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Oil and Industry University.

I. Perspective materials on the basis of petrochemical synthesis and oil raw materials.

PL7

INTENSIFICATION OF NATURAL HYDROCARBON AND CARBOHYDRATE RAW MATERIALS OF PETROCHEMICALS AND FUELS

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Abstract. The article is devoted to the prospects of using natural raw materials, both hydrocarbon and non-hydrocarbon in solving issues of life support. The main types of liquid, solid and gaseous hydrocarbon raw materials are named. Design parameters of naphthalan oil components are used in the work, which allow to interpret peculiarities of their bioorganic and behavioral properties. The reasons why declining hydrocarbon reserves may well be replenished by plant-based raw materials through the use of green chemistry technologies in the production of the necessary products are justified. In addition, the degree of resource renewal of the green chemistry feedstock significantly exceeds the similar characteristics of the hydrocarbon feedstock. Information is given on the composition and content of aromatic cinnamon alcohols in the composition of lignin macromolecule, hemicellulose polysaccharides in the structure of the carbohydrate part of lignin, its sulfo derivative - lignosulfonate and wood as a whole. The result of the application of plant non-hydrocarbon raw materials is promising monomers, polymers, reagents and compounds with practical properties for the needs of various fields of industry, including oil field chemistry. The possibilities of mathematical chemistry, computer calculations are used, the application of which allows creating and confirming the possibility of using plant biomass processing products to obtain qualitatively new and necessary products, including those having fungicidal and antimicrobial properties.

Keywords: Keywords: hydrocarbons, petroleum gases, vegetable raw materials, wood, polysaccharides, lignosulfonate.

1.İntroduction

The presented material is dedicated to the 100th anniversary of the oil formation and I wanted to start it with the thought of the President of Azerbaijan about "turning oil capital into non-oil capital" I.G. Aliyev.

The development of the petrochemical industry dates back to the beginning of the twentieth century, when the need arose for the development and production of various products for petrochemistry. And the main component of petrochemical production, of course, is raw materials, which are based on oil, gas, shale and coal [1].

The main types of hydrocarbon raw materials are: natural and associated hydrocarbon gases, gaseous and liquid products of oil refining, synthesis gas ($CO + H_2$), coke gas and industrial resins obtained during thermal processing of wood, coal, shale, peat.

After several decades, declining oil raw materials began to be replenished with gas, shale and coal hydrocarbon raw materials. Gas hydrocarbon raw materials, developed in the second half of the twentieth century, in the 60-80s [1.2], were considered especially promising.

At the beginning of the 21st century, we can talk about the production of petrochemicals, which we would not want to call alternative, but they are becoming increasingly important - these are products of green chemistry: biomass, natural polysaccharides, gums, mucus, etc.

These products are already beginning to be used quite intensively in almost all industries and agriculture, as well as medicine, pharmaceuticals and the food industry. Therefore, the first part of the report is devoted to hydrocarbon feedstock and its transformations, namely, oil processing, petroleum field gas, natural gas.

Oil and gas production is an integral part of the fuel and energy complex of Russia. Today, this is the most important component of the development of many industries. An important place today is occupied by gas processing, as the main raw material base of petrochemistry.

Table 1. Production and consumption of oil by world states for the period of 2015-2019

Place	Country	Production, billion m^3/year	Consumption, billion m^3/year
1	Saudi Arabia	542	135
2	Russia	531,4	153
3	US	446	830
4	China	208	507
5	Canada	193	756
6	Iran	166	96
7	Arab Emirates	165	80
8	Iraq	153	86

No less convincing is the hydrocarbon feed data in the gas phase.

Table 2. Gas production and consumption by world states for the period of 2013-2019

Place	Country	Production, billion m^3/year	Consumption, billion m^3/year
1	US	687	737
2	Russia	604,8	1035
3	Iran	166	212
4	Qatar	158	895
5	Canada	154	103,5
6	China	117	161,6
7	Norway	108	556

It should be noted that SiburTyumen Gas OJSC and SIBUR Company, which produce, i.e. process NPG (oil commercial gas) and process it into hydrocarbon fractions, individual hydrocarbons and their isomers, oxygen-containing compounds, polymers, rubbers, rubber and mineral fertilizers, thereby increasing their consumption.

The gas processing complex of the Sibur group has an extensive geography:

N.Novgorod, Tchaikovsky, Perm, Voronezh, Moscow, Novokuybyshevskaya NHK CJSC,

OJSC Uralorgsintez, OJSC Sibur-Neftekhim, CJSC Sibur-Khimprom, OJSC SiburTyumen Gas, Tver, Yaroslavl, Kiev, Minsk, Tomsk, LLC Tobolsk-Neftekhim, Tobolsk, Nizhnevartovsk, Samara

Development of production tactics and strategy, introduction of new methods of production process management [3,4]

The possibility of producing metals from oil, especially from heavy and super-heavy oils with a density of more than 100 kg/m3, seems promising and interesting. The reserves of such oil are very large both in Russia and in the CIS countries.

Significant amounts of vanadium, nickel, silver have been found in the oils of many Russian deposits. as well as gold, chromium, manganese. A deeper analysis showed, in addition to the above, the presence of scandium, beryllium, gallium, germanium, mercury, palladium. In total, more than fifty types of valuable metals were found in oil. Separation of metals from oil is possible by such methods as catalytic sorption, resistivity with acids and alkalis, hydrocracking and hydrotreating with light solvents, ultrasound, ozonation, bacterial strains, radiation irradiation, etc. [4]

The next part of the report is devoted to raw materials of non-hydrocarbon origin, namely raw materials of natural origin. The use of non-hydrocarbon raw materials results in promising monomers, polymers, reagents and compounds with practical properties for the needs of oilfield chemistry. They are actively used in almost all industries, and the history of their use is rooted in the XV-XVI-XVII centuries [5].

2.Expermental part

This section of the report is presented in 40 slides.

Using the possibilities of green chemistry, including wood processing products, I would like to note that the promising modern composites for drilling and oil production are reagents and reagent systems based on the by-product of lignosulfonate (LST) wood processing, cellulose, starch and other natural polysaccharides [5,6]. They are produced and used in many sectors of Russia, as well as in Azerbaijan.

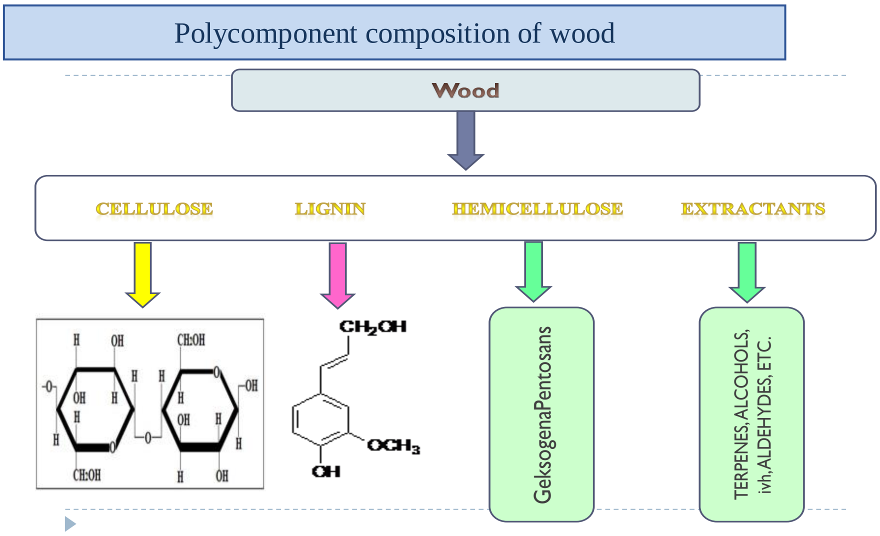


Fig.1. Schematic diagram of chemical composition of wood

It is lignin, as a polymer of the mesh structure in the composition of wood, that goes into sulfo-derivative - lignosulfonate (the main substance of sulfite liquor - a by-product of the wood delignification process). Lignosulfonate serves as the basis for the production of a number of products in oilfield chemistry: drilling reagents, plasticizers, cement setting retardants, binder and much more [7-9].

The lignin macromolecule contains both aromatic and carbohydrate components connected by various bonds and can be represented as a product of polymerization of n-hydroxycoric alcohols - p-coumaric (I), coniferyl (II) and synapic (III), which are: primary structural units of lignin (Fig. 2).

p-cumaryl alcohol (I), coniferyl alcohol (II) Synapic alcohol (III),

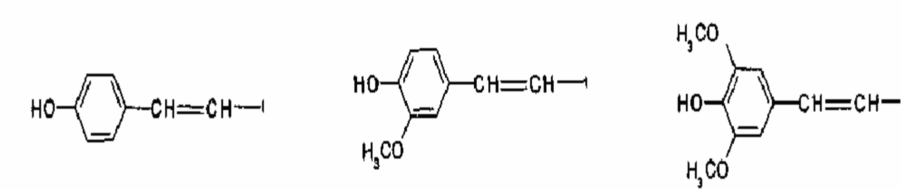


Fig. 2. Lignin monomers

The aromatic part of lignin (fragment) has the following conditional appearance (Fig.3).

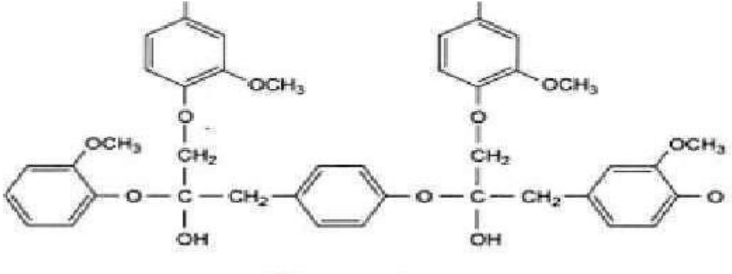


Fig. 3. Fragment of the aromatic part of lignin

The formation of lignin macromolecules in a plant (lignification) is a system of complex biological, biochemical and chemical processes.

The carbohydrate part of the macromolecule is cellulose and hemicellulose (Fig. 4).

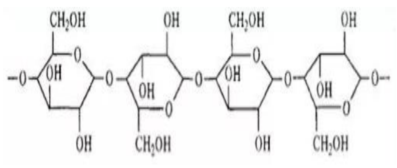
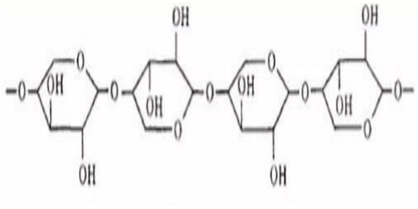
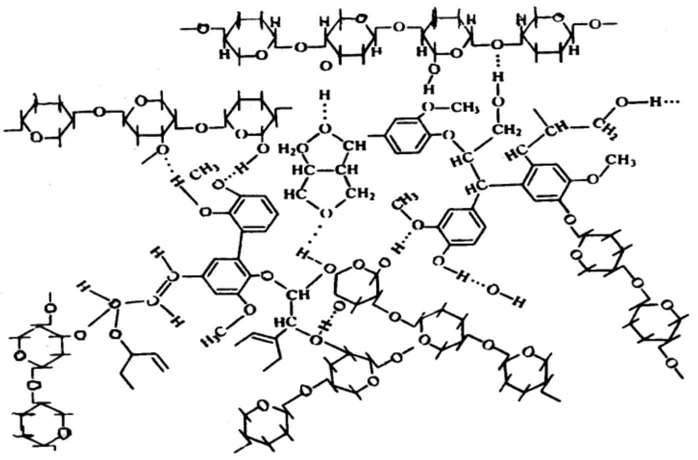
	
a) structure of cellulose	b) structure of hemicellulose

Fig. 4. Conventional structure of cellulose (a) and hemicellulose (b)

Chemically, analogues of these components can be considered: phenol, vanillin, guayacol for lignin; analogues of cellulose - glucose; analogues of hemicelluloses - arabinose and xylose (pentose), galactose and mannose (hexose) as reflected by the structure scheme of the lignocarboxylic matrix (Fig. 5) [7.10].

Fig. 5. Structure of lignocarboxylic matrix



3. Results and discussion

It can be seen that the structure of the lignocarboxylic matrix is due to the presence of hydrogen, carbon-carbon, ether chemical bonds of the aromatic and carbohydrate components. Since cellulose and lignin are thermodynamically incompatible substances, they form microheterogenic regions surrounded by hemicellulose gel. It is known that if two components are incompatible, then by adding a third component compatible with each of the two separately, the incompatible components become compatible [6,7,10]. Among wood components, hemicellulose is the third component that promotes compatibility of incompatible biopolymers - cellulose and lignin.

Hemicelluloses play a part-time role due to the formation of a transition layer on the surface of elementary cellulose fibrils and its limited thermodynamic compatibility with lignin. The composition of hemicelluloses can be represented by polysaccharides such as arabinans, xylanes, glucans, xyloglucans, mannans, arabinogalactanes, glucomannans, galactocomannans, some halactals The names of these polysaccharides come from the names of analogues of monomeric units of the macromolecule backbone.

Hemicelluloses can be detected by the presence of monomeric units - monosaccharides. Of the pentosans, xylan is best known in nature, which is part of most plant materials. The content of xylan in softwood is about 12%, in hardwood it is contained up to 25%, and in annual plants up to 37% of the weight of plant material.

In fact, it is a polymer composition, the mechanical strength of which is imparted by the engagement of segments of lignin macromolecules and hemicelluloses both among themselves and with cellulose.

In general, according to K. Freidenberg, the formula of lignin, which takes into account the presence of both aromatic and carbohydrate constituents, has the form: (Fig. 6)

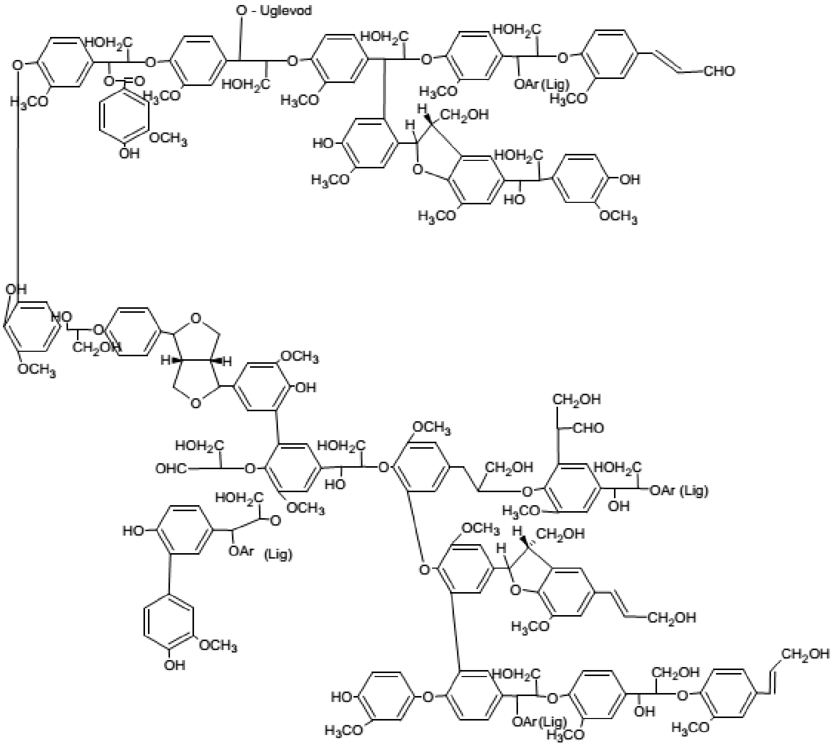


Fig.6. Formula of lignin macromolecules by K. Freidenberg

When sulfonated during delignification, the sulfo group HSO_3- occupies α, β or gamma position in the propane chain of FPE lignin (Fig. 7).

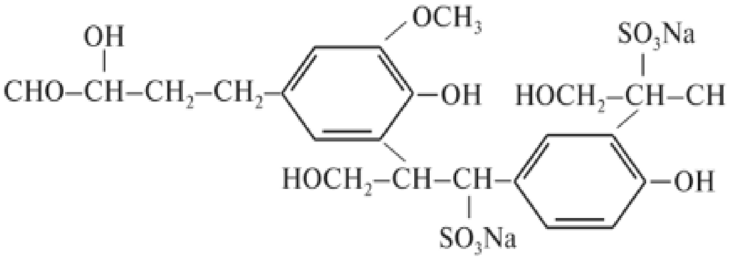


Fig.7. Structural formula of lignosulfonate macromolecule fragment

We have developed and proposed new reagent systems of polysaccharide nature, including those with fungicidal and antimicrobial properties. Joint studies and applications of fungicides and antiseptics are particularly important and interesting today [9.11].

I would also like to note that many chemical compounds are studied by methods of mathematical (computer) chemistry, the capabilities of which allow, based on the determined physicochemical properties, to prepare the appearance of many chemical compounds and transformations with practical properties (slides

As an example, we present the calculated parameters of naphthalan oil components, which allow us to interpret the features of their bioorganic and behavioral properties. The slides (56-70) show characteristics of biomarkers of naphthalan oil [12,13].

4. Conculusion

The results of our research on the transformations of hydrocarbon (oil, gas, coal, shale, oil field gas) raw materials and carbohydrate (processing of wood, waste of agricultural products and plants, waste of the pulp and paper industry) raw materials open up wide prospects and opportunities for obtaining qualitatively new materials and ways of using them for the life support of mankind.

5.References

1. Movsum-zade E. M. Events and facts of Russian oil: the birth of the oil business in the Russian Empire/E. M. Movsum-zade. - St. Petersburg: Nedra, 2008. - 151 p.
2.Movsumzade E.M. "Formation of gas processing in Bashkortostan" E.M. Movsumzade, A.M. Syrkin, N.S. Teplov. Moscow. "TsNIITEneftekhim" 1998.- 105s.
3. Development of automation and telemechanization systems in the oil and gas industry/A. E. Movsumzade, A. E. Soshchenko. - M.: Nedra, 2004 (State Unitary Enterprise Resin. region type. named after V.I. Smirnova). - 331
4. Mathematical methods in oil and gas chemistry [Text] = Mathematical methods in oil and gas chemistry/N. C. Movsum-zade, E. M. Zade. - Moscow: Chemistry, 2012. - 234 p.: il., porter, table.; 20 cm.; ISBN 978-5-98109-098-1
5. Karimov O.Kh., Teptereva G.A., Ismakov R.A. Chetverneva I.A. Wood products as an alternative to petroleum hydrocarbons Oil and gas chemistry, No. 3-4, S. 35-40
6 Karimov O.Kh., Kolchina G.I., Teptereva G.A., Movsumzade E.M. Chetvertneva I.A. Study of structural features and thermodynamic parameters of cellulose and derivatives. Industrial production and use of elastomers No. 4, 2019. C. 14-18.
7. Bogolitsyn K.G. Development of scientific foundations of environmentally safe technologies of integrated chemical processing of wood raw materials ./Bogolitsyn K.G. Izv. universities Forest Journal. 1998. №2-3. Page 40-52.
8. Teptereva G.A., Shavshukova S.Yu., Konesev V.G., Ismakov R.A. Functional analysis of lignosulfonates used in drilling technology: monograph - Ufa: Publishing House "Oil and Gas Business" 2017. - 92 s.
9. Patent of the Russian Federation No. 2709043 Method of producing lignosulfonate reagent for treatment of drilling mud/Tepterev G.A., Akchurin H.I., Konesev G.V., Nebit A.N., Zhestovsky M.P.
10. Teptereva, G. A. Study of the features of the carbohydrate composition of sulfite liquors used in drilling technology/G.A. Teptereva, R.A. Ismakov, F.A. Agzamov, G.V. Konesev, A.N. Popov//Sokar.- 2017.- № 3.- S. 5-11.
11 Teptereva, G.A. Preparation of drilling reagents by modification of neutral-sulfite liquors with phosphone compounds/G.A. Teptereva, G.V. Konesev, R.A. Ismakov, E.A. Kantor, M. Dikhtyar//Izvestia Tomsk Polytechnic University. Georesource Engineering. - 2017.- T.328, No. 9.- S. 94-101.
12.G.Yu.Kolchina, V.A. Adigezalov, E.M. Movsumzade "Physical and chemical properties of biomarkers of Naftalan oil" Moscow. "OBR
13. .Polnikova T.I., Bong H.K. Features of technology of primary carbon sorbents on the basis of lignin for environmental purposes. Fine Chemical Technologies. 2014;9(5):94-95. (In Russ.)

PP-I-3

STUDY OF BACTERICIDE-INHIBITORY PROPERTIES OF AMINOESTERS, OBTAINED ON THE BASES OF SYNTHETIC PETROLEUM ACIDS

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Abstract. Aminoesters were synthesized on the bases of ethanolamines and the mixture of synthetic petroleum acids, obtained by liquid-phase catalytic oxidation of naphthene-paraffinic hydrocarbons, separated from the fraction of Azerbaijani petroleums mixture boiling at 220-330°C temperature range. Simultaneously, Ba and Al salts were obtained on the bases of synthesized synthetic petroleum acids using double replacement reaction. Physical-chemical properties of the synthesized compounds were determined. Effect of 60% solution of these reagents in isopropyl alcohol on the activity of sulfate-reducing bacteria (SRB) was tested at 30-32°C in 15 days. It was found, that the synthesized aminoesters and metal salts of synthetic petroleum acids completely inhibit SRB activities even at very low concentrations. It was proved, that synthesized aminoesters (Exp.1, Exp. 2, Exp. 3) had 100% of bactericidal effect at 700 mg/l concentration, while metal salts of synthetic petroleum acids (Exp.4, Exp.5) had 100% of bactericidal effect at lower – 500 mg/l concentration. The studies proved, that the synthesized aminoesters completely prevent the growth of sulfate-reducing bacteria at much lower concentrations in comparison to the industrially used bactericidal inhibitors AMDOR-IK-7 and AMDOR-IK-10 (100% at 700 mg/l of concentration opposite 97-98%) taken as standard.

Keywords: diesel fraction, synthetic petroleum acids, biocorrosion, inhibitor, SRB

1.Introduction

Expansion of the assortment of industrially used metals and alloys, use of them under more severe conditions leads to a broader study of corrosion effects and development of the models for controlling corrosion process. One of the corrosion types is corrosion, caused by biological factors that it wasn't previously in great importance [1].

The studies showed, that biocorrosion may lead to significant economical losses in the oil industry. It's noted in literature, that more than 20% of corrosion losses are caused by biocorrosion. This figure is more than 30% in the gas industry [2, 3].

The oil industry is one of the areas, where the fixed assets are subjected to biological corrosion. It's known, that H_2S-corrosion is more common in oil industry than other types of corrosion and sulfate-reducing bacteria (SRB) are the main source of H_2S in well products. These types of bacteria are mainly found in separators, reservoirs, oil pipelines, etc. Hydrogen sulfide, in turn, may be found in tubing, process pipelines, raw material reservoirs and mainland pipelines, used for oil extraction from wells [4-6].

It's known, that bacteria have an important role in biocorrosion process. Bacteria need an aqueous medium and certain substrates for growth, the rate of their development depends on temperature, osmotic pressure, nature of environment and pH. This medium should contain organic compounds, hydrogen, carbon, nitrogen, sulfur, phosphorus, calcium and other trace elements [7].

Currently, the use of bactericidal substances against plankton and biocoatings that cause corrosion is widely studied. It's clear, that processes of biocorrosion and chemical corrosion occur comprehensively. In this regard, study of the substances that prevent chemical corrosion and affect the destruction of microorganisms becomes one of the main and important problems [8-10].

Thus, the main goal of this paper is obtaining synthetic petroleum acids (SPA) on the basis of catalytic liquid-phase oxidation of naphthene-paraffinic hydrocarbons of diesel fraction of Azerbaijani oils mixture, synthesis of nitrogen- and metal-containing derivatives of these acids and studying the effect of these compounds on life activity of sulfate-reducing bacteria.

2.Experimental Part

For this purpose, the fraction of Azerbaijani oils mixture with a boiling range of 220-330°C was taken as the object of the study. Before starting the oxidation process, the fraction was purified from aromatic hydrocarbons. Dearomatization process was carried out in the presence of 98% of H_2SO_4. The mixture of naphthene-paraffinic hydrocarbons, obtained by the dearomatization was oxidized in liquid-phase with catalytic presence of transition metal salts (Mn and Cr). Oxidation process was carried out by the known method [11-15]. The physical-chemical properties of SPAs were determined, and structural-group composition was studied by IR spectroscopy. The IR spectrum was recorded on ALPHA IR Fourier spectrometer manufactured by the German company BRUKER in the wavelength range of 600-4000 cm^{-1} [13]. Aminoesters were synthesized on the basis of oxidation process of SPAs and ethanolamines (monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA)). SPA and ethanolamine were taken at 1:1 of molar ratio for obtaining aminoesters. The reaction was carried out at 80-85°C with catalytic presence of NaOH in benzene as a solvent for 7-8 h. The catalyst amount was ~ 2-3% of the raw material mass. The yield of aminoester amounted to 98-99%.

The composition of the synthesized aminoesters was determined by the method of IR spectroscopy and the IR spectrum of the aminoester, obtained on the bases of SPA and DEA is illustrated in Fig. 1.

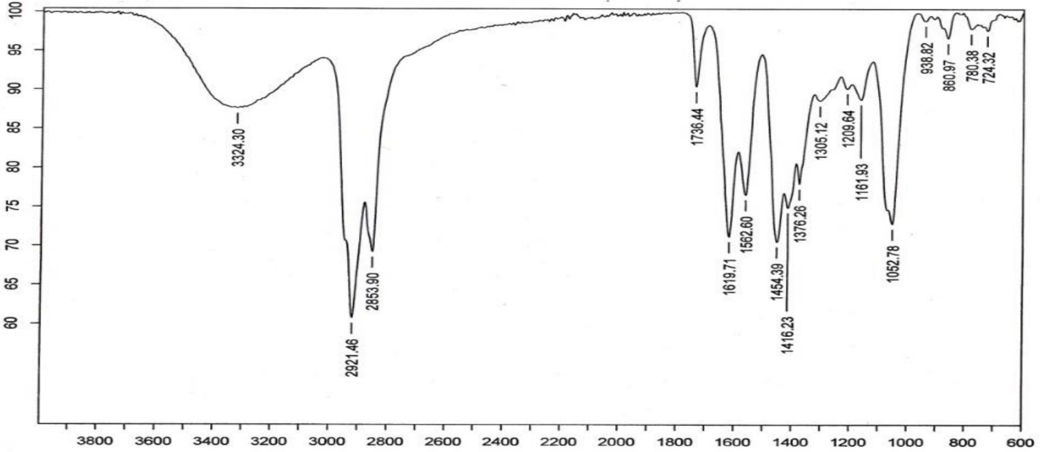

Fig. 1. IR-spectrum of the aminoester, obtained on the bases of SPA and DEA

As is evident from Fig. 1, the following absorption bands are observed in IR spectrum:

- deformation (724, 1376, 1454 cm^{-1}) and stretching (2853, 2921 cm^{-1}) vibrations of C-H bond of CH_3 and CH_2 groups;
- deformation (1619 cm^{-1}) vibrations of N-H bond;
- stretching (1209 cm^{-1}) vibrations of C-N bond;
- stretching (1161 cm^{-1}) vibrations of C-O bond of ether;
- stretching (1736 cm^{-1}) vibrations of C=O bond of ether;
- stretching (1052 cm^{-1}) vibrations of C-O bond of alcohol;
- stretching (3324 cm^{-1}) vibrations of H-O bond of alcohol.

Physical-chemical parameters of the synthesized aminoesters were also determined by known methods.

Simultaneously with aminoesters, Ba and Al salts were synthesized on the basis of SPA using double replacement reaction. Physical-chemical parameters of the synthesized salts were determined and structural-group composition was found using spectral analysis methods.

3.Results and Discussion

Effect of 60% solutions of the synthesized compounds in isopropyl alcohol on the life of SRB was studied as follows.

1143 strain of “Desulfovibrio desulfuricans” type, taken on the basis of OST 39-151-83 of Absheron-Binagadi deposit was studied as the object. Postgate B was used as the culture medium for SRB growth. The medium pH was in the range of ~7-7.5. Composition of the culture medium Postgate B: KH_2PO_4 – 0.5 g; NH_4Cl - 1 g; $CaSO_4$ - 1 g; $MgSO_4 \cdot 7H_2O$ – 2 g; sodium lactate – 3.5 g; NaCl - 2 g. The additives have the following composition: 5% solution of $FeSO_4 \cdot 7H_2O$ in 2% solution of HCl in water, 5% solution of $NaHCO_3$ in water, 1% solution of $Na_2S \cdot 9H_2O$ in 1% solution of Na_2CO_3 in water. 1143 strain of SRB was used for the experiments. The experiments were carried out in previously sterilized test tubes according to the method [16]. The effect of the synthesized compounds on SRB incubation period was studied in 15 days. Reagent-free and reagent media were used in comparison. 1 ml of bacterial medium was diluted with sterile water, transplanted into culture medium Postgate B in 10 ml tubes at a ratio of 1:9 and stored in thermostat at 30-32°C during 15 days. The amount of the bacteria germinated in the medium was determined under microscope at the end of the experiment. Effect of the reagents on SRB at concentrations of 50-700 mg/l is presented in Fig. 2.

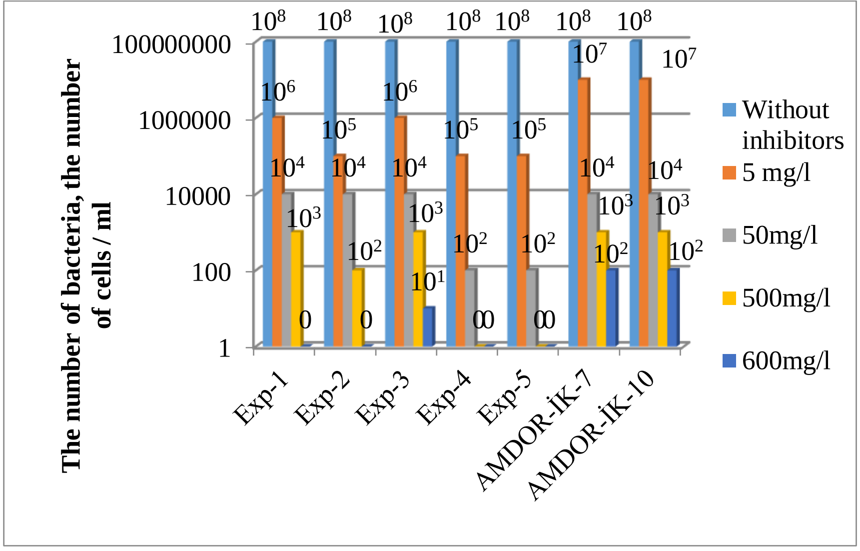

Fig. 2. Diagram of the influence of the samples Exp.1, Exp.2, Exp.3, Exp.4, Exp.5 on the amount of SRB
Note: Exp.1 – on the bases of SPA and monoethanolamine, Exp.2 – on the bases of SPA and diethanolamine, Exp. 3 – on the bases of SPA and triethanolamine, Exp.4 – Ba salt of SPA, Exp. 5 – Al salt of SPA

As is evident from the diagram, the bacteria amount to $n=1\times10^8$ in inhibitor-free medium, but in inhibitory medium bacteria amount decreases from 1×10^8 to 10^6 (from one hundred million to a million) in 5 mg/l concentration for Exp.1, Exp.2 and Exp.3; but for Exp.4 and Exp. 5 in 5 mg/l concentration bacteria amount decreases from 1×10^8 to 10^5(from one hundred million to one thousand); for Exp.1, Exp.2 and Exp.3 at concentration of 50 mg/l – to 10^4 (from one hundred million to ten thousands); bacteria amount at concentration of 50 mg/l decreases from 1×10^8 to 10^2 (from one hundred million to one hundred) for Exp.4 and Exp.5; at concentration of 500 mg/l to 10^3 (from one hundred million to one thousand) for Exp.1, Exp. 3; from one hundred million to one hundred for Exp.2; from 1×10^8 to 0 (from one hundred million to zero) for Exp.4, Exp.5; at concentration of 600 mg/l decreases from 1×10^8 to 0 for Exp.1, Exp. 3; from one hundred million to ten for Exp.2; for the complexes of Exp.1, Exp.2 and Exp. 3 at concentration of 700 mg/l bacteria amount decreases from 1×10^8 to 0 (from one hundred million to zero).

At the end of the studies the tested samples were titrated by iodometric method and protective effect was calculated on the amount of H_2S [17]. Fixed solutions of iodine and sodium hiposulfite were used for titration. H_2S content was calculated according to the following equation:

$$X\ \text{mg/l}\ H_2S=\frac{N(J)\cdot V(J)\ -\ N(Na_2S_2O_3)\cdot V(Na_2S_2O_3)}{VH_2O}\cdot 17000$$

N (J) = 0.1 n
V(J) =10 ml
N ($Na_2S_2O_3$) = 0.1 n
V ($Na_2S_2O_3$) = 7 ml
V (H_2O) =20 ml
17000 – indicates solubility of 0.1 n hiposulfite in 1000 ml.

Protective effect of inhibitor on the basis of the found content of H_2S is determined by the following equation:

$$Z=\frac{(C_0\text{-}C_{inh})}{C_0}\cdot 100\%$$

C_0- hydrogen sulfide content in control medium, mg/l;
$C_{inh.}$- hydrogen sulfide content in the reagent medium, mg/l.

Bactericidal effect of aminoesters and metal salts was calculated (Exp.1, Exp.2, Exp.3, Exp.4, Exp.5) (Tab. 2).

Table 2. The results of dependence of the complexes Exp.1, Exp.2, Exp.3, Exp.4, Exp.5 bactericidal effect on concentration

Symbol and composition	**Substance concentration, C-mg/l**	**Bacteria amount (number of cells/ml)**	**H_2S content, mg/l**	**Bactericidal effect Z, %**
Exp. 1	5	10^6	272	47
	50	10^4	213	58.2
	500	10^3	136	73.3
	600	**-**	**4.5**	**99.1**
	700	**-**	**-**	**100**
Exp. 2	5	10^5	255	50
	50	10^4	187	63.3
	500	10^2	93.5	82
	600	**-**	**-**	**100**
	700	**-**	**-**	**100**
Exp. 3	5	10^6	280.5	45
	50	10^4	221	57
	500	10^3	153	70
	600	**10^1**	**24**	**95.2**
	700	**-**	**-**	**100**
Exp. 4	5	10^5	238	53.3
	50	10^2	102	80
	500	-	-	100
Exp. 5	5	10^5	230	55
	50	10^2	76.5	85
	500	-	-	100
AMDOR-IK-7 (standard)	50	10^4	84.8	60
	500	10^3	53.2	75
	700	10^1	43	97
AMDOR-IK-10 (standard)	50	10^4	84.8	60
	500	10^3	44.8	80
	700	10^1	12	98
Control-I: H_2S content in the medium without a test-culture – 24 mg/l				
Control-II: H_2S content in the medium with a test-culture – 510 mg/l				
Control III: Bacteria amount in culture medium – 10^8 , number of cell/ml				

* test I and test II reveal H_2S content in control medium withour test-culture and in bacterial medium (test I – in SRB-free medium H_2S content amounts to 34 mg/l, test II – in SRB medium H_2S content amounts to 442 mg/l)

As is evident from Tab.2, the complexes Exp.1, Exp. 2, Exp.3 at concentration of 50 mg/l demonstrates 47-63.3% of bactericidal effect, but Exp.4, Exp.5 at concentration of 50 mg/l have 80-85% of bactericidal effect, Exp.1, Exp.2, Exp.3 at concentration of 700 mg/l – 100% of bactericidal efect, but Exp.4, Exp. 5 at lower concentrations (500 mg/l) have higher bactericidal effect (100%).

The complexes were compared with industrially-used bactericide-inhibitors (AMDOR-IK-7 and AMDOR-IK-10).

It was determined, that industrial reagents at concentration of 50 mg/l have 60%, but at concentration of 700 mg/l – 97-98% of biocidal effect.

Thus, it may be concluded, that if a reagent-free medium contains hundreds of millions of bacteria (10^8), then the number of bacteria in the medium with a reagent decreases from 10^8 to 0 in 500-700 mg/l of concentrations. Bactericidal nature of the synthesized compounds is due to their easily interact with intracellular enzymes, dissolving the cell walls and causing their destruction.

4.Conclusions

1. Synthetic petroleum acid (SPA) was obtained with the yield of 40% by liquid-phase catalytic oxidation of naphthene-paraffinic hydrocarbons, separated from the fraction of a mixture of Azerbaijani oils at the temperature range of 220-330°C.
2. Aminoesters were synthesized with the yield of 98-99% on the bases of ethanolamines (monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA)) and synthetic

petroleum acids (SPAs), obtained as a result of oxidation. Simultaneously, Ba and Al salts were obtained on the bases of SPAs using double replacement reaction.

3. The effect of the synthesized inhibitors in microbiological corrosive medium on SRB type of *"Desulfovibrio desulfuricans"* was tested and their high bactericidal effect was determined. The bactericidal effect of the samples was calculated on the basis of the amount of hydrogen sulfide. It was revealed, that the aminoesters synthesized at molar ratio of 1:1 (Exp.1, Exp.2 and Exp.3) at the concentration of 70% have 100% of bactericidal effect, but (Exp.4, Exp.5) of lower concentrations (500 mg/l) have higher bactericidal effects (100%).
4. The studies resulted in founding out, that the synthesized aminoesters and salts of SPA completely inhibit the growth of sulfate-reducing bacteria at much lower concentrations in comparison to the industrially used bactericide-inhibitors AMDOR-IK-7 and AMDOR-IK-10 (100% at 700 mg/l concentration opposite 97-98%) taken as standard.

5. References

1. Alagta, A., Felhosi, I., Bertoti, I, Kalman, .E.: Corrosion protection properties of hydroxamic acid self-assembled monolayer on carbon steel. Corrosion Science 50, 1644-1649 (2008). DOI:10.1016/j.corsci.2008.02.008
2. Quraishi, M., Danish J.: Fatty Acid Triazoles: Novel Corrosion Inhibitors for Oil Well Steel (N-80) and Mild Steel. JAOCS 77 (10), 1107-1113 (2000).
3. Olivares-Xometl, O., Likhanova, N., Dominguez-Aguilar M., Arce, E., Dorantes, H., Arellanes-Lozad, P.: Synthesis and corrosion inhibition of α-amino acids alkylamides for mild steel in acidic environment. Materials Chemistry and Physics, 110, 344-351 (2008). https://doi.org/10.1016/j.matchemphys.2008.02.010
4. Wang, D., Li, Sh., Ying, Y., Wang, M., Xiao, H., Chen, Z.: Theoretical and experimental studies of structure and inhibition efficiency of imidazoline derivatives. Corrosion Science 41, 1911-1919 (1999).
5. Xi, Sh., Qiu, M., Yu, L., Liu, F., Zhao, H.: Molecular dynamics and density functional theory study on relationship between structure of imidazoline derivatives and inhibition performance. Corrosion Science 50, 2021–2029 (2008). https://doi.org/10.1016/j.corsci.2008.04.021
6. Migahed, M.: Corrosion inhibition of steel pipelines in oil fields by N,N-di(poly oxy ethylene) amino propyl lauryl amid. Progress in Organic Coatings 54, 91–98 (2005).
7. Abdallah, M.: Ethoxylated fatty alcohols as corrosion inhibitors for dissolution of zinc in hydrochloric acid. Corrosion Science 45, 2705–2716 (2003). https://doi.org/10.1016/S0010-938X(03)00107-0
8. Sherar, B., Power, I., Keech, P., Mitlin, S., Southam, G. and Shoesmith, D.: Characterizing the effect of carbon steel exposure in sulfide containing solutions to microbially induced corrosion. Corrosion Science 53 (3), 955-960 (2011).
   https://doi.org/10.1016/j.corsci.2010.11.027
9. Mamedbeyli, E., Babayeva, V., Aghamaliyeva, D., Abbasova, Kh., Ibragimli, S. Synthesis of the complex of norborn-5-en-2-carboxylic acid amide with hexyl bromide and study of their effect on biocorrosion process. Oil Processing and Petrochemistry (Neftepererabotka i neftekhimiya) 3,·21-26 (2019).
10. Asadov, Z., Ahmadova, G., Rahimov, R, Hashimzade, S.: Micellization and Adsorption Properties of New Cationic Gemini Surfactants Having Hydroxyisopropyl Group. Journal of Chemical & Engineering Data. 64, 952−962 (2019). https://doi.org/10.1021/acs.jced.8b00815
11. Abbasov, V., Aliyeva, L., Afandiyeva, L. et all.: Aerobic oxidation of naphthene-paraffinic hydrocarbons of petroleum in the presence of γ-Al_2O_3 modified by transition metals. Processes of petrochemistry and oil-refining (PPOR) 21 (1) 80-89 (2020).
12. Purohit, S., Milind, P. Kanaad, A. et al.: Paraffin oxidation in a foam reactor. International journal of Engineering Research and Technology 5 (1), 81-98 (2012).
13. Litvintsev, I. Oxidation processes in industrial organic chemistry. Sorosov educational journal 8 (1), 24-31 (2004).
14. Matienko, L., Mosolova, L., Zaikov G. Selective catalytic oxidation of hydrocarbons. New perspectives. Russian Chemical Reviews (Uspekhii khimii) 78 (3), 227-247 (2009).
15. Aliyeva, L., Efendiyeva, L., Babanly, N., Guliyev, A., Abbasov, V.M.: Reactivity of β-dicetonates of metals with variable valencies and their nitroderivatives in liquid-phase oxidation reaction of naphthenic hydrocarbons. Processes of petrochemistry and oil-refining (PPOR) 20 (4), 389-400 (2019).
16. Postgate, J.R., Campbell, L.L. Classification of desulfovibrio species the nonsporulating sulfate-reducing bacteria. Bacteriol. Revs. 30 (4), 732-738 (1966).
17. OST 39-234-89 Iodometric method for the determination of hydrogen sulfide in water.

PP-I-6

STUDY OF THE EFFECT OF DIFRON-4201 REAGENT ON THE STRUCTURE OF HIGH-MOLECULE OIL COMPOUNDS IN LABORATORY

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Abstract. For the first time, the effect of the "Difron-4201" depressant additive on asphalt-resin-paraffin deposits on a metal surface was studied under laboratory conditions by the "cold finger" method. The experiments were carried out at different temperatures of the " cold finger" (0^0C, 5^0C, 10^0C, 15^0C, 20^0C, 25^0C, 30^0C) and with different concentration (300, 500, 700, 900, 1100 g/t) of the depressant additive "Difron-4201". The duration of the experiment was 3 hours. The amount of paraffin deposited at different times (0, 20, 40, 60, 80, 100, 120 minutes) on the finger surface was determined using an analytical balance and it was found that with a decrease in the finger temperature, the amount of oil deposits on the surface increase, and over time the intensity sedimentation decreases and, after 120 minutes, stabilizes.

From the analysis of the dependence of the mass of asphalt-resin-paraffin deposits on the concentration of the depressor additives additive, it was found that, with an increase in the concentration of the additive in oil, the amount of deposits decreases, and at an additive concentration of 900 g / t, the maximum level of decrease in deposits is observed.

On the basis of the experimental results obtained, the efficiency of the depressant additive and the maximum percentage of paraffin deposits on the finger surface were evaluated. The highest effect was observed at a concentration of 900 g / t of the depressant additive Difron-4201 (85%). Depending on the temperature of the cold finger, the maximum percentage of paraffin deposits on the metal surface 0^0C-12.8, 5^0C-9.16, 10^0C-6.76, 15^0C-5.82, 20^0C-5.04, 25^0C-2.96,30^0C-1.63.

Key words: cold finger, Difron-4201, cryostat, asphaltene-resin-paraffin deposits, the effectiveness of additives, gravimetric method.

1.Introduction.

At present, the fight against oil deposits forming on the inner surface of pipelines and other equipment has become sharp in many countries of the world's oil industry, including Azerbaijan, in connection with the commissioning of large, highly paraffinic oil deposits. That is why, in the oil industry, effective control of asphaltene-resin-paraffin deposits are considered one of the decisive tasks. Oil sediments, worsening the technical and economic indicators of oil production processes, collection, transport through pipelines and storage, increase energy needs and increase the likelihood of accidents.

Deposits on the inner surface of pipelines and other equipment by chemical composition are multicomponent systems consisting of inorganic and organic compounds. The organic compounds are mainly kinds of paraffin and high molecular weight compounds of oils. In oil deposits, the number of paraffinic hydrocarbons can reach up to 75%, resin from 8 to 35%, and asphaltenes from 1.5 to 5%. That is why, in most cases, oil deposits are called asphaltene-resin-paraffin deposits (ARPD). The composition of inorganic substances (ARPD) includes water, minerals, and mechanical impurities; they are mostly less than 5% [1].

When transporting commercial oil through pipelines, the temperature is the main factor in the formation of ARPD. In accordance with the change in the temperature of the oil flow, in the oil pipelines, the ARPD differentiates on the inner surface of the pipe wall. At the same time, in the process, the initial crystallization temperature of paraffin hydrocarbons plays a decisive role, which determines their transition to a solid-state. The nature of the distribution of deposits along the inner surface of pipelines shows that the dependence of the number of paraffin deposits on temperature is nonlinear.

Thus, the processes of formation and accumulation of ARPD depend on the composition of the oil, hydro- and thermodynamic conditions, and it can be characterized as follows [2].

During the movement, the oil cools, and at a certain temperature, solid hydrocarbons are released and at the same time, at the same temperature, they are deposited on the walls of the pipes. Paraffin crystals occur and grow both in the entire volume of oil and on the surface of the pipe wall. Crystallizing kinds of paraffin on the surface of the pipe wall mainly form ARPD. With a decrease in temperature, the amount of paraffin released from oil increases and, accordingly, the number of precipitation increases.

Due to the weak nature of crystals adhesion to the walls of the pipes, formed in the volume of oil, during its transportation, most of them are carried out by the flow of oil without adhering to the inner surfaces of pipelines.

Currently, there are numerous methods for combating paraffin deposits. But experiments show that under difficult geotechnological conditions of transport and storage of highly paraffinic oils, the optimal method of counteracting ARPD is the use of depressant additives [1].

In the fight against the formation of paraffinic deposits, the use of depressant additives differs from other methods not only in technological efficiency. The effect obtained when adding the reagent at temperatures higher than the initial temperature of paraffin crystallization does not depend on the thermodynamic conditions of oils transported through pipelines [3].

Thus, it can be concluded that depressant additives not only improve the rheological properties of highly paraffinic oils, but also act as inhibitors of paraffin deposits.

Recently, in the technology of transporting highly paraffinic oils with a higher freezing point, a more promising and the environmentally friendly method is transporting with the use of depressant additives. On the other hand, the effect of additives on oil is selective. For this reason, the selection of effective depressant additives and determination of their optimal concentration is possible only based on the results of numerous experiments carried out in laboratory conditions.

On the basis of the foregoing, the process of formation of ARPD of highly paraffinic model oil with the participation of depressant additive Difron-4201 was investigated in laboratory conditions. For this purpose, at the assessment of the effectiveness of depressant additives and determining the optimal rate of consumption, we used the “cold finger” method [4].

The purpose of the work: Evaluation of effectiveness and determination of the optimal consumption rate of the "Difron-4201" depressant additive for highly paraffinic model oil by the "cold finger" method.

2.Experimental part

The effect of the "Difron-4201" depressant additive in highly paraffinic oil with a higher freezing point was investigated by the "Coldfingertest" method. This method is based on the formation of ARPD from transported oil on a cold surface.

It is for this reason that the “cold finger” method is one of the main methods for evaluating the effectiveness and determining the optimal rate of consumption of a depressant additive when taking measures to prevent the deposition of paraffin crystals [5, 6].

In the "cold finger" method, under the influence of a moving stream of oil, the stages of formation and accumulation of ARPD are implemented, including such processes as dispersion (crushing) of sediments, the growth of heavy oil components and paraffin crystals, sedimentation, and the emergence of new crystallization centers. The advantage of the "cold finger" method is also that the lowest amount and the initial temperature of paraffin crystallization can be determined during experiments. On the other hand, this method combines the experimental conditions for the formation of paraffinic deposits in the oil, moving under the influence of a magnetic stirrer, with its real condition for flow in pipelines, since at this time, the flow of paraffins dissolved in oil is provided to the surface of the cold metal. But in the absence of mixing, the precipitation of paraffin crystals are observed less, and they remain in suspension in the medium of the dispersed oil system [7].

During the experiments, a noticeable temperature the gradient is created between the medium of the investigated dispersed oil system and the "cold finger", as a result of which it is possible to accurately observe the processes taking place.

The experiments in laboratory conditions by the "cold finger" method was carried out in the following sequence:

1. To the metal beakers intended for use in the experiments (d = 36mm, ℓ = 130mm), the same volumes of the investigated model oil were added and they were provided with magnetic stirrers.
2. While stirring with magnetic stirrers at a speed of 350 cycles/min, the metal beakers were heated to 55-60^{0}C and under these conditions a pre-calculated amount of a depressant Difron-4201 was added to each of them (for comparison, no additives were added to one of the beakers). A magnetic stirrer ensured the distribution of the reagent throughout the oil volume.
3. The chemical beakers were placed in an external thermostat and a U-shaped finger (d = 15 mm, ℓ = 110 mm) with a working surface length of 70 mm was introduced into it.
4. A metal finger was connected to a circulating cryostat thermostat and its temperature was controlled by a refrigerant circulating inside it (The temperature gradient between the surface of the “cold finger” and the liquid provides ideal conditions for crystallization and deposition of high molecular weight oil compounds).

5. After the completion of the experiment, a magnetic stirrer was turned off, and the “cold finger” was removed from the metal beaker introduced into the acetone solution to remove liquid oil residues.
6. To transfer the asphaltene-resin-paraffin residues into a liquid state, the “cold finger” was heated with a cryostat to 70^0C and the deposited mass was determined by the gravimetric method. The relative error was ±1-3%.

3. Results and discussion

The experiment was carried out for 3 hours at temperatures of 0^0C, 5^0C, 10^0C, 15^0C, 20^0C, 25^0C, 30^0C of the “cold finger”. At each finger temperature, the mass of oil sediments accumulated during 0, 20, 40, 60, 80, 100, 120 minutes was weighed on an analytical balance and corrected.

Table 1. The number of sediments deposited on the surface of the "cold finger" from highly paraffinic model oil.

Time, seconds	“cold finger” temperature						
	0^0C	5^0C	10^0C	15^0C	20^0C	25^0C	30^0C
	Weight of paraffin deposits, g.						
0	0.092	0.078	0.07	0.065	0.057	0.055	0.028
20	0.151	0.131	0.093	0.088	0.082	0.055	0.028
40	0.211	0.161	0.128	0.123	0.111	0.049	0.023
60	0.281	0.181	0.151	0.146	0.126	0.053	0.027
80	0.321	0.221	0.160	0.155	0.146	0.057	0.032
100	0.326	0.241	0.180	0.175	0.148	0.063	0.038
120	0.341	0.251	0.182	0.177	0.161	0.057	0.032

Experiments for oil samples, with the addition of the depressant Difron-4201 with the concentration of 300, 500, 700, 900, 1100 g / t, were repeated and the amount of precipitation on the cold surface was determined by the gravimetric method. Based on the results obtained, the effectiveness of the additive was calculated using the following mathematical expression:

$$K = \frac{m_{1}{-}m_{2}}{m_{1}} \cdot 100\%$$

Here: K–effectiveness of the depressant additive,
m_1–mass of ARPD in the absence of additive in the medium,
m_2 –is the mass of ARPD in the presence of an additive in the medium.
At the estimate of the effectiveness of the depressant additive by this method, taking into account the mass of oil on the surface of the "cold finger" is one of the decisive factors. Numerous experiments carried out show that at temperatures of 30 ° C and higher, paraffin deposits on the finger surface are small or almost absent. At these temperatures, the mass on the surface of the cold finger simply softens the oil film. When calculating the effectiveness of the additive, taking this mass into account is the main condition. It has been established that the mass of oil on the surface of the "cold finger" varies in the range of 0.026-0.031 g. Table 2 shows the effectiveness of "Difron-4201" at different concentrations.

Table 2. Effectiveness of the depressant "Difron 4201" at different concentrations

Concentration of the depressant additive, g / t	Depressant efficiency,%
300	62
500	68
700	77
900	85
1100	65

The maximum percentage of paraffin deposited on the surface of the cold finger, of the total amount of paraffin in the oil, is estimated by the following expression:

$$\delta = \frac{M}{V \cdot \rho \chi_p}$$

M– is the mass of paraffin deposited on the surface of the cold finger t^0C, g.
V–volume of oil in a beaker, ml
ρ–density of the investigated oil, g / ml

χ_p –mass percentage of paraffin present in oil, g.

Based on the above expression, the percentage of paraffin deposition on the surface of the “cold finger” at different temperatures was calculated, and the following results were obtained.

The amount of paraffin deposits, (%)						
0^{0}C	5^{0}C	10^{0}C	15^{0}C	20^{0}C	25^{0}C	30^{0}C
12.8	9.16	6.76	5.82	5.04	2.96	1.63

Thus, the results of investigations carried out using the “cold finger” method shows that a depressant additive can be used as an effective means of counteracting ARPD in highly paraffinic oils and its optimal consumption rate is 900 g / t.

4.Conclusion

1. For the first time, the effectiveness and optimal consumption rate of the "Difron-4201" depressant additive were investigated in laboratory conditions using the "cold finger" method. The experimental process was carried out using beakers with parameters d = 36mm, ℓ = 130mm and a U-shaped metal finger (d = 15 mm, ℓ = 110mm) for 3 hours.
2. The amount of ARPD precipitated from highly paraffinic model oil with and without the addition of Difron-4201 additive, on the metal surface, at different temperatures of the “cold finger”, during 0, 20, 40, 60, 80, 100, 120 minutes, was determined by the gravimetric method.
3. Based on the mass of paraffin deposits, the effectiveness of the “Difron-4201” depressant additive in different concentrations and the maximum percentage of deposits from the volume of the model oil on the surface of the “cold finger” were calculated.
4. It was found that the highest effect of the pour point depressant "Difron-4201" against ARPO is achieved at the concentration of 900 g / t and is 85%.
5. Depending on the temperature of the “cold finger”, the maximum percentage of deposits on the metal surface were 0^{0}C-12.8%, 5^{0}C-9.16%, 10^{0}C-6.76%, 15^{0}C-5.82%, 20^{0}C-5.04%, 25^{0}C-2.96% and 30^{0}C-1.63%.

5.References

1.Olenov L. M., Mironov T. P. The use of solvents and inhibitors to prevent the formation of ASPS. Moscow: VNIIOENG, 1994, 32 p.

2.Santanna V.C., Silva A.C.M., Lopes H.M., SampaioNeto F.A. Microemulsion flow in porous medium for enhanced oil recovery, Journal of Petroleum Science and Engineering, № 105, 5, 116 p. (2013)

3.Gubin V. E., Gubin V. V. Pipeline transport of oil and petroleum products. Moscow: Nedra, 296 p. (1982)

4.Ivanova L. V. Removal of asphalt-resin-paraffin deposits of different thickness, Oil and gas business, № 2, pp. 257-270, (2011)

5.Shadrina P. N. Methodological aspects of ensuring phase stability of oilfield fluids during oil production, transportation and preparation, Oil and gas business, № 6, pp.218-233, (2015).

6.Jennings D.W. Effect of shear and Temperature on WOX Deposition Cold finger investigation with a Gulf of Mexico Crude Oil. Energy. Fuels.19: pp.1376-1386, (2005)

7.Glushchenko V. N., Shapiguzov L. M., Uralov I. A. Evaluation of the effectiveness of asphaltene resin-paraffin deposits inhibitors, Oil industry, № 5, pp. 84-87, (2007)

8.Meclaflin G.G., Whitfill, D.L. Control of paraffin deposition in production operation. Journal Petoleum Technology, 1984, V.36, № 2, pp.1965-1970, (1984) http://dx.doi.org/10.2118/12204-PA

PP-I-2

REAGENTS FOR OIL PRODUCTION BASED ON LIGNOSULFONATE AND STARCH SULFOESTERS

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Abstract. The article shows the need to develop systems that reduce the risks of complications in oil production. One of the promising compositions can be the reaction products of a by-product of the pulp and paper industry - lignosulfonate, moreover, its modified form, obtained as a result of cooking wood in a neutral cooking solution under conditions significantly different from those of sulfite cooks. Another component of the composition is natural polysaccharide starch. Certain modifications of starch and neutral lignosulfonates have similar properties, due to which they are able to form compounds of the ester class, where the alcohol component is starch, the acid component is the lignosulfonic acid anion. The article proposes a reaction scheme for the preparation of ether. In laboratory conditions, as a result of a two-stage process, we obtained the preparation of sulfo ligno corboxy starch. The formation of ether is confirmed by the presence of absorption bands at 822 cm-1 (v C-O-S) and 1240 cm-1 (v S = O) on IR spectra, which were measured in the frequency range 400-4000 cm-1 on the IR-Fourier spectrometer. The experimental batch of the obtained preparation was produced as a ЛКР-1 reagent and tested in field drilling conditions at Russian fields with abnormally high pressures and bottom-hole temperatures.

Keywords: lignosulfonate, esters, starch, infrared spectrum, deposit

1.İntroduction

In oil production, issues of reducing complications during oil and gas well drilling are always relevant. One of the most profitable directions in both economic and technological terms is the chemical treatment of flushing liquids (drilling fluids) with reagents of various nature, the addition of which can give solutions the necessary rheological properties, reducing the risks of complications by ten times and increasing the efficiency of oil production in General. In our opinion, a group of modified starches capable of forming complex starches is promising for the purpose of creating reagent systems with the function of stabilizing clay suspensions.

2.Experimental part

The study of the combined effect of the starch component and the polymer structure – lignosulfonate (LST) on the stabilization function of drilling systems is promising. We have studied and tested the use of lignosulfonate compositions in field conditions when drilling intervals composed of unstable clay rocks. Phosphonic fragments of (H2RO3-) oxy-ethylene diphosphonic acid (OEDFC) can be embedded in the propane chain of the lignosulfonate monomer link, which contributes to the strengthening of the complexing and stabilizing properties of drilling fluids. Such replacement of the phosphonate ion with a distorted tetrahedron by stereochemistry is justified, while other functional groups of the phenylpropane link of lignosulfonate are characterized by a flat configuration. Phosphonic groups are represented by a number of protonated forms: PO_3^{2-} ; PO_3H^- ; PO_3H^{2-} . In this case, PO_3^{2-}-has a significantly greater electronegativity than the COO^--group. Replacing the carboxyl group with a phosphonic group leads to the formation of stable complexonates. All said complexes containing phosphone groups combine the absence of bound water in their composition. For lignosulfonate, protonation of the PPE propane chain can lead to the formation of large agglomerates of the lignosulfonic acid anion around the complexing cation.

3. Results and discussion

The possibility of forming a complex compound of LST with OEDPC has been proved by UV spectra, which show that LST compositions with phosphone groups contribute to the formation of complexonates and the appearance of ziphyr groups. This is confirmed in field practice by positive changes in overestimated rheological parameters of drilling fluids with additives of phosphone-modified PHLS reagent (Table 1).

Table 1. Effect of different PHCL compositions on polymer-clay solution parameters

№	Solution composition	Solution parameters					
		ρ, г/см^3	HC, s	PF, ml/30 min	η, MPa •s	ДНС, дПа	pH
1	Starting polymer-clay solution (No. 1)	1,15	62	6,0	38	124	8,4
2	No. 1 + PHL with OEDFC	1,15	29	5,8	24	66	8,1
3	No. 1 + PHL with TPF	1,15	30	5,6	24	70	8,3
4	No. 1 + PHCL with modified starch	1,15	32	5,2	28	74	8,0

This gives rise to a similar effect when using polysaccharide compositions of LCT, in particular with modified starches.

Certain modifications of starch and various lignosulfonates, having similar technological characteristics, are able to interact with each other to form esters - sulfocarboxyethers of starch [1,2]. As acylating agent we used anion of lignosulfonic acid.

The preparation of ether by us is considered as a two-step process, where in the first stage starch oxidation is carried out to obtain a carboxy derivative, in the second stage sulfation of the obtained carboxy starch (LCR-1 reagent), as confirmed by the presence of absorption bands at 822 cm-1 (v C-O-S) and 1240 cm-1 (v S = O) on IR spectra which are measured (Fig. 2).

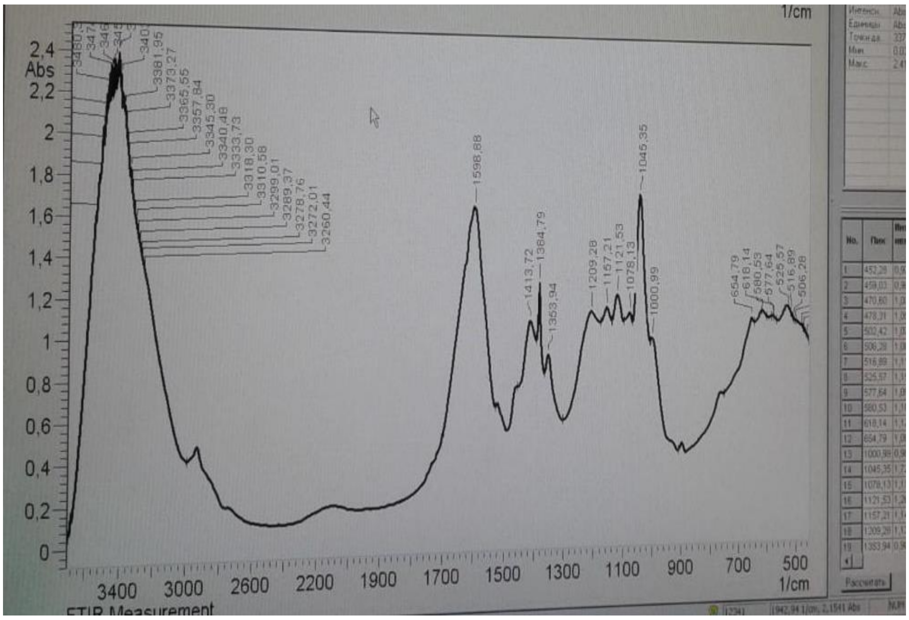

Fig. 2. IR spectrum of the obtained preparation ЛКР-1

Purification from low molecular weight impurities was carried out on cellophane membranes until there was no reaction to sulfate ion. The resulting substrate was dried at room temperature.

The appearance of absorption bands in the IR spectrum (Figure 8) of starch sulfolignocarboxy ester at 822 cm-1 (v C-O-S) and 1240 cm-1 (v S = O) are consistent with the chemical analysis data and clearly indicate the formation of sulfoester groups in the composition of modified starches (Fig. 3).

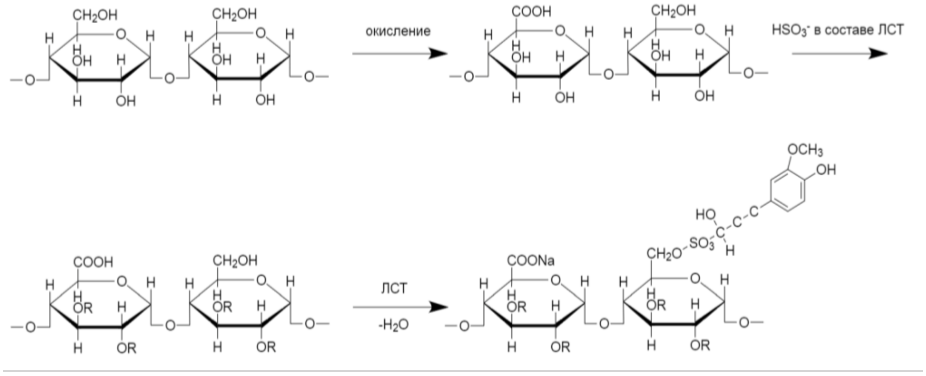

Fig. 3. Starch Sulfolignocarboxyester Production Scheme (ЛКР-1)

A distinctive property of the obtained composition is increased stability under aggressive well conditions. Drilling fluid system is stable to action of polyvalent cations, contamination with cement, supply of high content of active clay phase, action of acid gases, high temperatures.

This shows the possibility of obtaining a synergistic effect in the form of enhancing the structural-rheological properties manifested as a result of the reaction of the interaction of natural polymers of starch and lignosulfonate. The interaction product can be used in solving issues of drilling technology as a reagent capable of working in difficult mining and geological conditions as part of drilling fluids.

Further development of the synergistic effect was found in the form of a monophase composition of specially selected esters of lignosulfonic acids and polyhydric alcohols, which form a spatially structured network with macromolecules of polysaccharides.

4. Conculusion

Thus, the use of plant-derived materials allows improving the quality of well construction and reducing the volume of waste generation, and also partially solves the problem of prioritizing the use of domestic reagents in drilling solution systems in difficult mining and geological conditions.

In addition, the oxidation products of starch-containing plant raw materials with molecular oxygen in alkaline gels are effective as retardants for setting plugging solutions, and can also be used in other fields of industry [3-7].

5.References

1. Prospects of Application of By-Product of Cellulose-Sulfite Cellulose Extract Processing in the Oil Industry/G.A. Teptereva,, I.A. Chetverneva, E.M. Movsumzade//Oil Industry Chemistry. Materials of the VI International Scientific and Practical Conference (XIV All-Russian Scientific and Practical Conference). Moscow: RSU of Oil and Gas (NIU) named after I.M. Gubkin, 2019. FROM 59-61.
2. Starch reagents in drilling fluid technology: traditions and perspectives/Schitz L.A.//Starch and new starch-containing sources - structure, properties and new technologies: mater. 1st Moscow international. Conf., October 30 - November 1. M., 2001. C. 55.
3. Introduction of environmentally friendly structured hydrogel drilling fluids based on vegetal raw materials/V.I. Nosdra, S.V. Mazykin, E.V. Belenko, V.P. Polishchenko, etc//Drilling and oil, 2017. No. 10, C 20-24.
4. Recent achievements of chemistry and technology of starch derivatives/V.N. Kryazhev, V.V. Romanov, V.A. Shirokov//Chemistry of plant raw materials, 2010, No. 1. FROM 5-12.
5. Appearance, development and improvement of various types of drilling fluids in world and domestic practice/Chetvernev I.A., Tepterev G.A., Shavshukova S.Yu., Konesev V.G.//History and pedagogy of natural science. 2019. № 2. C. 25-29.
6. Functional analysis of lignosulfonates used in drilling technology/G.A.Tepterev, S.Yu. Shavshukova, V.G. Konesev, R.A. Ismakov. Ufa: Oil and gas business. 2017. 92 s.
7. E.M.Movsumzadeh, R.B.Valikov, G.K.Aminova "Growth and harvest regulators" Ufa. "GINTL," "Reagent" 2000-205s.

OR-I-2

COMPARATIVE STUDY OF THE EFFICIENCY OF MONOETHANOLAMINE SALTS OF SULPHO DERIVATIVES OF OLEIC AND LINOLEIC ACIDS AS STEEL CARBON CORROSION INHIBITORS

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Abstract Comparative study of monoethanolamine salts of sulpho derivatives of oleic and linolenic acids as inhibitors of carbon dioxide corrosion of steel grade C1018 were carried out and it was found that with an increase in the unsaturation of the used fatty acids, the effectiveness of the inhibitors increased. By using 50-100 ppm linolenic acid-based inhibitor the corrosion efficiency is between 91.7-98.2%, while at the same concentrations for an oleic acid-based inhibitor, the degree of protection is between 57.03-92.6%.

Keywords: inhibitor, corrosion, fatty acids, sulpho derivatives of fatty acids, corrosion rate

1. Itroduction.

The main reasons for reducing the resource of almost all types of oil refining equipment are corrosion damage and their erosion-mechanical wear. In the oil and gas industry 25% of all equipment failures accidents caused by corrosion [1].

In view of the widespread use of CO_2 to increase oil recovery, it is CO_2 corrosion that is the focus of researchers' attention.

The mechanism of carbon dioxide corrosion of steel has established the electrochemical nature of the process, which consists in the fact that under the influence of carbon dioxide, hydrogen evolution at the cathode increases and carbonate-oxide films form on the metal surface.

Nowadays, there are many methods to against this type of corrosion: coating products with protective corrosion-resistant metals (chrome plating, galvanizing), painting metal products with paints and varnishes, alloying metal, using special materials to create equipment that does not experience the effect of corrosion or is less least, electrochemical protection (protection by attaching an anode metal to the equipment, which will subsequently corrode), changing the properties of a corrosive environment, etc. [2].

Among all the methods mentioned above, the use of corrosion inhibitors is one of the practical methods of protecting metal equipment.

The mechanism of action of corrosion inhibitors is explained by adsorption on the metal surface with the blocking of active centers and, as a result, a decrease in the intensity of corrosion. The possibility of adsorption of inhibitors on the metal surface depends on the nature and surface charge of the metal, the chemical composition of electrolytes, the molecular structure and electronic characteristics of the inhibitor molecules.

The number of corrosion inhibitors used today is growing exponentially, and the raw material base for their production is quite wide [3,4].

Market analysis of modern corrosion inhibitors made it possible to identify promising raw materials for their production. This is, first of all, raw materials of plant origin, which is renewable and safer from an environmental point of view, which can be various vegetable oils.

The inhibitors obtained on the basis of vegetable oils and their derivatives can be classified as film-forming, the adsorption of which depends on the interaction of the π-orbitals of the inhibitor with the d-orbitals of metal atoms on the surface, which leads to the formation of a protective film. The adsorption capacity of inhibitors depends on atoms or functional groups in the molecules that provide the active adsorption interaction of the inhibitor with the metal. Such active groups can be nitrogen, sulfur, oxygen, and phosphorus groups that are adsorbed on the metal due to donor – acceptor and hydrogen bonds [5, 6].
Taken account all the above, monoethanolamine salts of derivatives of sulpho fatty acids are of interest as effective corrosion inhibitors. Studies conducted earlier at the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan established high anticorrosion properties of anionic surfactants obtained from cotton oil fatty acids [7].

Further studies in this area are devoted to identifying the nature of the used fatty acids on the anticorrosive properties of corrosion inhibitors obtained on their basis.

As a result, monoethanolamine salts of sulpho derivatives of oleic and linolenic fatty acids were synthesized and the obtained compounds were studied as corrosion inhibitors of CO_2 on an ACM GILL AC apparatus by a standard method with a 1% NaCl standard solution.

2. Experimental part

A standard 1% NaCl solution was prepared by dissolving chemically pure sodium chloride in distilled water. The tests were carried out using a solution of salts in water and isopropyl alcohol in a ratio of 70:30 at a concentration of 50-100 ppm. The parameters of the corrosion test process are given in Table 1.

Table 1. Corrosion test process dimensions

Material	C1018 low carbon steel
RCE outer surface area, cm2	7,9
Volume of solution, l	1,0
Temperature, °C	50
PH	6.7-5.7
CO2 pressure, bar	0,90
CO2 purity	>99,7
Corrosion measurements	Linear polarization resistance General measurement of metal loss

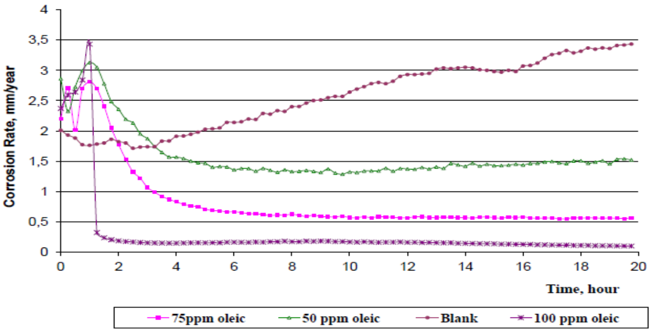
Physico-chemical properties of the obtained monoethanolamine salts of sulpho derivatives of oleic and linolenic fatty acids are given in Table 2.

Table 2. Physico-chemical properties of the obtained monoethanolamine salts of sulpho derivatives of oleic and linolenic fatty acids

	Property			
Name of Inhibitor	Molecular weight	Density kg/m^3	Solidification temperature, °C	Iodine number, gJ/100 g
Monoethanolamine salt of the sulpho derivative of oleic acid (MEASO) (MEASO)	459	958.5	-18	0
Monoethanolamine salt of the sulpho derivative of linolenic acid (MEASL) (MEASL)	455	958.1	-20	78

3.The discussion of the results

The kinetics of the corrosion process of a plate of low-carbon steel C1018 with and without the use of inhibitors (MEASO) and (MEASL) at concentrations of 50.75 and 100 ppm for 20 hours are shown in Figure 1 and 2.



Fiqure 1. Change of corrosion rate with respect to time for carbon steel C1018 in a 1% solution of NaCl saturated with CO_2 at concentrations of the MEASO inhibitor of 50-100 ppm

As can be seen from Figure 1, the corrosion rate in the absence of an inhibitor tends to increase over time. An increase in the corrosion rate in the initial period of testing is attributed to the galvanic effect between the phases of ferrite and cementite (Fe_3C), which are an integral part of steel in the non-oxidized state and accumulate on the surface after dissolution of ferrite (α-Fe) in Fe_2 + [9]. Fe_3C is known to be less active than the ferrite phase. Thus, ferrite acts as an anode, while cementite as a cathode with the accumulation of hydrogen released during the corrosion process.

Within 1.5 hours after the introduction of the MEASO inhibitor in an amount of 50-100 ppm, the corrosion rate of the test plate begins to decrease significantly, the most noticeable decrease is observed for a MEASO concentration of 100 ppm. Approximately after 4-5 hours, the corrosion rate of the tested samples decreases more smoothly, however, the braking efficiency for 100 ppm concentration of the MEASO inhibitor is 92.61% and far exceeds those for concentrations of 50 and 75 ppm (Table 3).

A somewhat different picture of a decrease in the corrosion rate of steel plates is observed when identical concentrations of the MEASL inhibitor are used (Figure 2).

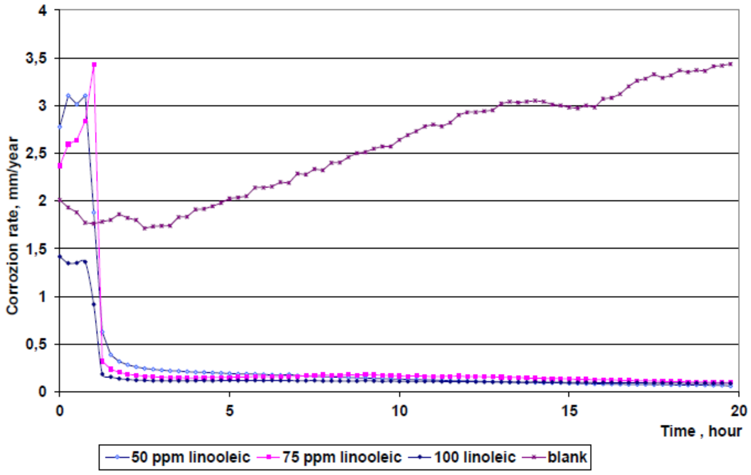


Figure 2. The change in the corrosion rate with respect to time for carbon steel C1018 in a 1% solution of NaCl saturated with CO_2 at concentrations of the MEASL inhibitor of 50-100 ppm

When using the MEASL corrosion inhibitor, in contrast to the MEASO inhibitor having two double bonds in the carbon chain, for all three concentrations, a decrease in the corrosion rate to 0.28-0.06 mm / g is achieved with a braking effect of up to 91.8 -98.20 % (Table 3).

Table 3. The characteristics of the process of corrosion of steel C1018 in a 1% solution of sodium chloride saturated CO_2 with and without corrosion inhibitors MEASO and MEASL

Inhibitor	Inhibitor concentration, ppm	Corrosion rate, mm/g	Braking efficiency,%	Total metal loss,mgcm^2/h	Surface coating values, θ
-	0	3,5	-	6,48 x10^{-3}	-
MEASO	50	1,50362	57,03	3,69 x10^{-3}	0,570
	75	0,62473	82,15	1,16 x10^{-3}	0,821
	100	0,25848	92,61	4,8 x10^{-4}	0,926
MEASL					
	50	0,28768	91,78	5,1 x10^{-4}	0,918
	75	0,09316	97,3	1,8 x10^{-4}	0,970
	100	0,06234	98,2	1,1 x10^{-4}	0,982

4. Conclusion

As a result, according to the data given in Table 3, it can be concluded that the MEASL corrosion inhibitor is more active in slowing down the corrosion of steel platinum than the MEASO inhibitor. The difference between these inhibitors is that the MEASL inhibitor molecule contains two double bonds, while in the molecule of the MEASL inhibitor they are not, as evidenced by the values of the iodine number of these compounds are given in Table. 2. Therefore, the effectiveness of the studied inhibitors depends on both adsorption of functional groups and adsorption of molecules on a double bond.

5.References

1. Groysman, A .; Street, D .: Corrosion in systems for storage and transportation of petroleum products and biofuels. In: Proceedings of the NACE Corrosion (2014)
2. Finšgar, M .; Jackson, J .: Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. Corros. Sci. 86, 17–41 (2014) https://doi.org/10.1016/j.corsci.2014.04.044
3. Olvera-Martínez, M.E .; Mendoza-Flores, J .; Genesca, J .: CO2 corrosion control in steel pipelines. Influence of turbulent flow on the performance of corrosion inhibitors. J. Loss Prev. Process ind. 35, 19–28 (2015) https://doi.org/10.1016/j.jlp.2015.03.006
4. Vigdorovich V.I. , Tsygankova L.E. Inhibition of hydrogen sulfide and carbon dioxide corrosion of metals. Universalism of inhibitors. M.: Publishing house KARTEK. (2011)
5. Hany M. Abd El-Lateef, V. M. Abbasov, L. I. Aliyeva, T. I. Ismayilov, E. E. Qasimov, T. U. Ahmadov, Novel anionic surfactants based on cottonseed oil and their corrosion inhibition efficiency for carbon steel in CO_2 saturated solution . Global J. Phys. Chem. 3(14), 1-12. (2012)
6. Hany M. Abd El-Lateef, Vagif M. Abbasov, Leylufer I. Aliyeva, E. E. Qasimov, I. T. Ismayilov, Ahmed H. Tantawy, Application of Complex Surfactant Based on Cottonseed Oil as CO_2-Corrosion Inhibitor and for Removing Thin Oil Slicks from Water Surface . Caspian Journal of Applied Sciences Research, 1(9), 57-67. (2012)
7. V. M. Abbasov, *Hany M. Abd El-Lateef, L.I. Aliyeva, I.T. Ismayilov, E.E. Qasimov, T.U. Ahmedov, Novel anionic surfactants based on cottonseed oil and their corrosion inhibition efficiency for carbon steel in CO_2 saturated solution .Processes of petrochemistry and oil-refining, 2(50),112-135 (2012).

PP-I-4

EFFECT OF TEMPERATURE ON HYDROCRACKING OF VACUUM GASOIL

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Abstract. The aim of done work was to obtain environmentally friendly diesel fuel and high-quality raw materials for catalytic cracking process by hydrocracking of vacuum gas-oil obtained from Baku oils in the presence of modified aluminosilicate catalyst containing Ni, Mo. The hydrocracking process of vacuum gas-oil conducted at 3-8 MPa pressure, 400-450 °C temperature range, in a flow-type Hungarian unit with a reactor capacity of 200 ml. The liquid product obtained from the process distillated to gasoline (o.p.-200ºC), diesel fraction (200-360 ºC) and residue > 360 ºC in an atmospheric vacuum unit. Each fraction studied separately. The effect of regime parameters on hydrocracking process of vacuum gas-oil was studied. During the investigations of temperature on hydrocracking process it was revealed that, when temperature rises from 400 to 450°C the yield of diesel fraction increases from 35 to 50 % wt. The yield of gasoline fraction constitutes 0-6 % wt. and the produce of residue fraction decreases from 65% to 45%. With increasing of temperature from 400 ºC to 450 ºC the amount of sulphur decreases from 0,01 % to 0,005 % wt and iodine number from 9 to 5 g J_2/100 g in composition of diesel fraction.

Keywords: vacuum gas-oil, hydrocracking, diesel fraction, aluminosilicate catalyst, cetane number.

1.Introduction

In recent years, a rapid increase in diesel engines is being observed due to economic and ecological challenges. In connection with the transition to diesel fuel in many countries, it is necessary to meet the needs of the country's economy in diesel fuel. Hydrocracking is the most effective of the secondary refining processes to obtain the diesel fraction from heavy crude oil. Hydrocracking is considered not only as an additional source for the production of diesel fraction, but also as one of the most effective methods for the hydro-enrichment of catalytic cracking raw materials [1].

The main factor in the successful implementation of hydrocracking process of various raw materials in the industry is the correct choice of catalysts. In addition to their high hydrodesulfurization activity, these catalysts must have high hydrogenation and decomposition ability at low temperatures to fully hydrogenate unsaturated, diene and partially polycyclic aromatic hydrocarbons. Listed hydrocarbons not only reduce the thermal stability of fuels, but also cause rapid coking of catalysts and technical equipment during subsequent processing. [2, 3].

For the realizing of hydrogenation function, oxides or sulfides of VI and VIII group elements of periodic table are being used in individual form or in the form of various compounds [4-5]. Effective catalysts of hydrocracking process contain molybdenum, nickel, cobalt, tungsten, precious metals – platinum, palladium and other metals. The most widespread acid carriers are– amorphous and crystal inorganic oxides: aluminum oxide, amorphous aluminum silicates and magnesium silicates, crystal aluminum silicates [6- 8].

Cobalt or nickel with molybdenum over the porous carrier (mainly aluminum oxide) and sometimes nickel-tungsten sulfide are being used as catalysts in most modern processes. Usually, catalysts are produced in the form of oxides; in the hydrogenation of sulphurous raw material cobalt (or nickel) and molybdenum oxides completely or partially pass to sulfid form. In many cases after catalyst loading it being sulfurized with hydrogen sulfide or sulfur compounds and hydrogen [9].

The most widely used catalysts in hydrocracking processes were alumocobaltmolybdenum catalysts, which are catalysts of hydrotreating processes. These catalysts, which have been proven in practice, have been gradually replaced by more efficient and inexpensive alumonickelmolybdenum catalysts. The latter has high decomposition, hydrogenation and denitration properties when used for heavy raw materials, and high selectivity and low inclination to coking when used for medium distillates [6-8]. Many attempts have been made to optimize the amount of active components and improve their quality properties by modifying these types of catalysts.

In this regard, the study of the hydrocracking process of heavy oil products in the presence of new zeolite catalysts modified with Ni, Mo metals has a great importance.

In presented article, the aim of done work was to obtain environmentally friendly diesel fuel and high-quality raw materials for catalytic cracking process by hydrocracking of vacuum gas-oil obtained from Baku oils in the presence of modified aluminosilicate catalyst containing Ni, Mo.

2.Experimental Part

Qualitative characteristics of vacuum gasoil obtained from Baku oils are shown in table 1. As seen from table, vacuum gasoil contains up to 15% vol. heavy diesel fraction.

The hydrocracking process of vacuum gas-oil conducted at 3-8 MPa pressure, 400-460 °C temperature range, 0,7-2,0 h^{-1} weight hour space velocity, at H_2: raw material = 1000 *l*/*l* ratio, in a flow-type Hungarian unit with a reactor capacity of 200 ml (Figure 1).

The catalyst (200 g) was pelletized, placed into the reactor (1), and activated under air flow at 500 °C for 3 h, followed by nitrogen purge to remove oxygen from the system and reduction under a hydrogen gas flow at 400 °C for a few days, until no moisture is observed at the outlet of the reactor (tested by filter paper). Hydrogen gas is used to sustain the pressure inside the reactor and inhibit coke formation on the catalyst. High-sulfur gasoline is pumped to the reactor from the reservoir (2) with varying liquid hourly space velocities in the range of 0.7−2 h−1, where it is mixed with H_2 from a cylinder (4). The pressure of the hydrogen gas was set at 3-8 MPa. The reactor is made of stainless steel and set in a block of aluminum bronze, which provides a uniform temperature distribution across its volume during the overall process. The temperature in the reactor was regulated by an electronic potentiometer and set the range of 400−450 °C. The reaction products and leftover hydrogen gas proceed to the shell-andcoil condenser (5) from the bottom of the reactor and then further to the ice-cooled separator−receiver (6), in which the separation of liquid hydrocarbons from gaseous products of reaction and hydrogen takes place. Liquid products are collected from the bottom cock of the receiver.

The liquid product obtained from the process distillated to gasoline (o.p.-200^{0}C), diesel fraction (200-360 ^{o}C) and residue > 360 ^{o}C in an atmospheric vacuum unit. Each fraction studied separately.

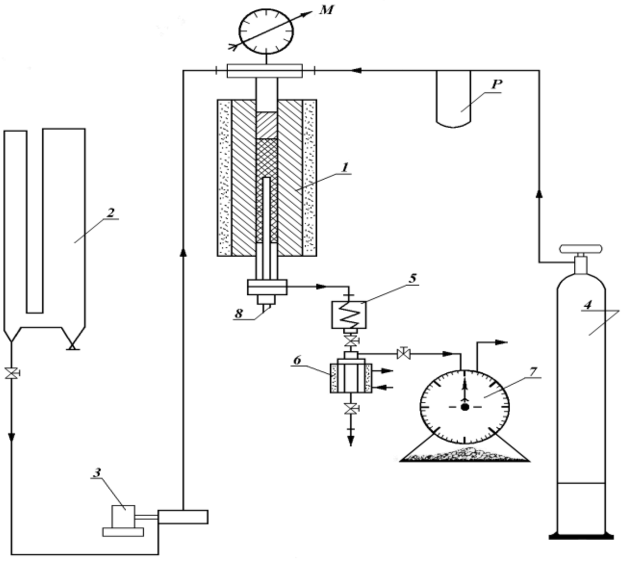

Fig. 1. Scheme of the experimental unit for hydrocracking of vacuum gas-oil: (1) reactor, (2) feed vessel, (3), feed pump, (4) H_2 gas cylinder, (5) condenser, (6) separator−receiver, (7) gas flowmeter, (8) thermocouple, (P) pressure regulator, and (M) pressure gauge.

The catalyst was regenerated under air flow at 500 °C for 3 h as described in ref [10].

Compositions of the products were analyzed using gas chromatography (AutoSystem XL, PerkinElmer). Chromatographic separations were achieved using helium gas in a Zebron ZB-1 capillary column coated with a dimethyl polysiloxane polymer as the stationary phase. Octane numbers were calculated on the basis of compositions of the gasoline fractions obtained from gas chromatography (AutoSystem XL, PerkinElmer). Distillation fractions were determined with a crude oil distillation system (B/R Instruments Company, Easton, MD, U.S.A.) by ASTM D2892 and ASTM D86 standards. Compositions of gasoline fractions were analyzed using gas chromatography (AutoSystem XL-230, PerkinElmer), Fourier transform infrared spectroscopy (FTIR, Infralum FT-02), and nuclear magnetic resonance (NMR, Tesla BS-487C). The sulfur content in gasoline was determined with a SLFA-20 X-ray fluorescence sulfur-inoil analyzer (Horiba Scientific) by the ASTM D4294 method. Densities of the gasoline were measured with density meters (DMA 4500 M, Anton Paar) by the ASTM D5002 method. The iodine number was determined by reacting the sample with iodine in chloroform solution and titrating residual iodine with sodium thiosulfate as described in ref [11].

Table 1. Qualitative characteristics of vacuum gasoil obtained from Baku oils

İndices	Vacuum gasoil
Density, 20 °C, kg/m^3	916.3
Fraction content, °C	
i.b.p.	280
< 330 °C, % vol.	5
< 360 °C, % vol.	15
end of boiling	500
Temperature, °C	
freezing (closed bowl)	0
ignition (closed bowl)	165-180
Coking, % wt.	0,23
Viscosity, 50 °C	17,8
Sulfurization, % vol.	32
Content of sulphur, % wt.	0,26
Asphaltenes	Not
Hydrocarbon content with using of adsorption method; % wt.	
Paraffin-naphthenes	70,7
Light aromatics	8,1
Middle aromatics	9,5
Heavy aromatics	10,5
Resins	1,2

3.Results and Discussion

Effect of regime parameters on hydrocracking process of vacuum gasoil in the presence of alumosilicate catalyst modified with Ni and Mo metals was investigated. Influence of temperature on hydrocracking process was studied at 400-450°C range. The results of hydrocracking process conducted at different temperatures are given in table 2.

From the analysis of obtained results it is clear that, at 400°C hydrocracking process passes weakly and therefore the yield of diesel fraction constitutes minimum 35% wt. The yield of diesel fraction increases with further increasing of temperature. It was observed that conversion degree of raw material rises with increasing of temperature and decreasing of weight hour space velocity (weight hour space velocity 1 h^{-1}). As, the yield of diesel fraction rises from 35 to 50% wt. with increasing of temperature from 400 to 450°C. The yield of gasoline fraction constitutes 0-5 % wt., the produce of residual fraction lessens from 65% to 45% wt.

Table 2. Temperature dependence of indices of hydrocracking process of vacuum gasoil obtained from Baku oils (P = 6,0 MPa, H_2 : raw material = 1000 *l/l*, V = 1,0 h^{-1})

Indices	Temperature, °C				
	400	420	430	440	450
Density, 20 °C, kg/m^3	877	873	854	863	858
Fraction content, °C					
i.b.p.	164	123	96	92	88
10 %	282	270	195	195	185
30 %	340	330	300	286	275
50 %	-	360 °C –47%	346	324	319
60 %	-	-	360 °C – 55 %	359	332
70 %	-	-	-	-	355

Yield of fraction, % wt:					
Also i.b.p.-200 °C	-	-	2	3	5,0
200-360 °C	35	39	45	49	50,0
> 360 °C	65	61	53,0	48,0	45,0
Iodine number, gJ_2/100g product	9,0	4,0	4,0	4,5	5,0
Sulfurization of obtained liquid product, % vol.	26	24	20	23	25
Sulphur content, % wt.	0,01	0,007	0,006	0,006	0,005

With increasing of temperature from 400 °C to 450 °C the content of sulphur decreases from 0,01 % to 0,005 % wt. in diesel fraction, iodine number lessens from 9 to 5 g J_2/100 g.

The qualitative characteristics of diesel fraction obtained from hydrocracking process of gasoil, conducted in the presence of alumosilicate catalysts modified with Ni,Mo, are given in table 3.

From qualitative characteristics of diesel fraction obtained from hydrocracking of vacuum gasoil it is clear that, temperature increase significantly influence to qualitative characteristics, especially hydrocarbon content of diesel fraction. As, with increasing of temperature the yield of aromatic hydrocarbons in diesel fraction at first decreases, at 430°C constitutes minimum, further rise of temperature causes to the gradually increase of the yield of aromatic hydrocarbons (table 3). This is due to the fact that as the temperature rises, the direction of the reaction changes to hydrogenation and hydrodealkylation path. According to qualitative characteristics of liquid product obtained from hydrocracking process, with rising of temperature to 430 °C the density of obtained liquid product, its sulfurization and the content of sulphur decrease.

Table 3.Qualitative characteristics of diesel fraction (200-360 °C) obtained from hydrocracking of vacuum gasoil of Baku oils (P = 6,0 MPa, H_2 : raw material = 1000 *l*/*l*, V = 1,0 h^{-1})

Indices	**Temperature, °C**			
	420	430	440	450
Density, 20 °C, kg/m^3	854,0	843,0	847,9	853
Fraction content, °C				
i.b.p.	146	157	166	165
10 % boiling temperature	154	168	181	211
50 % boiling temperature	298	272	271	270
end of boiling	361	360	360	362
Iodine number, g J_2/100 g	2,5	3,7	4,5	4,3
Sulfurization, % vol.	25	20	22	24
Temperature, °C				
Freezing	-20	-25	-23	-24
Ignition	-	70	75	-
Sulphur content, % wt.	0,006	0,005	0,005	0,004
Coking, % wt.	-	0,032	0,030	0,028
Ash content, % wt.	not.	not.	not.	not.
Hydrocarbon content, % wt:				
Paraffins	42,4	49,4	48,2	46,2
Naphthenes	31,3	27,9	27,0	26,6
Aromatics	25,3	21,2	23,0	25,0
Unsaturated	1,0	1,5	1,8	2,2
Molecular weight	203	200	202	190
Cetane number	47	48,5	48	47
Kinematic viscosity, 20 °C, mm^2/s	5	4,5	4,3	4

Thus, the optimal regime parameters of investigated hydrocracking process (in the presence of new synthesized alumisilicate catalysts), for the purpose of obtaining diesel fraction from vacuum gasoil and getting qualitative raw material for catalytic cracking, are these: temperature - 430°C, pressure 6 Mpa, weight hour space velocity of crude material 1,0 h^{-1}. Meantime, the yield of diesel fraction, gasoline fraction (fr. i.b.p.-200°C), and residual fraction (fr> 360 °C) - qualitative raw material for catalytic cracking process constitute 45, 2 and 53,0% wt., respectively.

The octane number of gasoline fraction obtained from hydrocracking of vacuum gasoil is 73-74 (motor method) and it can be used as raw material in reforming process. As, it was defined that in composition of gasoline fraction the content of sulphur and unsaturated hydrocarbons is 0,0001 % wt. and 0%, respectively.

The cetane number of diesel fraction obtained from hydrocracking process (which is conducted in the presence of alumosilicate catalyst modified with Ni, Mo at optimal regime parameters) of vacuum gasoil (from mixtures of Baku oils) is equal to 47-48 p. and can be added as a component to diesel fuels according to qualitative indicators.

The residual fraction obtained from hydrocracking of vacuum gasoil (fr> 360 °C) has some advantages in comparison to initial raw material. As, coking number is 0,02% wt. against to 0,09% wt., the amount of sulphur is 0,015% wt. against to 0,01% wt. and the quantity of aromatic hydrocarbons is 26% wt. against to 34% wt. The residual fraction can be used as high quality raw material for catalytic cracking process.

4.Conclusions

- Thus, the possibility of obtaining of high quality diesel fraction and quality crude material for catalytic cracking process from hydrocracking of vacuum gasoil (obtained from mixture of Baku oils) in the participation of alumosilicate catalyst modified with Ni, Mo metals, was shown.
- It was revealed that depending on temperature the yield of diesel fraction obtained from hydrocracking of vacuum gasoil increases from 35% to 50% wt. The cetane number of getting diesel fraction constitutes 47-48 (by motor method).
- Depending on temperature, 0-5% wt. gasoline fraction is obtaining from hydrocracking of vacuum gasoil. The octane number of obtaining gasoline constitutes 73-74 (by motor method) and can be used as raw material in reforming process.
- The residual fraction (fr> 360 °C) obtained from hydrocracking of vacuum gasoil has some advantages in comparison to initial raw material and it can be used as high quality crude material for catalytic cracking process.

5.References

1. Rustamov, M.I., Abad-zade, Kh.I., KAsimova, Z.A., Mukhtarova, G.S. “Production of pollution-free motor gasoline in Refinery named after H.Aliev”. Processes of petrochemistry and oil-refining (PPOR) 26 (3), 36-42 (2006)
2. Nasirov, I.R., Gureev, A.A:. Influence of sulfide agent on catalytic activity of Al-Co-Mo catalyst of hydrocracking. Oil chemistry 40 (4), 295-298 (2000)
3. Shakun, A.N., Yasyan, Yu.P., Litvinova S.M.: Some aspects of stability of new zeolite catalysts of selective hydrocracking. Chemistry and technology of fuels and oils 2, 39-40 (2001)
4. Magendie, G., Guichard, B., Chaumonno,A., Quoineaud, A., Legens, C., Espinat, D.: Toward a better understanding of residue hydroconversion catalystsusing NiMo catalysts supported over silica grafted Al_2O_3. Applied Catalysis A: General, 468, 216– 229 (2013) https://doi.org/10.1016/j.apcata.2013.08.044
5. Carolina, L., Jorge, A., Guillermo, C.: Effect of alumina and silica–alumina supported NiMo catalysts on theproperties of asphaltenes during hydroprocessing of heavy petroleum., Fuel 138, 111–117 (2014) DOI: 10.1016/j.fuel.2014.08.023
6. Radchenko, E.D., Nefedov, B.K., Aliev, R.R.: Industrial catalysts of hydrogenation processes of refining. M., Khimiya, 224 p. (1987) (in Russian)
7. Kimbara, N. New type of LIN support for hydroprocessing catalyst . Catalysts letters 6 (3), 409-416 (1990)
8. Scheffer, B., Arnolgu, P., Moulum, I.A.: Sulfidability and hydrodesulfurization activity of Mo catalysts, supported on alumina, silica and carbon. Journal of Catalysis 112 (2), 516-527 (1998)
9. Chary, K.U.R.: Highly active alumina-supported molybdenum sulphide and related hydroprocessing catalysts derived from precipitation from homogeneous solution . Journal of Molecular Catalysis 63 (2), 121-124 (1990)
10. Abbasov, V., Ibrahimov, H., Mukhtarova, G., Rustamov, M., Abdullayev E.: Adsorptive desulfurization of the gasoline obtained from low pressure hydrocracking of the vacuum residue using a nickel/ bentonite catalyst. Energy Fuels 31, 5840−5843 (2017) DOI: 10.1021/acs.energyfuels.7b00081
11. Abbasov, V., Mammadova, T., Aliyeva, N., Abbasov, M., Movsumov, N., Joshi, A., Lvov, Y., Abdullayev, E.: Catalytic cracking of vegetable oils and vacuum gasoil with commercial high alumina zeolite and halloysite nanotubes for biofuel production. Fuel 181, 55− 63 (2016) https://doi.org/10.1016/j.fuel.2016.04.088

PP-I-5

SEPARATION OF NAPHTHALENE FROM LIQUID PYROLYSIS PRODUCTS FORMED ON THE EP-300 UNIT AND ITS BASIS SYNTHES

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Abstract: Our Republic produces a large number and a large count of products of the petrochemical industry and organic substances. The presence of the richest hydrocarbon reserves in our country encourages the use of petroleum residues as raw materials for industrial production.

The EP-300 unit is currently operating at the Ethylene-polyethylene plant under the SOCAR production Association. The plant is undergoing a pyrolysis process, which uses liquefied low-octane gasoline produced at the SOCAR H. Aliyev oil refinery as raw material. According to the raw material obtained in the plant, along with the main products, a heavy pyrolysis resin (HPR) is also formed, called a 4-6% cubic residue.

As a result of research, it became known that the composition of HPR includes extremely valuable substances, including naphthalene and its derivatives.

For the first time, chloromethyl naphthalene and 4-ammonium salt were synthesized as a part of the cubic residue by cleaning naphthalene with trifluorbenzene. these additives were tested as multifunctional high-quality additives that improve the rheological properties of oil and are used in other fields.

Keywords: pyrolysis, naphthalene, picric acid, chloromethyl naphthalene, heavy pyrolysis resin, trifluorbenzene, clathrate, additives, paraformoldehyde, naphthylmethyl-triethyl-ammonium-chloride, molecular complex.

1.Introduction.

It is known that selective solvents are used to isolate naphthalene and other arenes from oil mixtures that have a complex composition. Extraction and extractive rectification methods are used simultaneously to separate condensed aromatic carob hydrogens from oil residues using these solvents.

Methods were developed for the synthesis of 4-ammonium salt from the reaction products and for conducting a chlorination reaction with the release of naphthalene from a heavy pyrolysis resin formed in the EP-300 unit. The isolated naphthalene, synthesized chloromethyl naphthalene and 4-ammonia salt were confirmed using physical and chemical analysis methods. The isolation of chloromethyl naphthalene allows the synthesis of other halogen organic compounds, as well as surfactants. The content of heavy pyrolysis resin, which is 4-6% of the main products and forms as a by-product, is 70-75% of the content of polytypical aromatic hydrocarbons, where the content of naphthalene exceeds 20% [7, 8].

In the research work, a comparison was made with the use of several extrogents to isolate naphthalene from the composition of cubic residues. Optimal conditions for the separation of naphthalene, the synthesis of chloromethyl naphthalene and ammonium salt 4 [6], as well as the positive and negative sides of solvents used for the separation of naphthalene [3] were studied. The main attention was paid to the economic availability of extraction solvents, their toxic properties, easy to find and return to reuse. The main advantage of solvents in them is given to picric acid and trifluorobenzene. In addition to naphthalene, the heavy pyrolysis resin contains other arenas, including anthracene, phenontren, methyl naphthalene, and other combinations. Since the amount of naphthalene in these compounds is greater than in other arenas, the research work was carried out on the basis of naphthalene [4].

In addition to obtaining surfactants from chloromethyl naphthalene synthesized on the basis of naphthalene, it can also be used as a modifier to improve the quality of tread rubber [1, 5].

2.Relevance of the work

Such rapid development of scientific and technological progress in the country and the world requires the development of new methods of petrochemical synthesis and increasing the efficiency of using oil residues. Along with this, the main issues are obtaining inexpensive additives to improve the quality of petroleum products, i.e. fuel, motor oils. In the research work, cubic wastes accumulated in the form of multi-tonnage waste are used as raw materials, isolated on the basis of the method of molecular addition of naphthalene and multifunctional high-molecular additives are synthesized on its basis. Synthesized additives improve the rheological properties of heavy paraffin oils. At this time, even in freezing weather, oil transportation is facilitated, and paraffin deposits do not occur in the pipes. At the same time, adding surfactants used in firefighting from the obtained additives to the composition provides greater foam formation and a longer stay of the resulting foam. In addition, when these additives are added to engine oils, the freezing point of the oil is sharply reduced and rapid engine failure is prevented.

Chloromethyl naphthalene, synthesized on the basis of naphthalene extracted from liquid pyrolysis products, can be used as a modifier in the vulcanization process to increase the resistance of tread rubber to friction and provide thermal stability used in the tire industry.

Statement of question

Heavy pyrolysis resin is characterized by high aromaticity and the absence of heterocyclic compounds in its composition, as well as a unique chemical composition [1, 5]. The amount of the composition of heavy pyrolysis resin with components is determined by the Markusson method.

Enrichment of the resin composition with multi-components makes it difficult to use it. For this reason, the effective use of resin requires the release of valuable substances contained in it.

The hydrocarbon composition of heavy pyrolysis resin using gas-acid chromatography LHM-80 MD and other modern physical and chemical analysis methods is reflected in table 1.

Table 1. Hydrocarbon composition of heavy pyrolysis resin

Hydrocarbons	Before treatment (mass %)	After treatment (mass %)
Naphthalene	20.0	27.0
α,β-methylnaphthalene	5.28	11.19
α,β- ethylnaphthalene	3.00	4.05
1,7- dimethylnaphthalene	1.47	1.99
1,3-+1,6- dimethylnaphthalene	4.72	6.38
2,3- dimethylnaphthalene	1.24	1.68
1,4- dimethylnaphthalene	0.59	0.80
1,5- dimethylnaphthalene	0.70	0.95
diphenyl+methyldiphenyl	4.58	7.81
Acenaphtane	6.13	8.28
Fluorine	0.80	1.08
Phenantrane	4.09	5.53
Anthracene	1.42	1.92
Other compounds	4.78	20.34
∑ unsaturated compounds	37.00	1.0

LXM– 80 MD gas-liquid chromotography indicators are as follows:

Length of the sleeve – 2 m. Adsorbent – polyethylene glycol, inert gas carrier-nitrogen.

The content of chloromethyl naphthalene synthesized on the basis of naphthalene extracted from resin is higher than 16%, and was confirmed using the method of elementary analysis. This also makes it possible to obtain organohalogen compounds other than chloromethyl naphthalene, and once again proves that research work is of scientific significance [2].

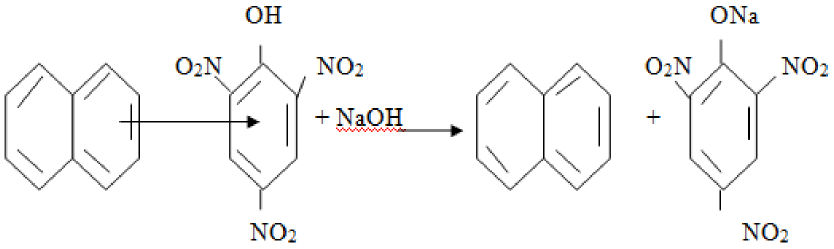
For the first time, together with naphthalene (1), the isolation of anthracene and phenanthrene was confirmed using the clathrate method [1, 5, 9].

Condensed aromatic hydrocarbons were isolated from the resin using picric acid (2) (trinitrophenol). Aromatic hydrocarbons are deposited as crystalline compounds from the resin, forming stable compounds of clathrate (3) with picric acid. Since the reaction is a reversible process, an optimal temperature of 50^0C weakens the clathrate adsorption process, while at a temperature below 50^0C the complex decays [10]. The clathrate reaction looks like this:

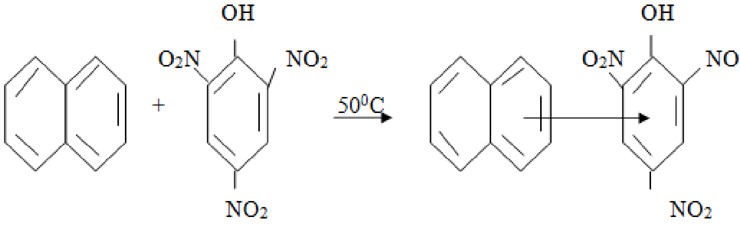
Since naphthalene acts as a donor and picric acid as an acceptor, naphthalene forms a stable compound with picric acid, and clathrates are easily separated from the resin by a solvent.

To separate naphthalene from clathrate it is neutralized by a molecular complex of alkalis:

Sodium picrate (4),



(1) (4)



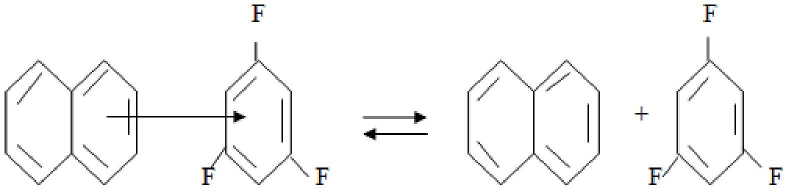
(1) (2) (3)

formed as a result of the neutralization reaction, is again converted to picric acid by the action of sulfuric acid and returned to reuse, which leads to the prevention of loss of picric acid:

Polycyclic does not pass into the free sodium picrate (4) condensate layer, which does not form clatrates with aromatic hydrocarbons. The only negative aspect of the implementation of the process of glatrate formation with picrinic acid is the formation of industrial discharge water when using sulfuric acid in the neutralization process.

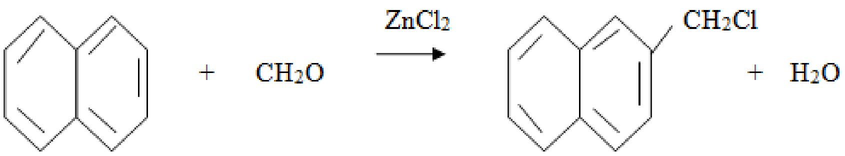
Unlike other methods, the separation of aromatic hydrocarbons condensed into a solid pyrolysis resin was first performed on the basis of a molecular complex (1,3,5) using trifluorbenzene (5):

The main advantage of using trifluorbenzene is that it is easily removed from the system, forming weak clathrates with aromatic carbohydrates, and trifluorbenzene does not need to be re-processed. An interesting and practical value of the work also lies in the fact that for the grinding of clathrates of this type, it is not necessary to use alkalis and other reagents. Their accounting proves the environmental friendliness of the process. Of resin through trifluorobenzoic is recommended other arenas.



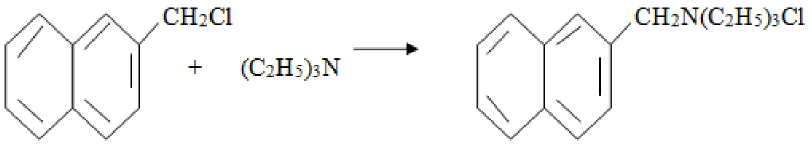
(5)

For targeted use of naphthalene extracted from the solid pyrolysis resin formed as a by-product of the EP-300 installation, β-chloromethyl naphthalene (6) was synthesized with the participation of para-formaldehyde and a zinc chloride catalyst using the classic Blanc method [2, 9, 10].



(5)

The synthesis of β-chloromethyl naphthalene from 4 ammonia salts, which are scientifically interesting and large industrial products, including naphthylmethyl-triethyl-ammonium chloride (7), was carried out by the following reaction:



(6) (7)

The reaction was carried out using triethylamine, and the resulting 4-ammonia salt has a high surface activity.

Application of physical and chemical analysis methods

The synthesized substances were confirmed using gas-hydraulic and thin-layer chromatography (plate silhouette) and nuclear magnetic resonance (NMR). It turned out that the center of the multiplet signal of 9 protons of the atomic nucleus is 7.1 m.s. [7]. Protons of the chloromethyl group manifest themselves as singlets. 7.1 m.s. the intensity of the signal generated in the field is also 9 protons.

In the study of heavy pyrolysis resin, infrared spectral analysis was used, and it became known that the main part of the resin composition consists of conical benzene rings and its derivatives.

Research of the IQS-SPECORD-80 Begmann device.

Characteristic absorption strips were observed during the IQS analysis of the 4-th ammonium salt. The presence of a signal 3262 cm^{-1} in this combination proves the presence of the NH-group.

3.Experimental part

Picric acid obtained from Merck was used as a complex absorber for the separation of naphthalene from heavy pyrolysis resin. 100 g of heavy pyrolysis resin is dissolved in 1 liter of acetone, and the asphalt contained in the resin is immediately destroyed and separated from the solution. Then 7.5 g of picric acid is added to the solution released from the precipitate, stirring at room temperature. The mixture is heated, stirring for 2 hours at 50^{0}C, and the mixture is cooled to 10^{0}C. At this time, the polycyclic aromatic hydrocarbons in the residue are crystallized and destroyed by a molecular complex formed under the action of picric acid. After the crystals separate from the liquid and dissolve in the ether, 5% NaOH is neutralized at room temperature for 30 minutes and the complex disintegrates. At this time, sodium picrate passes through the water layer, and aromatic hydrocarbons are released into the sediment. Polycyclic aromatic hydrocarbons separated as a mixture are washed off with a solution of K_2CO_3 and distilled, then separated into separate hydrocarbons with a purity of 99.9%.

Physical parameters of naphthalene extracted from the remains of the cube coincide with the data in the literature.

Preparation of β-chloromethyl naphthalene. In a three-layer round sausage with a volume of 500 ml, equipped with a mechanical blender, 32 g of solid pyrolysis resin, 13.75 g of paraformaldehyde, 107 g of hydrochloric acid and 3 g of zinc chloride as a catalyst are placed. The mixture is mixed at a temperature of 70^{0}C for 6 hours. The reaction occurs with the absorption of light. At the end of the chlorination process, the reaction mass is cooled to 15^{0}C, 10% through K_2CO_3, washed 2 times with distilled water and becomes neutral. The resulting crystalline solution is dried in a $CaCl_2$ desiccator for 8 hours. The product yield with 99.9% purity is 70%. When synthesized β-chloromethyl naphthalene is heated in a high vacuum (mercury column 105-107^{0}C / 0.2 mm), it turns into a colorless crystalline substance. The physical parameters of the obtained β-chloromethyl naphthalene correspond to the data in the literature.

Preparation of naphthylmethyl-triethyl-ammonium chloride. In an oval flask of 100 ml, equipped with an axoudalitel and a flywheel, 10.5 g of β-chloromethyl naphthalene and 55 ml of triethylamine are placed. The reaction mixture is quickly mixed and brought to a boil. Full absorption of β-chloromethyl naphthalene indicates that the reaction is complete, which is controlled by thin-layer chromatography.

A quaternary ammonium salt with a melting point of 178^{0}C is obtained, which is confirmed by nuclear magnetic resonance.

4. Conclusion

1. From the composition of heavy pyrolysis resin, which is still not used effectively, formed as a cubic residue at the plant “Ethylene-polyethylene”, a new method isolated naphthalene with high purity.
2. Synthesis of β-chloromethyl naphthalene was carried out by applying the well-known method of Blanc from naphthalene isolated by complex adhesion.
3. With the purposeful use of β-chloromethyl naphthalene, a 4-ammonium salt was obtained, which has a high surface activity, scientific, practical and industrial significance.

The resulting ammonia salt 4 was tested on 25^0C taken from the Muradkhanli field, on heavy oil with a viscosity of 4.28 minutes. Thus, the viscosity of the oil fell by 2.64 minutes, when 100 ml of heavy oil formed 2 ml of 4-x ammonia salt.

Offer

It is more appropriate to use synthesized β-chloromethyl naphthalene. Thus, the synthesis of other halomethyl derivatives of naphthalene by creating an interphase catalysis.

5.References

1. F.M. Sadigov, Z.K. Magerramova, G.N. Hajiyev, N.I. Heydarli, G.G. Hasanzade, I.G. Mammadova, N.S. Sadigova. "Combination of pyrolysis process mode and high-quality composition of heavy resin”, Azerbaijan chemical journal, № 4, 2016.
2. Bogamolov A.I., Gaile A.A., Gromova V.V. Chemistry of oil and gas. - L.: Chemistry, 1989. – 424p.
3. Brautman L. Compositional materials. Moscow: Chemistry, 1978, 283p.
4. Sh.Z. Goyushov. “The release of phenanthrene from the wastes of petrochemical plants and synthesis on its basis”. "Ecoenergetics" Scientific and Technical Journal, №.1, 2019, pp. 38-42.
5. Goyushov Sh.Z., Agayeva M.A., Movlaev I.G. "Composition based on butadiene-styrene rubber modified with enriched heavy pyrolysis resin". “Modern sciense”. Moscow, № 05(2), 2019, pp.182-186.
6. Movsumzade M.M., Goyushov Sh.Z. Separation of polycyclic condensed aromatic hydrocarbons from the remains of petrochemical industries // Azerbaijan chemical journal. 2009, №3. - P.115-118.
7. Sh. Z. Goyushov, M.M. Movsumzade, L.R. Makhmudova, A.L. Shabanov. Isolation of condensed aromatic hydrocarbons from the resin formed during pyrolysis of the gasoline fraction and syntheses based on them // oil refining and petrochemistry. -2015. -№2. - P.21-23.
8. Bazhenov S.L. Mechanics and technology of composite materials. Moscow: Chemistry, 2014, p.325.
9. Kamyanov V.F., Golovka A.K., Kurakolova E.A. and others. High-boiling aromatic hydrocarbons of oils // Reprint. - Novosibirsk: Institute of petroleum chemistry SOAN USSR, -1982, - p.265.
10. Sh.Z. Goyushov. Synthesis and prospects for the use of alkylmethyl naphthalenes // Azerbaijan chemical journal. - 2011, - № 2, - pp. 163-165.

OR-I-5

NITROGEN CONTAINING ALKYLPHENOLATE ADDITIVE FOR MOTOR OILS

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Abstract. The results on synthesis and research of high alkaline alkylphenolate AKI-137 additive have been introduced. AKI-137 additive is a carbonated calcium salt of the condensation product of dodecylphenol, formaldehyde, ammonia and 4-aminopyridine acid. Due to the presence of 3 nitrogen atoms and phenolate groups, the additive shows high anticorrosion, antioxidative and detergent properties. Using AKI-137 additive and commodity additives the M-10G$_2$ motor oil has been developed that by their physical-chemical and functional properties meet the standards.

Key words: dodecylphenol, formaldehyde, ammonia, 4-aminopyridine acid, additive, motor oil.

1.Introduction

The improve ement of the design of internal combustion engines leads to increased demands on the quality of motor oils.

The quality increase of motor oils with the help of effective additives is one of the more progressive methods that are used in obtaining high quality motor oils.

In composition of modern motor oils as one of the main components a significant part is given to detergent-dispersant additives.

This group of additives includes alkylphenolates, sulphonates and alkylsalicylates. Alkylphenolate additives are found in most modern motor oils. This is due to the availability of raw materials, simple technology of production and multifunctionality of alkylphenolate additives [1-3].

Up to the middle of 1990 in the republics of CIS, most of the alkylphenolate type detergent-dispersant additives produced in industry were barium containing products (БФК, ИХП-101, ЦИАТИМ-339 and others). Low alkalinity and high ash content of these additives were the main reason for the reduction or cessation of production of these obsolete additives [4], that didn’t meet modern requirements and were inferior to foreign analogues (Амоко-9230, Paranox-51 and others). However they had fulfilled their mission, at that time. By using them various types of motor oils were developed. In this regard, there is an urgent need to update the range of alkylphenolate additives and improve their quality.

Analysis of scientific, technical and patent literature of the last decade showed that of particular interest are high alkaline carbonated alkylphenolates containing metal (most often calcium).

The most perspective are high alkaline multifunctional additives that in low in small concentrations at the same time improve some properties of lubricating oils [5].

High alkalinity indicates high neutralizing properties of additives [6].

The need in high alkaline multifunctional additives is due to their ability to show high neutralizing and detergent properties in composition of lubricating oils.

By introducing various heteroatoms and functional groups into the additive molecules, their antioxidant, anticorrosive and detergent properties are improved [7, 8].

It is known that among metal containing additives for oils alkylsalicylate additives that possess high detergent, thermo-oxidative and other properties have also found wide application. However, in industry they are produced by multi-stage technology, which ultimately complicates the creation of the production technology of this type of additives [9].

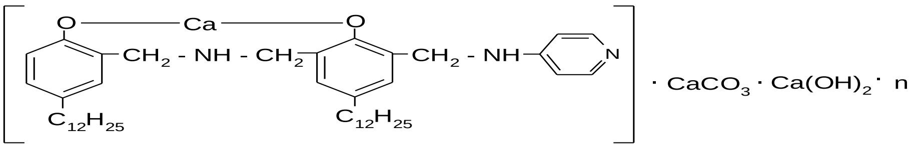
2.Experimental part

In connection with the above, we have proposed a method of obtaining new multifunctional additive for motor oils- AKI-137, which contains both the properties of alkylphenolate and alkylsalicylate additives.

The process of obtaining the additive includes the following main stages:

–sequential condensation of dodecylphenol with formaldehyde, ammonia and 4-aminopyridine;
–neutralization of condensation product with calcium hydroxide;
–carbonation of neutralization products and desiccation;
–separation of mechanical impurities by centrifugation;

The estimated formula for AKI-137 additive is:



The additive is a viscous liquid that has 140-160mgKOH/g alkaline number.

Following optimal conditions for obtaining additives: dodecylphenol: ammonia: formalin: 4-aminopyridine: Ca(OH)$_2$ – 100:30-35:30-35:4.0-4.7:35-40 were established. During carbonation 5% (of alkylphenol) ethylene glycol was used as a promoter.

3.Results and discussion

Physical-chemical and functional properties of AKI-137 additive have been studied in the composition of the M-8 oil using the following standard methods.

Anticorrosive properties were determined according to GOST 20502-75, anti-oxidative properties according to GOST 11063-77, detergent properties according to GOST 5726-2013.

Physicochemical and functional properties of test additive in composition of M-8 oil are shown in table, where for comparison foreign commodity additives ВНИИНП-714, OLOA-218A and MASК have also been tested.

Table. Physicochemical and functional properties of alkylphenolate additives

Additive	Physicochemical and functional properties of additives			M-8 oil + 5% additive		
	Alkali number, mgKON/g	Sulfate ash content, %	Kinematic viscosity, at 100°C, mm^2/s	Corrosiveness(in lead plates), g/m^2	Stability by induction period of precipitation (IPP 30 h. of prec., %	Detergent properties (on PZV), point
AKI-137	148.2	15.5	66.6	1.2	absent	0.5
AKI-137	155.8	16.7	67.8	0.85	absent	0.5
ВНИИНП-714	143.0	17.2	–	6.4	absent	0.5
OLOA-218A	147.0	17.6	–	9.8	absent	0.5
MASК	140.0	16.8	–	4.5	absent	0.5

*procipitation up to 0.5% is considered absent

4. Conclusions

As can be seen on data from table under the conditions of the tests of test additive AKI-137 on anticorrosion properties surpass comparable industrial analogues, and on antioxidative and detergent properties are on the same level with them.

The improvement of exploitative properties of the additive is apparently related to the mutual influence of 3 nitrogen atoms and phenolate groups on the formation of a stable colloidal dispersion.

5.References

1. Kirichenko G.N., Glazunova V.I., Desyatkin A.A., Ibragimov A.G., Dzhamilov U.M. Synthesis of new poly-functional additives for lubricating oils // Journal of Applied Chemistry. 2009. T 82. No. 1. from 94-98
2. Moiseeva L.S. Multifunctional additives - alkylphenolates: improving production methods // Mechanical engineering technology. 2012. No. 10. c. 37-47
3. Kyazim-zade A.K., Nagieva E.A., Mamedova A.Kh., Mamedova R.A., Nasirova S.I. Multifunctional additive for lubricating oils // Azerbaijan Oil Industry. 2013. # 9. from. 59-61
4. Selezneva I.E., Levin A.Ya., Monin S.V. Detergent-dispersing additives for motor oils // Chemistry and technology of fuels and oils. 1999, no. 6, p. 39-43,
5. Selezneva I.E., Levin A.Ya., Trofimova G.L., Ivanova O.V., Budanovskaya G.A. New super alkaline alkylphenol additive for motor oils // Chemistry and technology of fuels and oils. 2009, no. 4, p. 10-12
6. Lashkhi V.L., Leimeter T, Shor G.I., Falkovich M.I. Silk number as an indicator of compatibility of additives to motor oils // Chemistry and technology of fuels and oils. 2000. No. 4. from. 10-12
7. Kazimzade AK, Nagiyeva EA, Mammadyarova HN, Gadirov AA, Ibadova SY Modification of multifunctional alkylphenolate additive // Azerbaijan Oil Industry 2016, №5, p. 44-46

8. Kazimzade AK, Nagiyeva EA, Gadirov AA, Mammadova RA, Nasirova SI New multifunctional alkylphenolate additive modification // Azerbaijan Oil Industry, 2015, №5. s. 41-43.
9. Zhurba AS, Burlakova GG, Burgov VA The efficiency of the production of additives to oils Kiev: Naukova Dumka. 1990

PP-I-7

ENUMERATING SULFATE-REDUCING BACTERIA AND SOME OTHER MICROORGANISMS IN SAMPLES OF FORMATION WATERS, OIL AND SEA WATER OF THE ABSHERON PENINSULA

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Abstract. It is known that the main cause of biocorrosion of steel and reinforced concrete port facilities, metal structures of drilling platforms, cisterns, industrial gas, oil and water pipelines under anaerobic conditions due to the formation of hydrogen sulfide (a very active corrosion agent) by sulfate-reducing bacteria cells and their consumption of hydrogen formed on the surface of iron when it comes into contact with water

Work was carried out to determine the number of sulfate-reducing bacteria and some other microorganisms in samples of formation waters, oil and sea water of the Apsheron Peninsula. and also the study of the possibility of the development of sulfate reduction due to the oxidation of organic substances present in the collected oilfield waters.

In the course of the study, a microbiological analysis of samples of formation water, oil and sea water taken from the Balakhani and Bibi-Heybat fields was carried out, the number of bacteria and fungi was determined. Enrichment cultures were also identified and described from these samples of formation water and oil.

In the course of the work, a microbiological analysis of samples taken from different layers of formation water of the Bibi-Heybat deposit was also carried out. For comparison, the amount of sulfate-reducing bacteria, common bacteria and fungi in four different layers of formation water was determined.

Keywords: biocorrosion, formation water, sulfate-reducing bacteria, microorganisms in the extraction of oil, sulfate-reducing bacteria in seawater

1.Introduction

Microorganisms (algae, bacteria, yeast and fungi) found in the aquatic environment and soil are capable of provoking serious corrosive destruction called biological corrosion (biocorrosion) [1]. They can use the metal as a food medium or release products that destroy it.

In recent years, there has been an increased interest in microbiological phenomena and their practical application in the exploration of oil reserves and production. However, excessive uncontrolled development of microorganisms leads to microbiological contamination of a specific environment and changes in the composition of oil products. These changes take place in biodeterioration processes which in turn result in significant economic losses.

In the process of oil production by use of water flooding, bacteria also along with the injected water enter the reservoir pressure maintenance system, the reservoir and the oil collection and treatment system. Increased contamination of oilfield water by various groups of bacteria leads to a decrease in the permeability of rocks, plugging of bottom-hole zones and, as a consequence, decrease in oil recovery. The vital activity of microorganisms in the oil gathering system and maintaining reservoir pressure leads to an increase in the rate of the most dangerous local corrosion of the equipment. It has been proven that the main danger is so-called sulfate-reducing bacteria (SRB). Getting into reservoirs and sedimentation tanks, bacterial cells attach to the metal surface of containers or pipelines, forming colonies, cells fixed on a solid surface are called adhesive forms of SRB, and bacteria floating in the liquid are planktonic ones. Hydrogen sulfide produced by SRB in the course of its vital activity degrades the quality and composition of oils, as a result of which their viscosity and specific gravity increase. In addition when metal interacts with hydrogen sulfide, iron sulfide precipitates are formed which in a mixture with the extinct biomass of bacteria lead to the clogging of capillaries and a decrease in the permeability of the oil reservoir. It should be noted that biocorrosion of oilfield equipment is largely caused not by plankton, but by bacterial colonies attached to the surface that form a biofilm on it.

The most common method of suppressing the vital activity of microorganisms in oil production conditions is use of organic reagents - bactericides. However, the experience of their use has shown that there are no universal bactericides. In each specific case a thorough laboratory study of the protective effect of a number of reagents on the isolated bacterial cultures is necessary [2,3].

Among the wide range of biocides available in the oil industry market, effective prevention corrosion of oilfield equipment can be provided only by reagents which are highly efficient against planktonic and adhesive SRB.

In oil reservoirs, there are common types of bacteria with biogenic corrosion processes: hydrocarbon-oxidizing, methane-forming bacteria.

Typical representatives of fungi that cause biocorrosion in different climatic zones are fungi of the genus Aspergillus, Penicillium, Fusarium, Cladosporium.

As a result of biocorrosion the oil hydrocarbons are actively subjected to microbiological destruction. Hydrocarbon molecules are distinguished by stable chemical bonds and are degraded by microorganisms only with the participation of molecular oxygen, i.e. with the participation of aerobic organisms (hydrocarbon-oxidizing microorganisms). All other physiological groups of microorganisms, in particular anaerobic ones use the metabolic products of hydrocarbon-oxidizing bacteria.

The aim of this work is the enumeration of SRB and some other microorganisms in the samples of formation waters, oil and sea water of the Absheron Peninsula and also the study of the possibility of the development of sulfate reduction due to the oxidation of organic substances existing in the collected oilfield waters.

2. Materials and research methods

In the course of the study, a microbiological analysis of samples of formation water, oil and sea water taken from the Balakhani and Bibi-Heybat Oil Fields was carried out, the amount of bacteria and fungi was determined (Table 1).

The enumeration of bacteria and fungi was carried out by sowing on a dense nutrient medium (Koch's method): for bacteria - MIA (meat infusion agar) and for fungi - WA (wort agar) were used. After seeding by use of Limiting Dilutions Analysis, the cultivation of microorganisms was carried out in a thermostat at 30-32°C for 1-3 days for bacteria, 5-7 days for fungi.

Forn enumerating SRB, the McCready table was used, quantitative accounting was carried out in the Postgate's liquid medium of the following composition, g/l; KH_2PO_4 – 0.5 ; NH_4Cl –1.0; $CaSO_4$ –1.0; $MgSO_4{\cdot}7H_2O$ – 2.0; C_2H_5ONa (50% solution) – 4.0; NaCl – 5.0

Additives (g/l):

Yeast extract (5%-solution) – 1.0
$FeSO_4{\cdot}7H_2O$ – 0.5
$NaHCO_3$ – to determine pH (pH-7.2)
$Na_2S{\cdot}9H_2O$ – 0.2

The number of SRB in formation waters was determined by use of Limiting Dilutions Analysis according to the McCready table compiled on the basis of processing numerous results by the method of variation statistics. The cultivation was carried out in a thermostat at a temperature of 30 ± 2°C. Already on the 4th day gas formation was observed, and after 3 days a black sediment appeared, which indicated the presence of SRB.

Enrichment cultures were also isolated from samples of formation water and oil.

During the study the study a microbiological analysis of the samples taken from different layers of the Bibi-Heybat Oil Field was also carried out (Table 2).

3. Results and discussion

Cultures were isolated from formation water and oil samples.

Description of cultures of the selected samples

1) *Formation Water Sample*:
1. White, round, with smooth edges, shiny, 2-4 mm diameter.
2. Pale pink, slimy, elongated, smooth, smooth edges, 7 mm length, 4 mm width.
3. Bright yellow, round, with smooth edges, slimy, shiny, 2-3 mm diameter.
4. Matte, round, orange, smooth edges, flat, 7 mm diameter.
5. Round, orange, smooth edges with a rim, shiny, 5 mm diameter.
6. Pale brown, flat, round with uneven edges, shiny, slightly convex in the middle, 3-7 mm diameter.
7. Pale yellow, glossy, with irregular edges, elongated, not symmetrical.

2) *Oil Sample*
1. Pale pink, round, shiny, 5-6 mm diameter with smooth edges.
2. Orange, round, with uneven edges, 6-7 mm diameter

3. Yellow, round, slimy with smooth edges, 3-5 mm diameter

Microbiological analysis of oil samples, formation waters of the Balakhani and Bibi-Heybat Oil Fields has been carried out. The amount of SRB, common bacteria and fungi in 1 ml of formation water or oil has been determined. According to the results of the experiment the number of microorganisms in the formation water samples from the Bibi-Heybat Oil Field is slightly higher (SRB - $14·10^4$, bacteria - $15·10^4$, fungi – $29·10^3$) than in the formation water samples from the Balakhani Oil Field (SRB - $11·10^2$, bacteria - $13·10^4$, fungi - $16·10^2$). This is probably connected with the amount of oil available in the formation water, as the formation water samples from the Bibi-Heybat Field contain 7.5%, and the formation water samples from the Balakhani Field contain 9% of oil (Table 1).

Table 1. Microbiological analysis of samples of formation water, oil and sea water taken from Balakhani and Bibi-Heybat fields

Number of microorganisms	Balakhani field		Bibi-Heybat field		Sea water	
	Formation water	Oil	Formation water	Oil	Oil-contaminated sea water	Clean sea water
Bacteria	$13·10^4$	$24·10^5$	$15·10^4$	$19·10^4$	$54·10^5$	$78·10^7$
Fungi	$16·10^2$	$80·10^1$	$29·10^3$	$36·10^5$	$52·10^2$	$23·10^3$
SRB	$11·10^2$	-	$14·10^5$	$16·10^6$	$15·10^3$	$9·10^3$

When enumerating microorganisms in the composition of oil in the samples of both fields it was revealed that microorganisms predominated in the oil samples from the Bibi-Heybat Field (SRB -$16·10^6$, bacteria - $36·10^5$, fungi - $19·10^4$). This may be due to the fact that when oil is displaced mixing with formation water leads to contamination with microorganisms (Table 2).

Table 2. The number of microorganisms in formation water

№	Samples	Number of bacteria	Number of fungi	Anaerobic SRB
1	4AJ- water	$33·10^2$	3 colonies	$14·10^4$
2	The upper formation water 16 layer N 3617	$22·10^4$	2 colonies	$3·10^2$
3	Lower formation water 7 layer N 924	$42·10^6$	2 colonies	$20·10^2$
4	Bibi-Heybat N 924 (oil)	4 colonies of bacteria	—	$5·10^1$

4. Conclusions

The data shows that the number of sulfate-Reducing bacteria in oil-contaminated seawater is much higher ($15·10^3$) than the number of these microorganisms ($9·10^3$) in clean seawater. It is known from the literature that, in aquatic ecosystems, the possibility of aerobic decomposition of organic substances is limited by the limited solubility of oxygen in water. When organic matter accumulates in water, oxygen is consumed fairly quickly, and then the degradation of organic substances is carried out by anaerobic microbial communities that contain, among other things, sulfate-reducing microorganisms [5].

5.References

1. R.J.Akhiyarov, Yu.Matveyev, A.B. Laptev, D.Y.Buqay : Resource-saving technologies for preventing bio-contamination of reservoir waters of oil production enterprises. In: Oil and Gas business, 2011, №5, pp.232-242.
2. V.I.Levashova, T.P.Mudrik : Synthesis of reagents for suppressing the growth of sulfate-reducing bacteria in oil production. In: Petrochemistry 2008, volume 48, №4, pp.311-314.
3. A.R.Panteleyeva, S.B.Upakhovich, R.F.Tishankina, A.B.Kuznetsov : Corrosion protection with complex reagents in conditions of contamination of oilfield systems with sulfate-reducing bacteria. In: Oilfield equipment 8/2004, pp.106-110
4. A.S.Qalushko : Sulfate-reducing bacteria of flooded oil reservoirs of the Apsheron Peninsula, Abstract. In: Moscow 1990, p. 1-17
5. V. Korneeva : Biodiversity of sulfate-reducing substances bacteria in oxygen-containing waters in Black and Baltic Seas. In: Dissertation work, Moscow 2015, p.22

OR-I-6

RESEARCHES IN THE FIELD OF COKING OF COMPOSITE RAW MATERIALS FOR PRODUCTION OF ELECTRODE COKE

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Abstract: Development of a coking technology for composite raw materials based on heavy oil residues.

Key word: coke, heavy tar of pyrolysis, tar, extracts from selective cleaning of oils, mixed raw materials

1.Introduction

One most important problem in the field of heavy residues processing is increase of efficiency by feedstock rescurces expansion ,processing extending with simultaneous icrease of hight grade oil products yield. One of large-scale process allowing to gain a solution of the above metioned problem is coking one in which heavy residues and high-aromatic craking residues are used as a feedstock.

Super pure graphites produced from refinery coke are used for fast neutron moderatio in nuclear reactors.

Electrode coke may be obtained only from specially selected stable in composition and properties low sulfur high-aromatic feedstock with minimum content of asphalthenes, as admixtures and hetero-elements.

Extracts of lubricating oils selective purification after their pre-oxidation and as well thir compounds with a prospective feedstock for coking process allowing to obtain hight grade electrode coke which finds application in blast furnaces and ectrolyzers for aliuminium production lining in chemical engineering apparatuses,absorbers,condersers manufacturing in order to substitute expensive non-ferrous metals and alloys.

Purpose of this research consiste in designing of coking technology of extracts of lubricating oils selective purification in mixture with common feedstock,ta,intended to coke qulity up-grading,in particular its structural characteristics, in investigation of effect of extracts of distillate and residual lubricating oils selective purification preoxidation on yield and quality of ccoke obtained,developing variants of compounded feedstock preporation.

An active state of compouned feedstock is established as the result of investigation of extremum changes of structural-mechanical stability of compounded mixtures of various composition.

It is established that in conditions of cokig the compounded feedstock is a dispersed system processing ability to change its properties extremely in dependence on asphltenes and tars content in feedstock.Optimum composition of compounded feedstock giving maximum coke yield with simultaneous quality performances up grading is found.

It is necessary to note that thought there are results of sufficient number of researches in literature concerning coking of extracts of lubricating oils selective purification in which coke yield is range 8-15%,but comparative results of coking of extracts of distilled and residual lubricating oils selective purification as well effect of feedstock origin on pre-thermooxidation results with subsequent coking are absent.

In table 1 physicochemical researches of rsidues (density,coking,ability and sulfur content) in correspondence with standards are cited as well as by up to date methods of residues physic-chemical researches(X-ray analysis,derivatographic investigations of the feedstocks and their constituents) technique of aggregative stability determination of various feedstocks and their mixtures.

Result of investigation coking feedstocks extracts of distilled and residual lubricating oils selective purification by furfurol and tar which is basic feedstock for cokig plant,quality physicochemical analysis are cited.

Extract of residual lubricating oil selective purification has the best perphomances from the viepoint of anisotropic coke production.This extract differs from distilled lubricating oil one EDLOSP by physical properties as well as group composition. The results of the research are summarized in table 1.

More oil (ERLOSP) that the letter contains aromatic hydrocarbons in significantly large quantities basically owinig to polycyclic aromatics.

Asphalthenes content are almost four time less than in than in tar and slightly higher than in axtract of lubricating oil selective purification.in the same time quality factor as well as density of extracts of residual lubricating oil fraction selective purification are essentially higher in comparison with tar and extract of distillate lubrication oil purification. Therefore the extracts of lubricating oils selective purification are more favorable feedstock in viewpoint of graphitized coke obtaining in comparison with tar.

However, in viewpoint of relatively low coking abitily of ERLOSP (it is by 2,4% lower than one of tar) apparently it is expediently to use the aromatized extract in mixture with tar. Physicochemical performaces of tar and ERLOSP mixures are cited in the same table1.

Upon estimation of aromacity degree of coking feedstock and its applicability for special purpose coke production one must not limits oneself only by group composition because of quality of separate components for various resides may be different in principle.Its estabilished by us that there are signal of aromatic ring protons in the PMR spectrum which belongs to CH_3 and CH_2 groups in a-position to aromatic nuclear. Intensity of CH_2 group signal is much higher than one of CH_3 group that reveals about predomination of long alkyl substituens of normal structure in the investigated fractions.Relative distribution of hydrogen among structural groups for shows tha predominant proton type in ERLOSP groupcomponents are ones directly bonded with aromatic rings (H_a-38.5-41,3%).Then protons bounded with CH_3-,CH_2- and CH-groups in a-position to aromatic rings (H_a- 26,2-28,9%) follow.Least of all are protons bounded with terminal methyl groups (H_y-8,9-10,2%).

For ERLOSP components H/C atomic ratio has comparatively low value (0,77-0.83) that confirms the presence of condense rings I these fractions .

H/C atomic ratio for tar has relatively high value (1.27-1.48).ERLOSP group components has lower number of alkyl substituents and lower number of atoms in them. ERLOSP molecular mass lower the tar molecules of the same type.

Table1. Physicochemical performances of extracts of lubricating oils selective purification ,tar and mixtures of tar and ERLOSP

Perfomances	Extracts of lubricating oils selective purification		tar	Mixtures tar: extract in ratio , weight%				
	Distilled lubricating oil fraction of "Sangachaly-more"oil field	residual lubricating oil fraction of deasphaltized "Sangachaly-more"oil field		90:5	90:10	85:15	80:20	75:25
Desity,kg/m	962,5	1013,6	979,2	980 , 5	981,2	982,8	984,9	985,4
Coking ability,%	6,8	8,9	12,3	12,1	11,9	11,9	11,7	11,5
Viscosity at 100C	4,1	5,2						
Group hydrocarbon composition%								
Paraffinic naphtenic	31,2	18,5	36,9	35,1	34,0	34,0	33,9	33,15
Aromatic	54,5	62,3	38,8	41,2	42,1	43,3	44,1	44,8
Including light	9,9	10,0	7,3	7,25	7,3	7,2	57,2	7,1
Medium	22,5	19,5	6,5	7,0	7,5	8,3	9,2	10.0
Heavy	20,8	32,8	24,4	25,1	26,8	27,5	28,3	29,5
Tars	14,9	18,0	17,5	17,0	16,7	17,5	18,9	18,3
asphaltenes	1.3	2.0	7,8	7,5	7,2	6,9	6,6	6,3
Quality factor	0,64	1,6	0,56	0,60	0,63	0,67	0,70	0,75

To determine a dependence of tar and ERLOSP mixture properties on components ratio 12 compositions were prepared with extract content from 5 to 9 weight percent.

The dependences of the factor of aggregative stability and dynamic viscosity of prepared samples on extract content are showing in fig.1 from which one can see the factor of aggregative stability for ERLOSP is higher than one for tar 0.82 against 0.74 that in all probability is connected with lower content of tars and asphalthenes.

The dependence of aggregative stability and dynamic viscosity from components ratio have extremum character.

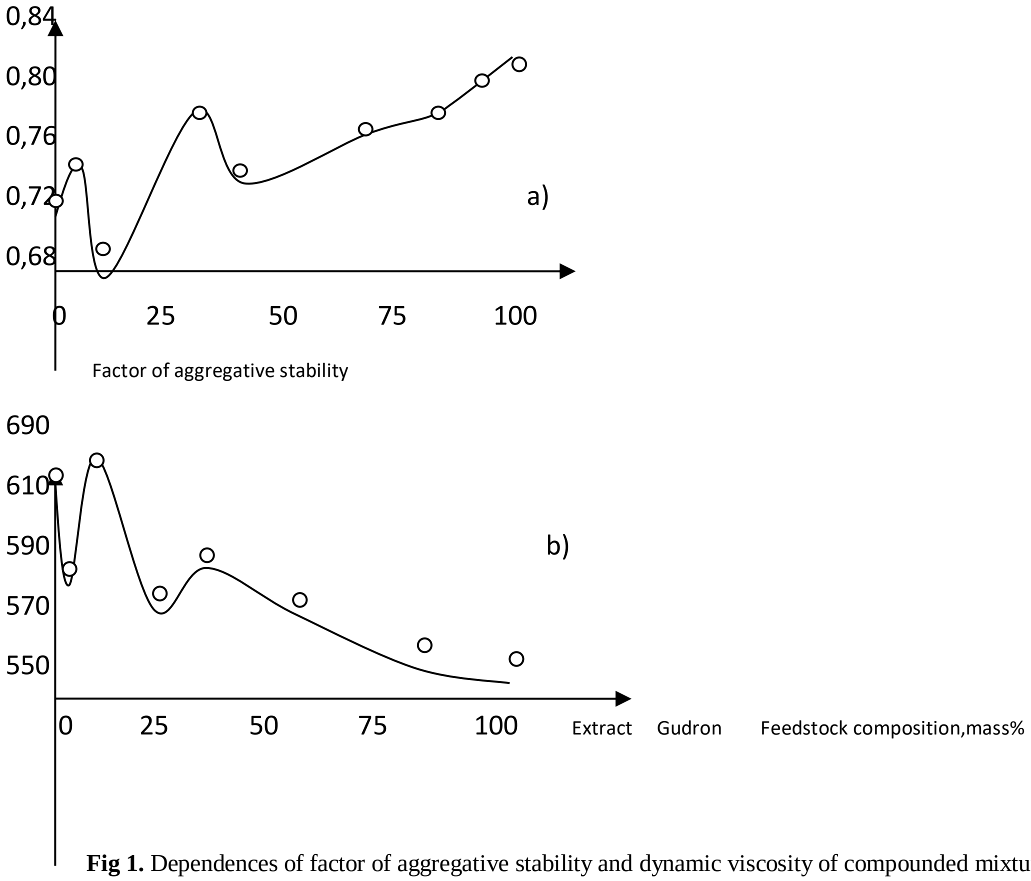

Fig 1. Dependences of factor of aggregative stability and dynamic viscosity of compounded mixture on components ratio.

A new grown of aggregative stability of at extracts concentrations above 30% weight is connected with ELOSP stability predomination. Thus, upon tar with high-aromatized ERLOSP the properties of compounded mixtures change extremely that gives possibility for determination of active state of coking feedstock. The optimum from viewpoint of aggregative stability are mixtures containing respectively 5 and 25 weight of ERLOSP.

Upon ERLOSP content increase above 25%weight aggregative stability of the mixture drops sharply.

Thus, compounded feedstock containing 25%weight of ERLOSP processes maximum aggregative stability. Usage of the feedstock with this components ratio in industrial coking plant will decrease possibility of furnace pipes coking and the process will reach high efficiency.

5.References

1.Petrukhina N.N; Tumanyan B.P. “Options for improving the residues processing schemes at modern oil refineries "Oil & Gas Technologies, 2010 No. 6-s 24-29
2.Komensky E.F; Khavkin VA "Deep refining of oil: Technological and environmental aspects." Moscow: Technics.-2001.-384s

OR-I-1

DIESEL-ALCOHOL -SURFACE-ACTIVE SUBSTANCE BLENDS AND THEIRS USE IN DIESEL ENGINES

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Abstract. The core objective of carried experiment is to investigate the way of improving stability period for alcohol diesel fuel mixture and compounds with 95, 90 and 85% purity methanol mixing with commercial diesel fuel (CDF) by using surfactant of 3.3-dilinolenate dimethylol-1,1dimethylol-cyclohexanol-2 ethers (SAS1) studied. Hydrophilic-lipophilic balance (HLB) of the synthesized SAS1 determined. Stability factors of the compounds obtained by adding different amounts to the SAS1 into the CDF / methanol mixture were analyzed and identified that by mixing alcohol-methanol (95% purity) and SAS1 with the ratio of 1: 0.25 by 1% into the CDF increases the stability period of the compounds up to 150 days while increasing the alcohol and SAS1 volume up to 5% with the same ratio causes the stability drop till 120-95 days. For other alcohols it is 115-135 days and better transperancy kept. Futhermore, if the mixtures are stored at low temperatures the content of methanol in diesel fuel can be increased up to 3%. Comperative combustion products of compounds obtained from 90% of commercial diesel fuel with methanol and SAS1 in a ratio of 1:0.25 were investigated. CO content in exaust gasses in mixtures of 1-10% with its absolute methanol is 0.717-0.507% and reduced by 7-42%. Accordingly for NOx ranged from 0.0681% mass decreased to 0.0647-0.0490% mass, and SOx oxides decreases from 0.0630% mass to 0.0586-0.0510% mass that corresponds to 5-28% and 7-19% decreement respectively

Keywords: diesel fuel, alcohol, emulsifier, methanol, surface-active-substance, exhaust gas

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1.Introduction

Nowadays one of the main trends in the production of environmentally friendly diesel fuel is the production of oxygen contained emulsion diesel fuel. Fossil derived oil and fatty acid based ethers and simple alcohols as oxygen-containing additives are considered one of the most effective means of this application. The presence of an oxygen atom in these additives ensures a more complete combustion of the fuel and ensures that the combustion content and limits are in complience with environmental regulation.

C_1-C_4 monohydric alcohols are used in two directions as additives in diesel fuels: either in the form of an aqueous alcohol (as an azeotropic mixture of water and alcohols) in an emulsion with diesel, or in the form of a mixture of diesel with completely anhydrous alcohols. The use of alcohol diminishes the environmental emission rate of diesel fuel. This is possible based on the factors listed below:

- First, as mentioned above, the presence of an oxygen atom in an alcohol molecule reduces the amount of harmful substances in the exhaust gases of internal combustion engines.
- Second, the high evaporation temperature of C1-C4 alcohols (the evaporation temperature of oil-based diesel fuel is 230-250 kC / kg when the evaporation temperature of ethanol is 870 kC / kg) reduces the amount of nitrogen oxides released into the atmosphere by reducing the maximum combustion temperature [1-3].

Another factor that improves the composition of exaust gases is the low boiling point of simple C1-C4 alcohols compared to diesel fuel, which contributes to the quality of the mixture formation process, as low boiling temperatures cause rapid evaporation of alcohol from the fuel mixture and oil-based diesel that creates additional turbulence in the fuel. This effect noted for a wide range of emulsion fuels, also provides economic advantage to the engines performance.

As mentioned above, from an environmental point of view the simple alcohols considered reasonably better oxygen-containing additives to diesel fuel. However, there are some difficulties in their use, as the direct use of these alcohols is possible only for completely dry (absolute) alcohols, and the resulting mixtures must be stored in airless conditions, otherwise the air will absorb moisture and phase out alcohol-containing fuels. In addition, due to absolute alcohols are more expensive, the cost of compounds based on them increases.

Currently researchers are focusing on methods for obtaining long-term, non-phase mixtures of diesel fuels with different amounts of water-containing alcohols. It should be noted that in this case, the water containing alcohols can also be labeled as an oxygen additive [4-6].

2. Experimental part

Emulsified diesel fuel was obtained using 3,3-dilinolenate dimethylol-1,1dimethylol-cyclohexanol-2 ether as a surfactant with methanol, ethanol, propanol, butanol alcohols containing up to 15% water in commercial diesel fuel (CDF), the physicochemical, operational properties and combustion products were studied.

At the initial stage, at room temperature, using a mixer with a speed of 600 rpm, 1-10% mixtures of water-retaining C1-C4 alcohols with 5-15% mass in the composition of diesel fuel were obtained and stability periods of these mixtures were determined (Table 1)

Table 1. Stability of 1-10% mass mixtures of C1-C4 alcohols with commercial diesel fuel containing 5-15% mass water, minutes

	95% alcohol content in commercial diesel fuel,% mass				
	1	3	5	7	10
Method of preparation	600 rpm mixer at room temperature,				
Appearance	cloudy	Cloudy	cloudy	cloudy	cloudy
Methanol	21	18	13	8	5
Ethanol	22	18	14	8	5
Prophanol	22	19	14	9	5
Buthanol	25	21	18	13	7
	90% alcohol content in commercial diesel fuel,% mass				
Appearance	cloudy	cloudy	cloudy	cloudy	cloudy
Methanol	17	14	11	6	3
Ethanol	18	15	12	7	3
Prophanol	18	15	13	7	3
Buthanol	21	18	15	9	4
	85% alcohol content in commercial diesel fuel,% mass				
Appearance	cloudy	cloudy	cloudy	cloudy	cloudy
Methanol	12	9	5	2	1
Ethanol	13	10	5	3	2
Prophanol	13	10	6	3	2
Buthanol	16	12	9	6	4

It is clear from Table 1 that the stability time of compounds obtained by mixing commercial diesel fuel with 95% alcohol (i.e. methanol) is very short and is only 21-25 minutes for 1% mixtures and 18-21 minutes for 3% mixtures, 13-18 minutes for 5% mixtures, 8-13 minutes for 7% mixtures, and 5-7 minutes for 10% mixtures. In this case, the results for methanol-propanol alcohols are approximately the same, while the use of butanol alcohol increases slightly, but does not make a sharp difference.

The same regularity and less stability periods are observed for compounds obtained using 90 and 85% alcohols.

Obviously, compounds with such a short stability period cannot be recommended for use, and the next step is to obtain stable compounds with 95, 90 and 85% methanol of commercial diesel fuel by using surfactant as 3.3-dilinolenate dimethylol-1,1dimethylol-cyclohexanol-2 ethers.

The hydrophilic-lipophilic balance (HLB) of the synthesized 3.3-dilinolenate dimethylol-1,1dimethylol-cyclohexanol-2 ether (SAS1) was determined according to Equation (1) and equal to 8.55.

$$H = 7 + \sum_{i-1}^{m} H_i - 0.475 \cdot n, \qquad (1)$$

Here:
m- number of hydrophilic groups molecule,
Hi- coefficient for i-hydrophilic group:
Value for -COOH group is 1.1; for -OH group is 1.9; for groups -CH, CH2, CH3, = CH- is 0.475,
n - number of lipophilic groups in the molecule

$$HLB_{SAS1}=6*(-0,475)+3*1,9+7+2,1+36*(-0,475)+2*2,1=8,55$$

In order to obtain a stable emulsion with methanol containing 5-15% water in commercial diesel fuel, the stability times of the compounds obtained by adding different amounts to the SAS1 CDF / methanol mixture were determined. The results obtained is presented in Table 2.

Table 2 Research outcomes for emulsifier of SAS1 with the mixture of CDF and Methanol containing of 5-15% water

	Amount of 95% purity methanol in CDF,% mass														
	1			3			5			7			10		
Method of preparation	600 rpm mixer														
Methanol:SAS1 ratio	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1
Duration of the resulting mixtures, days at 25 °C	150	-	-	150	-	-	120	135		85	95	-	75	90	-
Appearance at 25 °C	T			T			C	T		C	T		C	T	
Duration of the resulting mixtures, days at 0 °C	120	-	-	120	-	-	95	115		65	80	-	55	75	-
Appearance at 0 °C	T			T			C	T		C	C		C	C	
	Amount of 90% purity methanol in CDF,% mass														
Methanol:SAS1 ratio	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1
Duration of the resulting mixtures, days at 25 °C	120	140	-	110	120		100	120		50	75		35	50	70
Appearance at 25 °C	C	C	C	C	C		C	C		C	C		C	C	C
Duration of the resulting mixtures, days at 0 °C	90	110	-	80	95		75	85		40	55		25	30	45
Appearance at 0 °C	C	C		C	C		C	C		C	C		C	C	C
	Amount of 85% purity methanol in CDF,% mass														
Methanol:SAS1 ratio	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1	1:0.25	1:0.5	1:1
Duration of the resulting mixtures, days at 25 °C	100	110		90	105		85	100		30	55	85	15	35	60
Appearance at 25 °C	C	C		C	C		C	C		C	C	C	C	C	C
Duration of the resulting mixtures, days at 0 °C	75	85	-	60	75		50	65		15	25	40	10	25	35
Appearance at 0 °C	C	C		C	C		C	C		C	C	C	C	C	C
Note: C-cloudy, T-transparent															

As obvious from the data that the addition of 0.25% alcohol to SAS1 diesel / methanol mixture for a 1% of 95% methanol in CDF increases the stability period of the compounds up to 150 days. The same result is observed when the mixtures are stored at low temperatures and the content of methanol in diesel fuel increases up to 3%. In both cases, the resulting compounds are completely transparent. Given that the stability time of these mixtures without the use of SAS1 that was only 21 minutes, there is no doubt that SAS1 is an effective emulsifier.

Although the stability time is slightly reduced when the alcohol: SAS1 ratio is 1: 0.25, the compound obtained by adding 5% to 95% methanol in diesel fuel is slightly different at room and low temperatures, but becomes cloudy at 120 and 95 days, respectively. Compounds obtained when the amount of SAS1 in the ratio of alcohol:SAS1 corresponded to 1: 0.25 is transparent and retain their stability for 135 and 115 days.

For mixtures of 95% methanol with diesel fuel of 7 and 10%, the stability period was 85 and 75 days for alcohol:SAS1 ratio of 1: 0.25, and 95 and 90 days for alcohol: SAS1 ratio of 1: 0.5..

As the amount of water in the used alcohols increases, the stability of the compounds obtained from their use in commercial diesel fuel and SAS1 as an emulsifier decreases. Thus, at room temperature, the SAS1:alcohol ratio of 1-3% mixtures of 90% methanol with diesel fuel is 120 and 110 days, which is 30-40 days less than the use of 95% alcohol. Increasing the alcohol: SAS1 ratio to 1: 0.5 increases the stability times of the obtained compounds by 20 and 10 days, but the mixtures obtained in both ratios become cloudy. Keeping the mixtures at low temperatures further reduces their stability periods to 90-80 and 110-95 days respectively.The stability times of diesel fuel mixtures with 90% methanol and 5-7% are reduced to 100-50 and 120-75 days, respectively, when the SAS1: alcohol ratio is 1:0.25 and 1:0.5.

The lowest stability period is observed for 10% mixtures, and even when the SAS1: alcohol ratio is 1: 1, it is 70 and 45 days, depending on the temperature.

Also, the quality indicators of the compounds obtained by adding 5% to 95-85% methanol with diesel fuel in a ratio of 1: 0.25 with SAS1 were determined and summarized in Table. 3.

Table 3 Quality indicators of 5% compounds of CDF 95-85% with the ratio of methanol:SAS1 to 1:0.25

Parameters	EN-590	CDF	CDF + 5% Methanol		
			95%-li	90%	85%
Density at 20°C, кg/m3, max	860,0	847,4	845,0	845.4	845,9
Cetane number, min	51	46	42	42	42
Fractional composition, °C					
50% distilled	280	280	276	277	277
90% distilled	350	340	333	334	334
96% distilled	360	355	341	343	343
Flash point in closed cup, °C, min	55	74	52	52	52
Kinematic viscosity at 20°C, mm2/s, max	2-6	3,20	3,1	3,15	3,18
Pour point, °C, max	-10 (-35)*	-31	-32	-34	-34
Cloud point, °C, max	-25 (-10)*	-20	-20	-20	-22
Test on a copper plate at 50°C for 3 h	+	+	+	+	+
Aromatics content, %mass	15,0	18,0	16,7	16,5	16,5
Acidity, mg KOH/100 sm3 fuel, max	5	1,5	1,4	1,4	1,4
Iodine number, g I/100 g fuel, max	6	0	0	0	0
Total sulphur content, % mass, max	0,005	0,0112	0,010	0,010	0,010
Actual residue content in 100 sm3 fuel, mg, max	25	18	16,5	16,1	15,7
Low heating value, kJ/kq, min	-	42880	41450	41270	41200

As can be seen from Table 3, the quality characteristics of the compounds obtained by adding 95-85% methanol to 5% diesel fuel in a 1: 0.25 ratio with SAS1 are different from the original diesel fuel. Thus, as the amount of water in methanol increases, the density and kinematic viscosity of the obtained compounds increase slightly. The effect on the composition of the fraction is that the expulsion temperature of 50% increases by 1-2 °C, but in this case the above parameters remain in accordance with the requirements of EN-590.

3. Results and discussion

At the same time, the actual amount of tar in 100 cm3 of fuel, the total amount of sulfur and aromatic hydrocarbons in the obtained compounds are reduced, and these factors can be considered as a positive effect. Also, the low temperature properties of the obtained mixtures improve such as freezing, turbidity temperatures that is reduced by 2-3 °C. Further improvement in low temperature properties can be explained by the effect of SAS1 used.

On the other hand, for compounds obtained from 95-85% methanol with SAS1 in a ratio of 1: 0.25, a lower flash point is observed, which depends on the flash point of methanol.

Also, for the obtained compounds, there is a decrease in the low combustion temperature compared to the original diesel fuel, which is explained by the addition of oxygen atoms to the diesel fuel with SAS1 and water molecules.

In subsequent studies, comparative combustion products of compounds obtained from 90% of commercial diesel fuel with methanol and SAS1 in a ratio of 1:0.25 were investigated and presented in Table 4.

The data show that the combustion products of 90% methanol and SAS1 in a ratio of 1: 0.25 are more environmentally friendly than the combustion products of commercial diesel fuel compounds with absolute methanol. Thus, the content of carbon monoxide in the exaust gases of commercial diesel fuel is 0.874%. When present, the amount of CO in the combustion products of mixtures of 1-10% with its absolute methanol is 0.717-0.507% reduced by 7-42%. For compounds obtained from 90% diesel fuel with methanol and SAS1 in a ratio of 1:0.25, this reduction is already 8-47%.

Table 4. Individual and common compounds' exaust gases composition in mixture of CDF and methanol:SAS1 ratio of 1: 0.25

Exhaust gases composition, % mass	CDF	CDF + methanol (abs), %mass					CDF methanol (90%)+ SAS1:0,25) % mass				
		1	3	5	7	10	1	3	5	7	10
CO	0,874	0,813	0,717	0,588	0,550	0,507	0,786	0,655	0,577	0,516	0,463
NOx	0,0681	0,0647	0,0599	0,0545	0,0517	0,0490	0,0630	0,058	0,052	0,049	0,046
SOx	0,0630	0,0586	0,0567	0,0542	0,0529	0,0510	0,0580	0,054	0,052	0,051	0,049
Smoke, % mass	22,4	20,61	19,48	17,92	16,13	12,32	19,71	18,37	17,02	15,23	11,65

The same outcomes observed for nitrogen and sulfur oxides, and NOx oxides ranged from 0.0681% mass decreased to 0.0647-0.0490% mass, and SOx oxides decreases from 0.0630% mass to 0.0586-0.0510% mass. This decrease corresponds to 5-28% and 7-19%, respectively. Also, for compounds obtained from 90% diesel fuel with methanol and SAS1 in a ratio of 1:0.25 corresponds to 7-33% mass and 8-23%mass reduction.

4. Conclusion

As per outcomes of carried experiments it is determined that the 3,3-dilinolenate dimethylol-1,1dimethylol-cyclohexanol-2 ester synthesized in the production of high-stability emulsion fuels with 95-85% purity methanol of commercial diesel fuel can be used as an effective emulsifier. The content of carbon monoxide in the combustion products of the compounds obtained using this emulsifier is 8-47%, and the content of sulfur and nitrogen oxides presents 8-23%, 7-33%.

5.References

1. Abbasov V.M, Məmmədova T.A, Abbasov A.R., Məmmədxanova S.Ə, Lətifova T.S. Research over the physical and chemical properties and composition of exhaust gases of diesel-ethanol mixtures . Processes of Petrochemistry and Oil-Refinery, 3(20), 247-255 (2019).
2. Şahin, Z., Durgun, O., Kurt, M., Experimental investigation of improving diesel combustion and engine performance by ethanol fumigation-heat release and flammability analysis, Energy Conversion and Management, 89 (1), 175-187 (2015). doi: 10.1016/j.enconman.2014.09.053
3. Valentino, G., Iannuzzi, S., Marchitto, L., Merola, S., Tornatore, C., Optical Investigation of Postinjection Strategy Effect at the Exhaust Line of a Light-Duty Diesel Engine Supplied with Diesel/Butanol and Biodiesel Blends, J. Energy Eng., 140, 123-128 (2014). doi 10.1061/(ASCE)EY.1943-7897.0000155
4. Wang, Q., Wei, L., Pan, W., Yao, C., Investigation of operating range in a methanol fumigated diesel engine, Fuel, 140, 164-170 (2015). doi: 10.1016/j.fuel.2014.09.067
5. Jamrozik, A. Tutak, W., Gnatowska, R., Nowak, L. Comparative Analysis of the Combustion Stability of Diesel-Methanol and Diesel-Ethanol in a Dual Fuel Engine Energies , 12 (971), 1-17 (2019). doi:10.3390/en12060971
6. Atmanli, A.; Yilmaz, N. A comparative analysis of n-butanol/diesel and 1-pentanol/diesel blends in a compression ignition engine. Fuel 234, 161–169 (2018) doi: 10.1016/j.fuel.2018.07.015.

PP-V-2

DETERMINATION OF OPTIMAL CONDITIONS OF THE PROCESS OF CATALYTIC CRACKING OF OIL

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Abstract. In this article the question of determination of optimum conditions of process of catalytic cracking of oil is considered. With a view of realization of a rational thermal mode in a reactor-regenerative contour limiting limits of speed of circulation of the catalyst in system are defined. It is noted that the solution of the problem is simplified on the basis of static characteristics of the process, as well as the dependence of the values of the criterion of optimality on the conditional contact time at different values of the circulation rate and the temperature of the catalyst.

Keywords: cracking, upflow, catalyst, optimization.

1. Introduction

To increase the depth of oil refining and increase volumes the production of motor fuel at refineries is being modernized and the introduction of recycling processes petroleum feedstock, including catalytic cracking. In addition, catalytic cracking wet gas is of interest as a feedstock for the petrochemical industry and the production of other valuable chemicals.

To date, a significant number of research projects are aimed at the development of new operating catalytic cracking units and modern catalysts for processing heavy oil fractions. As is known, in the process of catalytic cracking, raw materials of various types are processed, such as vacuum and atmospheric gas oils and fuel oils, coking gas oils, hydrocracking bottoms, etc.

At most modern plants today, catalytic cracking units with a lift reactor and the use of microspherical zeolite-containing catalysts are widely used.

Optimizing the operation of catalytic cracking units is a multifactorial task and is determined by the characteristics of the processed feedstock and catalyst. Along with intensive scientific work in the field of improving the technology of catalytic cracking, it is important to determine the optimal conditions for the process of catalytic cracking of oil, which is discussed by us in this article.

2.Discussion and results

As you know, the implementation of optimal conditions for conducting the process is the main indicator of the perfection of a chemical reactor. Therefore, before choosing the design parameters of the reactor on the basis of a mathematical description of the process, a stage of theoretical optimization is required.

The study of the choice of the optimization criterion for the catalytic cracking process [I] showed that the most fully characterizing its efficiency is the depth of selection of motor gasoline.

An analysis of the statistical characteristics of the process under study, obtained on the basis of a mathematical model of the catalytic cracking of oil [2], shows that the depth of extraction of motor gasoline depends on the value of the conditional contact time τ, the catalyst circulation rate K, and the temperature in the reaction zone T:

$$Z = f(\tau; K; T) \qquad (1)$$

It should be noted that the final choice of the optimal process mode is associated with finding the rational thermal mode of the system as a whole. The mass circulation rate of the catalyst in reactors with an upward flow of the catalyst relates the distribution of heat between the concurrently operating main and auxiliary apparatus included in the catalyst circulation loop, in particular, the reactor-regeneration apparatus [3].

An increase in the catalyst circulation rate can result in insufficient balance coke generated by the process to achieve the optimum temperature in the regenerator. In this regard, it will be necessary to burn additional heat from the outside. If the amount of heat received by the catalyst in the regenerator exceeds the needs of the reactor, then there will be a need to remove a certain amount of heat from the catalyst before it enters the reactor, i.e., a ballast potential of heat will be created in the system.

Therefore, in order to implement a rational thermal regime in the reactor-regenerator loop, it is necessary to specifically determine the limiting boundaries of the catalyst circulation rate in the system. In this formulation, the solution to the optimization problem for the catalytic cracking of oil in a system with an upward flow of a catalyst based on a mathematical model represents a boundary value problem with incomplete assignment of boundary conditions (raw material consumption is known, the catalyst temperature at the bottom of the reactor is the conditional contact time, the catalyst circulation rate is unknown, the amount of coke in the top reactor.

Consequently, it is necessary to repeatedly calculate the reactor model, choosing the catalyst circulation rate so that the required amount of balance coke is obtained at the top of the reactor.

The solution of the problem is simplified by the presence of static characteristics obtained on the basis of the mathematical model of the process, the dependences of the values of the optimality criterion Z on the conditional contact time τ at various values of the catalyst inlet temperature and the frequency of its circulation.

Table 1 shows the dependences of the Z values on the contact time τ at various values of the circulation ratio K and the catalyst temperature T at the inlet. This dependence is extreme. With an increase in the temperature and frequency of the catalyst circulation, the extremum shifts to the left and the maximum output of motor gasoline is achieved at a smaller value of the conditional contact time. At the same time, with the shift of the optimality regions to the left, the value of the optimality criterion almost does not change and remains within the range of 1.21-1.22.

Table 1. Table of the dependence of the optimality criterion Z on the contact time

	T=823K		T=833K		T=843K	
Circulation rate K	Contact time τ	Optimality criterion Z	Contact time τ	Optimality criterion Z	Contact time τ	Optimality criterion Z
3	0.1	0.52	0.1	0.51	0.1	0.54
	0.2	0.68	0.2	0.62	0.2	0.62
	0.3	0.72	0.3	0.70	0.3	0.71
	0.4	0.81	0.4	0.74	0.4	0.77
	0.5	0.90	0.5	0.80	0.5	0.81
5	0.1	0.64	0.1	0.61	0.1	0.62
	0.2	0.81	0.2	0.77	0.2	0.76
	0.3	0.90	0.3	0.84	0.3	0.82
	0.4	0.96	0.4	0.94	0.4	0.91
	0.5	1.15	0.5	0.98	0.5	0.97
7	0.1	0.78	0.1	0.74	0.1	0.70
	0.2	0.88	0.2	0.86	0.2	0.84
	0.3	1.12	0.3	0.92	0.3	0.92
	0.4	1.14	0.4	1.04	0.4	1.05
	0.5	1.16	0.5	1.09	0.5	1.10
9	0.1	0.82	0.1	0.85	0.1	0.78
	0.2	0.94	0.2	0.92	0.2	0.90
	0.3	1.16	0.3	1.04	0.3	1.02
	0.4	1.18	0.4	1.12	0.4	1.11
	0.5	1.22	0.5	1.17	0.5	1.18

The critical fluid concentration of the catalyst in the reactor can be calculated using the following formula:

$$\mu_{kr} = \frac{R}{t_r - t_e} \frac{g_c[q - l(C_f t_p - C_a t_o) - C_k(t_p - t_k)]}{t_k C_{kat}(1 + \alpha x)} \qquad (2)$$

Where t_r is the temperature in the regenerator; t_e is the temperature at the end of the reactor; g_c-the amount of coke formed in the process; q-calorific value of coke and fuel; l is the amount of air for combustion 1 kg. coke; C_{kat}, C_f, C_a - heat capacity of the catalyst, flue gases entering the air regenerator; q-calorific value of coke and fuel; α is the sum of stoichiometric reaction coefficients; x is the conversion depth of raw materials.

Based on (1-2), we calculated the values of the critical fluid concentration of the aluminosilicate catalyst under the optimal conditions for conducting the catalytic cracking of oil. The corresponding values of the catalyst circulation ratio were determined according to the expression:

$$K = \frac{\mu_{kr}}{\gamma} \qquad (3)$$

$$\gamma = \frac{M_r 23{,}1(273+t)}{p273} \qquad (4)$$

where γ is the specific weight of raw materials during the process under optimal conditions, kg / m^3 ; μ_{kr}- critical fluid concentration of the catalyst in the reactor, kg / m^3; Mr is the molecular weight of the raw material; p-pressure in the system.

The optimal conditions for conducting the process were those at which the catalyst circulation rate K coincided with the rate from (2).

Research of various options τ, K, T, at which the maximum value of the optimality criterion is achieved, showed that the optimal mode of the process, when the maximum depth of selection of motor gasoline is 1.007 (42.09 wt.%), Should be considered the conditional contact time τ = 0, 2 kg / kg * mol / h, catalyst circulation rate K = 13 and catalyst temperature at the inlet T_2 = 833˚K. In this case, the initial temperature of the process after the phase shift is T = 790˚K, and the temperature difference along the reactor height ΔT = 10 ˚K.

When choosing the optimal conditions for conducting the process of catalytic cracking of oil in a reactor with an upward flow of the catalyst, the limitations imposed on the temperature and conditional contact time were also taken into account, since at high values of τ and T, a sharp decrease in the current concentration of diesel fuel and increased gas formation are observed.

5.References

1. Ganiev GG, Amirkhanov K.SH Optimization of the laboratory method for determining the activity of catalytic cracking catalysts. Bashkir Chemical Journal. 2012, Vol. 19, No. 1, pp. 128-129.
2. Mircea C., Agachi S., Marimoiu V. Simulation and Model Predictive Control of a UOP Fluid Catalytic Cracking / Chemical Engineering and Processing - 2003. - Vol. 42 - 67p.
3. Pashayeva B. Mathematical model of the fluid catalytic cracking for work in testing control systems for the cracking plant / PCI, Baku, Azerbaijan - Vol.1 - 2010. pp. 328-331.

PP-I-1

GEOCHEMICAL CONDITION OF THE LANDSCAPES AND THEIR IMPACT ON HUMAN HEALTH (on an example Kura lowland)

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Abstract. Geochemistry of landscapes studies the migration patterns of chemical elements in the Earth's geographical envelope. It deals with the patterns of matter migration in the Earth's shell, which is the human habitat.

Geochemistry of the landscape, as well as geochemistry in general, uses three methodological approaches. The first is to study the migration of chemical elements in different landscapes. The second approach is a systematic study of the types of elemental and geochemical landscapes of the biosphere and the nonosphere as a whole, the behaviour of paragenic associations of elements in forest, steppe, tundra and other modern natural landscapes, as well as in landscapes of past geological eras.

The article is devoted to the study of the peculiarities of the geochemical transformation of landscapes of the Kura intermountain basin based on the patterns of concentration and migration of macro-compounds and trace elements found in samples of mountain rocks, soil, plants and water, for which a comparative method of research and the relationship of landscape components was used. For the first time, a medium-scale "Ecogeochemical landscape map of the Kurin intermountain basin" and "Medico-ecological geochemical landscape map" of this region were compiled. The article reveals the characteristic features of the compiled maps and the features of the geochemical transformation of the study area.

Keywords: geochemistry, landscapes, microelements, macroions, anthropogenic transformation, chemical elements.

1.Introduction

Kura lowland is one of the largest morphological structures in Azerbaijan and has ancient landscapes exposed to intensive anthropogenic transformation. The bioaccumulative potential of the research area, transit water resources, favorable geographical conditions enabled rich biological diversity to create agro complexes that can develop in irrigation and freshness and have different structural and functional characteristics [4-7].

The main purpose of the study is to investigate and map out the deterioration of natural geochemical conditions associated with anthropogenic transformation of landscapes and to assess the impact on human health.

The object of the research is geochemical landscapes of the Kura lowland. In landscapes, soil creating layers are mainly consist of clay, gill, carbonate, tuff-breccias and limestone. These rocks are carbonate, with gypsum and deeply soluble salts in deep layers. Therefore, saline problems are observed in the area.

2.Material and Methods

Chemical analysis of soil, rocks, plants and water was carried out at the Institute of Geography of ANAS, during the analysis we obtained:

- soil, soil and water samples (pH),
- soil hygroscopic moisture,
- amount of organic carbon and total humus in soil,
- Undertaking component of the soil (HCO3, Cl, SO4, Ca, Mg, Na + K) was determined by known methods [1-8] with the analysis of total volume of water.

The percentage of organic carbon and humus in the soil is determined by I.V.Tyurin's method [2; 4], the environment of different landscape components (rocks, soil samples and water) is determined by the pH-type of "OP-201/2" [3-5]. All soil, rocks, plants and water samples were studied by X-ray fluorescence spectrometry with Elvax-CEP 01 spectral analysis method. Various schedules, geochemical formulas and other geochemical indicators were drawn on the basis of the obtained results.

Strontium (Sr), calcium (Ca), zirconium (Zr), and manganese (Mn) content are mainly clarity in the composition of samples taken from the Kura lowland sediment, which is characterized mainly as the area of accumulation. According to the results of spectral analysis, the number of tin (Sn) and Mercury (As) from microelements is higher than that of claws, chlorine (Cl), stibium (Sb), indium (Y) and scandium (Sc) several times, terbium (Tb) and cadmium (Cd) was found to be 100 times higher. It has been established that manganese (Mn), iron (Fe), zinc (Zn), rubidium (Rb), indium (Y), zirconium (Zr), potassium (K), titanium (Ti) and strocyum (Sr) micelaments that constitute a small fraction of their content, relatively small in size.

The spectral samples of the soil samples taken from the Kura lowland basin and the results of the chemical analysis of these samples are given. (Table 2, 3)

Table 1. The microelement compositions of taken rock patterns from Kura lowland k-59 Neftchala hydrometeorological station (selection)

Row №	Atomic №	Element	Average, with %		Concentration clark, CC
			In composition of the rock	Clark on the Earth's crust, CEC	
1	20	Ca	0,9193	2,96	0,31
	22	Ti	0,2660	0,45	0,59
	25	Mn	0,0322	0,10	0,32
	26	Fe	2,7105	4,65	0,58
	30	Zn	0,0025	0,0083	0,30
	37	Rb	0,0021	0,015	0,14
	38	Sr	0,0155	0,034	0,45
	39	Y	0,0019	0,0029	0,65
	40	Zr	0,0179	0,017	1,05
	41	Nb	0,0005	0,0020	0,25
	64	Gd	0,0275	0,0008	34,37
	65	Tb	0,0669	0,00043	155,58

Table 2. The microelement compositions of taken soil patterns from Kur lowland areas k-46 main Shirvan collector (selection)

Elements		Average, with %		Concentration clark, CC
Atomic №	Chemical sign	In composition of the soil	Clark on the Earth's crust, CEC	
1	2	3	4	5
26	Fe	0,1988	4,65	0,04
37	Rb	0,0014	0,015	0,09
38	Sr	0,0050	0,034	0,15
39	Y	0,0004	0,0029	0,14
40	Zr	0,0014	0,017	0,08

The main geochemical formulas we get as a result of the mathematical processing of actual indicators obtained from the results of spectral and chemical analysis, quantitative indicators of macroion-specific, terrestrial and deficit micronutrients (Table 4).

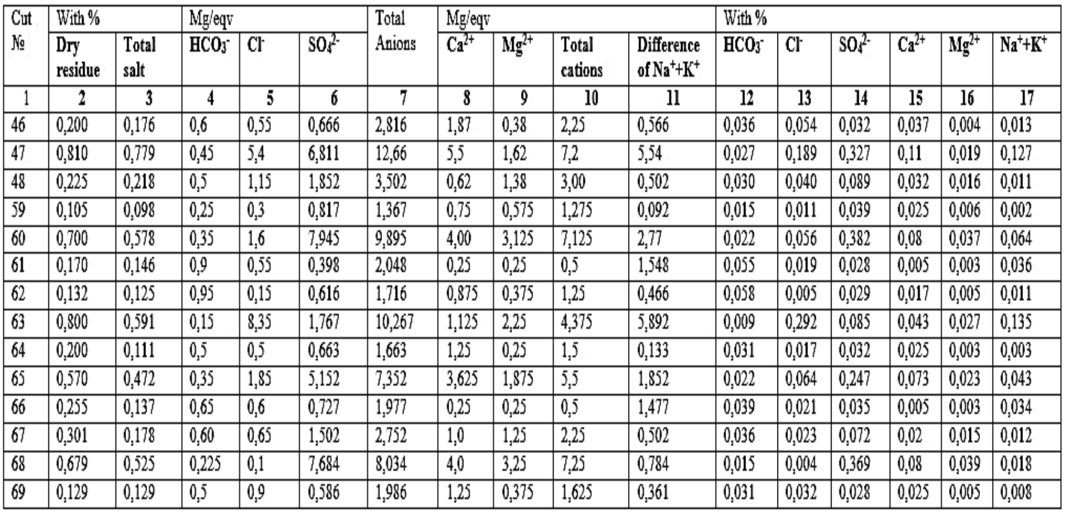
Sulfate-calcium-natrium is dominating (SO_4–Na–Ca) in Salyan, Imishli, Sabirabad, Saatli, Aghjabedi, in Kur district of Ceyranchol, Sulfat-sodium-calcium (SO_4–Ca–Na), Aghdash, Kurdemir, in Khirmanli village of Bilasuvar district , and Sulfate-calcium-magnesium (SO_4–Ca–Mg) compounds are dominating in Qarabagal village of Goychay.

Hydrocarbonate-natrium-calcium (HCO_3–Na–Ca) compounds are widely spread in the Hajigabul district, Varvara village of Yevlakh, in the village Poylu, village of Ceyranchol. It is noteworthy that hydrocarbonate-calcium-magnesium compounds in Mingachevir are dominant.

The chemical characteristics of scattered deficits and densely micronutrients in the area are clearly demonstrated in the right side of the column in Table 4. Apparently, Tb, Ag, Sn, Mo, As, Cu, Zn, Pb are the most common micronutrients in the area. Defective microelements which are characteristic for the area are Y, Zr, Sr, Rb and Fe.

Spectral analysis of the ash of the plant samples gathered from the area, determine quantitative and qualitative indicators of microelements contained in the major components of the landscape. The results obtained are shown in Table 5.

Table 3. Definition of total water release (general table)



Cut №	With %		Mg/eqv			Total Anions	Mg/eqv				With %					
	Dry residue	**Total salt**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**		**Ca^{2+}**	**Mg^{2+}**	**Total cations**	**Difference of Na^++K^+**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**Ca^{2+}**	**Mg^{2+}**	**Na^++K^+**
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
46	0,200	0,176	0,6	0,55	0,666	2,816	1,87	0,38	2,25	0,566	0,036	0,054	0,032	0,037	0,004	0,013
47	0,810	0,779	0,45	5,4	6,811	12,66	5,5	1,62	7,2	5,54	0,027	0,189	0,327	0,11	0,019	0,127
48	0,225	0,218	0,5	1,15	1,852	3,502	0,62	1,38	3,00	0,502	0,030	0,040	0,089	0,032	0,016	0,011
59	0,105	0,098	0,25	0,3	0,817	1,367	0,75	0,575	1,275	0,092	0,015	0,011	0,039	0,025	0,006	0,002
60	0,700	0,578	0,35	1,6	7,945	9,895	4,00	3,125	7,125	2,77	0,022	0,056	0,382	0,08	0,037	0,064
61	0,170	0,146	0,9	0,55	0,398	2,048	0,25	0,25	0,5	1,548	0,055	0,019	0,028	0,005	0,003	0,036
62	0,132	0,125	0,95	0,15	0,616	1,716	0,875	0,375	1,25	0,466	0,058	0,005	0,029	0,017	0,005	0,011
63	0,800	0,591	0,15	8,35	1,767	10,267	1,125	2,25	4,375	5,892	0,009	0,292	0,085	0,043	0,027	0,135
64	0,200	0,111	0,5	0,5	0,663	1,663	1,25	0,25	1,5	0,133	0,031	0,017	0,032	0,025	0,003	0,003
65	0,570	0,472	0,35	1,85	5,152	7,352	3,625	1,875	5,5	1,852	0,022	0,064	0,247	0,073	0,023	0,043
66	0,255	0,137	0,65	0,6	0,727	1,977	0,25	0,25	0,5	1,477	0,039	0,021	0,035	0,005	0,003	0,034
67	0,301	0,178	0,60	0,65	1,502	2,752	1,0	1,25	2,25	0,502	0,036	0,023	0,072	0,02	0,015	0,012
68	0,679	0,525	0,225	0,1	7,684	8,034	4,0	3,25	7,25	0,784	0,015	0,004	0,369	0,08	0,039	0,018
69	0,129	0,129	0,5	0,9	0,586	1,986	1,25	0,375	1,625	0,361	0,031	0,032	0,028	0,025	0,005	0,008

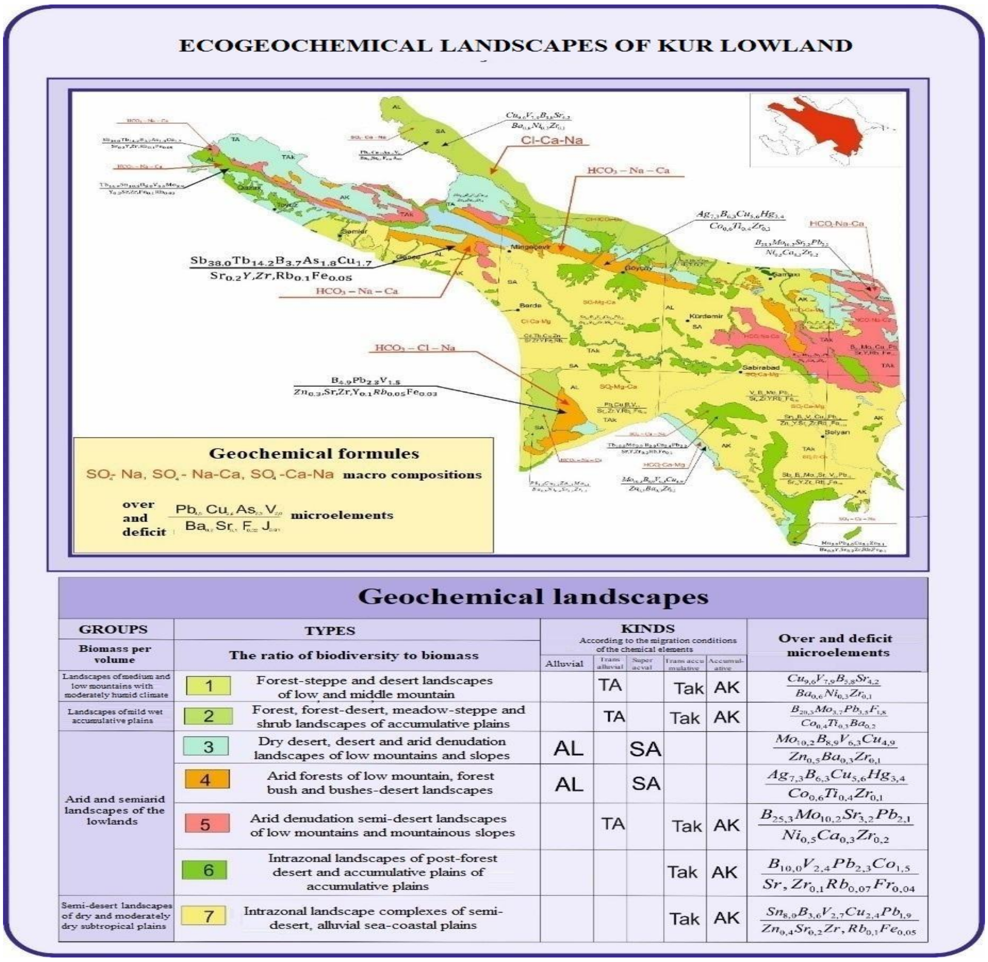
Table 4. Main geochemical indicators of transformated landscapes of Kura lowland

	Landscapes taken from the cut patterns	**Macroions**	**Above over, below (denominator) deficit microelements**
6	Main Shirvan collector. Accumulative semi-desert	SO_4 – HCO_3 – Ca	$\frac{Cu_{4.9}\,Pb_{4.1}\,Zn_{2.9}B_{2.0}}{Sr_{0.3}\,Y,\ Rb,\ Zr_{0.2}\,Fe_{0.04}}$
7	Salyan c. Selitep landscapes	SO_4 – Na – Ca	$\frac{Ag_{61.4}\ Tb_{14.2}\,Br_{1.2}}{Sr_{0.2}\,Y, Zr, Rb, Fe_{0.1}}$
8	Bilasuvar, Khrimandal v. Accumulative semi-desert	SO_4 – Ca – Na	$\frac{Tb_{18.8}Mo_{3.9}B_{2.8}Cu_{2.4}Pb_{2.2}}{Sr, Y, Zr_{0.2}Rb, Fe_{0.1}}$
9	Neftchala. Accumulative semi-desert	SO_4 – Cl – Ca	$\frac{Sb_{36.0}B_{10.2}Mo_{6.4}Sr_{3.1}V_{2.9}Pb_{1.9}}{Sr_{0.2}Y, Zr_{0.1}Rb_{0.05}Fe_{0.04}}$
0	Salyan hydrological station. Tugai forest	SO_4 – Ca – Mg	$\frac{Sn_{8.0}B_{3.6}V_{2.7}Cu_{2.4}Pb_{1.9}}{Zn_{0.4}Y, Sr_{0.2}Zr, Rb_{0.1}Fe_{0.05}}$
1	Yevlakh, Varvara v. Hydromorphic landscapes	HCO_3 – Na – Ca	$\frac{Mo_{7.9}B_{6.7}Cu_{1.9}Pb_{1.8}}{Sr, Zr, Y_{0.1}Fe_{0.05}Rb_{0.04}}$
2	Hajigabul c. Selitep landscapes	HCO_3 – Na – Ca	$\frac{B_{20.0}Mo_{5.0}Cu_{2.0}Pb_{1.9}}{Sr, Y, Rb_{0.1}Fe_{0.05}}$
3	Shirvan c. Technogenic urban landscapes	Cl – Na – Mg	$\frac{B_{24.5}Mo_{4.8}Pb_{2.9}V_{1.9}}{Sr_{0.4}Zr_{0.2}Y, Fe_{0.1}Rb_{0.05}}$
4	Sabirabad c. Selitep landscapes	SO_4 – Ca – Mg	$\frac{V_{3.9}B_{2.8}Mo_{2.7}Pb_{2.3}}{Sr_{0.2}Zr, Y, Rb_{0.1}Fe_{0.05}}$
5	Saatli c. Selitep landscapes	SO_4 – Ca – Mg	$\frac{B_{3.1}Cu_{2.9}Zn_{2.2}Y_{1.8}}{Sr, Zr_{0.2}Y, Rb_{0.1}Fe_{0.05}}$
6	Imishli, Cafarli v. Agrolandscapes	SO_4 – Na – Ca	$\frac{B_{7.9}Mo_{6.8}Sr_{2.9}Pb_{2.2}}{Sr_{0.2}Zr, Y_{0.1}Rb_{0.05}Fe_{0.04}}$
7	Beylagan, Ikinji Ashigli Agrolandscapes	SO_4 – Mg – Ca	$\frac{Pb_{4.3}Cu_{3.9}B_{2.1}V_{2.0}}{Sr_{0.2}Zr, Y, Rb_{0.1}Fe_{0.05}}$
8	Aghjabadi c. Selitep urban landscapes	SO_4 – Ca – Mg	$\frac{Cu_{3.6}B_{2.6}Mo_{2.2}}{Sr, Y, Zr, Rb_{0.1}Fe_{0.05}}$
9	Barda C. Selitep urban landscapes	Cl – Ca – Mg	$\frac{Cd_{46.1}Tb_{26.5}Cu_{4.0}Zn_{2.9}}{Sr, Zr, Y, Fe_{0.1}Rb_{0.03}}$

Table 5. General mass of microelements of the plants taken from Kur lowland and the biological absorption coefficients k-47 Salyan city, (selection)

Plants	Atomic №	Micro-elements	The mass of Microelements with %		(Kb) BAC
			In the composition of ash	In soil	
Tamarisk	26	Fe	0,0353	0,2739	0,13
	35	Br	0,0024	0,0003	8,00
	37	Rb	0,0009	0,0010	0,90
	38	Sr	0,0037	0,0080	0,46
Decrease row of BAC: $\frac{Br}{8{,}00} > \frac{Rb}{0{,}90} > \frac{Sr}{0{,}46} > \frac{Fe}{0{,}13}$					

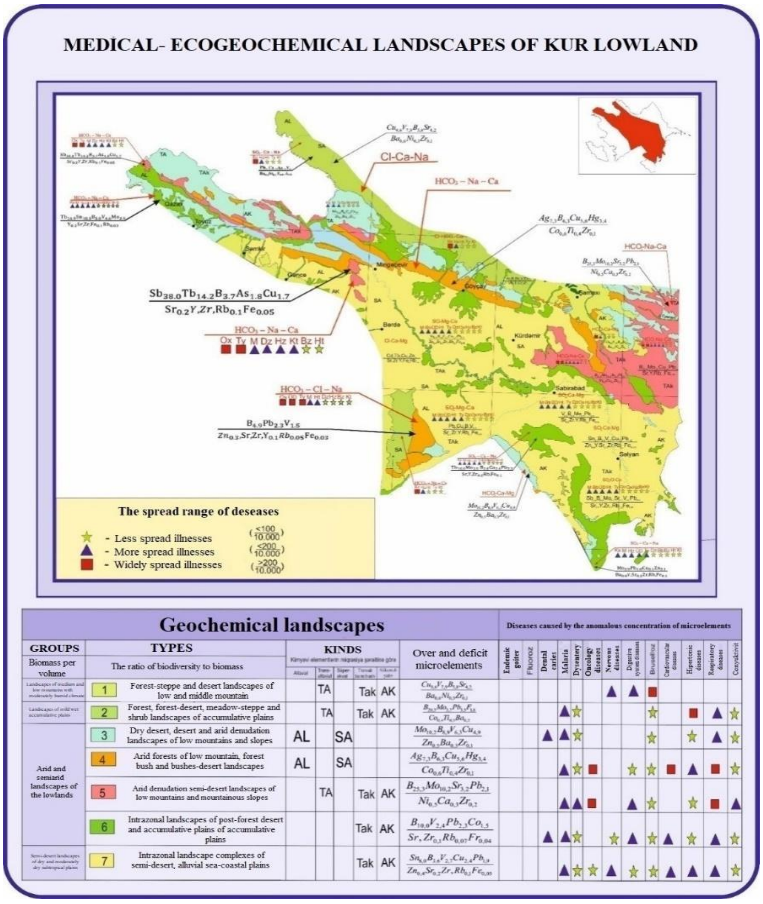
Figure 1. Geochemical landscape map of the Kura terrain



Geochemical landscapes

GROUPS	TYPES		KINDS					Over and deficit microelements
Biomass per volume	The ratio of biodiversity to biomass		According to the migration conditions of the chemical elements					
			Alluvial	Trans alluvial	Super acval	Trans accumulative	Accumulative	
Landscapes of medium and low mountains with moderately humid climate	1	Forest-steppe and desert landscapes of low and middle mountain		TA		Tak	AK	$\frac{Cu_{9,6}V_{7,9}B_{5,8}Sr_{4,2}}{Ba_{0,6}Ni_{0,3}Zr_{0,1}}$
Landscapes of mild wet accumulative plains	2	Forest, forest-desert, meadow-steppe and shrub landscapes of accumulative plains		TA		Tak	AK	$\frac{B_{20,3}Mo_{3,7}Pb_{3,5}F_{1,8}}{Co_{0,4}Ti_{0,3}Ba_{0,2}}$
Arid and semiarid landscapes of the lowlands	3	Dry desert, desert and arid denudation landscapes of low mountains and slopes	AL		SA			$\frac{Mo_{10,2}B_{8,9}V_{6,3}Cu_{4,9}}{Zn_{0,5}Ba_{0,3}Zr_{0,1}}$
	4	Arid forests of low mountain, forest bush and bushes-desert landscapes	AL		SA			$\frac{Ag_{7,3}B_{6,3}Cu_{5,6}Hg_{3,4}}{Co_{0,6}Ti_{0,4}Zr_{0,1}}$
	5	Arid denudation semi-desert landscapes of low mountains and mountainous slopes		TA		Tak	AK	$\frac{B_{25,3}Mo_{10,2}Sr_{3,2}Pb_{2,1}}{Ni_{0,5}Ca_{0,3}Zr_{0,2}}$
	6	Intrazonal landscapes of post-forest desert and accumulative plains of accumulative plains				Tak	AK	$\frac{B_{10,0}V_{2,4}Pb_{2,3}Co_{1,5}}{Sr, Zr_{0,1}Rb_{0,07}Fr_{0,04}}$
Semi-desert landscapes of dry and moderately dry subtropical plains	7	Intrazonal landscape complexes of semi-desert, alluvial sea-coastal plains				Tak	AK	$\frac{Sn_{8,0}B_{3,6}V_{2,7}Cu_{2,4}Pb_{1,9}}{Zn_{0,4}Sr_{0,2}Zr, Rb_{0,1}Fe_{0,05}}$

Figure 2. Map schame of medical-ecogeochemical landscapes of Kur lowland



To find out how alluvial (AL), transallvale (TA), superacval (SA), transaclimative (TAC) and accumulative (AK) landscape species [6] separated by migration conditions of chemical elements, it is enough to look at the legend of the "geochemical landscape map of the Kura terrain" (Figure 1).

Due to the study of the correlation between the concentration of toxic salts and trace elements [3, 7, 8], studied for the effects of macroions and trace elements on human health, the correlation between the characteristic features of the terrain [5-10], it was possible to compile the Medical Ecosystemic Landscape Map of the Kura Trench (Figure 2).

The distribution of these complexes by groups, the types of available landscapes, as well as the distribution of macroions, deficiencies and relative microelements in the region by types of landscapes are given in the legend of the "Eco-chemical landscape map of the Kura terrain" (Figure 1).

The medical and ecochemical landscape map of the Kura terrain was compiled, a correlation between the detection and deficiency of chemical elements was revealed to study the effect of existing ecochemical conditions on human health (Figure 2). The map contains various symbolic illnesses and their rate of spread (red squares, blue triangles and green stars).

3.Results

- In the landscapes of Kura lowland bruseliosis is very widespread, digestive system and nervous diseases are widespread diseases.

-In hyacinth, forest-desert, grass-bushes and bush landscapes of the accumulative plains, hypertension is very wide, malaria and respiratory diseases are common, dysentery, brucellosis and conjunctivitis.

- The most common diseases in the desert, desert and arid denidation landscapes of low mountains and slopes are not common. Dental caries, malaria and respiratory tract diseases are widely spread here, dysentery, bruseliosis, hypertension and conjunctivitis are less common.

- In the arid forest, forest bush and slopes-desert landscapes complex of the lowlands, the most common diseases of oncological diseases, cardiovascular and respiratory tract are malaria and hiportolic diseases. Dysentery, brucellosis, conjunctivitis, and digestive tract disorders are characterized by low-spread disease.

- Oncological diseases and respiratory diseases are very common in the arid denudation semi-desert landscapes of low mountains and mountainous slopes. Widespread diseases include dysentery, malaria, digestive tract and conjunctivitis; less common illnesses are brucellosis and hypertension.

-Donudative accumulative plains do not coincide with the most widespread diseases in the intrazonal landscape complex of post-forest desert and accumulative plains. Dental caries, malaria, digestive tract, respiratory tract and cardiovascular diseases are commonly associated with dysentery, nervous disorders, brucellosis, hypertension and conjunctivitis.

- There are not too wide spread diseases in the semi-desert of cumulative alluvial coastal plains and in the introductory landscapes of the alluvial marine coastal zone. In these landscapes, malaria, nerves, cardiovascular, digestive tract and respiratory tract diseases are widely spread, dysentery, digestive system, brucellosis, conjunctivitis and oncological diseases are the most common diseases.

4.Conclusion

Because of the anthropogenic transformation of natural landscapes in the Kura mountainous basin, changes in natural geochemical conditions of the landscapes were assessed as weak, moderate and strong (3 levels). The analysis of the large-scale medical ecochemical landscape mapping on this basis revealed that the risk geography of a number of diseases (brucellosis, cardiovascular, hypotonia, etc.) has changed in accordance with ecogeochemical conditions.

5.References

1. Alekseenko V.A. Geochemical Ecology. Moscow, Logos, 2010.
2. Budagov B.A., Ahmedov A.H., Rustamov G.I., Gahramanov A.I. Geochemical landscape map of Azerbaijan. Baku, 2000.
3. Fortescue. J.A. 1980. Environmental Geochemistry: A Holistic Approach. Springer-Verlag, New York, USA.
4. Glazovskaya M.A. Geochemical bases of typology and methods of studying original landscapes. Smolensk. Oikumen, 2002.
5. Perelman A..I., Kasimov N.S. Geochemistry in the landscape. Astirea. Moscow. 2000, pp. 183.
6. Yu. G. Kopylova., E. M. Dutova., and T. I. Romanova. “Ecological–Geochemical State of the Groundwaters of Mountain Taiga Landscapes of the Salair,” Obskoi Vestn., Nos. 3–4, 100–104 (1999).
7. Yu. G. Kopylova, T.I., Romanova, I. V., Smetanina. and A. A. Khvashchevskaya, “Conditions of the Formation of Fluorine-Bearing Waters in the Main Landscape Zones of Southeastern Western Siberia,” Obskoi Vestn., No. 1, 6–12 (2001).
8. Gyulakhmedov A.N. Microelements in the plants and soils of the Azerbaijan SSR. / ISD. AN Azerb. The USSR, Baku, 1987.
9. Penin R.S. Eco-geochemical Investigations of Aqual Landscapes. Proceedings of the International Scientific Session – 50th anniversary of the Institute of Geography of BAS, Sofia, November, 2000.
10. Zornitza C. Geochemical peculiarities of migration and concentration of some heavy metals in the Iskar river basin in Stara Planina mountain. Conference paper, "Human Dimensions of Global Change in Bulgaria", 22-24 April 2004, Sofia, Bulgaria.

II. Catalysis in oil refining and petrochemistry.

PHASE COMPOSITION AND ACTIVITY OF MG-ZN-O CATALYSTS IN THE REACTION OF CONVERSION ETHANOL TO ACETONE

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Abstract. The reaction of ethanol conversion on a number of binary Mg–Zn–O catalysts was studied. It is shown that the main reaction product of ethanol conversion on the studied catalysts is acetone and as byproducts are acetic aldehyde, carbon dioxide and ethylene.

It is found that ethanol conversion reaction on a studied catalyst begins at 250°C and output of acetone passes throw maximum with increasing of temperature. Also, on activity Mg–Zn–O catalysts influences the atomic ratio of magnesium to zinc. The yield of acetone with an increase in the content of magnesium oxide in the composition of the catalyst passes through two maxima on the samples Mg-Zn=4-6 and Mg-Zn = 7-3.

X-ray study of the phase composition of the prepared catalysts was carried out. It is found that in the Mg-Zn-O catalyst system, the formation of two phases is observed, only magnesium oxide and zinc oxide. The calculated degree of crystallinity of the Mg-Zn-O catalytic system slightly depends on the catalyst composition. It is established that increasing of catalyst crystallinity leads to rising of yield of acetone.

Keywords: Ethanol Conversion, Binary catalysts, Crystallynity.

1.Introduction

One of the interesting methods for producing acetone is the reaction of vapor-phase conversion of ethanol [1,2]. From the periodic literature it is known that zinc-containing catalysts selectively increase rate of the reaction of the conversion of ethanol to acetone [3,4]. Selectivity of the zinc containing catalysts in reaction of formation of acetone depends on type and properties of additives [5,6]. In the previous article, we explained that the magnesium zinc oxide catalytic system shows high activity in the reaction of conversion of ethanol to acetone. In this connection this work is devoted to studying the influence of phase composition of binary magnesium-zinc oxide catalysts on its activity in the reaction of the conversion of ethanol to acetone.

2.Experimental part

Magnesium-zinc oxide catalysts were prepared by co-precipitation of aqueous suspensions of magnesium carbonate and zinc carbonate. The mixture was evaporated at 95-100°C, dried at 100-120°C and decomposed at 250°C until initial salts will completely be decomposed and then calcined for 10 hours at 700°C. The activity of the synthesized catalysts was studied on a flow-through installation unit with a quartz reactor in the temperature range of 250-700°C. 5 ml of the studied catalyst with a grain size of 1.0–2.0 mm was loaded into the reactor and its activity was studied in the reaction of ethanol conversion. The yields of the ethanol conversion products, as well as quantity of unreacted ethanol were determined by chromatography method. X-ray studies of binary copper-tungsten oxide catalysts were carried out on a Bruker D2 Phaser automatic powder diffractometer (CuKα radiation, Ni filter, $3 \leq 2\theta \geq 80°$), we also degree of crystallinity of studied samples calculated using the DIFFRAC.EVA program.

3.Results and discussions

Based on the conducted research we can say that over magnesium-zinc oxide catalysts main product of ethanol conversion reaction is acetone. and. Other products, such as acetic aldehyde, ethylene and carbon dioxide are a byproduct. The results of the effect of temperature on the reaction of ethanol conversion on binary magnesium-zinc oxide catalysts it is shown on figure 1. Obtained results show that ethanol conversion reaction on binary magnesium-zinc oxide catalysts begins at 250°C. At this temperature, a small amount of acetaldehyde (1.2%) is obtained. A further increase in the reaction temperature leads to an increase in acetic aldehyde and the formation of other reaction products. The highest yield of acetaldehyde is achieved at 350°C and is equal 16.4%. With increasing temperature, the yield of acetone also passes through a maximum.

Table 1. Effect of temperature on the yields of reaction products of ethanol conversion.

Temperature	Reaction products				Selectivity on acetone	Conversion
	CO_2	C_2H_4	CH_3CHO	CH_3COCH_3		
200			0			0
250			1,2			1,2
300			9,1	0	0	9,1
350	0		16,4	8,4	33,9	24,8
400	6,1	0	14,3	35,6	52,4	68
450	10,7	4,3	3,1	68,7	77,4	88,8
500	12,2	9,3	0	37,9	41,1	92,3
550	15,9	8,15		23,2	23,6	98,5

The maximum yield of acetone is observed at 450°C and is equal 68.7%. It was also found that the conversion of ethanol sharply increases with increasing reaction temperature and at 550°C almost reaches 100%. Such dependences were obtained for all binary magnesium-zinc oxide catalysts.

We found that the activity of Mg-Zn-O catalysts in the conversion of ethanol to acetone also depends on the atomic ratio of magnesium to zinc in the composition of the binary catalyst. Below in the table 1 it is shown the effect of the atomic ratio of magnesium to zinc on the activity of the studied catalysts.

Table 2. The conversion of ethanol to binary magnesium-zinc oxide catalysts at a temperature of 400°C.

Reaction products	The yields of reaction products in % on samples with different atomic ratios of magnesium to zinc								
	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
CO_2	10,7	15,3	11,3	11,3	7,2	8,1	7,9	5,3	4,7
C_2H_4	4,3	5,3	10,1	7,6	9,4	13,4	15,3	12,7	9,4
CH_3CHO	3,1	5,7	4,1	3,6	4,5	16,2	9,8	13,7	16,6
CH_3COCH_3	68,7	62	59,8	55,8	48,7	36,9	30,7	16,9	6,4
Ethanol conversion	88,8	89,5	90,8	79,9	78,9	71,5	69,3	58,3	53,5

As can be seen from the table 1, the yield of acetone with an increase in the content of magnesium oxide in the composition of the catalyst passes through two maxima on the samples Mg-Zn=4-6 and Mg-Zn = 7-3. The yield of acetic aldehyde increases with increasing magnesium content in the composition of the catalyst and on the sample Mg-Zn = 9-1 is equal 16.6%. The table also shows that with an increase in the content of magnesium oxide in the composition of the catalyst, the graph of the dependence of ethylene yields on the composition has the form of a curve with two maxima, while the yield of carbon dioxide decreases slightly with increasing magnesium content in the composition of the catalysts.

Thus, based on the obtained results, it can be said that binary catalysts based on magnesium oxide and zinc have high activity in the reaction of the conversion of ethanol to acetone. It was found that the catalyst with the composition Mg-Zn =4-6 is most active in the reaction of acetone formation. The yield of acetone on this catalyst is equal 67.8%.

In the figure 1 have shown the diffractograms of results of X-ray studies of Mg-Ni-O catalysts.

Based on the X-ray studies, it was found that in the Mg-Zn-O catalyst system, the formation of two phases is observed, namely magnesium oxide and zinc oxide. The peak ratio of these compounds, as can be seen from the diffraction patterns, varies according to the composition of the binary catalysts. We also found that the formation of chemical compounds between magnesium and zinc oxides is not observed.

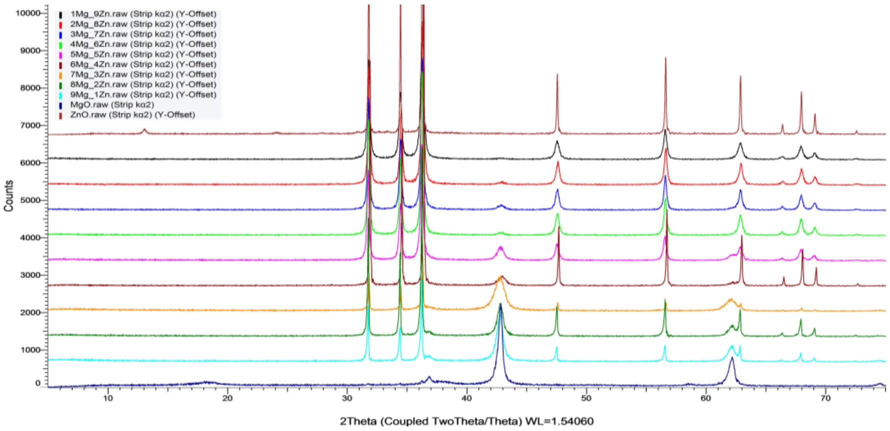

Figure 1. Diffractograms of all samples of Mg-Zn-O catalytic system

We also calculated the crystallinity of all samples using the DIFFRAC.EVA program. Obtained results presented on the table 1.

Table 3. The degree of crystallinity of binary magnesium-zinc oxide catalysts of different composition.

Atomic ratio of magnesium to zinc	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1
The degree of crystallinity, %	84.4	85.1	84	84.8	84	87.3	71.3	85.6	83.7

As can be seen from table 1, the degree of crystallinity of the Mg-Zn-O catalytic system slightly depend on the catalyst composition.

The phase composition and, accordingly, the degree of crystallinity of binary solid oxide catalysts somehow influences their catalytic activity. Therefore, we have compared the degree of crystallinity and activity of binary magnesium-zinc oxide catalysts in the reaction of converting ethanol into acetone. Results of this research is shown in Figure 2. As can be seen from Figure 2, with increasing degree of crystallinity of the catalyst, the outputs of acetone slightly increase while the conversion of ethanol practically does not change.

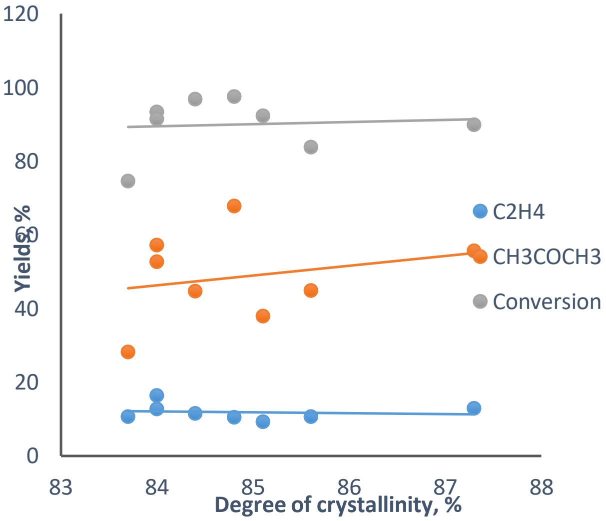

Figure 2. Dependence activity of binary magnesium-zinc oxide catalysts in the reaction of converting ethanol into acetone on the degree of crystallinity

4.Conclusion

- Binary magnesium zinc oxide catalysts have high activity in the reaction of the conversion of ethanol to acetone. Catalyst with the composition Mg-Zn =4-6 is most active in the reaction of acetone formation and yield of acetone on this catalyst is reaches 67.8%.

- In the Mg-Zn-O catalytic system formation of only magnesium oxide and zinc oxide phases is observed, formation of chemical compounds between magnesium and zinc oxides is not observed.
- Increasing degree of crystallinity of the catalyst leads to the rising of acetone yields and selectivity of conversion ethanol to acetone.

5.References

1. V. V. Borovik, V. M. Vorotyntsev & G. I. Golodets: Catalytic properties of oxides in vapor phase oxidation of acetone. Theoretical and Experimental Chemistry volume 24, pages107–110 (1988).
2. Muhammad Mahfuzur Rahman, Stephen D. Davidson, Junming Sun & Yong Wang: Effect of Water on Ethanol Conversion over ZnO. Topics in Catalysis volume 59, pages37–45 (2016)
3. Clarissa Perdomo Rodrigues, Priscila da Costa Zonetti & Lucia Gorenstin Appel: Chemicals from ethanol: the acetone synthesis from ethanol employing Ce0.75Zr0.25O2, ZrO2 and Cu/ZnO/Al2O3. Chemistry Central Journal volume 11, Article number: 30 (2017).
4. Gabriella Garbarino, Paola Riani, María Villa García, Elisabetta Finocchio, Vicente Sánchez Escribano & Guido Busca: A study of ethanol conversion over zinc aluminate catalyst. Reaction Kinetics, Mechanisms and Catalysis volume 124, pages503–522 (2018).
5. Tsuyoshi Nakajima, Kozo Tanabe, Tsutomu Yamaguchi, Isao Matsuzaki, Shozi Mishima: Conversion of ethanol to acetone over zinc oxide—calcium oxide catalyst optimization of catalyst preparation and reaction conditions and deduction of reaction mechanism. Applied Catalysis Volume 52, Issue 3, Pages 237-248 (1989).
6. R.SreeramaMurthyP.Patnaik1P.SidheswaranM.Jayamani: Conversion of ethanol to acetone over promoted iron oxide catalysis. Journal of Catalysis Volume 109, Issue 2, Pages 298-302 (1988).

PL-11

SPIN CATALYSIS OF N-SULFINYLAMINES CYCLOADDITION WITH DIENES

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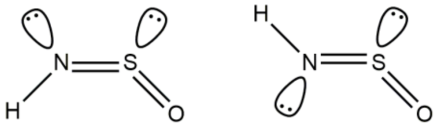
Abstract. Density functional theory has been applied to a number of N-sulfinylamine molecules in the ground singlet closed-shell state (S_0) and in the triplet excited state (T_1). DFT calculations show that these compounds are characterized by the low-lying T_1 excited state with a strong spin-density localization on the -N=S=O group, which can explain a number of specific chemical properties of N-sulfinylamines such as their reactions with acidic proton-active compounds, Diels-Alder cycloaddition with dienes and instability in the moisture. The relatively large calculated spin-orbit coupling matrix element between T_1–S_0 states explains an efficient rate constant for the $S_0 \rightarrow T_1$ excitation induced by heating and internal magnetic forces. We explain some chemical reactions of N-sulfinylimines by spin-catalysis concept.

Keywords: N-sulfinylimines, singlet-triplet transition, energy gap, spin-catalysis, Diels-Alder cycloaddition, DFT.

1.Introduction

Compound containing the NSC groups are known as N-sulfinylamines (also called as sulfinylimides, iminooxosulfuranes, N-sulfinylimine, N-sulfinylanilines in the literature) [1-4]. The N-sulfinylamines were first synthesized and investigated by Michaelis 130 years ago [1]. After discovery of the Diels-Alder reactions these compounds have found numerous application in cycloaddition processes, which mainly proceed across the S=N bond [1-4]. Reactions of N-sulfinylamines (R–N=S=O) with water strongly depend on the R substituent [1,4]. Thus, the chloro-N-sulfinylamines (R = Cl) react with water explosively. At the same time aromatic N-sulfinylamines participate in hydrolyzes more slowly, while N-sulfinylhydrazines (Ph-NH-NSO) are stable toward water [1]. Besides this inertness and of N-sulfinylhydrazines toward moisture they are active as pesticides and anticancer agents [1,2]. In this paper we shall try to explain peculiarities of N-sulfinylamines by their triplet excited state properties.

The *N*-sulfinylamine compounds, R–NSO, could be presented in two possible structural forms, *cis* and *trans* (or *syn*, *Z* and *anti*, *E*) [2]. HNSO species (as well as anion NSO^-) are isoelectronic with a non-linear SO_2 molecule; thus, they are also bent to non-linear form and two structural isomers are possible for HNSO.



Cis Trans

Scheme 1. Two configurational forms of H–N=S=O

The same analysis can be applied to other R-N=S=O molecules. Meanwhile, the trans-form is mainly observed in spectroscopic and X-ray experiments [2]. They are supported by our (and others [1-2]) quantum chemical calculations since repulsion of N and O lone pairs is minimized in the *trans* form. This is clearly seen from Fig. 1.

2. Method of calculation.

Density functional theory (DFT) with the B3LYP functional [4,5] is used in present work for geometry optimization, electronic structure and force field analysis. The global minimum on potential energy surface (PES) is supported for the studied molecules by the real values of all 3N-6 vibrational frequencies calculated by the PES gradient and the Hessian matrix diagonalization. For the transition state optimization the only one imaginary vibrational mode is found. The basis set 6-31G(d) [7] is used throughout the whole paper. For the triplet excited state calculations the spin-unrestricted DFT method is used. Spin square expectation values are less than 2.0001 after spin annihilation procedure; thus the correct triplet state character is achieved in the non-relativistic part of our calculations. Spin-orbit coupling calculation is done by the method described in Ref. [8]. All calculations in this work correspond to vacuum condition and are performed with the Gaussian09 code [5]. Atomic numeration is given in Fig. 1.

3. Results and Discussion

3.1. Analysis of IR spectrum

The calculated and experimental IR spectra of the C_6H_5–N=S=O molecule are presented in Fig. 1 and Table 1. Vibrational frequencies for NSO modes are equal to 1298, 1163, 636 and 1035 cm^{-1} for the asymmetric N=S=O stretching vibration, symmetric N=S=O stretching, bending (delta) N=S=O and C–N stretching modes, respectively, as being obtained by the Raman spectra [2]. The calculated IR frequencies are corrected by scale factor 0.955 for CH stretching and 0.97 - for other vibrations. The most intense calculated IR bands are presented in Table 1 and show a good agreement with the observed IR absorption. The assignment of Raman spectrum [2] is also reliable. Thus, all 36 modes have a complete interpretation from the first principles. All NSO vibrations are mixed with C-N and phenyl ring distortions. The low frequency modes are not scaled and omitted from Table 1. In the T_1 state almost all vibrations are changed dramatically, especially those of the NSO group.

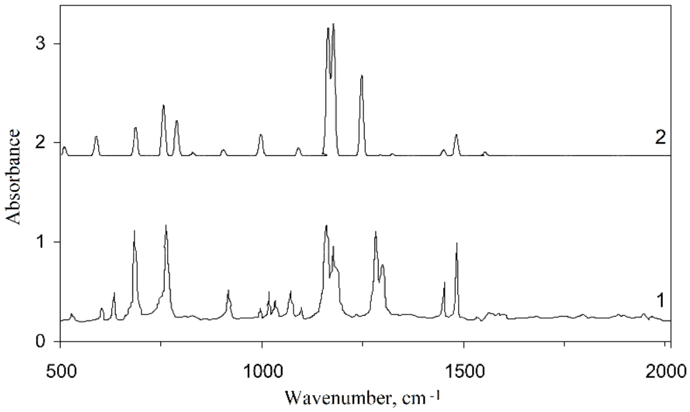


Fig. 1. IR spectra of N-sulfinylaniline. 1 – experimental [9], 2 – calculated spectrum with the B3LYP/6-31G(d) method. Frequency (cm^{-1}), I_{IR} – IR intensity (km/mol)

Table 1. Calculated with the B3LYP/6-31G(d) method vibrational frequencies (cm^{-1}) of N-sulfinylaniline in the singlet (S_0) state; I_{IR} is the calculated intensity (km/mol)

Mode	Freq. cal.	Freq. scaled	Freq. exp.[9]	I_{IR}	Assignment
36	3225.0	3079.8		6.8	CH_{benz} str., s. scale=0,955
35	3214.9	3070.2	3067	19.6	CH_{benz} str., as.
34	3205.1	3060.8		16.4	CH_{benz} str., as.
32	3189.1	3045.6		2.1	CH_{benz} str., as.
31	1647.8	1598	1590	0.3	CC_{benz} str., s.
30	1627.0	1578	1569	2.8	CC_{benz} str., s.
29	1527.9	1482	1482	15.1	$C_{benz}N$ str.
28	1495.4	1451	1452	4.3	CC_{benz} str., as.
27	1364.5	1324	1315	1.5	CC_{benz} str., as.
26	1333.8	1294		0.5	CC_{benz} str., Kekule.
25	1286.0	1247	1283	56.5	$C_{benz}N$, N=S=O str., as.
24	1213.7	1177	1177	92.0	S=O str., CH bend.
23	1200.4	1164	1162	88.4	$C_{benz}N$ and S=O, str., out-of-phase
22	1192.8	1157	1162	3.2	CH bend.
21	1112.9	1091	1096	5.8	CH bend.
19	1018.5	998	1018	13.3	Def. benz., as.
14	845.5	827	827	2.3	CH bend., out-of-plane
13	804.5	788	762	24.8	C_{benz}–N=S out-of-plane

12	771.6	756	762	36.4	CH bend., out-of-plane, in-phase
11	700.4	686	683	20.3	CH bend., out-of-plane, in-phase
10	628.6	616		0.1	Def. ring benz., as., in-plane
9	601.0	601	634	14.0	Def. ring, as., in-plane, N=S=O bend.
8	521.2	521	529	6.1	Def. ring benz., out-of-plane
5	344.8			1.9	–N=S=O bend

3.2. Electronic structure of the N-sulfinylamines in the ground singlet and triplet excited state

Few typical examples of N-sulfinylamines optimized by in the singlet and triplet states by DFT/B3LYP method are considered in Fig. 2 and Tables 2-3.

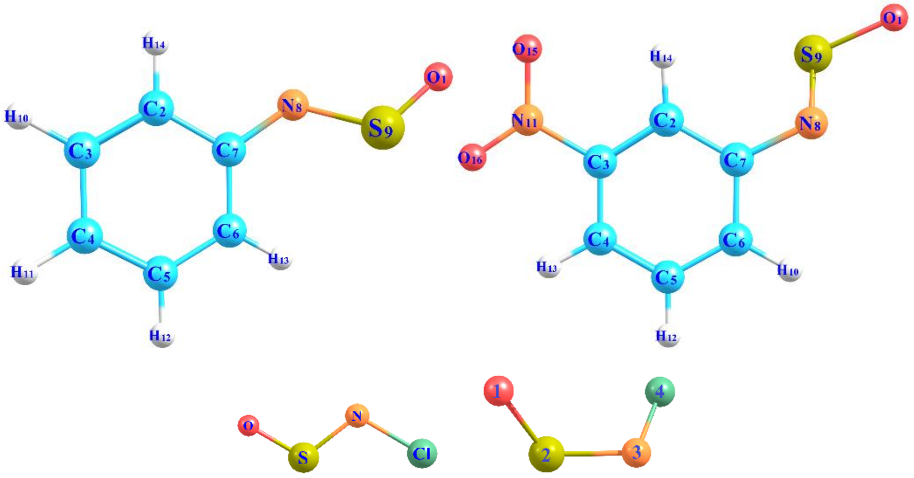


Fig. 2. Atomic numbering of phenyl- and *m*-nitro-N-sulfinylaniline including the structure of the singlet (left) and triplet (right) states of the Cl-N=S=O molecule.

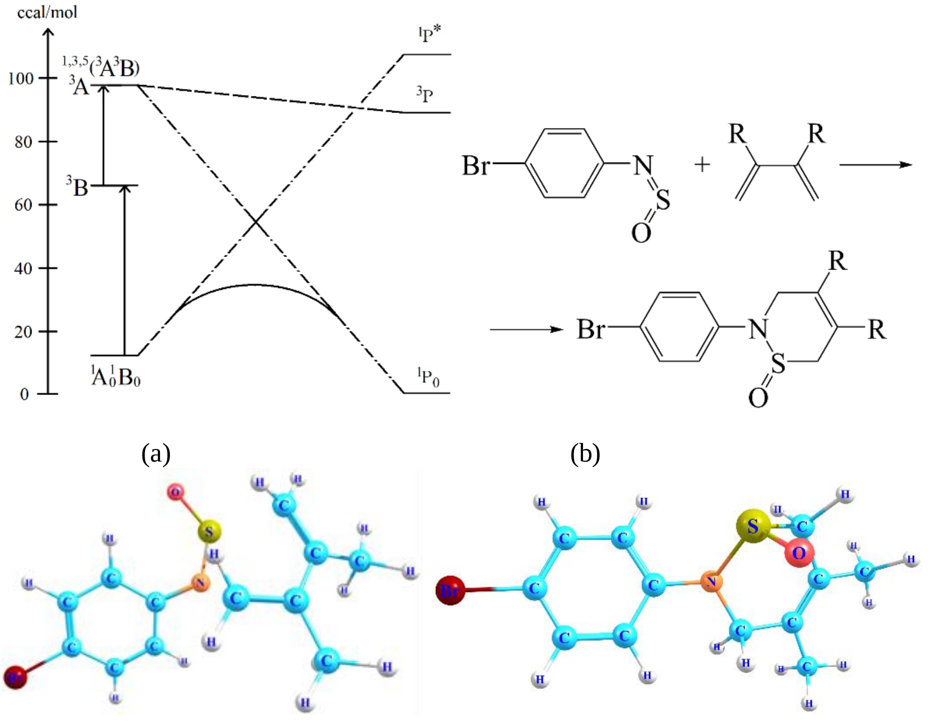
Table 2. Energy (a.u.), Mulliken atomic spin densities and atomic charges of aromatic N-sulfinylanilines. Hydrogen charges are summed to heavy atoms, ΔE$_{TS}$ is T$_1$-S$_0$ energy gap (eV).

Molecule	*p*-Cl-N-sulfinylaniline			*m*-nitro-N-sulfinylaniline		
Atom	Singlet	Triplet		Singlet	Triplet	
	Mulliken atomic charges	Mulliken atomic charges	Mulliken atomic spin densities	Mulliken atomic charges	Mulliken atomic charges	Mulliken atomic spin densities
1 O	-0.512	-0.489	0.474	-0.461	-0.476	0.486
2 C	0.048	0.061	0.242	0.063	0.086	0.247
3 C	0.027	0.040	-0.133	0.015	0.023	-0.138
4 C	-0.056	-0.060	0.312	0.047	-0.064	0.299
5 C	0.024	0.037	-0.134	0.267	0.267	-0.136
6 C	0.054	0.054	0.248	0.007	0.052	0.276
7 C	0.238	0.282	-0.100	0.227	0.277	-0.125
8 N	-0.525	-0.560	0.550	-0.511	-0.550	0.600
9 S	0.702	0.608	0.500	0.735	0.626	0.496
11 Cl, N	-0.001	0.023	0.037	0.386	0.392	0.008
15,16 O				-0.389	-0.377	-0.014
-Energy	1219.359	1219.308	E$_{TS}$=1.39	964.2491	964.2078	E$_{TS}$=1.12

Table 3. Mulliken atomic spin densities and Mulliken atomic charges of NSO^--group

Molecule	NSO^-			Cl–NSO		
Atom	Singlet	Triplet		Singlet	Triplet	
	Mulliken atomic charges	Mulliken atomic charges	Mulliken atomic spin densities	Mulliken atomic charges	Mulliken atomic charges	Mulliken atomic spin densities
1 O	–0.660	–0.718	0.238	–0.452	–0.426	0.515
2 S	0.313	0.294	0.386	0.784	0.655	0.473
3 N	–0.653	–0.576	1.376	–0.461	–0.413	0.810
4 Cl				0.129	0.183	0.202
-Energy	528.1200	528.0581	$E_{TS}=1.68$	988.2495	988.2077	$E_{TS}=1.13$

One can see that a strong charge transfer from N, O to S occurs in the triplet R-NSO molecules (Table 2,3). In the anion the largest T_1-S_0 energy gap is predicted (1.7 eV). The gap is droped to 1.1 eV upon R-NSO binding. The typical ΔE_{TS} value is about 3.5 eV in aromatics [10,11]. A very low ΔE_{TS} gap can influence the ground state chemical reactivity in terms of spin-catalysis concept [12,13] as in the cycloaddition reactions



(a) (b)

(c) (d)

Fig. 3. Schematic presentation of states correlation diagram for PES along reaction path for concerted cycloaddition reaction of N-sulfinylaniline (A) and diene (B).

In Fig. 3 the PES correlation diagram (a) for cycloaddition reaction between *para*-Br- N-sulfinylaniline (A) and diene (B) [13] is presented (b). The double-triplet ${}^{1,3,5}({}^3A{}^3B)$ states, like in the triplet-triplet annihilation [10], can possess the singlet, triplet and quintet multiplicity. In Fig. 2 the singlet part is taken into account and correlation with ${}^3P$ product is shown by dased line. The singlet ${}^1({}^3A{}^3B)$ state correlates well with the ground product ${}^1P_0$, but the starting reactants (${}^1A_0{}^1B_0$) diabatically correlate with the highly excited ${}^1P^*$ product [13] since their orbital and spin structure does not fit new bindings. Optimized structures of transition state (c) and product (d) are also shown in Fig. 3. Activation barrier of reaction is formed by avoiding crossing of two singlet states of the whole reacting system A+B. The lower ΔE_{TS} energy gap in the A molecule, the lower crossing point between $^1(^3A^3B)$ state and the ground state of the reactants $^1(^1A_0{}^1B_0)$ is predicted. That is why the N-sulfinylamines are prone to Diels-Alder cycloaddition.

All calculated N-sulfinylanilines are planar in the ground state and show the *trans* form, but in the T_1 state they are non planar with a strongly distorted NSO group intermediate between *cis* and *trans* structures (Table 3). This T_1 state shows n-π* type orbital structure with NSO spin localization and low repulsion of lone pairs (Scheme 1) which affords the cycloaddition reactions (Fig. 3).

Table 4. Geometry parameters of N–sulfinylanilines calculated by DFT methods

Molecule	*p*–Br–N–sulfinylaniline			*m*–nitro–N–sulfinylaniline	
Bond, angle	Experiment S_0 [2]	^{1}DFT	^{3}DFT	^{1}DFT	^{3}DFT
S–O	1.467	1.494	1.527	1.477	1.525
S–N	1.513	1.549	1.720	1.558	1.728
N–C^7	1.397	1.392	1.341	1.404	1.345
OSN	120.5	120.0	111.3	112.9	110.3
SNC^7	133.5	131.1	120.9	120.2	120.6
OSNC^7	1.3	0.002	57.6	175.5	–57.8
SNC^{7}C^2	–1.2	–0.016	–4.7	146.4	–177.5

Molecule	NSO–		Cl–NSO	
Bond, angle	^{1}DFT	^{3}DFT	^{1}DFT	^{3}DFT
O–S	1.533	1.572	1.475	1.515
S–N	1.497	1.650	1.585	1.771
OSN	124.242	116.483	111.0	108.7
O,S,N,Cl			180.0	73.2
N-Cl			1.751	1.721

In Table 5 we present some DFT calculated thermochemical parameters for transition state (TS) of reaction shown in Fig. 3. The calculated activation energy is 91 kJ/mol, $\Delta_r H^0_{298} = -39.4$ and $\Delta_r G^0_{298} = 19.7$ kJ/mol, $\Delta_r S^0_{298} = -198.27$ J/mol×K.

Table 5. Energy parameters of Diels-Alder reaction between p–Br–N–sulfinylaniline and 2,3-dimethyl-1,3-butadiene calculated with DFT method

Molecular system	B3LYP/6-31g(d)		
	Total energy E_{tot}, a.u.	Zero vibrational energy E_0, kJ/mol	S^0_{298}, J/mol·K
p–Br–N–sulfinylaniline	-3330.8682306	236.44	403.89
2,3-dimethyl-1,3-butadiene	-234.6227440	373.18	342.72
TS	-3565.4575171	613.63	559.17
Product of cycloaddition	-3565.5115360	624.20	548.34

The unexpectedly low ΔE_{TS} energy gap in the N-sulfinylamine molecules (about 1.1 eV) can influence their activity in terms of spin catalysis for various chemical reactions. The large spin density on oxygen atom (Table 2) opens reactivity in etherification and in H atom abstraction. For N-sulfinylhydrazines the extended π-conjugation through the -NH-NSO group produces a sulfide-like resonance which is responsible for N-sulfinylhydrazines inertness toward moisture. The strong decrease of positive charge on sulfur atom of the NSO group in the T_1 state with simultaneous increase of negative charges on other atoms of the group can explain some trends in photochemical oxidation reactions in the air [15,16]. Spin-orbit coupling (SOC) between T_1 and S_0 states is calculated to be relatively large (21 cm-1) which explains an efficient rate constant for non-adiabatic $S_0 \rightarrow T_1$ quantum transition upon heating. This might be useful for interpretation of anticancer activity of N-sulfinylhydrazines. In sulfinylamine hydrolysis water reacts as nucleophil and activation barrier is low because of big positive charge on sulfur in the ground state and low activation barriers can be explained by the singlet S_0 state reactivity [1-4]. All these results could be useful being predictive tools in the explanation of many general reactivity trends of N-sulfinyl compounds.

4. Conclusions

We applied DFT B3LYP method to a number of N-sulfinylamine molecules (also known as sulfinylimides, iminooxosulfuranes, N-sulfinylimines, N-sulfinylanilines). Spin-unrestricted DFT calculations show that the N-sulfinylaniline molecules are characterized by the low-lying triplet excited (T1) state which can explain a number of specific chemical properties. With account of spin-orbit coupling calculation between the singlet ground (S_0) and T_1 states we have explained the prone of the N-sulfinylimine substances to oxidation in a wet air. The $S_0 \rightarrow T_1$ quantum transition can be initiating by heating and interaction with water.

We have calculated the transition state of the Br-substituted N-sulfinylaniline Diels-Alder cycloaddition reaction with diene and interpreted this in terms of spin-catalysis concept accounting the low-lying T_1 state energy.

5.References

1. Ivanova E.V., Muchall H.M.: From Inert to Explosive, The Hydrolytic Reactivity of R-NSO Compounds Understood: A Computational Study. Journal of Physical Chemistry A. 115, 3095-3105 (2011). doi: 10.1021/jp110107p
2. Romano R.M., Della Ve´dova C.O.: N-Sulfinylimine compounds, R–N=S=O: a chemistry family with strong temperament. J. Mol. Structure. 522 1-26 (2000). doi: 10.1016/S0022-2860(99)00453-6
3. Ulrich H.: Cycloaddition reactions of heterocumulenes. Organic Chemistry, A Series of Monographs; Blomquist. 9, 1-364 (1967)
4. Verbeek W., Sundermeyer W.: Bis(sulfiny1amido)mercury(II). Angew. Chem., Int. Ed. Engl. 8, 376 (1969) doi: 10.1002/anie.196903761
5. Gaussian 09, Revision D.01, Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., et al. Gaussian, Inc., Wallingford CT, (2016).
6. A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652
7. [2] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789
8. 6-31П AO [4] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J.Phys.Chem. 98 (1994) 11623-11627
9. NIST Chemistry WebBook; IR spectrum; Coblentz no. 5727; https://webbook.nist.gov/cgi/cbook.cgi?ID=C1122834&Units=SI&Type=IR-SPEC&Index=1#IR-SPEC (accessed August 12, 2020)
10. Agren H., Vahtras O., Minaev B.F.: Response theory and calculations of spin-orbit coupling phenomena in molecules. Advances in Quantum Chemistry. 27, 71-162 (1996). doi: 10.1016/S0065-3276(08)60251-8.
11. Loboda O., Minaev B., Vahtras O., Ruud K., Schimmelpfennig B.: Ab initio calculations of zero-field splitting parameters in linear polyacenes. Chemical Physics. 286, 127-137 (2003). doi: 10.1016/S0301-0104(02)00914-X.
12. Minaev B.F., Agren H.: Spin uncoupling in molecular hydrogen activation by platinum clusters. Journal of Molecular Catalysis A. 149, 179-195 (1999). doi: 10.1016/S1381-1169(99)00173-9
13. Minaev B.F.: Spin effects in activation of hydrocarbons: The role of triplet states in catalysis. Journal of Molecular Catalysis A. 171, 53-72 (2001). doi: 10.1002/chin.200148292
14. Veremeichik Yu.A., Tevs O.A., Krivolapov D.B., Lodochnikova O.A., Plemenkov V.V.: Synthesis and structure of novel substituted *N*-sulfinylanilines. Russian Journal of General Chemistry. 87, 1143-1147 (2017). doi: 10.1134/S107036321706007X
15. Minaev B.F., Kobzev G.I.: Response calculations of electronic and vibrational transitions in molecular oxygen induced by interaction with noble gases. Spectrochimica Acta Part A. 59, 3387-3410 (2003). doi: 10.1016/S1386-1425(03)00165-3
16. Minaev B. F., Knuts S., Ågren H.: On the interpretation of the external heavy-atom effect on singlet-triplet transitions. Chemical Physics. 181, 15-28 (1994). doi: 10.1016/0301-0104(94)85010-0

PP-II-1

ACTIVITY OF CR-CU-O CATALYSTS IN THE ETHANOL CONVERSION REACTION

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Abstract. In this work, the reaction of the conversion of ethanol was studied over chromium copper oxide catalysts. Acetic aldehyde was shown to be the main product of the ethanol conversion reaction. The effect of the reaction temperature on the product yields was studied. It has been established that with increasing temperature, the direction of the ethanol conversion reaction shifts toward dehydration of ethanol to ethylene. Studies have shown that the atomic ratio of chromium to copper in the composition of the catalyst also has a strong effect on the activity of chromium-copper oxide catalysts. It has been established that the samples with a high copper content in the composition of the catalyst have the greatest activity in the reaction of acetic aldehyde formation. The isomerization reaction of butene-1 to cis- and trans-butenes-2 was studied. It was found that with an increase in the chromium content in the catalyst, the degree of butene-1 isomerization decreases. The dependence of the activity of chromium copper oxide catalysts on their acid properties is established. It was found that with an increase in surface acidity, ethanol conversion remains virtually unchanged, and the yield of acetic aldehyde and its selectivity decrease.

Keywords: Ethanol Conversion, Binary Catalysts, Isomerization.

1.Introduction

One of the promising raw materials for the production of various chemical compounds is ethanol [1-3]. This is due to the fact that ethanol is obtained in large quantities from biomass and is a renewable raw material. For the reactions of ethanol conversion, various catalytic systems are used based on oxides of chrome, zinc, copper, etc. [4, 5]. We have previously shown that ethanol is converted at high speed into acetone, acetic acid on various binary chromium-copper containing catalysts [6,7]. From the periodic literature it is known that the activity of the catalysts depends on their surface properties [8,9]. In this regard, the present work is devoted to the study of the dependence of the activity of chromium-copper oxide catalysts on their acidic surface properties.

2.Experimental part

Binary chromium copper oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of chromium and copper nitrate. The resulting mixture was successively evaporated and dried at 100-120°C, decomposed until nitrogen oxides were completely isolated at 250°C, and then calcined at 600°C during 10 hours. Thus, 9 catalysts with an atomic ratio of elements from Cr:Cu = 1:9 to Cr:Cu = 9:1 were synthesized. The activity of the synthesized catalysts in the reaction of ethanol conversion and butene-1 isomerization was studied in a flow unit with a tubular reactor in the temperature range 100 – 500°C. 5 ml of the studied catalyst with a grain size of 1.0–2.0 mm was loaded into the reactor, and its activity in the ethanol conversion reaction was studied. Ethanol conversion was carried out in a stream of nitrogen. Ethanol and its conversion products were determined by chromatography method.

3.Results and discussion

Studies have shown that the main product of the conversion of ethanol over chrome-copper oxide catalysts is acetic aldehyde. Ethylene, acetone, ethyl acetate, carbon dioxide, and carbon dioxide and other decomposition products are also formed as a by-product. Figure 1 shows the effect of the reaction temperature on the yields of ethanol conversion products on a Cr:Cu = 6:4 catalyst. As can be seen from Figure 1, acetic aldehyde is formed in the greatest amount on the Cr:Cu = 6:4 catalyst. Figure 1 shows that the reaction of ethanol conversion on the studied catalyst starts at a temperature of 150°C and at this temperature only acetic aldehyde is formed in an amount of 9.9%. An increase in the reaction temperature leads to the formation of other reaction products. The maximum yield of acetic aldehyde reaches 82.5% at 300°C.

The formation of ethylene, acetone and carbon dioxide begins at a temperature of 350°C. Figure 1 shows that the yields of ethylene and acetone increase with increasing reaction temperature. The highest yields of ethylene and acetone are observed at a temperature of 450°C and are respectively 30.2 and 28%.

The formation of ethyl acetate is observed in the temperature range 350 and 450°C and does not exceed 5.6%. The maximum ethanol conversion on the Cr:Cu = 1:9 catalyst reaches 92.1% at 450°C.

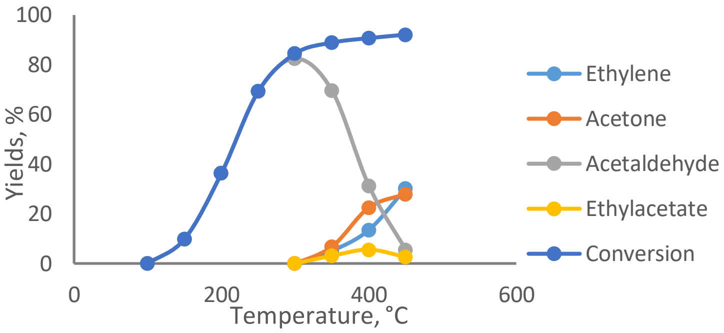

Fig. 1 Effect of temperature on the yields of ethanol conversion products on a Cr:Cu=6:4 catalyst.

Our preliminary studies showed that the atomic ratio of cerium to copper strongly affects the activity of chromium-copper oxide catalysts in the reaction of ethanol conversion. In this regard, we studied the effect of the composition of chromium copper catalyst on its activity. Table 1 shows the ethanol conversion, yields and selectivity of acetic aldehyde on chromium copper oxide catalysts of various compositions at a temperature of 300°C.

As can be seen from table 1, the yield of acetic aldehyde with an increase in the chromium content in the catalyst composition first decreases from 46.2% on the catalyst Cr:Cu = 1:9 to 32.3% on the catalyst Cr:Cu = 3:7 and then increases and passes through a maximum of 82.5% on the catalyst Cr:Cu = 6:4. The table also shows that the selectivity of the reaction for acetic aldehyde with an increase in the chromium content in the catalyst increases to almost 98% and then remains unchanged. The maximum ethanol conversion in the studied samples reaches 84.5%.

Table 1. The dependence of the yield and selectivity of acetic aldehyde on the atomic ratio of chromium to copper. T = 300°C.

Cr/Cu atom ratio	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Reaction products	Yields, %								
CH$_3$CHO	46,2	42,3	32,3	53,9	70,9	82,5	75,9	61,1	57
Conversion	73,8	63,3	58,6	67,9	72,6	84,5	75,9	62,5	57,8
Selectivity	62,6	66,8	55,1	79,4	97,6	97,6	100	97,8	98,6

Thus, based on the conducted studies, it can be said that acetic aldehyde is the main reaction product on chromium-copper catalysts and its yield reaches 82.5% with a selectivity of 97.6%. The yield and distribution of reaction products on chromium copper catalysts depends on both the reaction temperature and the atomic ratio of chromium to copper.

The acid-base surface properties of heterogeneous catalysts quite often correlate with their catalytic properties. In this regard, we studied the dependence of the activity of binary cobalt-containing catalysts in the reaction of steam conversion of ethanol to hydrogen on their acidity, for which we measured the rate of butene-1 isomerization to butene-2.

The results of a study of the reaction of butene-1 isomerization in butene-2 over chromium copper oxide catalysts are presented in Table 2. As can be seen from the figure, with an increase in the chromium content in the composition of the catalysts, the yields of trans and cis butene-2 decrease from 67.2% on the Cr-Cu = 1 sample -9 to 24.5% on a Cr-Cu catalyst = 9-1. From the data given in table 1 it is also seen that the ratio of the yields of trans and cis butenes-2 on the studied catalysts varies between 0.31 - 0.48.

Table 2. The dependence of the yields and ratios of trans and cis butenes-2 on the atomic ratio of chromium to copper. T = 300°C.

Cr/Cu atom ratio	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9
Reaction products	Yields, %								
trans-butene-2	19,4	12,5	11,9	10,6	9	8,2	8,1	7,3	7,6
cis-butene-2	47,8	32,8	29,2	28,7	27,4	22,7	19,7	19,8	16,9
Σ (t+c) butene	67,2	45,3	41,1	39,3	36,4	30,9	27,8	27,1	24,5
trans/cis ratio	0,41	0,38	0,41	0,37	0,33	0,36	0,41	0,37	0,45

Figure 2 shows the dependence of the yield of acetic aldehyde, the selectivity of the process for acetic aldehyde, and the conversion of ethanol on the degree of isomerization of butene-1 to butene-2 on binary chromium-copper oxide catalysts.

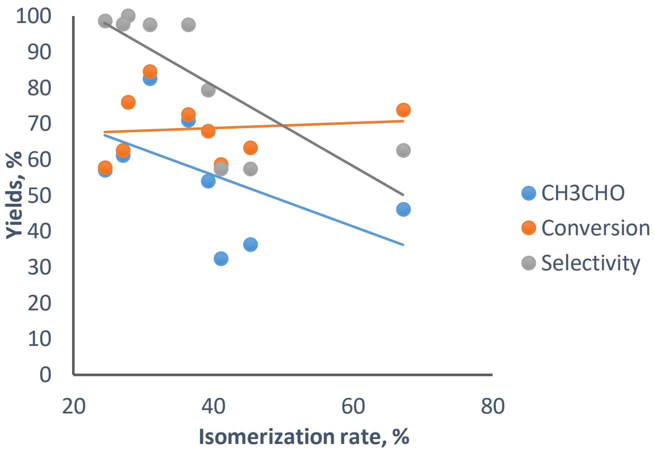

Fig. 2. Dependents of the yields of ethanol conversion products on isomerization rate.

As can be seen from Fig. 2, with an increase in the activity of chromium-copper oxide catalysts in the isomerization of butene-1 to butenes-2, the yield of acetic aldehyde and the selectivity of the process for acetic aldehyde decrease, while the overall conversion of ethanol does not change. This suggests that an increase in surface acidity leads to an increase in the rate of reaction by-products. Based on this, it can be assumed that the dehydrogenation of ethanol to acetic aldehyde proceeds at non-acidic sites.

4.Conclusions

- The main product of the ethanol conversion reaction over chromium-copper oxide catalysts is acetic aldehyde, and its yield reaches up to 82.5% with selectivity 97.6%.
- Increase in surface acidity of chromium-copper oxide catalysts leads to decrease of yield of acetic aldehyde and its selectivity in the ethanol conversion reaction.

5.References

1. Megumu Inaba, Kazuhisa Murata, Masahiro Saito & Isao Takahara: Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. Reaction Kinetics and Catalysis Letters volume 88, pages 135–141 (2006).
2. Weiping Wang, Zhifei Wang, Yan Ding, Jinyu Xi & Gongxuan Lu: Partial Oxidation of Ethanol to Hydrogen over Ni–Fe Catalysts. Catalysis Letters volume 81, pages 63–68 (2002).
3. Dapeng Liu, Yan Liu, Eileen Yi Ling Goh, Christina Jia Ying Chu, Chuandayani Gunawan Gwie, Jie Chang, Armando Borgna: Catalytic conversion of ethanol over ZSM-11 based catalysts. Applied Catalysis A: General, Volume 523, Pages 118–129 (2016).
4. Hala R. Mahmoud: Highly dispersed Cr2O3–ZrO2 binary oxide nanomaterials as novel catalysts for ethanol conversion. Journal of Molecular Catalysis A: Chemical, Volume 392, Pages 216–222 (2014).
5. Isabel C. Freitas, Jean Marcel R. Gallo, José Maria C. Bueno & Clélia M. P. Marques: The Effect of Ag in the Cu/ZrO2 Performance for the Ethanol Conversion. Topics in Catalysis volume 59, pages357–365(2016).
6. Mammadova S.H., Aghayeva K.Kh.: Conversion of ethanol over binary copper containing catalysts. Chemical Problems 2(18), 199-205 (2020).
7. Mammadova S.H., Garaybayli S.A., Baghiyev V.L.: A study of the phase composition of copper-cerium oxide system. In: 5th International School-Conference on Catalysis for Young Scientists, Catalyst Design: From Molecular to Industrial Level, May 20-23, 2018, Moscow, Russia, ABSTRACTS, Novosibirsk, PP-V-12, p.188.
8. S. Sugunan, T. Radhika & H. Suja: Surface properties and catalytic activity of sulfated rutile. Reaction Kinetics and Catalysis Letters volume 79, pages27–33 (2003).
9. V. Vishwanathan, Hyun-Seog Roh, Jae-Woo Kim & Ki-Won Jun: Surface Properties and Catalytic Activity of TiO2–ZrO2 Mixed Oxides in Dehydration of Methanol to Dimethyl Ether. Catalysis Letters volume 96, pages 23–28 (2004).

OR-II-6

EFFICIENT REMOVAL OF SULFUR AND NITROGEN COMPOUNDS FROM TRANSPORTATION FUELS USING IONIC LIQUIDS VIA MICROWAVE OXIDATION TREATMENT

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Abstract. Effective and complete removal of sulfur (S) and nitrogen (N) compounds from fuel oil is important to meet the new requirements of environmental agency. Two Bronsted acid pyridinium-based ionic liquids (IL) were synthesized via microwave irradiations and used as both catalyst and extracting agent for the oxidation of real diesel fuel in the presence of combined oxidants. It was shown that increasing the acid site strength leads to an increase of S-removal from diesel fuel. The best results were obtained in the presence H_2O_2/H_2SO_4-[$CH_2COOHPy$][HSO_4] catalytic system. The main factors affecting the process consisting of IL dosage, temperature, oxidant dosage, time and power of microwave irradiations (MW) were investigated in detail. The proposed method was demonstrated to be potentially applicable for the simultaneous extractive oxidesulfurization (ODS) and oxidenitrification (ODN) of diesel fuel (S= 541 ppm, N= 178 ppm) and real transportation fuels without any specific adaptation. Under optimal conditions oxidation, the S-removal reaches 98.34% and more than a 84 % denitrification degree of real diesel fuel were obtained (the oxidation conditions: oxidant/fuel volumetric ratio=0.03, 3 mL of IL, 400 rpm, 60°C, 700 W, 120 s). The synthesized IL could be reused/recycled for consecutive treatment-runs.

Keywords: Desulfurization, Denitrogenation, pyridinium-based IL, Fuel, Microwave

1. Introduction

Owing to the rapid economic expansion in the worldwide, the Organization of the Petroleum Exporting Countries (OPEC) estimated that demand for middle distillates will increase by 6.8 mb/d during the period 2016–2040. In terms of crude, it is projected that OPEC will need to supply an additional 7.7 mb/d during forecast period [1]. In regards to the continuous augmentation demand for energy and dwindling light crude oils reserves, the utility of low-quality feedstock (e.g.: sour, heavy oil and residuum) has become inevitable to exceed the world oil supply. The burning of liquid fuels derived from the residual oil leads to the increased emission of undesirable SOx and NOx gases, with well-known consequences on environmental and human health (e.g: acid rain, cancer etc.) [2,3]. For these reasons, the environment protection agencies across the word have imposed severe policies on the sulfur level of liquid fuels. Especially, for the transportation purposes, the developed countries have now recommended to utilize the gasoline/diesel containing with very limited sulfur (10-15 ppm) since 2018, and the tendency goes to sulfur-free oils [4].

In the industries, sulfur and nitrogen compounds are typically removed from feedstock by hydrotreating (e.g.: hydrodesulfurization (HDS) and simultaneous hydrodenitrification (HDN)) using a bimetallic catalyst. Chemically, during HDS, the S-compounds are converted into the corresponding aliphatic hydrocarbons and H_2S. Nitrogen-components are simultaneously converted to ammonia and the corresponding hydrocarbons. Though well optimized and industrialized, HDS has been relatively ineffective in converting benzothiophenes (BTs) and dibenzothiophenes (DBTs), especially DBTs having alkyl substituents on their 4 and/or 6 positions. Similarly, nitrogen-compounds, such as quinoline and carbazole, are relatively resistant to this treatment. To produce fuel oils with ultralow sulfur/nitrogen levels, in most of the cases a two-step deep hydrotreationg is required; this also implies the need of expensive H_2 gas in large quantity, more severe operating conditions and special active catalysts [5,6]. This prompts the researchers to find alternative approaches to meet the new standards for the liquid fuels under the H_2-free mild conditions with the expectation to lower the final fuel price and economize the HDS-energy consumption. Several trends toward reducing the S/N content in fuels are currently coming to the fore; these include oxidative desulfurization and denitrification (ODS/ODN) [7], bio-process [8], selective adsorption [9], and extraction methods with solvents [10] or ionic liquids as detailed in the review of Zolotareva et al. [11]. However, these alternative methods are still in the laboratory scale. At the same time, amongst all the aforementioned alternative HDS-methods, the ODS is endorsed as a suitable replacement or complementary to HDS for deep desulfurization of fuel oils. Till now, various studies on the ODS process have reported the use of differing oxidants, such as H_2O_2 in combination with H_2SO_4 [12], H_2O_2 with acid formic and H_2SO_4 [13], etc. A major part of these publications is dedicated to ODS procedure carried out on model molecules mostly BT, DBT and DMDBT. It has certainly been stated that the catalytic behavior may differ in the ODS of model and real feeds [13], and the simultaneous ODN could be operated at the same conditions of ODS process [11]. Currently, more efficient ODS/ODN systems in the presence of ionic liquid as extractant and catalyst have been stated. For example, Nie et al. [14] managed to increase the conversion of dibenzothiophene (DBT) from 11.86% to 90.64% by adding an ionic liquid to the reactional mixture, and the pyridine, pyrrole, and quinoline removal could reach nearly 100% at optimal conditions: IL/oil = 1:3 (mass ratio), O/N = 4:1 (molar ratio), 25 °C. It is known from the literature that the oxidation of S- and N-compounds proceeds easily in acidic media in which Brønsted acids (formic acid, acetic acid, sulfuric acid, phosphoric acid, etc.) are frequently used as catalysts for the oxidation of heteroatom compounds [9,15]. Catalytic systems based on ionic liquid containing Brønsted acidity are also used to enhance the oxidation and the extraction processes [15-17]. Therefore, in this work two Brønsted acids pyridinium-based ILs ($[CH_2COOHPy][HSO_4]$, and $[CH_2COOHmPy][HSO_4]$) were prepared and employed as catalysts and extractants in the simultaneous ODS/ODN of transportation fuels. Varying conditions for the oxidation reaction have been investigated, including reaction system, oxidant dosage, temperature, and microwave parameters. Besides, catalytic system possible reusability and recyclability were also studied.

2. Experimental procedure

2.1 Chemicals and methods

Analytical grade sulfuric acid, peroxide, pyridine, 3-methyl pyridine and other chemicals were purchased from Merck (Germany). All fuels were obtained from the Algiers petroleum processing. The infrared spectra of the title substrates as KBr pellets (4000–400 cm^{-1}) were recorded on a Varian 3100 FT-IR Excalibur series spectrophotometer (Germany). ^1H and ^{13}C NMR spectra were recorded in D_2O by using an internal standard on a Bruker 300 MHz Spectrometer (Germany). S and N elemental analyses were performed on X-ray Fluorescence analyzer (OXFORD LAB X-3500) and a Kjeldahl distillation apparatus, respectively, in accordance standards (ASTM D 5453 and D 3228). The samples before and after treatment were directly analyzed using gas chromatography/mass spectrometer (CG-MS), with 30 m ×250 μm inner diameter ×0.25 μm film thickness HP-5 capillary column, the injector and detector temperature was set to 300 and 290 °C, respectively. The GC-process for diesel started at 100 °C and the temperature was raised to 250 °C at 5 °C/min.

2.2 Pyridnium-based ILs synthesis

Synthesis of ionic liquids are presented in Fig.1. The synthesis of ILs based on sulfuric acid was accomplished in two stages. In the first stage, an equimolar amounts of pyridine (or picoline) and chloroacetic acid were put in a microwave assisted-reactor. The mixture was stirred mechanically for 5 min at 80°C at 150 W until obtaining a white solid precipitate ($[CH_2COOHPy]Cl$ or $[CH_2COOmHPy]Cl$). In the second stage, the resulting product was dissolved in distilled (Milli-QTM) water, and an equimolar amount of sulfuric acid (0.05:0.05) was dropwise under stirring until obtaining viscous liquid. The product was purified and dried under vacuum and the IL acidity measurement was performed at by mean Hammett method using UV–vis spectroscopy, wherein a methyl-orange in methanol solvent (pKa = 3.39) as a basic indicator was used to trap the dissociative proton. Then, the Hammett function (H_0) is calculated by using the formula [18]:

$$H_0 = \mathrm{pKa}\,[\mathrm{I}] + \mathrm{Log}\,\frac{[\mathrm{I}]}{[\mathrm{IH}^+]} \qquad (1)$$

where pKa[I] is the pKa value of the methyl-orange indicator, [I] and $[IH^+]$ are the percentages extracted from UV–vis absorbance band peak of respectively the unprotonated and protonated forms of the indicator in aqueous solution.

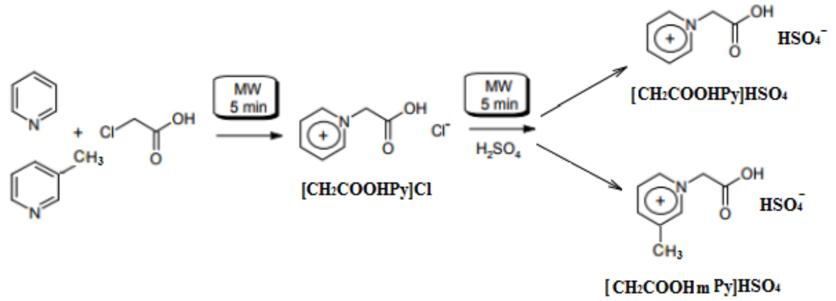


Fig. 1: Preparation pyridinium-based ionic liquids used in this work.

2.3 ODS and Simultaneous ODS/ODN of actual diesel experiments

All combined ODS/ODN experiments were conducted in a 100 mL single jacketed-glass column placed in a domestic microwave (Model Brandt SE2612S-900W), equipped with a mechanical stirrer, an infrared thermometer, and placed in a circulating water bath in order to set the temperature. At first, 50 mL of the diesel and oxidants (H_2O_2 and H_2SO_4) were poured into the column and heated to the desired temperature and then, a proper amount of selected IL was added to the system leisurely under controlled stirring. Then the mixture was settle for 10 min to obtain a clear phases and fuel was withdrawn from the upper phase for S, N-content analysis.

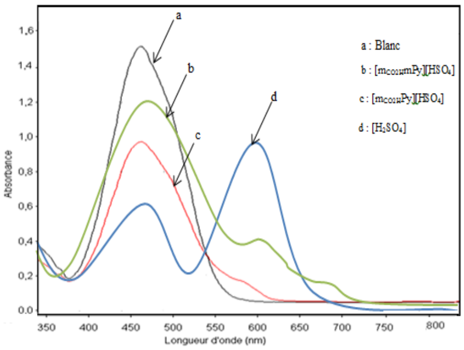
3.Results and discussions

3.1 Pyridnium-based ILs synthesis and characterization

The obtained ionic liquids were identified by NMR and FTIR analysis (see Supporting Informations), and the obtained data are listed below:

N-carboxymethylpyridine hydrosulphate ([CH_2COOHPy][HSO_4]): Yield: 92%. FTIR (KBr, γ /cm^{-1}): 3396, 2924, 1735, 1638, 1490, 1229, 1063, 839, 641, 585, 455. ^{1}HNMR (300 MHz, D_2O): 5.36 (s, 2H), 7.95 (t, 2H), 8.46 (t, 1H), 8.65 (d, 2H); ^{13}C NMR (300 MHz, D_2O): 60.89, 127.89, 145.66, 146.84, and 168.81. Density: 1.78 g/cm^3 and viscosity: 0.35 Pa.s. **Carboxymethyl-3-methylpyridine hydrosulphate [CH_2COOHmPy][HSO_4]:** Yield: 89.1%. FTIR (KBr, γ /cm^{-1}): 3436, 3425, 2924, 2488, 1738, 1640, 1507, 1289, 1172, 1008, 1006, 882, 773, 678, 613. ^{1}HNMR (300 MHz, D_2O): 2.39 (s,3H), 2.91 (s, 2H), 4.31 (t, 2H), 7.47 (t, 1H), 8.15 (d, 2H); ^{13}C NMR (300 MHz, D_2O): 27.84, 53. 11, 128.36, 146.19, 147.23, and 169.11. The density and 1.83 g/cm^3 and viscosity 0.39 Pa.s.

The UV–visible spectra of ILs are shown in Fig. 2. The maximal absorbance of the unprotonated form of the methyl-orange indicator (blank) was observed at 465 nm in methanol. The addition of IL or H_2SO_4 to the blank solution leads to decrease the absorbance of the unprotonated form of the basic indicator. The Hammett acidity (H_0) values calculated by using formula (1) are given in Table 2. As can be seen, [CH_2COOHPy][HSO_4] IL showed higher acidity than [CH_2COOHmPy][HSO_4] IL.



Fig; 2. U–vis absorption spectra of methyl-Orange for [CH_2COOHPy][HSO_4] IL, [CH_2COOHmPy][HSO_4] IL or H_2SO_4 in methanol solvent.

Table 2. Calculation of Hammett function H_0 of pyridinium-based ionic liquids and H_2SO_4 in methanol at ambient temperature.

Ionic liquid	Indicator	A_{max}	[I] (%)	[IH$^+$] (%)	H_0
-	Methyl-orange	1.53	100	00.00	-
$[CH_2COOHPy][HSO_4]$	Methyl-orange	0.92	39.87	60.13	3.21
$[CH_2COOHmPy][HSO_4]$	Methyl-orange	1.21	20.92	79.08	2.81
H_2SO_4	Methyl-orange	0.67	51.21	48.79	3.41

3.2. Optimization of parameters in extractive ODS process

Initially, the influence of different ionic liquids on the simultaneous desulfurization of diesel in the presence of H_2O_2/H_2SO_4 (H_2O_2/H_2SO_4= 1/2 volumetric ratio) at 30°C was investigated. During the initial extraction procedure of 15 minutes before adding the oxidant, the extractive abilities of each ionic liquid can be compared for the S-removal and the results presented in Fig. 3 (A) showed that $[CH_2COOHmPy][HSO_4]$ exhibits highest extraction performance (23.29%) than $[CH_2COOHPy][HSO_4]$ IL (19.59 %). This work confirms the results obtained by Gao et al. [19]. However, by adding oxidants, it is surprising that $[CH_2COOHPy][HSO_4]$ IL is better than $[CH_2COOHmPy][HSO_4]$ IL, which may because $[CH_2COOHPy][HSO_4]$ with high acidity and low density is favorable for the desulfurization of diesel fuel. Thus, more acidity can lead to more formation of peroxycarboxylic acid group (–COOOH) with strong oxidation tendency generated easier by the reaction of acidic IL with H_2O_2 [19]. Fig. 3 (B) shows the effect of oxidant on the extractive ODS-performance. It appear that extractive-ODS behaviors display the same trend with the corresponding oxidant/diesel (O/D) volumetric ratio at operating conditions: initial S-content= 541 ppm, diesel/$[CH_2COOHPy][HSO_4]$= 50:1, 400 rpm at 30°C. Sulfuric acid at low concentration is added to increase the medium-acidity by intensifying the member of protons leading to facilitate and accelerate the formation of peroxyacid groups, and also to prevent the thermal decomposition of H_2O_2 [12, 20]. The S-content in diesel fuel decreases with oxidant amounts (e.g.: O/D= 0 to 0.03) and finally flattens out, which may be attributed to the highest redox potential of oxidants [13]. After a reaction time of 1.5 h, the ODS-efficiency was about 55.82 % (239 ppm) when the O/D= 0.03 but the O/D= 0.04 shows a slightly lower ODS-performance (252 ppm). As a whole, the introduction of H_2SO_4 solution leads to increasing the ODS-ability for removing S-compounds but the decomposition of the acid solution into SO_4^{-2} and the formation of water by product charged with the excess of oxidant may decelerate the ODS-performance [12].

The effect of IL amounts on the process was evaluated. As illustrated in Fig. 3 (C), the S-removal percentage reaches 82.07 % (97 ppm) with 3 mL of IL. The high ODS-efficiency displayed by IL amount may be attributed to the highest mass transfer and the diesel-immiscibility in IL, which leads to the formation triphasic ODS-system (diesel/oxidant/IL). Figure 3 (D) shows the fitting results for H_2O_2-$H_2SO_4/[CH_2COOHPy][HSO_4]$ system towards S-compounds at various temperature. The kinetic plots of ODS tendency are similar at the different temperatures, the S-removal decreases with temperature and resulted in of S-removal from diesel from 103 ppm at 30°C to 57 ppm at 60°C after 1.5 h. As a reasonable explanation, the increasing temperature gradient contributes to increasing the desulfurization rate by making the transfer of S-compounds into complexing species quickly, which are easily dissolved in the mixture. From an economically and technically point of view, 60 °C may be a suitable reaction temperature for the present ODS system, since higher temperature means higher operation cost.

The main effects of microwave-parameters (time and power) are shown in Fig. 3 (E). Microwave-assisted ODS-process was carried out at optimized conditions: Vdiesel= 50 mL, O/D=0.03, VIL= 3 mL, 400 rpm and T=60°C. Interestingly, microwave-assisted ODS could reached (98.34 %, i.e., 532 ppm removed) of S-removal from diesel in 120 s at 700 W. This high S-removal may be due to the fact that microwave transferring energy from the irradiation source to the mixture led to the microwave thermal excitation which brought additional polarity to the S-compounds and oxidant agents; this can effectively accelerate the ODS rates [21].

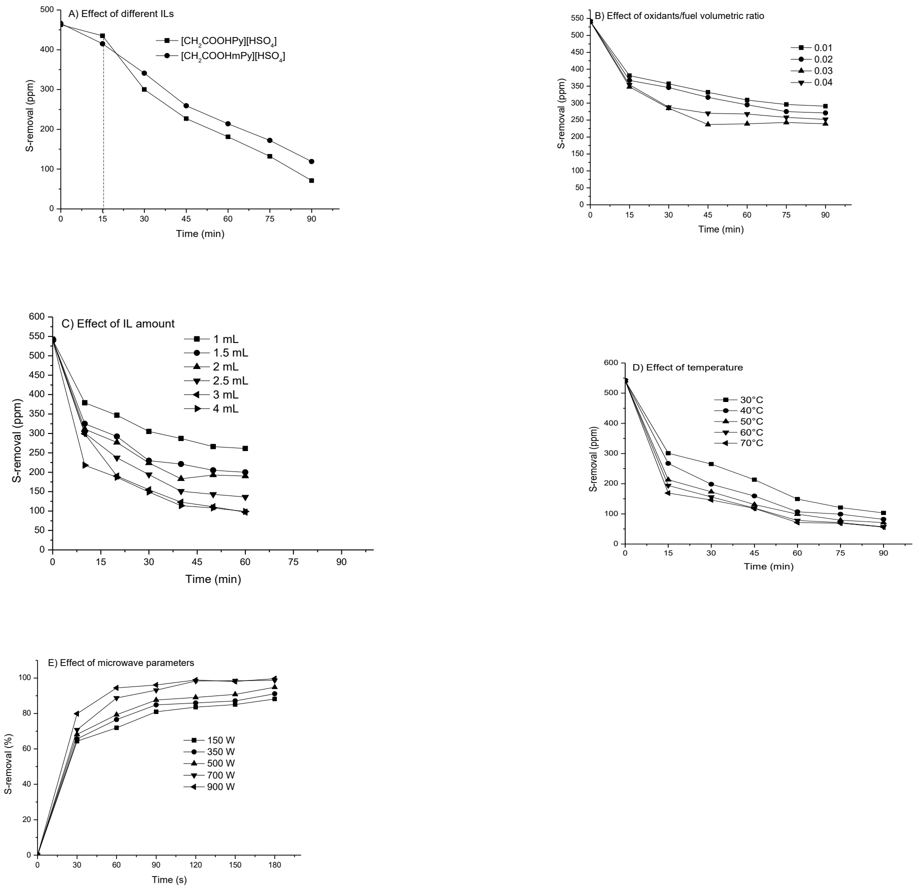


Fig.3. Effect of various operating parameters on S-removal from diesel fuel (541 ppm): A) IL type, B) oxidant/diesel amount, C) IL amount, D) temperature and D) microwave parameters (time and irradiations power).

Reusability and recyclability of IL

It was of interest to explore the activity of H_2O_2-H_2SO_4/[$CH_2COOHPy$][HSO_4] system for several cycles through recycling and reutilization processes. In both "reused" and "recycled" methods, the diesel phase was removed, but in the reused process fresh amounts of diesel was added without performing any other treatments, while in the recycled method the IL was regenerated by a mixture of water and carbon tetrachloride and then fresh amount of oxidants were added to the mixture. Each cycle was performed under the same optimal experimental conditions used during the first. As presented in Fig. 4, the ODS-efficiency decreases gradually from cycle 1 to process cycle 3 by using non-regenerated IL. This might be attributed to accumulation of oxidation products. While, the recycled-IL can be used at least five times for ODS-cycles with negligible loss in its activity.

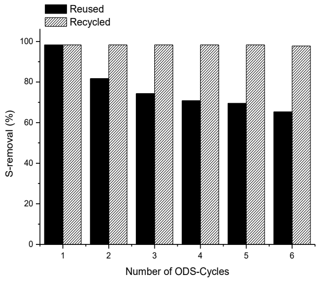


Fig.4. Microwave-assisted extractive ODS by reused and recycled [$CH_2COOHPy$][HSO_4]. Experimental Conditions: Vdiesel= 50 mL with initial S-content= 541 ppm; oxidant/diesel=0.03; 1 mL of H_2O_2 30% aq.; 2 mL of H_2SO_4 solution at 0.1 N; 3 mL of [$CH_2COOHPy$][HSO_4] IL; 400 rpm, T=60°C at 700 W for 120 s.

3.3 Simultaneous microwave-assisted ODS and ODN of a diesel

Simultaneous ODS/ODN was carried out at optimal conditions using a diesel (S=541 ppm, N=178 ppm) (V_{diesel}= 50 mL with initial S-content= 541 ppm; oxidant/diesel=0.03; 1 mL of H_2O_2 30% aq.; 2 mL of H_2SO_4 solution at 0.1 N; 3 mL of [$CH_2COOHPy$][HSO_4] IL; 400 rpm, T=60°C at 700 W for 120 s using first the diesel fuel (S=541 ppm, N=178 ppm). The results obtained for simultaneous ODS/ODN (Fig.5 (a)), indicate that S-compound are significantly better removed than N-compounds; this may be due to the competitive oxidation between ODN and ODS-reactions [14]. Both N- and S-compounds can be significantly removed from the diesel fuel, with nearly 85.4 % of desulfurization degree and 98,34 % of denitrification degree. It seems that most of the remaining S- and N- compounds (S=9 ppm, N=26 ppm) should be sterically hindered or highly stable to this treatment. Simultaneous ODS/ODN performances were subsequently checked using real transportation fuels such as gasoline, kerosene and marine fuel at same optimal conditions mentioned-above without any specific adaptation and high S- and N-removal were obtained (see Fig. 5 B). The difference between the combined ODS/ODN-efficiency of the considering fuels may related to the chemical composition of each fuel.

Some simultaneous ODS and ODN results of fuels oils using ILs are summarized, our results obtained seem very competitive. The proposed treatment process in this study provides satisfactory ODS and ODN efficiencies.

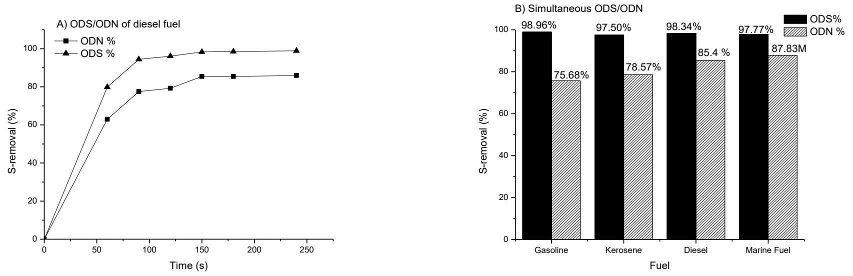


Fig.5. Simultaneous microwave assisted-ODS/ODN of transportation fuels. Experimental Conditions: V_{fuel}= 50 mL; oxidant/fuel=0.03; 1 mL of H_2O_2 30% aq.; 2 mL of H_2SO_4 solution at 0.1 N; 3 mL of [$CH_2COOHPy$][HSO_4] IL; 400 rpm, T=60°C at 700 W for 120 s.

Identification of oxidation byproducts in simultaneous ODS/ODN process

FTIR spectra of original, oxidized and treated diesel is shown in Fig. 6. As can be seen, the most intense bands at (3000–2800 cm^{-1}) and angular deformations (1462 cm^{-1} and 1377 cm^{-1}) were attributed to stretching vibration of C–H groups. Aromatic compounds bands were located at 1603 cm^{-1} and 900–675 cm^{-1} from the C–H out-of-plane angular deformation. The sulfur is present in original diesel as sulfides, which was observed by C–S axial stretch at very weak band in 700–650 cm^{-1} and by C=S axial stretch at 1206 cm^{-1} as stated in literature [27]. The bands at 1302 cm^{-1} and 1168 cm^{-1} indicated the presence of sulfones compounds in oxidized diesel without IL extraction step as showing in Fig. 6 (b). It seems that the sulfones peaks have disappeared in the FTIR spectra of treated diesel (see Fig. 6 (c)).

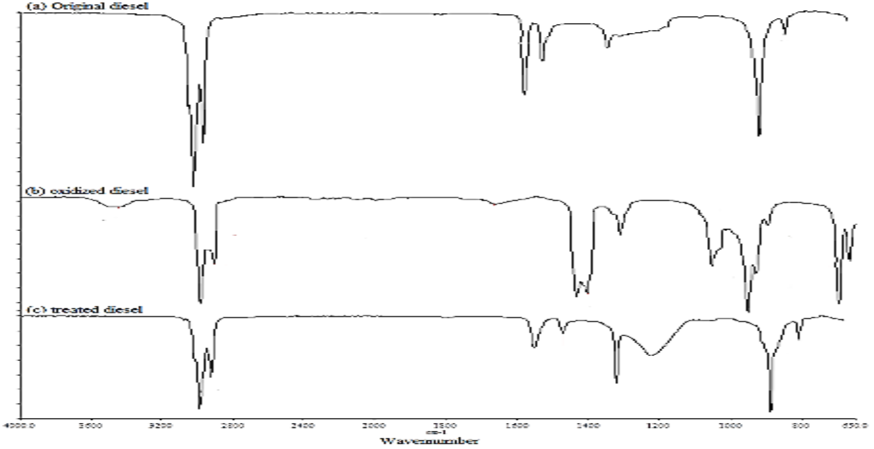


Fig.6. Infrared spectra of diesel samples: (a) original diesel, (b) oxidized diesel and treated diesel.

The chromatograms obtained after and before treatment by simultaneous ODS/ODN of diesel under MW radiations are illustrated in Fig. 7. These chromatograms presented a large number of peaks and reveal the presence of complex chemical mixtures composed mainly of paraffinic, naphthene, and aromatic hydrocarbons ranging from 8 to 26 carbon Fig.7a and b) as reported in literature [28]. Unfortunately, with a careful examination of the fragmentary ions the S- and N-compounds were undetectable because they were masked by other more-dominant species in the feedstock. Therefore, it was necessary to extract these compounds from diesel phase by solvent. The chromatograms of polar phase extracted from diesel (see Fig. 6c and d and), revealed the presence of S- and N-containing compounds. The main S-compounds observed are dibenzothiophene, alkyldibenzothiophene and naphthothiophene; while the identified N-compounds are: indole, carbazole derivatives, pyridine, acridine, and quinoline derivatives. The Fig.7e confirms the conversion of S- and N-compounds to their corresponding substrates. The proposed process did not show any deleterious effects on the distillation profile and other characteristics of the diesel or others real fuels.

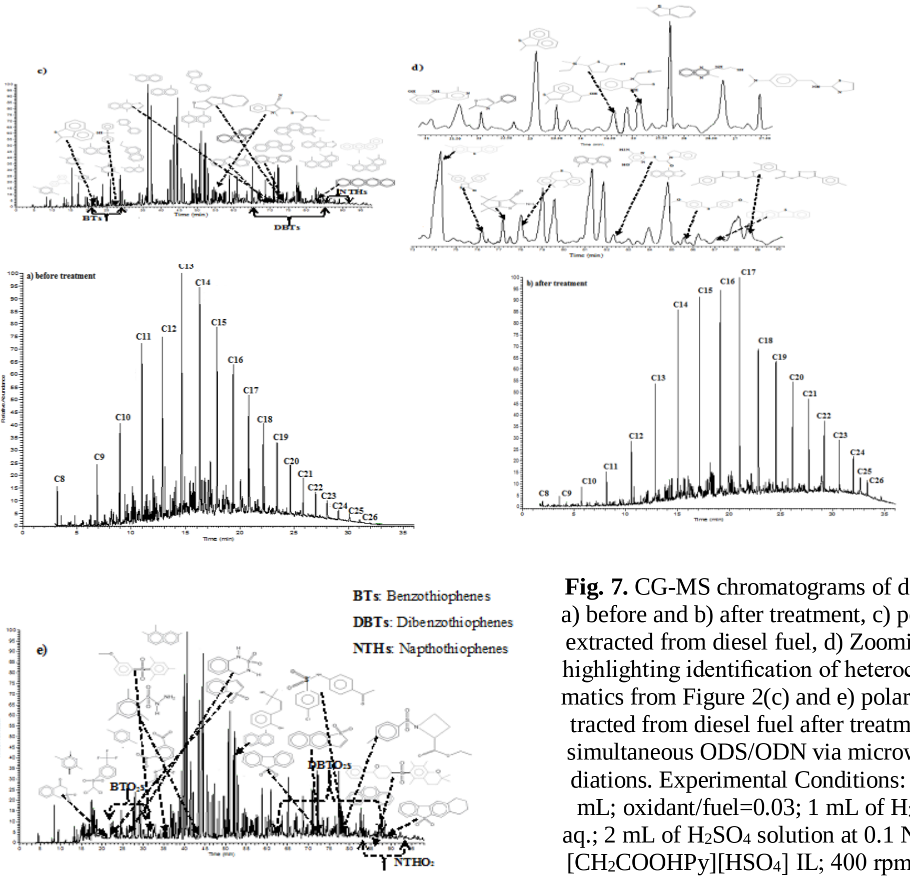


Fig. 7. CG-MS chromatograms of diesel fuel: a) before and b) after treatment, c) polar phase extracted from diesel fuel, d) Zooming in and highlighting identification of heterocyclic aromatics from Figure 2(c) and e) polar phase extracted from diesel fuel after treatment using simultaneous ODS/ODN via microwave irradiations. Experimental Conditions: V_{fuel}= 50 mL; oxidant/fuel=0.03; 1 mL of H_2O_2 30% aq.; 2 mL of H_2SO_4 solution at 0.1 N; 3 mL of [$CH_2COOHPy$][HSO_4] IL; 400 rpm, T=60°C at 700 W for 120 s.

4.Conclusion

In this work, simultaneous extractive oxidesulfurization and oxidenitrification of transportation fuels via microwave-radiations in the presence of payridinium IL and combined oxidants was demonstrated. The results suggested that experimental parameters, the structure and acidity of the IL cation, and the fuel chemical composition can greatly affect the treatment performance. Under the optimal conditions: Vfuel= 50 mL; oxidant/fuel=0.03; 1 mL of H_2O_2 30% aq.; 2 mL of H_2SO_4 solution at 0.1 N; 3 mL of [$CH_2COOHPy$][HSO_4] IL; 400 rpm at 60°C, high desulfurization and denitrification of diesel (S=541 ppm, N=178 ppm) was achieved within a reaction time of 120 s via microwave irradiations (700 W). The proposed method was also applied without any specific adaptation to treat other fuels such as gasoline, kerosene and marine fuel, and the results obtained were satisfactory. This can be attributed to the synergetic effect between microwave activation heating energy and the additional protonation from the addition of acid sulfuric solution, which multiplied the corresponding S and N-compounds formation pathways and thus accelerated the extractive oxidation reactions. According to the results, the proposed method is concurrency and offers a huge potential fort petroleum streams treatments.

5.References

1 Organization of the Petroleum Exporting Countries. OPEC World Oil Outlook(2018). Available from: http://www.opec.org.

2 Kobotaeva, N.S., Skorokhodova, T.S.: Ionic liquids as extractants of diesel sulfur compounds. Pet. Chem. **60**, 762–767 (2020).

3 Lei, Z., Gao, L., Chen, H. W., Wang, Z., Ren, S. Hydrotreatment of heavy oil from a direct coal liquefaction process on sulfided Ni-W/SBA-15 catalysts. Fuel. Process. Technol. **92**, 2055-2060 (2011).

4 houda, S., Lancelot, C., Blanchard, P. Oxidative desulfurization of heavy oils with high sulfur content: A review. Catalysts. **8**: 344 (2018).

5 Mochida, I., Choi, K. H. An overview of hydrodesulfurization and hydrodenitrogenation. J. Jpn. Petrol. Inst., **47**, 145-163 (2004).

6 Anantharaj, R., Banerjee, T. Fast solvent screening for the simultaneous hydrodesulfurization and hydrodenitrification of diesel oil using ionic liquids. J. Chem. Eng. Data, **56**: 2770-2785 (2011).

7 Carnaroglio, D., Gaudino, E. C., Mantegna, S., Moreira, E. M., Vicente de Castro, A., Flores, E. M., Cravotto, G. Ultrasound-assisted oxidative desulfurization/denitrification of liquid fuels with solid oxidants. Energy. Fuels. **28**, 1854-1859 (2014).

8 Monticello, D. J. Biodesulfurization and the upgrading of petroleum distillates. Curr. Opin. Biotechnol. **11**, 540-546 (2002).

9 Shahriar, S. A., Lin, H., Zheng, Y. Adsorptive denitrogenation and desulfurization of diesel fractions by mesoporous SBA15-supported nickel (II) phosphide synthesized through a novel approach of urea matrix combustion. Ind. Eng. Chem. Res. **51**: 14503-14510 (2012).

10 Kobotaeva, N.S., Skorokhodova, T.S., Andrienko, O.S., Marakina, E.I, Sachkov, V.I. Extractants based on coordinating liquid polar solvents for removal of sulfur compounds from diesel fuels. Appl. Sci. **8** (2018). doi:10.3390/app8080000.

11 Darya, Z., Alexey, Z., Khadichakhan, R., Valery, M. D., Anuar, D. Y. Ionic liquids assisted desulfurization and denitrogenation of fuels: review. Vietnam. J. Chem. **57**, 133-163 (2019). doi: 10.1002/vjch.201900008.

12 Karaca, H., Z. Yıldız. Desulfurization of fuel by leaching using H_2O_2 and H_2SO_4. Petrol. Sci. Technol. **23**, 285-298 (2005). doi:10.1081/LFT-200028294.

13 Mamaghani, A. H., Fatemi, S., Asgari, M..Investigation of influential parameters in deep oxidative desulfurization of dibenzothiophene with hydrogen peroxide and formic acid. Inter. J. Chem. Eng. **10** (2013) 10, Article ID 951045. doi:10.1155/2013/951045

14 Nie, Y., Gong, X., Gao, H., Zhang, X., Zhang, S. Simultaneous desulfurization and denitrogen of liquid fuels using two functionalized group ionic liquids. Sci. China. Chem. **57**, 1766-1773 (2014).

15 Z. Zhou, W. Li, and J. Liu. Removal of basic nitrogen compounds from fuel oil with [Hnmp]H_2PO_4] ionic liquid. Chem. Biochem. Eng. Q. **31**, 63–68 (2017).

16 Abro, R., Gao, S., Chen, X., Yu, G., Abdeltawab, A. A., Al-Deyab, S. S. Oxidative desulfurization of gasoline by ionic liquids coupled with extraction by organic solvents. J. Brazilian. Chem. Society **27**, 998-1006 (2016). doi:10.5935/0103-5053.20150355.

17 Benmabrouka, H., Mesdour, S, Boufades, D., Moussiden, A., Berrabia, N., Tliba, L., Hamada, B. 2019. Vanadium-catalyzed extractive oxidesulfurization of commercial diesel in ionic liquid with combined oxidizing agents. Petrol. Sci. Technol. **37**, 662-670 (2019).

18 Duan, Z., Gu, Y., Zhang, J., Zhu, L., Deng, Y. Protic pyridinium ionic liquids: synthesis, acidity determination and their performances for acid catalysis. J. Mol. Catal. A Chem. **250**, 163-168 (2006). doi:10.1016/j.molcata.2006.01.035.

PP-II-5

HYDROGEN PRODUCTION FROM CARBON DIOXIDE REFORMING OF METHANE OVER HYDROTALCITES CATALYSTS DERIVED

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Abstract. Considerable attention has been paid to the catalytic reforming of CH_4 with CO_2 to synthesis gas in recent years. This reaction has very important environmental implication since both CH_4 and CO_2 contribute to the green house effect. Therefore, it is important to develop new catalyst with a high activity and selectivity. In this paper, we intend to compare different types of catalyst: NiMgAl, CoMgAl, NiMgLa and CoMgLa. These samples were prepared by coprécipétation at constant basic pH and calcined at 450°C. The catalysts obtained are characterized by ICP method, XRD, FTIR and BET methods. The data obtained from chemical analysis of the calcined catalysts confirmed that $(M^{+2})/n(M^{+3})$ ratio is close to the intend value of 2. The XRD patterns exhibit the characteristic diffractions of hydrotalcite-like layered double hydroxide materials. Room temperature FT-IR spectra were recorded in the range 4000-400 cm^{-1}, on a Perkin Elmer spectrometer. These catalysts are tested for methane dry reforming reaction versus time on stream at 650°C. It was found that performances of catalysts after 8h in reaction indicates that within this period nor or little deactivation takes place over them. In these experiments conditions, co-catalysts did not show any catalytic activity. However, when CoMgAl catalyst is reduced at higher temperature (650°C) for 8h, the better catalytic performances were observed

Keys words: Hydrotalcite, green house effect, catalysis, CH_4, CO_2, Ni, Co

1. Introduction

Reforming of methane with carbon dioxide to synthesis gas, which is also referred to as dry reforming of methane (Eq.1), represents an industrially relevant process [1] that meets the criteria of green chemistry and of environmental protection: it employs two gases that are major components of greenhouse gases, converts them into a valuable feedstock of synthesis gas:

$$\mathbf{CH_4 + CO_2 \longrightarrow 2H_2 + 2CO} \quad \text{.... Eq (1)}$$

Great efforts have been focused on the development of catalysts which show high activity and stability. Supported metal catalysts have been used in the reforming reaction of hydrocarbons and are conventionally prepared by impregnation of different supports. This method is not fully reproducible and may give rise to some inhompgeneity in the distribution of the metal of the surface. Moreover, the fine metal particles tend to sinter at high temperature, resulting in the catalysts deactivation. It is recognized that most of the group VIII metals are more or less effective for CH_4/CO_2 reaction in terms of CH_4 conversion and selectivity to synthesis gas.

Noble metals such as Ru,Rh, Pt and Ir…etc have successfully been employed as highly active catalyst for CO_2 reforming of CH_4 [2]. However, the high cost and limited availability of noble metals have simulated researching for cheaper metals such as Ni and Co.

Use of the precursors containing metal ions such as Ni^{+2} and Co^{+2} in the crystal structure, which on further calcination and reduction, may result in the formation of highly dispersed metal particles [3].

The hydrotalcite structure can be considered as positively charged brucite-type octahedral sheets, in which a part of the Mg^{+2} is substituted by a trivalent metal like Al^{+3} generating a partial positive that is compensated with carbonates anions and water molecules located in the interlayer space. Nevertheless, it is possible to prepare different hydrotalcite by the partial or total substitution of Mg^{+2} and Al^{+3} with other divalent or trivalent metals. Hydrotalcite retain the layered structure up to 400°C, but a higher temperature yield to high surface area metal mixed oxides. Calcined hydrotalcites are potentially useful as catalysts or catalysts precursors if the advantage of their properties of high surface areas, rédox and basic character can be utilized **[4].** The corresponding chemical formula is: $\mathbf{[M_{1-x}^{2+}\ M_x^{3+}\ (OH)_2]^{x+}\ [A^{n-}]_{x/n}\ .m\ H_2O}$**,** where and M^{+2} and M^{+3} are di-and trivalent metals, respectively. As reported recently, the combination of two active transition metals Ni and Co present in hydrotalcite structure caused after calcination increasing catalytic performances in CH_4 dry reforming. In this context, the objective of this work is to study the influence of both M^{+2} nature and reduction temperature on the catalytic properties of Ni^{+2} and CO^{+2} hydrotalcite based catalysts.

2. Experimental

2.1. Catalysts synthesis

The samples derived hydrotalcites were prepared by continuous coprecipitation method reported by Miyata et al **[5],** from two aqueous solutions. The first solution contained nitrates of the metals (Ni^{+2} or CO^{+2}, Mg^{+2} and Al^{+3} or La^{+3} cations) and the second solution contained sodium carbonates as precipitant. The coprécipétation was carried out under constant agitation at 60°C maintaining the pH constant (11±0.1) by adjusting the flow rate of solutions. The material was cooled to room temperature, filtered and washed with a large amount of deionised water up to a pH 7 for complete removal of Na^+ and dried at 80°C for 12h. The resulting precursors were calcined at 450°C for 6h (4°C/min). The solids obtained was named M(II) M'(II) M(III).

2.2 Characterization of catalysts

The elemental composition of the samples was determined by atomic absorption spectroscopy (AAS). The samples were digested with a mixture of HNO_3 and HF acids. The measurements were obtained by the method of addition of standard solution using a Perkin-Elmer analyst equipment. BET surface areas were measured with NOVA 2000e apparatus by adsorption of nitrogen. X-Ray powder diffraction patterns were recorded in a X' PERT PRO MPD diffractometer using Cu Kα radiation and varying 2θ values from 5to 80°. FTIR spectra, in the region 4000-400 cm^{-1} were obtained with a Perkin-Elmer spectrometer using KBr pellet technique.

2.3 Catalytic experiments

The catalytic activity runs, were carried out at atmospheric pressure in a tubular quartz reactor. Quartz wool was used as support for the catalytic bed. For reaction tests, usually 100 mg of catalyst were pretreated under hydrogen at 500°C (or 650°C) for the night. Reaction temperature monitored by the thermocouple placed close to the reactor wall, increased from room temperature to 650°C at the heating rate of 4°C/min. Reactants feeding was regulated by mass flow controllers (Brooks 5850 TR). Reaction mixture CH_4: CO_2: Ar in proportion 20:20:60 at a flow rate 20 ml/min was used for reaction tests. This mixture was allowed to pass through the sample by switching a for-way valve located at the reactor inlet. Reactants and products were analysed in an on-line gas chromatograph (Delsi) equipped with a thermal conductivity detector (TCD) with Carbosieve-B column using Argon as carrier gas

3. Results and discussion

3.1. Catalysts characterization

The molar ratios of metal cations in prepared catalysts presented in Table 1, were calculated from results of chemical analysis were close to the intended value of 2.

Table 1: Molar ratios of metal cations, chemical composition and surface areas catalysts

Catalytsts	M^{+2}/M^{+3}	Chemical formula	Ni(Co) /Mg ratio	Surface area (m^2/g)	
				non calcined	calcined
NiMgAl	1.97	$Ni_{0.2}Mg_{0.45}Al_{0.33}$	0.45	31.93	117.13
NiMgLa	2.20	$Ni_{0.13}Mg_{0.55}La_{0.31}$	0.23	34.59	30.49
CoMgAl	2.20	$Co_{0.14}Mg_{0.54}Al_{0.31}$	0.26	77.61	70.68
CoMgLa	2.20	$Co_{0.11}Mg_{0.57}La_{0.31}$	0.19	8.28	16.65

Surface areas (Table1) determined by means of physical sorption and desorption of nitrogen moved from the highest value (117.13m^2/g) for NiMgAl catalyst to the lowest value (16.65m^2/g) for CoMgLa. As it was reported in the literature, the textural properties depend strongly on the thermal treatments **[6].** Several groups have reported results concerning the specific area of hydrotalcite-based catalysts as a function of temperature. The general trend is an increasing in surface area.

Figure-1presents XRD patterns of synthesized precursors. A well-cristallized hydrotalcite-like phase was found in the powder XRD patterns of the dried NiMgAl and CoMgAl samples.

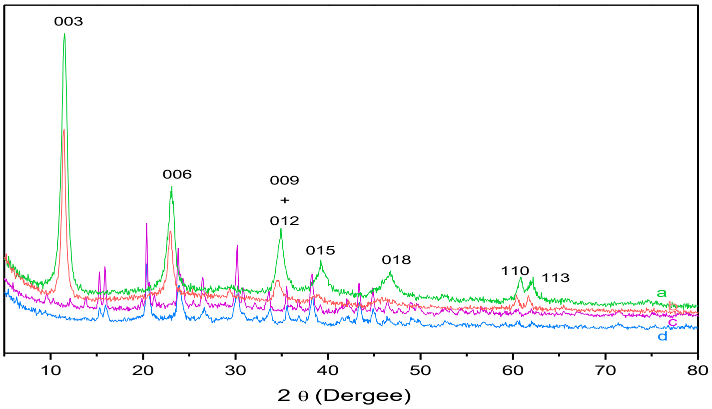


Figure 1: XRD patterns of non-Calcined samples: NiMgAl (a), CoMgAl (b), CoMgLa (c), NiMgLa (d).

The XRD patterns of NiMgAl sample (curve a) exhibits sharp and symmetrical reflections for (003), (006), (110) and (113) planes characteristic of a well-crystallized NiMgAl-hydrotalcite. Line of $Al(OH)_3$ was observed together with those of hydrotalcite phase just after drying of the precipitate.

The XRD patterns of CoMgAl sample (curve b) show formation of the single phase typical of hydrotalcite like-structure, exhibiting harmonics close to 2θ= 35°,38° and 46°,the reflections (009) and (012) overlapping **[7].** Finally, no shift was observed in the position of a peak at 2θ = 60.4, attributed to a reflection from (110) and (113) planes, indicating that the average cation-cation distance in the brucite-like layers remained unchanged regardless of the kind of anionic species introduced **[8].**

According to the literature **[7],** the position of the peak (003) was used to calculate the "c " parameter (c= 3d (003)) and the "a" parameter was calculated from the position of the peak near 2θ= 60.4°, due to the diffraction by planes (110) as a= 2d (110).

The calculated value of the parameter a are 3.038A° and 3.054A° for NiMgAl and CoMgAl respectively. The value of parameter c, 22.9A° and 21.9A° respectively for NiMgAl and CoMgAl is typical of hydrotalcites containing carbonates as interlamellar anions **[7].**

This is not the case of NiMgLa and CoMgLa samples (not reported), where XRD patterns show the presence of poor cristallinity. This can be due probably to the large ionic radius of La cations.

The powders patterns of calcined catalyst are reported in figure 2. Calcinations of NiMgAl and CoMgAl catalyst (curves a and b) at 450°C, for 6h resulted in the disappearance of a part of the layered structure of hydrotalcite and the formation of peaks attributed to the NiO and MgO oxides (peaks at 2θ equal to 35.70°, 43.40° and 63°), for CoMgAl sample and formation of peacks at 2θ equal 36.7°, 44.8°, 65.2° attributed to the Co_3O_4 and $Co^{+3}/^{+2}$ incorporated into the aluminium and magnesium oxide structure **[9].**

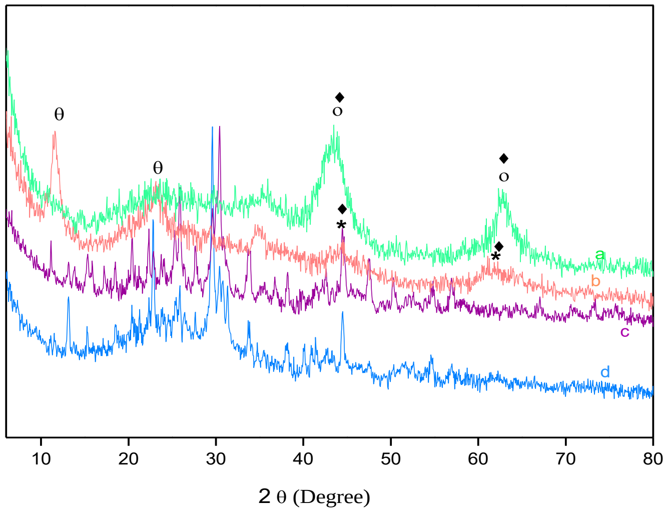


Figure 2: XRD patterns of Calcined samples at 450°C: NiMgAl (a), CoMgAl (b), CoMgLa (c), NiMgLa (d). O NiO, ♦ MgO, θ Al_2O_3, * CO_3O_4

The powder XRD paterners of NiMgLa and CoMgLa calcined as show on figure 2 (curves c and d), exhibited a low crystallinity and oxides formation like NiO, MgO, La_2O_3 and Co_3O_4 have been observed.

By infrared spectroscopy, in the non-calcined samples the obtained spectra reproduce the general features often reported for hydrotalcite-like compounds **[10].**

The FTIR spectra of calcined catalyst are shown in figure 3. The mixed oxides are formed during thermal decomposition of samples but a trace amount of remaining carbonate was found in the spectra of all calcined samples as shown by the bands at about 1460-1500 and 1340-1370 cm^{-1}. The absorption bands at 3430 and 1620-1630 cm^{-1} were shown in all spectra and indicated the presence f OH$^-$ and/or water but the dehydroxylation of samples should be complete at applied calcinations temperature 450°C. An adsorption of air humidity during preparation and handling of KBr pellet can be expected. The lattice vibration in the 800-250 cm-1 range decreases especially in the NiMgAl hydrotalcite derived catalyst.

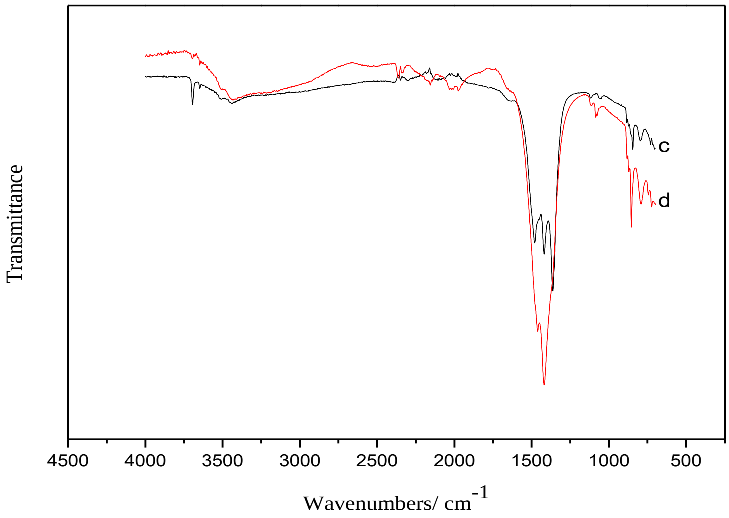
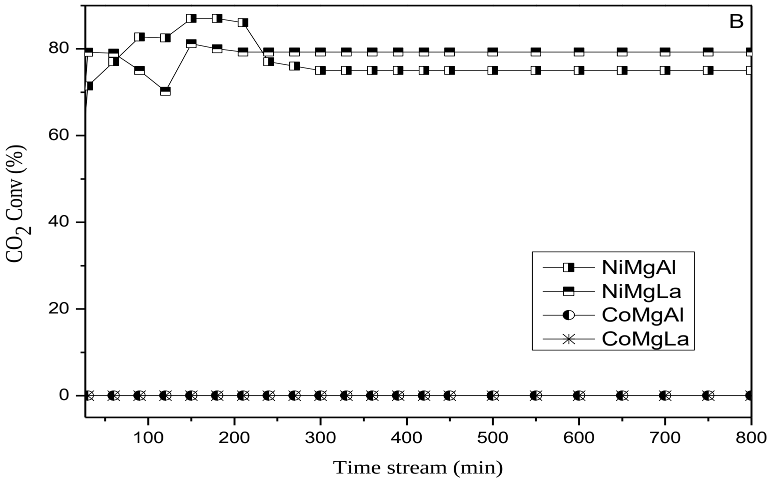


Figure 3: FTIR spectra of Calcined samples at 450°C: NiMgAl (a), CoMgAl (b),



CoMgLa (c), NiMgLa (d).

The IR spectra of Co based catalyst show bands in the wavenumber below 800cm^{-1}. These bands are characteristic for ν_1, ν_2 vibration of Co^{+3} in octahedral coordination.

3.2 Dry reforming of methane over Ni and Co-based catalysts

The stability of the reduce Ni and Co catalysts was examined at 650°C and a 1:1 CO_2/CH4 feed ration, after in-situ reduction at 500°C for 12 h. The variations of CH4 and CO2 conversions versus time on stream are represented in figure-4 (A and B) respectively.

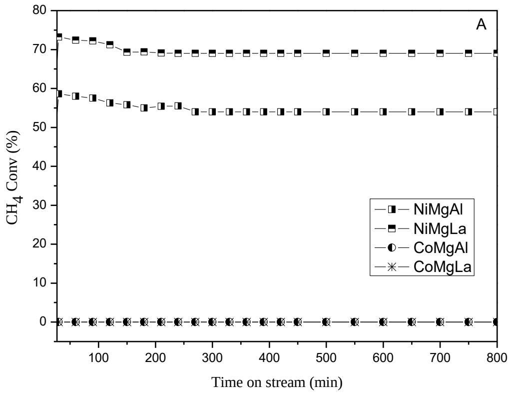


Figure 4: Evolution of CO_2 and CH_4 conversion vs. Time stream for Ni and Co based catalysts (P=1 atm, CO_2/CH_4= 1, F=1.2 L/h, Tred = 500°C).

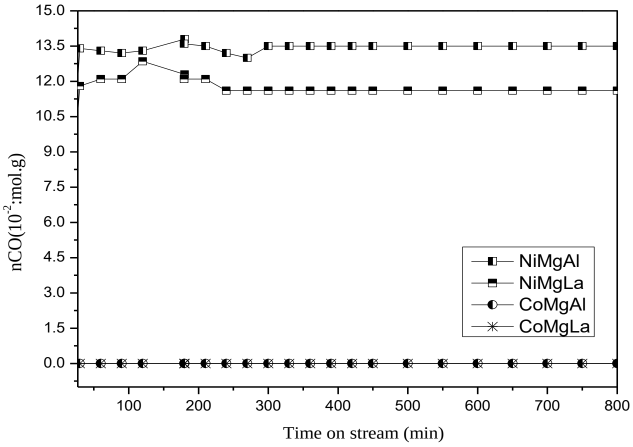
The NiMgAl and NiMgLa, catalysts exhibited effective catalytic activity and stability, and provided over 54.0% and 69.0% respectively, of methane conversion versus 75.0% and 79.3% respectively of CO_2 conversion.

As it shows, the catalytic conversion of CH_4 is lower than the one of CO_2 which indicates that probably the CO_2 is consumed in parallel in the reverse water gas shift reaction (RWGS) **[11,12]:** $CO_2 + H_2$ $CO + H_2O$ ΔH= 41.0 KJ/mol.

The RWCS reaction consumed more CO_2 and H_2 and produced more CO. The unequivalence of CO_2 and CH_4 conversions reveals the presence of secondary reaction under the reaction conditions adopted. For this reason, the H_2/CO ratio always attains values superior than unity **[13].**

These differences on selectivity can be related mainly to differences in acid-base character as suggested by Casenave et al. **[14].** According to these authors, a middle basic character and the better catalytic performances are obtained by the sample with higher Ni/Mg ration which is the case of NiMgAl derived hydrotalcite catalyst.

Moreover, the performance levels of the catalysts stabilize after 1 hour, and remain constant beyond 8 hours of reaction time.



Fuqure 5: Evolution of nCO versus Time on stream for Ni and Co based catalysts
(P=1 atm, CO_2/CH_4= 1, F=1.2 L/h, Tred = 500°C)

As shown in figure-5, the rate of Co formation increased such as the carbon monoxide yields are equal to 13.5 x 10^{-2} mol/g.h and 11.6 x 10^{-2} mol/g.h respectively on NiMgAl and NiMgLa. These results clearly confirmed than NiMgAl catalyst is more active (in terms of CO yield).

However, in these same experimental conditions (reduction at 500°C for 12 h), the CoMgAl and CoMgLa catalyst did not show any catalytic. This behavior can be related to the formation of new phase CoO-MgO solid solution as shown by XRD analysis, during catalysts calcinations, which is reduced at much higher temperature (500-700°C) **[15].**

It was also reported, that the presence of Al^{+3} ions influenced the reducibility of Co ions strongly and caused an increase in reduction temperature [**15].**

The influence of reduction temperature on methane dry reforming was examined in presence of CoMgAl derived catalyst. Figure -6, presents the CH_4 and CO_2 conversions after in-situ reduction at 650°C of CoMgAl hydrotalcite derived catalyst.

The in-situ temperature reduction has a different behavior when CoMgAl is reduced at 500°C or 650°C. According to the literature the reductibility of the cobalt ions depends on the number of Al^{+3} ions around cobalt. Although, reduction of surface Co^{+2} species at 580°C is also reported **[16]**, which can explain the better catalytic obtained on CoMgAl catalyst after in-situ reduction at 650°C. As it can be noticed on figure 6, CH_4 and CO_2 conversions are respectively 67,8% and 74,7% while reduction at 500°C did not give rise to any activity catalytic as shown in figure 5. However, the rate of CO formation increased such as the carbon monoxide yields are equal to 15.0. 10^{-2} mol.h-1.g-1 on CoMgAl, catalyst when temperature reduction is 650°C against 00, 0 against when temperature reduction is 500°C.

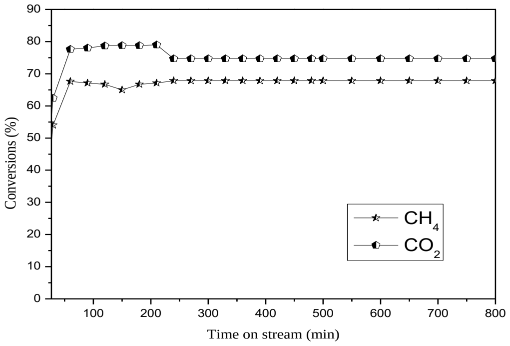


Figure 5: Evolution of CO_2 and CH_4conversion versus Time on stream for CoMgAl catalysts (P=1 atm, CO_2/CH_4= 1, F=1.2 L/h, Tred = 650°C)

These results confirmed that the CoO-MgO active phase is formed during calcinations and reduced at high temperature (> 500°C) and are in agreement with other works found in literature that show a greater reduction of metal oxides (Ni or Co) to metallic phase which takes place at higher temperature (> 500°C) and the extent of the reduction should be responsible for increasing of the activity [**17].**

We can therefore conclude that the catalytic performances of hydrotalcites derived catalysts depend essentially on the structure and physic-chemical properties considered as a whole and of course on the operating conditions such as temperature reduction before reaction of methane dry reforming.

4.Conclusion

A series of Ni and Co-hydrotalcite type catalyst were prepared by coprecipitation method. They were characterized by ICP method, XRD, FTIR, TPR and BET. The data obtained from chemical analysis of the calcined catalyst confirmed that the $n\ (M^{+2})/\ n(M^{+3})$ ratio is close to the intended value of 2. The XRD patterns exhibit the characteristic diffractions of hydrotalcite-like layered double hydroxide materials. Room temperature FT-IR spectra were recorded in the range 4000-400 cm-1. The Ni studied catalysts present catalytic performances at 650°C that vary in the following sequence: NiMgLa >NiMgAl. However, the CoMgAl and CoMgLa catalysts did not show any catalytic activity when samples are reduced at 500°C. The reduction of CoMgAl at 650°C for 8h, leads to the better catalytic conversion of CH_4 conversion and selectivity to synthesis gas.

To summarize, a middle basic character can be more favourable for methane dry reforming reaction under our operating conditions and Ni-hydrotalcite derived catalysts.

5.References

1 J.R.H Ross, Catal.Today 100 (2005) 151.
2 S.Wang, G.Q.Lu, G.J.Millar, Energy Fuels 10 (1996) 896.
3. K.Takehira, T.Shishido, M.Kondo, J.Catal.207 (2002) 307.
4 A.I.Tsyganok, T.Tsunoda, S. Hamakawa, K. Suzuki, K.Takehira, T.Hayakawa, J.Catal. 213(2003) 191
5 M.Miyata, A.Okada, Clays Clay Miner. 25 (1977) 14.
6 D.Tichit, R.Durand, A.Rolland, B.Coq, J .Lopez, and P.Marion, J.Catal. 211 (2005) 511.
7 A.H.Iglesias, O.P.Ferreira, D.X.Gouveria, A.G.S.Fillo, J.A.C. de Paiva, J.M.Filho, O.L.Alves, J.Solid State Chem . 178 (2005) 142.
8 A.I.Tsyganok, M.Inaba, T.Tsunoda, K.Uchida, K.Suzuki, K.Takehira, T.Hayakawa. Appl.Catal.A:Gen.292 (2005) 328.
9. A.F. Lucrédio, E.M.assaf,J.Power Sources 159 (2006) 677.
10. J.T.Kloprogg,D.Wharton, L.Hickey, R.L.Frost, Am.Mineral.87 (2002) 623.
11.Y.H. Hu,E. Ruckenstein, H.K.Bruce C. Gates,Adv.Catal., Academic Press, (2004) 297.
12 J.R.Rostrup-Nielsen, J. Sehested, J.K. Norskov.Adv.Catal., Academic Press, (2002) 65.
13.J.A.Montoya, E.Romero-Pascal, C.Gimon, P.Del Angel, and A.Monzon, Catal.Today 63 (2000) 71-85.
14.S.Casenave,H.Martinez, C.Guimon,A.Auroux, V.Hulea,A.Cordoneau, E.Dimitriu,Thermochim. Acta 373 (2001) 85.
15 L.Obalova´ K.J ira´, F.Kovanda, K. Pacultova´, Z.Lancny, Z.Mikulova´ Appl. Catal. B: Environm. 60 (2005) 289.
16 L.F.Liotta, G.Pantaleo,A.Macaluso,G.Di Carlo,G.Deganello, Appl.Catal. A: Gen. 245 (2003) 167.
17 N.T.Dung, D.Tichit, B.H.Cchiche,B.Coq, Appl. Catal.A 169 (1998) 179.

OR-II-2

DEHYDROALKYLATİON OF DİMETHYLCYCLOHEXANE İSOMERS BY METHANOL İN THE PRESENCE OF MODİFİED FORMS OF MORDENİTE

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Abstract. The reaction of dihydroalkylation of dimethylcyclohexane isomers by methanol in a flow system on a stationary layer of the H-form of mordenite modified with Fe (III), Ga (III), and Nd (III) oxides has been studied. It was found that the prepared catalyst samples exhibit high activity in the cyclic dihydroalkylation reaction.

Keywords: isomers of dimethylcyclohexane, xylene, trimethylbenzene,methanol, HNa- mordenite modified with Fe (III), Ga (III), and Nd (III) oxides.

1. Introduction

Zeolite catalysts and mesoporous materials are widely used in aromatic hydrocarbon alkylation reactions. Currently, research is developing on the alkylation of benzene [1,2], toluene [3-5], ethylbenzene [6-8], naphthalene [9,10], styrene [11,12], xylene isomers [13] and phenol [14, 15] with methanol and other monohydric alcohols. Particular attention was paid to the alkylation of toluene and ethylbenzene with steam, with obtaining isomers of xylene and ethyltoluene which were used as solvents, high-octane fuel components, as well as intermediates of various petrochemical synthesis.

We have previously studied the oxidative dehydrodisproportionation(DHD) of methyl and ethylcyclohexanes [18, 19], as well as the dehydroalkylation of methylcyclohexane (MCH) with methanol [16, 17] in the presence of modified forms of zeolites such as ZSM-5 or mordenite. As a result of the studies, it was suggested that the dehydrodisproportionation of MCH proceeds according to a bimolecular scheme, through an intermediate stage of the formation of methylcyclohexene and methylenecyclohexane radicals.

The dehydroalkylation of MCH with methanol or ethanol also proceeds according to a complex multi-route scheme with conjugation of the stage of dehydrogenation of the starting compounds and alkylation of intermediate unsaturated and aryl intermediates. Judging by the qualitative and quantitative composition of aromatic hydrocarbons, the main directions of the transformation of alkyl-substituted cyclohexane are:

- dehydroalkylation of these hydrocarbons with methanol or ethanol at the cyclohexane fragment with the formation of xylene or ethyltoluene isomers;
- dehydrogenation of MCH to toluene and alkylation of the latter at the phenyl or methyl fragment;
- dehydrodisproportionation of MCH to benzene and xylene isomers

In the development of research in this direction, it is interesting to investigate the reaction of dihydroxylation of dimethylcyclohexane isomers with methanol on HNa-mordenite, modified with various oxides of metals. Considering that some fractions of straight-run gasoline of oil from various fields consist of mainly paraffinic and naphthenic hydrocarbons [20], this direction of obtaining polyalkylbenzenes, in particular, trimethylbenzene isomers, seems to be very promising.

2.Experimental part

The catalysts were prepared on the basis of the H-form of mordenite (the degree of substitution of Na^+ cations is 75 eq.%). The modification was carried out by sequential impregnation of zeolite samples dehydrated at 500-550 ° C with aqueous solutions of Ga^{3+}, Nd^{3+}, and Fe^{3+} nitrates. After impregnation of each portion of the salt solution, the samples were dried at 150-200 ° C. The received powders were treated with a calculated amount of a 10% solution of H_3PO_4 and mixed with a binder component — an aluminum oxide hydrogel in an amount of 30 weight%. After mixing, the resulting paste was granulated and dried at

200 ° C (2 hours) and calcined at 400-550 ° C (4 hours). The content of Ga^{3+}, Nd^{3+}, Fe^{3+} and phosphorus in the composition of the samples in terms of oxides Ga_2O_3, Nd_2O_3, Fe_2O_3 and P_2O_5 was 1.5-7.3 weight.

As an initial hydrocarbons were used isomers of dimethylcyclohexane (DMCH), obtained by hydrogenation of individual o-, m- and p-xylenes, grade "chemically pure”. They were hydrogenated in an autoclave in the presence of nickel on kieselguhr at a temperature of 150-200 ° C and a pressure 10.1-12.1 MPa until stoichiometric absorption of hydrogen. The obtained hydrocarbons were isolated by atmospheric distillation. Their physicochemical indicators correspond to the literature data.

The experiments were carried out in a flow-through reactor with a fixed bed of catalysts in the temperature range 430-600 ° C at 0.1 MPa with a volumetric feed rate of liquid feed of 0.5-2.0 h^{-1} and a molar ratio of DMCH: CH_3OH = (1-3): 1. The duration of the experiment was 0.1-1.0 hours. Nitrogen was used as a diluent. Analysis of the reaction products obtained over stabilized catalyst samples were carried out by GLC and gas chromatography-mass spectroscopic methods. The initial samples were stabilized with their reaction mixture in a nitrogen flow for 3 hours at a temperature of 450-500 ° C. The stability of the catalysts was measured by obtaining reproducible results within 30 min. after this processing.

3.Results and Discussion

Preliminary studies have shown that, along with the dehydroalkylation reaction, the hydrodisproportionation of DMCH isomers to benzene, toluene, and trimethylbenzene isomers also occurs. The ratio of the speed of these reactions depends on the conditions of catalysis, and especially on the temperature and composition of the prepared catalysts (Table 1). Dehydrodisproportionation of DMCH mainly proceeds with the formation of toluene and trimethylbenzene isomers (preferably 1,2,3- and 1,2,4-trimethylbenzene). Practically no benzene was formed.

At the beginning of the study, we tested the most active catalyst samples in the aromatization of methanol by dehydrodisproportionation of DMCH; the results of these experiments were presented in Table. 1 and 2. As it can be seen from the presented data at a temperature of 430–475 ° C, all samples exhibit high activity in the conversion of methanol, but were practically inactive in the reactions of dehydrogenation and dehydrogenation of DMCH. Only starting from a temperature of 500 ° C in the liquid products of the DMCH transformation were noticed the accumulation of a noticeable amount of aromatic hydrocarbons. Therefore, the study of the dehydroalkylation reaction of DMCH with methanol was carried out at a temperature of ≥500 ° C (Table 3).

The main products of this reaction are toluene, xylene and trimethylbenzene isomers. In addition to them, the chromatograms also contain traces of benzene, C10-aromatic hydrocarbons - isomers of methyl- and dimethylcyclohexene, as well as methylstyrene. The gas phase contains C1-C4 hydrocarbons, carbon oxides and dimethyl ether, the amount of which were 4-12% by weight of the catalysis.

The prepared catalyst samples exhibit high activity in the dehydroalkylation reaction of DMCH for 8-10 hours.

Table 1. Conversion of 1,3-dimethylcyclohexane on modified forms of mordenite V=0,5 $hour^{-1}$).

	T°, C	Con., %	Content of liquid catalyst, weight%							
			Light hydrocarbons	1,3-DMCH	Unsaturated hydrocarbons	benzene	toluene	C_8-aromatic hydro-carbons	C_9-aromatic hydro-carbons	Undefined compounds
Ga_2O_3/HNaM (cat.1)	450	5,7	-	94,3	2,3	-	-	3,4	-	-
	475	9,4	-	92,0	2,1	-	0,6	5,3	-	-
	500	16,2	-	84,6	2,0	-	1,7	11,4	-	-
	530	22,6	2,0	80,7	1,1	1,3	2,9	10,6	1,4	-
	550	24	2,4	77,0	1,0	1,1	2,9	12,5	1,7	0,4

Ga_2O_3+ Fe_2O_3/HNaM (cat.2)	450	8,2	-	92,0	3,7	-	-	4,3	-	-
	475	13,5	-	87,0	4,6	-	0,7	6,8	0,9	-
	500	19,4	1,6	81,4	4,8	0,6	1,7	7,5	2,4	-
	530	28,6	2,5	72,5	2,6	1,1	2,5	13,7	4,0	1,1
	550	33,0	3,8	68,3	2,2	1,8	3,5	13,2	6,0	1.2
Fe_2O_3+Ga_2O_3+ Nd_2O_3/HNaM (cat.3)	450	9,8	-	90,6	3,7	-	-	5,7	-	-
	475	15,2	-	85,4	4,2	-	-	10,4	-	-
	500	19,5	1,3	81,1	3,8	-	1,7	8,9	3,2	-
	530	30,6	2,4	70,6	2,4	1,7	3,3	11,9	5,8	1,9
	550	35,0	3,2	65,9	2,0	2,1	3,8	11,5	7,8	3.7
Fe_2O_3+Ga_2O_3+Nd_2 O_3 +P_2O_5/ HNaM (cat.4)	450	8,3	-	92,0	2,7	-	-	5,3	-	-
	475	13,0	-	87,6	3,8	-	0,8	7,8	-	-
	500	18,2	1,0	82,5	3,2	0,8	1,7	6,9	3,9	-
	530	26,4	2,2	74,9	3,5	1,4	3,5	10,1	4,4	-
	550	34,2	2,8	67,0	2,0	2,2	4,7	11,5	7,4	2,4

Table 2. Convertion of methanol on modified forms of mordenite

Catalyst	T°,C	Convertion of methanol, %	Content of aromatic hydrocarbons, weight.,%				Yield of conversion. CH_3OH, %	
			benzene	toluene	C_8- aromatic hydrocarbons	C_9-aromatic hydrocarbons	C_8- aromatic hydrocarbons	C_9- aromatic hydrocarbons
Cat.1	430	41,0	6,2	17,9	49,5	26,4	17,4	9,3
	475	69,2	5,8	21,6	52,8	19,3	15,4	5,6
	500	87,3	4,2	20,5	59,7	15,5	24,2	9,1
	530	100	4,5	25,2	59,0	10,6	26,8	4,8
Cat.2	430	49,6	4,0	32,4	36,3	26,0	21,5	15,3
	475	72,4	4,4	30,8	40,0	23,7	21,4	12,6
	500	89,0	3,6	34,0	43,6	18,0	25,9	10,6
	530	100	3,0	37,6	44,0	15,0	23,2	7,8
Cat.3	430	43,2	3,8	28,2	41,6	24,7	21,8	12,9
	475	70,0	4,2	25,4	42,8	26,3	22,1	13,5
	500	92,4	4,6	25,8	46,9	19,4	26,4	10,9
	530	98,5	3,6	23,2	48,6	19,0	29,0	11,3
Cat.4	430	43,8	3,8	30,7	42,0	22,4	22,7	12,0
	475	68,7	4,7	30,3	43,0	20,6	23,6	11,2
	500	85,3	3,0	26,4	48,3	21,0	27,8	12,0
	530	95,6	3,0	25,0	48,7	21,6	28,1	9,2

Table 3. Dehydroalkylation of dimethylcyclohexane isomers with methanol in the presence of Fe-Ga-Nd-P-O/HNaM (DMCH : CH_3OH = 2:1, V-0,5h^{-1}, m_{DMCH} = 11,2g)

T°,C	Conv., %		Yield, weight %		Content of liquid catalyst, weight.%						
	DMCH	methanol	gas	Liquid cat.	DMCH	methanol	benzene	toluene	C_8-aromatic hydrocar-bons	C_9-C_{10} aroma-tic hydro-carbon	Undefined compounds
1,2 – dimethylcyclohexane											
430	4,7	32,0	1,0	99,0	86,1	8,8	-	0,2	4,9	-	-
475	9,4	48,3	1,4	98,6	93,6	6,7	trce	0,8	8,4	0,5	trce
500	16,9	70,6	2,0	98,0	78,8	4,0	0,2	2,3	12,3	2,4	trce
530	26,0	79,7	2,3	97,7	71,2	2,6	0,6	4,2	16,9	4,0	0,5
550	33,8	90,2	2,7	97,3	64,7	1,4	1,1	7,6	16,7	7,8	0,7
1,3 – dimethylcyclohexane											
430	9,6	33,7	0,9	99,1	82,2	8,6	-	0,3	8,8	0,1	-
475	13,5	50,4	1,4	98,6	80,1	6,6	0,1	1,1	11,4	0,7	-
500	20,4	65,4	1,9	98,1	75,2	4,7	0,2	2,9	14,2	2,5	0,3
530	33,6	77,6	2,3	97,7	64,0	3,1	0,7	5,3	19,7	6,7	0,5
550	40,2	92,4	2,8	97,2	58,7	1,1	1,2	9,9	18,9	10,0	0,2
1,4 – dimethylcyclohexane											
430	10,6	32,4	0,9	99,1	81,2	8,8	-	0,3	8,7	-	-
475	13,0	47,6	1,4	98,6	80,3	6,9	0,1	0,8	11,1	0,7	0,1
500	19,7	75,6	2,2	97,8	76,7	3,3	0,3	2,4	14,0	3,2	0,1
530	29,4	82,2	2,4	97,6	68,2	2,5	0,6	4,2	17,6	6,7	0,2
550	35,0	93,0	2,8	97,2	63,7	1,0	1,0	6,8	17,5	10,0	-

4.Conclusions

The reaction of dehydroalkylation dimethylcyclohexane isomers with methanol was carried out in the presence of a modified Fe-Ga-Nd-P-O / HNaM zeolite catalyst. It was found that the used catalyst samples exhibit high activity and selectivity in the reaction As a result, the yield of tri and tetramethylbenzene at 530 ° C in the catalyst was obtained 17-20%.

5.References

1. Odedairo T., Al-Khattaf S.//Catalysis Today. 2013. V. 204. p. 73-84. doi: 10.1016/j.cattod.2012.05.052
2. Hualei Hu, Qunfeng Zhang, Jie Cen, Xiaonian Li. //Catalysis Letters, 2015, V.145. №2. p.715-722.doi: 10.1007/s10562-014-1458-3
3. Alabi W., Atanola L., Jermy R., Al-Khattaf S. //Chem. Engineering Journal, 2012, V.195-196, p.276-288.doi: 10.1016/j.cej.2012.04.100
4. Inagaki Satoshi, Kamino Kohei, Kikuchi Eiichi, Matsukata Masahiko //Applied Catalysis A: General.2007, V318, p.22-27.doi: 10.1016/j.apcata.2006.10.036
5. Usachev N..Y., Lapidus A.L., Usacheva O.N., Savelev M..M., Krasnova L.L., Minachev X.M.// Neftximiya, 1993, V.33, №4, p.305-312.
6. Vos A/, Rozanska X., Schoonheydt R.A., Van Santen Ratger A.//J.Amer.Chem.Soc. 2001, V.123, №12.p.2799-2809.
7. Villarreal N.E., Kharisov B.I., Ironova I.I., Romanovski B.V.// Appl. Catal. A. 2002.V.224, № 1-2. p.161-166
8. Liu Q., Wang J., Wu W., Wang Ya.// J.Nanjing Univ. Technol. Natur. Sci.,2003. V.25.№1. p.23-27
9. Zhang M., Chen S., Shen Sh., Sun Y., Wu D.// J.Catal.,2000.V.21.N 2.p.143-146
10. Ponomareva O.A., Moskovskaya I.F., Romanovskiy B.V.//Nefteximiya, 1999, V.39, №2, p.101-108
11. Ponomareva O.A., Moskovskaya I.F., Romanovskiy B.V.//Nefteximiya, 2001, V.41, №4, p.282-286
12. Raj A., Reddy J., Kumar R.//J.Catal., 1992. V.138.N2, p.518-524.doi: 10.1016/0021-9517(92)90303-Y
13. Moon G., Bohringer W., O'Cannor C.T.// Catalysis Today, 2004. V. 97. N4. p.291-295.doi: 10.1016/j.cattod.2004.07.012
14. Bavornpon Jansang, Tanin Nanok, Jumras Limtrakul //Journ. Phys.Chem.C, 2008, V.112, N2, p.540-547.doi: 10.1021/jp077246b
15. Алимарданов Х.М., Велиева Ф.М., Сулейманова Э.Т., Таирова Л.А., Садыгова Р.Ш.//Нефтехимия, 2005.Т.45.№2,с.115-125
16. Алимарданов Х.М., Велиева Ф.М., Дадашева Л.А., Рустамов М.И.// Нефтехимия, 2006.т.46.№5,с.381-390

OR-II-5

CONVERSION OF ETHYLBENZENE TO STYRENE ON A PHOSPHATED ZIRCONIUM-MAGNESIUM-ALUMINUM CATALYST

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Abstract. An efficient catalyst for the oxidative dehydrogenation of ethylbenzene to styrene was synthesized by jointly supported ZrO_2 and MgO on γ-Al_2O_3. It was found that, on this catalyst in the presence of atmospheric oxygen, the conversion of ethylbenzene and the styrene selectivity reach 63 and 92%, respectively. The jointly supportion of ZrO_2 and MgO on γ-Al_2O_3 leads to a decrease in the reaction temperature to 475-480°C, while the selectivity of the target reaction increases. Modification with phosphoric acid improves the stability of the catalyst. The study of the effect of water vapor on the activity of the phosphated catalyst shows that the introduction of water vapor up to 5 vol% has an insignificant effect on the process, but improves the stability of the catalyst functioning. An increase in the concentration of water vapor in the reactant to 10 vol% leads to a significant decrease in the styrene yield. The oxidative dehydrogenation of ethylbenzene to styrene in the presence of CO_2 on a phosphated zirconium-magnesium-aluminum catalyst proceeds with high selectivity. It has been established that with an increase in the molar ratio of CO_2: EB to 4-5, the conversion of EB increases by more than 5 times (up to 53-54%), and the selectivity reaches 96%. The process is realized by a mechanism close to the mechanism of reverse steam conversion of carbon monoxide.

Key words*:* zirconium dioxide, magnesium oxide, aluminum oxide, phosphating, oxygen, carbon dioxide, cupper

1. Introduction

One of the largest catalytic processes today is styrene production. Currently 90% of this monomer is obtained by direct dehydrogenation of ethylbenzene. But this method has important disadvantages, such as high energy consumption, relatively low equilibrium yield of styrene, consumption of a high amount of water vapor heated to 7000C, etc. All these disadvantages require finding new, more efficient ways of producing styrene. One of the promising methods for producing styrene is the oxidative dehydrogenation of ethylbenzene to styrene. For several decades the intensive researches in this directionit have been conducting. Research are being conducted in the direction of creating active catalysts and finding effective oxidants.

Until now, intensive research continues on the optimal catalysts for the oxidative dehydrogenation of EB in St. Studies have shown that catalysts with an optimal balance of acid-base and redox properties have high activity and selectivity for styrene [1]. Certain metal oxides deposited on aluminum oxide [2]; catalysts with activity in the reverse steam conversion of carbon monoxide [3], metal oxides supported on mesoporous materials have a high activity in the conversion of EB into styrene [4].

Many substances have been studied as oxidants, such as N_2O, SO_2, O_2, CO_2, etc. [5-11]. The latter compound, as a mild oxidizing agent, is the subject of more and more research.

In connection with the aforesaid, the goal of this work is to create a highly efficient catalyst for the oxidative dehydrogenation of ethylbenzene to styrene based on magnesium, zirconium and aluminum oxides (as a carrier) and to study its activity in the conversion of EB to styrene in the presence of oxygen, CO_2, and water vapor.

2. Experimental part

The catalysts were prepared on the basis of powdered aluminum oxide from Sasol (γ-Al_2O_3) by impregnation with aqueous solutions of magnesium and zirconium nitrate salts at room temperature.

For this purpose, the calculated required amounts of $A1_2O_3$ were placed in separate porcelain cups and poured with a given solution of magnesium and/or zirconium nitrate. After 48 h of keeping $A1_2O_3$ in these solutions, the aqueous part was evaporated, with stirring, until a homogeneous jelly-like mass was obtained. The resulting mass was formed and dried in air, and then the granulated samples were again placed in porcelain cups and dried at 80-120 ° C (5 h) and a gradual increase in temperature to 550-570^{0}C, calcined (3 h).

Some of the samples synthesized as described above were treated with a solution of H_3PO_4 (24 hours) and, then, the aqueous phase was evaporated, and the resulting extrudates were dried at 80-120 and 300^{0}C for 3 hours and calcined at 500-600^{0}C. The amount of phosphorus was 5% (in terms of P_2O_5).

The catalysts were tested on a flow-through catalytic unit equipped with a quartz reactor.

Catalytic studies were carried out in the temperature range 480-500^{0}C, space velocity for styrene 0.5 h^{-1}, molar ratio of ethylbenzene : air = 1 : 6 and CO_2 : EB = 1-5. The products were analyzed by chromatographic method.

3. Results and its discussion

The support (γ-Al_2O_3) of the synthesized catalysts and one of the supported components - ZrO_2 show little activity in the oxidative dehydrogenation of ethylbenzene to styrene, while the other component - MgO is practically inactive in this process. The introduction of ZrO_2 and MgO separately on the surface of γ-Al_2O_3 increases the activity of these contacts in the oxidative dehydrogenation of ethylbenzene to styrene [12]. Of interest is the activity of samples synthesized by the joint introduction of these oxides on γ-Al_2O_3. In this work, varying the concentration of ZrO_2 and MgO oxides supported on γ-Al_2O_3 and modifying the obtained samples with phosphoric acid, we synthesized the most efficient catalyst for the oxidative dehydrogenation of EB in St. The results of these studies are shown below.

Figure 1 shows the results of studying the effect of the concentration of added MgO on the activity of a zirconium-alumina catalyst containing 0.4% ZrO_2 (catalyst 0.4% ZrO_2/γ-Al_2O_3). As can be seen from this figure, an increase in the MgO concentration on 0.4% ZrO_2/γ-Al_2O_3 to 4.0% promotes both an increase in the activity (from 52% to 63%) of the sample and an increase in the yield of the target product, styrene (from 45% to 52 %) at 500^{0}C. A further increase in the amount of MgO leads to a decrease in the activity and selectivity of the catalyst.

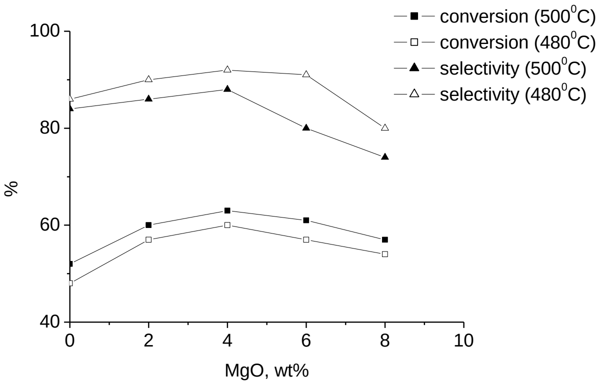

Fig. 1. Influence of the added MgO concentration on the activity and selectivity of 0.4% ZrO_2/γ-Al_2O_3 in the oxidative dehydrogenation of EB to St in the presence of oxygen. LHSV = 0.5 h^{-1}; EB: air = 1: 6; τ = 1 h.

Lowering the temperature of the process from 500 to 480^{0}C leads to significant changes in the catalytic parameters of the conversion of EB to St. Along with a natural decrease in the activity of catalysts, an increase in the St selectivity is observed.

Figure 2 summarizes the results of studying the effect of the ZrO_2 concentration on the activity of magnesium-alumina catalysts containing 4% MgO in the conversion of EB to St. From those presented in fig. 2 data shows that the introduction of ZrO_2 up to 1% leads to an increase in the activity (from 54% to 64%) and selectivity (from 85% to 90%) of the catalyst. A further increase in the ZrO_2 content (up to 2.0%) leads to a decrease in the activity of the catalyst.

Modification of 4.0%MgO/Al_2O_3 samples with zirconium dioxide, as in the case of modification of 0.4%ZrO_2/Al_2O_3 samples with MgO, leads to a decrease in the reaction temperature to 475-480^{0}C. In this case, the selectivity of the target reaction increases to 92%.

It is known that the monoclinic modification of ZrO_2, which is sufficiently stable at ordinary temperatures, at a temperature of ~ 600^{0}C transforms into the metastable tetragonal oxide ZrO_2 [13, 14]. When the samples are calcined, the presence of MgO can lead to the formation of solid solutions (a crystallographic analog of feldspar). Apparently, the presence of an excess amount of MgO (fig. 1) or ZrO_2 (fig. 2) in the composition of ZrO_2, MgO/ Al_2O_3 leads to the formation of similar surface structures that are not active in the reaction of oxidative dehydrogenation of EB to St. This can explain the decrease in the activity of ZrO_2,MgO/Al_2O_3 contacts with a total increase in the applied activating components.

Thus, 1.0%ZrO_2,4.0%MgO/Al_2O_3 is the optimal catalyst for the oxidative dehydrogenation of EB to St in the presence of oxygen.

In fig. 3 was shown the dependence of the EB conversion and St selectivity on this sample from the duration of the experiment. A characteristic feature of the formation of St on 1.0%ZrO_2, 4.0%MgO/Al_2O_3 is the development of catalyst activity in the course of the reaction, which is completed, approximately, within 1 hour. Another feature of the catalyst is its instability in the studied reaction. As seen from fig. 3, after the catalyst reaches the maximum EB conversion and a short operating time with this activity, the catalyst is deactivated.

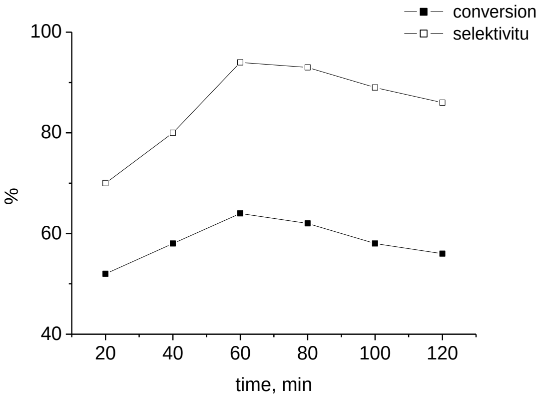

Figure. 3. Influence of the duration of the experiment on the oxidative dehydrogenation of ethylbenzene to styrene on the catalyst 1.0%ZrO_2,4.0%MgO/Al_2O_3. T = 480^0C, LHSV = 0.5 h^{-1}; EB: air = 1: 6.

It is known from the literature and our earlier studies that the treatment with phosphoric acid of catalysts for the oxidative dehydrogenation of EB in St leads to stabilization of their functioning [15]. Coming out of this fact, the synthesized 1.0%ZrO_2,4.0%MgO/Al_2O_3 was treated with phosphoric acid. The results of testing of 1.0% 1.0%ZrO_2,4.0%MgO/Al_2O_3 catalyst modified with phosphoric acid (1.0%ZrO_2,4.0%MgO/Al_2O_3 + 5% P_2O_5) are shown in fig. 4. The data in fig. 4 show that the 1.0%ZrO_2,4.0%MgO/Al_2O_3 + 5% P_2O_5 catalyst has, practically the same maximum activity in the conversion of ethylbenzene (63%) and the maximum St yield (58%), as the unmodified samples.

It follows from fig. 4 that the modification of 1.0%ZrO_2,4.0%MgO/Al_2O_3 with H_3PO_4 does not eliminate the effect of catalyst activity development, although it may somewhat accelerate this process (the initial yield of St at 15 minutes is 42% versus 30%). The data in fig. 4 show that the activity of the catalyst after the completion of the activity development does not decrease even after five hours of operation, and the yield of St is characterized by high selectivity (92%), which is achieved after the visible development of catalyst activity (2 h). Despite the noted stability of the operation of the catalyst modified with H_3PO_4, the latter was also used for regeneration - reaction cycles. These preliminary experiments indicate the stability of the phosphoric acid-modified zirconium magnesium aluminum catalyst in the indicated cycles.

As for the catalyst activity development observed at the beginning of the reaction and the effect of the phosphoric acid modification on the stability of the catalyst operation, this can be a consequence of both the accumulation of compaction products as a result of the interaction between reactant and catalyst, and the interaction between the supported oxides of zirconium and magnesium.

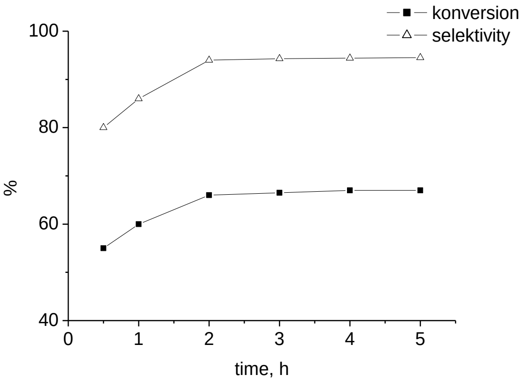

Fig. 4. Oxidative dehydrogenation of EB in St on a catalyst 1.0% ZrO_2,4.0% MgO/Al_2O_3 + 5% P_2O_5, T = 480^0C. LHSV = 0.5 h^{-1}, EB: air = 1: 6.

Indeed, the reduction of the active components of the catalyst by interaction with the reactant or its conversion products is excluded due to the chemical properties of these components. The only possible reason for the development of the catalyst seems to be the accumulation of carbonaceous deposits. The regeneration treatment of the catalyst with air at elevated temperatures helps to burn out these surface deposits. An increase in the stability of the catalyst modified with H_3PO_4 can be associated with the accumulation of other forms of carbonaceous deposits that differ from the compaction products responsible for the development of the sample.

Possibly applied phosphorus makes it difficult for unwanted carbon deposits to form. However, another explanation of the stabilization of the catalyst operation under the influence of H_3PO_4 is not excluded. It is known that ZrO_2 easily fuses with such oxides as MgO, forming compounds (salts) with them - zirconates [16]. These compounds, possibly due to instability, decompose again into the original oxides as a result of oxidative treatment. Therefore, it is possible to introduce H_3PO_4 prevents the formation of magnesium zirconates inactive in this reaction and thereby stabilizes the work of the ZrO_2, MgO/Al_2O_3 catalyst.

As is known, the direct dehydrogenation of ethylbenzene to styrene on industrial catalysts proceeds in the presence of steam. It is of interest to study the effect of water vapor on the activity of catalysts synthesized and studied in this work. The results of these studies are shown in fig. 5. As follows from fig. 5, the introduction of water vapor up to 5 vol.% has little effect on the process, but improves the stability of the catalyst. An increase in the concentration of water vapor in the reactant to 10 vol.% leads to a significant decrease in the yield of St on the 1.0%ZrO_2, 40% MgO/Al_2O_3 + 5% P_2O_5 catalyst. Probably, an increase in the content of water vapor helps to block the interaction of acid sites of the catalyst with EB and thereby reduces the activity of the catalyst and lowers the yield of St.

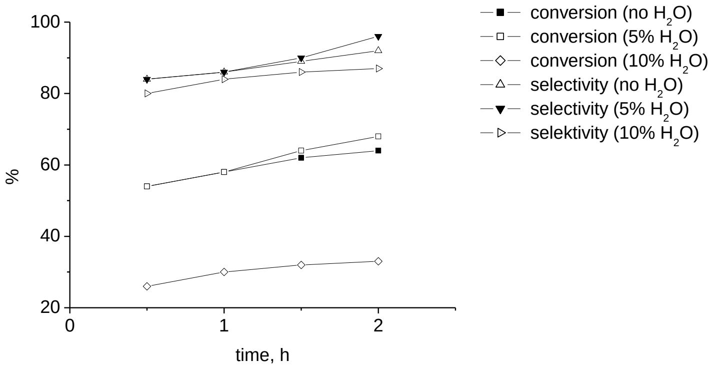

Figure: 5. Influence of H_2O vapors on the styrene yield in the oxidative dehydrogenation of ethylbenzene to styrene on the 1.0%ZrO_2, 40% MgO/Al_2O_3 + 5% P_2O_5 catalyst. T = 480^0C; LHSV = 0.5 h^{-1}; EB: O_2 = 1: 6.

In the following experiments, the effect of CO_2 on the activity of the 1.0%ZrO_2, 40% MgO/Al_2O_3 + 5% P_2O_5 catalyst in the conversion of EB to St was investigated. The results of these experiments are shown in Fig. 6.

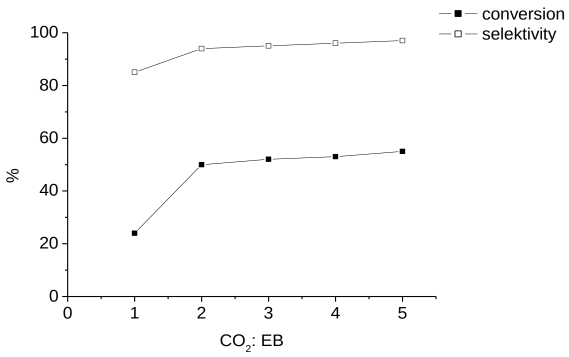

Fig. 6. Conversion of EB to St in the presence of CO_2 on a catalyst 1.0%ZrO_2, 40% MgO/Al_2O_3 + 5% P_2O_5. T = 500^0C; LHSV=0.5 h^{-1}, GHSV=500h^{-1}, τ = 2 h.

As can be seen from these data, with an increase in the molar ratio of CO_2: EB to 4-5, the conversion of EB increases more than 5 times (up to 53-54%), and the selectivity reaches 96%. At the same time, hydrogen is practically absent in the reaction products, and therefore carbon dioxide plays the role of an oxidizing agent. The realization of the process, apparently, occurs by a mechanism close to the mechanism of reverse steam conversion of carbon monoxide, proposed by K. Tomar [16].

Comparison of the data in fig. 6 with the data in fig. 4 shows that in the presence of CO_2, the conversion of EB (54%) is lower than in an oxygen atmosphere (63%), but the St selectivity in the first case is higher (96%) than in the second (90%). These results show that the oxidative dehydrogenation of EB to St on 1.0% ZrO_2, 4.0%MgO/ Al_20_3 + 5.0% P_2O_5 in the presence of CO_2 is more selective than in the presence of O_2.

4.Conclusion

Thus, based on the joint introduction of zirconium and magnesium oxides on the surface of aluminum oxide and modification of the obtained samples with phosphoric acid, it is possible to create highly efficient catalysts for the oxidative dehydrogenation of EB in St.

5. References

1. Nanzhe J., Abhishek B., Park S.E. Ethylbenzene to styrene over ZrO_2-based mixed metal oxide catalysts with CO_2 as soft oxidant. Chinese Journal of .Catalysis. **37**, 3 – 15 (2016). https://doi.org/10.1016/S1872-2067(15)60901-9
2. Itika K., Venkata R.B.G., Jayesh T.B., Kamaraju S.R.R., Bhari M.M. Development of stable MoO_3/TiO_2-Al_2O_3 catalyst for oxidative dehydrogenation of ethylbenzene to styrene using CO_2 as soft oxidant. Journal of CO_2 utilization.**18**. 309 – 317 (2017).
3. Tehua W., Siying C., Tongtong W., Huiyi L., Min J. The physicochemical properties and catalytic performance of carbon-covered alumina for oxidative dehydrogenation of ethylbenzene with CO_2. Applied Surface Science. **427**, 1011 – 1018 (2018). https://doi.org/10.1016/j.apsusc.2017.08.139
4. Ramudu P., Anand N., Mohan V., Murali D.G., Prasad S.S.P., David R.B., Kamaraju S.R.R. Studies on ethylbenzene dehydrogenation with CO_2 as soft oxidant over Co_3O_4/COK-12 catalysts. J.Chem. Sci.**127**, 701 – 709 (2015).
5. Jie Xu, Bing Xue, Yong-Mei Liu, Yong-Xin Li, Yong Cao, Kang-Nian Fan. Mesostructured Ni-doped ceria as an efficient catalyst for styrene synthesis by oxidative dehydrogenation of ethylbenzene. Applied Catalysis A: General. **405**, 142 -148 (2011). https://doi.org/10.1016/j.apcata.2011.08.001
6. Zarubina V., Talebi H., Nederlof C., Kapteijn F., Makkee M., Cabrera I.M. On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions. Carbon. **77**, .329 - 340 (2014). https://doi.org/10.1016/j.carbon.2014.05.036
7. Nederlof C., Zarubina V., Ignacio V.M.C., Erik H.J.H., Talebi H., Kapteijn F., Makkee M. Application of staged O_2 feeding in the oxidative dehydrogenation of ethylbenzene to styrene over Al_2O_3 and P_2O_5/SiO_2 catalysts. Applied Catalysis A: General. **476**, 204 - 214 (2014). https://doi.org/10.1016/j.apcata.2014.03.002
8. Wei Liu, Chao Wang, Dangsheng Su, Wei Qi. Oxidative dehydrogenation of ethylbenzene on nanocarbon: Kinetics and reaction mechanismJ. Catal. **368**, 1 - 7 (2018). *DOI: 10.1016/j.jcat.2018.09.023*
9. Antonio J. R.C., Joao M.,S., Jouse M.F., Alcineia C.O., Adriana C., Adwin R.C.M. Oxidative dehydrogenation of ethylbenzene with CO_2 for styrene production over porous iron-based catalysts. Fuel. **108**, 740 - 748 (2013).

10. Nederlof C., Kapteijn F., Makkee M. Catalysed ethylbenzene dehydrogenation in CO_2 or N_2—Carbon deposits as the active phase. Applied Catalysis A: General. **417 - 418**, 163 – 173 (2012).
11. Ramudu P., Anand N., Mohan V., Murali D.G., Prasad S.S.P., David R.B., Kamaraju S.R.R. Studies on ethylbenzene dehydrogenation with CO_2 as soft oxidant over Co_3O_4/COK-12 catalysts. J.Chem. Sci. **127**, 701- 709. (2015).
12. Mamedova M.T Oxidative dehydrogenation of ethylbenzene to styrene on MgO, ZrO_2/Al_2O_3 catalyst. In: International scientific conference "Actual problems of modern chemistry" dedicated to the 90th anniversary of the Mammadaliyev Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan., pp. 28 – 33. Baku (2019).
13. Nanzhe Jiang, Abhishek Burri, Sang-Eon Park Ethylbenzene to styrene over ZrO_2-based mixed metal oxide catalysts with CO_2 as soft oxidant. Chinese Journal of Catalysis. **37**, 3 – 15 (2016)
14. Jin-Nam Park, Jermim Noh, Jong-San Chang, Sang-Eon Park Ethylbenzene to styrene in the presence of carbon dioxide over zirconia. Chemistry Letters. **65**, 75 – 78 (2000).
15. Tagiev D.B., Gasimov G.O., Rustamov M.İ. Carbon deposits on the surface of CaO/SiO_2 as active catalysts for the oxidative dehydrogenation of ethylbenzene. Catalysis Today. **102 – 103**, 197 – 202 (2005).
16. Remy G. Course inorganic chemistry. Mir, Moscow (1966).
17. Krylov O.V. Heterogeneous catalysis. Akademkniga, Moscow (2004).

OR-II-4

SYNTHESIS AND CHARACTERIZATION OF ZnAl-LDHs USING DIFFERENT BASE SOLUTIONS

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Abstract. Zinc aluminum layered double hydroxides (ZnAl-LDHs) were synthesized using different base solutions: ammonium citrate tribasic and urea. 1M NaOH and $NaHCO_3$ mixed solution were used as a pH adjuster. X-ray powder diffraction (XRD) and Ultraviolet-visible (UV-Vis) spectroscopy were used to characterize the physicochemical properties of obtained solid materials. The XRD pattern of ZnAl-$LDH_{(ACTB)}$ shows high-intensity peaks while this intensity decreased for ZnAL-LDH_{urea}. E_{g1} and E_{g2} of ZnAl-LDH_{ACTB} are higher than ZnAl-LDH_{urea}. Because the interlamellar space of ZnAl-LDH_{urea} is higher than ZnAl-LDH_{ACTB}, the electronic transition energy from oxygen 2p to zinc metal's 4s and aluminum metal's 3s and 3p levels decreases, which is explained with the decrease of band gap energy.

Keywords: ZnAl -LDHs; base solutions; ammonium citrate tribasic (ACTB); urea.

1.Introduction

Layered double hydroxides (LDHs) are a famous group of layered materials known as anionic clays as well as positively charged hydrotalcite-like compounds. LDH are represented by the general formula$[M^{2+}_{1-x}M^{3+}_{x}(OH_2)]^{x+}(A^{n-})_{\frac{x}{n}}.m(H_2O)$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively and A^{n-} is the intercalated anion. They have received considerable attention due to their specific layered structure [1]. These promising materials have wide potential applications in catalysis, ion-exchange and adsorption by their high anion- and cation- exchange capacities, pharmaceutics, biochemistry, photochemistry, electrochemistry [1-5], etc. But there are extremely few works in synthesis, physicochemical characterization depending on the synthesis parameters of ZnAl -LDH. In this paper, we report and discuss the synthesis of ZnAl LDH applying different base compounds.

2.Experimental

Zinc nitrate heptahydrate $[Zn(NO_3)_2 \cdot 7H_2O]$, aluminum sulfate nonahydrate $Al_2(SO_4)_3 \cdot 9H_2O$, sodium hydroxide (NaOH), ammonium citrate tribasic (ACTB) ($C_6H_{17}N_3O_7$), urea (CH_4N_2O) and sodium bicarbonate ($NaHCO_3$) were analytical grade and used without purification. For the preparation of ZnAl -LDHs two equal pieces of solutions containing 3:1 ratios of Zn^{2+} and Al^{3+} ions were used as cation sources. 2.4g of ACTB and 3g urea were added into every each flask. 1M NaOH and 1M $NaHCO_3$ mixed solution were added to adjust the pH=9. The obtained white suspension was heated at 90°C for 24 hours, washed with distilled water and dried at room temperature. The obtained compounds are denoted as ZnAl –$LDH_{(ACTB)}$ and ZnAl –$LDH_{(urea)}$ according to base solutions.

The optical characterization of obtained samples was carried out by Ultraviolet spectrometer (UV-Vis) (Specord 250). Bruker D2 Phaser Powder X-ray diffractometer (XRD) in CuKα radiation, $\lambda = 1.541$ Å, was used to characterize the structural properties of the samples.

3. Results and discussion

The XRD patterns of ZnAl -LDHs obtained using ACTB and urea are shown in Fig. 1.

Both samples show characteristic reflections of hydrotalcite-like compounds along (003), (006), (012), (015), (018), (110) and (113) planes corresponding to JCPDS Card no. 48-1023 [6]. The XRD pattern of ZnAl-$LDH_{(ACTB)}$ shows high-intensity peaks while this intensity decreased for ZnAL-LDH_{urea}. The lamellae distance in a structure and the average particle size were calculated and shown in Table 1. The average particle size has been calculated by Debye–Scherrer equation:

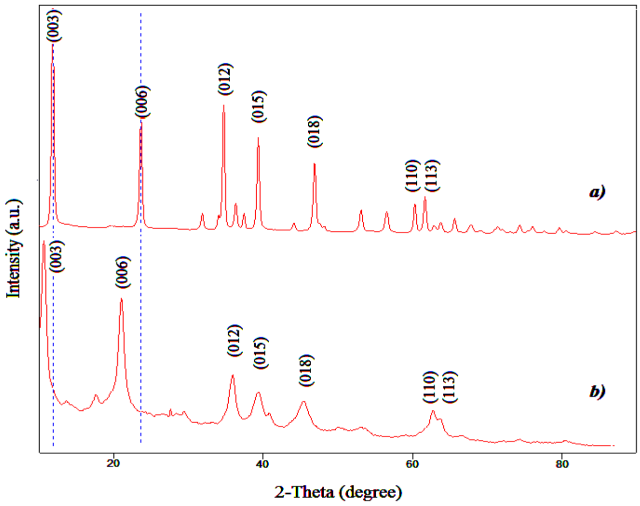

Fig.1. XRD pattern of ZnAl-LDH obtained using a) ACTB and b) urea.

$$D = \frac{\alpha\lambda}{\beta cos\theta} \quad (1)$$

Where, D- is the particle diameter, α- is the Scherrer constant (0.9), λ- the X-ray wavelength (1.5418 Å), and β- is the line broadening at half the maximum intensity (FWHM).

Table 1. Structural parameters for ZnAl-LDH obtained using ACTB and urea determined by XRD patterns.

Parameters	ZnAl-LDH$_{(ACTB)}$	ZnAl-LDH$_{(urea)}$
D (particle size) (nm)	22.37	9.58
d$_{(003)}$ (Å)	7.491	8.383
2θ $_{(003)}$- plane peak position (degree)	11.8°	10.55°

As can be seen from Table 1, the interlamellar distance (d$_{(003)}$) for ZnAl- LDH$_{urea}$ is wider than ZnAl-LDH$_{(ACTB)}$. During the hydrolysis of urea, the formed CO_3^{2-} caused the formation of wider interlamellar distance LDH structures.

3.2. Optical properties

Optical properties of ZnAl -LDH$_{(ACTB)}$ and ZnAl -LDH$_{(urea)}$ were studied by UV-Vis spectrometer and band gap energy was calculated from the transmittance spectra. Fig.2 shows two optical band gaps for of LDH structures, where the high-value (E$_{g1}$) band gaps are attributed to the presence of NO_3^- anions in the ZnAl -LDH$_{(ACTB)}$ interlayer galleries and NO_3^- and CO_3^{2-} anions in ZnAl- LDH$_{urea}$ structure [7, 8]. E$_{g1}$ and E$_{g2}$ of ZnAl-LDH $_{ACTB}$ is higher than ZnAl-LDH$_{urea}$. Because the interlamellar space of ZnAl-LDH$_{urea}$ is higher than ZnAl-LDH$_{ACTB}$, the electronic transition energy from oxygen 2p to zinc metal's 4s and aluminum metal's 3s and 3p levels decreases, which is explained with the decrease of band gap energy.

Table 2. Optical band-gap results of ZnAl -LDH determined by UV-Vis.

Samples	E$_{g1}$ (eV)	E$_{g2}$ (eV)
ZnAl -LDH$_{(ACTB)}$	5.2	3.5
ZnAl -LDH$_{urea}$	4.8	3.0

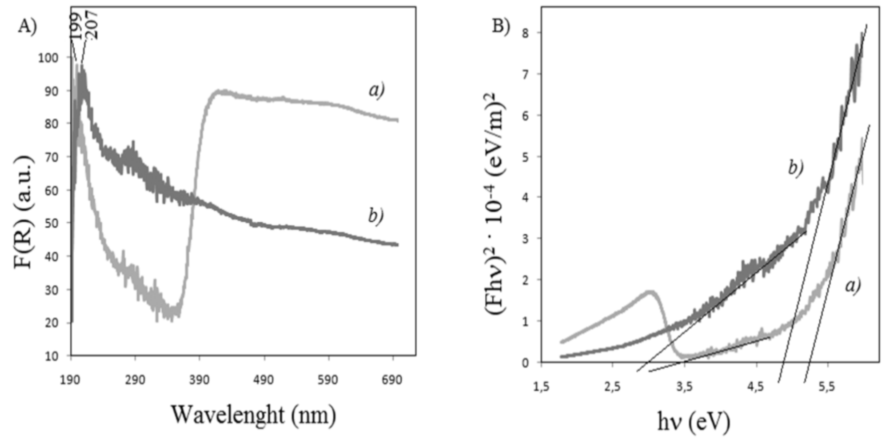

Fig.2. A) - Diffuse reflectance (R) UV–visible spectra and B) - variation of $[F(R\infty)h\nu]^2$ versus hν of (a)-ZnAl - $LDH_{(ACTB)}$ and (b)- ZnAl-LDH_{urea}

5.References

1. Bukhtiyarova, M.V.: A review on effect of synthesis conditions on the formation of layered double hydroxides. Journal of Solid State Chemistry 269, 494-506 (2019)
2. Sipos, P.; Pálinkó, I.: As-prepared and intercalated layered double hydroxides of the hydrocalumite type as efficient catalysts in various reactions. Catalysis Today 306, 32–41, (2018)
3. Álvarez, M.G.; Plíšková, M.; Segarra, M.A.; Medina, F.; Figueras, F.: Synthesis of glycerol carbonates by transesterification of glycerol in a continuous system usingsupported hydrotalcites as catalysts. Applied Catalysis B: Environmental 113–114, 212–220 (2012)
4. Li, F.; Duan, X.: Applications of Layered Double Hydroxides. Structure and Bonding 119, 193–223 (2006)
5. Xue, J.; Chen, T.; Meng, Y.; Zhou, X.; Pan, G.; Ni, Zh.; Xia, Sh.: Efficient detoxication of heterocyclics by layered double hydroxides contained different cobalt components as photocatalysts based on controllable application of active free radicals. Journal of Photochemistry and Photobiology A: Chemistry 371, 33-43 (2019).
6. Bernardo, M.P.; Ribeiro, C.: [Mg-Al]-LDH and [Zn-Al]-LDH as Matrices for Removal of High Loadings of Phosphate. Materials Research 21(3), e20171001(2018).
7. Balayeva O.O.; Azizov A.A.; Muradov M.B.; Alosmanov R.M.; Eyvazova G.M.; Mammadyarova S.J. Cobalt chromium-layered double hydroxide, α- and β- $Co(OH)_2$ and amorphous $Cr(OH)_3$: synthesis, modification and characterization. Heliyon 5 (11), e02725 (2019).
8. Chai, H.; Xu, X.; Lin, Y.; Evans, D.G.; Li D.: Synthesis and UV absorption properties of 2,3-dihydroxynaphthalene-6-sulfonate anion-intercalated Zn–Al layered double hydroxides. Polymer Degradation and Stability, 94, 744–749 (2009).

PP-II-2

AEROBIC OXIDATION OF CUMENE CATALYZED WITH N- (2,5-DYCHLOROPHENYL) DICHLOROMALEYMIDE

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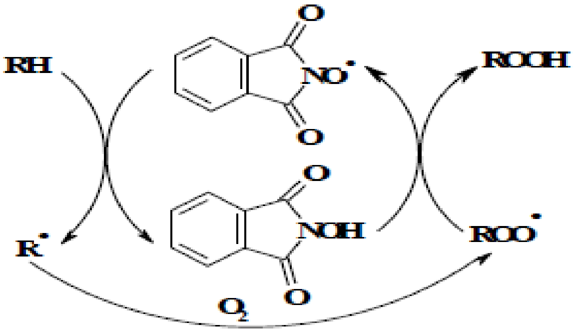
Abstract. Contemporary processes of the liquid phase catalytic oxidation of alkyl aromatic hydrocarbons have been generally analyzed with emphasis on non-metallic catalysis. It has been shown that hydrocarbon's conversion in such type of reactions may be increased by 2-3 times compared with that of peroxide initiated. In the presented work, N-(2,5-Dichlorophenyl) dichloromaleimide was used for the first time as non-metallic catalyst in the aerobic oxidation of cumene. It was determined that the imide possesses high catalytic activity affording a number of valuable organic substances containing oxygen (phenol, acetophenone, 1.2-benzoldicarboxylic acid), as well as oxygen-saturated and unsaturated compounds (phenyl-o (alpha-alpha-dimethyl) benzyl, 2.4-diphenyl-4-methylpentene- 1).In order to test the catalytic effect of N- (2,5-Dichlorophenyl) dichloromaleimide, an oxidation process was performed in parallel with molecular oxygen in air without a catalyst. N- (2,5-Dichlorophenyl) dichloromaleimide exhibits catalytic activity, leading to higher conversion of hydrocarbons compared to the oxidation process without a catalyst.Both oxide products obtained after the oxidation reaction were analyzed by chromium-mass spectrometry on the device "Agilent Technologies, 7820A GS system". Oxidation products do not contain cumolhydroperoxide.The catalyst may be considered as one of the active non-metallic additives for liquid-phase aerobic oxidation of alkyl aromatic hydrocarbons.

Keywords: 1N- (2,5-Dichlorophenyl) dichloromaleimide, 2oxidation, 3catalyst, 4cumene, 5imide, 6phenol, 7acetone,8 1.2-benzoldycarboxylic acid.

1.Introduction

Research on the selection of catalysts for the synthesis of industrially important organic substances obtained from the oxidation of hydrocarbons of various structures is important. In recent years, a study of the literature has shown that the selective oxidation of cumene synthesizes a number of valuable, industrially important organic compounds, and the choice of catalysts plays an important role in this process. Both metallic and non-metallic catalysts are used in the process. If oxidation reactions in the presence of metalphthalocyanins take place in the range of 80-1000C, they can be carried out at lower temperatures with metalporphyrins. Co, Cu, and Zn teraphenylporpyrins are highly active catalysts that, in addition to activating oxygen, accelerate the breakdown of cumene hydroperoxide (KHP) [1-11].The effect of phthalimide catalysts, temperature, initiator and their combination, on the conversion and oxidation of cumene, as well as on the selectivity of hydroperoxide formation was studied [12-13].The choice of phthalimides as the main catalyst is due to the availability of raw materials for their production and simplicity of synthesis. Studies of the concentration of N-phthalimides show that an increase in the catalyst content from 1.35% to 2.7% increases the rate of oxidation of cumene. However, a subsequent increase in concentration from 2.7% to 4.05% results in a slower reaction rate and a decrease in the amount of hydroperoxides formed. This is most likely due to the limited solubility of N-hydroxyphthalimide in the hydrocarbon under study. Re-use of N-hydroxyphthalimide does not reduce the main parameters of the process for 4-5 cycles. Additional oxidation products (acetophenone, benzoic acid, and benzaldehyde) reduce the selectivity of KHP formation. It was found that the content of additional products in the initial hydrocarbon is 0.05mol / l. Also, the effect of temperature on the oxidation and selectivity of technical cumene was studied and it was noted that the conversion of cumene in 60 minutes is about 22%, and the selectivity of KHP formation is 90.5%. The use of N-hydroxyphthalimides allows to increase the rate of oxidation of cumene by 2-3 times and therefore intensify this process with a selectivity of 90% for the formation of hydroperoxid. A comparison of the patterns of accumulation of hydroperoxides in the catalytic and non-catalytic oxidation of cumene shows the expediency of the use of phthalimide catalysts to increase the efficiency of this process. The duration of oxidation in industrial-scale reactors is up to three hours, during which an oxide containing 20-25% of KHP is obtained. When using N-hydroxysoftalimide, this result can be achieved within 75 minutes, which increases the efficiency of the reactor by 15-20%. Oxidation of cumene to hydroperoxides follows a chain radical mechanism. Acceleration of the oxidation process of N-hydrosoftalimides is associated with the formation of N-oxypthalimide radical from the N-hydroxycalimide molecule based on the interaction of the oxidizing agent with the peroxide radical. The formation of N-oxypthalimide has been experimentally confirmed by the EPR method. The basis of this process is the following catalytic cycle [14-15].



Chain excitation in the system is one of the important conditions for the implementation of this cycle, because the oxidation of isopropylbenzene in the liquid phase at a temperature of $100-120^0$C and in the presence of N-hydroxyphthalimides is practically impossible. The choice of catalysts for the synthesis of industrially important organic compounds obtained as a result of selective oxidation of cumene is of great importance.

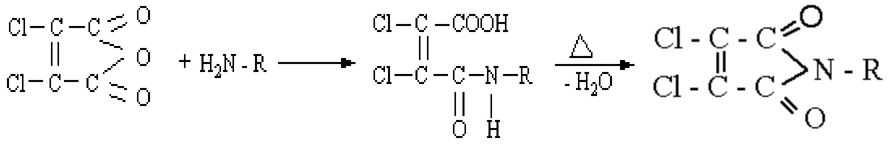
Thus, modern works on the processes of oxidation of cumene in the liquid phase with the participation of various catalysts were analyzed and it was determined that non-metallic catalysts are easier and cheaper than others. Therefore, in recent years, imides have been proposed as new effective catalysts in the aerobic oxidation of hydrocarbons [16]. It was noted that the most studied, researched and applied catalyst among imides is N-hydroxyphthalimide. Such information about other imides is almost non-existent. Therefore, it is expedient to study new types of imides in the oxidation processes of hydrocarbons. In the present study, the results of the oxidation of cumene with atmospheric oxygen at a temperature of 100^0 C in the presence of N- (2,5-Dichlorophenyl) dichloromaleimide are given.

2.Experimental part

N- (2,5-Dichlorophenyl) dichloromaleimide was synthesized under laboratory conditions by heating dichloromalein anhydride with 1: 1 mole of dichloromalein anhydride in an icy acetic acid environment, and its composition and structure were determined by spectral and chemical methods.

3.Results of experiments and their discussion

Preparation of N- (2,5-Dichlorophenyl) dichloromaleimide. Pour 16.7 g (0.1 mol) of dichloromalein anhydride (DXMA), 60 g of glacial acetic acid into a 4-neck flask equipped with a refrigerator, thermometer, dropper funnel and mechanical stirrer, and add 16.2 g (0.1mol) of 2.5-dichloraniline with a dropper funnel adds. The mixture is stirred for 30 minutes at 80^0C and 90 minutes at 118^0C. The solution is then mixed and cooled to 10^0C. The precipitate is filtered, washed with water and dried in a vacuum at 60^0C.The yield is 28 g (85%). The reaction proceeds in two stages according to the following scheme. First, amidobutyric acid, and then the separation of water closes the cycle and imide is formed [17-20].



R= *2*,5-$Cl_2C_6H_3$

The structure of the obtained substance was determined by IR-spectrum and elemental analysis. The IR spectrum was recorded in CBR on a Nicolet IS10 Thermo Scientific USA type spectrophotometer. IQ-spectrum,, sm-1 1755-1710 (C = O), 1642 (C = C), 1340 (= N-), 835 (C6H3), 739 (C-Cl). Found,%: C 38,58; H 0.92; Cl 45,76; N 4.54. $C_{10}H_3Cl_4NO_2$. Calculated,%: C 38,59; H 0.97; Cl 45,66; N 4.57.

The obtained imide is a yellowish crystal with benzene, toluene, acetone, etc. soluble in organic solvents. $T_{\text{meltinq point}} = 185\text{-}186\ ^0C$.

Aerobic oxidation of cumene with N- (2,5-dichlorophenyl) dichloromaleimide

The study used cumene produced by Sigma-Aldrich Gmbh with a purity of 98%. Oxidation process at 100^0C for 5 s. was carried out in a bubble-type glass reactor. (Figure 1).The reactor is made of heat-resistant glass with a diameter of 4 cm oxidizing column (30 cm - direct cooling, 23 cm - reactor), equipped with continuous air oxygen with an air flow of 0.4-0.5 liters / h. A refrigerant is connected to the column to convert gaseous substances into liquids and return them to the reaction zone. At the top of the oxidation unit is a tap for samplin. The oxidation unit is heated using a glycerin thermostat (Thermostat U1). The reaction temperature is maintained using a contact thermometer (t = 105 ° C) integrated in the thermostat. 25 ml (21.55 g, 0.1793 mol) of cumene and 0.1 g (0.00036 mol) of N- (2.5-dichlorophenyl) dichloroleimide were added to the reactor and a constant stream of air was released from the reaction mixture in order to use molecular oxygen as an oxidizer. In order to test the catalytic effect of N- (2,5-Dichlorophenyl) dichloromaleimide, the process of oxidation of air without catalysts with molecular oxygen was carried out in parallel.

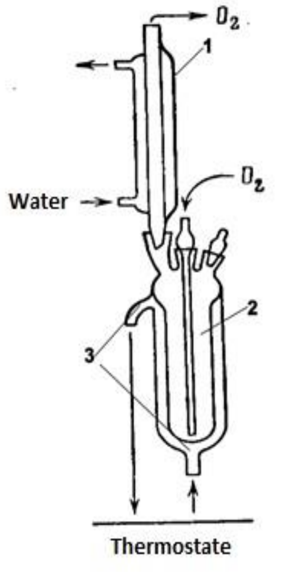


Fig. 1. Description of the oxidation device with molecular oxygen.

1 - refrigerator;
2 - volume of the reaction part;
3 - T-shirt for heating the reactor.

Both oxide products obtained after the oxidation reaction were analyzed by chromium-mass spectrometry on the device "Agilent Technologies, 7820A GS system". The main products of the obtained oxide are shown in Table 1.

Table 1. The main products of the oxide obtained by aerobic oxidation of isopropylbenzene with N- (2,5-Dichlorophenyl) dichlorolemeide and without a catalyst. (In the reaction, imide was taken by 1% by weight. Temperature 100^0C, time 5 hours.)

Names of products identified in the oxide	Catalyst and productivity, mass. %	
	Without catalysts	N-(2,5-Dichlorophenyl) dichlormaleimide (catalyst)
Cumene	43.846	10.586
Phenol	0.17	4.166
Acetophenone	11.561	2.499

2.4-Dimethylbenzoic acid	1.045	-
1-Metilenpropilbenzol	0.6045	-
2.4.4.6- Tetramethyl-6-phenylheptene-1	2.9085	-
Phenyl-o (alpha-alpha-dimethyl) benzyll	-	1.482
2.4-Diphenyl-4-methylpentene-1	-	3.906
4- (1-Methyl-1-phenylethyl) phenol-	-	2.396
1.2-bezoldycarboxylic acid	-	14.37

The table shows that the total conversion of cumene is 89.42%. In this case, various organic products: phenol, ketone (acetophenone), phenyl-o (alpha-alpha-dimethyl benzyl), 4-methyl-2,4- diphenyl-pentene-1, 4- (1-Methyl-1-phenylethyl) phenol, 1,2-benzoldycarboxylic acid, etc. ingredients are taken. The results show that N- (2,5-Dichlorophenyl)dichlorolemeide exhibits catalytic activity, leading to higher conversion of hydrocarbons compared to the oxidation process without a catalyst. Cumenehydroperoxide is not mentioned in oxidation products. For comparison, Table 2 shows the production of KHP as a result of aerobic oxidation of cumene at different temperatures.

Table 2. The effect of temperature on the conversion of isopropylbenzene to its hydroxyperoxide in the presence of N-hydroxyphthalimide. (N-hydroxyphthalimide was taken at a ratio of 2.7% by weight).

Temperature, ^{0}C	Reaction time h.	Amount of KHP in oxide,%	Selectivity of KHP,%	Average rate of KHP formation,% mass / h
100	3.0	29.3	91.3	9.8
110	3.0	37.2	92.0	12.4
120	2.5	47.9	95.0	19.6
130	1.0	50.1	91.3	50.1

Table 2 shows that 30% KHP is formed at 100 ° C and 3 hours. Under these conditions, in the reaction with N- (2,5-Dichlorophenyl) dichloroleamide, KHP is completely converted into organic products (phenol, ketone (acetophenone), phenyl-o (alpha-alpha-dimethyl benzyl), 4-methyl -2,4- diphenyl - pentene-1, 4- (1-Methyl-1-phenylethyl) phenol, 1,2 -benzoldycarboxylic acid, etc.).The total conversion of cumene as a result of oxidation at 120 ° C and 2.5 hours (Table 2) is 50%, while the reaction with N- (2,5-Dichlorophenyl) dichloroleamide is 89.42% at 100 ° C. Thus, summarizing all the above, we can draw the following conclusions.

4.Conclusions

1. During the oxidation of cumene in the presence of imide, intensive oxidative dehydrogenation reactions occur, which, along with a number of oxygen-containing organic products - acetophenone, phenol, etc., either unsaturated structural compounds are obtained, or oxidative alkylation reactions occur.
2. The choice of catalysts for the synthesis of industrially important organic compounds obtained as a result of selective oxidation of cumene is of great importance.
3. It has been determined that N- (2,5-Dichlorophenyl) dichloromaleimide has catalytic activity and the KHP obtained during the reaction is converted into appropriate oxidation products.
4. The total conversion of cumene to 1% by mass of the catalyst at 100^{o}C and 5 h is 89.42%.

5. References

1. Maravin G.B, Avdeev M.V, Bagriy E.I: Oxidative functionalization of saturated hydrocarbons in metal complexes of porphyrin series catalysts. Petrochemistry T.40, №1 (2000).
2. Giannini M.D., Shulpina L.S, Shuhardt U., Shulpin G.B: Oxidative functionalization of hydrocarbons in the presence of metal compounds. Petrochemistry T.45.№6. pp. 189-195 (2005).
3. Bukhtiyarov V.I, Slinko M.G: Metallic nanosystems in catalysis. Usp. Chemistry T.70, №2.s.167-181 (2001).
4. Poluboyarov V.A, Lapin A.E, Korotaeva Z.A, Prosvirin I.P, Bukhtiyarov V.A, Sirotkina E.E, Kobotaeva N.S: Neoorgan Materials T.41, №2. pp.151-161 (2005).
5. Askarov K.A, Berezin B.D., Sergeev G.B: Nanochemistry of metals Usp. khimii. T.70, № 10. pp.915-933 (2001).
6. Askarov K.A, Berezin B.D, Bystritskaya E.V and others: Porphyrins spectroscopy, electrochemistry, application.M. Nauka, pp. 384 (1987).
7. Bogdanova K.A, Askarov K.A: Metallocomplexes of porphyrin and azaporphyrin compounds as catalysts for molecular oxygen oxidation reactions. Successes of chemistry vol.52. №1. pp. 20-42. (1983).

8. Susana L.H. Rebelo, Mario M.Q.,Simes M.P., Graça .M.S. Neves, İose A.S.Cavaleiro: Oxidation of alkylaromatics with hydrogen peroxide catalyzed by manganese (III) porphyrins in the presence of ammonium acetate. Journal of Molecular Catalysis A.Chemikal vol.201. issues 1-2. pp.9-22 (2003).
9. Galen J. Supper, Ronald N. Occhiogrosso, Mark A. Mchugh: Oxidation of cumene in supercritical reaction media. İndustrial & Endineering Chemistry Research 28 (8), pp.1152-1156 (1989).
10. Shixia Liao, Feng Peng, Hao Yu, Hongjuan Wang: Carbon nanotubes as catalyst for the aerobic oxidation of cumene hydroperoxide. Applied Catalysis A General vol.478. pp.1-8 (2004)
11. Razyapov I.G: Intensification of isopropylbenzene oxidation in the presence of a catalyst based on cobalt. Author's dissertation for the degree of Candidate of Chemical Sciences pp.21 (2010).
12. Stepovik L.P, Dodonov V.A, Zaburdaeva E.A: Reactions of oxidation of alkylarenes trn-gret-butylate aluminum system - tert-butyl-hydroperoxide. Journal of General Chemistry vol.67. issue.1. p.116 -120 (1997).
13. Skibida I.P: Activation of molecular oxygen by metal complexes and its role in the mechanism of liquid phase oxidation. Success of chemistry vol. 54, T..9, p. 1487-1504 (1985).
14. Akhrem A.A., Metelitza D.I., Bielski S.M., Kiselev P.A., Skurko M.E., Usanov S.A: Selective heterogeneous-catalytic oxidation of C-H bonds of some hydrocarbons in the system of diacetate media (II) -three -butylhydroperoxide- oxygen in the air. Croat.Chem. Acta №49. p.223(1977).
15. Kurganova E.A: Liquid-phase oxidation of alkyls and cyclohexylaromatic hydrocarbons to hydroperoxides in the presence of phthalimide catalysts. Abstract of the dissertation in search of teaching. step. doctor of chem. Science p.17 (2013).
16. Nagiyev Y.M, Zeynalov E.B, Zeynalov S.B, Budagova R.N: Liquid-phase aerobic oxidation of cumola in the presence of N-phenylimide-endo dichlorobiciclo [2.2.1] hepta-5-en-2,3-dicarboxylic acids. XX Mendel Congress in general. and prikl. Chem. Yekaterinburg September 26-30, T. 1, Art. 464. pp.470 (2016).
17. Mendel Congress in general. and prikl. chem . Yekaterinburg September 26-30, 2016, T. 1, Art. 464. [Nagiyev Ya. M., Zeynalov E.B., Zeynalov S.B., Budagova R.N. Fundamental problems of chemical science 26-30 September, Ekaterinburg 2016, vol.1. pp.470 (2016)
18. Nagiev Ya.M. , Ahmedov R.M, Hasanov A.I, Kulieva T.A, Bagirova S.Sh. Obtaining some N-substituted adducts on the basis of aromatic nitroamines. Azerbaijan.chemical Journal, №2, p.180-186 (2008).

PP-II-3

STUDY OF CATALYTIC CYCLOALKYLATION REACTIONS OF PARA-CHLOROPHENOL WITH 1-METHYL- AND 4-VINYLCYCLOHEXENES

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Abstract. The paper presents the results of the researches carried out on kinetic regularities of catalytic alkylation reactions of p-chlorophenol (PCP) with 1-methyl- and 4-vinylcyclohexenes in the presence of KU-23 catalyst. Effect of kinetic factors (reaction temperature, time, mole ratios of initial components, catalyst amount) on the target products yield and selectivity has been studied. Thus, the optimal conditions have been determined for catalytic cycloalkylation reaction of p-chlorophenol with MCH in the presence of KU-23 catalyst: temperature - 120°C, reaction time – 5 h, mole ratio of PCP to MCH – 1:1, catalyst amount – 10% (according to PCP). Yield of 2(1-methylcyclohexyl)-4-chlorophenol to PCP is 77.5%, but selectivity for the target products amounts to 95.4% under this condition. Simultaneously, cycloalkylation reaction of PCP with VCH has been studied in the presence of KU-23 catalyst. There have been determined, that the yield of the target product – 2(cyclohexene-3-yl-ethyl)-4-chlorophenol amounts to 69.7% (according to PCP), but selectivity according to the target product is 92.5% under the following reaction conditions: temperature - 110°C, time - 5 h, mole ratio of PCP to VCH - 1:1, catalyst amount - 7%.It has been determined, that chemical reactions should be carried out under the following conditions for the purpose of having effective yield (69.7-77.5%) and selectivity (92.5-95.4%) of 2(2-methylcyclohexyl) and 2(cyclohexene-3-yl-ethyl-4-chlorophenols): temperature – 115-120°C, reaction time – 5-6 h, mole ratio of PCP to cyclen – 1:1, catalyst amount – 7-10% (according to taken PCP).

Keywords: p-chlorophenol, 1-methylcyclohexene, catalyst, cycloalkylation, 2(1-methylcyclohexyl)-4-chlorophenol, 2-ethylcyclohexenyl-4-chlorophenol

1. Introduction

Hundreds of effective antioxidizers, additives, stabilizers and other chemical additives to oils, fuels, polyolefins, rubbers which have already been used in industry are obtained as a result of phenols alkylation reactions with different alkylating agents. It's no coincidence, that most of industrially used chemical additives are obtained mainly on the bases of alkylphenols [1-9]. Alkylphenol-based chemical additives are mainly obtained by catalytic alkylation of aliphatic hydrocarbons with phenol. These chemical additives are non-soluble in applied objects and it is considered the most important disadvantage of them. Therefore, cycloolefin-based chemical additives containing a haloid fragment are of special significance.

The paper is devoted to the study of cycloalkylation reactions of p-chlorophenol with 1-methyl and 4-vinylcyclohexenes in the presence of the catalyst KU-23.

2. Experimental Part

p-chlorophenol, 1-methylcyclohexene (MCH) and 4-vinylcyclohexene (VCH) have been used as raw materials for the research. VCH is obtained by divinyl cyclodimerization [10] and has the following physicochemical properties: purity of 98.8-99%, b.p. 130°C, n_D^{20} 1.4648, ρ_4^{20} 0.8308, mol mas. 108; MCH is obtained by diene synthesis of isoprene with ethylene via Diels-Alder reaction and has the following physicochemical properties: b.p.111-112°C; n_D^{20} 1.4500; ρ_4^{20} 0.8800; mol mas. 96.

The catalyst KU-23 has been used for cycloalkylation reaction. KU-23 (10/60 of modification) contains 55-70% of water and it's thermally stable up to 170°C. Therefore KU-23 is heated to 110°C before use to get rid of water. The catalyst activity decreases by the cause of separation of sulfogroup from the catalyst under the influence of temperature and accumulation of resin like substances on it in the work process.

Unlike KU-2 catalyst, KU-23 catalyst is regenerated by hydrochloric acid of 2-4% and reused.

P-chlorophenol cycloalkylation reactions with cyclohexenes have been carried out in a three-necked flask on the following method: the flask is filled with calculated amount of p-chlorophenol and the catalyst (KU-23) and heated. Cycloolefin is added by drops at 40°C of temperature. The blend of the components is mixed in the reaction zone at 80-140°C for 2-8 h in the presence of a catalyst, filtered and separated from the catalyst at 45°C and rectified. MCH (VCH) is distilled firstly, then PCP and reaction products are undergone to vacuum distillation.

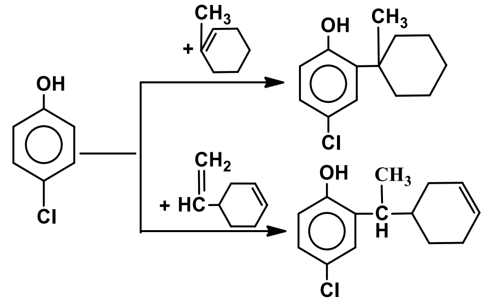
Chromatographic analyses of the reaction and rectification products have been conducted on LXM-72 chromatograph. The column length is 2 m, chromaton N-AW-/JMC in the size of 0.2 ±0.25 mm silanced by dimethylchlorosilane and washed by acid has been used as a solid carrier and SE-30 methylcyloxane of 5% – as inactive phase. The column initial temperature is 50°C, final temperature – 280°C, programming speed - 10°C/min, speed of helium – 50 ml/min., evaporator temperature - 355°C, detector temperature - 300°C, diagram tape speed – 60 mm/h .

100% of the the sum of the total peaks areas has been taken as the basis for calculating the percentage of the initial and final products compositions in both of the cases.

IR spectrum of the obtained compounds has been recorded on “Spectrum BX” produced by “Perkin-Elmer” and “ALPHA IR Fouirer” produced by “BRUKER”, NMR spectrum - on NMR spectrometer of 300 MHz by the company “BRUKER”.

3. Results and Discussion

P-chlorophenol (PCP) alkylation reactions by MCH and VCH in the presence of KU-23 catalyst are conducted on the equation below:



Effect of the reaction temperature, time, initial components mole ratios and catalyst amount on the yield and selectivity of the target products has been studied for the purpose of determining optimal conditions for catalytic reactions of para-chlorophenol with MCH and VCH.

PCP cycloalkylation reactions have been studued at the temperature of 80-140°C, duration of 2-8 h, PCP ratio to MCH (VCH) from 1:2 to 2:1 and 5-10% of the catalyst amount (according to the taken PCP).

The results of PCP cycloalkylation reactions with 1-methylcyclohexene in the presence of KU-23 catalyst are presented in the below figure as an example.

As is evident from the figure, 120°C of temperature is advisable to have higher yield of 2(1-methylcyclohexyl)-4-chlorophenol. The yield of the target product amounts to 77.5% and selectivity 95.4% at this temperature. The yield amounts to 51.8-68.3%, selectivity – 84.1-90.66 at 80-100°C of temperature. Increasing temperature up to 140°C isn’t considered acceptable for the process, because in this case the target product yield decreases to 72.5% and selectivity – to 88.4%; it’s explained by obtaining undesirable products.

The contact time of the initial raw materials with the catalyst is considered one of the main factors having an influence on the yield and selectivity of the reaction products. As is seen from the figure, 2 h of reaction time isn’t sufficient for running cycloalkylation reaction selectively, in this case the yield is 35.6%, but selectivity 96.8%. In 6h of reaction time the target product yield and selectivity amount to 77.5 and 95.4%, correspondingly.

One of the factors influencing on the yield and selectivity of 2(1-methylcyclohexyl)-4-chlorophenol is mole ratio of initial raw materials. As is seen from the figure (c), it is impossible to have higher yield and selectivity by increasing MCH concentration in the reaction mixture.The yield of mono-substituted PCP amounts to 53.6% and selectivity 68.1% in this case. The low yield and selectivity is explained by formation of 2,6-di-substituted PCP as a result of reacting excessively taken part of MCH with mono-substituted PCP.

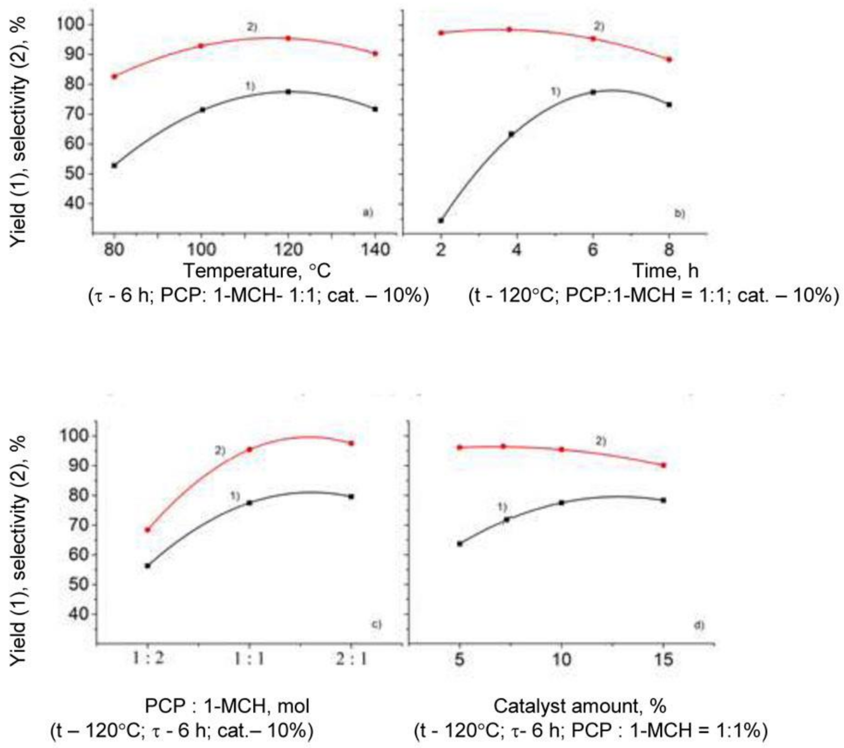


Fig. 1. Dependence curves of the yield (1) and selectivity (2) of 2(1-methylcyclohexyl)-4-chlorophenol on temperature (a), time (b), mole ratios of initial components (c), catalyst amount (d).

As is evident from the figure, it's more advisable taking of initial components amounts at 1:1 mole ratio in the reaction mixture. In this case the yield of 2(1-methylcyclohexyl)-4-chlorophenol is 77.5% and selectivity 95.4%.

As is seen from the figure, effective yield and selectivity of the target product is obtained in the amout of 10% of the taken catalyst. It's possible to have increase in the target product yield by increasing catalyst amount up to 15%, but the reaction selectivity decreases in this case.

Thus, the optimal conditions have been determined for catalytic cycloalkylation reaction of p-chlorophenol with MCH in the presence of KU-23 catalyst: temperature - 120°C, reaction time – 5 h, mole ratio of PCP to MCH – 1:1, catalyst amount – 10% (according to PCP). Yield of 2(1-methylcyclohexyl)-4-chlorophenol to PCP is 77.5%, but selectivity for the target products amounts to 95.4% under this condition.

IR spectrum results of 2(1-methylcyclohexyl)-4-chlorophenol: 654, 705 cm^{-1} – C-Cl bond; 809, 879 cm^{-1} - 1, 2, 4 substituted benzene ring; 973 cm^{-1} – C-H bond of cyclohexane ring; 1114, 1171 cm^{-1} – C-O bond; 1245cm^{-1}, 3555 cm^{-1} – deformation and stretching vibrations of O-H bond of phenol OH group; 1322, 1400, 1450, 1489 cm^{-1}- deformation vibration of C-H bond of CH_3 və CH_2 groups; 2856, 2923 cm^{-1} – stretching vibrations of CH_3 and CH_2 groups; 1597 cm^{-1} – C-H bond of benzene ring; 1698 cm^{-1} –C-H bond of benzene ring.

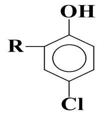
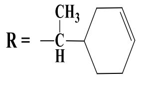
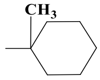
^{1}H and ^{13}C NMR spectra results of 2(1-methylcyclohexyl)-4-chlorophenol:

^{1}H NMR (300 MHz, acetone-d_6), δ, ppm: 1.33 (s., 3H, CH_3), 1.42-2.25 (m.,10H, CH_2), 6.84 (d., 1H, OH – C – $\underline{CH}$, J=8.7Hz), 7.02 (d.d., 1H, CH – $\underline{CH}$, J=5.7, 2.7Hz), 7.19 (d., 1H, Cl – C – $\underline{CH}$, J=2.7Hz), 8.58(s., 1H, OH) ^{13}C NMR (75 MHz, acetone-d_6), δ, ppm 22.62(CH_3), 24.87, 26.41, 36.34(CH_2), 38.05($\underline{C}$–CH_2), 117.85, 123.75, 126.14, 127.65, 129.17, 137.06(C,Ar), 154.8(OH–$\underline{C}$)

Simultaneously, cycloalkylation reaction of PCP with VCH has been studied in the presence of KU-23 catalyst. There have been determined, that the yield of the target product – 2(cyclohexene-3-yl-ethyl)-4-chlorophenol amounts to 69.7% (according to PCP), but selectivity according to the target product is 92.5% under the following reaction conditions: temperature - 110°C, time - 5 h, mole ratio of PCP to VCH - 1:1, catalyst amount - 7%.

Physicochemical properties of the synthesized 2(methylcyclohexyl)-4-chlorophenols are given in the table.

Table 1. Physicochemical properties of 2(methylcyclohexyl)-4-chlorophenols.

	Boil. point 10 mm mc	n_D^{20}	ρ_4^{40}	Mol. mas.	Elemental composition, %			
					Calculated		Found	
					C	H	C	H
	178-183	1.5476	1.0104	236	71.2	7.2	70.7	6.5
	207-211	1.5176	1.0308	224	69.6	7.6	69.0	7.8

4.Conclusion

Catalytic cycloalkylation reactions of p-chlorophenol with 1-methyl- and 4-vinylcyclohexenes have been studied in the presence of KU-23 catalyst. As a result of the researches, there have been determined, that yield of the target products amounts to 69.7-77.5% (according to the taken PCP), but selectivity – 92.5-95.4 (according to the target product) at 115-120°C, 5-6 h reaction time, at 1:1 mole ratios of initial components and 7-10% of catalyst amount.

5.References

1. Seleznova, I.Y., Levin, A.Ya., Trofilova, G.L.: New super-alkaline alkylphenol additive for motor oils. Chemistry and Technology of Fuels and Oils, № 4, pp. 10-12, (2009).
2. Chukicheva, I.Yu., Spirikhin, L.V., Kuchin, A.V.: Tandem molecular rearragement in the alkylation of phenol with camphene. Russian Journal of Organic Chemistry, vol. 44, № 1, pp. 69-73, (2008).
3. Mirzoye, V.G.: Interaction of phenol with 3-vinilcyclohexene a catalytic cycloalkenyl chlorination on a centinuosly operating unit. Prosesses of petrochemistry and oil refining, vol. 17, № 1, pp. 93-97, (2015).
4. Shakhmuradov, S.T., Dzhafarov, R.P., Mirzoyev, V.G.: Kinetic laws and the mechanism of reaction of orthocycloalkylation of para-chlorophenol with 1-methylcyclohexene. Neftepererabotka i neftekhimiya, № 1, pp. 29-31, (2018).
5. Vitvarova, D., Lupinkova, L., Kubu, M.: Akylation of phenols and acylation 2-methoxynaphthalene over SSZ-33 zeolites. Microporous and Mesoporous Materials, vol.210, pp.133-141, (2015).
6. Pokrovskaya, S.V., Korbut, Y.Ya.: Innovative ideas of phenol alkylation process modernization with the aim of alkylate quality improvement. Industry. Applied Science. Chemical Technology, № 11, pp. 101-107, (2018).
7. Medzhidov, E.A., Rasulov, Ch.K., Ibragimov, Kh.D.: Alkylation of phenol with 130-190°C fraction of pyrolysis liquid products in the presence of phosphorous-containing zeolite in a continuous installation. Azerbaijan Oil Industry, №7, pp.71-74, (2013).
8. Gürbüz, D., Çınarlı, A., Tavman A.: Synthesis and spectral characterization of 5-chloro-2-(5-chloro/methyl-1,3-benzoaxazol-2-yl)phenols / 1st International Turkic World Conference on Chemical Sciences and Technologies, (2015), p. 249.
9. Yoichiro, K., Takashi, M., Kazuhiko, T.: Rhenium-catalyzed regioselective alkylation of phenols. I.Am. Chem. Soc., 131(29), pp.9914-9915, (2009).
10. Aleksandrova, I.V., Tushakova, Z.R., Lomakin, I.A.: Dehydrogenation of 4-vinylcyclohexene-1 to styrene on industrial catalysts. Neftepererabotka i neftekhimiya, №12, pp.29-33, (2012).

PP-II-4

THERMAL AND CATALYTIC PROPANE-BUTANE FRACTIONS FACTORS AFFECTING PYROLYSIS

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Abstract: At present, research has been conducted to increase the yield of target products obtained in the process of thermal pyrolysis at high temperatures and at the same time to intensify the process. For this purpose, the effect of the process temperature on the pyrolysis raw material in the gas phase, the contact time of the raw material in the reaction zone, as well as the ratio of water vapor to the raw material on the output of the target product was studied. The obtained results were compared with the results obtained as a result of the application of catalysts to the process, and it was determined that the yield of ethylene can be increased by 0.19-0.33% (mass) at temperatures of 600-6500C. This creates effective conditions for lowering the temperature of the thermal pyrolysis process currently used in the petrochemical industry.

Keywords: thermal pyrolysis, Azerbaijani zeolite, mordenite, propane-butane, catalytic pyrolysis

1.Introduction

At present, the petrochemical industry uses various raw materials - gaseous and liquid hydrocarbons for the production of low molecular weight olefins. Thermal pyrolysis is a very strict process. The process is usually carried out in the temperature range of 700-900^{0}C. The high temperature in the process of thermal pyrolysis leads to its severe cracking process. Despite the fact that the process is carried out in such a strict mode, it is the most suitable process for the production of ethylene, propylene, butene, butadiene-1,3, which are widely used in industry. At the same time, it is possible to produce from this process various petrochemical products and additional components for motor fuels [1-2].

Along with gases, a certain amount of liquid resins are obtained from the pyrolysis process, which are rich in aromatic hydrocarbons. From these resins it is possible to obtain individual hydrocarbons - benzene, toluene, xylene, naphthalene, anthrapene, phenanthrene and other derivatives.

Taking into account the above, the process of thermal pyrolysis is one of the most destructive processes used in the petrochemical industry. In this regard, specialists are constantly searching for further development of the thermal pyrolysis process, increasing the yield of target products and at the same time mitigating the conditions of the process.

2. Experimental part

The flow method was used to determine the legitimacy of the thermal conversion of low-molecular hydrocarbon fractions in the presence of mordenite-type zeolite catalyst. This method is distinguished by its simplicity, allows to determine the catalytic activity of the catalyst at any stage of the reaction in the laboratory under stationary conditions and is a frequently used method [183-187].

The experiment was performed on a flow-type laboratory device operating under atmospheric pressure [188].

The conversion of hydrocarbon content of gaseous products into low-molecular-weight hydrocarbon fractions was tested on a chromatograph CVET-800 heat transfer detector. This device is based on DÜİST 26703 and belongs to the laboratory stationary chromatograph group.

The results of the analyzes were used with an accuracy of 0.1 from the arithmetic mean of two parallel results. The full composition of the pyrogas obtained as a result of the analysis was taken into account.

The following were used in the study of catalytic pyrolysis: $CaCl_2$ (for dehydration), technical nitrogen (DUIST 9293-74), hydrogen from a laboratory generator (brand GVCH-12).

3. Results and its discussion

We conducted our research with the propane butane fraction, which we used as a raw material. The indicators of raw materials are shown in Table 1 below

Table 1. Indicators of propane-butane fraction

Component composition,% by mass				
CH_4	C_2H_6	C_3H_8	i-C_4H10	H-C_4H_{10}
1.14	5.71	75.12	7.85	10.18

First, we tried to determine the regularity of the formation of low-molecular-weight olefin fractions formed during the transformation of this fraction. For this reason, we carried out thermal pyrolysis by keeping the rate of transfer of propane butane fraction to the pyrolysis process 900-570^{0}s-1, contact time 0.1-0.5s, and water vapor in the ratio of 0.2-0.6: 1 for raw materials.

In studying the mechanism of influence of the process temperature on the conversion of propane to butane fraction in the process of thermal pyrolysis, we carried out the process with the ratio of water vapor to raw material 0.4:1, maintaining the temperature of the process at 700-900°C and 0.1c in the reaction zone. We have recorded the results in Table 2.

As can be seen from the table, increasing the process temperature from 700°C to 900°C increases the yield of ethylene, and the maximum yield is obtained at 900°C. In this case, the maximum yield of propylene is 17.27% (mass) at 800°C. Then, with a gradual rise in temperature, a sudden decrease in propylene output is observed. It is assumed that this is due to the fact that as the temperature rises during the process, the breaking speed of the C-C bond is greater than the breaking speed of the C-H bond. As can be seen from the table, the maximum yield of unsaturated hydrocarbons C_2 - C_4 is 62.72% (mass) at 850°C. At the same time, it should be noted that as the process temperature rises, the output of by-products such as hydrogen, methane, resin and coke oven tar also increases. At the same time, the conversion of propane to butane fraction begins to increase with increasing temperature.

Table 2. The effect of temperature on the output of thermal pyrolysis products (contact time 0.1s and water vapor to raw material ratio 0.4: 1)

Experimental temperature, ^{0}C	700	750	800	850	900
Experimental results,% (mass)					
1. Product output,% (volume) H_2	0,13	0,35	0,70	1,11	2,66
CO	0,04	0,07	0,08	0,1	0,13
CO_2	0,01	0,03	0,05	0,06	0,08
CH_4	3,19	8,73	16,58	25,09	27,27
C_2H_2	0	0,02	0,18	0,43	0,58
C_2H_4	4,22	15,54	32,86	49,57	52,07
C_2H_6	6,28	6,06	5,74	3,84	1,07
C_3H_4	0	0,01	0,14	0,32	0,41
C_3H_6	1,68	11,1	17,27	9,97	2,97
C_3H_8	66,20	46,86	21,02	5,68	0,96
C_4H_6	0,33	0,76	1,02	0,85	0,68
$\sum C_4H_8$	0,07	0,83	2,17	1,54	1,45
$\sum C_4H_{10}$	17,69	9,36	1,54	0,20	0,08
Resin	0,09	0,11	0,42	0,57	8,20
Coke oven	0,08	0,16	0,24	0,65	1,40
Total	100	100	100	100	100
2. Yield of unsaturated hydrocarbons C_2- C_4,% (mass)	6,29	28,27	53,61	62,72	58,15
3. Conversion rate,% (gross)	8,84	37,03	71,39	90,17	97,87

In our research, we followed the mechanism of propane butane fraction pyrolysis at a temperature of 600-900^{0}C. In this case, we took the contact time in the reaction zone to be 0.25 s, and the ratio of water vapor to the raw material to be 0.4:1. The results obtained are shown in Table 3.

Table 3. The effect of temperature on the output of thermal pyrolysis products (contact time 0.25s and water vapor to raw material ratio 0.4: 1)

Experimental temperature, ^{0}C	600	650	700	750	800	850	900
1. Product output,% (volume) H_2	0	0,19	0,44	0,95	1,34	1,65	2,69
CO	followed	followed	0,05	0,09	0,09	0,13	0,17
CO_2	followed	followed	0,02	0,04	0,07	0,08	0,10

CH_4	1,46	1,25	4,01	10,12	20,65	24,63	27,82
C_2H_2	followed	followed	followed	0,04	0,12	0,58	0,93
C_2H_4	0,27	1,67	6,65	18,96	37,79	46,86	42,09
C_2H_6	5,52	5,54	5,41	5,29	4,57	2,91	1,39
C_3H_4	followed	followed	0,02	0,03	0,20	0,42	0,38
C_3H_6	followed	followed	4,69	13,72	15,12	6,02	1,55
C_3H_8	75,34	74,51	62,20	40,63	11,33	1,06	0,02
C_4H_6	followed	followed	0,05	0,09	0,80	1,72	1,93
$\sum C_4H_8$	followed	0,01	0,22	0,96	1,81	2,64	1,87
$\sum C_4H_{10}$	17,05	16,17	15,29	7,06	0,75	0,21	0,04
Resin	0,30	0,54	0,80	1,75	5,04	10,23	16,70
coke oven	0,06	0,12	0,15	0,27	0,32	0,86	2,32
Total	100	100	100	100	100	100	100
2. Yield of unsaturated hydrocarbons C_2- C_4,% (mass)	0,27	1,68	11,63	33,80	55,84	58,20	48,75
3.Conversion rate,% (gross)	1,01	2,72	16,19	46,44	83,17	95,77	98,53

Similarly, Table 3 shows that the conversion rate of the propane butane fraction increases with increasing temperature. The maximum yield of propylene occurs at a temperature of 800^0C. This is less than the amount of ethylene obtained during the 0.1s contact period, as shown in Table 2. Also, the amount of ethylene obtained during the 0.25s contact period is 4.9% higher than the amount of ethylene obtained during the 0.1s contact period.

It should be noted that in addition to the temperature factor, which has a greater impact on the conversion rate of the raw material, the distribution of reaction products in the reaction zone, as well as the duration of the raw material in the reaction zone also play an important role. If we pay attention to the results shown in Table 2, we can see that the maximum yield of ethylene at a temperature of 900^0C is 52.07% (mass) when we ensure the contact time in the reaction zone of 0.1 s. The yield of slightly higher propylene is found at a temperature of 800^0C, which is 17.27% (mass). At the same time, the maximum yield of unsaturated hydrocarbons is 62.72% (mass) at 850^0C. Comparing the results shown in Tables 2 and 3, we see that the yield of ethylene during the 0.25s contact period was 46.86% (mass) at 850^0C, the yield of propylene was 15.12% (mass) at 800^0C, and the yield of unsaturated hydrocarbons was 85.20% at 850^0C.

Studies have shown that the rate of convection increases with increasing temperature, and that increasing the contact time from 0.1 s to 0.25 s leads to an increase in the conversion rate. In addition, we see that the coke oven output increased during the 0.25s contact period. At the same time, it is assumed that the decrease in the yield of the target product and the increase in the amount of coke tar were caused by secondary polymerization and condensation reactions.

Thus, based on the results obtained, it can be said that it is possible to increase the yield of ethylene by increasing the temperature during the thermal conversion of the propane butane fraction and reducing the time the raw material remains in the reaction zone. At the same time, the optimum yield temperature of unsaturated hydrocarbons was set at 850^0C. This is explained by the fact that raising the temperature and reducing the contact time increases the rate of primary cracking and dehydrogenation reactions and reduces the rate of secondary reactions - polymerization and condensation reactions. The decrease in the yield of unsaturated hydrocarbons (C_2 - C_4) at 850^0C is higher than the rate of cracking compared to the dehydrogenation reaction, which leads to an increase in the yield of decomposition by-products and a decrease in the yield of propylene and butene.

To further intensify the process, we continued to conduct our research with the participation of the catalyst. We studied the catalytic pyrolysis of propane butane fraction by applying a catalyst to the thermal pyrolysis process. As it is known from the literature, studies have been carried out using catalysts under different names for the application of catalysts to the pyrolysis process [4,5]. In contrast to the known studies, we used Azerbaijani zeolites for the first time in our research and tried to clarify how zeolites behave in the process of catalytic pyrolysis. The strength of the structural structure of Azerbaijani zeolite increases its resistance to high temperatures. From this point of view, we have chosen the zeolite catalyst obtained from the Aydag zeolite deposit as the Azerbaijani zeolites [7,8]. The main component composition of the catalyst is given in Table 3.

Table 4. The main component of Azerbaijani zeolite obtained from the Aydag field

Azerbaijani zeolite in the Aydag field	Ingredient component,% by weight	
	SiO_2	Al_2O_3
	64.6-66.19	10.08-12.32

The results of the research are shown in Table 5.

Table 5. Catalytic pyrolysis of propane butane fraction in the presence of mordenite (contact time 0.1s, water vapor to raw material ratio 0.4: 1)

Experimental temperature, ^{0}C	600	650	700	750	800
1. Product output,% (volume) H_2	followed	0,06	0,16	0,50	0,74
CO	0,01	0,04	0,06	0,09	0,11
CO_2	0,02	0,02	0,03	0,05	0,07
CH_4	1,26	2,72	3,62	5,92	8,7
C_2H_2	followed	followed	0,05	0,16	0,27
C_2H_4	0,56	2,07	4,98	17,88	34,27
C_2H_6	5,33	5,43	5,39	5,26	5,02
C_3H_4	followed	followed	0,01	0,02	0,10
C_3H_6	0,07	0,22	5,54	12,3	18,06
C_3H_8	74,67	72,73	64,44	47,42	24,64
C_4H_6	followed	0,05	0,08	0,29	0,93
$\sum C_4H_8$	followed	0,02	0,07	0,60	1,53
$\sum C_4H_{10}$	17,64	16,37	15,06	8,63	2,31
Resin	0,18	0,18	0,37	0,59	0,87
Coke oven	0,06	0,09	0,14	0,29	0,38
Total	100	100	100	100	100
2. Yield of unsaturated hydrocarbons C_2- C_4,% (mass)	0,63	2,36	10,73	31,25	55,16
3. Conversion rate,% (gross)	1,08	4,43	14,17	38,01	65,55

As can be seen from Table 5, during the pyrolysis process with the participation of the Azerbaijani zeolite catalyst, the conversion rate of the raw material is 65.55% (mass) at a maximum temperature of 800^{0}C. At temperatures of 600-650^{0}C, the yield of ethylene increased by 0.19-0.33% (mass). The yield of propylene decreased by 0.05-0.54% (mass).

The yield of the by-products of the reaction - hydrogen, methane, resin and coke tar - increased in the presence of the catalyst. This is due to the composition of the catalyst.

Thus, the catalyst does not change the course of the radical chain mechanism in the pyrolysis of hydrocarbons, it is its active centers involved in the reaction of continuous chain formation. The most important role here is played by the free valence concentration in the total reaction volume, some of which is on the surface of the active sites, and the other part is the hydrocarbon radicals in the gas phase. Buddha provides a heterogeneous-homogeneous index of the process [6]

Analyzing the obtained results, it can be noted that the catalyst used in the pyrolysis of propane butane fraction has a high catalytic activity. This activity allows us to obtain low-molecular-weight olefins from low-molecular-weight paraffin hydrocarbons by operating more efficient catalysts.

4.Conclusion

During the thermal conversion of the propane-butane fraction, it is possible to extend the yield of ethylene by increasing the temperature and reducing the time the raw material remains in the reaction zone. At the same time, by applying Azerbaijani zeolite as a catalyst to the process, the yield of ethylene was increased to 0.19-0.33% (mass) at temperatures of 600-6500C. This makes the process of thermal pyrolysis more economical and cost-effective.

5. References

1. 2144055 RU. The method of obtaining low olefins/Bukharkin AK, Pustynnikova ON, Tomenko KB and others. Application. 18.01.1999; Опубл. 10.01.2000.
2. G.C.Dadayeva.The issue of coking of heavy tar of the gasoline pyrolysis at slowed - up coking reactor- Science and world v/International scientific journal № 7 (47), 2017, Mid, 138-40.

3. Zhagfarov FG, Grigorieva H.A., Lapidus AL New catalysts in the pyrolysis process // Chemistry and technology of fuel and oil. - 2005. - №2.-C 41 -43.
4. Catalyst for pyrolysis of hydrocarbons, methods of its production and methods of catalytic hydrolysates of hydrocarbons in lower olefins: 2238142 RU Erofeev VI, Trofimova A.C., Koval LM and others. Application. 08.07.2004; Опубл. 20.10.2004.
5. AA Yusifzada, G.Ch. Dadaeva. Pyrolysis of fractions 130-2300C in the presence of zeolite-containing catalysts. “ECO ENERGY”. №2, 2018, p.22-25
6. Vasilieva H.A. Theoretical aspects of radical-chain unexplained reactions of hydrolysis of hydrocarbons with the participation of heterogeneous catalysts: Author. dis. Dr. chemist. Science: 02.00.15 / Novosibirsk Institute of Catalysis G.K. Борескова. - N., 1999.-32 p
7. Geology of Azerbaijan, volume VI. Useful fossils. Baku-2005.
8. Mineral resources of Azerbaijan. Baku-2005

PP-II-6

ACTIVITY OF BINARY Mo-V-O CATALYSTS IN THE REACTION OF PROPYLENE OXIDATION

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Abstract. In this work, we studied the reaction of propylene oxidation to acetic acid on molybdenum-vanadium oxide catalysts of various compositions. Their surface and structural properties were also investigated. It was found that the specific surface area of binary molybdenum-vanadium oxide catalysts varies in the range from 1.2 m2/g to 3.7 m2/g. X-ray diffraction analyzes show that all samples consist of several phases and all retain the percentage of the initial molybdenum and vanadium atoms. It is shown that the synthesized samples contain molybdenum and vanadium oxides, as well as chemical compounds of molybdenum and vanadium of various structures. The degree of crystallinity of binary molybdenum-vanadium oxide catalysts practically does not change with a change in the catalyst composition. It was shown that acetic acid is the main reaction product on the studied catalysts, and carbon dioxide, acetone, and acetaldehyde are also formed as by-products. Studies have shown that with an increase in the reaction temperature, the yields of acetic acid, acetone, and acetaldehyde pass through a maximum, while the yield of carbon dioxide increases over the studied entire temperature range. It was found that with an increase in the content of molybdenum in the composition of the binary catalyst, the propylene conversion and the yield of acetic acid change in the same way and have the form of a curve with two maxima, which may be due to the formation of solid solutions in these catalysts.

Keywords: Propylene, Acetic Acid, Binary Catalysts.

1.Introduction

As it is known, acetic acid is one of the important monomers used in the petrochemical industry. One of the promising methods for the production of acetic acid is the direct oxidation of olefins over heterogeneous catalysts [1,2]. Catalytic systems based on vanadium oxide are highly active in the oxidation of olefins to acetic acid [3,4]. It is also known from the periodical literature that oxides of molybdenum, tungsten, etc. have high activity and selectivity in the reaction of partial oxidation [5,6]. In this regard, we studied the effect of molybdenum oxides on the activity of vanadium oxide in the oxidation of propylene to acetic acid.

2.Experimental part

Binary molybdenum-vanadium oxide catalysts were prepared by mixing aqueous solutions of ammonium molybdate and ammonium metavanadate. The resulting solution was evaporated and dried at a temperature of 100°C, after which it was transferred into a porcelain dish and calcined at a temperature of 200-300°C until the complete release of nitrogen oxides. Thereafter, the catalyst was calcined at a temperature of 500°C for 10 hours. Thus, we have prepared nine samples with different ratios of molybdenum to vanadium.

The catalytic activity of the synthesized samples was studied on a flow-through unit with a tubular reactor in the temperature range 150-450°C. For this purpose, 5 ml of catalyst with a grain size of 1-2 mm was loaded into the reactor. The volumetric feed rate was 1200 h^{-1}. The ratio of the initial reagents was C3H6:air:H2O=1:5:4. Analysis of reaction products and feedstock was carried out by chromatography. The specific surface area of the synthesized catalysts was determined by thermal desorption of nitrogen. X-ray studies were carried out on an automatic powder diffractometer "D2 Phaser" from "Bruker" (CuKα-radiation, Ni-filter, $3 \leq 2\theta \geq 80$ °).

3.Results and discussions

Measurement of the specific surface area of the initial oxides, of which the binary molybdenum-vanadium containing catalysts are composed, showed that the specific surface area of vanadium oxide is 8.2 m2/g and that of molybdenum oxide is 1.9 m2/g. Table 1 shows the data of the study of the specific surface area of Mo-V-O catalysts by thermal desorption of nitrogen. As can be seen from table 1, the specific surface area of molybdenum-vanadium oxide catalysts slightly increases with an increase in the content of molybdenum in the catalyst composition. On this catalytic system, the maximum specific surface area is observed on a sample with a Mo:V=8:2 ratio. In this sample, the specific surface area is 3.7 m^2/g.

Table 2. Specific surface areas of Mo-V-O catalysts.

Mo/V atomic ratio	V_2O_5	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1	MoO_3
Specific surface area, m^2/g	8,2	1,2	1,3	1,5	2,1	2,7	2,0	3,2	3,7	1,5	1,9

Figure 1 shows the diffraction patterns of all nine ratios (mMo / nV) put together. At the beginning and at the end of these diffraction patterns, the X-ray patterns of MoO3 and V2O5 are also presented.

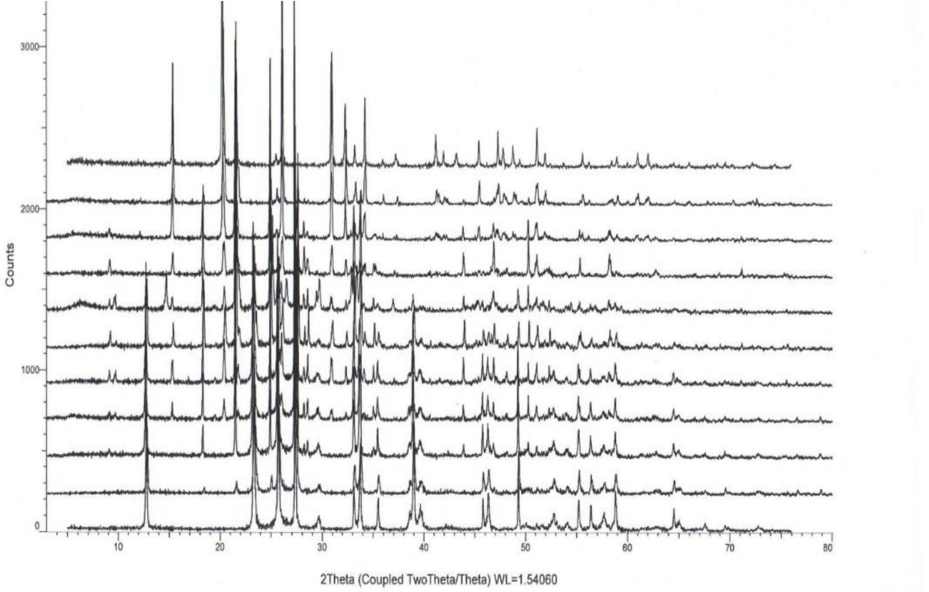

Figure: 1 Diffraction patterns of molybdenum and vanadium oxides, as well as all nine Mo-V-O catalysts.

Analyzes of X-ray diffraction patterns show that all samples consist of several phases and in all the percentages of components are preserved, which is evidenced by the regular change in the intensities of reflections in the diffraction patterns.

Table 2 shows the phases formed in the Mo-V-O system. Interpretation of the results obtained shows that at the ratios 1Mo/9V, 2Mo/8V, 3Mo/7V, 8Mo/2V and 9Mo/1V, three phases are formed, namely MoO3, V2O5 and Mo2.4V3.6O16. And when the ratios of the components are 4Mo/6V, 5Mo/5V and 6Mo/4V, in addition to oxides of Mo and V, other phases with different compositions of the Mo-V-O system are also formed.

Table 2. Phases formed in the Mo-V-O system.

Atomic ratio of molybdenum to vansdium	Образующиеся фазы
1 Mo-9V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$
2 Mo-8V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$
3 Mo-7V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$
4 Mo-6V	MoO_3, V_2O_5, MoV_2O_8, $(Mo_{0,86}V_{0,12})O_{2,94}$, $Mo_4V_6S_{25}$
5 Mo-5V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$, $(Mo_{0,08}V_{0,92})_2O_5$
6 Mo-4V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$, $(Mo_{0,88}V_{0,12})O_{2,94}$
7 Mo-3V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$
8 Mo-2V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$
9 Mo-1V	MoO_3, V_2O_5, $Mo_{2,4}V_{3,6}O_{16}$

We also calculated the degree of crystallinity of all formed phases using the DIFFRAC.EVA program on the D2 Phaser device, the results of which are presented in Table 3.

Table 3. Degree of crystallinity of molybdenum-vanadium oxide catalysts.

Mo/V atomic ratio	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1
Degree of crystallinity, %	82,6	78,3	79,6	75,7	80,5	77,5	81	77,6	77,9

As can be seen from Table 3, the crystallinity of Mo-V-O systems practically does not change with a change in the catalyst composition.

The study of the oxidation reaction of propylene on the studied catalysts showed that the main product of the reaction is acetic acid, and carbon dioxide, acetone and acetaldehyde are also formed as by-products. It was found that both the temperature and the composition of vanadium oxide catalysts have a strong effect on the yields of the reaction products. Studies have shown that with an increase in the reaction temperature, the yields of acetic acid, acetone, and acetaldehyde pass through a maximum, while the yield of carbon dioxide increases over the entire temperature range studied.

Our research has shown that the activity of Mo-V-O catalysts also depends strongly on the ratio of the elements that make up the catalyst. In fig. 2 shows the dependence of the activity of Mo-V-O catalysts on their composition at 400°C. It can be seen that with an increase in the content of molybdenum in the composition of the binary catalyst, the propylene conversion and the yield of acetic acid change symbatically and have the form with two maxima on the catalysts Mo:V=1:9 and Mo:V=6:4. The conversion of propylene and the yield of acetic acid reach 30% and 22.6%, respectively. Figure 2 also shows that with an increase in the content of molybdenum in the composition of the catalyst, the yields of acetaldehyde and acetone change little and do not exceed 0.4%. The yield of carbon dioxide decreases slowly with an increase in the content of molybdenum in the catalyst composition.

Table 4. Dependence of the activity of molybdenum-vanadium-oxide catalysts in the oxidation of propylene on their composition.

Reaction products	Outputs, %								
Mo/V atomic ratio	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
CO2	4,4	5,2	4,5	4,3	4,6	3,4	3,4	3,4	2,9
CH3COOH	22,6	20,2	10,6	15,4	19,8	22,6	22,6	20,1	14,2
Selectivity, %	80,7	79,5	51,7	75,1	81,1	85,6	86,2	84,8	82,6
Conversion, %	28	25,4	15,6	20,5	24,4	26,4	26,2	23,7	17,2

4.Conclusion

- The specific surface area of molybdenum-vanadium oxide catalysts slightly increases with an increase in the content of molybdenum in the catalyst composition.
- All samples of Mo-V-O catalytic system consist of phases initial oxides and chemical compositions between them. Degree of crystallinity of Mo-V-O systems practically does not change with a change in the catalyst composition.
- Catalysts with a predominance of molybdenum or vanadium oxides exhibit high activity and selectivity in the oxidation of propylene to acetic acid. Apparently, this is due to the formation of solid solutions in binary molybdenum-vanadium-oxide catalysts.

5.References

1. Arab K.El-Qisiari, Hanan A.Qaseer, Patrick M.Henry: An air oxidizable bimetallic palladium(II) catalyst for asymmetric allylic oxidation of olefins in acetic acid. Tetrahedron Letters, 43, 23, pp 4229-4231(2002).
2. S. Szakács, H. Wolf, G. Mink, I. Bertóti, N. Wüstneck, B. Lücke, H. Seebot: On the mechanism of the selective oxidation of butane and 1-butene on vanadyl phosphates. Catalysis Today, 1, 1–2, pp 27–36 (1987).
3. K.M.Abd El-Salaam∗, E.A. Hassan: Studies on the heterogeneous oxidation of 1-butene over V2O5-WO3 catalysts. Surface Technology, 9, 3, pp 195–202 (1979).
4. P.Concepción, P.Botella, J.M. LópezNieto: Catalytic and FT-IR study on the reaction pathway for oxidation of propane and propylene on V- or Mo–V-based catalysts. Applied Catalysis A: General, 278, 1, pp 45-56 (2004).
5. K.M.Abd El-Salaam, E.A. Hassan: Studies on the heterogeneous oxidation of 1-butene over V2O5-MoO3 catalysts. Surface Technology, 9, 3, pp 195–202 (1979).
6. P.Botella, B.Solsona, J.M.López Nieto: Selective oxidation of C3–C4 olefins over Mo-containing catalysts with tetragonal tungsten bronze structure. Catalysis Today, 141, 3–4, pp 311-316 (2009).

PP-II-7

SYNTHESIS OF A TARGET CATALYST FOR THE PROCESS OF OXIDATIVE DEHYDROGENATION OF SEC-BUTANOL AND STUDY OF THE KINETICS AND MECHANISM OF THE PROCESS

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Abstract. The catalytic activity of CaA zeolite modified with metal cations (Cu, Zn, Pd) by the method of ion exchange in the reaction of partial oxidation of sec-butanol to methyl ethyl ketone in the temperature range 240-350^{0}C, space velocities 1500-4000 h^{-1} and partial pressures of butanol-2 P_{B-2} = 0.12-0.36 atm, oxygen P_{O_2} = 0.12-0.24 atm. at atmospheric pressure. It has been established that the metal zeolite catalyst CuZnPdCaA containing 3.0 wt% Cu^{2+}, 2.0 wt% Zn^{2+} and 0.1 wt% Pd^{2+} exhibits the highest activity and selectivity in the reaction under consideration. The kinetic regularities of the reaction on the indicated catalyst have been studied. On the basis of experimental data, a probable stepwise mechanism of the reaction was proposed and a theoretically substantiated kinetic model of the process was developed.

Key words: butanol-2, zeolite catalyst, oxidative dehydrogenation, kinetics, methyl ethyl ketone, ion exchange.

1.Introduction

Methyl ethyl ketone (MEK) is used as a solvent and extractant, in some cases superior to acetone, it is not so volatile and safer in terms of fire. On an industrial scale, methyl ethyl ketone is produced by oxidation of butylenes on $PdCl_2$ and a two-stage method, which consists of hydration of n-butylene to butanol-2 with the participation of sulfuric acid as a catalyst and oxidative dehydrogenation of sec-butanol in MEK on mixed oxide catalysts [1-3].

The main disadvantages of the first method are the irretrievable consumption of a part of the expensive catalyst $PdCl_2$ and the formation of by products - chloroketone and crotonaldehyde. The disadvantages of the process of oxidative dehydrogenation of sec-butanol in MEK are a relatively high temperature (400–500^{0}C) and low selectivity for methyl ethyl ketone [4-6].

For the production of methyl ethyl ketone, the method of oxidative dehydrogenation of sec-butyl alcohol is used more [1]. However, due to these disadvantages, this method is characterized by low economic efficiency.

In previous works [7-14], we found that zeolites modified with metal cations by ion exchange exhibit high catalytic activity and selectivity in the reactions of oxidative dehydrogenation of aliphatic alcohols at relatively low temperatures (250-350^{0}C).

Based on the analysis of experimental data in the literature, as well as physicochemical methods of analysis, it has been established that, similarly to the liquid-phase version of the process, which proceeds in the acid sphere with the participation of protons through the formation of an intermediate compound of chromate ether, during heterogeneous alkoxides, which are formed during the interaction of medium-strength Bronsted acid sites with molecules of aliphatic alcohols adsorbed on the catalyst surface. The reaction of heterogeneous partial oxidation of aliphatic alcohols on the surface of metal zeolite catalysts occurs as a result of the interaction of these alkoxide formations with surface nucleophilic oxygen [15–17].

The aim of this work is to select an active and selective catalyst for the reaction of partial oxidation of butanol-2 to one of the most important products of the chemical industry, methyl ethyl ketone, and to study the kinetics and mechanism of the reaction with the participation of an active metal zeolite catalyst.

2.Experimental part

The catalysts were prepared on the basis of CaA zeolite synthesized by ion exchange from NaA. Modification of the specified zeolite with metal cations; Cu, Zn, and Pd were carried out by ion exchange in aqueous solutions of $CuCl_2$, $ZnCl_2$, and $[Pd(NH_3)_4]Cl_2$, followed by drying (80–120^{0}C, 5 h) and calcining in an air stream at a temperature of 300^{0}C, a space velocity of 2400 h^{-1} within 30 minutes. The amount of metal cations introduced into the zeolite composition was determined by mass spectrometric analysis on an ICP-MS Agilent 7700 instrument.

The experiments were carried out on a flow-through installation directly connected to an Agilent 7820A gas-liquid chromatograph with a DB-624 column, with a gas carrier (He) flow rate of 1.5 ml / min and a pressure of 7.5 psig. A reactor made of Pyrex glass was loaded with 2 cm^3 of a catalyst with a particle size of 0.23–0.63 mm, activated in a nitrogen flow at a temperature of 400^{0}C (3h), then the temperature was lowered to the reaction temperature and the reaction was fed at a certain volumetric rate. mixture. The feedstock was fed using an NE-1600 microdosing device into a mixer located in a thermostated cabinet equipped with an electric heater and a fan; a stable temperature in the thermostat was maintained using a "Micromax" microelectric thermostat. The mixer also receives oxygen and a diluent gas, nitrogen. The reactor is placed in a thermostated cabinet. The reaction products at the reactor outlet were taken for analysis from a sampling loop connected to a six-way valve.

The kinetics of the reaction was studied in the temperature range 280–340^{0}C, space velocities of 2000–4000 h-1, partial pressures of the P_{B-2} reagents = 0.12–0.36 atm and P_{0_2} = 0.12–0.24 atm under conditions that ensure the flow reactions in the kinetic region. The purity degree of butanol-2 (B-2) grade "analytical grade" was 99.5%.

3.Results and discussion

On the basis of CaA zeolite and metal cations Cu^{2+}, Zn^{2+}, and Pd^{2+}, catalyst samples containing different amounts of these cations were synthesized by ion exchange. The results of testing the catalytic activity of some of these samples, as well as unmodified zeolite, CaA in the oxidative dehydrogenation of butanol-2 (B-2) to methyl ethyl ketone (MEK) are presented in Table 1. From the data given in Table 1 it follows that the reaction of oxidative dehydrogenation of 2-butanol to methyl ethyl ketone on these catalysts is accompanied by deep oxidation and dehydration of 2-butanol with the formation of carbon dioxide and butylenes. The yield of individual products is significantly influenced by the distribution of acid sites (when metal cations are introduced into the zeolite, the distribution of acid sites on the surface changes), the concentration and nature of the cation. From table 1 it follows that the reaction of oxidative dehydrogenation of butanol-2 to methyl ethyl ketone on zeolite, CaA proceeds with a relatively low conversion (experiment No.1), which can be explained by the insufficient concentration of dissociatively adsorbed oxygen molecules. The introduction of copper cations into the zeolite increases the yield of methyl ethyl ketone (experiments No.2-4). With an increase in the concentration of copper cations from 0.5 wt% to 3.0 wt%, the yield of methyl ethyl ketone significantly increased from 45.0% to 58.0%, a further increase in the concentration of copper cations (up to 4.0 wt%) (experiment No.5) slightly affects the IEC output. This can be explained with a change in the distribution of acid sites on the catalyst surface in the direction of a decrease in the number of Bronsted acid sites of medium strength at relatively high concentrations of copper cations.

Table 1. Results of testing the catalytic activity of CaA zeolite (synthesized on the basis of NaA zeolite) modified with metal cations Cu^{2+}, Zn^{2+}, and Pd^{2+} in the oxidation of butanol-2 to methylethyl ketone at a temperature of 300^{0}C, a space velocity V = 2500 h^{-1} and a molar ratio of reagents alcohol: O_2: N_2 = 1: 0.69: 2.5

№	Zeolite	Composition in wt.%			Conversion, X, %	Yield, A %		
		Cu^{2+}	Pd^{2+}	Zn^{+2}		MEK, A_1	Butylenes, A_2	CO_2, A_3
1.	CaA (synthesized on the basis of NaA zeolite)	-	-	-	18,4	12,1	6,0	0,3
2.		0,5	-	-	48,1	45,0	2,5	0,6
3.		1,0	-	-	58,5	54,6	3,0	0,9
4.		3,0	-	-	63,8	58,0	4,3	1,5
5.		4,0	-	-	64,1	57,6	4,6	1,9
6.		0,5	0,1	-	80,4	74,7	3,7	2,0
7.		3,0	0,1	-	84,9	78,8	4,0	2,1
8.		3,0	0,1	1,0	88,0	82,4	3,4	2,2
9.		3,0	0,1	2,0	91,1	86,9	2,0	2,2
10.		3,0	0,1	4,0	87,2	80,0	4,4	2,8
11.		3,0	1,0	4,0	95,3	81,8	9,1	4,4

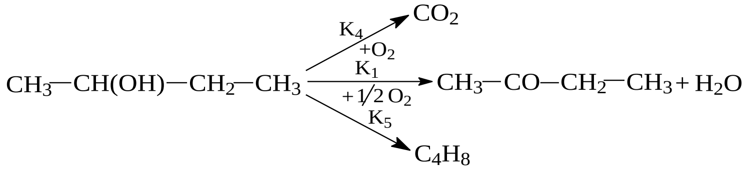
$$\left(\frac{k_1P_{O2}}{k_2P_{B-2}}+\frac{k_1P_{O2}}{k_3}\right)\theta_1^2+\theta_1-1=0$$

The introduction of small amounts of palladium cations (0.1 wt.%) And zinc (1.0– 2.0 wt.%) Creates a favorable distribution of acid sites on the surface of the catalyst for the reaction under consideration (experiments No. 6-9). In addition, these cations increase the concentration of dissociatively adsorbed oxygen molecules.

As a result of the analysis of the data given in Table 1, it can be concluded that the catalyst synthesized on the basis of CaA zeolite by the ion exchange method, containing 3.0 wt% Cu^{2+}, 2.0 wt% Zn^{2+} and 0.1 wt% Pd^{2+}, exhibits the highest activity in the reaction of oxidative dehydrogenation of butanol-2 to methyl ethyl ketone.

The kinetic regularities of the reaction under consideration were studied on a CuZnPdCaA metal zeolite catalyst of the indicated composition in the absence of diffusion inhibition.

The experiments allow us to offer the following kinetic scheme of reactions in the process of partial oxidation of 2-butanol on the catalyst CuZnPdCaA:



(1)

Based on the analysis of literary materials [4-6] can suggest the following mechanism of the MEK. In the adsorption of 2-butanol is its protonation with Brønsted acid sites of the catalyst to the further elimination of water and formation of a surface alkoxide. Conversion of surface alkoxide MEK occurs when it interacts with the surface through the formation of a nucleophilic oxygen ketonopodobnogo surface compound. Then there is the collapse ketonopodobnogo surface connection to the MEK and restores the initial state of the catalyst. A simplified diagram of the staging mechanism is as follows:

$$\begin{array}{l|c|}
O_2 + 2Z \xrightarrow{k_1} 2ZO & \frac{1}{2} \\
ZO + B\text{-}2 \xrightarrow{k_2} ZOB\text{-}2 & 1 \\
ZOB\text{-}2 \xrightarrow{k_3} Z + MEK + H_2O & 1 \\
\hline
\frac{1}{2}O_2 + B\text{-}2 = MEK + H_2O &
\end{array}$$

All these stages are almost irreversible. Assuming their simplicity, we find the following expressions for the rates of stages:

$$r_1 = k_1P_{O_2}\theta_1^2;\quad r_2 = k_2P_{B-2}\theta_2;\quad r_3 = k_3\theta_3 \qquad (2)$$

where $\theta_1, \theta_2, \theta_3$ - the proportion of vacant lots modified zeolite-coated atomic oxygen molecules of 2-butanol and ketones like surface intermediates; k_1, k_2, k_3 - the rate constants of the respective stages of the index; P_{O_2}, P_{B-2} partial pressures of the respective index components; r_2, r_1, r_3 - speed corresponding to index steps.

In stationary conditions:

$$r=r_1=r_2=r_3 \qquad (3)$$

where, r-total rate of formation of MEK.

Based on these equations and the total surface of constant education sector θ_i and the overall reaction rate as a function of concentration of reactants:

$$\theta_1+\theta_2+\theta_3=1 \qquad (4)$$

$$\theta_2=\frac{k_1P_{O2}}{k_2P_{B-2}} \qquad \theta_3=\frac{k_1P_{O2}}{k_3}\theta_1^2$$

$$k_1P_{O2}\theta_1^2=k_2P_{B-2}\theta_2; \qquad k_1P_{O2}\theta_1^2=k_3\theta_3;$$

Substituting expression θ_2, θ_3, in the equation (4) we get:

Solving the equation (5) we obtain an expression for θ_1. Substituting θ_1 in equation (2) we obtain

$$r_{MEK} = \kappa_1 P_{O2} \left\{ \frac{\sqrt{1+4\left(\frac{\kappa_1 P_{O2}}{2\kappa_2 P_{B\text{-}2}} + \frac{\kappa_1 P_{O2}}{2\kappa_3}\right)} - 1}{2\left(\frac{\kappa_1 P_{O2}}{2\kappa_2 P_{B\text{-}2}} + \frac{\kappa_1 P_{O2}}{2\kappa_3}\right)} \right\}^2 \qquad (6)$$

Carbon dioxide is formed by reacting weakly adsorbed molecules of 2-butanol adsorbed oxygen molecules according to the Langmuir-Hinshelwood mechanism. Kinetic equation corresponding to this mechanism is as follows:

$$r_{CO2} = \frac{\kappa_4 K_1 K_2 P_{O2} P_{B\text{-}2}}{\left(1 + K_1 P_{O2} + K_2 P_{B\text{-}2}\right)^2} \qquad (7)$$

where k_4 - forming reaction rate constant of carbon dioxide, K_1, K_2 - constant of adsorption of oxygen molecules and 2-butanol at the active centers of the catalyst surface for reaction.

Butylenes are formed by dehydration of 2-butanol, which is a reversible reaction. The observed rate of the reaction:

$$r = \overrightarrow{r} - \overleftarrow{r} = \overrightarrow{r}\left(1 - \frac{\overleftarrow{r}}{\overrightarrow{r}}\right) \qquad (8)$$

Where

$$1 - \frac{\overleftarrow{r}}{\overrightarrow{r}} = 1 - \frac{P_{C_4H_8} \cdot P_{H_2O}}{K_p P_{B\text{-}2}} = \gamma \qquad (9)$$

γ - irreversibility criterion, then:

$$r = \overrightarrow{r}\gamma \qquad (10)$$

$\overrightarrow{r}$ -can be expressed:

$$\overrightarrow{r} = KP_{B\text{-}2} \qquad (11)$$

Substituting (9) and (11) into (10) we have:

$$r = \kappa P_{B\text{-}2}\left(1 - \frac{P_{C_4H_8} \cdot P_{H_2O}}{K_p P_{B\text{-}2}}\right) = \kappa\left(P_{B\text{-}2} - \frac{1}{K_p} P_{C_4H_8} \cdot P_{H_2O}\right) \qquad (12)$$

In view of the reaction rate of inhibition adsorbed molecules of alcohol and water, the observed rate of the reaction is as follows:

$$r_{C_4H_8} = \kappa_5 \frac{P_{B\text{-}2} - \frac{1}{K_p} P_{C_4H_8} \cdot P_{H_2O}}{K_3 P_{B\text{-}2} + K_4 P_{H_2O}} \qquad (13)$$

where K_p - equilibrium constant dehydration sec-butanol

$$lgKp = -A + B/T \qquad (14)$$

where A and B are empirical constants determined from experimental data; K_3 and K_4 are constants of equilibrium adsorption of molecules of water and alcohol on the active centers of the catalyst for dehydration reaction of 2-butanol, respectively; k_5 - dehydration reaction rate constant. (To calculate the constants a and K in equations (6), (7) and (13) used the formula $\kappa = \kappa_0 \cdot e^{-\frac{E}{RT}}$, $K = K_0 \cdot e^{\frac{Q}{RT}}$).

Equations (6) and (7) and (13) form a kinetic model of the sec-butanol oxidation.

A kinetic model of the reaction subjected to statistical analysis based on kinetic data. Calculation of pre-exponential factors of reaction constants $\ln k_i^0 \left(\ln K_i^0\right)$, activation energies $\left(E_i^0\right)$ and heat of adsorption $\left(Q_i^0\right)$ by the method of "rolling admission" and Powell using software system "Search".

Table 3. Numerical values of the kinetic model constants for the oxidative conversion of sec-butanol alcohol to MEK.

$\ln k^0, \ln K^0$		$E, Q,$ kkal/mol	
$\ln k_1^0$	7,19	E_1	5,15
$\ln k_2^0$	4,03	E_2	6,47
$\ln k_3^0$	7,67	E_3	5,28
$\ln k_4^0$	20,91	E_4	21,27
$\ln k_5^0$	9,98	E_5	16,40
$\ln K_1^0$	–3,21	Q_1	1,98
$\ln K_2^0$	4,08	Q_2	4,00
$\ln K_3^0$	–4,67	Q_3	1,50
$\ln K_4^0$	4,54	Q_4	4,19

A kinetic model of the reaction of oxidation of secondary butyl alcohol MEK adequately describes the experimental data. Calculations have shown that the relative error of the experimental and calculated data does not exceed 7%.

5.References

1. Lebedev N.N. Chemistry and technology of basic organic and petrochemical synthesis. Moscow: Chemistry, 1975.P. 538
2. Karina L.N., Davudov A., Osipova N.A. // V International Symposium Relations between Homogeneous and Heterogeneous Catalysis. Novosibirsk. 1986. P. 140.
3. Santaceraia E., Gelora D., Danice P. // J. Catalysis. 1983. V.80. P.427.
4. Brailovsky S.M., Temkin O.N. Oxidation of alcohols on metals of the copper subgroup // Problems of kinetics and catalysis. 1985. T. 29. S. 146-175.
5. Balandin A.A. et al. // DAN SSSR. 1954.98, 5.P. 783
6. US Pat. No. 743004.1944.2.796.
7. Aliev A.M., Kasum-zade A.Yu., Matiev K.I. et al. // Catalytic activity of CaA zeolite modified with copper, zinc and palladium cations in the oxidation reactions of butyl alcohols // Azerb. chem. magazine. 2012. No. 2. P.9.
8. Aliyev A.M., Shabanova Z.A, Sarıcanov A.A. Oxidative dehydrogenation of C1-C2 alcohols over modified zeolites // International Conference “Catalysis in organic synthesis” (ICCOS - 2012), 2012 p.104.
9. Patent AP I 20130021
10. Patent AP I 20090200
11. Patent AP I 20100114
12. Shakhtakhtinsky T.N., Aliev A.M., Kuliev A.R. et al. Selection of an active catalyst and kinetics of the reaction of partial oxidation of isoamyl alcohol // Kinetics and Catalysis. 1996. T. 37. No. 2. S.286-293.
13. Aliev A.M., Matiev K.I., Medzhidova S.M. Comparison of the catalytic activity of zeolites A, X, Y modified with copper and palladium cations in the oxidation reaction of isoamyl alcohol // Azerbaijan Oil Industry. 1996. No. 6. S. 44-45.
14. Patent SU 1826925 A3 1993 (State Patent of the USSR)
15. Shakhtakhtinsky T.N., Aliev A.M., Kuliev A.R. and others. Construction of a polyfunctional metal zeolite catalyst for a nontrivial reaction of oxidative conversion of ethyl alcohol to ethyl acetate. // Dokl. Academy of Sciences of Russia. 1995. T. 343. No. 4. S. 496-499.
16. Aliev AM, Medzhidova SM, Sarydzhanov AA et al. Ion-exchange method for modifying zeolites with metal cations as a limiting model of the supported catalyst // Azerb. chem. magazine. 2011. No. 4. P.9.
17. Aliyev A.M., Shabanova Z.A., Aliyev F.V., Guseynova A.M. Zeolites modified metal cations as catalysts in reactions of oxidation of hydrocarbons and alkyl alcohols // European Researches. Internationals Multidisciplinary Journal. 2014. V. 82. No. 9-1. R.1564-1591.

III. Synthesis of macromolecular substances and polymer composite materials.

OR-III-1

SKN-40 FOOTBOARD WITH SODA AND MORNING EFFECTS ACKNOWLEDGMENTS GETTING CHEMICAL DECREASES

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Abstract. Modern development of science and technology requires the creation of polymer-based binder rods and other components capable of working in aggressive environments. Taking all of this into consideration, a rubber blend recipe was selected for the production of rubber capable of working in aggressive environments. I chose the volcano mode for the composite systems I had for 20 min at a temperature of 160^0C. I have determined the physical and mechanical properties of the volcano.

Keywords: butadiene-nitrile rubber (SKN-40), chemical durability, compound and simple ether, compression, rastifier, rubber, physical-mechanical properties, vulcanization, adaptation, diphenylolpropane dicaprilate and diphenylolpropene oxypropyl [1-8].

1.Introduction

The purpose of the work is to adapt the SKN-40 rubber with other ingredients, to quickly blend and to enhance the physical and mechanical properties of the volcano. The purpose of this is to make a comparative study of the physical and mechanical properties of rubber based on diocytylftalate, dibutylftalat and their combinations based on standard indicators. In laboratory conditions, the synthesis of diphenylolpropane oxypropylene esters of dicaprilate and diphenylolpropa is used as a plasticizer in SKN-40 rubber. Using this synthesized new plasticizer, it is able to obtain durable rubber-resistant rubber. To achieve this goal the following issues have been resolved:

- development of polymeric compositions using new types of plasticizers;
- to study the technological compatibility of the polymer-plastic system, to study the structure and properties of the inter-phase space, polymer composition;
- to study the rheological properties of the polymer composition depending on the type of polymer base and plasticizer;
- to study the physical and mechanical properties of polymer composition depending on the ratio of components of the mixture[9-15]

2.Experimental part

Results of research for improvement of chemical dynamics

Polyvinyl chloride was modified with butadiene-nitrile rubber at different rates at 125-1350C for 3-4 minutes. Composite material was developed on the basis of PVC/SKN/dolomite/DOF-100/20/10/10 modification and the physical and mechanical properties of the composite mixture obtained were investigated. It has been established that the composition obtained meets the standards and requirements of harsh operating conditions. It is recommended that the material used for this purpose be used in the manufacture of lambrine, as well as lineleum, as a plastic window clamping tool (rods).

It is shown in Table 1 that studying the length of the PVC / SKN-40 binary mixture at a temperature of $170\text{-}175^0$C with the S = 20 mm distance from the impact of different loads on the IRC-5 capillary viscometer

Table 1. that studying the length of the PVC / SKN-40 binary mixture at a temperature of $170\text{-}175^0$C

	Leakage of alloy			
№	13,06	19,12	24,56	32,08
1	68"04"	49"09"	31"75"	17"63"
2	38"73"	18"24"	11"808"	8"36"
3	29"18"	15"25"	10"90"	6"96"
4	17"32"	13"93"	8"30"	6"08"
5	9"22"	7"05"	4"45"	3"08"

We calculate the pressure affecting each square centimeter of the dual mix sample surface in the capillary viscosimeter cylinder by the following formula:

P = G / ((πD_S ^ 2) / 4)

Here: G-sample load (13.06 kg; 19.1 kg; 24.56 kg; 32.08 kg)

DS-cylinder diameter (0.954).

Let us calculate the pressure (P) on the sample according to the weight of the load

$$P_1 = \frac{13{,}06}{\frac{3{,}14 \cdot (0{,}954)^2}{4}} = \frac{13{,}06}{0{,}785 \cdot (0{,}954)^2} = \frac{13{,}06}{0{,}7144} = 18{,}281 \ \text{kg / cm}^2$$

$$P_2 = \frac{19{,}02}{0{,}7144} = 26{,}623 \ \text{kg / cm}^2$$

$$P_3 = \frac{24{,}56}{0{,}7144} = 34{,}378 \ \text{kg / cm}^2$$

$$P_4 = \frac{32{,}08}{0{,}7144} = 44{,}904 \ \text{kg / cm}^2$$

We calculate the displacement voltage (τ) of the binary mixture sample from the end point of the device's capillaries according to the calculated pressure:

$$\tau = \frac{P \cdot r}{2l}$$

Where: p - capillary radius (0.05 cm);

l - capillary length (0.8 cm).

Let us calculate the displacement stress based on the pressure on the polymer alloy

$$\tau_1 = \frac{18{,}281 \cdot 0{,}05}{2 \cdot 0{,}8} = \frac{0{,}91405}{1{,}6} = 0{,}5712 \ \text{kg / cm2} = 0{,}5712 \cdot 9{,}806 \cdot 10^4 = 5{,}6012 \cdot 10^4 \ \text{Pa}$$

$$\tau_2 = \frac{26{,}623 \cdot 0{,}05}{1{,}6} = 0{,}8319 \ \text{kg / cm2} = 0{,}8319 \cdot 9{,}806 = 8{,}1576 \cdot 10^4 \ \text{Pa}$$

$$\tau_3 = \frac{34{,}378 \cdot 0{,}05}{1{,}6} = 1{,}0743 \ \text{kg / cm2} = 1{,}0743 \cdot 9{,}806 = 10{,}5346 \cdot 10^4 \ \text{Pa}$$

$$\tau_4 = \frac{44{,}904 \cdot 0{,}05}{1{,}6} = 1{,}40325 \ \text{kg / cm2} = 1{,}40325 \cdot 9{,}806 = 13{,}7603 \cdot 10^4 \ \text{Pa}$$

The displacement voltage logarithm is calculated:

$\log \tau_1 = \log (5{,}6012) = 4{,}75$ $\log \tau_3 = \log (10{,}5346) = 5{,}02$

$\log \tau_2 = \log (8{,}1576) = 4{,}91$ $\log \tau_4 = \log (13{,}7603) = 5{,}14$

Calculate the volume consumption (Q) of the specimen by the following formula:

Q = S / t · (πD_S ^ 2) / 4

Where: S is the specified distance of the sensor (0.02 cm);

t is the time (in seconds) that crosses the specified distance of the indicator.

Table 2. The size of the alloy depends on the amount of consumption

№	G_1 (13,06 kilograms)	G_2 (19,12 kilograms)	G_3 (24,56 kg	G_4 (32,08 kg)
Q_1	2,09994	3,1	4,5001	8,1043
Q_2	3,6893	7,8337	12,10027	17,0909
Q_3	4,89678	9,369718	13,10105	20,52873
Q_4	8,249896	10,25699	17,20202	23,60
Q_5	15,49764	20,266	32,1078	46,3896
Q_6	20,29662	31,0608	44,0987	64,6515
Q_7	27,4785	42,1475	59,5333	90,4303

170^0C - the average displacement rate during capillary movement of specimens corresponding to each of the displacement voltage (τ) in the temperature regime is calculated by the following formula:

$$\gamma = \frac{Q}{\pi \cdot r^3}$$

Table 3. Dependence of displacement rate (γ) on displacement voltage (τ)

№	τ_1, seconds $^{-1}$	τ_2, , secondssan- 1	τ_3, , seconds- $^{-}$ 1	τ_4, , seconds - $^{-1}$
$\bar{\gamma}_1$	0,535	0,7898	1,1465	2,0648
$\bar{\gamma}_2$	0,93995	1,9958	3,0829	4,3543
$\bar{\gamma}_3$	1,2476	2,3871	3,3378	5,2302
$\bar{\gamma}_4$	2,1019	2,6132	4,3826	5,9873
$\bar{\gamma}_5$	3,9484	5,1634	8,1803	11,8190
$\bar{\gamma}_6$	5,1711	7,9136	11,2353	16,4717
$\bar{\gamma}_7$	7,0009	10,7382	15,1677	23,0395

They use the following equation to calculate the sliding rate:

$$\gamma = (3 + \text{n}) \cdot \bar{\gamma}$$

Where n is the tangent angle of the curve, reflecting its abnormal velocity.

τ₁ from the effects of displacement tension

γ_1 = (1,9965 + 3) · 0,535 = 2,67313
γ_2 = (1,812 + 3) · 0,93994 = 4,5229
γ_3 = (1,913 + 3) · 1,2475 = 6,12896
γ_4 = (1,845 + 3) · 2,1018 = 10,18322
γ_5 = (1,925 + 3) · 3,9484 = 19,4458
γ_6 = (1,920 + 3) · 5,1711 = 25,4418
γ_7 = (1,821 + 3) · 7,00089 = 33,7512

τ₂ from the effects of displacement tension

γ_1 = (1,831 + 3) · 0,7898 = 3,8155
γ_2 = (1,921 + 3) · 1,9958 = 9,8213
γ_3 = (1,882 + 3) · 2,3871 = 11,6538
γ_4 = (1,931 + 3) · 2,6132 = 12,8856
γ_5 = (1,879 + 3) · 5,1634 = 25,1922
γ_6 = (1,852 + 3) · 7,9136 = 38,3968
γ_7 = (1,825 + 3) · 10,7382 = 51,8118

Let us summarize some of the rheological properties of the system according to the reports.

According to the results obtained in Figure 1 it is shown that the mixing of alloy mixtures under the temperature of 1750C depends on the amount of LCD in the mixture as a result of different loads (G_1; G_2; G_3 and G_4). It is clear from the character of some that the amount of polymer alloy increases as the amount of SKN rubber in the polymer mixture increases. From this we conclude that the SKN-40 rubber plastics PVC. However, the amount of SKN-40 in the PVC / SKN mix is 20 kHh. - when taken upwards, the volume of alloy increases rapidly due to the effect of all loads. We also know that 20 kh. Delivery of SKN-40 in addition to plastic PVC also creates mutual structural changes. Subsequent growth of SKN-40 will lead to the formation of 175^0C. The largest target is G_2 = 19.12 kg; G_3 = 24.56 kg and G_4 = 32.08 kg. During the comparison it is clear that the mixing capacity (Q4) is 8.24 m^3/sec due to the impact of the G1 load, respectively; 10.25 m^3 / sec due to the impact of G3 and G4 loads; It is 17.2 m^3 / sec and 23.6 m^3 / sec. That is, the volume consumption of the PVC/SKN-40 blend depends on the G_1 load, G_2; It is 2-3 times higher than the impact of G_3 and G_4 loads. This comparison contains 20 kHz. The SKN-40 applies to the blend.

The PVC/SKN-40 blend efficiency is determined by the following equation:

$$\eta_{ef} = \frac{\tau}{\gamma}$$

Table 4. Dependence of effective alloy (η), alloy tension (τ)

№	τ_1	τ_2	τ_3	τ_4
η_1	2,0953	2,13801	1,9044	1,3889
η_2	1,2384	0,8306	0,71264	0,65699
η_3	0,91389	0,6999	0,652774	0,54868
η_4	0,550042	0,63286	0,49621	0,476816
η_5	0,28804	0,32384	0,26330	0,241045
η_6	0,2201	0,21245	0,19513	0,17407
η_7	0,16595	0,15744	0,14435	0,12440

We calculate the logarithm of effective self-efficacy:

τ₁ due to the displacement stress

log η_1 = log (2,0953) = 4,321246 log η_4 = log (0,550042) = 3,740395
log η_2 = log (1,2384) = 4,09286 log η_5 = log (0,28804) = 3,4594
log η_3 = log (0,91389) = 3,9603 log η_6 = log (0,2201) = 3,3426
log η_7 = log (0,16595) = 3,2199

4.Conclusions

The kinetics of the vulcanized process of rubber mixture obtained on the basis of butadiene-nitrile rubber was found. The volcanic mode is set as follows: T = 155^0C, P = 5MPa, t = 20 minutes.

The physical and mechanical properties of the volcano have been investigated to show that the obtained product meets the standard requirements.

The durability of these rubber products in aggressive environments (fat, oil, alcohol, acid, alkaline) has been studied from 1 to 8 months.

For the first time, we used dichaprilate and oxypropylene ethers of diphenylolpropa as a plasticizer, and the results allow these plastics to be used in the future in obtaining oil and gas resistant rubber.

We recommend that the rubber offered by us at engine temperature of 70^0C has been studied. Working temperature for 72 hours was only 0.01%. This means that the product is fully responsive to swelling in aggressive environments.

5.References

1. Pramila Devi D.S., Nair A.B., Jabin T., Kutty S.K.N. Mechanical, thermal and microwave properties of conducting composites of polypyrrole/ polypyrrole-coated short nylon fibers with acrylonitrile butadiene rubber. Appl.Polym.Sci., -2012, - No. 6, - C.1965.
2. Petrova N.P., Tarasov N.A., Ushmarin N.A., Reznikov M.S., Koltsov N.I. Investigation of the effect of flame retardant combinations on the kinetics of burning rubber based on butadiene-nitrile rubber. Chemistry and Chem. technol., -2014, - No. 4, C.52-54.
3. Sandalov S.I., Feofanova O.N., Reznikov M.S., Ushmarin N.F., Gnezdilov D.O., Koltsov N.I. Development of thermally aggressive rubber based on nitrile butadiene rubbers. Vesmn. Kazan. mechnol. un-ma., -2014, -№3, -C. 108-110.
4. Voronchikhin V.D., Lesik E.I., Dubkov K.A., Ivanov D.P., Semikolenov S. B. International scientific-practical conference "Rubber industry. Raw materials. Materials. Technologies", Moscow, - 2014, - C.56-58.
5. KaradenizKemal, Ergüller Neşe. İnvestigation of plasticizer effect of hazelnut oil and its epixidized derivative on chloroprene and nitrile rubbers. Kautsch und Gummi. Kunstst., -2012, -№10, -p. 49-54.
6. Mansour S.A., El-Salam M.A., Moharram A.H., Hussein M., Al-Agel F.A.M. The order addition effect of carbon black / graphite on the electrical properties of rubber composites. Apply.Polym.Sci.-2012, -№2, - p. 593-600.
7. Slobodkina K.N., Rudakov A.A., Makarov T.B., Vofson S.I. Adhesive and protective properties of compositions based on nitrile butadiene rubber and thiacol. . Vesmn. Kazan. mechnol. Un-ma., 2014, - No. 10, -C. 94-96
8. Suzdaltseva E.S., Klochkov V.I., Petrova G.I., Kurlyand S.K. Features of the mechanical destruction of vulcanizates of nitrile butadiene rubber. Abstracts of the 3rd All-Russian Conference "Rubber and Rubber-. Moscow -2013, -№4, -C.47-48
9. Tuzhikov O.O., Tuzhikov O.V., Khokhlova T.V., Lukasik V.A., Orlova S.A. Elastomeric compositions based on nitrile butadiene rubber modified with 2-styrene-benzimidazole. Rubber and rubber., - 2012, -№4, -C 30-33

[eleven]. Kerem Shixaliyev. Minavar Ibrahimova, Irada Abdullayeva .THE Researching of the Polyvinylchloride and Butadiuene –Nitrile Rubber. Internationai Journal of Research in Science, Engineering and technoiogy.-2019, -volme6, issue6, - 27-33

10. Magg G. Vulcanizing systems for special rubbers // Polymer materials - 2014. - No. 14. - S. 22-29.
11. Zaikin A.E., Bobrov G.B. Morphology of a mixture of polypropylene and nitrile butadiene rubber of peroxide vulcanization. Vesmn. Kazan. mechnol. un-ma 2013, No. 10, -C .122-125
12. Baranova N.V., Pashina L.A., Kosmochko A.V. The relationship of the chemical structure of the surface of butadiene nitrile rubbers with surface energy and acid-base characteristics. Vestn. Kazan. technol. University .-2012- No. 15- C.172-176
13. Wongthong P. Influences of the phenolic curative content and blend proportions on the properties of dynamically vulcanized natural rubber / acrylonitrile – butadiene – styrene blends / P. Wongthong, C. Nakason, Q. Pan, GL Rempel, S. Kiatkamjornwong // Journal of Applied Polymer Science. - 2015 .-- p132.
14. Ugbesia, S. and Ekabafe, L. O. Effect of Carbonization Temperature of Filler on the Tensile Properties of Natural Rubber Compound Filled with Cassava Peel Carbon. Turkish Journal of Science and Technology, 2011. p. 75.
15. Kerem Shixaliyev.Theory and practice of obtaining composite materials based on polymer blends . Proceedings of the Fouth International Confrense of European Academy of Science BONN,GERMANY. 2019,-pp32.

PP-III-1

PREPARATION AND RESEARCH OF COMPOSITIONS BASED ON THERMOPLASTICPOLYMERS

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Abstract. The scientific basis of industrial technology for the production of composite materials with a wide range of performance properties based on polyolefins and heterocain polymers using existing production facilities and technological equipment, to ensure the production of the first in the domestic practice of high-performance injection-molded cordless tires and other severely deficient products.

Keywords: compatibility, composition, polymer, multi-tonnage polymers, polymer compatibility, solubility, thermoplastic polymers, polyvinyl chloride(PVC), polyurethane thermoplastic(PUTEP) elongation, desirability.

1.Introduction

At present, in fact, there is not a single branch of the national economy where polymer materials are not used.[1-6]

Now in the field of multicomponent systems, empirical search is far ahead of the development of theory. However, only the presence of a well-developed theory, a scientifically based approach to choosing the composition of compositions, and finding out the regularities of changes in the macroscopic properties of the system due to its internal organization will allow us to obtain polymer composite materials with predetermined properties[7-13]

There are a number of fundamental approaches to the production of mixtures, of which the method of mixing thermoplastic polymers, carried out on an extrudes or rolls, favorably differs in the simplicity of the technology. Despite a number of limitations related to the stability of the mixture throughout the entire cooking cycle using this method, it was possible to obtain a number of PUTEP mixtures with other thermoplastics. Thus, by mixing PUTEP with PVC, a material is obtained that combines the impact strength and abrasion resistance of PUTEP with the rigidity and high modulus of elasticity of PVC. At the same time, the resulting composite is cheaper than a “pure” PUTEP. However, such compositions have a small relative elongation (about 100 ÷ 200 % at 200C), which is completely unsatisfactory for use in a number of RTI industries, in particular, for the production of cast polyurethane tires.[14-23]

In order to give optimal technological and physical - mechanical properties to mixtures, the modifying role of HCPE, which serves as a “carrier” for PVC incompatible with PUTEP, was studied on the basis of PUTEP.

2.Metod

Homogenization was carried out by research mixing of components on a two-roller mixer at a temperature of 1650C for 15 minutes, then the blades were cast, which after 7 days of exposure were subjected to rupture on a breaking machine P-0.5 according to GOST 270-75 with a drawing speed of 130mm/min and a temperature of 200C. Based on the literature data, the optimal indicators for cast tires were determined:

$dv = 1,0 = 45,0$ kN/m-tear resistance

$d\varepsilon = 1,0 = 375\%$ is the relative elongation, where dv and dε are functions of the desired factor.

The relation of the desirability index Y1 to the desirability function has the form:

$d = e\text{-}(Y1)p$

where n is the exponent whose value is determined by the parameter requirement.

By varying the desirability index from -4 to + 4, we determine the type of regression equation that connects the current value of the indicator under study with the desirability index, meaning the equation:

$Y_6 = AO + \alpha;\ Y1$

where Y1 is the current value of the indicator.

As a result of the calculation, we have:

ue_1 = -8.42 + 0.0276

Y_1 =17.35 – 0.0356

Taking the form of the desirability function d =x/Y_1 by /198/, we determine the desirability indicators for the break resistance of y1c and the relative elongation of Y_1, as well as the cor

2. an Increase in the content of HCPE from 5 to 20 m. h. leads to a Di with an extremum at the level of 12.5 m. h.

X_2 = 5 m. h. Di =0.067

X_2 =12, 5 m. h. Di =0.089

X_2 = 20 m. h. Di =0.078

3. In one pair of the system (for example, 3A-2B, etc.), the maximum with an increased content of oil resin SPP.

3.Results and Discussions

We used a MIN-8 polarizing microscope equipped with a specially made photo attachment with a Zenith-TTL SLR camera, magnification factor x 480, wedge-quartz L= ½ λ, polymer mixtures were studied at a temperature of 2980K.

Table 1. Desirability function and desira bility indicators for tear resistance and elongation

№№ п/п	$Y_{iG}{}^1$	d_i G	$Y_{i\varepsilon}{}^1$	d_i ε
1.	-2,78	0,01	4,78	1,0
2.	-3,40	0,01	0,37	0,45
3.	-2,97	0,01	-3,40	0,01
4.	-3,33	0,01	1,22	0,80
5.	-3,25	0,01	-3,23	0,01
6.	-3,67	0,01	0,81	0,61
7.	-2,99	0,01	-0,98	0,01
8.	-2,59	0,01	-1,73	0,50
9.	-2,84	0,01	-3,23	0,01
10.	-	-	-	-
11.	-3,84	0,01	-2,19	0,02
12.	-4,01	0,00	-3,01	0,01
13.	-3,01	0,01	-0,49	0,20
14.	-2,95	0,01	0,80	0,61
15.	-2,44	0,01	-2,69	0,01
16.	-2,74	0,01	-2,76	0,01
17.	-2,93	0,01	-2,41	0,01
18.	-3,16	0,01	-3,58	0,01

Table 2.Physical and mechanical properties and enrichment of the desirability function of the composition

№№ п/	Variables				Responses			
	Inside X_0	PVX X_1	XhCP E» X_2	SPP X_3	Co-rotation break , Mпа, $У_1$	Refers. extension, % $У_2$	Permanent elongation ., % $У_2$	Generalized function desirability D
1a 1	100	5,0	5,0	0,55	20,4	354	57,5	0,1
1б 2	100	5,0	5,0	2,2	18,2	477	89,5	0,067
2a 3	100	5,0	12,5	0,588	19,7	583	89,6	0,01
2б 4	100	5,0	12,5	2,35	18,4	453	81,3	0,089
3a 5	100	5,0	20,0	0,626	18,7	578	89,8	0,01

3б 6	100	5,0	20,0	2,5	17,2	510	77,1	0,078
4а 7	100	7,5	5,0	0,562	19,6	515	90,5	0,032
4б 8	100	7,5	5,0	2,25	21,1	536	87,4	0,071
5а 9	100	7,5	12,5	0,6	20,0	578	102,1	0,01
5б 10	100	7,5	12,5	2,4	-	-	-	-
6а 11	100	7,5	20,0	0,638	16,5	549	91,5	0,014
6б 12	100	7,5	20,0	2,55	15,9	572	106,4	0,00
7а 13	100	10,0	5,0	0,576	19,5	501	91,5	0,045
7б 14	100	10,0	12,5	2,3	19,8	465	80,0	0,078
8а 15	100	10,0	12,5	0,612	21,6	563	91,5	0,01
8б 16	100	10,0	12,5	2,45	20,5	565	84,4	0,01
9 а 17	100	10,0	20,0	0,65	19,8	555	89,8	0,01
9 б18	100	10,0	20,0	2,6	19,1	588	89,6	0,01

4.Conclusions

The analysis of generalized de suitability functions showed that the increase in PVC content from 5-10% by weight. Leads to an increase in D from 0.067 to 0.078

System PVC-UTEP is incompatible in a wide range of compositions.

The combination of polymers in the PUTEP-PVC system is thermodynamically possible at a concentration of PUTEP no more than 10% by weight.

A relatively wide area of the interphase boundary layer should be observed in the separating system.

Three-component compositions based on polyvinyl chloride and polyurethane with high physical and chemical parameters have bee

5.References

1 .Serenko O. A., Goncharuk G. P. et al. / Effect of temperature on the deformation behavior of a composite based on polypropylene and rubber particles // High Molecular Compounds.-2007.-No. 1.-P. 71-78.

2.Zaikin A. E., Bobrov G. B./Compatibilitation of mixtures of incompatible polymers by filling//High-molecular compounds.-2012. - №8. - p. 1275-1282

3.Kuleznev V. N., Surikov P. V.//Phase equilibria in three-component polymer mixtures/High-molecular compounds.-2012. - №11. - p. 1602-1609

4. Belov N. A., Safronov A. P., Yampolsky Yu. P.//Reverse gas chromatography and thermodynamics of sorption in polymers./High-molecular compounds.-2012. - №11. - p. 1631-1647

5. Bundjali B., Yudistira I., JAriah B, Sukria L.//Study on properties of Polymer Blends from Polypropylene with Polycaprolactone and their Biodegradability/Polymer Journal, -2007 - Vol.39, №12.-pp.1337-1344

6. Ermilova E. A., Sizova A. A., Ilyicheva N. N., Pleshakov D. V.//Investigation of thermodynamic compatibility of a three-component mixture of nitramines with a copolymer of methyl methacrylate and methacrylic acid./ Advances in chemistry and chemical technology.-2014-no. 2. - p. 65-67.

7. Rijhikova I.G., Volkov A.M., et all. Modification feature of binary mixtures PP / SKEP by the system of organic peroxide-polyfunctional vinyl monomer in the reaction extrusion process. Plastic masses, 8, 2013, p. 40–45.

8. Murtazina L.I., Garifullin A.R., Nikultsev I.A., et all. Influence of plastificators on the property of unhardened hermetics on the basis of ethylene-propylendiene rubber. Engineer-chemist's encyclopedia, № 8, 2014, pp. 31–35.

9. Kirsh I.A., Pomogova D.A. Study of the properties of secondary polymer materials based on polypropylene and polyethyleneterephtalat, obtained in the influence of ultrasonic vibrations on the polymer melts. – Moscow, Plastic masses, 2012, No. 1, pp. 48–51.

10.Turaev E. R., Beknazarov H. S., Akhmedov U. K., Jalilov A. T. //Interfacial interactions of three-phase polypropylene composite materials. / Universum.Technical Sciences. / - 2018-no. 12. - p. 57

11. Shastin D. A., Wolfson S. I., Makarov T. V.//Influence of modification of triple ethylene propylene rubber on physical and mechanical properties of rubbers./Bulletin of Kazan technological University.- 2010 - №4. - p. 5-7

12. Ryzhikov I. G., Volkov A. M, Baumann N. A. Kazakov S. M., vol'fson S. I.//Influence of the concentration of components of the modifying system peroxide/TMPTA and Mooney viscosity of the EPDM rubber for a balance of fluidity and impact resistance of EPDM batchas in the matrix of polypropylene./Bulletin of the technological University-2015-no. 4. - with 148-150.

13. Ryzhikova I. G., Volkov A. M., Bauman N. A., Kazakov Yu. M., Wolfson C. B. //Research of physical and mechanical properties of mixtures of PP/SKEPT modified by peroxide and peroxide system/tmpta-Bulletin of the technological University. - 2015. - no. 4. - p. 134-137

14. I. Klyuchnikov A., Klyuchnikov O. R., Stoyanov, O. V.//Bulletin of Kazan technological University.-2015. - №4-p. 224-225

15. Bazhenov S.L., Berlin A.A., Kul'kov A.A., Oshmyan V.G. Polimernyye kompozitsionnyye materialy [Polymer composite materials]. Dolgoprudnyy: Intellekt Publ., 2010, 352 p.
16. Misin V.M., Nikulin S.S., Dyumayev K.M. Vestnik Kazanskogo tekhnologicheskogo universiteta [Bulletin of Kazan Technological University]. 2013. vol. 16, no. 1, pp. 97-109
17. Kablov E. N. Strategic directions of development of materials and technologies of their processing for the period up to 2030// Aviation materials and technologies. 2012 No. S. S. 7-17.
18. Mikheeva V. A., Tkacheva E. N., Sofronova O. B., Pogrebtsov V. P. Influence of technological parameters of prizvodstvo on the structure and properties of new grades of ethylene propylene rubbers //Industrial production and use of elastomers. -2013. - №2. - P. 3-7.
19. Ososhnik I. A., Shutilin Yu. F., Karmanova O. V. Production of rubber technical products. Voronezh: Voronezh state technological University. Acad. -2007. -972 p.
20. Magg G. Vulcanizing systems for special rubbers //Polymer materials-2014. - №14. - Pp. 22-29.
21. Shykhaliev K. Development of a composition and products based on butyl rubber. SB Experimental and theoretical research in modern science. Sat Art. according to the material. 1 international scientific and practical conf. Novovbirsk, SIBAK.№1.-2017.-C.90-94.
23. Shixaliyev Kerem Sefi Exelolted thermoplastics based compositions. E uropean science review.Scientific journal ., Vienna -2017№ 5-6.- P.89-94.

PP-III-2

MODIFIED LINEAR POLYETHYLENE PROPERTIES

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Abstract: As result of the modification of polyolefin, composite materials based on them were obtained for the use in special equipment in order to entrain their heat resistance. Data analysis DTA (differential thermal analysis) of the DTA curve of this polyethylene sample suggests a bimodal nature of their MWD (molecular weight distribution) which differs from polyethylene with unimodal MWD and a series of endo oxidation effects with a maximum temperature of 245, 335, 358 and 435 °C.

X-ray structural studies showed that the crystal system and the size of the unit cells of the crystal lattice of LLDPE practically does not differ from those of LDPE. LLDPE as well as LDPE and HDPE has a layered structure with dense packing of macromolecules. In terms of crystallinity and crystallite sizes, LLDPE are on par with HDPE and significantly differ from LDPE. These data are in agreement with published data. The parameters of the unit cells of the crystal structure of UHMWPE are close to those of LLDPE, and by crystallinity it occupies middle ground between HDPE and LLDPE.

Key words: linear low density polyethylene (LLDPE), LLDPE-1 - ethylene-hexene-1 copolymer, LLDPE-2 -- ethylene-octene-1 copolymer, LLDPE-3 -- ethylene-decene-1 copolymer, supramolecular polyethylene (SMPE), EHC -- copolymer of ethylene with hexane, EOC -- copolymer of ethylene with octane, NMR -- nuclear magnetic resonance, TG -- thermogravimetric, MWD -- molecular weight distribution, Vinylidene groups, composition, aging

1. Introduction

Linear low density polyethylene (LLDPE) is synthesized in the presence of a titanium-chromium catalyst and differs from each other by the length of the side branch. LLDPE-1 is a copolymer of ethylene with hexene-1, where the butyl groups ($-CH_2-CH_2-CH_2-CH_3$) are side branches; LLDPE-2 is a copolymer of ethylene with octene-1, where the side branches are hexyl groups: ($-CH_2-(CH_2)_3-CH_2-CH_3$); LLDPE-3 is a copolymer of ethylene with decene-1, where the side branches are octal groups: ($-CH_2-(CH_2)_5-CH_2-CH_3$). With a constant composition of the copolymer, a relationship is found between the degree of crystallinity and the length of the hydrocarbon chain of the commoner. Namely, with an increase in the chain length of the commoner and, accordingly, the length of the branches from the macro chain, the effect of decreasing crystallinity increases and reaches a maximum when using α-olefins C_4-C_6 as commoners.

A further increase in the chain length of α-olefins does not cause a significant decrease in the degree of crystallinity and even leads to a slight decrease in the effect of disruption of the crystal structure [1-15].

2. Result

Thus, by varying the degree of crystalline LLDPE by introducing more or less commoner, materials with new properties can be obtained.

Unlike low density polyethylene, obtained at high pressure, the structure of which is characterized by the content of side branches of various lengths, LLDPE obtained at low pressure (up to 4.0 MPa) contains the same type of side branches. Moreover, the size of the latter, as indicated above, depending on the commoners, can vary from C_4 to C_8, in the case of LLDPE-1 and LLDPE-3, where α-C_6 and α-C_{10} were used as comonomers, respectively. This is a fundamentally important difference between LLDPE and LDPE and it largely determines a set of exceptionally high performance properties of LLDPE. Fig.1 presents a schematic representation of the structure of LDPE, LLDPE and HDPE.

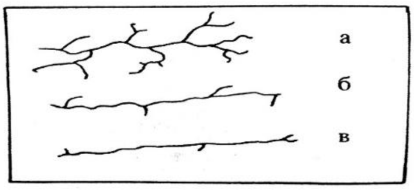

Fig. 1. Schematic illustration of the structure of LDPE - a, LLDPE - b and HDPE - c.

In terms of structural characteristics, LLDPE is close to HDPE and significantly differs from LDPE.

Violation of the linear structure of polyethylene is long and short-side chains and olefin saturation. Despite their small content in the general structure of linear polyethylene they have a significant impact on the physicochemical properties of the polymer [16-25].

3. Discussion

The results of an IR analysis of the structure of the synthesized LLDPEs show that the main saturated groups in the structure of LLDPE are vinyl, vinylidene and trans-vinyl groups (Table 1).

The increase in the content of commoner in the composition of LLDPE leads to an increase in vinylidene groups. In all circumstances, an increase in the commoner in the composition of the copolymer (LLDPE) leads to an increase in the amount of -CH$_3$ groups.

The content of individual fragments in the structure of LLDPE was also determined by appropriate processing of the NMR spectra of various types of LLDPE.

Table 1. Structural characteristics of LLDPE (Synthesis conditions: temperature -160 °C; pressure - 20 MPa; duration - 60 min; catalyst - titanium-chromium)

The monomers content in the copolymer, mole%	Σ C=C	Vinylidene groups, %	Vinyl groups,%	Trans vinyl groups,%	-CH$_3$- per 1000 C atoms
	per 100^{0}C atoms				
LLDPE -1 (EHC-1)					
0,08	0,24	10	83,5	6,5	0,05
0,150	0,25	10,2	84,3	5,5	0,07
0,450	0,42	9,8	82,9	8,1	0,21
1,10	0,44	15	76,6	8,4	0,51
1,50	0,57	25	60,9	14,1	0,65
LLDPE -2	0,40	5,9	90,1	4	0,05
(EOC-1)					
0,10	0,37	4,1	90,9	5	0,09
0,144	0,45	16,0	76	8	0,37
0,54	0,55	19,0	68	13	0,55
1,40	0,41	28,0	67	15	0,85
LLDPE -3 (EDC-1)					
0,15	0,25	10,4	85,1	4,3	0,09
0,88	0,38	14	73	13	0,51
1,67	0,39	26	55	19	0,8

The results of the quantitative determination of individual fragments of the structure of LLDPE obtained from NMR spectroscopy are compiled in Table 2.

Table 2.NMR spectroscopy data

Samples	The number of groups per 1000 C atoms			
	-CH	-CH$_2$	-CH$_3$	The commoner content in the reaction zone, mole%
LLDPE -1	3,3	93,4	3,3	0,1
LLDPE -2	4,4	91,2	4,4	0,1
LLDPE -3	6,2	87,6	6,2	0,2

With an increase in commoner content in copolymer an increase in the CH$_3$ groups shows that the commoner in the copolymer is distributed by separate units and the distribution is statistical in nature. The lack of large blocks of commoner in LLDPE is also shown by derivatographic data.

Block copolymers are usually characterized by two melting points whereas copolymers with a statistical distribution of copolymers in the composition are characterized by the same melting point, but differ from the melting point of photopolymers [10 - 20].

Figure 2 shows the derivatographic curves of HDPE synthesized in solution in the presence of a titanium-chromium catalyst. This HDPE sample is characterized by sufficiently high thermophysical properties. The melting point is 132 °C, the oxidation temperature is 245 °C and temperature of 50 % of weight loss is 480 °C.

From the TG curve of the dependence of the mass loss (Δm) of polymer on temperature (T) it is evident that this curve has two distinct temperature regions at which polyethylene, when heated, noticeably loses weight. These regions correspond to temperatures of 310 – 370 ° C and 370 – 420 ° C, respectively. This type of TG curve is characteristic of polymer samples predominantly with bimodal MWD.

The TG curve of polyethylene with a unimodal MWD distribution, as a rule, is characterized by a single temperature region at which polyolefins .

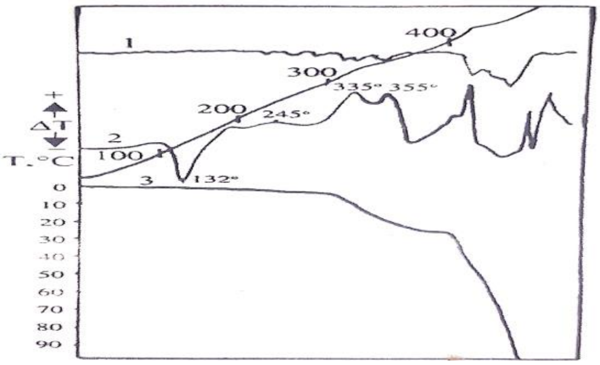

Fig. 2. Derivatogram of linear low density polyethylene, 1-DTG, 2-DTD, 3-TG curves

DTA data analysis of these polyethylene samples suggests a bimodal nature of their MWD which differ from polyethylene with unimodal MWD a series of oxidation endo-effects with a maximum temperature of 245, 335, 358, and 435 °C.

The dependence of the change in specific volume on the temperature of polyethylene is characterized by different values of V at a given T. The dependence of the change in V on T in LLDPE is quite different from other polyolefin. Namely, if we draw straight lines along the points of the upper branch of the dilatometry cooling curve, then we get two sections ~ 120 to 165 °C and from 165 to 230 °C (Fig. 3).

Apparently, upon cooling the LLDPE melt to the crystallization temperature, their macromolecules are partially ordered at higher temperatures. The indicated two sections of the upper branch of the dilatometry cooling curve of LLDPE are related to the nature and characteristics of the same type of lateral branches.

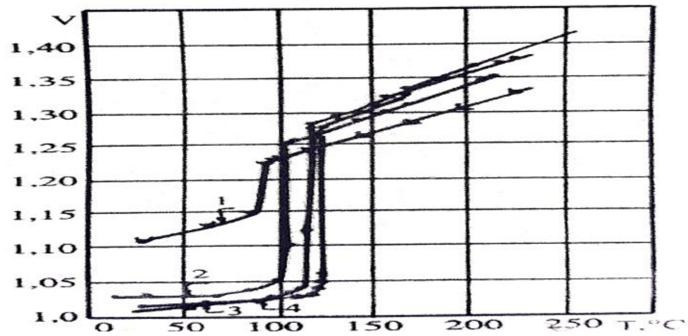

Fig. 3. The dependence of the change in specific volume (V) on temperature for: 1-LDPE; 2-HDPE; 3-LLDPE-2 and 4-LLDPE-3.

It is expected that during cooling of the LLDPE melt, namely, the EOC-1 and EDC-1 copolymer, the formation of microcrystalline regions precedes the beginning of their crystallization due to the laying of similar lateral branches having copolymers in the structure. Microcrystalline areas formed due to lateral branches concentrate along the main chain and lead to an increase in the strength properties and resistance of EOC-1 and EDC-1 to cracking.

This conclusion is in line with the data obtained by us in calculating the relative fraction of "free volume" (f_f) for low and high density polyethylene and for EOC-1 and EDC-1, which were equal: 0,028, 0,025, 0,008 and 0,007, respectively.

An increase in the content of $–CH_3$ groups from 0.5 to 80 per 1000 carbon atoms in copolymer of ethylene with propylene leads to a change in T_g from 121 K. The T_m/T_g and f/f_f ratios for narrow fractions of EOC-1 in the MW range from $15\cdot10^3$ to $90\cdot10^3$, and for the samples of CEP containing from 0.5 to 13-CH_3 branches per 1000 carbon atoms of the main chain, turned out to be quite close. A further increase in the content of - CH_3 leads to a slight decrease in the T_m / T_g and f / f_f ratios. This fact points to the large-scale character of the influence of short CH_3 branches on the most important characteristics of the CEP.

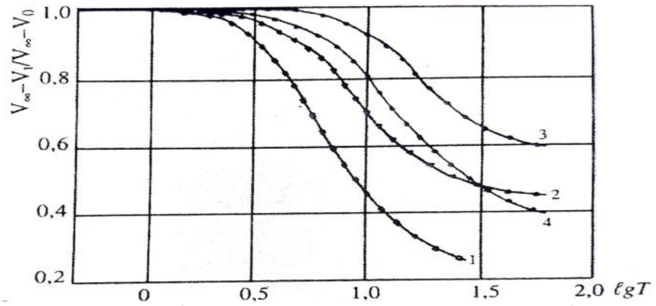

Fig.4. Kinetic crystallization isotherms of the initial LLDPE-2 (4) and its narrow fractions with MW-$7{,}5\cdot10^3$ (1); $90^3\cdot10^3$ (2); $150\cdot10^3$ (3).

The kinetics of isometric crystallization of the initial LLDPE-2 (EOC-1) and its narrow fractions was studied by dilatometry method by changing the specific volume. The results of isothermal crystallization of narrow EOC fractions in the coordinates $(V_\infty - V_t)/(V_\infty - V_0)$lgT are shown in Fig. 4

The narrow fractions of EOC-1 with different MW differ from each other in induction time of crystallization (τ_i) characterizing the nucleation rate, in the crystallization half-time ($\tau_{1/2}$), in the time of crystallization completion (τ_∞) and also in the crystallization kinetics at the final stage of the process when the formation and complication of supramolecular formations occurs.

The obtained values of τ_i, $\tau_{1/2}$ and $\nu=\frac{1}{\tau_{1/2}}$ are given in Table 5. The reciprocal of the crystallization half-time (during which half of the substance goes into the crystalline state) conditionally characterizes the crystallization rate - c_{cr}.

Kinetic isotherms show that, depending on the molecular mass, the maximum value crystalline state conversion at a given temperature of the narrow fractions of LLDPE-2 (EOC-1) could be 0,50 for high molecular weight and up to 0,85 for a low molecular weight sample (Fig. 4). Therefore, when evaluating $\tau_{1/2}$, it seems appropriate to take the half-conversion time $\tau'_{\frac{1}{2}}$during which the crystalline state transforms half of the maximum possible amount of a substance capable of crystallizing throughout the entire crystallization time τ_∞. When assessing the crystallization rate, it should be taken into consideration that during the time τ_i, taken as the induction period of crystallization, there is no noticeable increase in crystallinity, therefore, the time should be subtracted from the time $\tau'_{\frac{1}{2}}$ and the reciprocal of this difference ($\tau'_{\frac{1}{2}}$- τ_i) should be considered as crystallization rate:

$$C_{cr}= \frac{1}{\tau_{cr}} - \frac{1}{\tau'_{\frac{1}{2}}\cdot\tau_i}$$

While structural features, in particular, the uniformity of sufficiently long lateral branches, on the one hand, increase the rate of crystallization, on the other hand, it increases the viscosity properties of LLDPE melts.

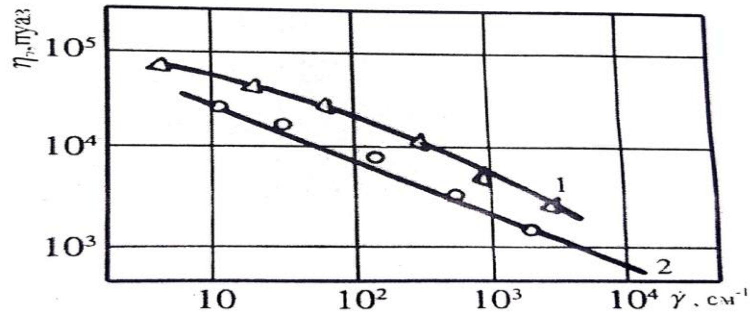

Fig. 5. The dependence of viscosity on shear rate for LLDPE-2 (1) and LDPE (2)

It has been shown that the shear rate of LDPE uniformly decreases with increasing viscosity for LLDPE-2, which is typical for the same viscosity with LDPEof lower shear rate. This fact is also related on the one hand to the conformational feature of the structure of macromolecules and, on the other hand, it is probably related to the crystallite sizes and the interaction of interlayer chains in the structure of LLDPE-2 (Fig. 5). This feature requires the development of special conditions for the processing of LLDPE.

On the basis of the data obtained, the true values of the velocity gradient were calculated, which, in turn, served to calculate the effective viscosity and the highest Newtonian viscosity ($\eta_{n\delta}$).

$$lg\eta_{n\delta} = f(\frac{1}{\eta})$$

$\eta_{n\delta}$ was found graphically by extrapolating the curve of the dependence of the logarithm of τ_e on τ (Fig. 10).

The graphical dependence of $lg\eta$ on the reciprocal temperature, according to the Frenkel-Eyring equation, $lg\eta_э = lgA + \frac{E}{2,3R}\cdot\frac{1}{T}$ gives a straight line, the slope of which allows determining the activation energy of the viscous flow of polymers.

The activation energy of the viscous flow of high density polyethylene and its copolymers with octane and hexane is 20,3 kJ/mol and 31,9 kJ/mol, respectively. The activation energy of the viscous flow of ethylene-octene copolymer is 35%, and the ethylene-hexane copolymer is 50% higher than the activation energy of HDPE (Fig. 6-7).

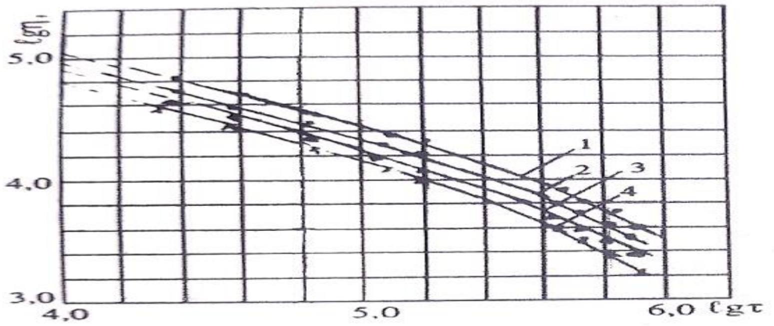

Fig. 6. The dependence of the effective viscosity of ethylene-hexane copolymer (LLDPE-1) on shear stress at 190 (1); 210 (2); 230 (3); 250 °C (4)

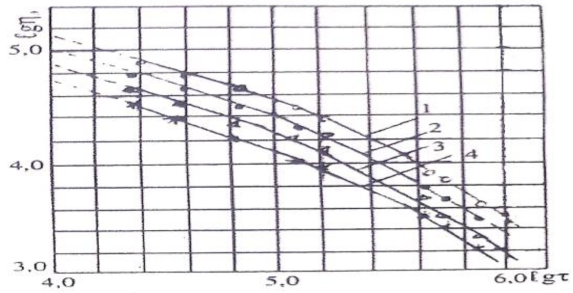

Fig. 7. The dependence of the effective viscosity of ethylene-octane copolymer (LLDPE-2) on shear stress at 190 (1); 210 (2); 230 (3); 250 °C (4)

The dependences of the reduced LLDPE viscosity on shear stress were established, as indicated in the figures, the reduced viscosity does not depend on temperature (Figs. 10-12).

Figures 8-10 show the curves of the dependence of the effective viscosity of the studied polyethylene's on the strain rate in the temperature range 190–250 °C where these experimental data are presented in an invariant form. The dependence of η_{sp} on γ_{sp} is universal for most polymers. The universal dependence also describes the regularity of viscosity at different temperatures. The flow curves for the same polymer at different temperatures merge into one common universal curve in the coordinates η_{sp} -- γ_{sp} independent of temperature, i.e. the universal curve is temperature-invariant.

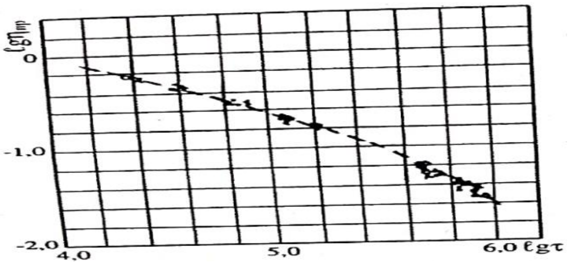

Fig.8 The dependence of the reduced viscosity of HDPE on shear ○ -190 °C; ● -210 °C; Δ-230 °C; x-250 °C

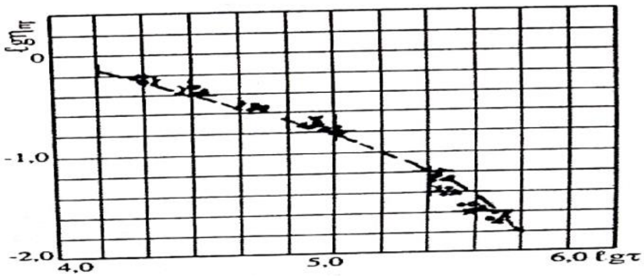

Fig.10. Dependence of the reduced viscosity of ethylene-hexene copolymer (LLDPE-1) on shear stress ○ -190 °C; ● -210 °C; Δ-230 °C; x-250 °C

Below are the results of a comparative study of the diffusion of liquid aggressive media through HDPE and LLDPE (copolymers with octane and hexane). Hexane, hexane, benzene and acetone were used as aggressive media.

There are various methods for studying the process of permeability of gases, vapors and liquids through a polymeric substance. The mass method differs in simple and relatively high accuracy, therefore, we dwelled upon this method [21-26].

The experiments were performed at room temperature. Exposure time consisted 400 hours. Polymer films were obtained by pressing at a temperature of 180 °C. Table 3 summarizes the sizes of the studied films obtained from LLDPE and HDPE.

To calculate the permeability coefficient (P) by the mass method, the formula is used:

$$P = \frac{\Delta Q \cdot \delta}{s \cdot \tau} \quad (2)$$

where ΔQ is the amount of substance (g) that has penetrated over time (τ) through the sample with the thickness of δ (cm) and an area of s (cm^2).

Table 3. Sizes of the investigated films

Polymer name	Name of aggressive environments							
	hexane		hexane		benzene		acetone	
	Thickness (δ), cm	Area, (s), cm^2	Thickness, cm	Area, cm^2	Thickness, cm	Area, cm^2	Thickness, cm	Area, cm^2
High Density Polyethylene (HDPE)	0,013	9,07	0,013	9,07	0,012	9,07	0,009	9,07
EOC-1 LLDPE -2	0,016	9,07	0,015	9,07	0,0115	9,07	0,012	9,07
EHC-1 LLDPE-2	0,007	9,07	0,007	9,07	0,0085	9,07	0,011	9,07

As is known, the permeability of crystalline polymers is usually explained using a two-phase model, and the amorphous phase is considered permeable. The higher the density and degree of crystallinity of polymers, the lower the vapor permeability coefficients [17-24].

An analysis of the rheological characteristics of polyethylene's with a MFR equal to 1,4–7,0 g/10 min in the temperature range 135–300 °C showed that in these temperature ranges the efficiency of the polymer melt viscosity varies slightly with temperature.

The transition of HDPE to the plateau of a highly elastic state, at a certain critical level of the dynamic loss modulus (E′ and E″) occurs clearly and E'_m and E''_{max} have the same values. The maximum value of $E_{max} = 7{,}28 \cdot 10^9$ N/m^2 is a measure of the stiffness of a fully crystalline polymer.

The functional dependence of the volume dynamic modulus of elasticity of monodisperse, polydispersity and branched polyethylene's with their main parameters –M, ρ, V_m and the ultrasonic propagation velocity of the polymer showed the invariance of the E_y-ρ dependence for polyethylene's.

With repeated loading and unloading of polyethylene samples, a known hysteresis pattern is revealed. Samples of polyethylene's with MW up to $2,5 \cdot 10^4$ are brittle and break down under primary loading. With increasing MW, the number of possible loading cycles before fracture of the samples at the beginning grows and then decreases, the apparent strength (σρ) grows, although its limiting values are less than that with stationary deformation. Another feature of hysterisation of polyethylene is the complete restoration of strength during repeated cycles.

Heat treatment has a significant impact on the bulk properties of polyethylene. With prolonged exposure of the polymer at high temperatures due to the simultaneous passage of crystallization, recrystallization, structuring, or partial destruction, the temperature dependence of the density changes significantly. At 200–250 °C crystallization is suppressed, the packing density of macromolecules decreases, and at room temperature samples with values of ρ 850 ÷760 kg/m^3 are obtained. In the temperature regions T_{cr} and T_m, their narrow temperature range is observed, and the smaller the MFR, the more V_{sp} and the less ρ.

4.Conslusion

The density of polyethylene samples strongly depends on the cooling rate, T_g increases from -106 °C to 62 °C with increasing cooling rate. With an increase in MFR, a pronounced induction period of crystallization is manifested. In general, the crystallization mechanism of single crystals and polymer obtained from the melt differs slightly. The dependence of the fraction of free volume on T-T_g presents an opportunity at any T and cooling rate to determine the value of V_{sp} or ρ, which proves the invariance of the results with respect to temperature. The generalized temperature invariant characteristic is established for the most important physical properties of linear polyethylene's - V_{sp}, V_f, f_f, coefficient of volumetric thermal expansion, etc.

The effect of polydispersity of polyethylene's on their properties has shown that the smaller the MW value, the higher the values of shear rates R_{max} (M) appears (the value of rheological functions in MW). Low-molecular weight polyethylene samples are characterized by a narrower MW. With increasing MW, the position of R_{max}(M) shifts toward ever smaller values of γ, and the value of R_{max} (M) decreases, i.e., there is a typical pattern of a wide distribution of MW. Narrow MWD polyethylene is characterized by a minimum value of the generalized rheological index of polydispersity RPI and for monodispersed polyethylene, the RPI value is zero.

In the DTA curve of the HDPE in the region of 300°C and above, a series of exon- and endo-effects are observed that relate to oxidative degradation, and above 300°C, molecular chains broken -- MW decreases, at more than 360°C, the formation of volatile decomposition products begins and at 475°C deep decomposition of polymer occurs. Narrow fractions of HDPE with $M_w/M_n \approx 1,02$, in contrast to the basic samples of polyethylene have a smaller T_m interval and at a value of MW from $3 \cdot 10^3$ to $5 \cdot 10^5$, do not depend on MW. The dependence of the thermal properties of HDPE on MW is large-scale and seems to be grouped in a certain MW interval, with increasing MW, the T_m interval expands and the overall rate of thermal oxidation and destruction increases.

The formation mechanism of LLDPE in the presence of a titanium-chromium catalyst with hexene-1 (LLDPE-1), octene-1 (LLDPE-2) and decene-1 (LLDPE-3) is practically the same and the distribution of the commoner in the composition of the copolymer occurs according to the law of the case. LLDPEs are characterized by high thermophysical properties $T_m=132^0$C and temperature of 50 % of weight loss is 480° C. LLDPE with a close degree of crystallization (0,64-0,68) and crystallite sizes (151-154 Å) has a higher tensile strength compared to LDPE. Depending on the MW the maximum conversion to a crystalline state at a given temperature for narrow LLDPE fractions can be 0,50 for a high molecular weight sample and up to 0,85 for a low molecular weight sample

An analysis of the rheological properties of LLDPE at 190–250 °C and shear stress of $10^2 \div 10^4$ MPa showed that at the same temperatures the dependence logy/logτ for the copolymers is the same and the reduced viscosity is independent of temperature. LLDPE can be processed by almost all known processing methods for thermoplastics. The presence in the structure of LLDPE of the same type and rather long lateral branches affects the permeability. Polymer films were obtained by pressing LLDPE at 180° C for 400 hours. At room temperature HDPE had a high vapor permeability. This is attributable to the relatively low density and crystallinity of LLDPE.

5.References

1. B. Huang and J. Liu, “The effect of loading rate on the behavior of samples composed of coal and rock,” International Journal of Rock Mechanics and Mining Sciences, vol. 61, pp. 23–30, 2013
2.J. Liu, E. Wang, D. Song, S. Wang, and Y. Nia, “Effect of rock strength on failure mode and mechanical behavior of composite samples,” Arabian Journal of Geosciences, vol. 8, no. 7, pp. 4527–4539, 2015.
3.S. Chen, D. Yin, F. Cao, Y. Liu, and K. Ren, “An overview of integrated surface subsidence-reducing technology in mining areas of China,” Natural Hazards, vol. 81, no. 2, pp. 1129–1145, 2016.
4.C.P. Lu, G.J. Liu, Y. Liu, N. Zhang, J.H. Xu, and L. Zhang, “Micro seismic multi-parameter characteristics of rock burst hazards induced by hard roof fall and high stress concentration,” International Journal of Rock Mechanics and Mining Sciences, vol. 76, pp. 18–32, 2015.
5. S. Chen, D. Yin, N. Jiang, F. Wang, and Z. Zhao, “Mechanical properties of oil shale-coal composite samples,” International Journal of Rock Mechanics and Mining Sciences, vol. 123, p. 104120, 2019.
6 S. J. Chen, D. W. Yin, H. M. Liu, B. Chen, and N. Jiang, “Effects of coal’s initial macro cracks on rock burst tendency of rock–coal composite samples,” Royal Society Open Science, vol. 6, no. 11, Article ID 181795, 2019.
7.R.-H. Cao, P. Cao, H. Lin, C. Z. Pu, and K. Our, “Mechanical behavior of brittle rock-like specimens with pre-existing fissures under uniaxial loading, experimental studies and particle mechanics approach,” Rock Mechanics and Rock Engineering, vol. 49, no. 3, pp. 763–783, 2016.
8.X. L. Li, L. J. Kang, H. Y. Li, and Z. H. Ouyang, “Three-dimensional numerical simulation of bust-prone experiments about coal-rock combination,” Journal of China Coal Society, vol. 36, no. 12, pp. 2064–2067, 2011.
9.D. W. Yin, S. J. Chen, X. Q. Liu, and H. F. Ma, “Effect of joint angle in coal on failure mechanical behavior of roof rock-coal combined body,” Quarterly Journal of Engineering Geology and Hydrogeology, vol. 51, no. 2, pp. 202–209, 2018.
10.D. W. Yin, S. J. Chen, B. Chen, X. Q. Liu, and H. F. Ma, “Strength and failure characteristics of the rock-coal combined body with single joint in coal,” Geotechnics and Engineering, vol. 15, no. 5, pp. 1113–1124, 2018.
11.S. J. Chen, D. W. Yin, B. L. Zhang, H. F. Ma, and X. Q. Liu, “Study on mechanical characteristics and progressive failure mechanism of roof-coal pillar structure body,” Chinese Journal of Rock Mechanics and Engineering, vol. 37, no. 7, pp. 1588–1598, 2017.
12.Z.-H. Zhao, W.-M. Wang, C.-Q. Dai, and J.-X. Yan, “Failure characteristics of three-body model composed of rock and coal with different strength and stiffness,” Transactions of Nonferrous Metals Society of China, vol. 24, no. 5, pp. 1538–1546, 2014.
13.S. J. Chen, D. W. Yin, N. Jiang, F. Wang, and W. J. Guo, “Simulation study on effects of loading rate on uniaxial compression failure of composite rock-coal layer,” Geotechnics and Engineering, vol. 17, no. 4, pp. 333–342, 2019.
14.Z. H. Zhao, W. M. Wang, L. H. Wang, and C. Q. Dai, “Compression-shear strength criterion of coal-rock combination model considering interface effect,” Tunneling and Underground Space Technology, vol. 47, pp. 193–199, 2015.
15.T. B. Zhao, W. Y. Guo, C. P. Lu, and G. M. Zhao, “Failure characteristics of combined coal-rock with different interfacial angles,” Geotechnics and Engineering, vol. 11, no. 3, pp. 345–359, 2016.
16.Y. L. Tan, X. S. Liu, J. G. Ning, and Y. W. Lu, “In situ investigations on failure evolution of overlying strata induced by mining multiple coal seams,” Geotechnical Testing Journal, vol. 40, no. 2, pp. 244–257, 2017.
17.Y. L. Tan, X. S. Liu, B. Shen, J. G. Ning, and Q. H. Gu, “New approaches to testing and evaluating the impact capability of coal seam with hard roof and/or floor in coal mines,” Geotechnics and Engineering, vol. 14, no. 4, pp. 367–376, 2018.
18.B. A. Paulsen, B. Shen, D. J. Williams, C. Huddleston-Holmes, N. Erarslan, and J. Qin, “Strength reduction on saturation of coal and coal measures rocks with implications for coal pillar strength,” International Journal of Rock Mechanics and Mining Sciences, vol. 71, pp. 41–52, 2014.
19.T. Wang, Y. D. Jiang, S. J. Zhan, and C. Wang, “Frictional sliding tests on combined coal-rock samples,” Journal of Rock Mechanics and Geotechnical Engineering, vol. 6, no. 3, pp. 280–286, 2014.
20. X. Qu, “Experimental study on influence of mechanical properties of roof and floor on stability of strip coal pillar,” Shandong University of Science and Technology, Qingdao, China, 2018, Master’s thesis.

OR-III-3

ETHYLENEDIAMINE PHOSPHATE CONTAINING SCALE INHIBITORS

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Abstract. A method has been developed for producing a scale inhibitor which builds on the interaction of ethylenediamine dihydrophosphate, bisethylenediamine monohydrophosphate and trisethylenediamine phosphate with 85 % phosphoric acid at a temperature of 40-45 ^{0}C and at a different molar ratio of chemicals. It is immediately followed by cooling of the generated phosphates to 20 ^{0}C, and dilution with water to produce a 10 % solution.

When the produced inhibitors are fed in sulfate and carbonate solutions with a rate of 20, 25, 30 mg/l, they exert a high protective effect which outreaches 80 %. The maximum protective effect (more than 90%) is observed when the inhibitor is introduced into solutions with a consumption rate of 30 mg/l.

Keywords: scale inhibitor, ethylenediamine, phosphoric acid, protective action.

1.Introduction

Salt deposition in oil production is a process of mass crystallization from supersaturated solutions under severehydroand thermodynamic conditions in the presence of oil components, gas phase and mechanical impurities. All these affect the intensity of accumulation, the nature and properties of deposition.

In order to increase the service life of oilfield equipment for each facility, it is required to conduct an individual selection of chemicals, develop an optimal application technology and dosage.

The most effective way of controlling salt deposition is the use of inhibitors. Inhibitors are designed to prevent the formation of mineral deposits of various compositions on the inner surface of oilfield equipment, pipelines, systems for collecting and transporting watercut oil, reservoir pressure maintenance systems and waste water disposal, as well as to protect wells and deep equipment.

The mechanism of action of scale inhibitors is based on adsorption processes. Adsorbed on the germ centers of the salt compound, inhibitors inhibit the growth, reshape and resize the crystal, prevent bonding to each other, and also worsen the adhesion of the crystal to metal surfaces [1].

There is a large number of scale inhibitors available nowadays. Phosphoric compounds-organic phosphate esters, organic phosphonates, organic aminophosphates, inorganic polyphosphates and organic polymers are the major scale inhibitors. The scale inhibitors minimize the scaling of salt deposits through a combination of dispersion of the crystals and the stabilization of deposits [2, 3]. The optimal choice of an inhibitor is crucial now to protect steel equipment from scaling and corrosion [4, 5].

The purpose of this work is to produce scale inhibitors based on ethylenediamine phosphates, as well as to study their scale control properties in reservoir water.

2.Experimental part

The primary target of the work is to develop a waste-free method for producing scale inhibitors, generate the end product in a simpler way which will help improve the effectiveness of protection of facilities water circulation systems, oilfield equipment and pipelines from mineral deposits, and expanding the raw material sources.

The technical result of this work is expressed in a waste-free technology for producing a scale inhibitor of mineral salts. The specified result of generating scale inhibitor of mineral salts, effective in saline environments is achieved through a method for producing scale inhibitor which builds on the interaction of amine compounds with 85 % strength phosphoric acid, where the amine compounds separately use ethylenediamine dihydrophosphate or bisethylenediamine monohydrophosphate or trisethylenediamine phosphate interaction at a temperature of 40-45 ^{0}C and at different molar ratio of chemicals, and the resulting phosphate is cooled to 20 ^{0}C, and diluted with water to produce a 10 % solution.

Ethylenediamine dihydrophosphate, bisethylenediamine monohydrophosphate and trisethylenediamine phosphate are generated by interaction of ethylenediamine with 85 % phosphoric acid at a molar ratio of 1:1, 2:1 and 3:1, respectively. Prior the reaction, water is fed to the system at a molar ratio of ethylenediamine: water =1:5.0. Aqueous solution of ethylenediamine is heated to a temperature of 40-45 ^{0}C. With the rotation of the mixer, phosphoric acid is fed into the ethylenediamine drop by drop through the separating funnel. Phosphoric acid is completely introduced into the flask, and the reaction continues for 2 hours at a temperature of 40-45 ^{0}C. During this time, a compound of ethylenediamine phosphates is produced in the form of a syrup. The general reaction scheme for the synthesis of ethylenediamine phosphates can be described as follows:

$H_3PO_4 + xH_2NCH_2CH_2NH_2 \rightarrow H_nPO_4(H_3N^+CH_2CH_2NH_2)_y$,

where x=1-3, y=1-3, n=0-2.

85 % phosphoric acid with molar ratio of 1:1 is drop wise fed in the syrup like compound of ethylenediamine dihydrophosphate, bisethylenediamine monohydrophosphate and trisethylenediamine phosphate using separating funnel. In the mean while the rotation of the mixer continues and the temperature is maintained in the range between 40 and 45 ^{0}C. Once the phosphoric acid is fully poured to the flask, the reaction is carried on for another hour. As the reaction proceeds, the mass in the flask thickens. Upon completion of the reaction, the generated phosphates are cooled to 20 ^{0}C, and white crystals emerge with a yellow tinge. The resulting substances in alignment with theoretical calculations are fed with water and 10 % aqueous solution is formed. The reaction network of producing ethylenediamine dihydrodiphosphate, bisethylenediamine monohydrodiphosphate and trisethylenediamine diphosphate is given below:

$$H_3PO_4 + H_2PO_4H_3N^+CH_2CH_2NH_2 \rightarrow H_2PO_4H_3N^+CH_2CH_2N^+H_3PO_4H_2;$$
$$H_3PO_4 + HPO_4(H_3N^+CH_2CH_2NH_2)_2 \rightarrow HPO_4(H_3N^+CH_2CH_2N^+H_3)_2PO_4H;$$
$$H_3PO_4 + PO_4(H_3N^+CH_2CH_2NH_2)_3 \rightarrow PO_4(H_3N^+CH_2CH_2N^+H_3)_3PO_4.$$

3.Results and discussion

The results of preparing aqueous solutions of scale inhibitors based on ethylenediamine and phosphoric acid are shown in table 1.

Table 1. Results of preparation of ethylenediamine phosphates

№ of samples	Inhibitor	Molar ratio of substances constituting the inhibitor		
		Nitrogen-containing compound	Phosphoric acid	Water
1	(Ethylenediamine+ phosphoric acid) +water	0,12	0,12	0,6
	(Ethylenediamine dihydrophosphate + phosphoric acid) + water	0,12	0,12	15,357
2	(Ethylenediamine +phosphoric acid)+ water	0,24	0,12	1,2
	(Bisethylenediamine monohydrophosphate + phosphoric acid) + water	0,12	0,12	18,963
3	(Ethylenediamine +phosphoric acid)+ water	0,36	0,12	1,8
	(Trisethylenediamine phosphate + phosphoric acid) + water	0,12	0,12	22,569

Tests of the protective effectiveness of prepared inhibitors to prevent deposition of calcium sulfate and calcium carbonate were carried out in reservoir water:

for $CaSO_4$		for $CaCO_3$	
$CaCl_2$	13,6 g/dм^3	$CaCl_2$	2,92 g/dм^3
$MgCl_2 . 6 H_2O$	1,24 g/dм^3	$MgCl_2 \cdot 6H_2O$	4,26 g/dм^3
Na_2SO_4	13,0 g/dм^3	Na_2SO_4	2,4 g/dм^3
NaCl	18,8 g/dм^3	NaCl	40,6 g/dм^3

As the testing procedure [6] dictates, after the inhibitor is fed to the reservoir water, the samples with and without the inhibitor, i.e. a "blank" sample, are kept in a thermostat at 80 ^{0}C for 5 hours. Upon cooling of the samples, the accumulated deposits are filtered out. The residual content in the solution of calcium cations was determined by trilonometry titration. The inhibition efficiency (E, %) was calculated using:

$$E= (C_i-C_b)\cdot 100/(C_0-C_b), \%,$$

where C_i - the content of calcium ions in the sample with an inhibitor after thermostating, mg/l; C_b-the content of calcium ions in the "blank" sample, mg/l; C_0-the content of calcium ions in the initial solution, mg/l.

The results of the tests to determine the protective effect of the produced scale inhibitors are shown in table 2.

Table 2. Determination of the protective effect of inhibitors of deposition of phosphate salts of ethylenediamine

№ of Samples	Inhibitor	The consumption of inhibitor, mg/l	Protective effectof the inhibitor	
			$CaSO_4 \cdot 2H_2O$	$CaCO_3$
1	Ethylenediamine Dihydrodiphosphate	20 25 30	81,4 86,2 92,7	84,4 88,3 94,6
2	Bisethylenediamine monohydrodiphosphate	20 25 30	83,3 88,4 93,1	85,2 89,9 95,3
3	Trisethylenediamine Diphosphate	20 25 30	82,2 86,3 92,9	85,0 88,1 94,8

It becomes evident from Table 2 that when the compositions are fed in sulfate and carbonate solutions with a consumption rate of 20, 25, 30 mg/l, they exerta high protective action which surpasses 80 %. The maximum protective effect is observed when the inhibitor is introduced into sulfate and carbonate solutions with a consumption rate of 30 mg/l. In these cases, the protective effect of inhibitors, as can be seen from the table, exceeds 90 %.

The results for determining the protective effect of the scale inhibitor ethylenediamine derivatives with phosphoric acid is shown as a graph in Fig. 1-3.

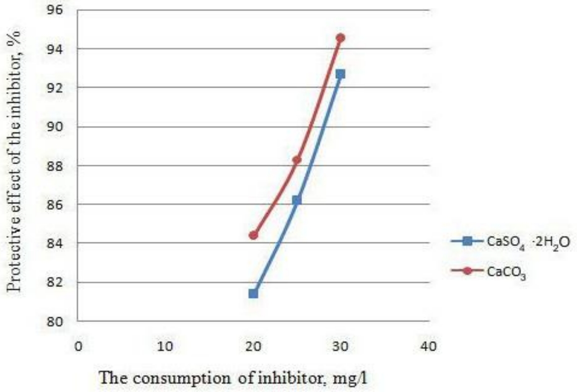

Figure 1. Determination of the protective effect of the inhibitor of salt deposits ethylenediamine dihydrodiphosphate from the consumption of the inhibitor

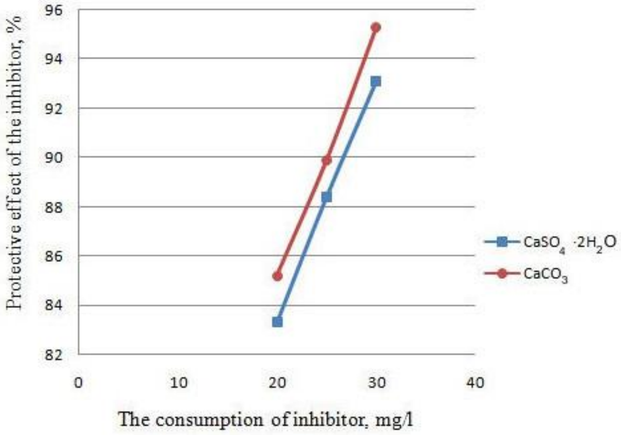

Figure 2. Determination of the protective effect of the inhibitor of salt deposits bisethylenediamine monohydrodiphosphate from the consumption of the inhibitor

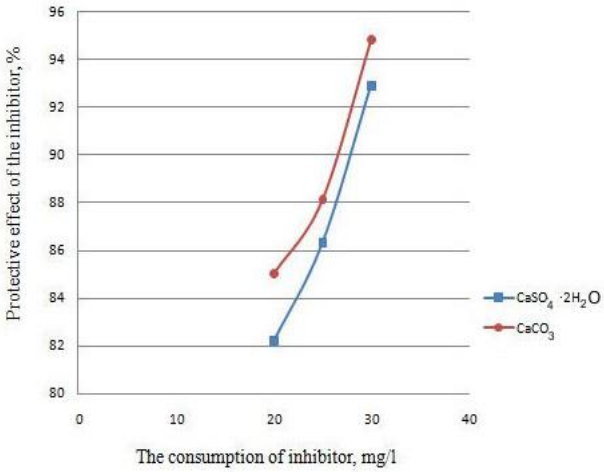

Figure 3. Determination of the protective effect of the inhibitor of salt deposits trisethylenediamine diphosphate from the consumption of the inhibitor

4. Conslusion

1. A method has been developed for producing a scale inhibitor which builds on the interaction of ethylenediamine dihydrophosphate or bisethylenediamine monohydrophosphate and trisethylenediamine phosphate with separately 85 % phosphoric acid at a temperature of 40-45 ^{0}C, and at a different molar ratio of chemicals, after which the resulting phosphates are cooled to 20 ^{0}C, and diluted with water to form a 10 % solution.
2. When applying the developed inhibitors in sulfate and carbonate solutions with a flow rate of 20, 25, 30 mg/l, they show a high protective effect-more than 80 %. The maximum protective effect (more than 90 %) is observed when the inhibitor is introduced into solutions with a consumption rate of 30 mg/l.

5.References:

1.Qlushenko V.N., Denisova A.V., Silin M.A., Ptashko O.A., Inqibitornaya zashita neftepromislovoqo oborudovaniya ot korrozii I soleotlojeniya. Ufa: Kitap, 2013. 592 s.
2. Nancollas G.H., Kazmierczak T.F., Schuttringer E. A Controlled Composition Study of Calcium Carbonate Growth: The Influence of Scale Inhibitors//Corrosion-NACE 37, no.2 (1981): 76-81
3. Dyatlova N.M.,Temkina V.Y., Popov K.I., Kompleksoni i kompleksonati metallov. M.:Khimiya, 1988. 544 s.
4. Chausov F.F., Effektivnost fosfonatochinkatnikh inqibitorov soleotlojeniy i korrozii. Sravnitelnie laboratornie issledovaniya//Ekoloqiya i promishlennost Rosii. 2008.№ 9. S. 28-33.
5. Chausov F.F., Sravnenie effektivnosti zashiti stali ot korrozii soleotlojeniy razlichnimi inqibitorami// Novosti teplosnabjeniya. 2008. № 9. S. 40-45.
6. Bikchantaeva N.V., Monakhova N.V., Aleshkina I.V., Issledovanie svoystv novoqo inqibitora soleotlojeniy SNPK-5312 (markos S i T) // Neftyanoe khozyaystovo. 11, 2000, S.39-40

PP-III-3

RESEARCHING OF STRUCTURE AND REACTION MECHANISM OF PHENOL-FORMALDEHYDE OLIGOMER MODIFIED WITH DIPHENYLAMINE BY METHOD OF IR-SPECTROSCOPY

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Abstract. The composition and structure of the modified resole phenol-formaldehyde oligomer were studied by method of IR-spectroscopy. In the same condition the mechanism of the probable reaction was determined by comparing the spectra of the unmodified oligomer with the spectra of the final product (modified).

Keywords: phenol-formaldehyde oligomer, modification, diphenylamine, IR-spectroscopy

1.Introduction

Due to its high reactivity and easy-to-obtain technology, phenol-formaldehyde oligomers are used in the preparation of polymeric materials with destructive environment, water, heat resistance, high strength, adhesion and dielectric properties, and they are widely used in various fields of industry.

In addition to having high physical-mechanical and exploitation performance, phenol-formaldehyde oligomer has a number of shortcomings such as brittleness, high content of environmentally harmful free phenol, low adhesive strength and this limits the applications of materials based on oligomers. In order to overcome these limitations, phenol oligomers are modified with compounds of different functional groups.

The low content of free phenol in modified oligomers, the use of nitrogen compounds as a modifier in the synthesis of phenol-formaldehyde oligomers, the development of new types of modified oligomers is more promising than the analogues of phenol-formaldehyde oligomers. On the basis of such compounds it is possible to obtain compositions for various purposes, as well as coating-forming and other effective materials. This is due to the influence of adhesive heteroatoms, high-polarity nitrogen-containing functional groups, which form a protective property [1-9**]**.

Modification of oligomer with different composition and multifunctional compounds causes changing of its physico-chemical, physico-mechanical, dielectric, thermal, exploitation properties. For this reason, the study of ways to modify phenol-formaldehyde oligomers, to improve their technological and exploitation properties is one of the current problems of polymer chemistry.

Thus, the composition and structure of the modified oligomer, as well as the exploitation properties vary depending on the nature of the modified agent, the amount of moles, the modification environment [10-13**]**.

2.Experimental part

The study is interested in the modification of the phenol-formaldehyde oligomer with diphenylamine, an aromatic compound containing nitrogen, as a modifying agent. The modification process was carried out in an alkaline environment [14]. During the process, the components were taken in different proportions. After numerous tests, the optimal ratios of the components - mole ratios of phenol, formaldehyde and modifier - were determined to be 1.0: 1.45: 0.05. In these ratios, the oligomer yield was high (99%). The dependence of the oligomer yield on the reaction time is shown in Figure 1.

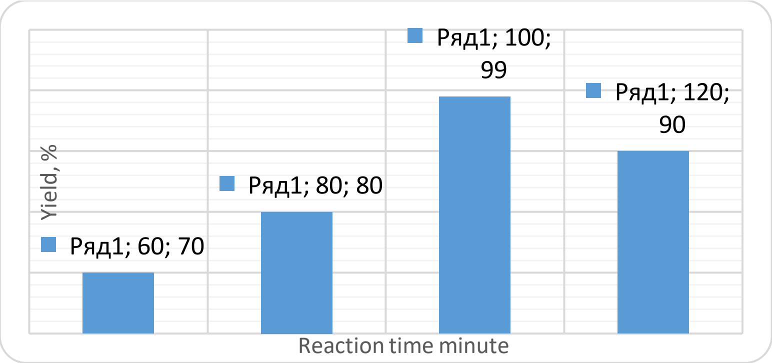


Figure 1. The dependence of the modified oligomer yield on the reaction time

Thus, the reaction was finished in an alkaline environment at a temperature of 85-90^{0}C for 1-1.5 hours.

3. Results and discussion

It is known that the process of modification is carried out in two ways: chemical and physical modification. In the study, the phenol-formaldehyde oligomer was chemically modified in the presence of a modifier. That is, the taken modifier participates in the formation of the main chain. For this reason, in order to determine the chemical composition and structure of the phenol-formaldehyde oligomer modified with diphenyamine, infrared spectra of the new oligomer were drawn.

Nicolet IS-10 infrared spectrophotometer (sensitivity 80, step ~42-45) was used to record the infrared spectra of the sample. In order to further clarify the obtained result, infrared spectra of phenol-formaldehyde oligomer (unmodified), modificator (diphenylamine) and modified FFO obtained in the same conditions were taken in the range of 400-4000 cm^{-1}.

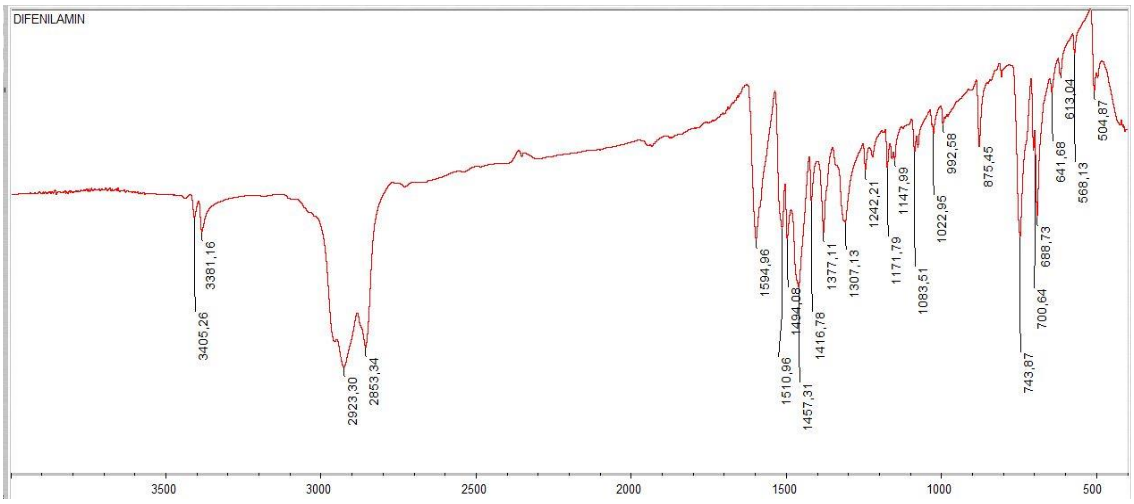


Figure 2. Diphenylamine

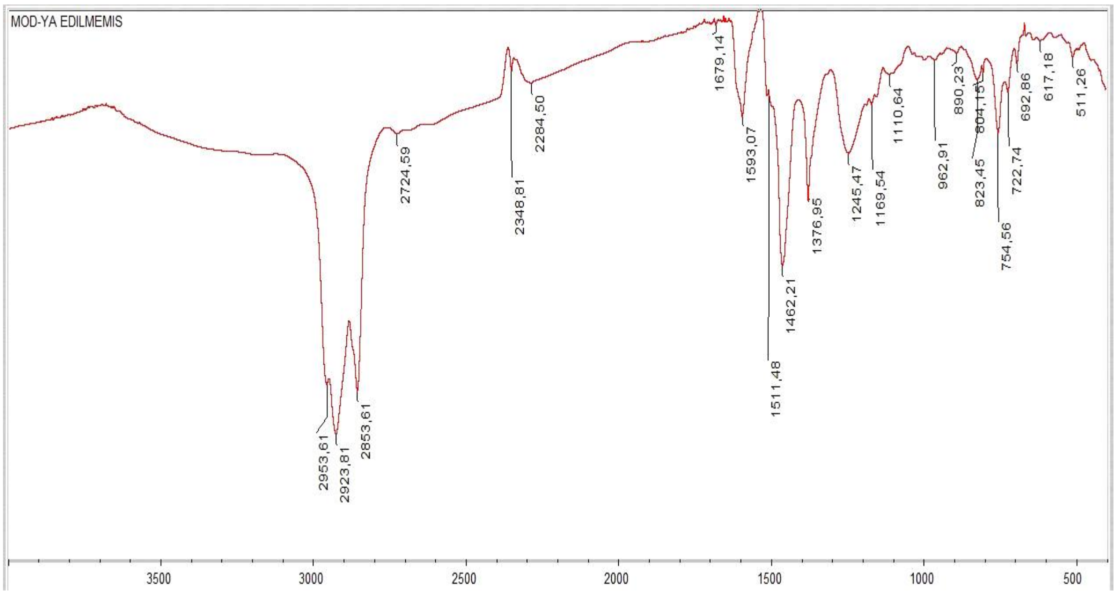


Figure 3. IR-spectroscopy of unmodified PFO

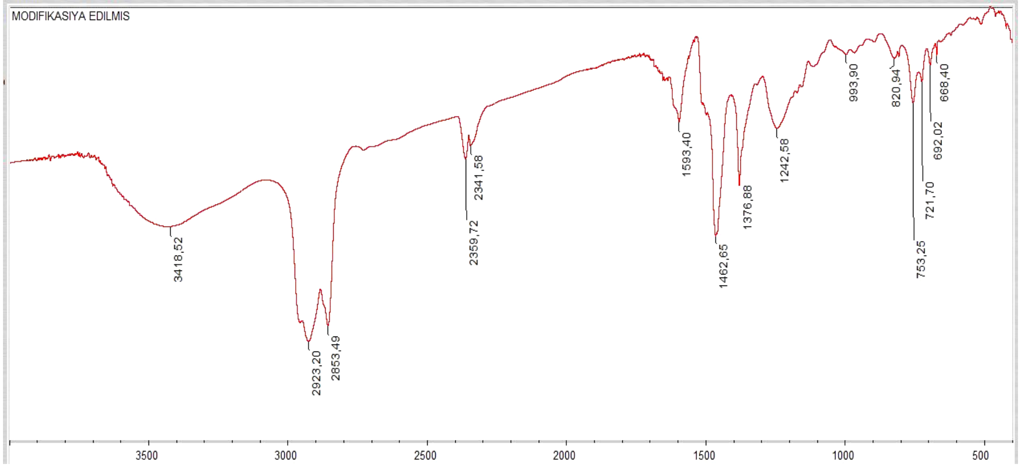
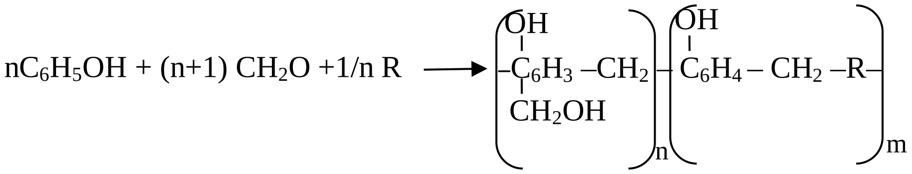


Figure 4. IR-spectroscopy of modified PFO

Identification of the infrared spectra of the modifying agent-diphenylamine, the unmodified phenyl-formaldehyde oligomer and the modified FFO confirms that this process is a chemical modification. As can be seen, the absorption bands of the valence vibrations of the C = C, CH bonds in the aromatic nucleus in all three spectra are $\nu_{c\text{-}c}$1593; 1511 cm^{-1}, $\nu_{C\text{-}H}$ 2953.61 cm^{-1} 2923.81 cm^{-1} 2853.61 cm^{-1} 1462 cm^{-1} 1376.95 cm^{-1}, the absorption band of deformation vibrations of CH bonds in the aromatic nucleus was observed in the intervals $\sigma_{C\text{-}H}$875 cm^{-1}, 743.87 cm^{-1}, 700.64 cm^{-1}, 688.73 cm^{-1}.

The absorption band of the N-H amino hydrogen bond in the IR spectrum of the modifier in the range of 3380-3434 cm^{-1} corresponds to the absorption band of valence vibrations corresponding to the position of the modified oligomer in the IR spectrum bound by $\nu_{N\text{-}H}$ = 3434 cm^{-1}, 3418 cm^{-1}.

The basis of the spectroscopic analysis can be shown as follows:



$$nC_6H_5OH + (n+1)\,CH_2O + 1/n\,R \longrightarrow \left(-\overset{OH}{\underset{CH_2OH}{C_6H_3}} - CH_2 \right)_n \left(\overset{OH}{C_6H_4} - CH_2 - R - \right)_m$$

There:$R=(C_6H_5)_2$ NH

4.Conclusions

Thus, the structure of the modified oligomer and the probable mechanism of the reaction were studied on the basis of comparison of the spectra of the obtained primary components (modifying agent and unmodified PFO) of diphenylamine-modified phenol-formaldehyde oligomer with IR-spectroscopy analysis.

5.References

1. A.S.Torlova, I.A.Vikalova, E.S.Pikalov. Production technology, properties and applications of composites based on phenol-formaldehyde resins. Technical sciences, №2, 2017, p. 96-98.
2. N.Pugazhenti, J.Thamilarasan, Sathesh Kumar. Preparation and properties phenol-formaldehyde resin reinforced with recycled cellulose fiber. Internation journal of mechanical engineering and technology. №8, 2017, p.59-64.
3. Наибова Т.М., Abdullayeva İ.Q.,Велиев М.Г.,Билалов Я.М., Гаибова Н.М. Модификация фенолоформальдегдных олигомеров непредельными хлор (бром) содержащими эпоксидными соединениями. Москва, Ж.Пластические массы, №12, 2005, 25-26 стр.
4. Naibova T.M., Abdullayeva İ.Q. Fenol-formaldehid oliqomerinin modifikasiya prosesinin ehtimal olunan kinetikası. J. Azərbaycan Ali Texniki Məktəblərinin Xəbərləri, ADNA, № 1 (47), 2007, s.12-18.

5. Poljansek and Krajne. Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. University of Ljubjana, Asta Chim.Slov. №52, 2005, p.238-244.
6. Abdullayeva İ.Q. Yapışqan kompozisiyası J. »Kimya problemləri». AMEA. №3, 2006, s.541-543.
7. Наибова Т.М., İ.Q.Abdullayeva. Modifikasiya olunmuş fenol-formaldehid oliqomeri əsasında inhibitor. J.«Azərbaycan Ali Texniki Məktəblərinin Xəbərləri», ADNA, №5-6 (69-70), 2010 , c 119-120.
8. Naibova T.M., Abdullayeva I.Q., Mammadova A.A. Materials of the III International Research and practice conference. Modifikatot of rubber mixtures. Science, Technology and Higher Education, Canada, 2013, p.121-122.
9. Л.И. Мачуленко, А.И. Нечаева, С.А.Донецкая, М.И.Бузин и др. Синтез и свойства новолаков на основе тройных смесей, содержащих фенол, фенолфталеин и фталимидинсодержащие бисфенолы, и сшитых сополимеров на их основе. Ж. Пластическая масс. №3-4, 2016, с.28-31.
10. М.Н. Амирасланова, А. М.Мустафаев, М. Дж.Ибрагимова, Р. А. Рустамов, Ф.Ю.Юсифзаде, П.Э.Исаева. Исследование физико-механических свойств защитных покрытий на основе азотсодержащих моноалкил (C_8-C_{12}) фенолоформальдегидных олигомеров, привитых с соевым маслом. Пластические массы, №11-12, 2018, 47-49.
11. Yuan Xin-hua, ShaoMei-xiu, Chen Min. Preparation and heat endurane of phenolic resin modified with linseed oil. Jiangsu Univ Natur Sci. №3, V.27, 2006, p.234-236.
12. Bilalov Yaşar Mahmud oğlu, Naibova Tamilla Muxtar qızı, Abdullayeva İradə Qurban qızı. Yapışqan kompozisiyası, Patent AR İ2009 0190. 02.11.2006
13.T.M.Naibova, F.Q. Seyfiyev, Y.Ə.Əzimov. Neft-mədən avadanlıqlarının elektrokimyəvi korroziyadan mühafizəsi üçün ingibitor. Azərbaycan Neft Təsərrüfatı, № 8, 2007, s. 37-40.
14. Maharramova U. Sa, Abdullayeva I. Gu. Determining the properties of adhesives based on modified phenol-formaldehyde oligomer with amine-aromatic compound, Актуальные проблемы гуманитарных наук, 2019, p. 7-10.

OR-III-5

COMPOSİTİONS BASED ON EPOXY OLİGOMER MODİFİED BY FİLLERS

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Abstract. In this work, we report that the epoxy oligomer was modified by mixing fillers with shavings, graphene oxide and diatomite separately for 1.5-2 hours, gradually adding at 50-70 degrees Celsius at different rates. Mix for 10-15 minutes while adding antioxidant to the epoxy oligomer (50-70 degrees Celsius) that has been modified with fillers. The adhesive composition is cooled to a temperature of 20-30 degrees. The physicomechanical and chemical properties of an adhesive composition based on epoxy oligomers modified with fillers have been investigated.

Keywords: epoxy oligomer, modification, graphene oxide, diatomite

1.Introduction

Epoxide oligomers (ED-16, ED-20) are widely used in the production of various materials - absorbents, coatings, adhesives and varnishes. Materials based on epoxide oligomers are used to cover or absorb different circuits and electrical conductivity in the electrical and radio industry [1,4]. Stickers are used to glue the metals, rubbers, plastics, woods, ceramics. Materials based on the epoxide oligomer are starting to be accumulated during the solidification process, so that the accumulation must be minimized. This remains a pressing problem.

2.Results and discussions

To address this urgent problem, the epoxide oligomer is first modified by a series of fillers (sludge, graphene oxide [2,3] and diatomite), and then, other components are included in the composition. Firstly, we have added different quantities of polyethylenepolyamine (PEPA) to the ED-20 oligomer. The physical and mechanical properties of the composition have been investigated. It has been found that adding 10 k.h. PEPA to the composition can result better properties [5,6]. (Table 1) Then, we have examined the effect of sludge filler on the properties of adhesive composition by giving the 10 k.h. PEPA to the adhesive composition based on the epoxide oligomer [7]. First, the epoxide oligomer has been heated at 50-70°C, then, stirred it for 1–2 hours. Afther that, a slurry filler has been gradually added at various ratios (Table 1). Then the antioxidant has been added and stirred for 10-15 minutes. The prepared mixture has been cooled to a temperature of 25-30°C, then (PEPA) has been added for 5-10 minutes.

Table 1. Ratios of mixture

№	The password of the mix	1	2	3	4	5	6	7	8
	Components:								
1	Epoxide Digomer (ED-20)	100	100	100	100	100	100	100	100
2	Sturdy	5.0	7.5	10.0	12.5	10	10	10	10
3	Sludge	-	-	-	-	3.0	6.0	9.0	12
4	Antioxidant	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Sum:	106.5	109.5	111.5	114.0	114.5	117.5	120.5	123.5

The surface of the metal plates has been purified by acetone and dried to determine the metal bond strength of the adhesive compositions based on epoxy oligomers. After cleaning and drying, glue has been applied to the surface and the metals have been placed over each other for 24 hours at room temperature. Then the adhesive metals have been heated and treated at 80-100°C for 1 minute and cooled. By pulling out and sliding the metals durability on gluing has been checked by the RMI-60 device.

Table 1.1. Results of composition properties

№	The password of the mix	1	2	3	4	5	6	7	8
	İndicators								
1	Strength limit in extension, Mpa	22.3	18.6	22.3	26.8	22.5	20.2	19.8	17.1
2	Relative extension (%)	35	18.8	35	20	30	20	18	15

3	Stacking during reinforcement(%)	1.6	0.8	1.6	2.2	1.3	0.9	0.6	0.2
4	Metal adhesion resistance, MPa	7.9	5.2	7.9	9.1	7.6	6.7	4.9	3.1
5	Sticky metal adhesion resistance,Mpa	8.2	6.0	8.2	9.3	7.2	7.0	5.7	4.3
6	TM-2 hardness	90.3	83.2	90.3	98.8	79.9	85.3	86.7	91.7
7	Rear bend elasticity, (%)	9	11.7	9.5	90	9.7	8.9	8.0	7.5
8	Tile adhesive, MPa	7.5	7.2	7.1	6.9	6.85	6.82	6.79	6.76
9	H_2SO_4 (28%)	28	30	31	31.5	33	33.2	34.3	35
10	KOH (40%)	17	18.5	18.8	19	19.2	19.6	19.8	19.9
11	Sea water (3%)	4	5.28	5.29	5.32	5.34	5.4	5.42	5.44

At the same time, the adhesive composition has been investigated in sheet form, room temperature, 24-hour drying shear strength, relative elongation, stiffness, and resistance to different aggressive environments. (H_2SO_4 (28%), KOH (40%), Sea water (3%)). All indicators are shown in Table 1.1.

When comparing the indices of the adhesive composition modified with the cuttings with the adhesive composition on the basis of the epoxy oligomer, we see that when the amount of sludge is 3-6 k.h. in the adhesive composition, the other properties improve against the aggressive environment without deterioration. This means that modifying the epoxide oligomer with cuttings does not have an effect on the properties of adhesive composition.

To improve the properties of the adhesive composition on the basis of the epoxide oligomer, the epoxide oligomer has been modified in various proportions with graphene oxide and calculated in the following composition. (table 2)

The adhesive composition has been made according to the specified technological process. Samples have been prepared to study the necessary properties of the prepared adhesive composition and compared with the properties of the adhesive composition obtained on the basis of the epoxy oligomer. (table 2.1)

When analyzing the results, we see that the number of air bubbles in the adhesive coating on the basis of epoxide oligomer modified with graphene oxide is lower than that of unmodified epoxide oligomers. This is explained by the fact that graphene oxide has been distributed in the epoxy oligomer volume, filling the gaps and reducing the number of air bubbles in the coating. However, the physical-mechanical properties of the adhesive composition based on epoxide oligomer modified by graphene oxide have shown lower values than the properties of adhesive compositions on the basis of unchanged epoxide oligomers. However, the adhesion of the adhesive coatings decreases during compression.

Table 2. Adhesive composition of ED-20 modified by graphene oxide

№	**Code of mixed compound**	**1**	**2**	**3**	**4**	**5**
	Components					
1	Epoxide oligomer (ED-20)	100	100	100	100	100
2	Sturdy (PEPA)	10	10	10	10	10
3	Graphene oxide	-	3.0	6.0	9.0	12.0
4	Antioxidant	1.5	1.5	1.5	1.5	1.5
	Sum:	111.5	114.5	117.5	120.5	123.5

Table 2.1. Physical-Mechanical properties of adhesive composition of ED-20 modified by graphene oxide

№	**The password of the mix**	**1**	**2**	**3**	**4**	**5**
	İndicators					
1	Strength limit in extension, Mpa	22.3	22.5	20.2	19.8	18.7
2	Relative extension (%)	35	37	32	28	18.9
3	Stacking during reinforcement(%)	1.6	1.4	1.0	0.8	0.6
4	Metal adhesion resistance, MPa	7.9	7.0	6.0	4.9	3.5
5	Sticky metal adhesion resistance, Mpa	8.2	7.2	6.1	5.0	3.7
6	TM-2 hardness	90.3	89.8	92.5	95.7	95.2
7	Rear bend elasticity, (%)	9	8.5	7.9	7.0	6.0
8	Tile adhesive, MPa	7.5	8.02	9.05	9.7	10.2
9	KOH (40%)	17	9.11	9.15	9.2	9.7
10	H_2SO_4 (28%)	28	15.2	15.7	15.9	16.2
11	Sea water (3%)	4	2.18	2.22	2.25	2.29

The composition of the adhesive based on the epoxide oligomer modified by the diatomite is given. (Table 3) The epoxide oligomer in various ratios with Diatomite has been modified according to the technology we mentioned earlier. Samples have been developed to study the properties of adhesive composition on the basis of diatomite modified epoxide oligomer. On the surface of the adhesive plate, designed to study physical and mechanical properties, air bubbles are rarely observed and the surface is very smooth. That's why the surface friction is clearly observed. The absence of bubbles can be explained by the fact that the epoxide oligomer has been fully absorbed by the diatomite and prevents the formation of air bubbles. The surface of the adhesive board is very smooth and has no bubbles. The physical-mechanical and chemical properties of the prepared adhesive composition have been studied. (Table 3.1.) An analysis of the properties of the adhesive composition shows that the (3-6 kh) adhesion composition based on epoxide oligomer modified by diatomite is 22.3-25.4 MPa, metal bonding strength to metal, 7.9 MP8. Mainly, adhesive metal bond strength - 8.2–10.3 MPa, adhesion-based bond strength to tree cutting - 7.5–8.9 MPa properties improved compared to adhesive composition based on unmodified epoxide oligomers.

Table 3. Composition of adhesive composition on the basis of diatomite modified epoxide oligomer

№	Code of mixed component	1	2	3	4	5	6
	Components						
1	Epoxide oligomer (ED-20)	100	100	100	100	100	100
2	Sturdy (PEPA)	10	10	10	10	10	10
3	Diatomite	-	3.0	6.0	9.0	12.0	15.0
4	Antioxidant	1.5	1.5	1.5	1.5	1.5	1.5
	Sum:	111.5	114.5	117.5	120.5	123.5	226.5

Table 3.1. Physical-mechanical properties of the glue composition based on the ED-20 modified by diatomite

№	The password of the mix	1	2	3	4	5	6
	İndicators						
1	Strength limit in extension, Mpa	22.3	23.9	25.4	26.8	25.6	25.0
2	Relative extension (%)	35	40	35	20	28	24
3	Stacking during reinforcement(%)	1.6	1.0	0.6	0.4	0.3	0.3
4	Metal adhesion resistance, MPa	7.9	8.9	9.8	10.0	8.2	7.0
5	Sticky metal adhesion resistance, Mpa	8.2	9.5	10.3	11.0	9.8	7.8
6	TM-2 hardness	90.3	91.6	95.2	97	97.5	98
7	Rear bend elasticity, (%)	9	9.8	9.2	9.0	8.0	7.6
8	Tile adhesive, MPa	7.5	8.5	8.9	9.2	9.8	9.9
9	KOH (40%)	17	2.71	2.75	2.86	2.87	2.91
10	H_2SO_4 (28%)	28	8.52	8.54	8.59	8.64	8.69
11	Sea water (3%)	4	0.075	0.076	0.079	0.082	0.086

On the other hand, the diatomite modified and unsaturated adhesive composition was fixed with 20% (1,2,4,8,16,18,20 hours) of 28% H_2SO_4, 40% KOH and 3% seawater. Dry to a fixed weight. By 18 hours, the weight of the adhesive composition increases, and after 18 hours the weight of the adhesive composition stabilizes. The weight of the unmodified adhesive composition reaches a constant weight and is less than its initial weight. that is, washing goes on. The adhesion composition on diatomite-modified and undamaged epoxide oligomers was 28% in H_2SO_4, 40% KOH and 3% salt solutions, respectively, with 8.53-28%, 2.75-17%, 0.076-4%. it is concluded that while the modified adhesive composition is swollen in the specified aggressive environments, the unchanged adhesive composition is also washed in the environment, that is, soluble. (except salty water)

A comparative analysis of the physical-mechanical and chemical properties of adhesive compositions based on cutaneous graphene oxide and diatomite modified epoxide oligomer shows that the adhesive composition on the epoxide oligomer (3-6 k.h.) diatomite has better performance. Not only does the diatomite modifier play a role in enhancing the epoxy oligomer construction process.

4.Conclusion

The epoxide oligomer has been modified by mixing the fillers with cuttings, graphene oxide and diatomite separately for a period of 1.5-2 hours, gradually adding at 50-70 degrees Celsius at different rates.

Blend for 10-15 minutes by adding antioxidant to the epoxide oligomer (50-70 degrees Celsius), which has been modified by fillers. The adhesive composition has been cooled to a temperature of 20-30 degrees and a mixture of 10 k.h. PEPA has been added to the mixture.

The physico-mechanical and chemical properties of the adhesive composition based on epoxy oligomers modified by fillers have been investigated.

Studies have shown that the adhesive composition based on the diatomite modified epoxide digomer has better performance than the adhesive composition modified by cutaneous and graphene oxide.

5.References

1. Методические указания к курсу «Высокомолекулярные соединения». Учебное пособие / сост.: Собанов А. А., Курамшин А. И., Бурнаева Л. М. и др. — Казань: Изд-во КазГУ, 2000. — 42 с.
2. Graphene Oxide Fundamentals and Applications Ayrat M. Dimiev, Siegfried Eigler
3. Hanaa M. Hegab, Linda Zou, Graphene oxide-assisted Membranes: Fabrication and potential Applications in desalination and water purification, Journal of Membrane Science, http://dx.doi.org/10.1016/j.memsci.2015.03.011
4. Ли Х., Невилл К. Справочное руководство по эпоксидным смолам. Пер. с англ. / Под ред. Н.В. Александрова – М.: Энергия, 1973 – 416с.
5. Черняк К.И. Эпоксидные компаунды и их применение – Л.: Судпромгиз, 1963 – 258с.
6. 4. Воробьев А. Эпоксидные смолы // Компоненты и технологии – 2003 – №8
7. Е.С. Ананьева, Л.Г. Полукеева, М.С. Чилизубова, А.В. Ишков Технологические характеристики пропиточных составов на основе эпоксидианового связующего и полиметилен-n-трифенилбората при изготовлении стеклопластиковых препрегов // Интернет-ресурс: http://all-epoxy.ru/tablizi/urow1/statia06.htm

PP-III-4

USAGE OF ACRYLIC ACID BASED POLYMER FOR STABILIZATION OF NICKELINE NANOPARTICLES

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Abstract: The synthesized Ni nanoparticles were stabilized with polyacrylic acid and SEM images of samples of nickel nanoparticles that stabilized with polyacrylic acid were presented in various magnifiers in a slow electron mode at a voltage of 15 kEv. Depending on the concentration, the solubility of nickel nanoparticles and the effect of pH and nanoparticle concentration on the average distribution of the suspension were studied.

Key words: Polyacrylic acid, suspension, nanoparticles, SEM

1.Introduction

Nanomaterials have been carefully studied from the point of view of fundamental scientific and technological interest in order to enter new classes of functional materials with unusual properties and applications. In recent years, nickel nanoparticles have been used in chemical catalysis, electrocatalysis, conductive dyes, magnetic notes, rechargeable batteries, medical diagnostics, superconducting devices and so on. Also, figure has become one of the most interesting metal nanomaterials in research due to various applications in the various fields [1-3].

Among all magnetic metal nanomaterials, nanostructured nickel materials are relatively difficult to prepare because, they are easily oxidized. Over the past decades, various chemical and physical approaches have been developed to overcome this challenge and produce high-quality nickel nanoparticles.

Among the developed various synthetic approaches, the solution can be provided in sensitive and different ways to gain control over particle size, morphology, crystal phase, and other suitable relationships.

İn conclusion, nanocrystals are also notable for their desired properties, manipulation and economic aspects of the process.

However, polymers have been widely used in chemical methods to prevent nanoparticles from crossing each other and to protect particles from sterility. Specially, polymers can stabilize metal nanoparticles through the steric mass of their frames and also bind weakly to the nanoparticle surface by heteroatoms acting as ligands. [5-7] Also, it has also been reported that polymers can control the shape and size of nanoparticles. Whereas, polymer-stabilized metal nanoparticles can disperse uniformly in organic solvents or water and can be mixed with reagents and products in a manner similar to homogeneous catalytic systems. Polyacrylic acid is used in this work and organized as a stabilizer.

2.Materials And Methods

Synthesis of polyacrylic acid (PAA).

Acrylic acid was bought from Merck company (Darmstadt, Germany) purified by vacuum distillation.

Materials used in the synthesis of polyacrylic acid in aqueous solution are: Acrylic acid (8.4 g), 30% hydrogen peroxide (0.3 ml) and distilled water (28 ml).

The synthesis of PAA process firstly, involves dissolving of hydrogen peroxide and acrylic acid in distilled water and secondly, starting from half time of the process, filling a clean dry ampoule made of semi-permanent refractory glass. The narrow end of the ampoule was sealed and placed in an oven at 100 degrees for 11 days for polymerization. After some period, the bulb is cooled and carefully opened. The final viscous liquid represents a solution of polyacrylic acid in water. Polyacrylic acid is released by evaporation of water in a vacuum.

Synthesis of nickel nanoparticles with polymer protection

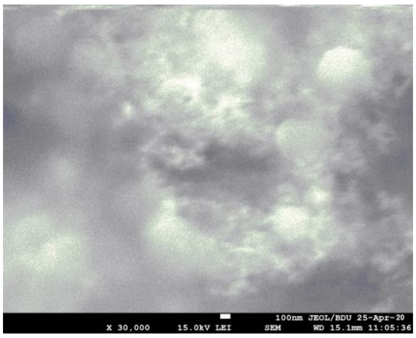
$NiCl_2$, $6H_2O$ (6 ml 2%, 0.50 mmol) were added to temporary mixing 36 ml water mixture and mixed well. After that, with better mixing, solid $NaBH_4$ (0.2 g, 5.29 mmol) was added. After adding of NaBH4, after 1 minute, 2 mol NaOH was added and immediately dissolved in 50 ml of water.

The following is an example for the preparation of nickel nanoparticles with PAA protection:

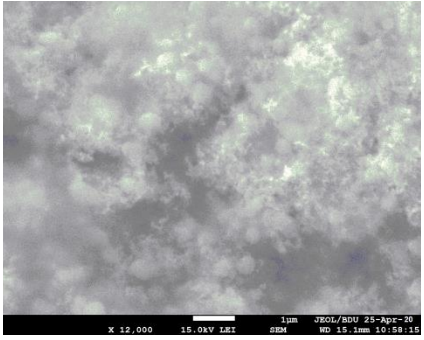
PAA (0.4 g. 63 vt% solution, 2.89 mmol in monomer units) was dissolved by slowly stirring in approximately 18 ml of water. NiCl2, 6H2O (6 ml 2%, 0.50 mmol) were added to the mixture, and after properly mixing, solid NaBH4 (0.2 g, 5.29 mmol) was added to the mixture. Then, one minute after the addition of NaBH4, 21 mmol NaOH was added and the volume of the solution was immediately raised to 50 ml of water. Other samples were prepared in a similar way and concentrations PAA and NaOH were changed. The amount of PAA solution taken for second and rhird samples were 1.6 and 6.4 g, and the pH of the samples was found to be between 11 and 12.

Characterization of nanostructure [4]: sem

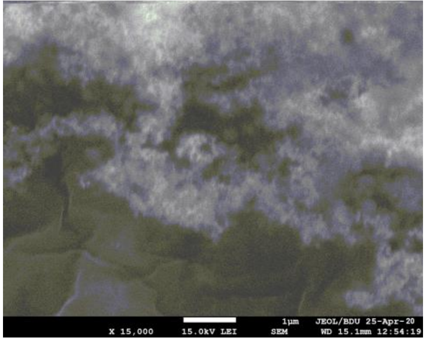
In the photo, SEM images of samples of nickel nanoparticles fixed with polyacrylic acid are presented in various magnifiers (12000) in slow electronic mode at a voltage of 15 kEv.



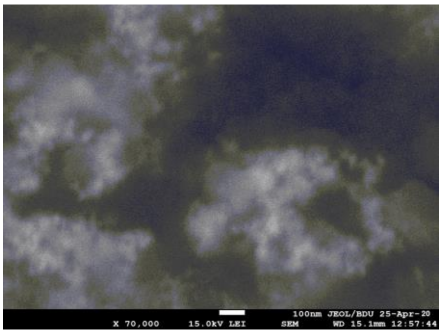
In the photo, SEM images of samples of nickel nanoparticles fixed with polyacrylic acid are presented in various magnifiers (15000) in slow electronic mode at a voltage of 15 kEv.



In the photo, SEM images of samples of nickel nanoparticles fixed with polyacrylic acid are presented in various magnifiers (30000) in slow electronic mode at a voltage of 15 kEv.



In the photo, SEM images of samples of nickel nanoparticles fixed with polyacrylic acid are presented in various magnifiers (70000) in slow electronic mode at a voltage of 15 kEv.



3.The discussion of the results

The easy reduction of aqueous nickel chloride with sodium borohydride results in sufficient monodisperse and electrochemically active nickel nanoparticles when using a coating polymer such as polyacrylic acid (PAA). The resulting nanoparticles were characterized by conductive electron microscopy, powder X-ray diffraction, infrared spectroscopy with Fourier transform, and cyclic voltameter. The size of Ni nanoparticles is very small and their concentration can be easily adjusted by changing the polymer.
Maintaining the correct pH level of the resulting solution is an important condition for the synthesis of Ni nanoparticles, otherwise Ni will later be converted to Ni2 +. It should also be noted that PAA cannot recover Ni2 + nickel at room temperature, so a reducing agent such as NaBH4 should be used as a stronger additive. In our case, the synthesis of the amount of NaOH used in the samples (in mmol) was determined using experiments and experiments. Polymer-nickel nanocomposites were separated by centrifugation.

After the addition of NaBH4, all solutions darken rapidly, regardless of the polymers and concentrations used.

Because Ni^{2+} ions are reduced by borohydride. The stoichiometric equation for the reduction of Ni^{2+} ions can be expressed as follows:

$$2Ni^{2+} + BH_4^- + 2H_2O = 2Ni^0 + BO_2^- + 2H_2 + 4H^+$$

All samples (pH 11 to 12) were very stable without discoloration over time. In all samples, a stable black color visually indicates the formation of stable spills, as in others.

t seems that the initial volume of the pH suspension has a weak effect on the average size of the suspension, but this effect decreases after the addition of the suspension. It appears that, the average particle size does not change when 200 mg / l suspension is added at pH = 5… 8; in a strongly acidic environment (pH = 9) the measurement decreases by 6%, but in an alkaline environment (pH = 9) it increases by 6.6%. A dependence is characteristic for more added suspensions: a decrease in particle size of 5.3% and 4.8% with a suspension concentration of 2 and 0.02 mg / l, respectively, when pH = 5 to pH = 4. are recorded. In other estimates, the pH may change if incorrect. The reduction in the size of nickel particles in an acidic environment may be due to its increasing rate. At the same time, a 100-fold reduction of nickel particles in the aqueous suspension indicates that it is nonlinear. It has been found that for suspensions with a concentration of less than 2 mg / l, the aggregate strength of the suspension does not depend on the concentration. Thus, the average particle size in aqueous suspension at pH = 7 is 3152, 232 and 214 hm, and in concentrated suspensions the particles are 200, 2 and 0.02 mg / l.

It has been shown experimentally that the solubility of the nanoparticles under study depends on the initial concentration of the suspension. Thus, in a suspension with a concentration of 100… 500 mg / l, the solubility does not exceed 1.5% (Table 2), and in this case the solubility decreases with increasing concentration as a whole (Table 1). According to the experimental results, the solubility of nanoparticles in 0, 10, 30 and 60 minutes is "0… 0.1… 0.2… 0.7%", respectively.

Long-term sample preparation of suspensions (up to two hours) leads to an increase in the solubility. It is likely that the sample will continue to settle in longer US (ultrasound) exposure.

Table 1. Dissolution rate of nickel in high concentration suspensions at pH = 7, measured after 120 minutes

	Concentration of nanoparticle, mg/l				
	100	200	300	400	500
Solubility degree, %	1,4 ± 0,3	1,1 ± 0,4	1,2 ±0,5	0,9 ±0,3	0,95 ±0,4

Table 2. Changes in the solubility of nickel nanoparticles in suspensions with a concentration of 200 mg/l

	Adjustment of Ultrasound time , minute.				
	0	10	30	60	120
Solubility degree, %	0	0,1 ±0,02	0,2 ±0,04	0,7 ±0,1	1,1 ±0,3

AThe solubility rate for a low concentration (0.02 mg / l) suspension varies from 63 to 82% depending on the acidity of the medium (Table 3.)

Table 3 .The degree of solubility of nanoparticles in suspensions with a concentration of 0.02 mg / l at different pH

	pH=4	pH=7	pH=9
Concentration of nanoparticle in suspension after using of ionchanging resins mkg/l.	4,26 ± 0,53	3,69 ±0,26	7,38 ±0,94
Solubility degree, %	78 ± 2,5	82 ± 3,3	63 ± 4,1

4.Conclusion

Nickel nanoparticles were synthesized and the size of Ni nanoparticles obtained as a result of the synthesis was determined. To study the effect of acidic environment on the dispersion of suspensions of nickel nanoparticles, different pH = 4… 9 was created. The pH was equalized with 1% HNO3 (65%, Fisher Scientific, TraceSELECT Ultra, Waltham, MA USA) and NaOH (98%, Sigma – Aldrich, SigmaUltra, St Louis, MO, USA) using acid-based titration. It has been shown that the acidity of the dispersion medium between pH 5 ... 9 has a small effect on the average particle size at the suspension of the same concentration (measurement varies within error), while for all suspensions studied in a strong acidic environment pH = 4, particle size decreases. The size of Ni nanoparticles is very small and can be easily adjusted by changing the polymer and concentration in each situation. At selected concentrations of polymers that provide a similar number of monomer units, polyacrylic acid has a very positive effect as a stabilizer. Research shows that polyacrylate anions at high positive potentials interact more with catalyst nanoparticles. The reduction of nickel chloride in aqueous solution with sodium borohydride results in electrochemically active nickel nanoparticles with sufficient monodisperse and separate use of a single-coated polymer such as polyacrylic acid (PAA).

5.Referens

1. Jortner J., Rao C.N.R., Nanostructured advanced materials. Perspectives and directions, Pure Appl. Chem 74 (2002) 1491–1506. DOI: 10.1351/pac200274091491
2. Panácek A., Kvítek L., Prucek R., Koláˇ r M., Veceˇ rová R., Pizúrová N., Sharma V.K., Nevˇ ecná T.J., Zboˇ ril R., Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity, Phys. Chem. J. B 110 (2006) 16248–16253. DOI: 10.1021/jp063826h
3. Li X., Elliott D.W., Zhang W., Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects, Critical Reviews in Solid State and Materials Sciences. 31 (2006) 111-122. DOI: 10.1080/10408430601057611
4. Hortola, P., SEM examination of human erythrocytes in uncoated bloodstains on stone: use of conventional as environmental-like SEM in a soft biological tissue (and hard inorganic material). Journal of Microscopy. 218 (2) (2005) 94-103. DOI: 10.1111/j.1365-2818.2005.01477.x
5. Tian H., Li J., Mu Z., Li L., Z.H. Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles, Sep. Purif. Technol. 66 (2009) 84–89. DOI: 10.1016/j.seppur.2008.11.018
6. Joo S.H., Zhao D., Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: effects of catalyst and stabilizer, Chemosphere 70 (2008) 418–425. DOI: 10.1016/j.chemosphere.2007.06.070
7. Satapanajaru T., Anurakpongsatorn P., Pengthamkeerati P., Boparai H., Remediation of atrazine-contaminated soil and water by nano zerovalent iron, Water Air Soil Pollut. 192 (2008) 349–359. DOI: 10.1007/s11270-008-9661-8

PP-III-5

SYNTHESIS AND TRANSFORMATIONS OF NITROGEN POLYCARBONYL COMPOUNDS OF THE CYCLOHEXANE SERIES AND RESEARCH OF THEIR ANTIMICROBIAL PROPERTIES

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Abstract: We have synthesized new derivatives of the cyclohexane series and screened the antimicrobial activity of some of the synthesized compounds and established the antimicrobial activity of derivatives of polycarbonyl compounds against test cultures of microorganisms. As a result of the study, it was found that all 4 samples exhibit pronounced bactericidal properties in relation to g (+) bacteria - S. aureus. All tested compounds showed the best efficacy against S. aureus and Ps. Aeruginosa.

Key words: dicarboxylate, antimicrobial activity, diazospirocycle, S. aureus and Ps. Aeruginosa.

1.Introduction

Carbonyl and polycarbonyl compounds occupy one of the leading positions in organic chemistry. The presence of an extensive raw material base in the form of available 1,3-dioxo compounds (acetylacetone, acetoacetic ether), aliphatic and aromatic aldehydes, a high chemical potential due to the presence of oxo groups of various types, makes these compounds very valuable building blocks of organic synthesis. Being polyfunctional compounds, they are capable of interacting with nucleophilic reagents, entering into condensation and heterocyclization reactions [1,2]. This makes it possible to design a wide range of derivatives on their basis, including those with antimicrobial, antiphage activity, analgesic, antipyretic and cryoprotective effects[2,3]. Despite the fact that certain successes have been achieved in the chemistry of compounds of this type, the selective reactivity of these compounds in a wide range of reactions with nitrogen-containing nucleophilic reagents, the conditions for cyclization into one or another heterocyclic system, and the spatial structure of the synthesized compounds remain unexplored or poorly studied. From these positions, it seems promising to develop new selective, multicomponent, cascade processes, to introduce new reagents into practice.

2.Materials and methods

All chemicals that we used in the synthesis were of analytical grade and were used after vacuum distillation in the form in which they were obtained: 4-methylbenzaldehyde, acetic acid, N-isobutylethylenediamine, phenacyl bromide, etc.

The antimicrobial action of some synthesized new chemical compounds was tested by the disk diffusion method and by the method of serial dilutions. To determine the sensitivity of the serial dilution method, the test substances were taken in the form of a 1% alcohol solution. Their dilutions were studied in the following concentrations: 1: 100, 1: 200, 1: 400, 1: 800.

Gram-positive (Staphylococcus aureus), gram-negative bacteria (Escherichia coli, Pseudomonas aeruginosa) were taken as test cultures. MPAc pH 7.2-7.4 was used as a nutrient medium, and Sabouraud's medium was used for Candida. The microbial load in all tests was 1 billion microbial bodies per ml, of which one drop was added to each tube. Sowings were carried out every 10, 20, 40, 60 minutes of exposure. For a comparative study of the activity of the studied drugs, known drugs (ethyl alcohol, rivanol, furacillin, nitrofungin) were taken as control.As a result of the tests, it was established that samples 2 and 4 have a strong antimicrobial effect. As can be seen from table 1, sample 4, at a dilution of 1: 400, kills E. coli in 10 minutes, staphylococci, and blue-green purulent sticks in 20 minutes, Candida in 40 minutes ... Sample 2 kills staphylococci in 20 minutes even at a dilution of 1: 800.

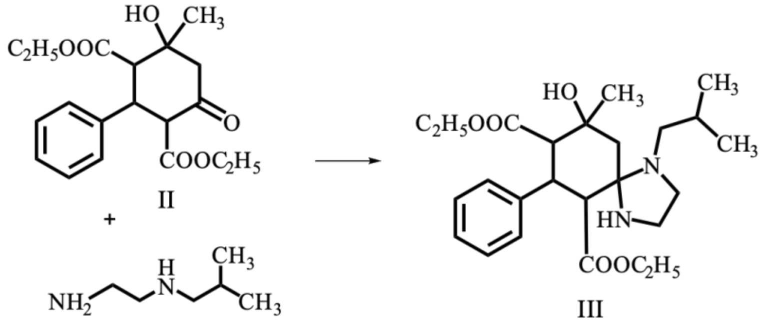
3.The discussion of the results

We carried out the diketone condensation [5] of 4-methylbenzaldehyde with acetoacetic ether in ethanol in the presence of catalytic amounts of piperidine (25 mol%), with the addition of a drop of glacial acetic acid. As a result, diethyl 4-hydroxy-4-methyl-2- (4-methylphenyl) -6-oxocyclohexane-1,3-dicarboxylate was isolated. We have carried out an X-ray diffraction study of a crystal of compound (I) obtained by slow crystallization from an alcohol solution. In the crystalline state, compound (I) exists exclusively in the ketone form. The cyclohexane ring has a chair conformation. All three bulky substituents (two ethoxycarbonyl and benzene ring) are located in the equatorial position.

Based on this dicarboxylate, we have synthesized new derivatives. Cyclohexane series. So, to begin with, we carried out a reaction to obtain diethyl 1-isobutyl-9-hydroxy-9-methyl-7-phenyl-1,4-diazaspiro [4,5] decane-6,8-dicarboxylate.

The reaction of diethyl 4-hydroxy-4-methyl-2-aryl-6-oxocyclohexane-1,3-dicarboxylates with nucleophilic aliphatic and aromatic monoamines has been relatively well studied. At the same time, the development of synthetic methods requires the search for new reagents and the development of techniques to expand their potential.

In this study, we studied the reaction of diethyl 4-hydroxy-4-methyl-2-phenyl-6-oxocyclohexane-1,3-dicarboxylate (II) with N-isobutylethylenediamine as a binukleophilic nitrogen nucleophilic reagent. The experiment showed that these reagents, taken in a molar ratio of 1: 1, form diethyl-1-isobutyl-9-hydroxy-9-methyl-7-phenyl-1,4-diaza-spiro [4,5] decane-6, 8-dicarboxylate (III) in 76% yield:



The structure of the synthesized compound (III) was studied by IR and NMR spectroscopy and X-ray diffraction.

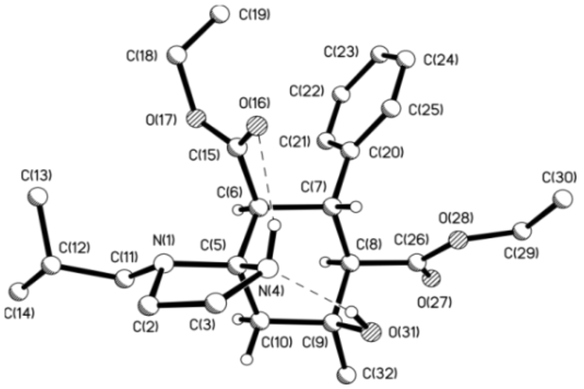
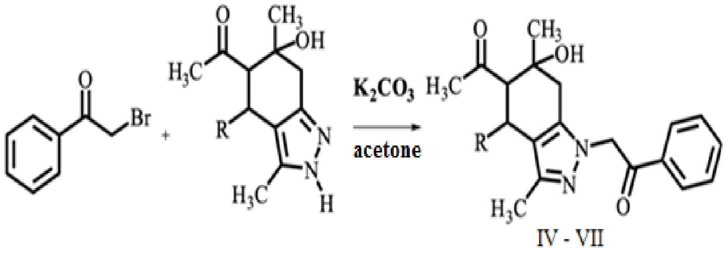


Fig. 2. Molecular structure of compound III according to X-ray diffraction data.

Molecule III contains a spirocyclic fragment consisting of two rings: a 5-membered heterocycle N1-C25-C3-N4-C5 (A) and a 6-membered carbocycle C5-C6-C7-C8-C9-C10 (B). Heterocycle A has a twist shape (half-chair). The B carbocycle has a chair shape. The isobutyl substituent has a pseudo-equatorial orientation (the N4-C5-N1-C11 torsion angle is -162.2 °). Apparently, our attempt to synthesize a spirocyclic system with a bulky substituent at position 1 was crowned with success precisely because the inversion of the nitrogen atom occurred during the reaction. Two intramolecular hydrogen bonds O (31) -H (10) ... N (4) and N (4) -H (1N) ... O (16) contributes to the stabilization of the form of the spirocyclic fragment.

In order to clarify the direction of further functionalization in alkylation reactions, the reaction of 4-aryl-4,5,6,7-tetra-hydro-2H-indazole derivatives of diacetyl (diethoxycarbonyl) substituted hydroxycyclohexanones with phenacyl bromide in boiling acetone in the presence of K_2CO_3 was studied. According to the results of reactions with yields of 70-77%, 2-(5-acetyl-6-hydroxy-4-R-3,6-dimethyl-4,5,6,7-tetrahydro-1H-indazole- 1-yl)-1-phenylethan-1-ones(IV-XII):



IV - VII

R = C_6H_5(IV), 4-CH_3O(V), 4-Cl-C_6H_5(VI), 2-furyl(VII)

X-ray diffraction analysis of a single crystal of 1- [6-hydroxy-4- (4-methoxyphenyl) -3,6-dimethyl-4,5,6,7-tetrahydro-2H-indazol-5-yl]-ethanone made it possible to determine the pyrrole and pyridine nitrogen atoms of the heterocycle. Alkylation with phenacyl bromide proceeds through the pyridine nitrogen, so it has greater nucleophilicity and basicity.

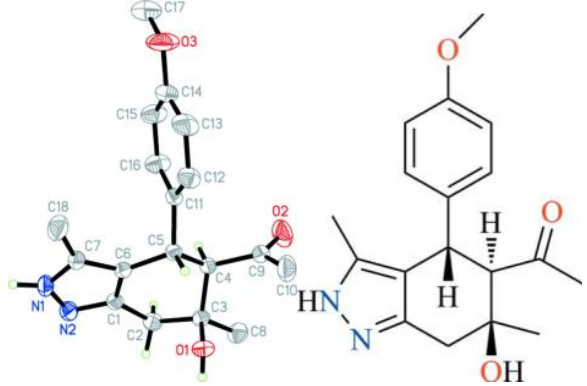
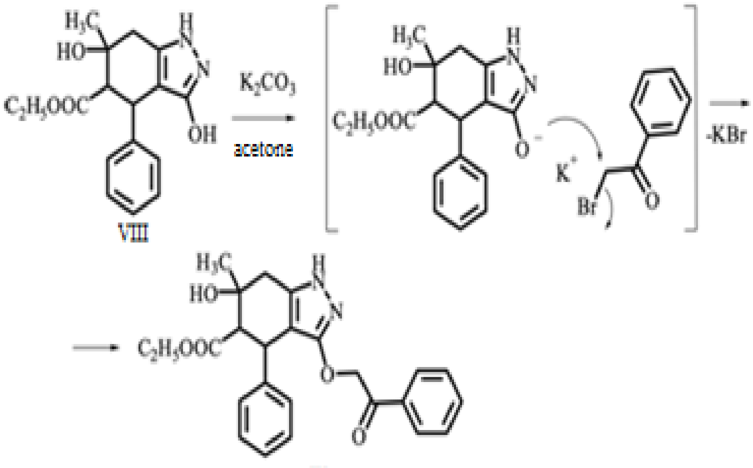


Fig. 5 Molecular structure of compound (1- [6-hydroxy-4- (4-methoxyphenyl) -3,6-dimethyl-4,5,6,7-tetrahydro-2H-indazol-5-yl]-ethanone)

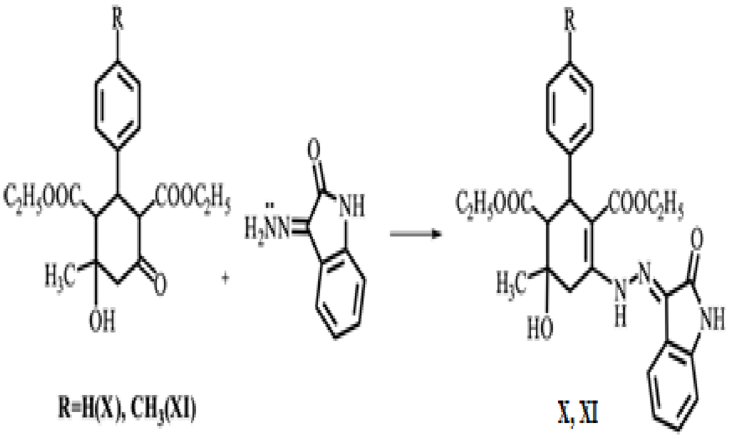
The reaction of phenacyl bromide with 3,6-dihydroxy-6-methyl-4-phenyl-4,5,6,7-tetrahydro-1H-indazole-5-carboxylate (VIII) in boiling acetone and in the presence of K_2CO_3 leads to the product O-alkylation - ethyl 6-hydroxy-6-methyl-3- (2-oxo-2-phenylethoxy) -4-phenyl-4,5,6,7-tetrahydro-1H-indazole-5-carboxylate (IX)



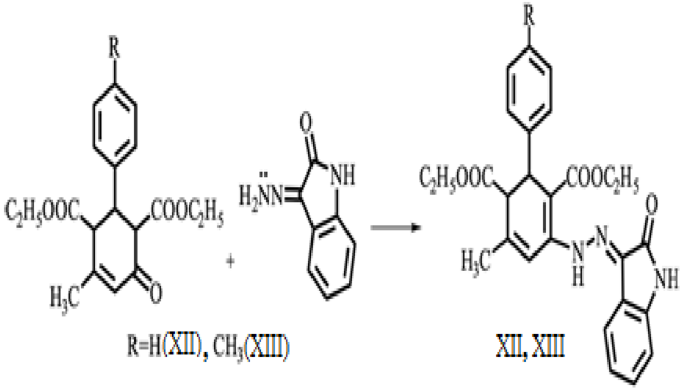
IX

Since the hydroxyl group is acidic, an anion is formed by the base. The negative charge is more dispersed on the oxygen atom, as on a more electronegative element. On the other hand, acetone, being a polar aprotic solvent, favors the separation of the O^- // K + ion pair, thereby promoting O-alkylation. The mass spectrum of compound (IX) contains the main peak (434) corresponding to a molecular ion.

We have found that the interaction of diethyl 2-aryl-6-hydroxy-6-methyl-4-oxo-cyclohexane-1,3-dicarboxylates with isatinhydrazone leads to diethyl 3-hydroxy-3-methyl-5- (2- (2-oxoindolin-3-ylidene) hydrazinyl) -1,2,3,4-tetrahydro- [4`-R-1,1`-bi-phenyl] -2,6-di-carboxylates (X, XI) (yields 80-87%)



The reactions of hydrazone with diethyl 5-methyl-3-oxo-1,2,3,6-tetrahydro- [4`-R-1,1`-diphenyl] -2,6-dicarboxylates were also studied. These compounds contain an α, β-unsaturated ketone fragment, along with the C = C bond of which nucleophilic addition of amines is possible.



It was found that the primary amine group of the hydrazone interacts with the ketone group of the alicyclic to form the corresponding enamine. Consequently, the Aza-Michael addition at the multiple C = C bond does not occur. Reaction products of diethyl 3-methyl-5- (2- (2-oxoindolin-3-ylidene) hydrazinyl) -1,2-dihydro [4`-R-1,1`-diphenyl] -2,6-dicarboxylates (XII, XIII) were isolated in 70-73% yields. We found that the rate of interaction of isatinhydrazone increases with the use of catalytic amounts of hydrochloric acid. The structure of the synthesized compounds (XII, XIII) was proved using IR and NMR spectroscopy.

Determination of the sensitivity of bacteria to some synthesized compounds.

The long latency period of the antimicrobial action can be explained by the unequal number of membranes surrounding those active centers with which the tested compounds interact. The increase in the efficiency of the diluted preparations proves good permeability through the cell membranes. The most important thing is that regardless of the content of various functional groups, they are effective against all microorganisms.

The data obtained show that the bactericidal action of the drugs is associated with their inhibitory effect on the formation of the cell wall of microorganisms, protein denaturation, impaired permeability of the cytoplasmic membrane, with inhibition of enzymes important for the vital activity of bacteria.

Table 1. Antimicrobial action of the synthesized new compounds.

Culturetest	Exposure time (min)	Compounds															
		(III) (sample**№ 1**)				**(IV)**sample**№2**)				**(V)** (sample**№3**)				**(IX)** (sample**№4**)			
		1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
St.Aureus	10	-	-	-	+	-	-	-	+	-	-	+	+	-	-	+	+
	20	-	-	-	+	-	-	-	-	-	-	-	+	-	-	-	+
	40	-	-	-	+	-	-	-	-	-	-	-	+	-	-	-	+
	60	-	-	-	+	-	-	-	-	-	-	-	+	-	-	-	+
Ps.Aeruginoza	10	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+	+
	20	-	-	+	+	-	-	+	+	-	-	+	+	-	-	-	+
	40	-	-	+	+	-	-	+	+	-	-	-	+	-	-	-	+
	60	-	-	+	+	-	-	+	+	-	-	-	+	-	-	-	+
E.coli	10	-	-	+	+	-	-	+	+	-	-	+	+	-	-	-	+
	20	-	-	+	+	-	-	+	+	-	-	+	+	-	-	-	+
	40	-	-	+	+	-	-	+	+	-	-	-	+	-	-	-	+
	60	-	-	+	+	-	-	+	+	-	-	-	+	-	-	-	+

4.Conclusion

The reaction of N-isobutylethylenediamine with diethyl 4-hydroxy-4-methyl-2-phenyl-6-oxocyclohexane-1,3-dicarboxylate was the first to synthesize a compound with a diazaspirocyclic framework. The X-ray diffraction analysis established the presence of intramolecular hydrogen bonds of two O-H ... N and N-H ... O types, the diequatorial position of ethoxycarbonyl substituents in the cyclohexane ring. The annelated tetrahydro-2H-indazole derivatives obtained on the basis of diacetyl (diethoxycarbonyl) substituted hydroxycyclohexanones and hydrazine hydrate was involved in the reaction with phenacyl bromide in the presence of K_2CO_3 in boiling acetone in order to determine the direction of their further functionalization.

It was found that, depending on the structure of indazoles, the reactions proceed as N- and O-alkylation. Reactions of diethyl 2-aryl-6-hydroxy-6-methyl-4-oxocyclohex-san-1,3-dicarboxylates and their dehydration products - diethyl -5-methyl-3-oxo-1,2,3,6-tetrahydro-[4'-R-1,1'-diphenyl]-2,6-dicarboxylates with isatinhydrazoneproceed as amination at the most active center - the carbonyl group of the alicyclic, with the formation of the corresponding cyclohexene (diene) amines. The study of the reactions of diethyl 5-methyl-3-oxo-1,2,3,6-tetrahy-dro- [4'-R-1,1'-diphenyl] -2,6-dicarboxylates with hydroxylamine hydrochloride showed for the first time that the use of potassium carbonate as a base contributes to the implementation of the direction of heterocyclization - the production of ethyl 6-methyl-3-oxo-4-aryl-1,3,4,5-tetrahydrobenzo [c] isoxazole-5-carboxylates. Among the synthesized compounds, substances with antimicrobial activity exceeding the activity of reference drugs were isolated.

5.Referens

1. Гейн В.Л., Левандовская Е.Б., Носова Н.В. Синтез и противомикробная активность N,N-диарилl-2-арил-6-гидрокси-6-метил-4-оксоциклогексан-1,3-дикарбоксамидов // Хим-фарм. журн., 2007, т 41, №.12, с.21-23
2. Гейн В.Л., Носова Н.В., Потемкин К.Д. и др. Синтез, строение и взаимо-действие с нуклеофильными реагентами диизопропил-2-R-6-гид-рокси-6- метил-4-оксоциклогексан-1,3–дикарбоксилатов // ЖОрХ, 2005, т.4, №7, с.1039-1045
3. Зинина Е. А., Поплевина Н. В., Сорокин В. В. Первый пример получения этил 4-арил 2-карбоксиметил-2-метил-5-оксодигидрофуран-3-карбоксила-тов в реакции Байера-Виллигера // ХГС, 2012, т.48, № 10, с.1675-1678
4. Зинина Е.А.,Шуршалова Н.Ф.,Нечаева О.В. и др. Антимикробная активность адамантилметиленаминоциклогексан дикарбоксилатов // Изв. Са-ратов. Ун-та, Сер. хим., биол., экол., 2012, т.12, №2, с.8-9
5. Hote B., Lokande P. Novel and efficient synthesis of 4-indazolyl-1,3,4-tri-substituted pirazole derivatives//Synth. Commun.,2014,v.44,No10,pp.1492-1500

OR-III-4

COORDINATION METHODS OF THIOLIGANDS IN TRINUCLEAR COMPLEXES OF PLATINUM (II)

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Abstract. The trinuclear complexes with simple and mixed ligands of platinum (II) with mercaptoethanol and mercaptoethylamine have been generated and their contents and structures investigated by numerous physico-chemical methods. Mercaptoethanol ($SHCH_2CH_2OH$) is coordinated monodentally with just sulfur atom and forms pentacyclic metalchelate ring, where as mercaptoethylamine ($HSCH_2CH_2NH_2$) is coordinated monodentally as well as bidentally and forms identical ring (pentacyclic metalchelate). The sulfur atom of ligands plays a bridge role between metals in the trinuclear platinum complexes. The hydroxyl group of mercaptoethanol does not participate in the coordination.

Keywords: mercaptoethanol, mercaptoethylamine, platinum, trinuclear, metalchelate cycle, bridge, terminal.

1.Introduction

The great interest in ligands containing sulfur hydroxyl, sulfur amine groups is related to their containing functional groups that belong to biological systems. In the other hand, it is possible to generate coordination compounds that are variously resistant with coordination sphere purposively synthesizing ligands with platinum salts [1].

As an investigating object, mercaptoethanol $HSCH_2CH_2OH$ and mercaptoethylamine $HSCH_2CH_2NH_2$ ligands containing sulfur-oxygen, sulfur-nitrogen donor atoms have been taken. These ligands have universal effect and form very stable and soluble in water complex compounds that are able to solve some problems of the science, technology and medicine [2]. There are reference informations about biological activity of the complex compounds of the ligands and their some derivations containing sulfur, oxygen and nitrogen donor atoms [3]. In the proffered work trinuclear complexes with simple and mixed ligands have been synthesized with palladium and investigated. Complexes with simple and mixed ligands have been synthesized and studied comparatively considering that the polynuclear mixed complexes of palladium are technically and medically important.

2.Experimental part

During experimentation 2-mercaptoethanol – $HSCH_2CH_2OH$ and 2-mercaptoethylamine (mercamine) – $HSCH_2CH_2NH_2$ produced by “Ferak” and “Serva” companies, respectively, have been used without decontamination. The IR-spectra of the synthesized complexes and ligands were drawn in “Thermoscientific, Nicoltis 10” and “Bruker IFS-113V” spectrometers, in vaseline suspension, fluorinated oil and pill-shaped KBr(in spectrum diapason of 200-500, 400-4000cm^{-1}). The electroconductivities of the complexes in aqueous or aqueous-alcohol solutions were measured by “KEL-1M2” conductometer at 25^{0}C. Thermical resistance and reactions were investigated in “STA 449 F3 Yupiter” derivatograph of “NETZSCH” company heating 10^{0}C in every minute. The element analysis of the synthesized complexes were carried out with “CHNSOE Carlo ERBA” analyzer.

Synthesis of $[Pt_3(SCH_2CH_2OH)_4(NH_3)_2Cl_2]\cdot 2H_2O$ complex (I). 0,60g (1,09mmol) of $K_2[PtCl_4]$ salt was dissolved in 20 mL of NH_4OH solution in compact flask regularly stirring at 55^{0}C and filtered through a paper filter to remove partially reduced metallic platinum. 0,50g (6,35mmol) of ligands – mercaptoethanol 10% more than stoichiometric ratio was added to filtered hot (45^{0}C) solution. Reaction mixture (pH=8,5) was continuously heated in compact flask for 3 hours at 55-65^{0}C. The dark pink complex compound was formed from obtained same-coloured solution. The complete precipitation process proceeds for 2 days at 6^{0}C. The precipitation was filtered and washed with cold water, alcohol and ester. The obtained substance first was dried at room temperature, then in vacuum over $CaCl_2$ till it got a stable weight. Yield was 0,69g (46%).

For $C_8H_{30}S_4N_2Cl_2O_6Pt_3$ formula:
Pt – 56,31; S – 12,18; N – 2,56; Cl – 6,63; C – 9,11; H – 2,73 were found.
Pt – 56,57; S – 12,39; N – 2,70; Cl – 6,85; C – 9,28; H – 2, 90 were calculated.
The compound dissolves well enough in hot water and alcohol.

Synthesis of [$Pt_3(SCH_2CH_2NH_2)_2(SCH_2CH_2OH)_2(NH_3)_2Cl_2$] complex (II). 0,36g (0,37mmol) of [$Pt_3(SCH_2CH_2NH_2)_4$]$Cl_2\cdot H_2O$ complex compound obtained by known way [4] was taken and prepared suspension mixing in 20 mL of hot NaOH solution. This suspension dissolved when reaction mixture was stirred at 55^0C for 40 minutes and it changed into transparent solution. 0,09g (1,15mmol) of mercaptoethanol $HSCH_2CH_2OH$ dissolved in 10mL water was added into reaction mixture, as a result of that light pink precipitation was formed. Reaction proceeded (pH=9) for 1,5 hours at 45^0C. When precipitation process finished completely the compound was filtered and removed from solution and washed first with cold water, then with alcohol and ester. Obtained complex compound was dried in vacuum over $CaCl_2$ until it got a stable weight. Yield was 0,28g (76 %).
For $C_8H_{28}N_4S_4Cl_2O_2Pt_3$ formula:
Pt – 58,56; S – 12,68; N – 5,49; Cl – 6,92; C – 9,57; H – 2,73 were found.
Pt– 58,73; S – 12,86; N – 5,61; Cl – 7,11; C – 9,64; H – 2,80 were calculated.
The compound dissolves well enough in hot water and alcohol.

Synthesis of [$Pt_3(SCH_2CH_2NH_2)_2(SCH_2CH_2OH)_2Cl_2$] complex (III). 0,32g of complex II was transferred into compact flask, 20mL of water and 10mL of 15% KOH solution added and regularly stirred for 1,5 hours at 65^0C. Ultimately, the light pink colour of reaction mixture was changed into dark yellow (pH=9,5), then transparent solution filtered and evaporated at 50^0C in water-bath until little volume. Obtained syrupy mass was treated with 70mL chloroform at first, then the exess amount of solvent dismissed, the yellowish compound precipitated in this step. Precipitation was filtered and washed with cold alcohol and ester. Formed compound was dried over $CaCl_2$ until a stable weight. Yield is 0,24g (83%).
For $C_8H_{22}N_2S_2Cl_2O_2Pt_3$ formula:
Pt – 65,39; S – 7,26; N – 3,35; Cl – 7,58; C – 10,47; H – 2,22 were found.
Pt – 65,15; S – 7,14; N – 3,12; Cl – 7,88; C – 10,69; H – 2,45 were calculated.
This substance dissolves well in water and alcohol.

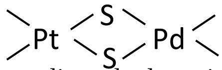
3.Results and discussion

Mercaptoethanol and mercaptoethylamine are soft hydroxides and contain not only OH and NH_2 groups, but also polar HS group has strong reaction ability. A sulfohydryl group differs bitterly from triol >S functional group with respect its reaction ability. Therefore, it can be presumed that complexes with simple and mixed ligands formed with palladium and ligands containing sulfohydryl group have different contents, structures, resistances and other properties.

The ratios, medium, solvents, temperature and other factors of synthesis are optimal. The high yield of pure complex compounds [$Pt_3(SCH_2CH_2OH)_4(NH_3)_2Cl_2$]$\cdot 2H_2O$ (I),
[$Pt_3(SCH_2CH_2NH_2)_2(SCH_2CH_2OH)_2(NH_3)_2Cl_2$](II) and
[$Pt_3(SCH_2CH_2NH_2)_2(SCH_2CH_2OH)_2Cl_2$] (III) is acquired only under above-mentioned condition seriously supervising.

To get whole results about structures of complexes IR-spectra of the ligands and newly synthesized coordination compounds have been studied and assayed comparatively. SH functional groups belong to both ligands – mercaptoethanol and mercaptoethylamine are characterized by 2568 and 2562 cm^{-1} adsorption bands in IR-spectra, respectively. These adsorption bands are identical to reference materials [4,5] and any adsorption band pertaining to HS-group was not recorded in IR-spectra of all synthesized I–III complexes. And it implicitly indicates that HS group is deprotonated with central atom and forms $\nu_{Pt\text{-}S}$ valence bond. 288, 294 and 330 cm^{-1} adsorption bands were recorded within 200–400 cm^{-1} adsorption zone in IR-spectrum of complex I. First two adsorption bands $\nu_{Pt-S}^{koord.}$ belong to bridge-shaped Pt-S valence bond. Other strong 330cm^{-1}adsorption band belongs to $\nu_{Pt-Cl}^{ter.}$ terminal bond [6]. The first two adsorption bands from 284, 286, 290 and 292 cm^{-1} partially slid and clearly expressed in IR-spectrum of complex II and are close to above-mentioned adsorption bands belong to mercaptoethanol that forms valence bond in Pt-S bridge position, the other two bands belong to mercaptoethylamine Pt–S valence bond [7]. Other ledgeless 328 cm^{-1} adsorption band belongs to $\nu_{Pt-Cl}^{ter.}$ terminal valence bond.

When complex II is treated in alkaline medium ammonia is ejected from coordination sphere by amine group of mercaptoethylamine and as a result of that trinuclear metalchelate complex III is formed. In consequence of chelateformation the innercomplex electronic density distributed samely among atoms and the adsorption bands in IR-spectrum of complex appear clearly. Three slightly slipped adsorption bands – 262, 276 and 293 cm^{-1} – of Pt-S bond indicate innercomplex high spin splitting and low spin splitting, in other words destroying its flat plane structure. Three adsorption bands of platinum sulfur bridge bond show that sulfur atom has pyramidal structure, and this makes its configuration “armchair-shaped” [8]. Expression of Me-S valence bond in bridge position with three adsorption bands indicates that complex has spin configuration. This case is known from reference source [9].



The complexed and complicated adsorption bands appear within 2400-3700cm^{-1}adsorption zone in IR-spectra of complexes I-II, it means that these complexes have hydrogen bonds like OH….Cl or NH$_2$…Cl. On the other hand, the adsorption bands belonging to OH and NH$_2$ groups of the ligands were not expressed in IRS of the complexes. Such situation is often faced in references [10].

The high intensive $\delta_{(N-H)}$ adsorption bands observed in IR-spectra of complex I (II) probably belong to N-H deformative bond and Pt-N valence bond. The expressions demonstrating mentioned adsorption bands find place in reference [11].

As a result of forming of pentacyclic

metalchelate ring in bridge form and of coordinating of mercaptoethylamine bidentally the Pt-N in terminal position is characterized by two – 371 and 382 cm^{-1} adsorption bands in IRS of valence bond unlike complexes I and II [11,12].

The hydrogen bonds existing between NH…Cl and H$_2$O…Cl in IR-spectra of complexes I-III stabilize the structures of the complexes, and this prompts structural changes not to happen in aqueous solution of the complexes.

The numerical values (40,52,47 Om^{-1}cm^{2}mol^{-1}) of electroconductivities of all three complexes in 10^{-3}M aqueous and aqueous-alcohol solution demonstrate that these complexes are nonelectrolates and the estimated formulas for them are correct.

Thermical decomposition of complexes I-III is different from each other depending on the ligand surroundings of central atom. Thus, the thermical decomposition of complex I takes place in two steps. In first step, in other words, at 165^{0}C dehydration happens, the second step is ended with decomposition of complex without melting at 290^{0}C. Complex II is decomposed at 270^{0}C, III at 320^{0}C without melting. The last product of thermolysis of all three complexes is PtO.

$$[Pt(SCH_2CH_2OH)_4Cl_2(NH_3)_2]\cdot 2H_2O) \xrightarrow{165^0 C} [Pt(SCH_2CH_2OH)_4Cl_2(NH_3)_2] \xrightarrow{290-600^0 C} PtO$$

In complex III with mixed ligand mercaptoethylamine is coordinated bidentally and forms two symmetrical pentacyclic metalchelate ring, therefore it is decomposed in higher temperature than its analogues.

The antimicrobial properties of every complex have been learned comparatively. The complex I unlike other complexes indicates strong antimicrobial property. The microbial properties decrease according to I>II>III order.

4.Conclusion.

1. It has been demonstrated by modern physicochemical ways that newly synthesized complexes with simple and mixed ligands containing sulfur-oxygen, sulfur-nitrogen donor atom are trinuclear.
2. In complex I four mercaptoethanol molecules from sulfur atoms are coordinated monodentally with platinum in bridge position. In complex II mercaptoethanol and mercaptoethylamine are coordinated monodentally and form coordination compounds with mixed ligand.
3. In complex III mercaptoethanol is coordinated monodentally, mercaptoethylamine is coordinated forming pentacyclic metalchelate ring, namely complex compounds with mixed ligands and mixed coordination.

5.References

1. H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe, H. Yasui.// Coord. Chem. Rev. 2002 (226) p.187-198
2. A.I. Matesanz, P. Souza.//J.Inor.Biochem.2007 (101) p.1354-1361.
3. T. Rosu, E. Pahontu, S. Pasculescu, R. Georgescu, N. Stanica, A. Curaj, A. Popescu, M. Leabu. //Eur. J. Med. Chem. 2010 (45) p. 1627-1634.
4. Hasanov Kh.I., Fatullayeva S.S., Tagiev D.B., Mirzai J.I.//J. Azerb.Chem.. 1998. №3. p. 38–42.
5. Yefimenko I.A., Hasanov Kh.I., Gorbunova Y.Y.//Pres. RAN. 1992.(326)p. 654–660.

6. Fedorova O.V., Koryanova O.V., Rusinova G.L.//General Chemistry J. 2000. (45) p.1654–1657.
7. D.Gambino, L.Otero, M.Vieites, M.Boiani, M.Gonzalez, E.J.Baran, H.Cerecetto, Spectrochim. Acta.//A 2007(68) p.341-348.
8. D. Vazquez-Garcia, A. Fernandez, J.J. Fernandez, M. Lopez-Torres, A. Suarez, J.M. Ortigueira, J.M. Vila, H. Adams.// J. Organomet. Chem. 2000 (595) p. 199-207.
9. V. Suni, M.R.P. Kurup, M. Nethaji, Spectrochim.// Acta Part A 2006 (63) p. 174-181.
10. A.P. Rebolledo, M. Vieites, D. Gambino, O.E. Piro, E.E. Castellano, C.L. Zani, E.M. Souza-Fagundes, L.R.Teixeira, A.A Batista, H.Beraldo.//J.Inorg.Biochem. 2005(99) p.698-706.
11. L. Papathanasis, M.A. Demertzis, P.N. Yadav, D. Kovala-Demertzi, C. Prentjas,A. Castineiras, S.Skoulika, D.X.West.//Inorg.Chim.Acta 2004 (357) p. 4113-4120.
12. R.A.Alderden, M.D.Hall, T.W. Hambley.//J.Chem. Ed. 2006 (83) 728-734.

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FORECASTİNG OF PRECİPİTATİON OF HİGH-MOLECULAR CHEMİCAL COMPOUNDS İN OİLS

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Abstract. The article examines the process of precipitation of high molecular compounds (asphaltene, resin, paraffin) in two different Azerbaijani oils by mixing them in different proportions. Experimental tests to determine the amount of ballast deposited from the oil mixture have shown that, in general, the sedimentation process can take months. The bulk of the total ballast can collapse during the first day of oil mixing. The amount of colloidal particles in the system increases, with the mixing of different types of crude oils, then some changes are observed in a number of parameters. The presence of these compounds is not only the causes of accidents, but also has a significant impact on the rheology of oils.

It has been established that, depending on the mixing ratio of the oils, it is very crucial to take into account the duration and behaviour of the precipitation process in oil in order to avoid problems during their storage and transportation or to prevent them in time. An empirical expression has been suggested in this review in order to analyze precipitation of ballasts.

Key words: blended oils, transportation, precipitation, physical-chemical properties, empirical model.

1.Introduction.

It is known that the deterioration of rheological parameters in the processes of recovery, transportation and storage of oils containing asphaltene, resin, paraffin especially occurs at lower temperatures. In the meantime, cyristallization and precipitation of high-molecular compounds occur, which leads to worsening and even disruption of technological processes. Therefore, depending on the time and temperature, the oils entering the transport networks are not homogeneous due to unstable quality indicators. It is possible not only to increase the efficiency of technological processes during oil storage, transportation and refinery, but also to achieve good economic results by mixing this type of heavy crude oils with light oils. The research has been carried out by Prof. I.N.Yevdokimov and others shows that it is an undeniable fact that specific problems arise when mixing different types of crude oil with each other or with light oil [1-4,8]. Interaction of oils with different chemical composition leads to deposition of solid particles in storage tanks and pipelines which resulting in the shutdown of the transportation process and fittings. In previous studies the formation of precipitation process is explained by the presence of organic solids – paraffin, resin and asphaltenes in the oils. During the blending of oils, asphaltenes in different crude oils begin to precipitate from the resulting mixture. The reason of precipitations that occur is not completely disclosed, but it is explained in different versions. It is known that there are water, mechanical impurities, various salts and other ballasts within crude oils. In most cases, they also precipitate along with paraffin, asphaltene and resins. Crude oil consists of real solutions, suspensions and colloids. The occurence of these precipitations is likely possible to be explained by coagulation of asphaltenes around salt solutions, as well as formation of colloids by asphaltene, resin and paraffin. The amount of colloidal particles in the system increases with blending of different types of crude oils, then some changes are observed in parameters such as density and viscosity.

Studies show that the presence of these compounds is not only the cause of accidents, but also has a significant impact on the rheology of oils. As the amount of asphaltene-resin constituents increases, so does the amount of metals in the oil [5,6].

2. Metod.

Due to differences in chemical composition, crude oils differ significantly in their ability to dissolve water, mechanical impurities and salts. Compared to paraffin hydrocarbons, aromatic and saturated hydrocarbons are relatively well dissolved in water. Resins and asphaltenes are dissolved in water and form durable compositions. These durable compositions are formed by heteroatomic compounds within asphalten-resin. Formed durable high-molecular compositions are one of the main causes of the problems mentioned above. In addition, the blending of different types of crude oil becomes often problematic. In this case, the study of the process of precipitation of high-molecular components such as asphaltene, resin and paraffin is very relevant.

Those mentioned were studied in the example of mixture of oils from various oil fields. Impact of the mixture of these oils in different proportions on physical-chemical properties have been investigated by the authors [7]. Laboratory research has been carried out in accordance with the current GOST(11858, 11851,6370, 2477,21534)

3. Results and Discussion.

The authors have studied the variation of the amount of resin-asphaltene-paraffin compounds, water and mechanical impurities in the mixture of two crude oils in a ratio of 20:80% depending on time and temperature. The experiments have been performed under standard conditions (t = 200°C) in 40 days. The amount of deposits within the mixture was measured every 5 days, and after 30th day every 2 days (table). As can be seen from the table, the amount of deposits increased monotonously in the following days. Based on the data in the table, a graph showing the amount of deposits change over time is plotted (Figure). As you see, most of the deposits (80%) precipitate within 1 day.

Table The amount of deposits in the oil mixture, % ($t=20^0C$)

Time, day	The amount of deposits		
	Factual	According to $y=ax^b$ model	Error, %
Actual			
1	30.07	29.06	3.4
5	33.25	33.68	1.3
10	34.48	35.88	4.1
15	36.36	37.24	2.4
20	37.33	38.24	2.4
25	38.51	39.03	1.4
30	39.56	39.68	0.3
Forecast			
32	41.03	39.92	2.7
34	41.82	40.14	4.0
36	41.16	40.35	2.0
38	42.42	40.55	4.4
40	41.97	40.74	3.0

Here, a=29.599, b=0.0786.
Then $R^2=0.966$

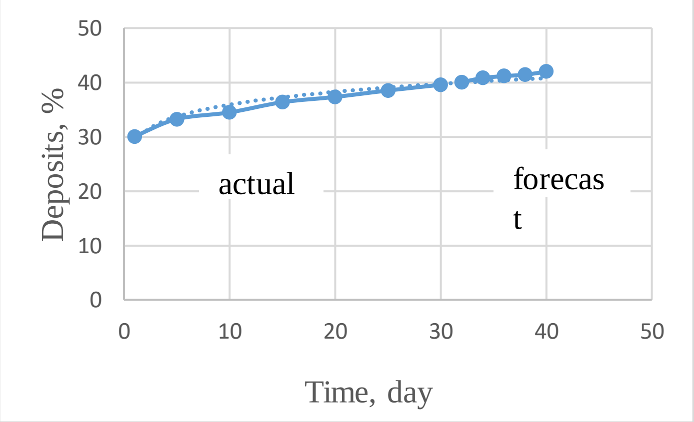

Fig . Change of the amount of deposits (%) with time

Precipitation process in itself under normal conditions and the intensive occurrence of this process are seldomly happening. The precipitation process usually intensifies during the blending of oils, and this process becomes sometimes long-lasting, even may continue for months. In general, deposits are formed by the formation of dispersed systems of resin-asphaltene-paraffins and mechanical impurities. These processes are more typical for undesirable oil mixtures. Taking into account the above, the issue of forecasting the precipitation process in oil mixtures has also been considered. As a result of the analysis, the following empirical model has been obtained to describe the precipitation process shown in the figure.

$$y=ax^b$$

Here, a and b coefficient of model; a = 29.599: b = 0.0786:

y – amount of deposits, mass %:

x – number of days.

It should be noted that when selecting the mathematical model, the preliminary data up to 30 days has been taken for “actual”, and the rest part of data, i.e. the data measured every two days from 30th up to 40th day has been used for “forecast”. The curve, which reflects the changes in the results of the calculations performed in accordance with the obtained mathematical expression, is shown with dotted line. As can be seen from the table and figure, the proposed mathematical dependency gives good results for the determination and forecasting of deposits . In this case, it can be considered applicable in order to solve engineering problems, as the average relative error for “actual” is not more than 2.2% and for “forecast” is not more than 3.2%.

4.Conclusion.

Thus, based on the studies have been carried out it has been determined that the precipitation process in oil mixtures can be long-lasting and continue for months. The bulk of deposits can precipitate from oil mixture in the first day of blending. An empirical expression has been proposed for the determination and forecasting of deposits, and the expediency of applying the mathematical expression to engineering problems has been shown.

5.References

1. Khafizov A.R. Pestretsov N.V, Chebotarev V.V et al. Collection and preparation of oil and gas. Technology and equipment, Tutorial. Ed. A.R. Khafizova, N.V. Pestretsov, V.V. Shaidakova, Ufa, p. 551, (2002)
2. Evdokimov I.N., Losev A.P. Features of the analysis of associative hydrocarbon media. Applicability of refractometric methods, Chemistry and technology of fuel and oils, № 2, pp.38-41ç (2007)
3. Sharifullin A.V., Baibekova L.R., Suleimanov A.T. Features of the composition and structure of oil deposits,Technology of oil and gas, № 6, pp.19-24, (2006)
4. Ismayilov Q.Q., Nurmammadova R.Q., Nurullayev V.X. and Zeynalov R.L. On specific problems arising during oil mixing, Azerbaijan Oil Industry, Baki, №10, pp.30-37, (2015)
5. Ismayilov GQ, Nurullayev VH, Adigozalova MB .. On the reo-nano chemical properties of oil mixtures, News of the Azerbaijan Academy of Engineering - International scientific and technical journal, V. 9, №4, pp.75-85, (2017)
6. Ismailov G.G., Adygezalova M.B., Zeynalov R.L. Manifestation of "incompatibility" in oil mixtures, Theoretical and Applied Mechanics, №3-4, pp.114-117, (2016)
7. Ismayilov GQ, Nurullayev VH, Adigozalova MB On the reo-nano chemical properties of oil mixtures, News of the Azerbaijan Academy of Engineering - International scientific and technical journal, V. 9, №4, 75-85, (2017)
8. Asomaning S. Test methods for determining asphaltene stability in crude oils, Petroleum science and technology,V.21, № 3-4, pp.581-590, (20003)

OR-III-6

CORROSION INHIBITOR OF STEEL

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Abstract. Various classes of organic compounds that differ in their chemical composition, principle of action, and solubility in corrosive environments can be used as corrosion inhibitors. Organic inhibitors mainly refer to compounds containing nitrogen, sulfur, or oxygen, i.e. elements that have undivided electron pairs in the outer orbit and are therefore capable of active donor-acceptor interaction. High protective properties are shown by guanamine derivatives. For example, acetoguanamine, benzoguanamine, benzodiguanamine, butyl-guanamine, as well as their condensation products with phenol-formaldehyde, glycidyl, or epoxy, have been studied as steel corrosion inhibitors in various media [1-3].

The benzoguanamin-formaldehyde oligomer has been modified with epixlohydrines. The main indicatots of the oligomers obtained are determined. comparison, benzoguanamin – formaldehyde oligomer was also studied under identical conditions. The new oligomers obtained are used as corrosions inhibitors for steel.

As a corrosive medium produced water is used. The corrosion rate, the protective effect and the degree of protection are calculated. It was revealed that the chemical composition,structure, inhibitor concentration, corrosive environment, etc. influence the corrosion process.

It has been found that oligomers containing amine functional groups can be used as a corrosion inhibitor of steel in the produced water environment.

Keywords: co-polycondensation, modified, oligomer, resin, synthesis and characterization, inhibitor, corrosion, produced water.

1. Introduction

About 10-15 % of the metal produced on a global scale is lost from corrosion. As a result of corrosion, metal is not only lost, but also the most complex technological equipment, products and structures that work together for the most part are destroyed. All factors that affect the rate and distribution of corrosion are divided into two groups: external and internal.

Therefore, all factors related to the conditions of corrosion, i.e. the nature of the environment, its chemical properties and the presence of substances in the composition that slow down or accelerate the corrosion process, are external factors. Corrosion factors related to the metal itself, its chemical nature, and structure are internal factors.

The main external factor is the chemical nature of the electrolyte in which the metal corrodes. Also, the specificity of corrosion failure is related to the heterogeneity of the liquid extracted from wells (oil - produced water). The regularities of the corrosion process are determined by many factors, among which the main role is played by the physical and chemical properties of the medium (mineralization, pH of the medium, the presence of hydrogen sulfide, etc.).

The study of the dependence of the corrosion rate on the mineralization of reservoir water allows us to characterize its corrosion aggressiveness. The salts dissolved in it are of great importance. As the salt concentration increases, the corrosion of metals increases markedly, which is mainly due to changes in the electrical conductivity of the medium. Along with this, the process of metal corrosion is influenced by chlorine ions.

The mechanism of protective action of inhibitors is related to their adsorption at the metal-medium interface. The adsorption of organic compounds on metals is caused not only by physical forces, but is also accompanied by chemosorption interaction and chemical changes in the adsorbed particles.

In the oil and gas industry, high-molecular substances of complex structure have become widespread as a corrosion inhibitor. High-molecular compounds used as corrosion inhibitors contain both polar (adsorption-active) and non-polar (hydrophobic) parts. The polar end of such a molecule is an active participant in the adsorption process, and when the polar (functional) group of the inhibitor interacts with the surface of the corroding metal, both physical and chemical adsorption occurs simultaneously.

It is known that the synthesis of an oligomer that does not contain phenol is a very urgent task. In solving these problems, an important role is played by the use of modern methods of system analysis, which allow us to reveal the mechanism and main kinetic patterns of reactions, to determine the optimal conditions for obtaining an environmentally friendly product [4-7]. The optimal pH values found by us, at which condensation products containing mainly methylol derivatives of benzoguanamine are formed under mild conditions, are 7.0 – 8.0.

2. Experimental part

A new inhibitor of electrochemical corrosion on oilfield equipment based on benzoguanamine-formaldehyde oligomer (BFO) modified with epichlorohydrin was developed in the research work. The synthesis of amino-epoxide-containing co-oligomers in aqueous media at pH = 7.0-8.0 proceeds in two stages: the first - benzoguanamine-formaldehyde was synthesized, the second - epichlorohydrin was introduced into their aqueous solutions. Depending on the molar ratio of benzoguanamine, amino-epoxide-containing co-oligomers (AES) with different characteristics were obtained [8]. Benzoguanamine-formaldehyde oligomer was also studied for comparison under identical conditions (Table 1).

To determine the temperature field of the effective use of synthesized co-oligomers studied their thermo-oxidative destruction on derivatograf Q-1500 D MOM in the temperature interval 200 – 500 ^{0}C in the following conditions. The mass of the test specimen equal to 0.2 g. The sensitivity of TG-scales equal to 200. The sensitivity of the galvanometers DTA = DTA =50 μv. The rate of temperature rise in the derivatograph furnace is 50/min. The speed of the recorder drum is 2.5 mm/min. The test was performed in an air atmosphere in RT/Pt – Rh crucibles.

The obtained thermal properties, degree of conversion, the time of thermal degradation, temperature degradation (half-life T½) were used to calculate the dissociation energy, activation energy process of thermal destruction, etc.

Table 1. Main indicators of BFO and AEC

№	Name of indicators	BFO	AEC
1.	Element content, % by weight Nitrogen Carbon Hydrogen Chlorine	 10.8 70.6 6.4 -	 11.4 74.2 7.6 5.8
2.	Free formaldehyde content, % by weight.	0.85	0.35
3.	Drop-off temperature for Ubbelohde, ^{0}C	70	78
4.	Density, kg/m^3	1155	1180
5.	Degree of hardening, % at 140 ^{0}C	96.8	98.9
6.	Adhesive strength, MPa	2.42	2.94
7.	Heat resistance according to Vika, ^{0}C	126	138
8.	Gelatinization time, sec.	56	52
9.	Conditional viscosity according to the viscometer VZ-4, at 20 ^{0}C,sec.	48	56

3. Results and Discussions

The conducted studies of the thermo-destruction of amino-epoxide-containing co-oligomers allow us to make the assumption that the thermo-destruction of co-oligomers is satisfactorily described by the equation:

$$d\alpha/d\tau = K_0 \cdot e^{-E/RT} \cdot \sqrt{(1-\alpha)/\alpha}$$

Thus, we can conclude that when heated to 200 - 250 ^{0}C, amino-epoxide-containing oligomers do not undergo significant changes. Intensive destructive processes in the co-oligomer occur at temperatures above 250 ^{0}C.

Upon further heating, dehydrogenation occurs and the co-oligomer turns into a residue with a high carbon content [9].

To identify the inhibitory properties of the tested substances, corrosion studies were carried out on plates made of non-alloy carbon steel of the St.3 brand, measuring 20x40x2 mm. After pretreatment –

cleaning, grinding, degreasing-they were loaded into a constantly mixed mixture of hydrocarbon and electrolyte.

At the end of the test, the steel samples were washed, cleaned of the corrosion product, and weighed. The effectiveness of the inhibitory action of the substance was evaluated and compared using a well-known method [10] and the corrosion rates (K, $g/m^2 \cdot h$) were determined based on changes in the metal mass, degree of protection (Z, %), and protective effect (γ). In all experiments, control tests of steel corrosion were performed in the same mixture, but without the addition of the test substance. The results of the research are presented in Table 2.

Table 2. The results of corrosion studies

Presence of an inhibitor	Inhibitor concentration, mg/l	Corrosion rate (K), $g/m^2 \cdot h$.	Degree of protection (Z), %	Protective effect, (γ)
Without inhibitor	-	2.5	-	-
Benzoguanamine	200	1.2	52.0	2.08
	500	1.0	60.0	2.50
Benzoguanamine-formaldehyde oligomer	200	0.78	66.4	2.80
	500	0.53	78.8	4.72
Amino-epoxide-containing co-oligomer	200	0.76	68.8	3.20
	500	0.22	91.2	11.30

As can be seen from the above data, with an increase in the concentration of the substance in a corrosive environment, the effect of inhibition increases in all cases. The inhibitor concentration was calculated per 1 liter of corrosive medium.

4. Conclusion

As an inhibitor, products of co-polycondensation of a benzoguanamine-formaldehyde oligomer modified with epichlorohydrin were tested.

The physico-chemical and physico-mechanical indicators of the amino - epoxy-containing co-oligomer, including its adsorption capacity and heat resistance, were further enhanced by the functional group with additional reactivity. At the same time, their use as an inhibitor of steel corrosion was of interest.

It was found that studies of various compounds (benzoguanamine, benzoguanamine-formaldehyde oligomer and amino-epoxide-containing co-oligomer) are related to the nature of the inhibitor, i.e. the presence of the active group is an acceptor or donor that shifts the electron density at the adsorption center. When introducing electrophilic substituents, the positive charge on the adsorption center of the molecule increases and its adsorption on the negatively charged metal surface is facilitated. This reduces corrosion, which increases the inhibitory effect.

5. References

1. Gonik A. A. Protection of oilfield equipment. Moscow: Chemistry, 1983, 193 p.
2. Rosenfeld I. L. Corrosion and protection of metals. Moscow: Chemistry, 1970, p. 352
3. Naibova T. M., Seifiev F. Q., Azimov Y. Sh. Azerbaijan Journal of Oil Economy, 2007, no. 8, p. 37-41
4. Kazimov F. M., Mamedyarova I. F., Naibova T. M., Seifiev F. G. Protection of underground oilfield equipment from corrosion. J. Azerbaijan oil industry, 2009, no. 3, pp. 37-41
5. Naibova T. M., Seifiev F. G., Akhundov I. Z., Tagieva S. E. The possibility of regulating the corrosion process based on laboratory and field research. J. Environmental Protection in the oil and gas industry complex. Moscow, 2009, no. 10, pp. 4-7
6. Rizaev R.G., Kazimov A.M., Mamedyarova I.F., Naibova T.M., Mammadova A.A. Corrosion inhibitor of steel . AR patent no. I 2000 0036 dated 04.02.2000.
7. Amirov F. A., Mammedova A. A. Modification of amine-aldehyde oligomers. International scientific conference "Functional monomers and polymer materials with special properties". Sumgait, 2017, pp. 212-213
8. Ramazanov B. G. Synthesis and structural analysis of amine-aldehyde oligomers. J. Encyclopedia of chemical engineer. Moscow, 2010, no. 2, pp. 20-24
9. Grassi N. Chemistry of oligomer destruction processes. Moscow: Mir, 1988, 252 p.
10. Mamedyarova I. F., Shakhmamedbekova A.V., Rasulova S. A. Zh. Corrosion and protection in the oil and gas industry. Moscow, 1989, no. 7, p. 9-11

OR-III-2

TIRE WASTE COMPOSITION

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Abstract. The sources of scientific literature on the research have been investigated, various approaches to the processing and modification of polymers have been analyzed and the main direction of the study have been identified.

The changes in the properties of thin layers of industrially produced low-density polyethylene (LDPE) grades 10803-20 and 16603-011 operating under different climatic conditions have been studied. It has been determined that changes with different intensities occur in the structure and in this connection in the physical and mechanical properties of LDPE that was in operation at different time intervals and in different climatic conditions of the Absheron Peninsula and the Aran region: melt flow index of polymer alloy, tensile strength at break, relative extension and values of other indicators are deteriorating. In polymer samples is formed ~24,2 – 28,6% of insoluble phase and as a result of oxidation up to ~ 12,3 – 16,8% carbonyl, hydroxyl and other functional groups.

Keywords: polymer, polyethylene, recycling, modification, mineral filler, physical and mechanical properties, waste, ecology, melting temperature, crumb rubber, polymer-bitumen, binder

1.Introduction

The expansion of the production of polymers and composite materials based on them exacerbates the problem of reusing of waste from the operation of polymer products. The solution to this problem is associated with the creation of low-waste or economically favorable non-waste production or the development of effective modification methods for reusing of polymer waste, taking into account their structure and properties.

Most polymeric materials retain the basic structure and properties from the beginning of the production process to the end of the operational period. The use of this qualitative feature of polymeric materials is of great practical importance and must be taken into account when processing polymeric materials.

Nowadays, it is impossible to imagine many industries without polymer composite materials. In this respect, development of polymeric materials production and processing industry, expansion of their use in various industries leads to increased environmental pollution, increased share of polymer waste and the emergence of new environmental problems.

The study of the physicochemical, physic mechanical and rheological properties of the used up LDPE showed that it is impossible to turn polyethylene waste into reusable raw materials without modification, associated with structural and chemical changes that occur in macromolecules during polymer processing and operation in natural climatic conditions. Therefore, to restore the original polymer properties recycling of polyethylene waste must be carried out along with the modification process.

2.Metod

Despite the fact that the cost of the polymer waste disposal process is 8 times more expensive than the cost of processing industrial waste, 3 times more expensive than the processing of household waste [1-12], the cost of polymer waste is 40-70% lower than the base price for original polymers, while their overall quality is slightly different from the quality of the original polymer material. Therefore, recycling of polymer materials is of great economic importance [13 - 17].

Recycling of polymer waste considerably reduces the need for original polymer and saves financial and labor resources. Hence, the recycling of polymer materials along with environmental problems also contributes to solving socio-economic problems – the conservation of natural resources [18-20]. One of the most common and widely used methods for producing polymer compositions is the use of different obsolete polymer products, which can significantly change the properties of polymer mixtures and thereby expand their scope [21-22].

3.Results and Discussions

The Republic of Azerbaijan produces low density polyethylene LDPE on an industrial scale, however, the demand for thermoplastic polymers in industrial areas is not fully met. By recycling the used up LDPE, the demand for thermoplastics is significantly satisfied, for example, it is possible to save on polyethylene by 20-30%, it becomes possible to obtain polymer compositions with relatively high physical and mechanical properties – heat resistance, chemically stable, flexural resistance and hardness, which is large interest and practical value for recycling.

Despite the fact that annually in the Republic of Azerbaijan up to 90.000 tons of used up polymer materials are released into the environment, their recycling has not yet been organized at the required level. This is clear evidence of landfills in the outskirts caused by discarded waste (Fig. 1).

Fig. 1. Obsolete polymeric materials

In these landfills the semi-finished products at least shown in Figure 2, can be obtained in the easiest ways and used for various purposes.

Fig. 2 Compositions from obsolete polymer waste

Therefore, from an economic and environmental standpoint, the most appropriate direction is the recycling of polymer wastes. And one of the major points of this direction is the maximum restoration of lost properties of obsolete polymer waste by mechanical and chemical and physical modification of its structure and properties.

Through recycling and modification of LDPE, which is a characteristic polymeric waste for the Republic of Azerbaijan, it is economically and environmentally viable to obtain multi-purpose composite materials. To investigate the properties change of LDPE grade 10803-020 during operation the polymer samples were stored for 6 spring-summer months in the open air at a temperature of 30-45 °C and their physical and mechanical properties change was studied. The results are presented in Table 1.

Table 1. Properties of the original and obsolete LDPE grade 10803-020

N	**Parameter name**	**Original LDPE**	**LDPE after 3 months of operation**	**LDPE after one year of operation**
1	Density, kg/m^3	925,0	930,0	918,0
2	Melt flow index, 190^{0}C, load 2,16 kg, gr/10 min	1,20	0,80	0,22
3	Crystallization rate, %	45,0	-	-
4	Tensile strength at break, MPa	15,5	11,4	4,6
5	Relative extension,%	500	170	115
6	Hardness, Mpa	1,5	1,7	2,5

7	Number of >C=0 groups, %	0,1	1,6	16,8
8	The amount of insoluble phase, %	0	20,0	28,6
9	Melting temperature, ^{0}C	105,4	110,0	119,2

As Table 1 indicates the initial properties of LDPE are changing dramatically. The change in the initial properties of LDPE of grade 16603-011 under the same conditions after 6 months of storage are shown in Table 2. Thermophysical properties of LDPE are given in Table 3.

Table 2. Physical and mechanical properties of LDPE (grade 16603-011)

N	**Parameter name**	**Original LDPE**	**LDPE after 6 months of operation**
1.	Density, kg/m^3	919,0	-
2.	Melt flow index of polymer alloy, 190^{0}C load 2,16 kg, gr/10min	1,1	0,075
3.	Crystallization rate, %	35-40	-
4.	Tensile strength at break, MPa	9,3	-
5.	Fracture resistance, Mpa	12,2	7,7
6.	Relative extension,%	600	260
7.	Hardness, Mpa	18-19	25
8.	Modulus of elasticity	98	42

Table 3. Thermophysical properties of LDPE

N	**Parameter name**	**Parameter value**
1.	Melting temperature, ^{0}C	103-108
2.	Vick heat resistance, ^{0}C	100-105
3.	Heat transfer, Vt/mK	0,32-0,36
4.	Specific heat capacity at 20^{0}C, J/(kgK)	-9,3
5.	Coefficient of linear thermal expansion from 0^{0}C to 100^{0}C, 1/^{0}C	(2,1-5,5) 10^{-4}
6.	Casting shrinkage, %	1,0-3,5
7.	Brittle temperature, ^{0}C	-100

Given the formation of various functional groups in LDPE during its operation, it has been modified with a reactive epoxy resin (ED-16, ED-20) capable of retaining functional groups, phenol-formaldehyde oligomer (PFO) modified with thiocarbamide and remainder of the alunite processing – sludge and natural mineral fillers – zeolite and shell limestone. It was shown that the restoration of the technological and physical-and-mechanical properties of LDPE, in which the amount of elastic phase decreased and brittleness increased as a result of operation is possible in the case of adjusting the amount of binders and mineral fillers, wetting the filler particles, their distribution in the mixture, adding a filler-binder, chemical binder in the composition of used up LDPE. The obtained results are given in Table 4 and Figure 3 .

Table 4. Effect of the optimal amount of dolomite-filler and binder on the physical and mechanical properties of RLDPE

N	***Formulation compositions (1)* and indicators (2) based on LDPE**	**Formulation compositions and property indicators**		
		LDPE after 1 year exposure (RLDPE)	**Composition based on RLDPE**	**Composition based on RLDPE with ED-20 binder addition**
1	The amount of ED-20 (per 100 w/w of RLDPE), w/w	-	-	15,0
2	Dolomite filler, w/w	-	8,0	8,0
3	Dispersive-stearic acid, w/w	-	2,0	2,0
4	Tensile yield stress, MPa	7,1	4,8	8,2
5	Tensile strength at break, MPa	4,6	11,8	14,8
6	Extension elongation, %	115	100,0	150
7	Melt flow index – MFI, gr/10 min	0,22	0,15	0,52
8	Relaxation modulus, 25^{0}C, ε=20%,MPa	2,7	2,8	2,2
9	Modulus of elasticity, MPa	80,2	72,8	70,0
10	Effective viscosity - $\eta_{\varepsilon,}$ 160^{0}C, Pa·s	12,2	13,8	10,1

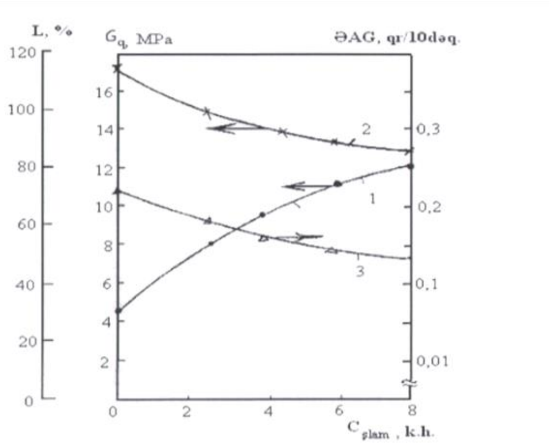

Figure 3. The effect of the amount of sludge on the change in the properties of LDPE after 1 year of operation (RLDPE): 1 - σ_q; 2 - Lq; 3 – MFI

Improving the complex properties of sludge and zeolite filled with RLDPE, FFO, modified thiocarbamide and its mixture with ED-16 in a ratio of 60:40 is associated with the functionality of the binder, its ability to wet the filler particles. Due to the fact that in the binders hydroxyl, epoxy, and thio groups coordinate the bond in the polymer-filler system, as well as carry out chemical bonding formed in the used polymer with hydroxyl, carbonyl, ether and other groups, an improvement in the complex properties of the compositions is observed. The intensity and character of these relationships was confirmed by IR spectroscopy, DTA and analytical methods for the study of functional groups.

It was established that during the recycling of used up LDPE modification of the structure and properties – restoration is possible only in the case of wetting particles of mineral filler and when dispersively mixing them with a polymer mass using mixtures ED-20, Modified Phenol Formaldehyde Oligomers(MFPO)

+ ED-16, which support functional low molecular weight groups.

As a result, an efficient recycling process of used up LDPE was achieved and the complex properties of RLDPE were improved, in addition to obtained compositions can be used not only to save raw materials, but also to solve environmental problems and produce multi-purpose products.

At the same time to study the possibilities of expanding the scope of use of obsolete tires, we have carried out a series of researches. Scientific studies have been conducted in the use of crumb rubber [1, 4, 8, 17] and it was found that the most profitable method of obsolete tires recycling is to modify them and obtaining based on them multi-purpose compositions. In order to recycle obsolete tires after their grinding to dust with the size of particles 1-2 mm it is possible to modify oil road bitumen and obtain a polymer bitumen binder on its basis. The resulting polymer bitumen was used for the manufacture of asphalt concrete. The results obtained are given in Table 8, 9 and 10.

Table 8. Physical and mechanical properties of the obtained bitumen grade Baku 85/25, as industrial bitumen

Indicator	Units of measurement	Baku 85/25
Penetration at 25 °C	mm/10	20-30
Softening point (the ring and ball)	^{0}C	80-90
Elongation at 25 ^{0}C	cm	2,5
Flash point	^{0}C	246
Ultimate tensile strength	^{0}C	- 10

Table 9. Formulation of the composition based on crumb rubber (CR)

Name of components	No of samples				
	1	2	3	4	5
	Content of the mass parts				
Bitumen	100	100	100	100	100
CR	2	4	6	8	10
Sulfur	-	-	-	1	2

Table 10. Physical and mechanical properties of a composition based on crumb rubber

N	Indicator	Samples				
		1	2	3	4	5
1	Needle penetration at 25 °C	38	72	100	71	96

2	Softening point, ^{0}C	49	68	82	56	75
3	Brittle temperature, ^{0}C	-10	-10	-26	-8	-20
4	Elongation at 25 ^{0}C	40	60	70	55	60
5	Density, g/cm^3	2,34	2,36	2,38	2,2	2,4
6	Temperature changes at T=65 °C within 5 hours	7	6	6	6	6
7	Ultimate tensile strength at 20 ^{0}C at 50 ^{0}C	2,4 0,9	3,0 1,0	3,5 1,2	3,1 1,1	3,4 1,3

Studies have shown that it is not possible to obtain the required complex properties in recycled low density polyethylene (RLDPE) which has been modified only by mineral filler – although durability, indicators of thermal stability are improving, technological and plastic and elastic properties – effective viscosity, elasticity, melt flow index are deteriorating. Improving the complex properties of RLDPE is observed in compositions obtained at optimal values of the binder.

The optimum quantity of binders per 100 w/w of used up LDPE has been shown: binders supporting functional groups – ED-20 modified PFO – 15-20 w/w, fillers – sludge and zeolite 6-8 w/w and shell limestone 20-25 w/w and at established optimal amounts it is possible to restore basic properties of RLDPE.

4.Conclusions

The changes in the properties of thin layers industrially produced low-density polyethylene (LDPE) grades 10803-20 and 16603-011 operating under different climatic conditions have been studied. The study revealed that in the structure and related the physical and mechanical properties of LDPE that was in operation in natural climatic conditions in different periods of time (6-8 months) and conditions (May-September and December-March) various changes occur: tensile strength at break, relative elongation and other indicators of polymers and composite materials are deteriorating. In polymer samples is formed ~24,2 – 28,6% insoluble phase and as a result of oxidation up to ~ 12,3 – 16,8% carbonyl, hydroxyl and other functional groups.

Having regard formation of various functional groups in used up LDPE, it has been modified with a reactive epoxy resin ED-16, ED-20 capable of retaining functional groups, PFO modified with thiocarbamide and remainder of the alunite processing – sludge and natural mineral fillers – zeolite and shell limestone. It was indicated that restoration of the technological and physical-and-mechanical properties of LDPE, in which the amount of elastic phase decreased and brittleness increased as a result of operation is possible in the case of adjusting the amount of binders and mineral fillers, wetting the filler particles, their distribution in the mixture, providing in the used up LDPE-binder-filler system chemical bond.

Studies have shown that when Recycled Low Density Polyethylene (RLDPE) is modified only with a mineral filler, it is impossible to obtain the necessary complex of properties. Thus, despite the fact that material strength, indicators of thermal stability are improving, technological and plastic and elastic properties – effective viscosity, elasticity, melt flow index are deteriorating. Improving the complex properties of RLDPE is observed in compositions obtained at optimal values of the binder. The optimum quantity of binders supporting functional groups partially providing basic properties recovery of RLDPE per 100 w/w of used up LDPE: ED-20 modified PFO15-20 w/w, fillers – sludge and zeolite 6-8 w/w and shell limestone 20-25 w/w.

Improving the complex properties of sludge and zeolite filled with RLDPE, FFO, modified thiocarbamide and its mixture with ED-16 in a ratio of 60:40 is associated with the functionality of the binder, its ability to wet the filler particles. When in the binders hydroxyl, epoxy, and this groups coordinate the bond in the polymer-filler system providing chemical bonding formed in the used polymer with hydroxyl, carbonyl, ether and other groups, an improvement in the complex properties of the compositions is observed. The intensity and character of these relationships was confirmed by IR spectroscopy, DTA, and analytical methods for the study of functional groups.

Thus, the studies revealed that during the recycling of used up LDPE modification its structure and properties – restoration is possible only in the case of wetting particles of mineral filler and when dispersive mixing them with a polymer mass using mixtures – ED-20, (MFPO) + ED-16, which support functional low molecular weight groups. Efficient recycling of used up LDPE and preparation of compositions providing improved complex properties of RLDPE, along with the production of multi-purpose products, make it possible to save raw materials and solve environmental problems.

5.References

1. Shykhaliev KS. Modification of petroleum bitumen by polymer waste (monograph) Exact science Kemerovo technical scientific journal .2017., 46.C
2. Shixaliyev Kerem Sefi Exelolted thermoplastics based compositions. E uropean science review. Scientific journal., Vienna -2017
No. 5-6.- P.89-94 E-mail: info@ew-a.org
3. Shikhaliev K. Compositions and products based on polyvinyl chloride. Coll. Articles of the X International Scientific and Practical Competition. Penza. 25.07.2017. C.19-25.

4. Shikhaliev K.S. Amirov Fariz. Studies of the process of obtaining coated for various purposes based on petroleum bitumen (monograph). Innovative develop science education. Under the general ed. Yu. Gulyaeva., Penza ICSN, science and education., - 2017.-318C.
E-mail: mon@naukaip.ru
5. Amirov Fariz Ali, Shixaliyev Kerem Sefi. Obtaning and application of rubber mixtures based on isopeene (SRI-3) and functional grup polimers. Austrian Journal of Technical and Natural Sciences Vienna. 2017.No 3-4. P 27-31 E-mail.info@ew-a.org
6. Shixaliyev Kerem Sefi Study on compatibility of, chemicals and other characteristics of therir mixtures. European Journal of Technical and Natural Sciences. Vienna.-No 3.4-2017.-P.41-46 E-mail.info@ew-a.org
7. Shixaliyev Kerem Sefi Exeloited termoplastics based compositions. Europeon Sciences revicw scientifiic journal., - Vienna.№5-6.-2017.- P.89-94 E-mail.info@ew-a.org
7. Shykhaliev K. Physical and chemical properties of plasticized PVC and products based on them. Innovations in science: scientific journal.-2017., - Novosibrsk., Ed. ANS "SIAK" ,. ., - No. 12 (73) -C. 54-58
8. Shikhaliev K. Obtaining rubber based on butadiene-nitrile rubber, polyvinyl chloride and their modification with a wooden stone Herald of science and education: scientific journal. Ivanovo., Ed. “Problems of Science”., - 2017.- No. 09 (33) - S.10-14.E-mail: info@p8n.ru
9. Shixaliyev K.S., Salimova Nigar. Termodinamics and mutual distribution of macromoleculos in the systems-shorine-shlorocontaining polimeris. European Scince review: Scientific journal.-Vienna., - 2017.-No 3-4 .-- P118-120.E-mail: info@ew-a.org
10. Shykhaliev K. Development of a composition and products based on butyl rubber. SB Experimental and theoretical research in modern science. Sat Art. according to the material. 1 international scientific and practical conf. Novovbirsk, SIBAK.№1.-2017.-C.90-94.
11. Amirov F.A. Theory and practice of obtaining composite materials based on polymer mixtures (monograph Premier Publishing. S.R.O Vienna, Austria. 2018 .318
E-mail: pub @ publishing.orgconference @ sibscience.ru
12. Ermilova EA, Sizova AA, Ilyicheva NN, Pleshakov DV.//Study of the thermodynamic compatibility of a three-component mixture of nitramines with a copolymer of methyl methacrylate and methacrylic acid. / Advances in chemistry and chemical technology. 2014 - No. 2.-p. 65-67.
13. Rijhikova I.G., Volkov A.M., et all. Modification feature of binary mixtures PP/SKEP by the system of organic peroxide-polyfunctional vinyl monomer in the reaction extrusion process. Plastic masses, 8, 2013, p. 40–45.
14. Murtazina L.I., Garifullin A.R., Nikultsev I.A., et all. Influence of plastificators on the property of unhardened hermetics on the basis of ethylene-propylendiene rubber. Engineer-chemist’s encyclopedia, No. 8, 2014, pp. 31–35.
16. Kirsh I.A., Pomogova D.A. Study of the properties of secondary polymer materials based on polypropylene and polyethyleneterephtalat, obtained in the influence of ultrasonic vibrations on the polymer melts. - Moscow, Plastic masses, 2012, No. 1, pp. 48-51.
17. Turaev ER, Beknazarov Kh.S., Akhmedov UK, Jalilov AT. // Interphase interactions of three-phase polypropylene composite materials. / Universum. Technical sciences ./- 2018-№12.- p.57
18. Shastin D.A., Wolfson S.I., Makarov T.V.// Influence of modification of triple ethylene-propylene rubber on the physicomechanical properties of rubbers./ Vestnik of Kazan Technological University.-2010-No. 4.-p.5-7
19. Ryzhikova I.G., Volkov A.M., Bauman N.A., Kazakov Yu.M., Wolfson S.I. // Influence of the concentration of components of the modifying system peroxide / TMPTA and the Mooney viscosity of rubber SKEPT on the balance of yield and impact resistance Master-batches of SKEPT in a polypropylene matrix. / Bulletin of the Technological University-2015-No. 4.-from 148-150.

PP-III-7

THE RESEARCH OF MAGNETIC COMPOSITE MATERIALS WITH POLYMER MATRIX

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Abstract. Studied interfacial interaction in elastic magnetic polymer composites based on diene and silicone rubbers filled with ferrimagnets with micro-particles Fe, and Fe_3O_4. Relationship of mechanical and magnetic properties of elastic magnetic composites with intensity of interphase interaction in them is established. The use of such materials in sorption processes makes it possible to replace the complex procedure for separating spent sorbent from solution with a simple magnetic separation method. Magnetic polymer granules can be obtained by depositing iron oxides directly in a polymer matrix that limits the growth of magnetic particles, as a result, their size becomes smaller than in the absence of polymer, and magnetic properties are improved. For the synthesis of magnetic elastomers used silicone polymer matrix. Silicone oligomer with vinyl and hydride groups at 100-150^{0}C interacts in the presence of a platinum catalyst. Magnetic particles are introduced into the matrix: Fe - 2 µm, Fe_3O_4 - 0.2-0.4 µm. In a magnetic field, the polymer macromolecules are oriented, and in the presence of magnetic particles, the elastomers are structured. Based on the conducted studies, it was found that the obtained magnetic composites with a low iron content have good solubility in water, while increasing the iron content to 15 and 20%, the metal-containing composites lose their solubility in water due to intermolecular cross-linking of polymer macromolecules with iron oxide particles.

Keywords: metal containing, composites, magnetic elastomers, iron oxide, solubility

1.Introduction

The article deals with the current problem of polymer technology – modifying the structure and properties of elastomers with functional compounds and fillers.

The introduction of various functional groups and excipients into the polymers allows their reactivity, properties, and therefore the intended purpose to be tested over a wide range. One of the most promising available and common methods for preparing composite materials with new properties is the mechanic chemical combination of different polymers using interfacial functional additives and fillers of compatibility-enhancing polymers. [1-2]

The need to create composite materials with improved operational properties based on industrial large-duty polymers, including elastomers, as well as the clearly emerging need to use natural organic raw materials - oil, have led to the search for practically effective ways to modify polymers in traditional processing conditions.

One of the important directions in the development of modern polymer technologies is the creation of magnetic polymer composites in which dispersed particles of magnetic material are evenly distributed in the polymer matrix. Improving the magnetic properties of both hard magnetic and soft polymer composites is achieved by increasing the proportion of magnetic powder in the composition and the use of powders with the best magnetic characteristics. [1] However, an increase in the degree of filling inevitably leads to deterioration in the mechanical properties of the composition. In this regard, studies of the interfacial interaction of the polymer and the magnetic filler, which provides the mechanical properties of magnetic polymer composites, are of particular importance. In addition, the interaction at the interface can affect the magnetic properties of the composites. Assessing the energy of this interaction is a complex experimental and theoretical task that requires taking into account the phase and relaxation states of the polymer matrix. The purpose of the work is to develop effective ways to obtain magnetically active polymer sorbent composites, which combine the presence of magnetic centers with the presence of pores suitable for sorption of certain substrates, and to establish factors affecting their structure, magnetic and sorption characteristics.

Metal-containing polymer materials are the subject of intensive research in connection with the prospects for their use in various fields of technology and technology. For the synthesis of metal-polymer composites, various methods can be used: treatment of polymer films with metal pairs, chemical reactions of metal salts in polymer solutions with the subsequent isolation of the corresponding polymer, polymerization of various metal-containing monomer systems.

The purpose of our research is to develop polymer compositions based on modified and combined mixtures of industrial elastomers with improved rheological, strain-strength, relaxation properties, chemical and thermal stability, as well as to develop elastomer containing compositions sensitive to magnetic field. The development of magnetic elastomers combining both high magnetic characteristics and elasticity (i.e., restore their shape and dimensions after the termination of external forces) is a relevant and sought-after industry.

The effect of the magnetic field arranges the structure of the compositions to improve compatibility, and as a result, the composition of the mixture becomes uniform. The use of a magnetic field changes the chemical potential of the system, and this determines the direction of the chemical reaction.

It is known that in order to achieve the highest magnetic characteristics, it is necessary to ensure the maximum possible degree of filling of the composite by reducing the proportion of the elastic polymer matrix, which conflicts with the requirements for elastic properties. Therefore, the main goal was to develop rubber mixture compositions and a technology for producing magnetic elastomers with improved operational properties.

2. Experimental method

The study of interfacial interaction in the magnet of filled polymer composites and the establishment of its connection with the properties of these materials is an urgent problem of modern science and the technology of polymer composite materials. Analysis of literary data on dependence of mechanical, magnetic and dielectric properties of magnet of soft and magneto-solid polymer composites on degree of filling, nature of polymer, size, shape and nature of magnetic particles of filler, method of composite production is carried out. It is noted that the number of studies on the interaction between the polymer matrix and filler particles is extremely small even for non-magnetic fillers, and for the magnet of polymer composites, there is no data on interfacial interaction. Mechanical properties and magnetic characteristics of composites based on industrial rubbers filled with ferrimagnets with Fe micro particles were investigated, and their connections with the amount of interfacial interaction Fe_3O_4 revealed. In our studies, poly chloroprene (PCP), silicone (SCV), isoprene (SKI) nitrile rubbers (SKN-18) were used as the polymer matrix for the magnet of filled polymer composites.

Interfacial interaction in polymer composites based on industrial rubbers filled with Fe and Fe_3O_4 established influence of polymer nature, dispersion of filler particles on value of adhesion interaction. Thermodynamic measurements of interfacial interaction in polymer composites based on silicone rubber, isoprene rubber, chloroprene poly, acrylonitrile and butadiene copolymer with content of acrylonitrile groups of 18 wt.%, polystyrene filled with ferrimagnets with micro particles Fe, and Fe_3O_4 modified by placing particles with active surface in hexane, toluene. Interfacial interaction was studied in elastic magnetic polymer composites based on diene rubbers (PCP, SKI, SKN-18) and silicone rubber (SCV) filled with ferrimagnets with micro particles Fe, and Fe_3O_4. Relationship of mechanical and magnetic properties of elastic magnetic composites with intensity of interphase interaction in them is established.

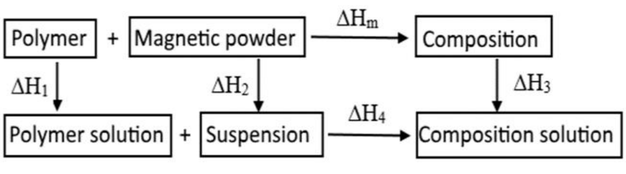

Fig. 1. Thermochemical cycle for counting mixing enthalpy magnetic polymer compositions.

The enthalpy of the interfacial interaction in the magnetic polymer composite was calculated using the thermochemical cycle shown in Figure 1 according to the following equation:

$$\Delta H_m = \omega_1 \Delta H_1 + \omega_2 \Delta H_2 - \Delta H_3 + \Delta H_4$$

where ΔH_m - enthalpy of composite mixing (enthalpy of interfacial interaction), J/g; ΔH_1, ΔH_3 - enthalpy of polymer and composite dissolution, J/g; ΔH_2 - enthalpy of filler particle surface wetting, J/g; ΔH_4 - enthalpy of polymer solution mixing with filler particle suspension, J/g; and is the weight fraction of the polymer and filler, respective.

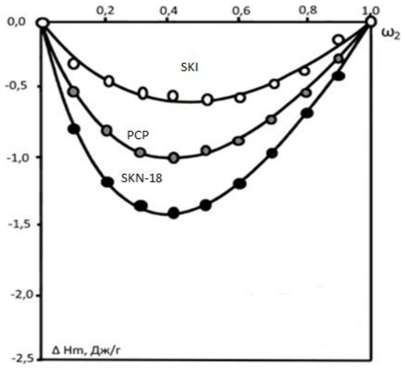

Fig. 2. Concentration dependence of mixing enthalpy at 298 K for elastic composites filled with micro Fe particles. Points - experimental data, lines - interpolation result equation (1).

Figure 2 shows the concentration relationships of the enthalpy of mixing elastic matrix composites filled with micro Fe particles. Diene rubbers of SKI, PCP, CKN-18 have negative mixing enthalpy values throughout the formulation area for all excipients studied. This corresponds to good adhesion of the matrix to the filler particles. The enthalpy of interfacial interaction for diene rubbers in absolute value reaches 2,5 J/g in the minimum of curves.

Increased dispersion of iron particles leads to an increase in the enthalpy of mixing composites by 1.5-2.5 times. Interfacial interaction in elastic-based composites matrix

is due only to adhesion interaction between composite components, which is described by the following equation [2]

$$\Delta H_m = \Delta H^{\infty}_{adq} \frac{K(1-\omega_2)\omega_2 S_{ud}}{K(1-\omega_2)+S_{ud}\omega_2} \qquad (1)$$

whereΔH_{adq} - enthalpy of adhesion in saturated adhesive layer (limit adhesion enthalpy), and *K* is the adsorption constant. Received mixing enthalpy concentration relationships were interpolated equation (1). Calculated enthalpy values of adhesion in saturated adhesive layer for elastic composites filled with micro particles Fe, Fe_3O_4 are given in table 1. As can be seen from Table 1, for all magnetic fillers the same dependency is observed: absolute value increases in the range of SKI < PCP < SKN-18. Polarity increases in the same row a polymeric matrix that can be characterized by a dipole the moment of the polymer μ - link, which indicates on a significant contribution to the energy of interfacial interaction electrostatic forces of attraction of dipole groups of polar polymer to particle surfaces.

Table 1. Enthalpy values of adhesion in saturated adhesive layer

Parameters	Polymers	micro Fe	Fe_3O_4	μ -link D
ΔH_{adq} J/m^2	SKI	-15,02	-29,08	0,2
	PCP	-32,10	-44,12	0,85
	SKN-18.	-45,00	-98,60	2,7

Adhesion Enthalpy Values in saturated adhesive layer calculated by interpolation according to equation (1), show that the modification surface of micro particles Fe allows strengthening the adhesive interaction in composites on isoprene rubber base in 1.5-9 times. Surface modification of particles installed iron promotes adhesion in composites and thickness growth adsorption layers in more than two times, with looseness of boundary layers of composites are reduced by one third. All this in aggregate leads

to increase the strength of composites, filled with modified micro particles micro Fe and Fe_3O_4.

3.Results and discussion

A new class of magnetic elastomers is obtained, which are a highly elastic polymer matrix with micro magnetic particles dispersed in it. The combination of magnetic and elastic properties results in such composite materials having a unique material capacity for the material's unique ability to reversibly change size and viscoelastic properties in the external magnetic field. The use of such materials in sorption processes makes it possible to replace the complex procedure for separating spent sorbent from solution with a simple magnetic separation method. Magnetic polymer granules can be obtained by depositing iron oxides directly in a polymer matrix that limits the growth of magnetic particles, as a result, their size becomes smaller than in the absence of polymer, and magnetic properties are improved. For the synthesis of magnetic elastomers used silicone polymer matrix. Silicone oligomer with vinyl and hydride groups at 100-150^{0}C interacts in the presence of a platinum catalyst. Magnetic particles are introduced into the matrix: Fe – 2 μm, Fe_3O_4 - 0.2-0.4 μm. In a magnetic field, the polymer macromolecules are oriented, and in the presence of magnetic particles, the elastomers are structured.

It has been proven that the modification active surface of Fe nanoparticles allows improving their adhesion interaction with elastic and glassy matrix 1.5-9 times. It is shown that the most effective surface modifiers

4. Conclusions

Fe nanoparticles are polystyrene and isoprene rubber. It has been determined that using modified nanoparticles as filler iron increases the strength of polystyrene-based composites on 70% with degrees of filling of 30 – 50 mass.%.

5.References

1. Pozdnyakov, A.S. Functional polymer nanocomposites containing triazole and carboxyl groups//High molecular weight compound. B. - 2014. - T. 56, No. 2. - C.226.
2. Bilalov Y.M., Mammedzade A.M. Polymer solutions sensitive to magnetic field, magnetic elastomers//Plastic masses. Moscow, 2011, 3, page 29-35

PP-III-8

SYNTHESİS OF METAL-CARBON NANOCOMPOSITES BASED ON THE HIGH PRESSURE POLYETHYLENE AND STUDYING THEİR PROPERTIES

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Abstract. Metal-carbon nanocomposites are of a great interest as new generation materials with a set of valuable practical properties.

The effect of cobalt nanoparticles and multilayer carbon nanotubes stabilized in a polyethylene matrix on the physicomechanical and thermal properties of these nanocomposites has been studied.

An improvement was detected in the strength and deformation parameters, as well as in the thermal-oxidative stability of the obtained nanocomposites. This can be attributed to the effects of structural and chemical stabilization of the polymer matrix.

Small amounts of these nanofillers introduced into the polymer, play the key role as structure-forming agents - artificial nuclei of crystallization, which contributes to the formation of a small-spherolite structure in the polymer, characterized by improved physical, mechanical and thermal properties in the resulting nanocomposite.

Keywords: cobalt-containing**,** nanoparticles; multilayer carbon nanotube; metal-carbon nanocomposites; high pressure polyethylene

1.Introduction

For recent years, there has been considerable interest in composite materials based on polymer matrices and nanosized metal particles, which is related to a widespread application - from catalysis to nanotechnology in information technology. The unique properties and improved characteristics of nanomaterials are related to their size, surface structure, and interfacial interaction. Metal-carbon nanocomposites are of great interest as new-generation materials with a set of valuable practical properties.

The use of metal nanoparticles of variable valence (copper, cobalt, nickel, etc.) incorporated in polymers allows to obtain fundamentally new materials, that can be widely used in radio and optoelectronics as magnetic, electrically conductive and optical medium [1-3].

Polymer nanocomposites can be obtained by the in-situ method, i.e. by polymerizing the monomer in the presence of a nanofiller previously dispersed in the reaction medium [4]. The method of introducing a nanofiller into a polymer melt is more preferable. This method is most convenient for application in modern industry. It makes possible to obtain nanocomposite polymers for a wide range of manufacturers, which makes this method promising and cost effective [5, 6].

Modification of polyethylene by generating various composite materials can significantly expand the scope of its application. Filled polyethylene takes one of the first places among filled thermoplastics. Currently, more and more attention is paid to the development of composites with nanoscale fillers. Such composite materials own higher performance than composite materials with micro- and macro-fillers. Even, the introduction of a small amount of nanosized filler into polyethylene can significantly increase the physical properties, improve the barrier properties, increase the thermal stability, electrical conductivity, etc. [1,3,6].

Carbon nanofillers provide ample opportunities for regulating the properties of substances without significant changes in their composition due to the manifestation of size effects that affect the electronic, thermal, mechanical, electrical and other properties of the filler and affect the properties of materials [7].

Most often, polymer composite materials with CNTs used as a filler are of interest from the point of view of their electrically conductive properties, but no less important are their physical, mechanical and operational properties (wear, oil, petrol resistance, etc.). It is also of great interest to increase the heat and temperature resistance of products made from such nanocomposites, their gas and air tightness, which is important in the production of pipes, containers and other similar products [8].

The presented work is devoted to preparation and study of the properties of nanocomposites based on the high-pressure polyethylene using metal-containing nanoparticles stabilized by a polymer matrix and multi-walled carbon nanotubes used as a nanofiller.

2.Experimental part

High-pressure polyethylene grade 15803-020 (PE), as nanofillers (NPh) was used cobalt-containing nanoparticles stabilized by a polymer matrix of high-pressure polyethylene, obtained by a mechanochemical method (NPhCoO) [9] and multi-walled carbon nanotubes MWCNT (CVD -179, purified from resins and Fe, hydrocarbon feedstock - cyclohexane).

Nanocomposite polymer materials are obtained from mixing PE with a cobalt-containing nanofiller and MWCNT on laboratory rollers at a temperature of 130-135 ° C for 15 minutes. For mechanical tests, the resulting mixtures were pressed in the form of 1mm thick plates at 170 ° C and a pressure of 10 MPa for 10 minutes.

The physicomechanical parameters of the obtained compositions were determined by using an RMI-250 device.

The thermal stability of the researched nanocomposite samples was studied on a Q-1500D derivatograph (MOM, Hungary). The tests were carried out in an air atmosphere in a dynamic mode when the sample was heated to 5 degrees • min^{-1} from 20 to 500^{0}C, a sample of 100 mg, the sensitivity of the channels DTA-250mkV, TG-100, DTG-1 mV.

3.Results and discussion

Nanocomposite polymeric materials based on PE with cobalt-containing nanofiller and MWCNT have been acquired. The physicomechanical, thermophysical and thermal properties of the obtained nanocomposites have been investigated. The data are presented in Tables 1 and 2.

Table 1. Physical and mechanical properties of the synthesized nanocomposites

Compositions (wt%)	The tensile strength, (σ_p), MPa	Elongation at break (ε_p), %	Vicat softening point, °C
PE	11.39	400	130
PE/NPhCoO (100/0.5)	10.94	450	134
PE/NPhCoO (100/1.0)	12.45	500	138
PE/NPhCoO (100/2.0)	10.79	440	133
PE/MWCNT (100/0.01)	9.56	215	137
PE/MWCNT(100/0.05)	10.05	220	140
PE/MWCNT (100/0.1)	9.17	210	135
PE/NPhCoO/MWCNT	11.83	680	145

As can be seen from the data in Table 1, the introduction of 0.5 - 1.0 mass% of NPhCoO into the composition of the composition leads to an increase in the strength index from 11.39 to 12.45 MPa and the deformation value at break of the composite from 400 to 500%. An increase in the concentration of NPhCoO more than 1.0 wt% leads to a decrease in the strength of the composite (10.79 MPa) and the magnitude of deformation upon fracture of the composite (440%), which is probably due to the aggregation of nanoparticles, which leads to the formation of micro-defects in the bulk of the polymer matrix.

Investigation of the Vicat heat resistance of the obtained compositions showed that the introduction of the nanofiller NPhCoO (1.0 wt.%) into the PE composition leads to an increase in the heat resistance index from 130 to 138 ° C. An increase or decrease in the amount of NPhCoO leads to a decrease in the heat resistance index, which is probably related to the microdefect of the obtained composite.

A necessary condition for obtaining the best properties of carbon nanomaterials in a polymer composite is to achieve the maximum degree of dispersion of the filler and its optimal orientation in the polymer matrix [8].

As can be seen from the data in Table 1, the introduction of 0.01-0.1 wt.% MWCNTs into the composition leads to a significant decrease in physical and mechanical parameters: σ_p from 11.39 to 10.05 MPa, ε_p from 400 to 220%, but the Wick heat resistance increases by 10 ° C.

To overcome the low affinity of MCNTs for the polymer, it is necessary to use low molecular weight compounds or polymers with functional groups [8]. We have used PE as a functionalized polymer, modified with cobalt oxide nanoparticles.

The combined use of both NPhCoO and MWCNTs in the PE composition increases the ultimate strength at break to 11.83 MPa, relative elongation to 680%, and Wick heat resistance to 145 ° C.

The thermal stability of the studied samples based on PE, containing separately or together NPs of copper oxide and MWCNTs, was estimated from the value of the activation energy (E_a) of the decomposition of thermal oxidative destruction, calculated by the method of double logarithm using the TG curve according to the method [10], at the temperature of 10% (T_{10}), 20% (T_{20}) and 50% (T_{50}) decay of the samples under study, as well as their half-life –$\tau_{1/2}$. The data, achieved as a result of derivatographic studies, are shown in Table 2.

Table 2. Thermal properties of the studied nanocomposite samples

Compositions (wt.%)	T_{10} °C	T_{20} , °C	T_{50} ,°C	$\tau_{1/2}$, min	E_a , кJ/mol
PE	325	345	380	63.2	191.45
PE/NPhCoO (100/0.5)	335	355	390	78.3	221.48
PE/NPhCoO (100/1.0)	340	360	400	79.8	229.56
PE/NPhCoO (100/2.0)	330	350	385	76.4	219.74
PE/MWCNT (100/0.01)	355	375	405	79.1	248.17
PE/MWCNT(100/0.05)	360	380	410	81.2	256,22
PE/MWCNT (100/0.1)	350	370	400	78.6	246.84
PE/NPhCoO /MWCNT (100/1.0/0.05)	370	390	420	83.1	291.38

It was shown, the insertion of copper oxide NPs containing NPh into the PE composition contributes an increase in the sample half-life (T_{50}) from 380 to 400 ° C, the half-life ($\tau_{1/2}$) increases from 63.2 to 79.8 min., the activation energy (E_a) of the decomposition for thermal oxidative destruction of the obtained nanocomposites increases from 191.45 to 229.56 kJ / mol. The introduction of only MWCNTs into PE leads to an increase in T_{50} from 380 to 410 ° C, $\tau_{1/2}$, from 63.2 to 81.2 min., E_a from 191.45 to 256.22 kJ / mol. The combined use of both NPhCoO and MWCNTs in PE promotes an increase in T_{50} to 420 ° C, $\tau_{1/2}$, to 83.1, E_a to 291.38 kJ / mol.

Thermal analysis studies have shown that the joint insertion of NPs of cobalt oxide and MWCNTs into the composition of the composition improves the thermal-oxidative stability of the obtained nanocomposites.

Numerous experimental data on the mechanical, strength, relaxation, and other properties of polymer-polymer and polymer-filler mixtures are explained within the framework of the concept of the presence of an interphase layer [10].

The properties of polymer composites are significantly influenced by the supramolecular structure of the polymer (the size of spherulites, the degree of crystallinity, the presence of C = O groups and various branches, etc.) and the interfacial interaction at the interface [11].

The metal-containing nanoparticles and MWCNTs used in this work, located in the interphase layer of the structural elements of PE, contribute to the formation of a composition of heterogeneous nucleation centers in the melt, which, in the process of stepwise cooling of the nanocomposite, contribute to an increase in crystallization centers, leading in general to an improvement in the crystallization process and the formation of a relatively small-spherulite structure.

4.Conclusions

1. A separate and joint effects of cobalt oxide nanoparticles stabilized by the high-pressure polyethylene matrix, obtained via the mechanochemical method and MWCNTs on the properties of metal-carbon composites based on high-pressure polyethylene have been studied.
2. An improvement in the strength, deformation parameters, and also thermal-oxidative stability of the obtained nanocomposites was revealed, which is apparently associated with the synergistic effect of the interaction of cobalt-containing nanoparticles with MWCNTs.
3. The results obtained indicate that small amounts of nanofillers introduced into the polymer obviously play the role of structure-forming agents - artificial nuclei of crystallization, which contributes to the appearance in the polymer a fine-spherolite structure imparted the improved physical, mechanical and thermal properties to the obtained nanocomposites.

5.References

1. S.P. Gubin, G.Yu. Yurkov, I.D. Kosobudsky, Nanomaterials вased on metal-containing nanoparticles in polyethylene and other carbon-chain polimers. International Journal of Materials and Product Technology. v. 23. no. 1 – 2. p. 2 – 25. doi:10.1504/.2005.006587. (2005).

2. A.D. Pomogajlo, A.S. Rozenberg, I.E. Uflyand, Metal nanoparticles in polymers,Nanochasticzy` metallov v polimerakh. M, Khimiya, 672s.(2000).
3. G.Yu.Yurkov, S.V.Kondrashov, I.D.Kraev, Nanocomposites based on high-pressure polyethylene and cobalt nanoparticles: synthesis, structure, properties Aviaczionny`e materialy`i tekhnologii, # S2, s.29-33.(2014))
4. E.M. Antipov., M.A. Guseva, V.A. Gerasin., Yu.M. Korolev, A.V. Rebrov, H.R. Fischer, I.V. Razumovskaya, Structure and deformation behavior of nanocomposites based on PE and modified clays, Visokomol. soed. A. T.45. №11. c.1874-1884.(2003).
5. M.E. Savinova, E.S.Semenova, M.D.Sokolova, Investigation of the physical and mechanical properties of PE80B modified with magnesium nanospinel and zeolites. Neftegazovoe delo. 2011. No.6. s.328-333.
6. N.I. Kurbanova, T.M. Kuliyeva , N.Ya. Ishchenko, Preparation and study of the properties of nanocomposites based on high-pressure polyethylene with metal-containing nanofillers, Perspektivnie materiali. no. 2. p. 48-54. doi: 10.35164/0554-2901-2020-5-6-12-14. (2020).
7. E`.G.Rakov, Carbon nanotubes in new materials, Uspekhi khimii. T. 82, No.1, S. 27 – 47. (2013).
8. V.Mordkovich, I.Arutyunov, S.Zaglyadova, A.Karaeva, I.Maslov, S.Kireev, Nanocomposites based on polyolefins and carbon nanoparticles and nanofibers Nanoindustriya., No.1, s. 20-22 .(2009)
9. E.B. Zeynalov, N.I.Kurbanova, N.A.Mirzoeva, A.I.Dunyamalieva, N.Ya.Ishchenko. Obtaining a polyethylene composition containing metal nanoparticles 6th International Caucasian Symposium on Polymers & Advanced Materials. Georgia, Batumi. 17-20 July. p.116 . (2019).
10. V.F.Kurenkova. Praktikum po khimii i fizike polimerov. Khimiya. 299 s. (1990).
11. A.D.Pomogajlo, Molecular polymer-polymer compositions. Synthetic aspects Uspekhi khimii. t.71, No.1, s.5-38. (2002).

PP-III-9

COMPOSITE COMPOSITIONS BASED ON PETROLEUM POLYMER PITCH OF GAS OIL FRACTION OF CATALYTIC CRACKING

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Abstract. This article presents the results of studies on the use of a petroleum pitch, synthesized based on a gasoil fraction from the catalytic cracking of oil process, as a binder in various composition compounds, as individually and in a composition with epoxy resin. The curing process was carried out thermally, and with the participation of cross-linking components, for which urotropine and polyethylene polyamine (PEPA) were used. The influence of the ratio of components, temperature and reaction time on the curing process was studied. It was found that during thermal curing of phenoformalite with epoxy resin, the formation of a cross-linked structure is observed only at temperature 160 ° C and the maximum value of the degree of curing is achieved with a curing time of 4 hours, ratio of phenol and aromatic hydrocarbons - 98.8%.

The process of curing the synthesized petroleum pitch, with the participation of a crosslinking component - urotropin, was carried out at temperature 100-120^0C, with the participation of PEPA at 20-90^0C. It should be noted that the use of PEPA as a cross-linking component, at all investigated mass ratios of the components, a sufficiently high degree of curing is observed (90.4-98.5 wt%).

The obtained results indicate the perspectivity of the synthesis of the oil-polymer resin by involving of aromatic hydrocarbons contained in the gasoil fraction from the process of catalytic cracking into process.

Keywords: Modified Phenoformaldehyde Resin, Phenoformolite, Polycondensation, Curing, Degree of Curing

1.Introduction

The rapid development of the chemical industry constantly requires new resources, as well as the rational use of natural resources, including by-products of secondary oil refining. The possibility of using oil residues as raw materials in the reactions of synthesis of phenoformoldehyde resins, so-called phenoformolites, is very important. In the aspect the using of light phlegm, from the catalytic cracking process, which rich with the set of aromatic hydrocarbons as raw materials for the production of thermosetting petroleum polymer resins - phenoformolites, is having a great practical interest [1].

2.Experimental part

We carried out the polycondensation reactions of phenol with formaldehyde, with the participation of aromatic hydrocarbons as a raw material component - contained in the product of light catalytic cracking gas oil, to obtain a modified petroleum resin - phenoformolite.

The impact of the mass ratio of aromatic hydrocarbons in the gas oil fraction, phenol and formaldehyde, catalyst concentration, temperature and reaction time on the conversion and yield of reactive petroleum resin was studied. The synthesis process was carried out using ionic-liquid as a catalyst, in particular, morpholinehydrosulfate or N-methylpyrrolidonehydrosulfate [2]. The use of an ionic liquid as catalyst provides a relatively high rate in the polycondensation reaction, in comparison with the participation of hydrochloric acid, and leads to the formation of a product with a high yield [3].

As expected, it was found that an increase of the mass ratio of phenol to gas oil fraction, as well as the ionic liquid catalyst, provide the increase of the yield of product was observed. So, all other things being the same, the maximum conversion of aromatic hydrocarbons in the gas oil fraction is observed at a threefold mass excess of phenol in relation to aromatic hydrocarbons with a phenoformalite yield - 75.92%.

3.Results and discussion

In this paper the results of studies of the use of modified petroleum resin obtained under the above conditions as a binder in various composition compounds have been presented. It should be noted that we have previously investigated the use of phenoformalite obtained at an equal mass ratio of phenol and aromatic hydrocarbons at a catalyst concentration of 5 wt% to obtain compositions.

Under current conditions, the synthesized petroleum resin as a binder separately and in a composition with epoxy resin (ED-20) with the implementation of the curing process thermally and with the participation of crosslinking components - urotropin, as well as polyethylene polyamine (PEPA) was used. The influence of various factors - the ratio of components (modified resin: epoxy resin), temperature and reaction time on the curing process was investigated. It was found that during thermal curing of the composition compounds of the modified phenoformaldehyde and epoxy resins, the formation of a crosslinked structure is observed only at temperature 160 ° C and above. The maximum value of the degree of crosslinking, depending on the conditions of synthesis of the modified petroleum resin, in particular on the ratio of phenol to aromatic hydrocarbons, is 65.96-97.6% of the mass with a curing time of 4-10 hours (Table 1).

Table 3. Results of thermal curing.

Mass ratio of PPP:ED-20	Mass ratio of phenole to aromatic hydrocarbons in synthesis of PPP	Time, h	Temperature, ^{0}C	Degree of curing, %
50 : 50	30:70	4	160^{0}C	57,5
		7		52,8
		10		65,9
	50:50	2		88,2
		4		96,09
		5		97,48
	70:30	2		88,9
		3		92,1
		4		98,8

The process of curing of the obtaining composition compounds based on the synthesized modified petroleum resin and ED-20 was also carried out with the participation of crosslinking agent - urotropin or PEPA. Curing with the participation of a cross-linking agent - urotropin at a concentration of 10% was carried out at temperature 100-120^{0}C, however with the participation of PEPA, taken in the same amount, at room and at the high temperatures (20-90^{0}C). The results obtained are shown in Table 2, as can be seen, regardless of the nature and conditions of curing, almost complete curing of the investigated compositions compounds is achieved within 30-240 minutes.

So, in the case of using PEPA and urotropin as cross-linking components, the structuring process of the petroleum polymer resin proceeds at a fairly high rate, with all the studied mass ratios of the components, a sufficiently high degree of curing (85.2-99.8% by weight) of the petroleum resin is observed (table-2).

Table 2. Dependence of degree of cross-linking of the petroleum polymer pitch on curing conditions.

Mass ratio of PPP:ED-20		Mass ratio of phenole to aromatic hydrocarbons in synthesis of PPP	Time, min	Temperature, ^{0}C	Degree of curing, %
Urotropine		30:70	30	100^{0}C	85,2
50 : 50			40		87,4
			60		90,9
		50:50	30		92,2
			40		94,09
			60		98,48
		70:30	30		95,9
			40		97,1
			60		99,8
	PEPA	30:70	60	25^{0}C	78,2
	50:50		180		83,8
			240		88,9
		50:50	60		83,2
			180		90,09
			240		93,0
		70:30	60		87,9
			180		92,1
			240		96,9

Phenoformolites are also widely used as the film-forming materials possessing high atmosphere resistance, decorative properties, good water resistance, adhesion and as well as resistance to yellowing [4, 5].

The film-forming properties of the composition compounds based on the synthesized phenoformolite with epoxide resin have been investigated with the participation of PEPA as a cross-linking agent in concentrations 7 and 9%.

The coatings on the basis of these compounds have been obtained by a method of the overflow from 50% mass of the solutions in methyl ethyl ketone. It has been established that the drying time to degree 3 is 15-18 min., the thickness of the coatings was 80-140 mcm, and the obtained coatings were characterized by sufficiently high index of hardness – 0.6, impact strength – 40-45 cm and adhesion –1 point.

The IR spectral analyses of the synthesized phenoformolite resin and composition compounds on its basis containing urotopine or PEPA as cross-linking components were produced on IR-Fourier spectrometer ALPHA (firm BRUKER, Germany) in the range of 600-4000cm^{-1} and were almost identical with the spectra of samples obtained using phenoformolite resin obtained at an equal mass ratio of components.

4.Conclusion

Based on the research, the possibility of modification of phenol formaldehyde resin in the oil refining process, obtained during catalytic cracking, was identified by using a light gasoil fraction containing a mixture of aromatic hydrocarbons as a raw material.

In the process of synthesis of phenol formaldehyde resin modified by gasoil fraction, the conditions for obtaining high yields using ionic liquid catalytic system were determined.

The structuring process of the synthesized new composition phenol formaldehyde resin in the presence of various building components was studied and the conditions for obtaining such a spatially structured polymer at room temperature with high yield were determined.

Thus, the proposed modification of phenol formaldehyde resin, along with defining a new, effective field of application of light gasoil fraction obtained in the oil refining process, partially improved the operational properties, revealed the possibility of obtaining environmentally friendly (low free phenol and formaldehyde) oil polymer resin.

5.References

1. Ugryumov S. A., Osetrov A. V.: Investigation of curing processes of modified phenol-formaldehyde resin. Polymer Science Series D. V.8, №. 4. – C. 304-306 (2015).
2. Pashayev, Z. N., Ibragimova D. M., Abdullayev F. M. et al.: The use of ionic liquids in the synthesis of esters of (meth) acrylic acid. Scientific works, 1(3), p.271-275 (2016)
3. Ibragimova M. D., Amirov F. A., Bayramova S. T., Ibragimova T. A., Pashaeva Z. N., Bagirova B. F.: Application of an ion-liquid catalyst-morpho-lingidrosulfate in the synthesis of phenoformalites based on light catalytic cracking gas oil. Paint and varnish materials and their application, No. 3, p. 98-99 (2019).
4. Kang S., Fu, J., Zhang G., Zhang, W., Yin H., Xu Y.: Synthesis of humin-phenol-formaldehyde adhesive. Polymers, V. 9, №. 8, p.373 (2017).
5. Hirano, K.; Asami, M.: Phenolic resins—100 years of progress and their future. React. Funct. Polym. 73, p.256–269 (2013).

PP-III-10

SYNTHESIS AND STUDY OF THERMAL PROPERTIES OF ALLYL CAPRINATE-STYRENE POLYMERS

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Abstract. The results of obtaining viscous additives that are resistant to destructive effects and meet the increased requirements of machines and mechanisms have been presented in the article. The reaction of copolymerization of allyl caprilate with styrene by the radical mechanism in the presence of a radical initiator was carried out, the influence of various factors on the process and quality of viscous additives to petroleum oils was studied. Research to determine the thermal stability of the synthesized copolymers in comparison with known viscous additives polyisobutylene and polyalkyl methacrylate also have been studied. The research results showed that the new samples in terms of the determined indicator are superior to the known ones - the decrease in the viscosity of oils thickened with polyisobutylene and polyalkyl methacrylate is 11.4 and 13.7, respectively; and for copolymers this figure is 7.7%.

Keywords: copolymers, allyl caprinat, styren, copolymerization, thermal destruction, mechanical destruction

1. Introduction

Oil-soluble polymers of many vinyl monomers have been used as viscous additives. Studies have shown that polyalkylmethacrylates are indispensable among these polymers: they are obtained by environmentally friendly technology (radical polymerization), are easily modified, and more effectively improve the viscosity-temperature properties of oils, especially at low temperatures. However, like other viscous additives, polyalkylmethacrylates are not resistant to destructive effects. Therefore, research is being conducted worldwide to obtain more modern polyalkylmethacrylate-type viscous additives [1-5]. Vinyl monomers have a high polymerization capacity, copolymer compounds obtained by using them have a high molecular weight distribution and the polymer chain becomes irregularly structured. The physical and mechanical properties of polymer compounds depend on their value in terms of molecular weight, molecular weight distribution, and the sequence of monomer manganese in the polymer chain. Involvement of allyl monomers in the synthesis of viscous additives not only increases the range of monomers used for this purpose, but also serves to expand their raw material reserves [6].

In this direction, purposeful researches are carried out at the Institute of Chemistry of Additives named after academician A.M. Kuliyev of ANAS. The essence of these studies is the chemical modification of polyalkylmethacrylates. The basic monomer is polymerized with a small amount of stabilizing monomer to obtain viscous additives with the required properties.

One of the most important exploiters of viscous additives is their resistance to thermal effects. If the viscous additives do not have a high thermal stability, viscosity of the additives concentrated oils may be abnormally degraded as a result of destruction, which is also unacceptable.

As thermal destruction occurs in the presence of oxygen, there are oxygen compounds in the polymer. These compounds can disintegrate to form free radicals, and the free radicals formed can harden the subsequent destruction of the polymer.

Thus, thermal destruction is a complex process and its oxidation products autocatalytic accelerate by a chain radical mechanism lead to the thermal destruction of the polymer.

The results of research in the field of synthesis and research of thermally stable copolymer for petroleum oils have been presented in this article. To obtain a copolymer, allyl caprinate styrene was copolymerized by a radical mechanism.

2. Experimental part

2.1. Synthesis of allyl caprinate with styrene

The reaction was carried out in the presence of azo- (bis) isoacetic acid dinitrile (DINIZ) at a temperature of 60-70^{o}C. Allyl caprinate was synthesized from the starting monomers in the laboratory and styrene was taken in the form of a reagent and used fresh. The results of the copolymerization process are summarized in table 1.

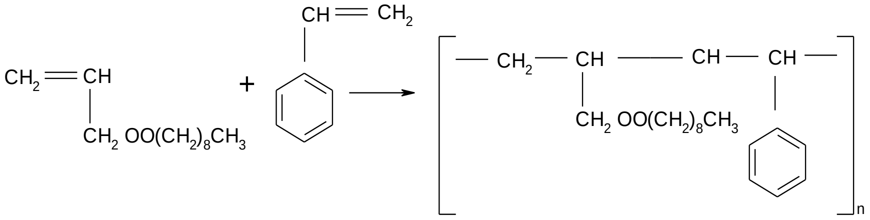
Table 1. Copolymerization of allyl caprinate with styrene

Conditions of copolymerization				Characteristics of copolymer	
amount of styrene in a mixture of monomers,%	the density of the initiator, %	duration, hour	reaction temperature, ^{0}C	yield of polymer, % wt.	molecular weight
5	1	4	75	25.3	3000
10	1	4	75	53.1	4000
15	1	4	75	60.9	5000
20	1	4	75	80.3	8000
25	1	4	75	91.2	9000
30	1	4	75	96.4	10000
20	0.5	4	75	71.2	10000
20	0.7	4	75	77.3	9000
20	0.3	4	75	50.1	11000
20	1	6	75	82.4	8000
20	1	3	75	77.8	8000
20	1	4	65	79.9	8300
20	1	4	85	81.5	7900

By changing the reaction temperature and the duration of the process, the reaction conditions were found to provide the required value of high yield and molecular weight - 750 ^{0}C and 4 hours.

In the synthesis of allyl caprinate-styrene copolymers, the probable reactions are as follows.

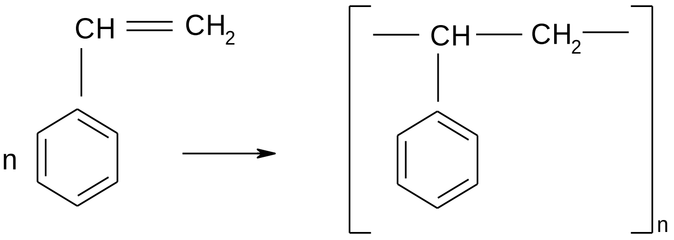
1. Copolymerization of allyl caprinate with styrene



where n=12-48

This is a highly probable reaction, since the allyl ether itself does not polymerize, and the formation of a polymer means the polymerization of allyl caprinate with styrene.

2. Homopolymerization of styrene



This reaction is probable. However, when making polystyrene, observation was observed. We did not observe this reaction in the study. This is due to the fact that compounds with different electronic densities tend to bind to the active center, formed by another monomer (allyl caprinate) during polymerization. Consequently, the homopolymer does not form during the reaction.

2.2. Thermal properties of allylcaprinate-styrene copolymers

There are various ways to evaluate the thermal destruction of polymers. Viscosity additives are working in oil solutions, so it would be better to carry out their destruction in solution. For this purpose a special method has been developed, and the essence of this method is that the 5% solution was heated in specially selected oil - turbine "L" at a temperature of 12 hours for 2000 hours.

At certain time intervals, samples are taken, their kinematic viscosity is determined at 100 ° C, comparing with the initial viscosity, the decrease in viscosity (VD)is determined and the thermal stability of the polymer compound is taken into account.

The calculations are carried out according to the following formula:

$$VD = \frac{Vi - Vp}{Vi} \cdot 100\%$$

where - initial viscosity of condensed oil at 100^0 C, mm^2/s,
V_P- post-test viscosity, mm^2/s.

3. Results and discussion

The results of the thermal destruction of allyl caprinate-styrene polymers in the turbine "L" are given in table 2.

Table 2. Thermal destruction of allyl caprinate-styrene copolymers in the turbine "L"

Molecular weight of copolymer	Initial viscosity of concentrated oil, mm^2/s	Decreased initial viscosity depending on the time (hour) from thermal exposure of concentrated oil,%,			
		1	4	8	12
3000	8.30	1,3	1,8	2,1	2,3
5000	9.81	2,1	2,4	2,7	3,1
8000	11.48	3	3,4	3,7	4,4
9000	13.36	3,1	3,3	4,1	4,7
10000	15.57	48,1	2,5	3,6	4,2
12000	18,74	4,8	5,1	5,5	5,8
Polyalkylmethacrylate					
12000	10,0	1,6	4,0	6,5	9,1

For comparison, the thermal destruction of an industrial viscous additive of polyalkyl methacrylate grade "B-2" with condensed oil was investigated. It was found that as a result of heating for 12 hours, the viscosity of condensed oil decreases to 9.1%, i.e. the copolymer has higher stability than polyalkyl methacrylate. Therefore, polymerization is a method of chemical modification and the synthesis of polymer compounds with the required performance properties by selecting the right level of monomer can be polymerized. Specifically, this is true in the case of the allylcaprinate-styrene copolymer — the incorporation of styrene into the polymer chain has given rise to resistance to thermal effects.

The thermal stability of polymer compounds is also determined by the mass. Such an analysis — that is, a thermogravimetric study — is performed on a derivatograph. Specifically, our research was carried out on a derivatograph brand OD-102T (F. Paulik, I. Paulik, L. Erderi system). Al_2O_3 was used as a standard. The heating rate is 50 ^{0}C/ min. The comparative conduct of thermal stability in two different ways allows us to speculate about the mechanism of thermal destruction (Table 3).

Table 3 Results of thermogravimetric study of allyl caprinate- styrene copolymers

Molecular weight of polymer	I Phase of the destruction		indicated temperature, ^{0}C, loss of matching mass,%			Activation energy, kJ / mol
	Temperature,°C	power loss,%	10	20	30	
3000	130-190	10	290	300	330	205
5000	165-270	6	280	296	320	198
8000	145-255	6	280	294	318	185
9000	140-260	6	270	286	312	170
10000	150-240	5	265	280	308	162
12000	160-272	2	260	270	302	158
Polyalkylmethacrylate						
12000	205- 220	2	258	264	300	156

The effect of the value of the molecular weight of allyl caprinate-styrene copolymers on the results of thermal destruction has been studied. When studying the effects of thermal effects on condensed oils, it was found that an increase in the molecular weight of a copolymer reduces its resistance to the thermal effects of condensed oils. Analogy is also evident in thermogravimetric studies. But here is an interesting fact: the destruction of a copolymer takes place in two stages - it is at a lower temperature in the first stage, and the value of mass reduction is relatively small (2-10%). This stage of destruction, though not so typical, requires explanation. The observed fact can also be explained by the fact that the subjects have a relatively low molecular weight (3000-9000).

This means that these compounds in the composition may contain lower molecular fractions and "weakly bound" polymers, therefore, when they are removed from the first stage of the process, significant weight loss is observed. As the process continues, an increase in temperature is observed, corresponding to a 10-30% weight loss of the copolymers. Commercial polyalkyl methacrylates were used for comparison. Copolymers are understood to be more stable than polyalkyl methacrylates. This is due to the presence of styrene units in the copolymers. It should also be noted that, depending on the mechanism of destruction, polymers react differently to thermal effects. If the destruction proceeds by the mechanism of depolymerization (reverse polymerization), then in thermogravimetric studies, a large weight loss is observed, that is, when the monomer unit is separated from the polymer chain, this causes weight loss. If the polymer breaks down according to the "law of chance", that is, the polymer chain breaks off in random places from heat exposure, then "flakes" are formed, and the loss of polymer mass is insignificant.

It is known that polymethacrylates and polystyrene are destroyed by the mechanism of depolymerization. There are similarities between the results of thermogravimetric analyzes of the studied copolymers of allylcaprate-styrene and a viscous additive, polyalkyl methacrylate (table 3). This means that the test samples are destroyed by the mechanism of depolymerization, depending on their chemical nature. Since the esters of the polymer type are destroyed by the mechanism of depolymerization. One of the most important performance characteristics of engine oils is their resistance to mechanical damage. As a result of mechanical destruction, the C-C bond in the polymer backbone is broken. The tendency of the C-C bond to rupture is associated with the uneven distribution of mechanical stress on individual bonds.

For some polymers, as the degree of polymerization increases, the rate of destruction increases according to the quadratic law of stability; the refraction of the C-C bond in macromolecules is approximately in the middle of the chain, and the molecular weight distribution of the polymers is reduced as a result of mechanical destruction.

Mechanical destruction of viscous additives is carried out in oil solution and there are various methods of conducting the process. Determination of mechanical destruction using ultrasound is widespread and this method is standardized (GOST 6794-75); a UZDN-1 disperser is used to carry out the destruction. The advantage of the method is that a very small amount of solution (20 ml) is required and the test time is 15-60 minutes. The polymer solution is poured into a glass beaker and exposed to ultrasound for a certain period of time. The stability of the polymer against mechanical stress, which compares the initial surface area of the solution with that of the post-test surface, is considered.

The results of the mechanical destruction of the synthesized polymers are given in table 4.

Table 4 Mechanical destruction of allyl caprinate-styrene copolymers

Additive		Copolymer solition in the transformer oil			
Molecular weight	fat hardness, %	Initial viscosity мм^2/с	Decrease in viscosity over a specified period of time(min).		
			15	30	60
3000	8	9.50	3,5	4,2	5,6
5000	5	9,56	7,3	9,1	10,0
8000	6	9,99	3,2	10,1	12,3
9000	7	9,76	8,5	12,4	15,5
10000	8	9,10	9,1	13,6	16,8
12000	5.5	9,74	10	14,1	18,7
	Polyalkylmethacrylate				
12000	6	9,0	18,6	21,3	27,2

As can be seen from the table, here, as with thermal destruction: with an increase in the value of the molecular weight and polymer concentration, the value of destruction increases. But with mechanical destruction, a higher amount of destruction is observed. The kinematic properties of copolymer solutions in transformer oils are approximately the same (~ 9-10 mm2 / s). Therefore, polymers with different molecular weights were used at different concentrations.

A comparative study of the results with industrially low content of polyalkyl methacrylates shows that some polymers have excellent properties - a decrease in surface area from 27.6% to 5.6-18.7%, respectively.

4.Conclusions

Thus, regardless of use, the problem of mechanical degradation of thickened oils is of great importance. Research is underway to improve the mechanical stability of polymers. One of the ways to increase the resistance of polymers to mechanical stress is to polymerize the base monomer with a small amount of stabilizing comonomer**.**

5.References

1.Kuliyev A.M (1985) Chemistry and Technology of Fuels and Oils. L: Chemistry 1985.
2. Akhmedov A.I, Farzaliyev V.M, Aliguliyev R.M (2000) Polymeric Additives and Oils. Baku: Elm; 2000.
3. Yukich A, Vidovich E, Yanovich Z (2007) Additives to improve the viscosity index oils, Chemistry and technology of fuels and oils, . № 5, 2007, pp. 23-27.
4. Yanovich Z, Yukich A, Vidovich E (2009) Triple polymers of maleic anhydride and long chain alkylmethacrylate as a viscosity additive. Chemistry and technology of fuels and oils, № 4, 2009, pp. 33-37.
5. Farzaliev V.M., Gasanova E.I., Akhmedov A.I. Synthesis of Copolymers of Decyl Methacrylate with o-Allylphenol and Their Investigation as Viscosity Improving Additives for Petroleum Oils, 2012, T.85, № 10, pp.1640-1642
6. Akhmedov A.I, Gasanova E.I., Mekhtiyeva S.T.: Thermostable polymers in obtainingof lube oils. J. Petroleum processing and petrochemistry, № 3, pp.40-42

PL-10

PREPARATION OF ELECTRO-CONDUCTIVITY OF NANO-COMPOSITIONS OF OLIGOMERS OF AROMATIC AMINES

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Abstract. The oligomers of aromatic amines (oligoaniline – OA, oligomethylaniline - OMA, oligoparaphenylendiamine - OPFDA) in nanosizes with more high electric conductivity has been synthesized by oxidative polycondensation of aromatics amines in the presence of $[NH_4]_2S_2O_8$ (APS) or $K_2S_2O_8$ in a medium of HCl under action of ultrasound waves. For revealing of aromatics amines optimal parameters of synthesis of aromatics amines in nanosizes the process has been carried out in atmospheres of air and nitrogen, at various values of pH medium and ratios monomer: oxidizer (mol) and measurement of the electric conductivity of each synthesized sample by a method of four points.

The oligomers of aromatic amines are prepared in the presence of new hydrophilic template: sulfanilic acid derivative of poly (styrene–alt–maleic anhydride) (PSMA-SU) as a matrix polymer during the in situ chemical oxidative polymerization of aromatics amines. PSMA-SU can be used template as matrix to linearly guide the growth of a secondary polymeric reaction. Template is made with grinding powder to form a fine powder of PSMA. Then sulfanilic acid was used for modification of PSMA fine powder in presence of trimethylamine. The acidic repeating group of sulfanilic acid derivative of PSMA acts as external dopant for prepared oligoaniline in oligomers of aromatics amines (oligoaniline – OA, oligomethylaniline – OMA, oligoparaphenylendiamine of aniline. Prepared OMA-PSMA-SU composites by this method have excellent solubility in water due hydrophilic interactions in its template and electrical conductivity values of 0.41 S/cm are obtained for it by the four probe method. Produced all polymers and copolymers were characterized by ^{1}HNMR and FT-IR spectroscopy. It has been determined that nanooligomers of aromatics amines and their oligomer-polymer nanocompositions show high and stable electroconductivity (6.1−24.5 Om^{-1}·cm^{-1}, 0.15−2.2 Om^{-1}·cm^{-1}), and the sizes of oligomethylaniline particles are 50-100 nm. This type of oligomers and their nanocompositions can be used in microelectronics, in the textile industry, in the preparation of coatings with protective and antistatic properties from the influence of UV rays and their nanocompostions are the perspective polymer materials for microelectronics.

Keywords: Oligomers of aromatics amines, oligoaniline, oligomethylaniline oligoparaphenylendiamine, electro-conductive polymers

1.Introductıon

In recent years it is of great interest a use polyfunctional reactive high-molecular compounds as the active additives to the industrially-produced polymers for improve of their operational indices, as well as to give them the complex of necessary and useful properties. These compounds are polyfunctional aromatic polyconjugated homo- and cooligomers. They show semiconductivity, paramagnetism, thermal stability, catalytic activity and in most cases possess solubility and meltability. As a result such high-molecular compounds and their compositions with fibres, thermoplasts, resins and elastomers are widely used in creation of sensors, transformers and «smart materials» of various purpose and also in textile industry [1-3]. The purposeful change and control of electrical properties of such materials at keeping of solubility and meltability is actual and important problem [3-5].

Usually the polymers on nature are good isolators. A number of polymers possessing relatively high own electric conductivity is comparatively small. They are mainly high-molecular compounds, macromolecules of which include developed system of polyconjugated bonds, i.e. polyacetylene, polyphenylenes, polymers of aniline, pyrrol, thiphene and their derivatives. However, these polymers, in its turn, have the serious lacks: practical absence of solubility in usual solvents and melting temperatures, very low adhesion, deformation and strength indices. In addition, the values of the electric conductivity of such polymers are changed depending on conditions of their synthesis in the very wide range and usually are not high. For elimination of such lacks the numerous investigations were carried out. For improvement of solubility and meltabilty and also adhesion and strength properties the functional derivatives of above-mentioned polymers have been synthesized. An essential increase of the electric conductivity, i.e. an increase of quantity of solitons, polarons and bipolarons in their composition has been reached by the methods of thermal and chemical influence and in more wide scale – alloying. The alloying can be realized by various ways and with use of compounds of various nature. We have synthesized new representatives of polyfunctional polyconjugated polymers synchronically possessing semiconducting properties, solubility and meltability by oxidative homo- and copolycondensation of mono- and dihydroxybenzenes, naphthols and aromatic mono- and diamines in the presence of various oxidizers. It has been established that homo- and copolymers of such kind in influence of various oxidizers and at high temperature in atmosphere O_2 form the stable microradicals of aroxyl type. Both the initial polymers and their macroradicals show paramagnetic and semiconducting properties. By change of conditions of synthesis one can purposefully vary the concentrations of paramagnetic centers (PMC) in composition of these compounds. The results of the investigations showed that the electric conductivity of the samples both in constant and in alternating electric fields is essentially (~3÷5 order) increased with concentration growth of PMC (~1÷2 order) in their composition.

However, the preparation of electro-conductive polymers in nanosizes, optimization and stabilization of their electric properties and also creation of their nanocompositions with matrix polymers are more interesting and tempting, as they have more wide possibilities for development of polymer materials with high and stable electric conductivity.

2.Experımental

The oligomers of aromatics amines (oligoaniline – OA, oligomethylaniline - OMA, oligoparaphenylendiamine - OPPhDA) in nanosizes with more high electric conductivity has been synthesized by oxidative polycondensation of aromatics amines in the presence of $[NH_4]_2S_2O_8$ (APS) or $K_2S_2O_8$ in a medium of HCl under action of ultrasound waves. For revealing of aromatics amines optimal parameters of synthesis of OA in nanosizes the process has been carried out in atmospheres of air and nitrogen, at various values of pH medium and ratios monomer : oxidizer (mol) and measurement of the electric conductivity of each synthesized sample by a method of four points.

For preparation of nano-sized OPPhDA, 0.05 mol (5.45 g) of PPhDA is weighed and 100 ml of HCl (1M) solution is added to it and PPhDA salt for 30 min is prepared. 0.022 mol (5.94) of $K_2S_2O_8$ is dissolved in 50 ml of distilled water and after the begining of reaction, this solution is gradually added for 30÷40 min., and carried out in an ice bath at temperature 273÷277 K for 3 hours. A yield of oligomer products depending on condition is ~40÷70%.

The composition and structure of the synthesized homooligomers have been determined by methods of elemental, chemical and spectral analyses and NMR, TGA, XRD and SEM methods. These compounds are substances of black color, soluble in polar organic solvents, have paramagnetic properties and are high-density semiconductors. As they contain functional groups of amines, they form the complex compounds with heavy metal ions undergoing the electron and ion-exchange reactions.

The FT-IR spectroscopy were recorded on a Bruker Alpha-P **(Wismar, Germany)** in ATR in range of 4000 cm^{-1}– 400 cm^{-1}

The UV-Vis spectrum of polymers was taken using Perkin Elmer Lamba UV-vis Spectrometer by dissolving the polymers in DMSO as a solvent.

Thermal stabilities of the polymer substance were examined by thermogravimetric analysis (TGA) on a STA 6000 model (Perkin Elmer Instruments). The samples (~ 5 mg) were heated from room temperature to 800 °C under nitrogen atmosphere at a scanning rate of 10°C/min.The XRD was measured with Bruker AXS D8 Advance. The samples were fixed on a conductive carbon tape and coated with (direct current) DC sputter at a thickness of 20 nm. Scanning Electron Microscopy (SEM) images were taken by Field Emission JEOL SEM 7001F with secondary electron imaging (SEI) mode.

3.Rezults and dıscussıon.

It has been established that the samples of OA prepared in a medium N_2 show more high electric conductivity than the samples synthesized on air. The electric conductivity of OA prepared under action of ultrasound in the presence of N_2 for 4 h becomes more high. During using of various concentrations of hydrochloric acid the more high results are reached at 1.5 mol/l concentration of HCl. At the same time, it was known that a molar ratio of APS/monomer during preparation of various polymers are differed: for polyaniline, polypyrrol and poly-3,4-ethylenedioxythiophene a use of the values 1.5; 0.5 and 1.0, respectively is recommended. However, the results of the carried out investigations showed that for samples of OA synthesized under action of ultrasound waves its optimal value is1.25 (mol). In this case, the electric conductivity of the prepared OA is higher and reached to 23.5 S/cm [6,7].

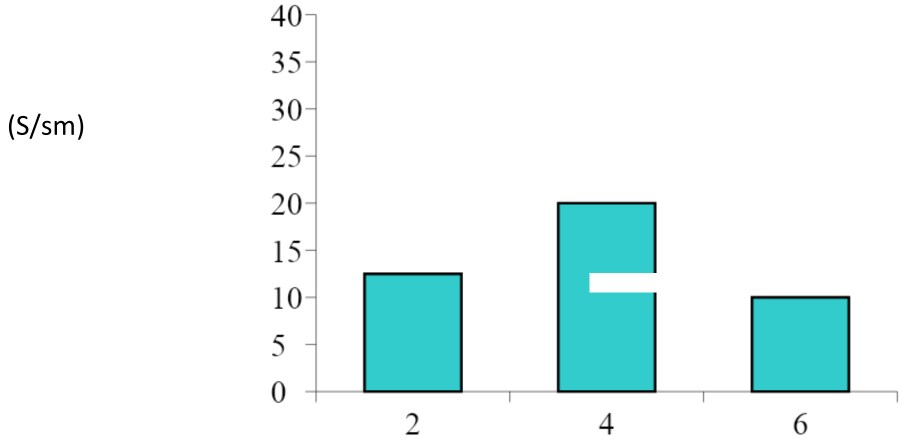

Fig. 1. Diagram ot influence of the synthesis time on electro-conductivity of nano-OMA $[MAn]_0$-0.044mol, $[APS]_0$-0.022mol, $[HCl]_0$-1.0 mol/l, T-277K and τ -4 h

The synthesis of OMA in nanostructures is carried out under various conditions and each time by measuring its electro- conductivity by a four-point method. It has been determined that the electro-conductivity of OMA samples (10,25 S/cm) synthesized in N_2 medium under the same conditions is higher than the electro-conductivity of OMA samples (9,80 S/cm) obtained in air, electro-conductivity of OMA samples (19,3 S/cm) treated under ultrasound waves for 4 h and electro-conductivity of OMA samples (12,8 S/cm) treated for 2 h. Electro-conductivity of OMA samples obtained under the influence of ultrasound waves in N_2 medium for 6 h was approximately twice less than the c orrespondig indice of the samples obtained for 4 h (Fig.1).

The influence of the used acid concentration on the electro-conductivity of OMA samples was also determined (Fig.2.). It is apparent that an increase of the acid concentration used for protonation of OMA in the range of 1.0-1.0 mol/l does not practically change the electro-conductivity value of OMA samples, but an increase of the acid concentration in the range of 1.0-1.5 mol/l leads to an increase of electro-conductivity of the samples.

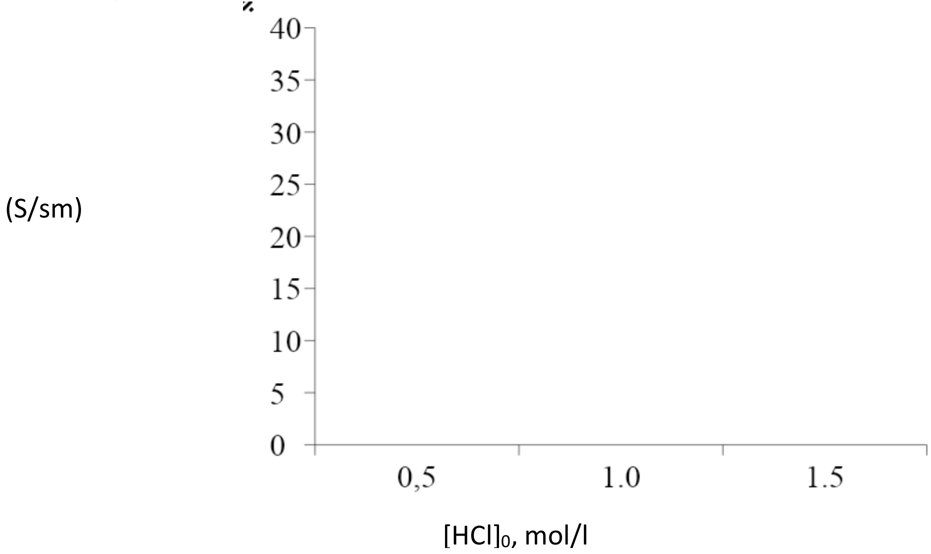

Fig. 2. Electro-conductivity of OMA samples treated with various acids. $[MAn]_0$ – 0.033 mol, $[APS]_0$ – 0.044 mol, T – 277K and τ – 4 h

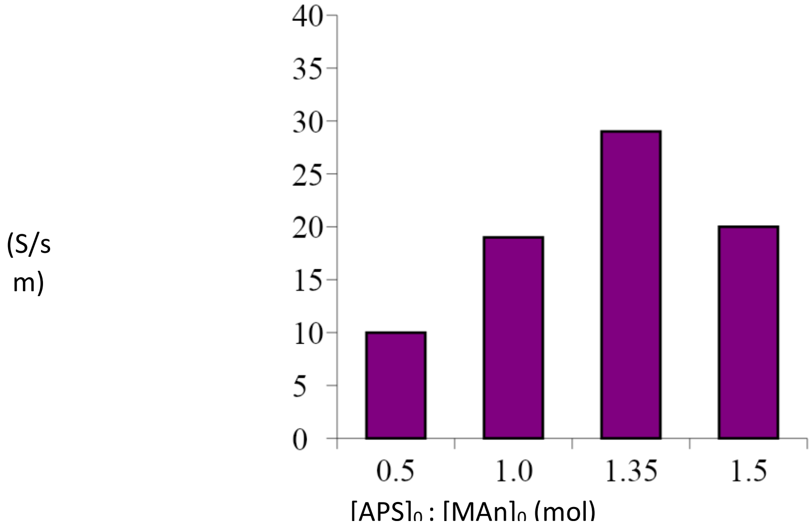

Fig. 3. Electro-conductivity of OMA samples at various ratios [APS]$_0$ **:** [MAn]$_0$. [MAn]$_0$-0.033mol, T-277K and τ -4 h

At the same time, it has been shown that the optimal value of APS/monomer ratio is different for polymers of various composition. For polyanylline, polypyrrol and poli(3,4 – ethylenedioxytiophene), this ratio taking at ratio 1.5; 0.5 and 1.0 is considered appropriate. However, it became clear from the results of experiments carried by us that the optimal value of this ratio for samples of oligomethylaniline synthesized under influence of ultrasound waves is 1.35 (mol). The electro-conductivity of OMA obtained under such conditions is higher and is 21.8 S/cm (Fig.3). In the UV spectrum in the aromatic ring of the synthesized OMA, there are peaks at 330 nm and 550 nm wavelengths, the first of which (330 nm) characterizes π→ π* excitation in the aromatic ring, and the second (550 nm) can refer to n → π* excitation. After alloing with HCl, three maxima – 800, 420 and 320 nm are observed in the UV spectrum of OMA. The first of them (320 nm) again refers to polyaron → π*, that is, π→ π* excitation. → π* polyaron excitation can be represented by a maximum at 420 nm, if this transition occurs in emeraldine salt, then the maximum recorded at 800 nm.

The structure of the synthesized nano-sized polymers has been analyzed using spectroscopic analysis (FT-IR) methods.

As follows from Fig.1, the wide absorption bands having 3327cm^{-1} are correspond to N-H double amine groups in the polymer chain. The absorption band at 3612 cm^{-1} can be attributed to the asymmetric valence vibrations of N-H bond. The absorption bands at 1576 and 1476 cm^{-1} correspond to C=N and C=C bond of the quinoid and benzenoid rings, respectively. The absorption band at 1206 cm^{-1} corresponds to C-N bond. The peaks with wavelength of 871 cm^{-1} can be attributed to non-plane vibrations of the benzene ring. Also, the absorption bands around 1095 cm^{-1} correspond to the electron bond used by delocalization. **[8,9]**.

The UV-Vis spectrum of PpPDA synthesized in the presence of potassium persulfate is shown in Figure-2. These spectra were taken in the presence of solvents of dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). PpPDA records maxima in the wavelengths at 275 nm and 550 nm, the first of which (330 nm) characterizes π→ π* excitation in the aromatic ring, and the second (550 nm) may refer to n → π* excitation (between N atom and rings) [10].

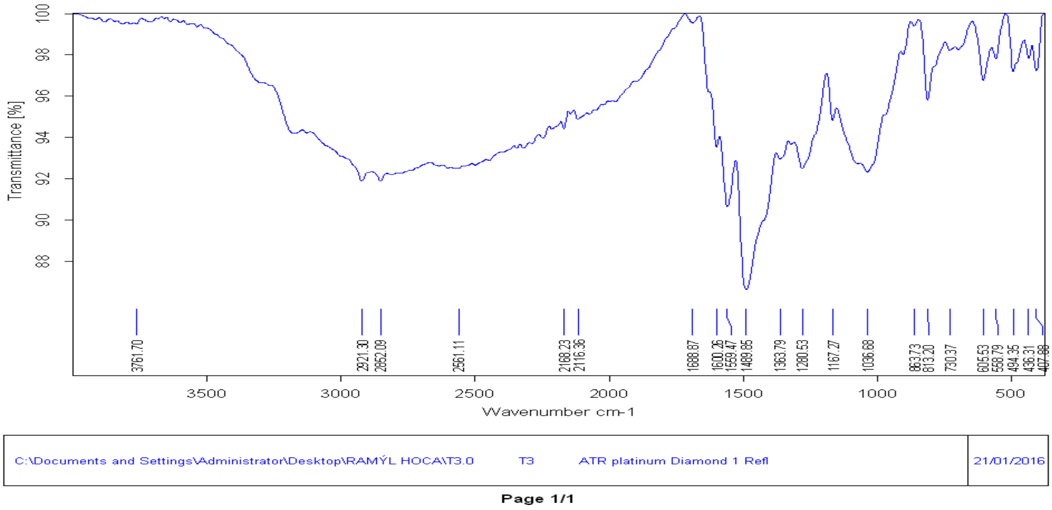

Fig.4. FT-IR spectrum of PpPDA in potassium persulfate ($K_2S_2O_8$).

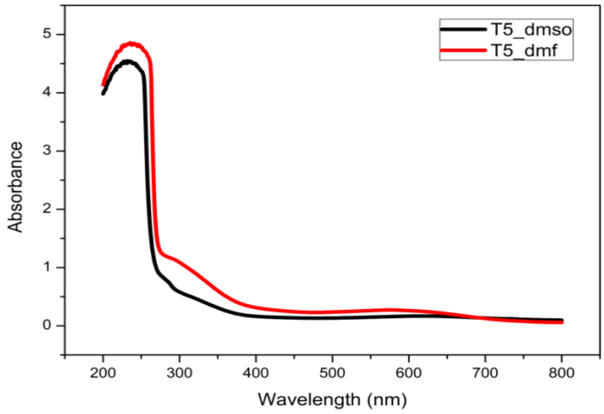

Figure-5. UV-Vis spectrum of OPFDA

X-ray diffraction: The XRD sectrum of OPFDA shows a series of sharp lines in the regions of $5^0<2\theta>35^0$, which depicts that the synthesized polymer samples has high crystallinity and long range ordering. From the spectrum it is evident thatthere is no broadening of peaks due to amorphous components as shown in figure 5 and found to be crystalline in nature. It becomes clear from XRD diagram (fig.4) and figure SEM (fig.5) of the synthesized samples of OPFDA that the particles of OPFDA have the sizes approximately 50–100 nm, i.e. the samples of OPFDA synthesized under action of ultrasound waves consist of nanoparticles.

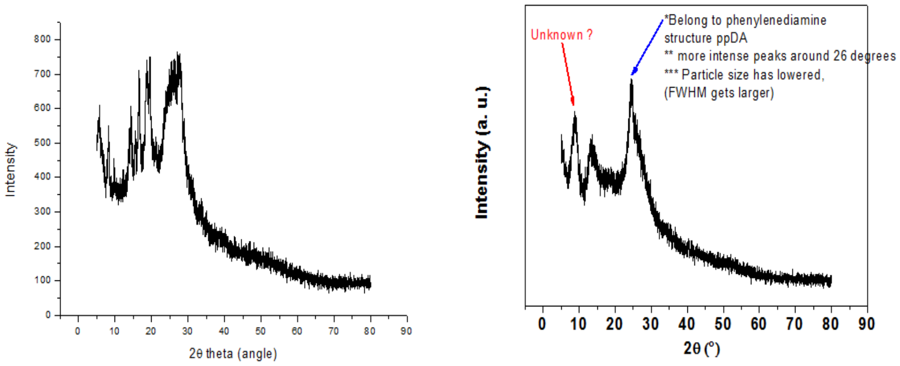

Fig. 7. Diagrams XRD for OPFDA

A comparison of value of the electric conductivity of the synthesized samples of OA after treatment by various alloying compounds shows that a nature of the alloying agent also influences on value of the electric conductivity of polyaniline. As, the values of the electric conductivity of the samples of OA prepared under action of ultrasound and treated with HCl and CSA are 23.5b and 16.0 S/cm, respectively.

We have also carried out the template oxidative polycondensation of aniline in the presence of APS and matrix polymer under action of ultrasound waves in a medium of nitrogen. As a matrix polymers were used:polystyrene-alt.-maleic anhydride (PSMA), products of its hydrolysis (PSMT) in interaction with isopropylamine and polyethyleneglycol and also aniline sulfoacid (PSMA-SAT). As a result, a number of nanocompositions of polyaniline with high and stable electric conductivity have been developed.

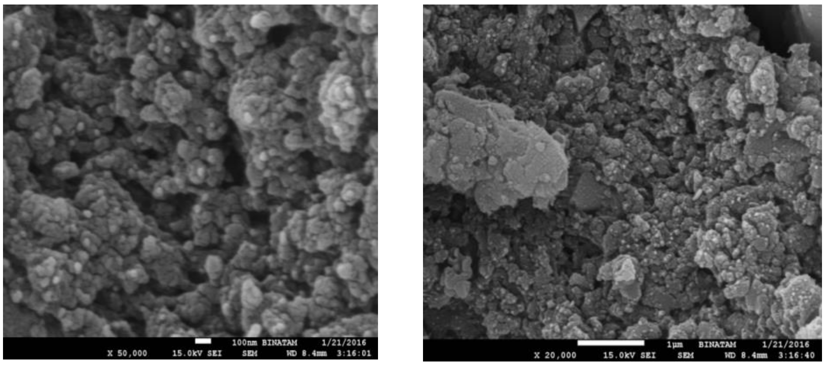

Fig. 8. Figures SEM of OPFDA.

The water-soluble polymers which can be stable as nanosized particles, attracting surface of molecules of other monomers create a possibility for carrying out of their oxidative polycondensation. As a result, the particles of again prepared polymer are formed in nanosizes. In addition, the polymer stabilizers acting by mechanism of phase stabilization can directly be used as a matrix polymer for prevention of accumulation of polymer nanoparticles. The compositions consisting of nanoparticles of spherical form in sizes about 100 nm have been prepared by the oxidative polycondensation in dispersions PSMT–PS and PSMT–SAT–PS in acidic aqueous medium. The electrical properties of these compositions have been studied for their thin films. The process has been carried out under action of ultrasound waves in a medium of nitrogen with use of APS as an oxidizer, HCl – alloying agent (37%) and PSMT – phase stabilizer, product of hydrolysis. The values of the electric conductivity of compositions of OMA–PS and OMA–PSMT–PS of various structure are changed in the interval of 0.17÷2.39 S/cm. The electric conductivity of compositions of OMA–PSMT–PS is more high. The electric conductivity of nanocompositions of OMA–PSMT(PEQ) and OMA–PSMT(IPA) are practically on level of the electric conductivity of compositions of OMA–PSMT, but they characterized by more high deformation and physical-mechanical indices. An introduction of PS into structure of these compositions leads to the decrease of their electric conductivity ~ in 20 times, however the prepared template of OMA–PSMT–PS is sufficiently homogeneous and elastic. A growth of quantity of OMA in structures of compositions and also a quantity of PSMT in a mixture of matrix polymers is accompanied by value growth of the elctric conductivity of film. This has been connected with the fact that OMA is the basic electro-conductive component and acidic groups of PSMT, apparently, fulfill the role of the alloyiong agent.

4. Conclusion

The synthesized new matrix polymer of PSMA–SU includes in composition of macromolecule simultaneously carboxyl aniline sulfoacidic groups (pk_a=4 и $pk_{a=}$ 0.7, and for aniline – $pk_{=}$ 4.63). In media of pH < 4.5 PSMA–SU becomes negatively charged and aniline positively charged. PSMA–SU fulfills the function of electrostatic template which creates a favorable condition for combination of molecules of aniline orderly through para-position and the polyconjugated macromolecules of linear structure are formed. A high concentration of cations of aniline near surface of template creates a favorable condition for proceeding of the oxidative polycondensation. As a result, it is formed OMA with more high molecular mass. Thus, the prepared nanocompostions of OMA possess considerably higher and stable electric conductivity than its known compositions made by other methods, for ex., by a method of displacement. The nanocompositon of OMA−PSMA–SU prepared at ratio OMA: PSMA–SU= 0.06:1.0 (mol) is characterized by sufficiently high electric conductivity. A value of its specific volume electric conductivity is 0.41 S/cm and with content growth of PSMA–SU in comparison with OMA the electric conductivity of compositions is decreased. At the same time, the electric conductivity of compositions of OMA prepared in the presence of various template polymers is noticeably differed. The distribution and sizes of components in nanocomposition have been determined with use of methods XRD and SEM.

5.References

1. Hu W.L., Chen S.Y., Yang Z.H. J.Phys. Chem. B 2011, № 115, p. 8453–8457.
2. Khastgir D. Nikhil K. Singha J. Progress in Polymer Science 2009 , №34, p.783–810.
3. Pud A., Ogurtsov N., Korzhenko A., Shapovol Q. Proq. Polym. Ski. 2003, v.28, p. 1701-1758.
4. Valipour A.Ya., Moghaddam P.N., Mammedov B.A. Archives des Science Journal, Switzerland, Geneva 2012; vol. 65, № 7, p. 14–20.
5. Valipour A.Ya., Moghaddam P.N., Mammedov B.A. Life Sci J. 2012, vol. 9 , № 4, p.409– 421.
6. Valipour A.Ya., Moghaddam P.N., Mamedov B.A. Processes of petrochemistry and oil refining; vol. 12, № 1(45), p. 20–32, 2011.
7. Valipour A.Ya., Moghaddam P.N., Mammedov B.A. Jokull journal ISSN:0449-0576. www.jkljournal.org po box 5128, Reykjavik,Iceland, volume 2013,.issue July, p.211-251, 2013.
8. Pham, Q. L.; Haldoral, Y.; Nguyen, V. H.; Tuma, D.; Shim, J. J. Bull Mater Sci 2011, 34, 37.)
9. Moslem Mansour Lakouraj, Ehsan Nazarzadeh Zare, Advances in Polymer Technology, 2014,Vol. 33, No. 1, DOI 10.1002/adv. March2014)
10. M.R.Huang, Q.Y.Peng, and X.G.Li, Chem. Eur. J., 2006,12, 4341

IV. Chemistry and technology of organic and inorganic materials.

OR-IV-6

ALKOXYHALOGENATION OF DICHLOROSTYRENES IN UNSATURATED C_3-ALCOHOLS AND INVESTIGATION ON LIFE ACTIVITY OF SULPHATEREDUCTION BACTERIA

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Abstract. One of the effective methods of obtaining β-halo ethers is alkylehalogenation of alkenes with halogen-carrying reagents - N-bromoxukinimide and cystic iodine in alcohol medium. Alkoxyhalogenation of dihalostyrenes with allyl or propargyl alcohol and *N*-bromosuccinimide or crystalline iodine in the presence of clinoptilolite $[(NaK)_4CaAl_6Ci_{30}O_{72}]$ afforded the corresponding unsaturated β-halo ethers with high yields. The reaction of alkoxyhalogenation of allylmethaacrylate with saturated alcohols with the participation of crystalline iodine proceeds chemo- and regioselectively at low temperature. The composition and structure of the synthesized compounds were determined by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. The synthesized compounds have high antimicrobial activity against sulfate-reducing bacteria (SRB) at low concentrations. It has been shown that they are more effective antimicrobial substances and at low concentrations they completely stop the activity of SRB. It was determined that the minimum bactericidal concentration of the obtained compounds. So that, 0.025 and 0.05 ppm

Key words*:* β-halo ethers, Alkoxyhalogenation, Allylmethaacrylate, Sulfate-reducing bacteria, Biocorrosion, Anaerobic Respiration IR, ^1H and ^{13}C NMR spectroscopy.

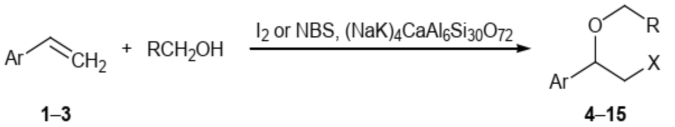
1.İntroduction

Currently, corrosion of metals in developing countries, including Azerbaijan, is one of the topical issues in the areas of processing oil and gas transportation, as well as other areas of industry. Because the corrosion problem brings great economic losses in various industries, especially in the oil and gas industry, it is always important to prevent [1-3]. Microorganisms growing on surfaces perform a variety of metabolic reactions, the products of which may promote the deterioration of the underlying substratum. These reactions refer to biocorrosion when the substratum consists of a metal or metal alloy.The action of microorganisms on petroleum products, such as fuels, oils, lubricants, etc., during their operation, storage, and transport, leads to sharp deterioration of their performance and physicochemical properties. Accumulation therein of microorganism waste products (carboxylic acids, peroxides, sulfurcontaining compounds, etc.) causes such undesirable consequences as corrosion, fouling of reservoirs and equipment, etc. [4]. Hydrogen sulfide, which is a waste product of sulfate -reducing bacteria (SRB), is one of the main factors that accelerates the corrosion process. The main method of protection against corrosion of metals is protection with inhibitors [5-6].

Aromatic unsaturated ethers that have shown the highest bactericidal effect were tested for anticorrosion activity in such aggressive media as seawater, strata water, oil-field water, oil-field water with oil, which contained hydrogen sulfide and sulfate-reducing bacteria [7]. The data accumulated until now indicate that many propargyl compounds efficiently protect metals from corrosion induced by mineral acids [8]. A rational method for the synthesis of β-halo ethers is based on alkoxyhalogenation of a double bond with unsaturated C_3-alcohols and iodine or *N*-bromosuccinimide (NBS) in the presence of mercury(II) oxide [9–11]. We have found that the use of safe and nontoxic clinoptilolite $[(NaK)_4CaAl_6Ci_{30}O_{72}]$ instead of HgO favors the reaction.

We have found that the use of safe and nontoxic clinoptilolite $[(NaK)_4CaAl_6Ci_{30}O_{72}]$ instead of HgO favors the reaction. The substrates were dichlorostyrenes **1**–**3**, and their alkoxyhalogenation with allyl and propargyl alcohols afforded up to 80% of β-halo ethers **4**–**15** containing a dichlorophenyl ring (Scheme 1).

Scheme 1.



1, **4**, **7**, **10**, **13**, Ar = 2,6-$Cl_2C_6H_3$; **2**, **5**, **8**, **11**, **14**, Ar = 2,4-$Cl_2C_6H_3$; **3**, **6**, **9**, **12**, **15**, Ar = 3,4-$Cl_2C_6H_3$;
4–**6**, **10**–**12**, X = I; **7**–**9**, **13**–**15**, X = Br; **4**–**9**, R = CH_2=CH; **10**–**15**, R = CH≡C.

Regioselective alkoxyhalogenation of the double bond in styrenes **1**–**3** was confirmed by the ^{1}H NMR data. The ^{1}H NMR spectra of iodine-containing compounds **4**–**6** and **10**–**12** showed one-proton doublets of doublets at ~3.21 and ~3.46 ppm (J = 8.3, 5.8 Hz) due to methylene protons of the CH_2I group, and their IR spectra contained C–I stretching band at 545–560 cm–1. The ^{1}H NMR spectra of bromomethyl analogs **7**–**9** and **13**–**15** displayed CH_2Br signals at δ ~3.42 and ~3.51 ppm (d.d, ^{1}H each, J = 10.3, 5.8 Hz). The ^{1}H and ^{13}C NMR and IR spectra, as well as elemental analyses, of compounds **4**–**15** were in agreement with the assigned structures.

2.Experimental

The IR spectra were recorded from samples dispersed in mineral oil on a Specord 75 IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker SF-300 instrument at 300 and 75 MHz, respectively, from solutions in $CDCl_3$ using hexamethyldisiloxane as internal standard. The elemental compositions were determined with a Carlo Erba 1106 analyzer. The melting points were measured on a Boetius hot stage.

1,3-Dichloro-2-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp-1). A mixture of 14 g (0.25 mol) of allyl alcohol and 44.8 g (0.25 mol) of 2,6-dichlorostyrene was cooled to –5 to 0°C, 2.6 g of clinoptilolite [$(NaK)_4CaAl_6Ci_{30}O_{72}$] was added with vigorous stirring, and 31.5 g (0.12 mol) of finely ground crystalline iodine was then added in 1g portions. The mixture was stirred at room temperature for 3–4 h and filtered, and the filtrate was washed with a solution of $Na_2S_2O_3$ and extracted with diethyl ether. The extract was dried over $CaCl_2$ and evaporated on a rotary evaporator, and the residue was recrystallized from an appropriate solvent. Yield 30.4 g (68%), mp 98–99°C (from EtOH). IR spectrum, ν, cm^{-1}: 3080, 3010, 1640, 1630, 1515, 1360, 1270, 842, 560. ^{1}H NMR spectrum, δ, ppm: 3.22 d.d and 3.51 d.d (^{1}H each, CH_2I, J = 10.3, 5.8 Hz), 4.00 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.43 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.17 d.d.t (^{1}H, H_2C=, J_{cis} = 10.4, ^2J = ^4J = 1.6 Hz), 5.26 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.89 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = 4J = 1.6, J_{trans} = 17.3 Hz), 7.29 d (^{1}H, C_6H_3, J = 8.8 Hz), 7.54 d.d (^{1}H, C_6H_3, J = 8.8, 2.7 Hz), 7.69 d.d (^{1}H, C_6H_3, J = 8.8, 2.7 Hz). ^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 133.1 (C_3), 135.6 (C_1), 134.9, 159.6. Found, %: C 37.41; H 3.55; Cl 19.46; I 35.58. $C_{11}H_{11}Cl_2IO$. Calculated, %: C 37.01; H 3.11; Cl 19.86; I 35.55.

2,4-Dichloro-1-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp-2) was synthesized from 2,4-dichlorostyrene, allyl alcohol, and crystalline iodine by similar mehod. Yield 66.8%, mp 96–98°C (from EtOH). IR spectrum, ν, cm–1: 3080, 3010, 1640, 1630, 1515, 1343, 1270, 845, 560. ^{1}H NMR spectrum, δ, ppm: 3.22 d.d and 3.46 d.d (^{1}H each, CH_2I, J = 10.3, 5.8 Hz), 4.01 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.43 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.16 d.d.t (^{1}H, H_2C=, J_{cis} 10.4, ^2J = ^4J = 1.6 Hz), 5.25 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.88 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = ^4J = 1.6, J_{trans} = 17.3 Hz), 7.28 d.d.d (^{1}H, C_6H_3, J = 8.8, 8.8, 2.4 Hz), 7.51 d.d (^{1}H, C_6H_3, J = 8.8, 2.4 Hz), 7.73 d.d (^{1}H, C_6H_3, J = 2.7, 0.4 Hz). ^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 133.1 (C_4), 135.6 (C_2), 134.9, 134.4, 159.6. Found, %: C 37.41; H 3.16; Cl 19.55; I 35.43. $C_{11}H_{11}Cl_2IO$. Calculated, %: C 37.01; H 3.11; Cl 19.86; I 35.55.

1,2-Dichloro-4-{2-iodo-1-[(prop-2-en-1-yl)oxy] ethyl}benzene (Exp-3) was synthesized from 34-dichlorostyrene, allyl alcohol, and crystalline iodine by similar method. Yield 66.8%, mp 97–99°C (from EtOH). IR spectrum, ν, cm–1: 3080, 3010, 1640, 1630, 1515, 1360–1340, 1270, 845, 560. ^{1}H NMR spectrum, δ, ppm: 3.20 d.d and 3.47 d.d (^{1}H each, CH_2I, J = 10.3, 5.8 Hz), 4.03 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.42 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.18 d.d.t (^{1}H, H_2C=, J_{cis} = 10.37, ^2J = ^4J = 1.6 Hz), 5.25 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.88 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = ^4J = 1.6, J_{trans} = 17.3 Hz), 7.28 d.d (^{1}H, C_6H_3, J = 8.3, 0.5 Hz), 7.53 d.d (^{1}H, C_6H_3, J = 8.8, 2.6 Hz), 7.66 d.d (^{1}H, C_6H_3, J = 2.6, 2.6 Hz). ^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 131.1 (C_2), 132.6 (C_1), 134.9, 159.6. Found, %: C 37.22; H 3.18; Cl 19.47, I 35.55. $C_{11}H_{11}Cl_2IO$. Calculated, %: C 37.01; H 3.11; Cl 19.86; I 35.55.

2-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,3-dichlorobenzene (Exp-4). A mixture of 14 g (0.17 mol) of 2,6-dichlorostyrene and 10 g (0.17 mol) of allyl alcohol was cooled to –5°C, and 14 g (0.17 mol) of *N*-bromosuccinimide was added in portions with stirring, maintaining at the temperature below 0°C. The mixture was then stirred for 3 h at room temperature, the precipitate of succinimide was filtered off, and the mixture was made alkaline by adding a solution of 15 g of sodium hydroxide in 100 mL of water, extracted with diethyl ether, and dried over $CaCl_2$. The solvent was removed under reduced pressure. Yield 71.8%, mp 94–96°C (from EtOH). IR spectrum, ν, cm–1: 3080, 3010, 1640, 1630, 1515, 1360, 1270, 850–840, 560. ^{1}H NMR spectrum, δ, ppm: 3.41 d.d and 3.51 d.d (^{1}H each, CH_2Br, J = 10.3, 5.8 Hz), 4.02 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.42 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.16 d.d.t (^{1}H, H_2C=, J_{cis} = 10.37, ^2J = ^4J =1.6 Hz), 5.25 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.88 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = ^4J = 1.6, J_{trans} = 17.3 Hz), 7.28 d (^{1}H, C6H3, J = 8.8 Hz), 7.54 d.d (^{1}H, C_6H_3, J = 8.8, 2.7 Hz), 7.69 d.d (^{1}H, C_6H_3, J = 8.8, 2.7 Hz). ^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 133.1 (C_3),135.6 (C1), 134.9, 158.4. Found, %: C 42.57; H 3.54;

Br 25.66; Cl 22.86. $C_{11}H_{11}BrCl_2O$. Calculated, %: C 42.62; H 3.58; Br 25.77; Cl 22.87.

1-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-2,4-dichlorobenzene (Exp-5) was synthesized from 2,4-dichlorostyrene, allyl alcohol, and *N*-bromosuccinimide by similar method. Yield 66.8%, mp 91–93°C (from EtOH). IR spectrum, ν, cm–1: 3080, 3010, 1640, 1630, 1515, 1313, 1270, 848, 560. ^{1}H NMR spectrum, δ, ppm: 3.42 d.d and 3.51 d.d (^{1}H each, CH_2Br, J = 10.3, 5.8 Hz), 4.00 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.43 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.17 d.d.t (^{1}H, H_2C=, J_{cis} = 10.4, ^2J = ^4J = 1.6 Hz), 5.26 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.89 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = ^4J = 1.6, J_{trans} = 17.3 Hz), 7.24 d.d (^{1}H, C_6H_3, J = 8.8, 2.4 Hz), 7.53 d.d (^{1}H, C_6H_3, J = 8.8, 2.4 Hz), 7.72 d.d (^{1}H, C_6H_3, J = 2.7, 0.4 Hz). ^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 133.1 (C_4), 135.6 (C_2), 134.9, 159.6. Found, %: C 42.77; H 3.51; Br 25.73; Cl 22.64. $C_{11}H_{11}BrCl_2O$. Calculated, %: C 42.62; H 3.58; Br 25.77; Cl 22.87.

4-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,2-dichlorobenzene (Exp-6) was synthesized from 3,4 dichlorostyrene, allyl alcohol, and *N*-bromosuccinimide by similar method.Yield 68.7%, mp 93–95°C (from EtOH). IR spectrum, ν, cm–1: 3080, 3010, 2100, 1640, 1630, 1515, 1360–1340, 1270, 850–840, 560. ^{1}H NMR spectrum, δ, ppm: 3.40 d.d and 3.52 d.d (^{1}H each, CH_2Br, J = 10.3, 5.8 Hz), 4.02 d.d (^{2}H, CH_2O, ^3J = 5.7, ^4J = 1.5 Hz), 4.42 d.d (^{1}H, CH, J = 5.8, 9.0 Hz), 5.17 d.d.t (^{1}H, H_2C=, J_{cis} = 10.4, ^2J = ^4J = 1.6 Hz), 5.25 d.d.d (^{1}H, H_2C=, J_{trans} = 17.3, ^2J = ^4J = 1.7 Hz), 5.88 d.d.t (^{1}H, CH=, J_{cis} = 10.4, ^2J = ^4J = 1.6, J_{trans} = 17.3 Hz), 7.30 d.d (^{1}H, C_6H_3, J = 8.3, 0.5 Hz), 7.53 d.d (^{1}H, C_6H_3, J = 8.8, 2.6 Hz), 7.67 d (^{1}H, C_6H_3, J = 2.6 Hz).^{13}C NMR spectrum, δC, ppm: 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 130.9, 131.1 (C_2), 132.6 (C_1), 134.9, 134.4, 159.6. Found, %: C 42.65; H 3.63; Br 25.71; Cl 22.57. $C_{11}H_{11}BrCl_2O$. Calculated, %: C 42.62; H 3.58; Br 25.77; Cl 22.87.

3.Results and discussion

The obtained compounds are liquids with a characteristic odor, insoluble in water, well soluble in organic solvents. The effect of samples on the life activity of SRB was studied by the following method [12]. The effect of Exp-1(1,3-Dichloro-2-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene), Exp-2 (2,4-Dichloro-1-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene), Exp-3 (1,2-Dichloro-4-{2-iodo-1-[(prop-2-en-1-yl)oxy] ethyl}benzene), Exp-4 (2-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,3-dichlorobenzene), Exp-5 (1-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-2,4-dichlorobenzene), Exp-6 (4-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,2-dichlorobenzene) samples on the vital activity of SRB was studied by the following procedure. In the experiments, the SRB of the species "Desulfovibrio desulfuricans" and strain 1143 were used. SRB are lobed anaerobic bacteria that restore sulfates to hydrogen sulphide. For the development of SRB, the most optimal medium is the Postqeyt B culture medium. The pH of the medium must be within range of 7.0-7.5 For the development of SRB in the environment of Posqeyt add the following supplements. The additives are as follows: ferrum sulphate $FeSO_4 \cdot 7H_2O$ (5% solution in 2% hydrochloric acid) - 0.5-2 mll, sodium bicarbonate $NaHCO_3$ (5% aqueous solution) - 1 ml, a solution of crystalline sodium sulphide prepared in a 1% solution of Na_2CO_3 ($Na_2S \cdot 9H_2O$ - 1 ml

The experiments were carried out in 10 ml pre-sterilized test tubes according to a known technique. To determine the content of bacteria in a non-inhibitory medium, bacteria are first diluted, inoculated and stored in a thermostat at a temperature of 30-32 ^{0}C with an incubation period of 7-14 days, and at the end of the experiment it was found that the content of bacteria in a non-inhibitor control medium, the number of bacteria is n = 108. Subsequently, the synthesized compounds were added at concentrations of 0.025 and 0.05 ppm they were again kept in a thermostat at a temperature range of 30-32 ° C for 7-14 days, and in the first 48 hours the effectivity of the complexes on the life activity of bacteria was observed. The effect of complexes on the SRB growth at concentrations of 0.025 and 0.05 ppm see in fig. 1.

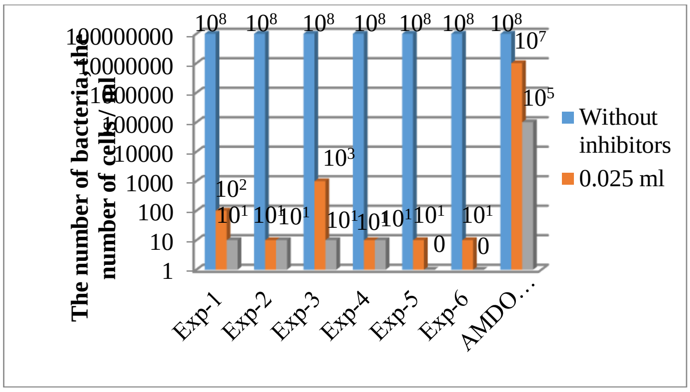


Fig. 1 Diagram of the influence of samples Exp-1, Exp-2, Exp-3, Exp-4, Exp-5, Exp-6 on the amount of SRB.

The number of bacteria / cell number without inhibitor
0.025 ppm
0.05 ppm

As can be seen from the diagram, in the medium without inhibitor the number of bacteria is n = 1 × 10^8, and in an inhibitory medium for 1,3-Dichloro-2-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp-1) the number of bacteria at a concentration of 0.025 ppm decreases from 1 × 10^8 to 10^2 and 0.05 ppm 10^1. 2,4-Dichloro-1-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp 2) at all concentration the number of bacteria decreases from 1 × 10^8 to 10^1. 1,2-Dichloro-4-{2-iodo-1-[(prop-2-en-1-yl)oxy] ethyl}benzene (Exp 3) at a concentration of 0.025 ppm decreases from 1 × 10^8 to 10^3, at a 0.05 ppm10^1. 2-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,3-dichlorobenzene (Exp 4) at a concentrations of 0.025 and 0.05 ppm decreases from 1 × 10^8 to 10^1. 1-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-2,4-dichlorobenzene (Exp 5) the number of bacteria at a concentrations of 0.025 ppm decreases from 1 × 10^8 to 10^1 at a 0.05 ppm to 0. 4-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,2-dichlorobenzene (Exp 6) at a concentrations of 0.025 ppm decreases from 1 × 10^8 to 10^1 at a 0.05 ppm to 0.

At the conclusion of the studies, the test samples were titrated by the iodometric method and the protective effect was calculated from the obtained amount of H_2S. For titration, we used fixed solutions of iodine and sodium hyposulfite. During the titration were used fixed solutions of iodine and sodium hyposulfite. The H_2S content was calculated using the following equation:

$$X \text{ mq/l } H_2S = \frac{N(J) \text{ x } V(J) - N(Na_2S_2O_3) \text{ x } V(Na_2S_2O_3)}{VH_2O} \text{ x } 17000 \qquad 1)$$

N (J) = 0.1 N, V(J) =10 ml, N ($Na_2S_2O_3$) = 0.1 N, V ($Na_2S_2O_3$) = 7 ml, V (H_2O) =20 ml
17000 - shows the solubility of 0.1 N hyposulfite in 1000 ml.
Based on the H_2S content, the protective effect of the inhibitor is determined by the following equation

$$Z = \frac{(C_0 - C_{inh})}{C_0} \cdot 100\% \qquad 2)$$

C_0 - hydrogen sulfide content in the control medium, ppm;
C_{inhi} - the content of hydrogen sulfide formed in the reagent medium, ppm.
Calculated bactericidal effect of samples (Exp-1, Exp-2, Exp-3, Exp-4, Exp-5, Exp-6) (table 1)

Table 1. Results of resulting compounds (Exp-1, Exp-2, Exp-3, Exp-4, Exp-5, Exp-6) bactericidal effect dependence on concentration

The resulting compounds	Substance concentration C-ppm	The number of bacteria (number of cells / ppm)	H_2S containing mg/l	Bacterisidal effect Z, %
1,3-Dichloro-2-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp-1)	0.025	10^2	60	76.4
	0.05	10^1	32	87.4
	0.025	10^1	23	91

2,4-Dichloro-1-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp 2)	0.05	10^1	10	96
1,2-Dichloro-4-{2-iodo-1-[(prop-2-en-1-yl)oxy] ethyl}benzene (Exp 3)	0.025	10^3	63	75
	0.05	10^1	13	94.9
2-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,3-dichlorobenzene (Exp 4)	0.025	10^1	11	95.6
	0.05	10^1	1.8	99.2
1-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-2,4-dichlorobenzene (Exp 5)	0.025	10^1	5	98.4
	0.05	-	-	100
4-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,2-dichlorobenzene (Exp 6)	0.025	10^1	2	99
	0.05	-	-	100
АМДОР-ИК-10	0.025	10^7	187	26
	0.05	10^5	142	45
Control-I H_2S content in medium without test culture-32 mg/l				
Control-II H_2S content in the medium with the test culture-255 mg/l				
Control -III-the number of bacteria in postgate medium 10^8 (number of cells / ppm)				

Control-I and Control –II is show H_2S content in a non test culture medium and in a test culture medium Control-I -is a medium without SRB, that H_2S content is -32 mq/l, control –II -is a medium with SRB that the H_2S content is -255 mq/l). Control -III-the number of bacteria in postgate medium 10^8 (number of cells / ppm)

As can be seen from Table 2, 1,3-Dichloro-2-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp-1) exhibit 76.4% bactericidal effect at 0.025 ppm concentration and at 0.05 ppm 87.4%. 2,4-Dichloro-1-{2-iodo-1-[(prop-2-en-1-yl)oxy]ethyl}benzene (Exp 2) exhibit 91% bactericidal effect at 0.025 ppm 96% at 0.05 ppm. 1,2-Dichloro-4-{2-iodo-1-[(prop-2-en-1-yl)oxy] ethyl}benzene (Exp 3) exhibit 75% bactericidal effect at 0.025 ppm and 94.9% at 0.05 ppm. 2-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,3-dichlorobenzene (Exp 4) exhibit 95.6% bactericidal effect at 0.025 ppm 99.2% at 0.05 ppm. 1-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-2,4-dichlorobenzene (Exp 5) exhibit 98.4% at 0.025 ppm, 100% at 0.05 ppm bactericidal effect. 4-{2-Bromo-1-[(prop-2-en-1-yl)oxy]ethyl}-1,2-dichlorobenzene (Exp 6) bactericidal effect is 99% at 0.025 ppm concentration and 100% at 0.025 ppm. The obtained compounds were compared with bactericide-inhibitors used in industry (AMDOR-IK-10). It has been established that industrial reagents at a concentration of 0.025 ppm exhibit 29-26%, and at a concentration of 0.05 ppm 48-45% biocidal effect.

Based on the results of the studies, it was found that the synthesized β-haloethers completely suppress the life activity of SRB at significantly at low concentrations in comparison with industrial inhibitors taken as a standard.

5.References

1. Abd El-Lateef H.M., Aliyeva L.I., Abbasov V.M., Ismayilov T.I., Ismayilova X.R. Development of New Eco-Friendly Corrosion Inhibitors Based on Vegetable Oils for Protection from CO_2 Corrosion. Chemistry Journal (2), pp. 74-93. (2012)

2. Hany M. Abd El-Lateef, Aliyeva L.I., Abbasov V.M., Ismayilov T.I. Corrosion inhibition of low carbon steel in CO_2 -saturated solution using anionic surfactant. Advances in Applied Science Research (3) 2, pp. 1185-1201 (2012)

3. V.M. Abbasov, A.R.Ezizbeyli, R.A. Jafarova, S.Y.Hajiyeva, E.E. Gasimov Corrosion Inhibition of Steel C1018 with Novel Complexes of Imidazoline. Chemistry journal (CJ) (02) 06, pp. 194-198. (2012)

4. Биоповреждения. Под ред. В.Д.Ильичева. М. Высшая школа, 1987. С. 219.

5. V.M. Abbasov, A.R. Ezizbeyli, R.A. Jafarova, A.T. Gambarogly, E.G. Mamedbeyli Synthesis and study of bactericidal properties of complexes of imidazoline derivatives of petroleum acids with alkylhalogens. Processes of Petrochemistry and Oil Refining (60)15.4, pp. 343-347. (2014)

6. A.R. Ezizbeyli, V.M. Abbasov, R.A. Jafarova, S.Y.Hajiyeva, E.E. Gasimov Corrosion Inhibition of Steel C1018 with Novel Complexes of Imidazoline. Chemistry journal (02) 06, pp.194-198. (2012)

7. Karaev S.F., Garaeva Sh.V., Mamedov F.V. Chemistry of Heteroatomic Propargyl Compounds, Moscow: Chemistry, pp. 145. (1993) [Караев С.Ф., Гараева Ш.В., Мамедов Ф.В. Химия гетереоатомных пропаргиловых соединений, М.: Химия, 1993.с.145].

8. Balezin S.A., Voskresensky A.G. Sat. Metal corrosion inhibitors. Moscow: MGPI im. VI Lenin, , N3, pp. 295-298. (1969) [Балезин С.А., Воскресенский А.Г. Сб. Ингибиторы коррозии металлов. М.: МГПИ им. В.И.Ленина, №3, с. 295-298 (1969)]

9. .[Talybov G.M., Mekhtieva V.Z., Karaev S.F.. *Russ. J. Org. Chem.* . (37)4, pp.600. (2001)]. doi.10.1023/A:1012462709589 Талыбов Г.М., Караев С.Ф., Мехтиева В.З. ЖОрХ., (37) 4 с.634. (2001)

10. Karaev S.F., Akperova M.A., Talybov G.M. Dihaloalkylpropargyl ethers: synthesis and properties. XIX Mendeleev Congress on General and Applied Chemistry. (1), Volgograd. pp. 232. (2011) [Караев С.Ф., Акперова М.А., Талыбов Г.М. Дигалогеналкилпропаргиловые эфиры: синтез и свойства. XIX Менделеевский съезд по общей и прикладной химии.(1)., Волгоград. с. 232. (2011)]

11. Akperova M.A., Talybov G.M., Karaev S.F .. Proceedings of the Higher Educational Institutions of the Russian Federation. Chemistry and chemical technology. (54) 8, pp.35. (2011) [Акперова М.А., Талыбов Г.М., Караев С.Ф.. Известия Высших Учебных заведений РФ. Химия и химическая технология., (54) 8, с.35. (2011)]

12. Postgate J.R., Campbell L.L., Classification of Desulfovibrio cpecies the non sporulating sulfate- redusing bacteria. Bacteriol. Revs., (30) 4, pp. 732-738. (1966)

OR-IV-1

EXTRACTION-PHOTOMETRIC DETERMINATION OF IRON

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Abstract. Spectrophotometric methods were used to study the complexation of iron (III) with 2-(piperidinomethyl)-4-methyl-6(3-methylcyclohexyl)phenol (L). Identification of the synthesized reagent was performed using elemental analysis, IR and NMR spectroscopy. The optimal conditions for the formation and extraction of the complex compound were found and the relations of the components in the complex were established. It was found that a complex compound is formed in a weakly acidic medium (pH_{opt} 3.6-5.4). The molar absorption coefficient is equal to $\varepsilon_{540} = 3.34 \times 10^4$. L maximally absorbs at 268 nm. The bathochromic shift is 267 nm. The yield of the complex is maximum at a concentration of 8.5×10^{-4} mol L^{-1} L. The complexing form of iron is $FeOH^{2+}$. The ratio of components in the complex is 1: 2 (Fe:L=1:2). During the electrolysis of the solution of the complex, its movement was not observed either to the anode or to the cathode even after prolonged current flow, that is, it is electrically neutral. The method of intersection of the curves calculated stability contants ($\lg\beta k = 10.49$). With a single extraction with chloroform, 98.2% of iron is extracted in the form of a complex.

Key words: iron, 2- (piperidinomethyl) -4-methyl-6 (3-methylcyclohexyl) phenol, extraction-photometric method, spectrophotometric measurements.

1. Introduction

Iron is an essential element in living organisms. Therefore, analytical control of the iron content in environmental objects should be carried out by reliable methods.

Iron forms coordination bonds with complexing ligands. Reagents containing donor oxygen and nitrogen atoms are considered the most suitable for the determination of iron (III) [1]. Photometric methods for the determination of iron (III) in the form of mixed ligand complexes (MLC) with this reagent in the presence of third components are highly sensitive [2-8].

Reagents containing OH and SH - groups are selective with respect to iron (III) [6-8].

The aim of this work is to develop a photometric method for the determination of iron (III) in oil and oil products using 2 - (piperidinomethyl) -4-methyl-6 (3-methylcyclohexyl) phenol (L).

2 Experimental

2.1 Reagents and Apparatus

An initial solution of iron (III) (1 mg / ml) was obtained by dissolving 8.6350 g $FeNH_4(SO_4)_2 \times 12H_2O$ (99.1%; Reanal, Hungry) in water containing 5 ml conc. H_2SO_4 [9] and standardization was carried out using α -benzooxime by gravimetric method [9]. Solutions with lower iron content were prepared sequentially dilution of the standard solution. A 0.01 M solution of L in chloroform was used. Purified chloroform was used as an extractant. The acidity was adjusted by adding solutions with acetate-ammonia buffer solutions and controlled with a glass electrode (I-130 ion meter). Optical density was measured using KFK-2 and SF-26. IR spectra were recorded on a Specord-M80 instrument.

2.2.Procedure for the synthesis of 2- (piperidinomethyl) -4-methyl-6 (3-methylcyclohexyl) phenol

A mixture of 27.5 g of *p*-cresol (254 mmol), 7.5 g of formaldehyde (250 mmol) and 27.5 g of benzene (352 mmol) are thoroughly mixed and heated. When the temperature of the reaction mixture reaches 40-45°C, 21 g (247 mmol) of piperidine are added dropwise from a dropping funnel. After the addition of piperidine, the temperature of the reaction mixture is raised to 80° C and stirred for 1 hour. In order to remove water and benzene, the temperature of the mixture is raised to 110°C. The resulting product is cooled to 40°C and 2- (piperidinomethyl) -4-methyl-6 (3-methylcyclohexyl) phenol is isolated by distillation under reduced pressure (mm Hg) Product yield: 59%.

The synthesized reagent was identified using elemental analysis and IR spectroscopy [13]. The results of chemical analysis:

	C	H	N	O
Found,%	79.73	10.30	4.65	5.31
Calculated,%	78.89	10.02	4.34	5.54

IR spectrum (KBr) - 3470 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2850 cm^{-1} ν (CH_3), 1610-1450 cm-1 ν (C_6H_5), 1420 cm^{-1} ν (CN), 1391 cm^{-1} ν (CO).

2.3 General Procedure

In 25 ml volumetric flasks with an interval of 10 μg, 10-100 μg of iron, 3 ml of a 0.01 M solution of L and 2 ml of chloroform are injected, the pH is controlled, water is diluted to the mark and the optical density of the solutions is measured relative to water. Based on the data obtained, calibration graphs are built.

2.4 Determination of the charge sign of the complex

During the electrolysis of the solution of the complex, its movement was not observed either to the anode or to the cathode even after prolonged passage of current, i.e., it is electrically neutral. The experiments were conducted in the usual way, in a U-shaped tube with two taps, at a voltage of 180-200 V and a current strength of 0.5-0.8 mA. The electrolysis was carried out for 3 hours.

3. Results And Discussion

Absorption spectra and effect of pH. The iron complex with L absorbs light at 540 nm. L is absorbed as much as possible at 256 nm. The bathochromic shift is 279 nm. The contrast of the reactions is high: the initial reagent is almost colorless, and the complex is red-violet-summer in color. The molar absorption coefficient is $\varepsilon = 3.29 \times 10^4$.

For the formation and extraction of the Fe (III) complex, the optimum pH is 3.6-5.4, and further analytical studies were carried out at pH 4.

The choice of the extractant. 2- (piperidinomethyl) -4-methyl-6 (3-methylcyclohexyl) phenol is poorly soluble in water. The reagent anion is transferred to the aqueous phase and the complex is formed in the aqueous phase. The complex is also poorly soluble in water, but the solubility in non-polar organic solvents is high. To clarify the possibility of complex extraction, the following solvents were tested: aromatic carbohydrates, cyclohexanone, tributyl phosphate, alcohols, carbon tetrachloride, chloroform, and their mixtures. Chloroform turned out to be the best solvent for the extraction. In a single extraction with chloroform, 98.2% of the iron is extracted as a complex.

Influence of ligand concentration, retention time and phase volume. To select the optimal conditions, the influence of the concentration of reagents, temperature and time on the formation of a colored complex was studied. The yield of the complex is maximal when the concentration of the reagent is 8.5×10^{-4} mol L^{-1}.

Iron extracts in the form of Fe-L obey the basic law of light absorption at concentrations of 0.25 - 16 μg / ml. Equation of the calibration graph: $0.036 + 0.041x$ (R = 0.9978).

The iron complex with L is formed within 10 minutes and does not decompose within two days, and after extraction - more than 10 days.

The degree of extraction does not depend on the ratio of the volumes of the aqueous and organic phases in a wide range (from 5: 5 to 105: 5), which makes it possible to simultaneously concentrate and photometrically determine iron.

Composition and structure. It has been experimentally established that the complexing form of iron is FeOH2 + [10].The stoichiometry of the studied complex was established by the methods of curve intersection, equilibrium shift, relative yield, and a straight line of Asmus [11]: Fe : L = 1: 2. Stability constants (10.49) are calculated by the curve crossing method.

The Fe (III) complex with L has been synthesized and studied by chemical analysis and IR spectroscopy. The disappearance of the absorption band in the region of 3600-3250 cm-1 shows that -OH takes part in the formation of bonds with iron. The vibration frequency νCN (1350 cm-1) is shifted towards low frequencies by 35 cm-1 compared to the IR spectrum of the free ligand (absorption band νCN = 1850 cm-1). This suggests that the ligand is coordinated with iron through the nitrogen atom of the piperidine ring. The absorption bands at 445 cm-1 and 576 cm-1 correspond to ν (Fe-O) and ν (Fe-N), respectively [12].

The results of chemical analysis:

	Fe	C	H	N	O
Found,%	8.54	73.17	9.14	4.27	4.88
Calculated,%	8.29	71.89	8.63	4.04	4.54

Considering the molar ratio of the components in the complex, the complexing form of the central ion, as well as the data of IR spectroscopic and chemical analysis, the structure of the Fe (III) complex with L can be represented as:

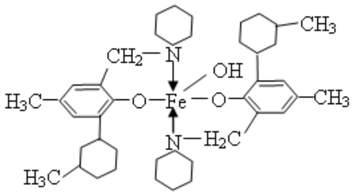

Table 1 shows the chemical and analytical characteristics of the method for determining Fe (III).

Table 1. Optimal conditions for formation and analytical characteristics of the complex

Color	H_{max}	H_{opt}	мах, nm	$\times10^{-4}$	lgK_{eq}	lgK_{ex}	R,%	Working Range, µg /ml
ed	.8-8.1	3.6-5.4	40	.34	.22	.82	8.2	0-22 0.2

Selectivity of determination of iron. Several metal ions as well as masking agents were studied under optimal conditions for the extraction spectrophotometric determination of iron. The determination of iron is not interfered with by acetate, aluminum, fluoride, and zirconium. Iron is interfered with: Cu (II), Mn (VII), Ti (IV), Nb (V), and Ta (V). Their interfering influence was eliminated by masking agents.

4. Conclusion

In the already established optimal conditions, the proposed method was used to determine the iron (III) content in oil and oil products. The proposed methods for determining the iron content in oil and oil products were tested using phenanthrolines [1]. The analysis results are presented in Table 2.

Table 2. Determination of iron

Prosedure	X, % *Oil*	Sr
phenanthroline	$(3.45\pm0.16)\times10^{-4}$	0.039
Fe-L	$(3.30\pm0.25)\times10^{-4}$	0.027
	Fuel Oil	
phenanthroline	$(4.43\pm0.24)\times10^{-3}$	0.036
Fe-L	$(4.65\pm0.29)\times10^{-3}$	0.028
	Hyudron	
phenanthroline	$(4.73\pm0.23)\times10^{-3}$	0.029
Fe-L	$(4.48\pm0.29)\times10^{-3}$	0.031

5.References

1. Marczenko, Z., Baltsejak, M. K.: Metodı Spectrophotometrii v UF I vidimoy oblastyax (Spectrophotometrically in the UV and visible regions in inorganic analysis). M. Binom. Laboratoriya znaniy (2007).
2. Upor, E., Makhoi, M., Novak, D.: Photometric methods for the determination of traces of inorganic compounds. M. Mir. (1985).
3. Safavi, A., Mir, M., Abdollahi, H.: Simultaneous spectrophotometric determination of iron, titanium and aluminium by partial least-squares calibration method in micellar medium. Journal Analytical Letters 36 (3), 699-717 (2003).
4. Rustamov, N. Kh., Alieva, A. A., Agamalieva, M. M.: Extractionphotometric determination of iron (III) with aromatic diamines and dinitrobenzene salicylic acid. Journal of Chemical Problems. (2), 83-86 (2003).
5. Rustamov, N.Kh., Keramova, A.A.: Extraction-photometric determination of iron (III) with heterocyclic diamines and azo derivatives of salicylic acid. Factory laboratory. 75 (5), 3-8 (2009).
6. Zalov, A.Z., Kuliev, K.A.: Extraction-photometric determination of cobalt (II) with 5- (4-Hydroxybenzylidene) - 2,4- tiazolidindion in different objects. Journal of pharmacognosy and phytochemistry. 8 (1), 2612-2616 (2019).
7. Zalov, A.Z., Kuliev, K.A., Mammadova, Sh.A.: Extraction-pho-tometric determination of iron in fruit, berries and in natural waters. International journal of chemical studies. 7 (1), 2379-2384 (2019).
8. Zalov, A.Z., Kuliev, K.A., Abasgulieva, U.B.: Composition and extraction of tungsten (VI) complexes with 2-hydroxy-5-bromtiphenol and aminophenols.Journal Chemical problems.1 (17), 50-58 (2019).

9. Korostelev, P. P.: Preparation of solutions for chemical analysis works. Publishing house of Academy of Sciences of the USSR. (1964).
10. Nazarenko, V.A., Biryuk, E.A.: Study of the chemistry of the reactions of ions of multivalent elements with organic reagents. Journal of Analytical Chemistry. 22 (1), 57–64 (1967).
11. Bulatov, M. I., Kalinkin, I. P.: Prakticheskoe rukovodstvo po fotokolorimetricheskim I spektrofotometricheskim metodam analiza (Practical Guide on Photocolorimetric and Spectropho-tometric Methods of Analysis), Moscow: Khimiya (1972).
12. Bellami, L.: Infrakrasnie spectri slojnikh molecul (The Infra-Red Spectra of Complex Molecules). Moscow, Mir, (1991).

PP-IV-2

EFFECT OF CRYSTALLINITY OF CU-W-O CATALYSTS ON THEIR ACTIVITY IN THE REACTION OF ETHANOL CONVERSION

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Abstract. In the work, 9 catalysts with an atomic ratio of elements from Cu–W = 1: 9 to Cu – W = 9: 1 were synthesized. The phase composition of the synthesized samples was studied by X-ray diffraction. It was found that in the Cu-W-O system, the formation of three phases is observed in all samples, namely, two phases of the initial copper and tungsten oxides, as well as the chemical compound of copper tungstate. It was found that in the synthesized samples the percentage ratio of the starting components is preserved, which is evidenced by the regular change in the intensities of reflections in diffraction patterns. It is also calculated the degree of crystallinity of the studied samples. It is found that the degree of crystallinity of the Cu-W-O catalytic system with an increase in the copper content in the catalyst composition first increases slightly to 85.7% for the sample Cu-W = 3-7 and then decreases to 41.3% for the sample Cu-W=9-1. Increase in the degree of crystallinity of binary copper-tungsten oxide catalysts leads to an increase in the yields of the partial oxidation of ethanol and a decrease in the yield of carbon dioxide.

Keywords: Binary Catalyst, Ethanol Conversion, Crystallinity.

1.Introduction

We have previously shown that tungsten oxide catalysts are highly active in the reactions of ethanol conversion into such compounds as acetic acid, acetone, etc. [1,2]. From the periodic literature it is known that catalysts based on copper oxides are highly active in the reactions of partial oxidation of organic compounds [3-5]. In this regard, we studied the effect of copper additives on the activity of tungsten oxide catalysts in the reaction of ethanol conversion [6]. It was found that the activity of binary copper-tungsten oxide catalysts strongly depends on their composition, which is apparently due to a change in the phase composition of the samples. That is why in this work, the phase composition of binary copper-tungsten oxide catalysts and its influence on catalytic activity was studied.

2.Experimental part

Mixed copper tungsten oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of copper nitrate and ammonium tungstate. The obtained mixture was successively evaporated and dried at 100-120°C, decomposed at 250°C until nitrogen oxides were completely separated, and then calcined at a temperature of 600°C for 10 hours. Thus, 9 catalysts were synthesized with an atomic ratio of elements from Cu:W=1:9 to Cu:W=9:1. X-ray studies of binary copper-tungsten oxide catalysts were carried out on a Bruker D2 Phaser automatic powder diffractometer (CuKα radiation, Ni filter, $3 \leq 2\theta \geq 80$ °)., we also degree of crystallinity of studied samples calculated using the DIFFRAC.EVA program. The activity of the synthesized catalysts was studied on a flow-through installation unit with a quartz reactor in the temperature range of 150-500°C. 5 ml of the studied catalyst with a grain size of 1.0–2.0 mm was loaded into the reactor, and its activity in the ethanol conversion reaction was studied. A mixture of ethanol with steam and nitrogen was passed through the catalyst loaded into the reactor with an ethanol: water: nitrogen ratio of 1:4:5. The space velocity of the feed mixture was 1200 h^{-1}. Ethanol and its conversion products were determined by a chromatographic method.

3.Results and discussion

We have synthesized 9 samples of Cu-W-O catalytic system in various component ratios satisfying the following conditions:

mCu/nW, where m, n = 1 ÷ 9; m + n = 10.

The results of X-ray diffraction studies showed that in the Cu-W-O catalytic system three phases are formed: CuO and WO3 and $CuWO_4$. Figure 1 shows the diffraction patterns of all nine samples of Cu-W-O catalytic system assembled together.

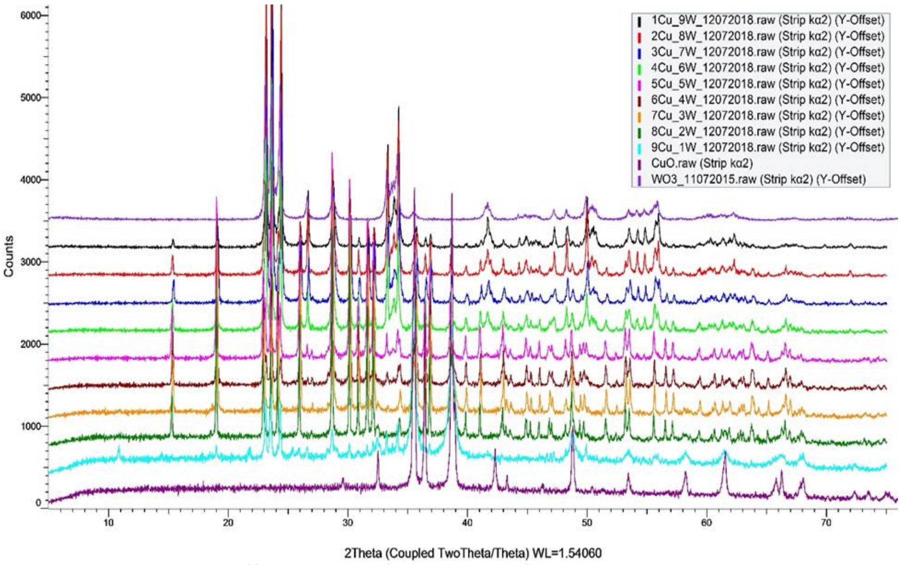

Figure 1. Diffractograms of all samples of Cu-W-O catalytic system

At the beginning and at the end of these diffraction patterns are also presented samples of ZnO and CuO oxides. Analysis of x-ray diffraction patterns shows that all samples consist of three phases and the percentage of components is preserved in all, which is evidenced by a regular change in the intensities of reflections in diffraction patterns.

We also using the DIFFRAC.EVA program calculated the degree of crystallinity of the studied catalysts. The phase composition and degree of crystallinity of studied samples are presented in the table 1. As can be seen from table 1, all studied samples contain CuO, WO_3, and $CuWO_4$ phases. An exception is the sample composition Cu-W=9-1 in which instead of a chemical compound $CuWO_4$ there is present a phase of metallic copper. From table 1 it is also seen that with an increase of the copper content in the catalyst, the degree of crystallinity practically does not change until the Cu-W=5-5 sample. Starting from sample Cu-W=6-4, the degree of crystallinity decreases sharply and reaches 41.5% on sample Cu-W = 9-1.

Table 4. Phase composition and degree of crystallinity of Cu-W-O catalytic system.

Cu/W ratio	Degree of crystallinity, %	Phases
Cu-W=1-9	84,2	CuO, WO_3, $CuWO_4$
Cu-W=2-8	85,5	CuO, WO_3, $CuWO_4$
Cu-W=3-7	85,7	CuO, WO_3, $CuWO_4$
Cu-W=4-6	84,1	CuO, WO_3, $CuWO_4$
Cu-W=5-5	83	CuO, WO_3, $CuWO_4$
Cu-W=6-4	79,8	CuO, WO_3, $CuWO_4$
Cu-W=7-3	77,6	CuO, WO_3, $CuWO_4$
Cu-W=8-2	66,6	CuO, WO_3, $CuWO_4$
Cu-W=9-1	41,3	CuO, WO_3, $CuWO_4$

The study of the activity of the studied samples showed that the reaction products of the conversion of ethanol to the Cu – W – O catalytic system are acetic aldehyde, acetone, ethylene, and carbon dioxide. Table 2 shows the dependence of the yields of the reaction products of ethanol conversion on the atomic ratio of copper to tungsten in the composition of Cu-W-O catalysts. It is seen that with an increase in the copper content in the catalyst composition, the yield of acetic aldehyde passes through two maxima on the samples Cu-W=3:7 (56.4%) and Cu-W=6:4 (52.6%). Similar output dependencies on the catalyst composition are also observed for the reaction of acetone formation. The yield of ethylene with an increase in the copper content in the composition of the catalyst decreases and is almost zero on samples rich in copper. The yield of the product of the deep oxidation of ethanol carbon dioxide with an increase in the copper content in the composition of the catalyst first slightly decreases, and then starting from the sample Cu:W=3:7 increases to 24.6% on the sample Cu:W=9:1. As can be seen from table 2, the dependence of ethanol conversion on the composition of the catalyst also has the form of a curve with two maxima, and the highest conversion of ethanol reaches 89.5%.

Table 2. Dependence of the yields of the reaction products of ethanol conversion on the atomic ratio of copper to tungsten in the composition of the catalyst.

Reaction products	Yields of reaction products, %								
The ratio of copper to tungsten	1-9	2-8	3-7	4-6	5:5	6-4	7-3	8-2	9-1
Carbon dioxide	21,6	19,7	16,8	17,8	20,4	19,8	23,2	20,3	24,6
Ethylene	18	13	9,4	5,4	4,8	4,3	0	0	0
Acetic aldehyde	32,2	50,8	56,4	52,4	44,4	52,6	45,6	40,4	37,4
Acetone	0	6	5,2	0	0	6,2	1,5	1,2	0
Ethanol conversion	71,8	89,5	87,8	75,9	69,9	83	70,3	66,3	63,5

The dependence of the yields of ethanol conversion reaction products on the degree of crystallinity of binary copper-tungsten oxide catalysts is shown in Figure 2. As can be seen from Figure 2, with increasing degree of crystallinity of the catalyst, the outputs of acetic aldehyde, increase, while the yield of carbon dioxide decreases. It can also be seen from Figure 2 that the conversion of ethanol also increases with an increase in the degree of crystallinity of the catalyst.

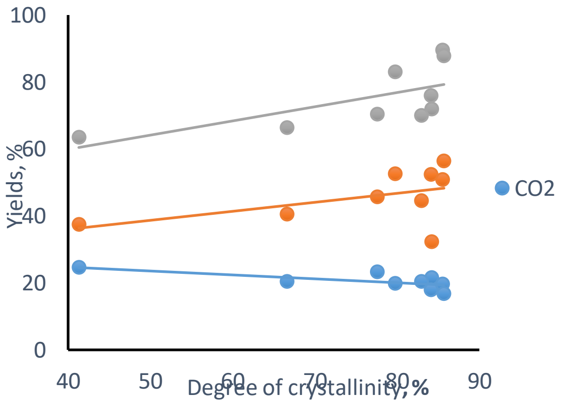

Figure 2. Dependence of the yields of the reaction products of ethanol conversion on the degree of crystallinity of binary copper-tungsten oxide catalysts.

4.Conclusion

- Phases CuO, WO_3, and $CuWO_4$ are formed in the copper-tungsten oxide system. With increasing copper content in the catalyst, the degree of crystallinity of the samples decreases.
- Increase in the degree of crystallinity of binary copper-tungsten oxide catalysts leads to an increase in the yields of the partial oxidation of ethanol and a decrease in the yield of carbon dioxide.

5.References

9. Aghayeva K.Kh., Baghiyev V.L.: Conversion of ethanol over Mo-W-O catalysts. Austrian Journal of Technical and Natural Sciences 7-8, 47-50 (2017).
10. Aghayeva K.Kh., Baghiyev V.L.: Ethanol Conversion over Binary Ti-W-O Catalysts. In: 5th International School-Conference on Catalysis for Young Scientists, Catalyst Design: From Molecular to Industrial Level, May 20-23, 2018, Moscow, Russia, ABSTRACTS, Novosibirsk, PP-V-22, p.279.
11. Gabriella Garbarino, Paola Riani María Villa García, Elisabetta Finocchio Vicente Sanchez Escribano, Guido Busca.: A study of ethanol dehydrogenation to acetaldehyde over copper/zinc aluminate catalysts, Catalysis Today 330, 121-130 (2019).
12. Shelepova E.V., Ilina L.Yu., Vedyagin A.A..: Theoretical predictions on dehydrogenation of methanol over copper-silica catalyst in a membrane reactor, Catalysis Today 331, 35-42 (2019).
13. Nauert S., Schax F., Limberg C., Notestein J.: Cyclohexane oxidative dehydrogenation over copper oxide catalysts, Journal of Catalysis 341, 180-190 (2016).
14. Mammadova S.H., Aghayeva K.Kh.: Conversion of ethanol over binary copper containing catalysts, Chemical Problems, 2(18), 199-205 (2020)

PP-IV-13

PHASE EQUILIBRIA IN THE GETE-RICH FIELD OF THE GETE-Bi_2Te_3 SYSTEM

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Abstract. The GeTe-Bi_2Te_3 system was re-examined in the 0-25 mol% Bi_2Te_3 composition in the range between 700-1000 K interval by using DTA, RFA, and SEM methods, and the corresponding fragment of the phase diagram was constructed. It was found that the system is characterized by the formation of large solid solutions based on both modifications of GeTe. The solubility of the cubic structure α-GeTe is maximum and rich 18 mol% at 870 K, and the solubility of the rhombic structure β-GeTe is ~ 9.5 mol%. An increase in bismuth concentration leads to a morphotropic transition to the cubic phase. $Ge_4Bi_2Te_6$ and $Ge_3Bi_2Te_6$ Van der Waals compounds decompose by solid-phase (858 K) and peritectic reaction (863 K) accordingly. The obtained results are compared with the phase diagrams illustrated in the literature.

Keywords: GeTe-Bi_2Te_3 system, phase diagram, solid solution, Van-der-Waals phases, phase transitions

1. Introduction

Tetradymite-like layered ternary compounds formed in $A^{IV}Te$-$B^{V}_2Te_3$ (A^{IV}- Ge, Sn, Pb; B^{V}-Sb, Bi) systems have been widely studied as promising thermoelectric materials since the second half of the last century [1-3]. The discovery of new innovative functional materials - topological insulators (TI) [4, 5] and the determination of the TI properties of these compounds [6-13], has aroused a great interest of researchers [6-12]. It has been determined that they are very promising for applications used in spintronics, the creation of quantum computers, scanning devices used in medicine and security systems, etc [13-16].

The above information highlight the importance of phase diagrams of multicomponent systems in materials science [17-19] and makes it necessary to study the data on $A^{IV}Te$-$B^{V}_2Te_3$ systems and obtain reliable schemes of phase equilibria. As noted in [13], many ternary compounds are not reported in the known phase diagrams of these systems. GeTe-$B^{V}_2Te_3$ systems are of particular interest in terms of the development of physico-chemical properties for the synthesis and investigation of new TI-specific phases, as they have formed representatives of two types of homologous series of layered compounds ($mGeTe\cdot B^{V}_2Te_3$ and $GeB^{V}_2Te_4\cdot nB^{V}_2Te_3$) [20,21].

Considering the above, we began detailed research of phase equilibrium in GeTe- $B^{V}_2Te_3$ systems. In the presented work, obtained results for the GeTe-rich area of the GeTe-Bi_2Te_3 system are demonstrated.

It should be noted that phase equilibria in this system were first studied in [22] and it was determined that this system is characterized by the formation of $GeBi_4Te_7$, $GeBi_2Te_4$, $Ge_3Bi_2Te_6$ compounds which melt by peritectic reaction and large solid solution areas based on both primary binary compounds. The phase diagrams given in [22] also show some other compounds which is mentioned in [20, 23]. However, the data about their melting character and temperatures are not provided.

The information about the crystal structure and various physical properties of many of these compounds has been reported in the literature [24-27].

2. Experimental section

Synthesis

Alloys of the GeTe-Bi_2Te_3 system were prepared by the melting of starting materials in a dry argon atmosphere and sealed off in evacuated quartz ampoules. The synthesis of the samples was carried out at 1120 K for 3-4 hours and then ampoules were quenched in ice water. Then the alloys were annealed at 700K for 1300 hours. Annealed tubes were taken out of the hot furnace and again quenched in ice water.

Methods

The investigations were carried out by using the powder X-ray diffraction (XRD), DTA, and SEM methods.

For the XRD analysis, the powder specimens are well ground in an agate mortar. XRD patterns collected with a Stadi-P (STOE, Darmstadt) powder diffractometer, using germanium monochromated Cu $K\alpha_1$ radiation and a Mythen 1 K detector. Lattice parameters of homologous series were indexed and calculated using Topas V3.0 software. The results are listed in Table.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. The analysis was carried out within room temperature and ~1400 K depending on the composition of the alloys at a heating rate of 10 K· min $^{-1}$. Temperatures of thermal effects were taken mainly from the heating curves.

SEM analysis was performed on the HITACHI SU8030 system.

3. Results and discussion

XRD patterns of [0-9.09] mol% of Bi_2Te_3 samples annealed at 700 K and quenched are shown in Figure 1. As can be seen, their diffraction patterns are qualitatively identical to the low-temperature rhombohedral modification of GeTe with some displacement of diffractions patterns. This is characteristic of substitutional solid solutions.

Diffractograms of Bi_2Te_3-richer samples prepared under the same conditions have a qualitatively different picture.The X-ray patterns of samples formed 10 and 11 mol % of GeTe showed that they crystallize in the cubic symmetry are homogenous, whereas the ones formed of 20 and 25 mol% adopt a tetradymite-like layered structure. The XRD patterns of 10 and 20 mol% GeTe are shown in Figure 2. We also found that the samples containing 12-19 mol% of GeTe consist of a mixture of cubic and Van der Waals phases.

Obtained XRD results show that a rhombohedral cubic morphotropic transition occurs in solid solutions at small intervals between 9.09 and 10 mol% GeTe. The possibility of such a cubic transition to Van der Waals phases is noted in [25, 28]. According to the authors, in the GeTe-Sb_2Te_3 and GeTe-Bi_2Te_3 systems, the replacement of germanium with antimony or bismuth in the GeTe crystal lattice increases the number of cationic defects, which leads to a transition from the cubic structure to the Van der Waals phase. We did not observe the last transition. This transition may occur at lower temperatures.

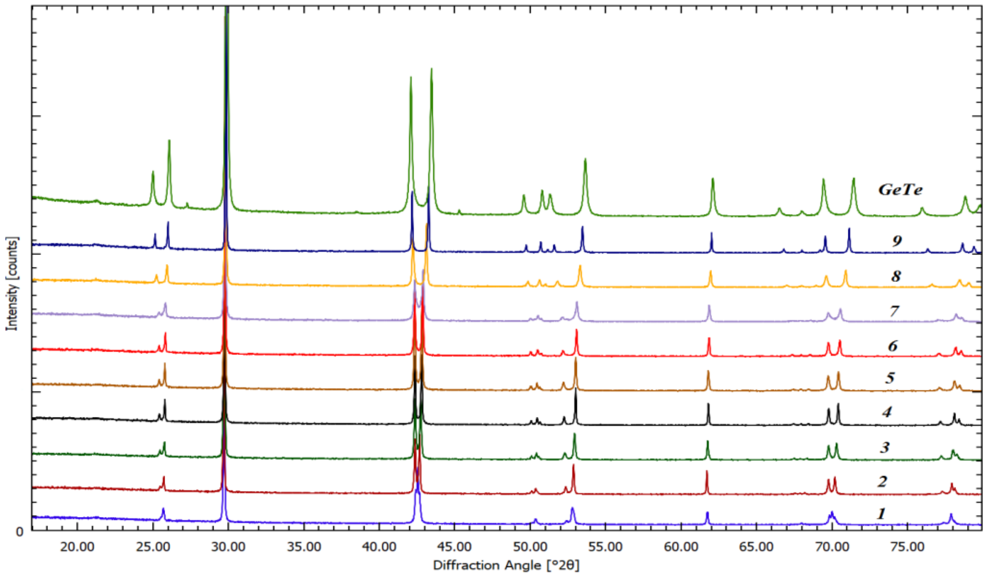

Fig. 1. Powder XRD patterns of some samples annealed at 700 K in the GeTe-rich area of the GeTe-Bi_2Te_3 system: 1- $Ge_{10}Bi_2Te_{13}$; 2- $Ge_{11}Bi_2Te_{14}$; 3- $Ge_{12}Bi_2Te_{15}$; 4- $Ge_{16}Bi_2Te_{19}$; 5- $Ge_{14}Bi_2Te_{17}$; 6- $Ge_{15}Bi_2Te_{18}$; 7- $Ge_{13}Bi_2Te_{16}$; 8- 96mol%GeTe; 9- 98mol%GeTe.

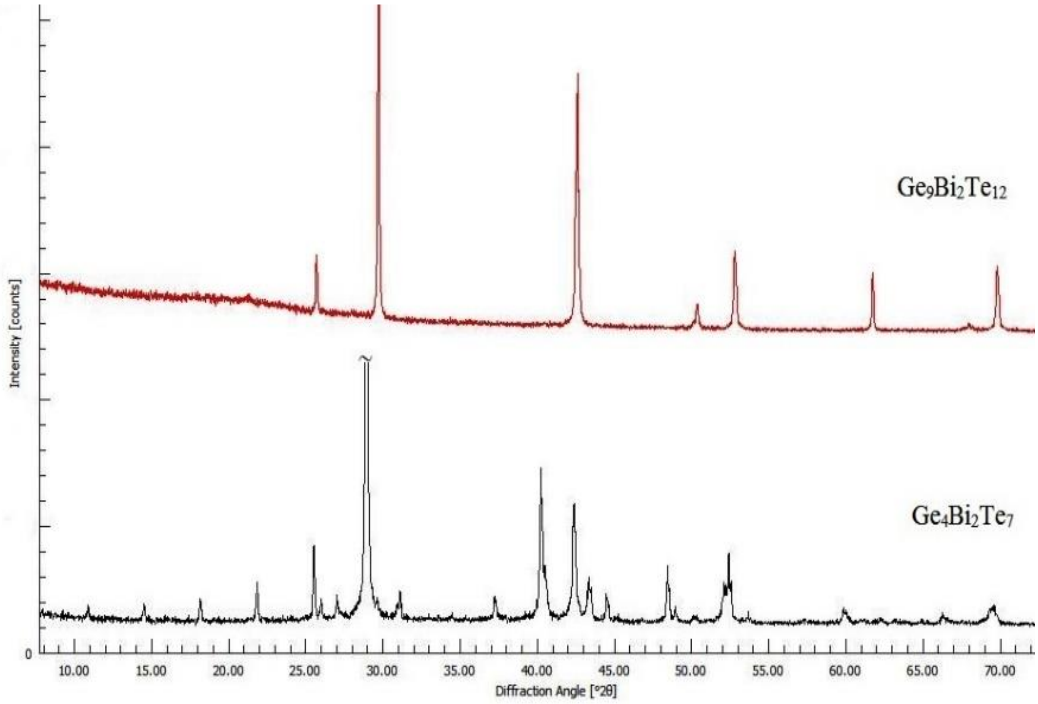

Fig. 2. Powder XRD patterns of the samples containing 10 and 20 mol% Bi_2Te_3 annealed at 700 K.

Samples containing 4, 9.1, and 15 mol% Bi_2Te_3 were annealed at 870 K for 10 hours followed by quenching in ice water to determine the solubility of α-GeTe at high-temperature. It was revealed that these samples crystallize in a cubic structure.

The crystallographic parameters of all samples were calculated by using Topas V3.0 software and are given in the Table.

Table 1. Crystallographic parameters of the phases in the $GeTe-Bi_2Te_3$ system

Composition	Crystal lattice type and parameters, Å	
	700K	870K Cubic, *Fm*3*m*
GeTe	Hexagonal, *R*3*m*, *a*=4.1628(3),*c*=10.6675(8)	*a*=5.9824(5)
2mol% Bi_2Te_3	Hexagonal, *R*3*m*, *a*=4.1788(3),*c*=10.6075(8)	
4mol% Bi_2Te_3	Hexagonal, *R*3*m*, *a*=4.1965(4),*c*=10.5582(9)	*a*=5.9904(5)
$Ge_{16}Bi_2Te_{19}$	Hexagonal, *R*3*m*, *a*=4.2097(4),*c*=10.4840(8)	
$Ge_{15}Bi_2Te_{18}$	Hexagonal, *R*3*m*, *a*=4.2157(3),*c*=10.4795(8)	
$Ge_{14}Bi_2Te_{17}$	Hexagonal, *R*3*m*, *a*=4.2192(4),*c*=10.4692(9)	
$Ge_{13}Bi_2Te_{16}$	Hexagonal, *R*3*m*, *a*=4.2236(4),*c*=10.4608(9)	
$Ge_{12}Bi_2Te_{15}$	Hexagonal, *R*3*m*, *a*=4.2288(3),*c*=10.4432(8)	
$Ge_{11}Bi_2Te_{14}$	Hexagonal, *R*3*m*, *a*=4.2341(4),*c*=10.4283(9)	
$Ge_{10}Bi_2Te_{13}$	Hexagonal, *R*3*m*, *a*=4.2417(3),*c*=10.3993(8)	*a*=6.0096(6)
$Ge_9Bi_2Te_{12}$	Cubic, *Fm*3*m*, *a*=6.0061(5)	
15mol% Bi_2Te_3		*a*=6.0238(6)
$Ge_4Bi_2Te_7$	Hexagonal, *R*3*m*, *a*=4.2638(2), *c*=73.271(3)	
$Ge_3Bi_2Te_6$	Hexagonal, *R*3*m*, *a*=4.2730(3), *c*=62.634(4)	

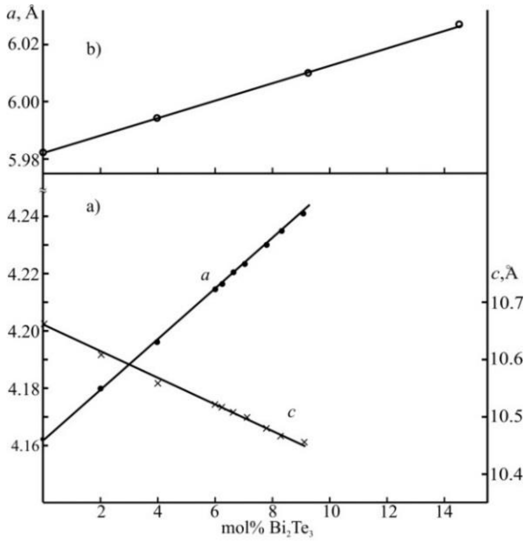

Fig. 3. Composition dependence of lattice parameters of annealed at 700 K (a) and 870 K (b) solid solutions in the GeTe-Bi_2Te_3 system.

For both series of samples, the composition dependences of the cell parameters are practically linear (Fig. 3). It should be noted, that with the Ge → Bi substitution in solid solutions, the *c* parameter decreases while *a* parameter of the (β-GeTe) phase increases.

The homogeneity of GeTe-based solid solutions and layered compounds has been confirmed by SEM method. Figure 4 indicates SEM images of compounds containing 20 and 25 mol% of Bi_2Te_3, annealed at 700K. The layered structure of $Ge_4Bi_2Te_7$ and $Ge_3Bi_2Te_6$ is clearly visible from the image.

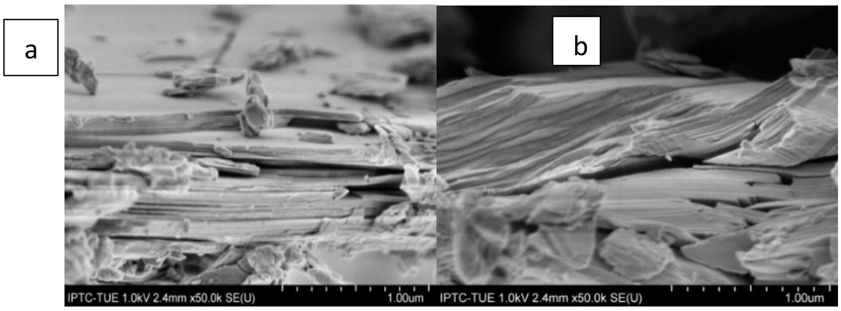

Fig. 4. SEM image of $Ge_3Bi_2Te_6$ (a) and $Ge_4Bi_2Te_7$ (b) compounds.

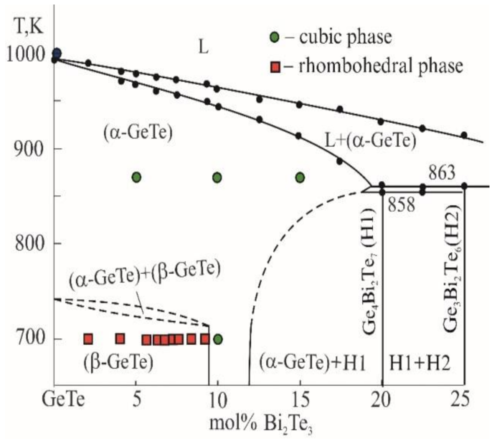

Fig. 5. A fragment of the phase diagram of the GeTe-Bi_2Te_3 system in the GeTe rich side.

By combining the results of DTA and XRD, a phase diagram of the GeTe-Bi_2Te_3 system was constructed in the 0-25 mol% Bi_2Te_3 composition range (Fig. 5). According to this diagram, a wide range of solid solutions based on both modifications of GeTe is formed in the system. The homogeneous area of the cubic phase (α-GeTe) is maximum at 860-870 K and is ~ 18 mol%, while the rhombohedral phase (β-GeTe) has a homogeneity area of ~ 9.5 mol% at 700 K. These results differ sharply from those given in [22, 23]. According to these studies, the solid solutions based on the high-temperature modification of GeTe with the cubic structure are present at >600 K, and the solution based on low-temperature modification is insignificant.

According to the phase diagram, in contrast to that in [22,23], the $Ge_3Bi_2Te_6$ compound melts with decomposition by peritectic reaction at 863K instead of 923K, while $Ge_4Bi_2Te_7$ decomposes by solid-state reaction at 858 K. It can be assumed that layered compounds, which are richer in GeTe, may exist at lower temperatures.

4. Conclusion

By re-examining the GeTe-Bi_2Te_3 system in a GeTe-rich field by DTA, RFA, and SEM methods, a new scheme of the phase equilibria differed from illustrated in literature was obtained. It was established that the system has a wide solid solution based on both modifications of GeTe. Solubilities based on high-temperature cubic α-GeTe reach ~ 18 mol% (870 K), and solutions based on low-temperature rhombic β-GeTe reach ~ 9.5 mol% (700 K). Approximately at ~ 9.5 mol% Bi_2Te_3 there is a morphotropic transition of solid solutions from rhombohedral into the cubic structure. The presented phase diagram reflects the layered compounds $Ge_4Bi_2Te_6$ and $Ge_3Bi_2Te_6$. At 700 K and above, layered compounds with a higher GeTe composition were not found. They may exist at lower temperatures.

5.References

1. Shevelkov A.V. Chemical aspects of the design of thermoelectric materials. Russ. Chem. Rev. 77, no. 1, 1-19 (2008). doi: 10.1070/RC2008v077n01ABEH003746
2. *Rowe, D.M. Thermoelectrics Handbook Macro to Nano*. CRC Press, Taylor and Francis Group, *Boca* Raton, London, New York. 1008, (2006)
3. Kanatzidis, M.G. The role of solid-state chemistry in the discovery of new thermoelectric materials. Semiconductors and semimetals. 69, 51-98, (2001)
4. Moore J.E. The birth of topological insulators. Nature. 464, 194-198 (2010). doi: org/10.1038/nature08916
5. Kane C.L. and Moore J.E.: Topological Insulators. Physics World. 24, 32–36, (2011). doi: 10.1103/RevModPhys.82.3045
6. Politano A., Caputo M., Nappini S., Bondino F., Aliev Z.S., Babanly M.B., Chulkov E.V., Exploring the surface chemical reactivity of single crystals of binary and ternary bismuth chalcogenides. J. Physical Chemistry C, 118, 21517-21522, (2014). doi: org/10.1021/jp506444f
7. Okamoto K., Kuroda K., Miyahara H., Miyamoto K., Okuda T., Aliev Z.S., Babanly M.B., Amiraslanov I.R., Shimada K., Namatame H., Taniguchi M., Chulkov E.V., Kimura A., Observation of a Highly Spin Polarized Topological Surface State in $GeBi_2Te_4$. Phys. Rev. B 86, 195304(5), (2012). doi: 10.1103/PhysRevB.86.195304
8. Okuda T., Maegawa T., Ye M., Shirai K., Warashina T., Miyamoto K., Kuroda K., Arita M., Aliev Z.S., Amiraslanov I.R., Babanly M.B., Chulkov E.V., Eremeev S.V., Kimura A., Namatame H., Taniguchi M. Experimental Evidence of Hidden Topological Surface States in $PbBi_4Te_7$. Phys. Rev. Lett. 111, 206803(5), (2013). doi: 10.1103/PhysRevLett.111.206803.
9. Niesner D., Otto S., Hermann V., Fauster Th., Menshchikova T.V., Eremeev S.V., Aliev Z.S., Amiraslanov I.R., Echenique P.M., Babanly M.B., Chulkov E.V. Bulk and surface electron dynamics in a p-type topological insulator $SnSb_2Te_4$. Phys.Rev. B. 89, 081404(5), (2014). doi: 10.1103/PhysRevB.89.081404
10. Nurmamat M., Okamoto K., Zhu S., Menshchikova T.V., Rusinov I.P., Korostelev V.O., Miyamoto K., Okuda T., Miyashita T., Wang X., Ishida Y., Sumida K., Schwier E.F., Ye M., Aliev Z.S., Babanly M.B., Amiraslanov I.R., Chulkov Evgueni V., Kokh K.A., Tereshchenko O., Shimada K., Shin S., Kimura A. Topologically non-trivial phase-change compound $GeSb_2Te_4$. ACS Nano. 14(7), 9059-9065, (2020). doi: org/10.1021/acsnano.0c04145.
11. Pacile D., Eremeev S.V., Caputo M., Pisarra M., Luca O. De, Grimaldi I., Fujii J., Aliev Z.S., Babanly M.B., Vobornik I., Agostino R.G., Goldoni A., Chulkov E.V., and Papagno M. Deep insight into the electronic structure of ternary topological insulators: A comparative study of $PbBi_4Te_7$ and $PbBi_6Te_{10}$. Physica status solidi (RRL)-Rapid Research Letters. 12(12), 1800341-8. (2018). doi:10.1002/pssr.201800341
12. Shvets I.A., Klimovskikh I.I., Aliev Z.S., Babanly M.B., Zúniga F.J., Sánchez-Barriga J., Krivenkov M., Shikin A.M., Chulkov E.V. Surface electronic structure of the wide band gap topological insulator $PbBi_4Te_4Se_3$. Phys. Rev. B 100, 195127, (2019). doi:10.1103/PhysRevB.100.195127

13. Babanly M.B., Chulkov E.V., Aliev Z.S., Shevelkov A.V., and Amiraslanov I.R. Phase diagrams in materials science of topological insulators based on metal chalcogenides. Russ. J. Inorg. Chem., 62(13), 1703–1729, (2017). doi: 10.1134/S0036023617130034
14. Viti L., Coquillat D., Politano A., Kokh K.A., Aliev Z.S., Babanly M.B., Tereshchenko O.E., Knap W., Chulkov E.V., Vitiello M.S. Plasma-Wave Terahertz Detection Mediated by Topological Insulators Surface States. Nano Letters, 16, 80−87, (2016). doi:org/10.1021/acs.nanolett.5b02901
15. Yonezawa S. Nematic Superconductivity in Doped Bi$_2$Se$_3$ Topological Superconductors. Condens. Matter, 4 (1), 2 (2019). doi:org/10.3390/condmat4010002
16. Walsh L.A., Smyth C.M., Barton A.T., Wang Q., Che Z., Yue R., Kim J., Kim M.J., Wallace R.M., Hinkle C.L. Interface Chemistry of Contact Metals and Ferromagnets on the Topological Insulator Bi$_2$Se$_3$. J. Phys. Chem. C, 121(42), 23551-23563 (2017)
17. Zlomanov V.P. Physicochemical analysis in materials science. Russ. J. Inorg. Chem. **55**, 1740–1753 (2010). doi:org/10.1134/S0036023610110112
18. Imamaliyeva S.Z., Babanly D.M., Tagiev D.B., and Babanly M.B. Physicochemical Aspects of Development of Multicomponent Chalcogenide Phases Having the Tl$_5$Te$_3$ Structure: A Review. Russ. J. Inorg. Chem. **63(**13), 1703, (2018). doi: 10.1134/S0036023618130041.
19. Babanly M.B., Mashadiyeva L.F., Babanly D.M., Imamaliyeva S.Z., Taghiyev D.B., Yusibov Y.A. Some issues of complex investigation of the phase equilibria and thermodynamic properties of the ternary chalcogenid systems by the EMF method. Russ. J. Inorg. Chem, **64(**13), 1649-1671, (2019). doi:org/10.1134/S0036023619130035
20. Shelimova L.E., Karpinskii O.G., Zemskov V.S. , Konstantinov P.P. Structural and electrical properties of layered tetradymite-like compounds in the GeTe-Bi$_2$Te$_3$ and GeTe-Sb$_2$Te$_3$ systems. Inorg. Mater., **36**, 235–242, (2000). DOI: 10.1007/BF02757928
21. Shelimova L.E., Karpinskii O.G., Kosyakov V.I., Shestakov V.A., Zemskov V.S. & Kuznetsov F.A. Homologous series of layered tetradymite-like compounds in Bi-Te and GeTe-Bi$_2$Te$_3$ systems. J. Structural Chemistry, **41**(1), 81–87, (2000). doi:org/10.1007/BF02684732.
22. Abrikosov N.X., Danilova-Dobryakova G.T. Study of the GeTe-Bi$_2$Te$_3$ phase diagram. **1**, 57-61, (1965) In Russian.
23. Shelimova L.E., Karpinskii O.G., Konstantinov P.P., Avilov E.S., Kretova M.A. & Zemskov V.S. Crystal structures and thermoelectric properties of layered compounds in the ATe-Bi$_2$Te$_3$ (A=Ge, Sn, Pb) systems. Inorg. Mater., **40,** 451–460, (2004)
24. Jung C.S., Kim S.H., Im H.S., Park K., Park J., Ahn Jae-P., Yoo S.J., Kim Jin-G., Kim J.N., and Shim J.H. In Situ Temperature-dependant transmission electron microscopy studies of pseudobinary mGeTe·Bi$_2$Te$_3$ (m= 3-8) nanowires and first principle calculations. *Nano Lett.* **15**(6), 3923–3930, (2015). doi: org/10.1021/acs.nanolett.5b00755
25. Wu D., Xie L., Xu X., He J. High thermoelectric performance achieved in GeTe-Bi$_2$Te$_3$ pseudo-binary via van-der-Waals gap-induced hierarchical ferroelectric domain structure. Adv.Func.Mater. **29(**18), 1806613, (2019). doi: org/10.1002/adfm.201806613
26. Kohri H., Shiota I., Kato M., Ohsugi Isao J., Goto T. Synthesis and thermoelectric properties of Bi$_2$Te$_3$-GeTe pseudo binary system. J. Advances in science and technology. **46,** 168-173 (2006). doi: org/10.4028/www.scientific.net/AST.46.168
27. Kim J.N., Kaviany M., and Shim Ji-H. Optimized ZT of Bi$_2$Te$_3$−GeTe compounds from first principles guided by homogeneus data. Phys. Rev. B **93,** 075119 (2016). doi: org/10.1103/PhysRevB.93.075119.
28. Rosenthal T., Schneider M.N., Stiewe C., Doblinger M. and Oeckler O. Real structure and thermoelectric properties of GeTe-rich germanium antimony tellu rides. J. Chemistry of materials. **23**(19), 4349–4356, (2011). doi: org/10.1021/cm201717z

OR-IV-5

RE-INVESTIGATION OF THE $SnTe-Sb_2Te_3$ SYSTEM AND CRYSTAL STRUCTURE OF $SnSb_4Te_7$

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Abstract. Phase equilibria in the $SnTe-Sb_2Te_3$ system were studied by a combination of differential thermal analysis (DTA), powder X-ray diffraction (PXRD), and scanning electron microscope (SEM) techniques. The system is quasi-binary and hosts two intermediate compounds. Beside the already known $SnSb_2Te_4$ compound, the existence of a new mixed layered compound $SnSb_4Te_7$ was revealed. Small homogeneity ranges were detected for both ternary compounds. DTA results confirm that $SnSb_2Te_4$ and $SnSb_4Te_7$ melt with peritectic reactions at 595 °C and 593 °C, respectively. The crystal structure of the newly discovered $SnSb_4Te_7$ phase was elucidated by means of Rietveld refinement of PXRD data. The system is also characterized by the formation of two wide solid solutions areas based on both initial compounds.

Keywords: $SnTe-Sb_2Te_3$ system, phase diagram, layered materials, tetradymite-like structure, thermoelectric materials, topological insulators.

1.Introduction

Layered materials have widely been studied for many years thanks to their intriguing chemical, physical and mechanical properties. Tetradymite-like layered ternary compounds, in particular, in the $A^{IV}Te-B^{V}{}_2Te_3$ (A = Ge, Sn; B = Sb, Bi) systems exhibit outstanding transport properties which are key factors for high-performance thermoelectric materials [1-3]. These materials promise many potential applications for solid-state cooling or heating and waste heat recovery from different energy sources [4-7]. In the last decade, these van der Waals chalcogenides have emerged as an important platform for topological insulator phases [8-11]. In addition, materials with topological insulating properties also exhibit good thermoelectric properties [12-14]. In this point of view, re-investigation of the phase diagram $SnTe-Sb_2Te_3$ is of interesting in order to evidence of new intermediate phases.

The earliest results on the phase equilibria investigations in the $SnTe-Sb_2Te_3$ system showed the formation of one intermediate compound - $SnSb_2Te_4$ and a wide field of solid solutions based on Sb_2Te_3 [15,16]. The compound $SnSb_2Te_4$ crystallizes in tetradymite-like layered hexagonal structure and melts incongruently at 603 °C [16]. According to the phase diagram [15], this compound also exhibits a certain range of homogeneity. The crystal structure and lattice parameters of $SnSb_2Te_4$ ($R\text{-}3m$, $a = 4.298(1)$ Å, $c = 41.57(1)$ Å) were determined by using resonant single-crystal diffraction [17]. It was reported that the $21R$-type structure consists of rocksalt-type blocks, loosely connected by van der Waals (vdW) interactions. Each block is composed of four anion and three cation layers. Although tin atoms are distributed over all cation positions, they are clustered in the middle of the blocks. The results of our research on the thermodynamic properties, such as Gibbs energy and enthalpy, as well as the electronic structure and dynamics at the surface of the $SnSb_2Te_4$ were given in [18,19].

The existence of the phase $SnSb_4Te_7$ was also mentioned in other references, [20, 21] where its crystal structure was determined by electron diffraction from thin-films, indicating space group $P\text{-}3m1$, and lattice parameters of $a = 4.37$ Å and $c = 23.78$ Å [20]. Theoretical calculations on its electronic and spin structure were given in [21]. However, polycrystalline bulk samples of $SnSb_4Te_7$ have been successfully synthesized for the first time in our recent work [22].

A present paper was devoted to updating and completing the new version of the phase diagram of the $SnTe-Sb_2Te_3$ system.

2.Experimental part.

The starting compounds - SnTe and Sb_2Te_3 of the title system were prepared by melting of high purity elements (99.999 wt.% Alfa Aesar) in evacuated (~10^{-3} Pa) silica ampoules at temperatures ~50 °C above their melting points. All starting compounds were identified by DTA and PXRD techniques.

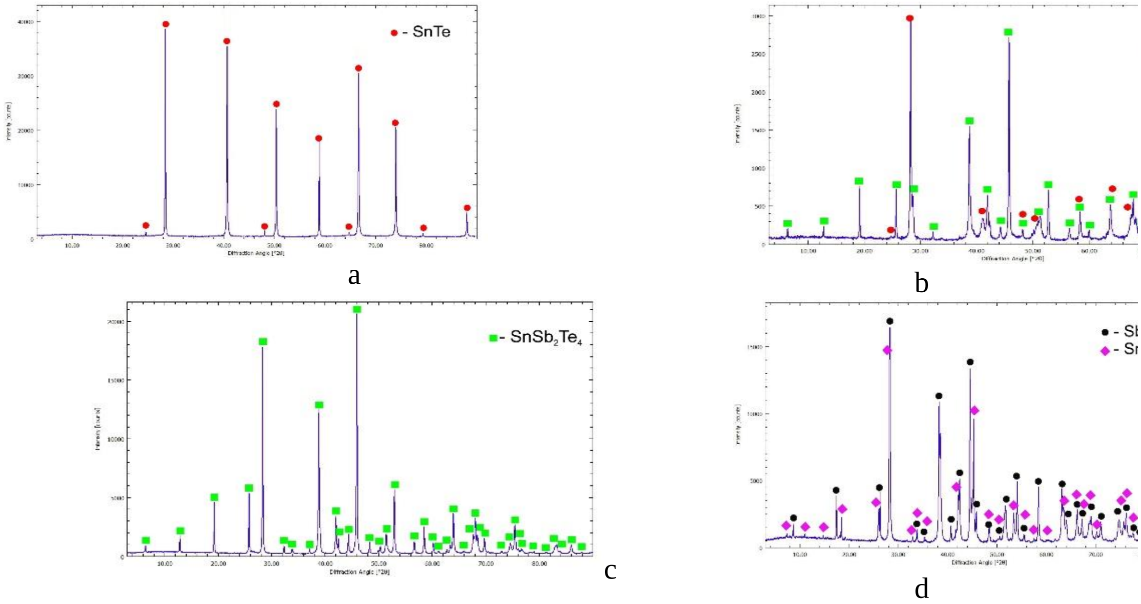
Seventeen alloys of the SnTe-Sb_2Te_3 system were prepared by melting at 800 °C from the pre-synthesized initial compounds followed by quenching in icy water. The alloys have been further annealed at 450° C for 720 h and then slowly cooled down to room temperature.

Crystals of about 3.5 cm in length and 0.8 cm in diameter were grown from the melt using the vertical Bridgman-Stockbarger method. The samples were placed into the conical-bottom quartz ampoules and sealed under vacuum 10^{-4} Pa. These ampoules were held in the "hot" zone (~650°C) for 6 h. and then moved to the cold zone with ate of 1.0 mm/h.

PXRD data collection was performed at room temperature with an Empyrean diffractometer (PANalytical) equipped with a curved Ge(111) monochromator using CuKα_1 radiation (1.54056 Å). Rietveld refinement using the fundamental parameter approach was performed with TOPAS academic (Version 5; Coelho, 2018). Morphological characterization of the samples was made using a SEM with SU8020 (Hitachi) with a tripledetector system (Ua = 5 kV). DTA of the annealed alloys was carried out using SETARAM Instrumentation system (temperature accuracy +/- 2 °C) between room temperature up tp 1000 °C with a heating and cooling rate of 5 °C·min^{-1}. Temperatures of thermal effects were taken mainly from the heating curves.

3.Results and discussion

In order to study the phase equilibria in the SnTe-Sb_2Te_3 system, seventeen samples with different compositions were synthesized. Fig. 1 shows the PXRD results of some of these samples. As can be seen, the XRD results of the samples with compositions near both end-members, have qualitatively identical diffraction patterns with the binary tellurides. Samples containing 10 % (Fig. 1*a*) and 85 mol% Sb_2Te_3 (Fig. 1*e*) have similar reflection lines with a slight shift compared to pure SnTe and Sb_2Te_3, respectively. These results confirm the existence of 11-12 mol% solubility based on SnTe and 20 mol% - solubility based on Sb_2Te_3. The sample with 40 mol % Sb_2Te_3 composition was a two-phase mixture of α(SnTe) + $SnSb_2Te_4$ (Fig. 1b). It should be noted that in the samples corresponding to the composition of the ternary compounds (50 and 66.7 mol% Sb_2Te_3), $SnSb_2Te_4$ can easily be synthesized as phase-pure compound (Fig. 1c), while the sample with the stoichiometric composition of $SnSb_4Te_7$ is a mixture of several phases.

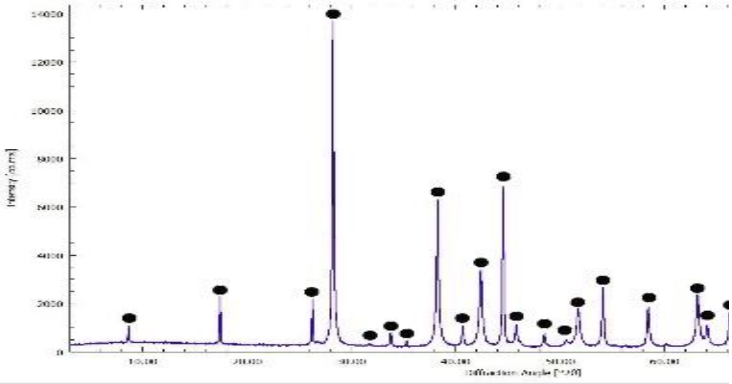


a

b

c

d



e

Fig. 1. PXRD patterns SnTe-Sb_2Te_3 alloys having : a) 10 mol% Sb_2Te_3, b) 40 mol% Sb_2Te_3 c) 50 mol% Sb_2Te_3, d) 75 mol% Sb_2Te_3, e) 85 mol% Sb_2Te_3

These results show that, despite long annealing time, some samples did not reach the thermodynamic eqilibrium. However, these ternary compounds can be easily distinguished in XRD analysis by their characteristic non-overlapping peaks at small angles. Besides the $SnSb_2Te_4$ and Sb_2Te_3 reflections, the sample with a composition of 65 mol% Sb_2Te_3 contains additional peaks, which are fully indexed with the structure model of $SnSb_4Te_7$ given in the literature [19]. Also, the XRD pattern of a sample containing 75 mol% Sb_2Te_3 (Fig. 1*d*) has a set of reflections that belongs to Sb_2Te_3 and $SnSb_4Te_7$. These results strongly prove the formation of the new $SnSb_4Te_7$ compound in the SnTe-Sb_2Te_3 system, in addition to the already known $SnSb_2Te_4$.

Analysis of the samples obtained by the Bridgman-Stockbarger method also confirmed the existence of the new phase $SnSb_4Te_7$. PXRD analysis of the sample taken from the upper part of the ingot (60 mol% Sb_2Te_3) shows that the sample has diffraction lines of the $SnSb_4Te_7$ phase along with $SnSb_2Te_4$ (Fig. 2).

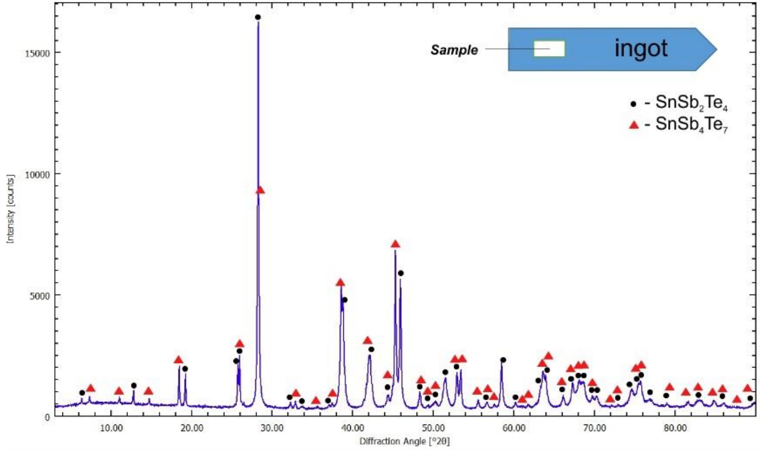
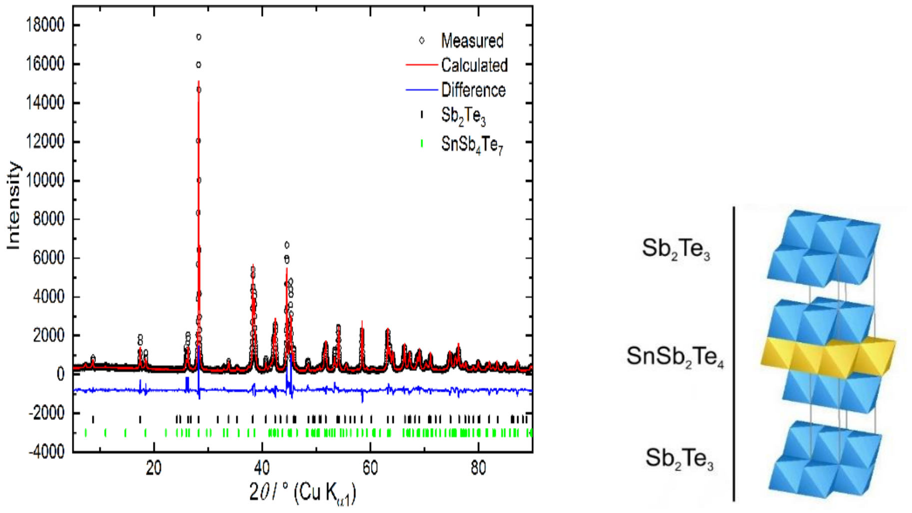


Fig. 2. XRD pattern of ingot composition of 60 mol % Sb_2Te_3 synthesized by direct crystallization.

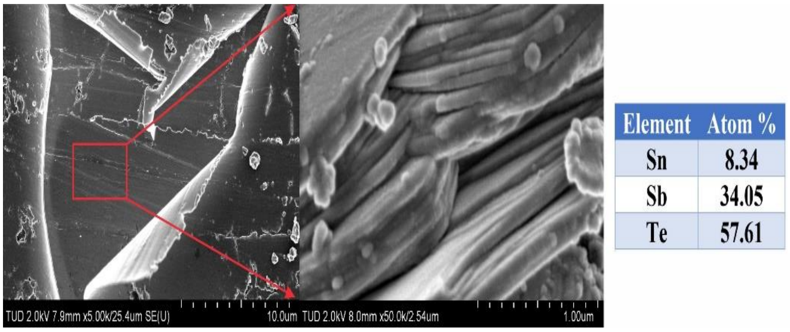
In general, PXRD results show that synthesized samples contain reflection lines corresponding to the compounds $SnSb_2Te_4$ and $SnSb_4Te_7$. However, we did not detect any characteristic patterns for expected higher members of the $(SnTe)_n(Sb_2Te_3)_m$ (n = 1, m > 1) homologous series which as formed in the related SnTe-Bi_2Te_3 system. The existence of large homogeneity ranges based on both end members indicate that tin and antimony can replace each other to some extent within the crystal lattice. It is also likely that such a mutual replacement of Sn and Sb atoms in the crystal lattice can also occur in the structure of intermediate ternary compounds consisting of stacking seven- and twelve-layer atomic blocks. This intermixing and the similar atomic sizes of Sn and Sb is considered as the main reasons preventing the formation of more complex layered structures than the $SnSb_4Te_7$.

In order to determine the crystal structure of the new phase - $SnSb_4Te_7$, the PXRD pattern of the sample with 75 mol% Sb_2Te_3 has been refined by the Rietveld method (Fig. 3), since no phase-pure product of the new phases was successfully synthesized. Details on the structure refinement and atomic parameters are summarized in Tables 1 and 2. An analysis of the XRD pattern shows that along with Sb_2Te_3, the sample contains the second phase - $SnSb_4Te_7$ which was indexed with unit cell parameters of a = 4.230(2) Å and c = 23.98(3) Å. The comparative analysis of the diffraction intensities shows that Sb_2Te_3 is the dominant phase in the sample. SEM-EDS measurements also confirm the presence of two phases in the sample and and the layered structure of $SnSb_4Te_7$ (Fig. 4).



a b

Fig. 3. (*a*) Rietveld analysis result of the sample having 75 mol% Sb_2Te_3 and (*b*) structural model of $SnSb_4Te_7$.



Element	Atom %
Sn	8.34
Sb	34.05
Te	57.61

Fig. 4. Scanning electron micrographs of ingot composition with 75 mol% Sb_2Te_3.

Table 1. Refined crystal structure data of the $SnSb_4Te_7$ phase.

Compound	**$SnSb_4Te_7$**
R-Bragg	2.083
Space group	*P*-3*m*1
Lattice parameters	
a (Å)	4.230(2)
c (Å)	23.98(3)
Unit cell volume (Å^3)	371.56(51)
Crystal Density (g/cm^3)	6.6989(91)

Table 2. Atomic positional parameters of the $SnSb_4Te_7$.

Site	**N_p**	**x**	**y**	**z**	**B_{eq}**
Te1	1	0.00000	0.00000	0.00000	1
Sb1	2	0.33333	0.66667	0.084(23)	1
Te2	2	0.66667	0.33333	0.145(22)	1
Te3	2	0.00000	0.00000	0.262(19)	1
Sb2	2	0.33333	0.66667	0.347(21)	1
Te4	2	0.66667	0.33333	0.423(25)	1
Sn	1	0.00000	0.00000	0.50000	1

A 3D image of the crystal strcuture of $SnSb_4Te_7$ is depicted in Fig 3*b*. It is a member of the homologous series of $(SnTe)_n(Sb_2Te_3)_m$ which crystallizes in the tetradymite-like hexagonal structure, space group *P*-3*m*1(#164). The structure is comprised of alternating quintuple layers of Sb_2Te_3 and septuple layers of $SnSb_2Te_4$ blocks along the *c*-axes, like the isostructural analog $SnBi_4Te_7$. Although atomic layers are mainly covalently bounded, weaker vdW interaction exists between each block.

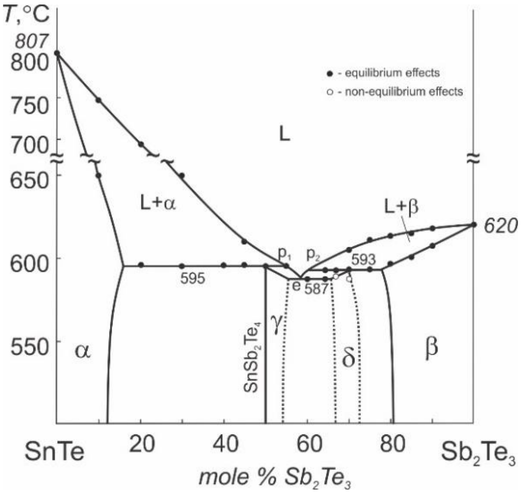


Fig. 5. The phase diagram of the SnTe-Sb_2Te_3 system.

The phase diagram of the SnTe-Sb_2Te_3 system was constructed based on the data from DTA and XRD analysis of the annealed samples (Fig. 5). The system is quasi-binary and characterized by the formation of the two intermediate compounds, which both melt by peritectic reactions:

L+α-phase (SnTe) ↔ $SnSb_2Te_4$ (p_1, 595°C)

L+β-phase (Sb_2Te_3) ↔ $SnSb_4Te_7$ (p_2, 593°C)

The coordinates of the peritectic points - p_1 and p_2, were found to be 53 and 59 mol% Sb_2Te_3, respectively. The temperature of eutectic transformation is 587 °C and the composition is 58 mol% Sb_2Te_3. It should be noted that $SnSb_4Te_7$ has a limited range of primary crystallization areas, making it extremely difficult to obtain a homogenous phase.

Besides, the system has 11-13 and 18-19 mol% solid solution areas based on SnTe and Sb_2Te_3, respectively. The presence of a small homogeneity areas based on both ternary compounds has also been determined. The newly constructed phase diagram differs from those shown in the literature in terms of the number of ternary compounds, and the peritectic and eutectic reaction temperatures [14,15]. Particularly, the crystal structure and melting character of the $SnSb_4Te_7$ compound were experimentally determined for the first time in this work.

4.Conclusion

New experimental data on the phase equilibria of the SnTe-Sb_2Te_3 system were obtained by means of DTA, XRD and SEM analyses and found to differ from previously reported data. It was revealed that the system is characterized by the formation of the two ternary compounds which melt peritectically: $SnSb_2Te_4$ (595° C) and $SnSb_4Te_7$ (593° C). The primary crystallization fields of both phases as well as types and coordinates of non-variant equilibria were determined. There are wide areas of solid solutions on the basis of the binary end members. The existence of small homogeneity areas based on both ternary compounds was observed, too. The crystal structure of the new $SnSb_4Te_7$ compound was investigated by the Rietveld method. It was found to crystallize in space group *P*-3m1 and the lattice parameters were refined to a=4.230(1) Å and c=23.98(3) Å.

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5.References

1. Shelimova, L.E., Karpinskii, O.G., Konstantinov, P.P., Avilov, E.S., Kretova, M.A., Zemskov, V.A. Crystal Structures and Thermoelectric Properties of Layered Compounds in the ATe-Bi_2Te_3 (A=Ge, Sn, Pb) Systems. Inorg. Mater. **40**(5), 530-540 (2004). doi: 10.1023/B:INMA.0000027590.43038.a8
2. Rohr, F. von, Schilling, A., Cava, R.J. Single-crystal growth and thermoelectric properties of Ge(Bi,Sb)$_4$Te$_7$. J.

Phys. Condens. Matter., **25**(7), 075804 (2013). doi: 10.1088/0953-8984/25/7/075804

3. Wu, D., Xie, L., Xu, X., He, J.Q. High Thermoelectric Performance Achieved in GeTe– Bi_2Te_3 Pseudo-Binary via Van der Waals Gap-Induced Hierarchical Ferroelectric Domain Structure. Adv. Funct. Mater., **29**(18), 1806613 (2019). doi: 10.1002/adfm.201806613
4. Ahluwalia G.K. (Ed.). Applications of Chalcogenides: S, Se, and Te. Springer (2016). doi:10.1007/978-3-319-41190-3
5. Duong, D.L., Yun, S.J., Lee, Y.H. van der Waals Layered Materials: Opportunities and Challenges. ACS Nano, **11**(12), 11803-11830 (2017). doi:10.1021/acsnano.7b07436
6. He, J., Tritt, T. M. Advances in thermoelectric materials research: Looking back and moving forward. Science **357**, 1369 (2017). doi:10.1126/science.aak9997
7. Tiejun, Z., Liu, Y., Fu, C., Heremans, J. P., Snyder, J.G., Zhao, X. Compromise and synergy in high-efficiency thermoelectric materials. Adv. Mater., **29**, 1605884 (2017). doi: 10.1002/adma.201605884
8. Wang, L.L., Johnson, D.D. Ternary Tetradymite Compounds as Topological Insulators. Physical review. B. Condensed matter., **83**(24), 241309 (2011). doi: 10.1103/PhysRevB.83.241309
9. Babanly, M.B., Chulkov, E.V., Aliev, Z.S., Shevelkov, A.V., Amiraslanov, I.R. Phase diagrams in the materials science of topological insulators based on metal chalcogenides. Russ. J. Inorg. Chem., **62**(13), 1703–1729 (2017). doi:10.1134/S0036023617130034
10. Nurmamat, M., Okamoto, K., Zhu, S. et al. Topologically non-trivial phase-change compound $GeSb_2Te_4$. ACS Nano. **14**(7)**,** 9059-9065, (2020). doi: 10.1021/acsnano.0c04145
11. Pacile, D., Eremeev, S.V., Caputo, M. et al. Deep insight into the electronic structure of ternary topological insulators: A comparative study of $PbBi_4Te_7$ and $PbBi_6Te_{10}$. Physica status solidi (RRL), **12(**12), 1800341-8. (2018). doi:10.1002/pssr.201800341
12. Heremans, J.P., Cava, R.J., Samarth, N., Tetradymites as thermoelectrics and topological insulators, Nat. Rev. Mater. **2**(10), 17049 (2017). doi: 10.1038/natrevmats.2017.49
13. Xu, N., Xu, Y., Zhu, J. Topological insulators for thermoelectrics. npj Quant. Mater., **2**(51) (2017). doi: 10.1038/s41535-017-0054-3
14. Baldomir, D., Faílde, D. On Behind the Physics of the Thermoelectricity of Topological Insulators. Sci. Rep., **9**, 6324 (2019). doi: 10.1038/s41598-019-42744-3
15. Stegherr, A., Philips Res. Repts. Semiconductors: Preparation, Crystal Growth, and Selected Properties 1. (Suppl. 6) (1969).
16. Elagina, E.I., Abrikosov, N.K. The investigation of the systems PbTe–Bi2Te3 and SnTe–Sb_2Te_3. Russ. J. Inorg. Chem., **4**, 1638-1642 (1959).
17. Oeckler, O., Schneider, M.N., Fahrnbauer, F., Vaughan, G. Atom distribution in $SnSb_2Te_4$ by resonant X-ray diffraction, Solid State Sci., **13**, 1057-1161 (2011). doi: 10.1016/j.solidstatesciences.2010.12.043
18. Guseinov, F.N., Seidzade, A.E., Yusibov, Y.A., Babanly, M.B. Thermodynamic Properties of the $SnSb_2Te_4$ Compound. Inorg. Mater., **53**(4), 354–357 (2017). doi: 10.1134/S0020168517040057
19. Niesner, D., Otto, S., Hermann, V., Fauster, Th., Menshchikova, T.V., Eremeev, S.V., Aliev, Z.S., Amiraslanov, I.R., Babanly, M.B., Echenique, P.M., Chulkov, E.V. Bulk and surface electron dynamics in a p-type topological insulator $SnSb_2Te_4$. Phys. Rev. B, **89**, 081404 (2014). doi: 10.1103/PhysRevB.89.081404
20. Imamov, R.M., Semiletov, S.A., Pinsker, Z.G. The crystal chemistry of semiconductors with octradral and with mixed atomic coordination. Kristallografiya, **15**, 239–243 (1970).
21. Vergniory, M.G., Menshchikova, T.V., Silkin, I.V., Koroteev, Y.M., Eremeev, S.V., Chulkov, E.V. Electronic and spin structure of a family of Sn-based ternary topological insulators. Phys. Rev. B, **92**(4). pp. 045134 (2015). doi: 10.1103/PhysRevB.92.045134
22. Seidzade, A.E. Phase diagram of the $SnSb_4Te_7$-$SnBi_4Te_7$ system. New Materials, Compounds and Applications, **3**(3),193-197 (2019).

PP-IV-14

PHASE COMPOSITION AND MAGNETIC PROPERTIES OF THE PRODUCTS OF HYDROTHERMAL TREATMENT OF Mn(Fe, Co)/Bi/La NITRATES MIXTURE

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Abstract. This work presents the results of a study of the influence of the medium (ethylene glycol (EG), formic acid (FA)) on the phase composition and magnetic properties of the products of hydrothermal treatment of a mixture of manganese nitrates (iron, cobalt), bismuth and lanthanum taken in different ratios (1:1:1 and 1:2:1), at a temperature of 200 °C for 3 hours in autoclave. The obtained solid products of processing were characterized by the methods of X-ray phase analysis (XRF), infrared (IR) spectroscopy and electron magnetic resonance (EMR). According to XRD data, the main products of this treatment are metallic bismuth - Bi, lanthanum carbonate hydroxide - $LaCO_3OH$, manganese carbonate - $MnCO_3$ (rhodochrosite), cobalt oxalate - CoC_2O_4, bismutite - $Bi_2(CO_3)O_2$ and magnetite - Fe_3O_4. The IR spectra exhibit bands characteristic of the vibrations of Fe-O, Mn-O, Co-O, La-O, Bi-O-Bi bonds and -OH, CO_3^{2-}, $C_2O_4^{2-}$ groups present in the above-mentioned compounds. It has been shown that, depending on the nature of the medium (ethylene glycol, formic acid), the composition of the resulting products practically does not change, although noticeable changes in the EMR spectra are observed for both the products of hyd-rothermal treatment of nitrate mixtures with different ratios of Mn(Fe,Co)/Bi/La and different nature of the environment (EG, FA). It is shown that for the case of a mixture with cobalt nitrate in EG, the EMR spectra exhibit only one broad inhomogeneous signal $g = 2.3011$, $\Delta H = 1466.7$ G for a 1:1:1 ratio, due to the formation of a ferromagnetic phase, and two EMR signals, a broad $g = 2.1174$, $\Delta H = 899.1$ G and narrow with $g = 2.0035$, $\Delta H = 4.7$ G, due, respectively, to the ferromagnetic phase and defects of the F - center type in bismuth-containing structures for a 1:2:1 ratio. We note that superpara/ferromagnetism appears for all synthesized samples.

Keywords: hydrothermal treatment, nitrates of Mn(II), Fe(III), Co(II), Bi(III), La(III), X-ray diffractometry, FTIR -, EMR – spectroscopy

1.Introduction

Currently, composite materials with magnetic fillers are of great interest. Over the past 10-15 years, a large number of composite materials with magnetic properties have been synthesized for their use in various fields, including the production of new generation electronic and computer equipment, contrast agents for magnetic resonance imaging, drug carriers, etc. A wide range of methods for the synthesis of these materials has been developed. The chemical methods used to obtain nanoparticles and nanostructured materials are mainly coprecipitation, pyrolysis of organometallic substances, microemulsion, sol-gel, and hydrothermal synthesis methods. Among the chemical methods for the synthesis of nanomaterials, sol-gel and hydrothermal synthesis methods are most often used, since it is possible to obtain nanoscale materials with the required parameters. It should be noted that at present the development of promising methods for the synthesis of highly dispersed composites based on metals / metal oxides with adjustable magnetic properties and the study of their applications is one of the most important tasks in the chemistry of nanomaterials [1-3].

This paper presents the results of the study of the influence of the medium (ethylene glycol, formic acid) on the phase composition and magnetic properties of the products of hydrothermally treated mixture of manganese (iron, cobalt), bismuth and lanthanum nitrates with different ratios at a temperature of 200 °C in autoclave.

2.Experimental section

2.1. Materials

All chemicals ($Mn(NO_3)_2{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ $Bi(NO_3)_3{\cdot}5H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $(CH_2OH)_2$-ethylene glycol, HCOOH -formic acid were of analytical grade and used as received from commercial sources without further purification. Hydrothermal treatment of the mixtures of Mn(II)[Fe(III),Co(II)] /Bi(III)/La(III) nitrates taken in a ratio 1 : 1 : 1 and 1 : 2 : 1 in 6.0 ml ethylene glycol (formic acid) was carried out in a stainless steel autoclave at 200 °C, for 3 hours. The resulting precipitate was separated from the reaction solution, washed with water and dried at 70 °C for 2 hours.

2.2.Methods

The phase composition, optical and magnetic properties of the obtained samples were characterized by X-ray diffractometry, FTIR - and EMR - spectroscopy. For this purpose X-ray diffractometer XRD TD 3500, China, Fourier-transform infrared spectrometer FTIR LUMOS, Bruker, Germany and electron magnetic resonance spectrometer EMR-micro, Bruker, Germany were used.

3.Results and discussion

In fig. 1. a, b, c X-ray diffraction patterns of a composite materials based on Mn(II), Fe(III), Co(II), Bi(III) and La(III) nitrates were given. The main products of the hydrothermal reduction of manganese nitrate with formic acid (fig. 1. a) at the temperature of 200 °C were metallic bismuth - Bi, $LaCO_3OH$ (lanthanum carbonate hydroxide), $MnCO_3$ (rhodochrosite), CoC_2O_4 (cobalt oxalate), $Bi_2(CO_3)O_2$ (bismutite), Fe_3O_4 (magnetite).

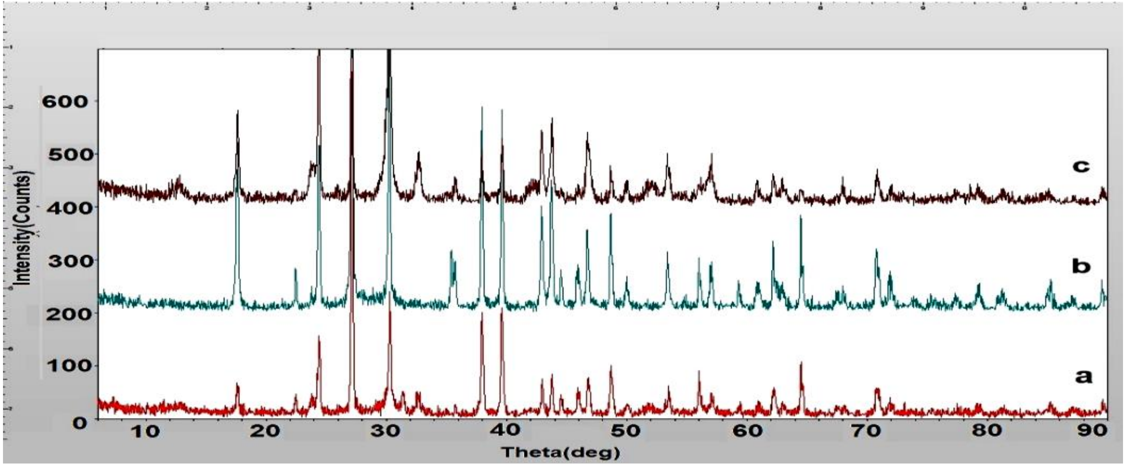


Fig. 2. a, b, c. X-ray diffraction patterns of solid samples after hydrothermal treatment at 200°C for 3 hours in autoclave of a mixture of nitrates taken in a ratio 1:2:1 in formic acid:
a) $Mn(NO_3)_2{\cdot}2H_2O$/ $Bi(NO_3)_3{\cdot}5H_2O$/ $La(NO_3)_3{\cdot}6H_2O$;
b) $Fe(NO_3)_3{\cdot}9H_2O$/ $Bi(NO_3)_3{\cdot}5H_2O$/ $La(NO_3)_3{\cdot}6H_2O$;
c) $Co(NO_3)_2{\cdot}6H_2O$/ $Bi(NO_3)_3{\cdot}5H_2O$/$La(NO_3)_3{\cdot}6H_2O$.

Metallic Bi - semimetal with a rhombohedral structure is appeared for all samples. For all samples $LaCO_3OH$ with hexagonal and orthorhombic structures are observed. The preparation of $LaCO_3OH$ powders with hexagonal structure by hydrothermal treatment in an autoclave is described in [4]. The diffraction peaks belong to a pure rhombohedral structure of $MnCO_3$ (rhodochrosite) is detected also.

Figure 1, b shows the XRD pattern for the Fe_3O_4 (magnetite) nanoparticles. Six characteristic peaks for Fe_3O_4 (2Θ=30.1°; 35.5°; 43.1°; 53.4°; 56.9° and 62.5°) marked by their indices ((220), (311), (400), (422), (511) and (440)) were observed for all samples with $Fe(NO_3)_3$ as precursor. The resultant nanoparticles were Fe_3O_4 with cubic spinel phase. The same particles of Fe_3O_4 are observed in the case as ethylene glycol and formic acid used as the reaction medium. The observed $Bi_2(CO_3)O_2$ (bismutite) were tetragonal phase particles (fig. 1, c). All the diffraction peaks can be perfectly indexed to the tetragonal $Bi_2(CO_3)O_2$ with lattice parameters of a = b = 3.87 Å, and c = 13.697 Å (JCPDS 41-1488). The strong and narrow diffraction peaks indicate that the synthesized product has been well crystallized. Cobalt oxalate CoC_2O_4 with monoclinic structure is also appeared in this samples (fig. 1, c).

In fig. 2 the IR spectra of ternary systems obtained by hydrothermal treatment of Mn(Fe,Co)/Bi/La nitrates with a ratio of 1:2:1 in formic acid are presented.

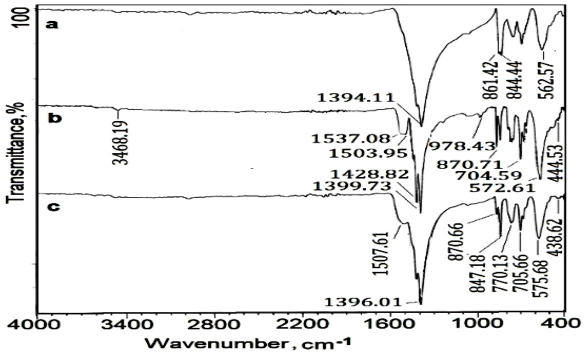
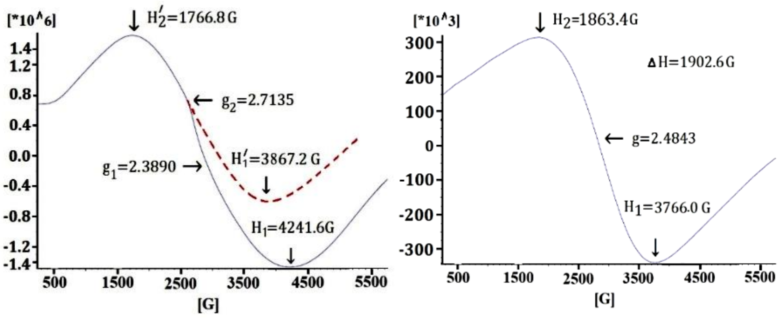


Fig. 2. a, b, c. IR-spectra of a) Mn/Bi/La; b) Fe/Bi/La and c) Co/Bi/La solid samples after hydrothermal treatment at 200 °C for 3 hours in an autoclave of a mixture of nitrates taken in a ratio of 1:2:1 in formic acid.

The observed peaks centered at 1070, 847.18, 1396.01, 1427.36 and 684.19 cm^{-1} are associated with the vibration modes of the CO_3^{2-} group, respectively (Fig. 2. a, b, c). The absorption peak centered at 570 - 580 cm^{-1} is attributed to Bi - O stretching mode. Meanwhile, the peaks at 700 - 400 cm^{-1} originating from the -Bi-O-Bi- vibration is still observed. The OH- stretching band appeared at 3468 cm^{-1}, 3617 and 3648 cm^{-1} for $LaCO_3OH$. The bands 1503, 1507 cm^{-1} in Figure 2 were assigned to the vibrational modes of coordinated CO_3^{2-} ion (v_3) and the weak peaks at 1070 - 870, 844 - 847, 776 - 705 cm^{-1} were assigned to the carbonate ion modes v_1, v_2 and v_4 respectively. A similar IR pattern for a hexagonal $LaCO_3OH$ sample was reported by Zhang et al. [5, 6]. However, the small peaks centered at around 415 - 420 cm^{-1} and the shoulder at 680 cm^{-1} may originate from the presence of small amounts of manganese oxides, band is observed at 704 and 684 cm^{-1} can be assigned to Mn-O vibrations (Fig. 2, a) and bands at 565 and 673 cm^{-1} can be assigned to Co-O vibrations (Fig. 2, c). It should be noted that it is difficult to assign IR frequencies for the obtained ternary oxide systems. This complexity is due not only to the structural features of the detected compounds, but also to the lack of a theoretical justification for assigning IR frequencies in such multicomponent oxide systems. From spectra given in fig. 2, b, it is possible to see an intensive peak at 572.61 cm^{-1} characteristics of the Fe-O bond absorption and ascribed it to Fe-O bond in magnetite nanoparticles.

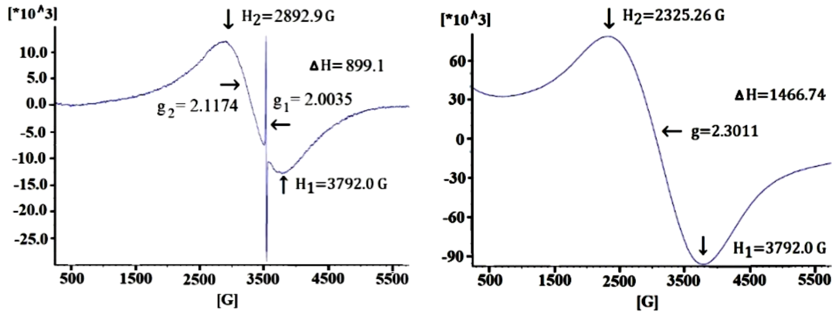
The observed EMR spectra (Fig. 3. a, b) are typical for systems with ferromagnetic properties, but differing in composition. Studies show that the magnetism of the decomposition products of the resulting nitrate mixture strongly depends on the nature and nature of the reducing agent. The EMR spectra obtained for Mn / Bi / La-ethylene glycol and formic acid media are practically identical in shape and values of the EMR parameters. These spectra can be attributed to $MnCO_3$. Studies have shown that the number and composition of ferromagnetic phases formed in ternary systems with iron nitrate vary depending on the molar ratio and the nature of the medium, and it is more likely that they are in an ethylene glycol medium for the Fe/Bi/La - 1:1:1 system. magnetic phases Fe_2O_3 and Fe_3O_4 are formed.



a) **b)**

Fig. 3. EMR spectra of the products of hydrothermal treatment of mixtures of iron, bismuth and lanthanum nitrates, taken in a ratio of 1: 1: 1, at a temperature of 200 °C for 3 hours in an autoclave in a medium: **a)** ethylene glycol and **b)** formic acid.

It is shown that for the case of a mixture with cobalt nitrate in EG, the EMR spectra (Fig. 4. a, b) exhibit only one broad inhomogeneous signal $g = 2.3011$, $\Delta H = 1466.7$ G for a 1:1:1 ratio, due to the formation of a ferromagnetic phase, and two EMR signals, a broad $g = 2.1174$, $\Delta H = 899.1$ G and narrow with $g = 2.0035$, $\Delta H = 4.7$ G, due, respectively, to the ferromagnetic phase and defects of the F-center type in bismuth-containing structures for a 1:2:1 ratio. We note that superpara/ferromagnetism appears for all synthesized samples [7, 8]. When ethylene glycol is taken as a reducing agent, the the Co / Bi / La system EMR spectra given below are observed.



a) **b)**

Fig. 4. EMR spectra of the products of hydrothermal treatment of mixtures of cobalt, bismuth and lanthanum nitrates, taken in a ratio of a) 1:1:1 and b) 1:2:1, at a temperature of 200 °C for 3 hours in an autoclave in a medium ethylene glycol.

4.Conclusion

In this work the influence of the medium (ethylene glycol (EG), formic acid (FA)) on the phase composition and magnetic properties of the products of hydrothermal treatment of a mixture of manganese (iron, cobalt), bismuth and lanthanum nitrates taken in different ratios (1: 1: 1 and 1: 2: 1), at a temperature of 200 ^{0}C for 3 hours in autoclave is discussed. Using the methods of X-ray phase analysis (XRF), infrared (IR) spectroscopy and electron magnetic resonance (EMR) the obtained solid products of hydrothermal processing were characterized. The difficulties were indicated in assigning of IR frequencies for the obtained ternary oxide systems. The complexity is due to the structural features of the detected compounds and the lack of a theoretical justification for assigning IR frequencies in such multicomponent oxide systems. An inte-resting case was detected in the EMR spectra for nitrate mixtures with different ratios of Co/Bi/La hydrothermally treated in ethylene glycol. It was shown that for this case the EMR spectra exhibit only one broad inhomogeneous signal $g = 2.3011$, $\Delta H = 1466.7$ G for a 1:1:1 ratio, due to the formation of a ferromagnetic phase, and two EMR signals, a broad $g = 2.1174$, $\Delta H = 899.1$ G and narrow with $g = 2.0035$, $\Delta H = 4.7$ G, due, respectively, to the ferromagnetic phase and defects of the F-center type in bismuth-containing structures for a 1:2:1 ratio.

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5.References

1. Russo P., Acierno D., Palomba M. et al.: Ultrafine magnetite nanopowder: synthesis, characterization, and preliminary use as filler of polymethylmethacrylate nanocomposites. In: Journal of Nanotechnology. vol. 2012, Article ID 728326, 8 pages, 2012. Hindawi Publishing Corporation (2012). doi: 10.1155/2012/728326
2. Na, H.B., Song, I.C. and Hyeon, T.: Inorganic Nanoparticles for MRI Contrast Agents. In: Adv. Mater. 2009. vol. 21, pp. 2133–2148. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (2009). doi: 10.1002/adma.200802366
3. Watcharenwong, A., Bailuang, Y., Kajitvichyanukul, P.: Synthesis and characterization of monodisperse magnetite nanoparticles by hydrothermal method. In: Key Engineering Materials 2017. vol. 737, pp. 367–372. Scientific.Net, Switzerland (2017). https://doi.org/10.4028/www.scientific.net/KEM.737.367
4. Zhong, S.-L.; Zhang, L.-F.; Jiang, J.-W.; Lv, Y.-H.; Xu, R.; Xu, A.-W.; Wang, S.-P.: Gelatin-mediated hydrothermal synthesis of apple-like LaCO$_3$OH hierarchical nanostructures and tunable white-light emission. İn: J.CrystEngComm 2011. vol. 13, pp. 4151-4160. Royal Society of Chemistry (2011). doi: 10.1039/c1ce00012h
5. Xie, J., Wu, Q., Zhang, D., Ding, Y.: Biomolecular-induced synthesis of self-assembled hierarchical La(OH)CO$_3$ one-dimensional nanostructures and its morphology-held conversion toward La$_2$O$_3$ and La(OH)$_3$. İn: J. Cryst. Growth Des. 2009. vol.9, pp. 3889–3897. American Chemical Society (2009). doi: 10.1021/cg801053p
6. Zahir, M.H., Rahman, M.M., Shafiullah, M., Rahman, M.M., Ali, A., Khan, F., Mohaisen, K.O., Al-Rasheidi, M.: LaCO$_3$OH nanoprisms and their luminescence and no reduction properties. İn: J.Catalysts 2020. vol.10, pp.394. 4052 Basel, Switzerland (2020). doi: 10.3390/catal10040394
7. Javier Bustamante Mamani, Lionel Fernel Gamarra, Giancarlo Espósito de Souza Brito.: Synthesis and characterization of Fe$_3$O$_4$ nanoparticles with perspectives in biomedical applications. In: Mat. Res. 2014. vol. 17, no 3, pp. 542-549. UFSCar - Dep. de Engenharia de Materiais, Rod. Washington Luiz, km 235 (2014). doi: 10.1590/S1516-14392014005000050
8. Hseih CT, Huang WL, Lue JT.: The change from paramagnetic resonance to ferromagnetic resonance for iron nanoparticles made by the sol-gel method. In: J. of Physics and Chem.of Solids. 2002. vol. 63, issue 5, pp. 733-741. Elsevier Ltd (2002). doi: 10.1016/ S0022-3697(01)00222-0

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THERMODYNAMIC PROPERTIES OF THE $BiTe$ and Bi_8Te_9 COMPOUNDS

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Abstract. Two-phase alloys Bi_8Te_9+Bi_4Te_5 and BiTe+Bi_8Te_9 were studied by the electromotive forces method (EMF) in the temperature range 300-450 K. From the EMF data, the relative partial molar functions of bismuth in the alloys were calculated. The potential-forming reactions responsible for these partial functions were compiled, the values of the standard thermodynamic functions of formation, and the standard entropies of Bi_8Te_9 and BiTe compounds were calculated. A comparative analysis of the data for BiTe with the literature data was carried out; for Bi_8Te_9, the thermodynamic functions were obtained for the first time.

Keywords: bismuth tellurides, thermodynamic functions, EMF method, ionic liquid

1.Introduction

The discovery of a new quantum state of matter - a topological insulator (TI) [1] has sharply increased interest in layered compounds, in particular, bismuth and antimony tellurides. It was found that these compounds are TI [2-6] and are extremely promising materials for various applications, including spintronics, quantum computers, medicine, security systems, etc. [6-9].

Thermodynamic functions are fundamental characteristics of compounds and, together with phase diagrams, form the basis of their synthesis, crystal growth, doping, etc. [6, 10, 11].

Despite the increased interest in bismuth tellurides, their thermodynamic properties have been studied extremely insufficiently. Analysis of the available literature shows that modern handbooks and electronic databases contain thermodynamic data mainly for Bi_2Te_3 and to a lesser extent for BiTe [12-15].

Taking into account the above, we have undertaken a comprehensive study of phase equilibria in the Bi-Te system and the thermodynamic properties of bismuth tellurides. In [16], a new refined phase diagram of this system in the composition range of ≤60 at% Te is presented, and the formation of some bismuth tellurides with incongruent melting was shown. The thermodynamic functions of Bi_2Te_3 and Bi_4Te_5 compounds obtained by the method of electromotive forces (EMF) are presented in [17].

In this work, we continued the thermodynamic study of the Bi-Te system and presented the results of the thermodynamic study of BiTe and Bi_8Te_9 compounds by using the EMF method.

This method is widely used to study binary and complex inorganic phases [18-20]. When studying solid chalcogenide phases, it is advisable to carry out the measurements at temperatures below the solidus. For this purpose, along with glycerol solutions of alkali metal salts [20-23], ionic liquids are also successfully used [24, 25], which we used in this work.

2.Experimental

To study the thermodynamic properties of the Bi-Te system by the EMF method, the concentration cells of the type

$$(-)\ \text{Bi (solid)}\ |\ \text{ionic liquid} + Bi^{3+}\ |\ \text{Bi-Te (solid)}\ (+) \qquad (1)$$

were assembled and their EMF was measured in the temperature range 300-450 K.

Elemental bismuth was used as the left electrode, and alloys from the two-phase regions Bi_8Te_9+Bi_4Te_5 and BiTe+Bi_8Te_9 were used as the right electrodes.

Alloys-right electrodes were synthesized by fusion of elementary bismuth and tellurium of high purity in vacuum (~ 10^{-2} Pa) quartz ampoules. After fusion at 900 K, the samples were quenched into cold water, followed by thermal annealing at 750 K (500 h) and 400 K (20 h). The phase composition of the obtained alloys was confirmed by XRD. As an example, Fig. 1 presents the powder X-ray powder diffraction pattern of an alloy with a composition of 54 at% Te. As can be seen, the diffraction pattern of this alloy consists of a set of reflection lines Bi_8Te_9 and Bi_4Te_5. This is in accordance with the refined phase diagram of the Bi-Te system [16].

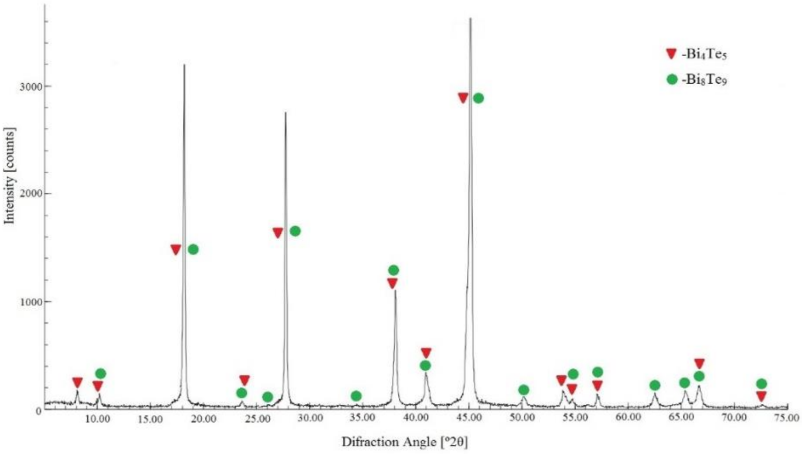

Fig.1. Powder X-ray powder diffraction pattern of an alloy with a composition of 54 at% Te.

An ionic liquid (morpholine formate) with the addition of $BiCl_3$ was used as the electrolyte. The ionic liquid was obtained following the procedure described in [25].

The assembly of electrochemical cells of type (1) and the method for EMF measurements are described in detail in [24, 25].

The first equilibrium EMF values were obtained after maintaining the electrochemical cell at ~350 K for 40-60 h., while the subsequent ones every 3-4 h. after a certain temperature. The EMF values were considered equilibrium, which did not differ from each other when repeatedly measured at a given temperature by more than 0.2 mV, regardless of the direction of the temperature change.

3.Results

As a result of the EHQ measurements, it was established that the EMF has a constant value in each of the phase areas of Bi_8Te_9+ Bi_4Te_5 and BiTe+Bi_8Te_9 of the Bi-Te system, and linearly depends on the temperature (Fig.2). This confirms the existence of pointed two-phase areas in the phase diagram and allows us to use this for the thermodynamic calculations.

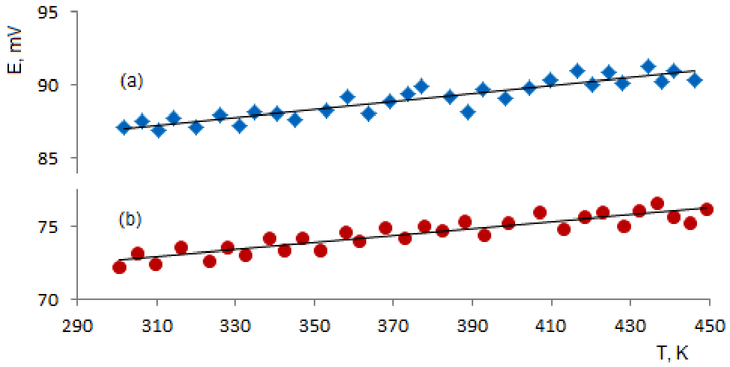

Fig. 2. Temperature dependence of the EMF of type (1) cells in the Bi_8Te_9+ Bi_4Te_5 (a) and BiTe+Bi_8Te_9 (b) two-phase regions

The obtained experimental data were processed using the Microsoft Office Excel 2003 computer program using the least-squares method and linear equations of the type E = a + bT were obtained. The linear equations obtained during the calculations are shown in Table 1 in the form recommended by modern handbooks [19, 20

$$E = a + bT \pm t\left[\frac{\delta_E^2}{n} + \delta_b^2(T - \overline{T})^2\right]^{1/2} \tag{2}$$

In equation (2), a and b are coefficients, n is the number of pairs of values of E and T; $\overline{T}$ - average temperature, K; Student's t-test, δ_E^2 and δ_b^2 - are dispersions of individual values of EMF and constant b. Given that the number of experimental points is n = 30, at a confidence level of 95%, the Student test is t≤2.

Table 1. Relations between the EMF and the temperature for type (1) cells in alloys of the Bi-Te system in the 300–450 K temperature interval

№	Phase area	E, mV=a+bT± t· $\delta_E(T)$
1	Bi_8Te_9 + Bi_4Te_5	$78.93 + 0.0268T \pm 2\left[\frac{0.23}{30} + 3.9\cdot10^{-6}(T - 376.17)^2\right]^{1/2}$
2	BiTe +Bi_8Te_9	$65.54 + 0.00238T \pm 2\left[\frac{0.23}{30} + 3.7\cdot10^{-6}(T - 376.38)^2\right]^{1/2}$

From obtained equations (Table 1) by using the thermodynamic expressions

$$\overline{\Delta G}_{Bi} = -zFE \tag{3}$$

$$\overline{\Delta S}_{Bi} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \tag{4}$$

$$\overline{\Delta H}_{Bi} = -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \tag{5}$$

the partial molar Gibbs free energy, enthalpy, and entropy of bismuth in the alloys were calculated (Table 4).

Table 2. Relative partial functions of bismuth in the alloys of the Bi-Se system at T = 298.15 K

Phase area	$-\overline{\Delta G}_{Bi}$	$-\overline{\Delta H}_{Bi}$	$\overline{\Delta S}_{Bi}$
	kJ/mol		J/(mol·K)
Bi_2Te_3 + Te	25.158±0,069	22.85±0.29	7.76±0.76
Bi_4Te_5 +Bi_2Te_3	21.024±0.067	18.97±0.28	6.89±0.74

The areas of homogeneity of the compounds Bi_8Te_9 and BiTe are very small [16], so these partial molar values are the thermodynamic characteristics of the following potential-forming reactions (the substances in the crystalline state) [19, 20]

$$Bi+2.25\ Bi_4Te_5=1.25Bi_8Te_9 \tag{6}$$

$$Bi+Bi_8Te_9=9BiTe \tag{7}$$

From relations (6) and (7) by using the equations

$$\Delta_f Z^0(Bi_8Te_9) = 0.8\Delta\overline{Z}_{Bi} + 1.8\Delta Z^0(Bi_4Te_5) \tag{8}$$

$$\Delta_f Z^0(BiTe) = \frac{1}{9}\Delta\overline{Z}_{Bi} + \frac{1}{9}\Delta_f Z^0(Bi_8Te_9) \tag{9}$$

$$S^0(Bi_8Te_9) = 0.8\Delta\overline{S}_{Bi} + 0.8S^0(Bi) + 1.8S^0(Bi_4Te_5) \tag{10}$$

$$S^0(BiTe) = \frac{1}{9}\Delta\overline{S}_{Bi} + \frac{1}{9}S^0(Bi) + \frac{1}{9}S^0(Bi_8Te_9) \tag{11}$$

the standard thermodynamic functions of the formation of Bi_8Te_9 and BiTe were calculated. In the relations (8) and (9) Z ≡ G or H. For the calculations, we used the thermodynamic data [17] for Bi_4Te_5 (Table.3) as well as the standard entropy of elementary bismuth (56.7 ± 0.5 $J\cdot mol^{-1}\cdot K^{-1}$) [12]. The obtained values are summarized in Table 3. In all cases, the estimated standard uncertainties were calculated by accumulating the errors. In Table 3, in addition to the results of the present work, the result of previous work [17] and literature data for BiTe are also presented.

As can be seen from Table 3, the standard enthalpy of formation and entropy of BiTe determined by us is in good agreement with the data [14] and differ significantly from the results of [26] obtained by high temperatures EMF measurements. The thermodynamic functions of Bi_8Te_9 were determined by us for the first time.

Table 3. Standard integral thermodynamic functions of the bismuth tellurides

Compound	$-\Delta_f G^o$ (298K)	$-\Delta_f H^o$ (298K)	S^o (298K)
	kJ·mol^{-1}		J·mol $^{-1}$·K^{-1}
Bi_8Te_9	268.2±1.5	286.8±2.3	897.0±12.0
BiTe	34.2±0.2	34.0±0.3	106.7±1.3
	25.6 [26]*	68.6 [26]*	-
		34.4[14]	110.9±12.6 [14]
Bi_4Te_5 [17]	147.8±0.8	149.2±1.1	469.7±6.2
Bi_2Te_3 [17]	76.9±0.2	79.2±0.5	254.2±3.0

* data for 766 K.

4.Conclusion

The thermodynamic properties of the alloys of the Bi_8Te_9 and BiTe compounds were studied by EMF measurements of the concentration cells relative to the bismuth electrode in the 300-450 K temperatures interval. Relative partial molar functions of bismuth in the alloys, standard thermodynamic formation functions, and standard entropies of above-stated compounds were calculated. The results obtained for BiTe supplement and refine the literature data, while the thermodynamic functions for Bi_8Te_9 are determined for the first time.

Acknowledgment

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5.References

1. Kane, C.L. and Moore, J.E.: Topological Insulators. Physics World. 24, 32–36 (2011). https://doi.org/10.1088/2058-7058/24/02/36
2. Holtgrewe, K., Mahatha, S. K., Sheverdyaeva, P. M., et al.: Topologization of β-antimonene on Bi_2Se_3 via proximity effects. Sci.Rep., 10, 14619-14622 (2020). doi: 10.1038/s41598-020-71624-4
3. Hogan, C., Holtgrewe, K., Ronci, F. et al.: Temperature driven phase transition at the antimonene/Bi_2Se_3 van der Waals heterostructure. ACS Nano, 13(9), 10481-10489 (2019). doi.org/10.1021/acsnano.9b04377
4. Lamuta, C., Cupolillo, A., Politano, A. et al.: Indentation fracture toughness of a single-crystal Bi_2Te_3 topological insulator. Nano Research, 9(4), 1032-1042 (2016). https://doi.org/10.1007/s12274-016-0995-z
5. Sultana, R., Neha, P., Goyal, R. et al.: Unusual non saturating Giant Magneto-resistance in single crystalline Bi_2Te_3 topological insulator. J. Mag. Mag. Materials, 428, 213-218 (2017). https://doi.org/10.1016/j.jmmm.2016.12.011
6. Babanly, M.B., Chulkov, E.V., Aliev, Z. S. et al.: Phase diagrams in materials science of topological insulators based on metal chalkogenides. Russ. J. Inorg. Chem., 62(13), 1703–1729 (2017). DOI:10.1134/S0036023617130034
7. Lawal, A., Shaari, A., Ahmed, R., Jarkoni, N.: First-principles investigations of electron-hole inclusion effects on optoelectronic properties of Bi2Te3, a topological insulator for broadband photodetector. Phys.B.Cond.Matter, 520, 69-75 (2017). https://doi.org/10.1016/j.physb.2017.05.048
8. Le, P.H., Liu, P.T., Luo, C.W. et al.: Thickness-dependent magnetotransport properties and terahertz response of topological insulator Bi_2Te_3 thin films // J. Alloys Compd., 692, 972-97 (2017). https://doi.org/10.1016/j.jallcom.2016.09.109
9. Viti, L., Coquillat, D., Politano, A. et al.: Plasma-Wave Terahertz Detection Mediated by Topological Insulators Surface States. Nano Letters, 16, 80−87 (2016). https://doi.org/10.1021/acs.nanolett.5b02901
10. Babanly, M.B., Mashadiyeva, L.F., Babanly, D.M. et al.: Some issues of complex investigation of the phase equilibria and thermodynamic properties of the ternary chalcogenide systems by the EMF method. Russ. J.Inorg.Chem, 64(13), 1649-1671 (2019). https://doi.org/10.1134/S0036023619130035
11. Voronin G.F., Gerasimov Ya.I. The role of chemical thermodynamics in the development of semiconductor materials science. In the book: Thermodynamics and semiconductor materials science. M.: MIET, 3-10 (1980) In Russian.
12. Data base of thermal constants of substances. Digital version, Eds.: V.S. Iorish and V.S. Yungman. (2006)

http://www.chem.msu.ru/cgi-bin/tkv.pl

13. Kubaschewski, O., Alcock, C.B., Spenser, P.J. Materials Thermochemistry. Pergamon Press, 350 (1993)
14. Mills, K.C.: Thermodynamic Data for lnorganic Sulphides, Selenides, and Tellurides, Butterworth, London, (1974).
15. Barin I. Thermochemical Data of Pure Substances, Third Edition, VCH (2008).
16. Hasanova, G.S., Agazade, A.I., Orujlu, E.N., Babanly, M.B.: Refinement of the phase diagram of the Bi-Te system in the Bi-Bi_2Te_3 composition area / 5th International Turkic World Conference on Chemical Sciences and Technologies (ITWCCST 2019)", 110 (2019)
17. Hasanova, G.S., Dashdiyeva, G.B., Yusibov, Y.A., Babanly, M.B.: Thermodynamic properties of the Bi_2Te_3 and Bi_4Te_5 compounds. Chem. Problems, 3, (2020) accepted.
18. Wagner, K. Thermodynamics of alloys. Metallurgizdat, 179 (1957)
19. Babanly, M.B., Yusibov, Y.A., Babanly, N.B. The EMF method with solid-state electrolyte in the thermodynamic investigation of ternary Copper and Silver Chalcogenides. Electromotive force and measurement in several systems. Ed.S.Kara. Intechweb.Org, 57-78 (2011)

OR-IV-3

EFFECT OF MODIFICATORS ON THE PROPERTIES OF BITUM AND ASPHALTOBETON

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Abstract Styrene-butadiene block copolymer-SBS and ethylene-vinyl-acetate copolymer-EVA are offered as high-molecular modifying additives in road bitumen. The effect of modifiers on the main parameters of the polymer-bitumen adhesive and the performance characteristics of asphalt concrete was studied. As the density of the modifier in bitumen increases, the depth of sinking of the needle, the softening temperature increases, the brittleness temperature decreases, and the operating temperature range of the road surface is significantly expanded. Studies show that the SBS copolymer, a thermoplastoelastomer, gives better results than EVA. As a result of the study of adhesion properties, the addition of polyethylene polyamine-containing MasterLife PVA 100 significantly improves the adhesion of bitumen to mineral materials. Studies have shown that the application of a polymer modifier improves many properties of asphalt concrete. Optimal proportions of components in the composition of asphalt concrete pavement with high-performance properties have been proposed.

Keywords: bitumen, polymer, modifier, compressive strength, asphalt concrete

1.Introduction

One of the promising directions in the modernization of bitumen-based pavements is the application of modifiers [1]. The use of polymeric substances such as EVA, Elvaloy, DST-30, butyl rubber and triple copolymer as a modifying additive, first of all, significantly improve their properties and strength [2-5]. However, the use of some high-molecular-weight modifiers causes the following technological problems: first, the uneven distribution of the polymer in the bitumen, and second, the insufficient adhesion of gravel to the bitumen coating, resulting in the collapse of the surface layer.

Analysis of the literature allows us to select the most widely accepted class of high-molecular compounds for the production of polymerbitum adhesive (PBY) [6,7]. For example, as a modifying additive, it is convenient to use easily copolymers of olefin and diene in a concentration that ensures that the main parameters of the polymerbitum adhesive are maintained at a technically reasonable level. In connection with the above, the current research is devoted to the possibility of using styrene-butadiene-styrene copolymer as a modifying additive in road bitumen to improve its performance properties.

2.Materials and research methods

In this case, TN AZ 3536601.242-2015 (production of Baku Oil Refinery named after H.Aliyev) from BNB 50/70 oil bitumen; Europrene SOL T 6302 styrene-butadiene block copolymer - from SBS (manufactured in Ravenna, Italy); LG EVA EA 28400 brand ethylene-vinyl-acetate thermoplastic (made in South Korea); MasterLife PVA 100 (manufactured by BASF) was used. Europrene SOL T 6302 styrene-butadiene block copolymer has a specific gravity of 0.94 g/cm^3, the tensile strength of 20 MPa, the viscosity of 4.0 Pa.s according to Brookfield. The density of MasterLife PVA 100 is 0.93 kg/l, pH = 8, boiling point is 350^{0}C, ignition temperature is above 160^{0}C. Forms of polymeric substances for bitumen are given in Figure 1.

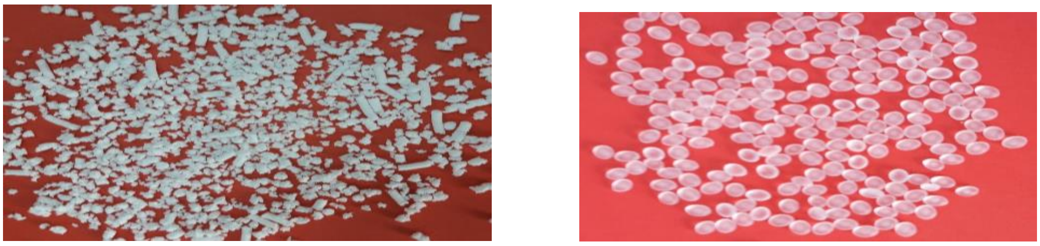

Figure 1. Polymeric substances for bitumen
1- Europrene SOL T 6302 brand SBS, 2- LG EVA EA 28400 brand EVA

In the laboratory, the modifier was mixed with bitumen at a temperature of 160°C in a heating device shown in Figure 2.

PBY softening temperature is determined by the method of KVS (QOST 11506-73). The brittleness temperature is measured in Fraas (QOST 11507-78). The depth of immersion of the needle at 25°C is determined in accordance with QOST 11501-78. Adhesion with mineral aggregates is determined by QOST 11508-74. The stability of bitumen, assessed for changes in quality during long-term storage at high temperatures (163^{0}C, 5 hours) is carried out by QOST 18180-72.

Figure 2. Mixer provided with heating

3.Results and discussion

The main physical and mechanical parameters of PBY were studied in the study to determine the role of the polymer in the composition of PBY, as well as in the asphalt concrete mix. First of all, the effect of SBS and EVA content on bitumen performance was considered. As can be seen from Figure 3, the depth of sinking of the needle, which determines its brand, increases with the amount of modifier in bitumen. In PBY obtained with the application of EVA in the amount of 2% of polymers, the depth of needle immersion is slightly higher than the results of SBS, but SBS shows better results in the range of 3-6%.

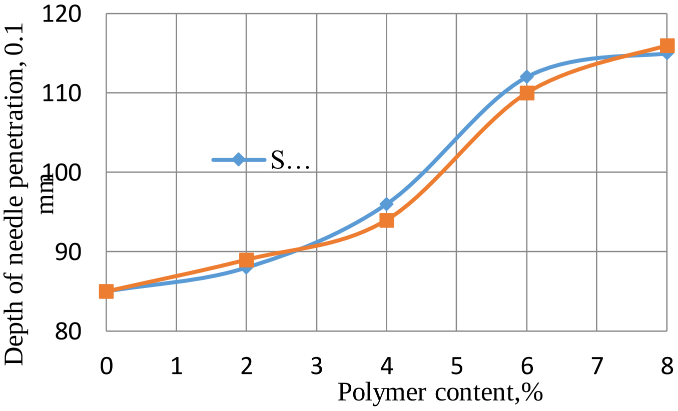

Figure 3. Dependence of needle sinking depth on the density of polymers in polymer-bitumen adhesive

Although the main indicator of heat resistance is the softening temperature, which reflects the transition from the elastoplastic state to the viscous state, the effect of the amount of high-molecular compounds added to it has been studied. It was found that SBS-based PBY results (5-15%) are better when the PBY softening temperature is 3-11% when the EVA content is 2-6% (Fig. 4).

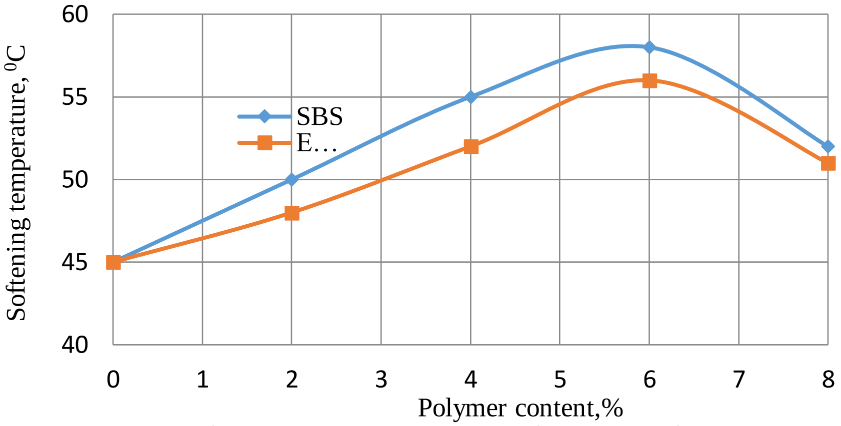

Figure 4. Softening temperature dependence of the amount of polymers in the polymer-bitumen adhesive

The observed dependence is probably explained by the formation of a spatial polymer lattice in PBY. Then there is a slight stabilization and decrease. It seems that at first the polymers act as a fine filler, while the softening temperature and viscosity increase. Then, as the mixture reaches a critical concentration in the formation, the peak of the softening temperature due to the saturation of the mixture with the polymer is recorded. Subsequent increase in viscosity leads to excessive saturation of bitumen with high molecular weight compounds, which leads to a decrease in the softening temperature of bitumen.

An increase in the concentration of styrene-butadiene-styrene copolymer leads to a decrease in the brittleness temperature of PBY and is -32-35^{0}C when used in an amount of 4-6% (Fig. 5).

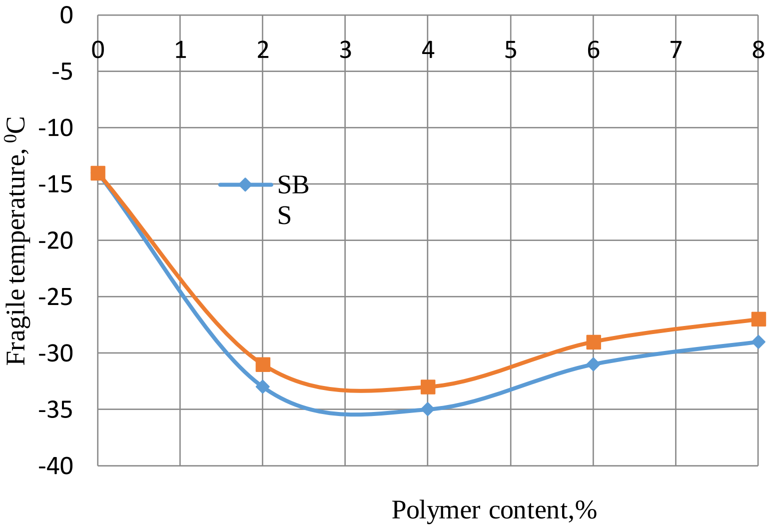

Figure 5. Dependence of brittleness temperature on polymer viscosity in polymer-bitumen adhesive.

For all experimental samples of PBY prepared with different amounts of modifiers, the indicators that meet the requirements of QOST R 52056-2003 are indicated (Table 1). Given that nitrogen-containing substances are used as additives to enhance adhesion properties [8,9], BASF's MasterLife PAV-100 surfactant (polyethylene polyamine - PEPA) has also been studied. The "passive adhesion" method was chosen to study the adhesion properties.

As can be seen from the table, the addition of the SBS modifier to bitumen improves its key performance. First of all, there is a significant increase in the plasticity range, which characterizes the operating temperature range. Bitumens with a wide plasticity range have a higher deformation ability, which increases the resistance to cracking at low temperatures and the shear strength of the coating at high temperatures. The addition of polymer to bitumen eliminates the problem of cracking of the road surface due to the improvement of the main parameters of the adhesive, which are characterized by crack resistance (Table 1).

Table 1. Physical and mechanical properties of polymer-bitumen adhesive

№	Quantity of PBY components, in% by weight			Penetration at 25 °C, 0.1 mm	Softening tempera-ture, °C	Fragility tempera-ture, °C	Elongation at 25°C, cm	Plasticity interval, °C	Adhesion of miner-als with
	Bitumen	SBS	PEPA						
1	100	0	0	85	45.1	-14	>100	59.1	№3
2	95	2	0	92	54.4	-32.9	>150	97.3	№2
3	90	4	0	112	58.8	-34.7	>150	103.5	№1
4	85	6	0	114	49.8	-30.7	>150	80.5	№2
5	95	0	3	122	49.8	-30.9	103	80.7	№2
6	93	4	2	106	64.8	-37.8	>150	106.6	№1
7	90	4	3	111	54.1	-34.5	>150	92.6	№1
8	85	4	4	130	50.7	-30.4	>150	84.1	№2
QOST R 52056-2003				91-130	50	-30	>30	-	№2

The results show that the adhesion strength of the mineral material is significantly improved and MasterLife PAV-100 corresponds to the control sample 2№ (Table 1) when used in the amount of 1% to 2%. In this case, other parameters of the adhesive are within the requirements of the standard.

One of the reasons for the premature collapse of the road surface is the wear and tear that occurs during its long-term operation. In this case, complex physical and chemical transformations occur in the structure of the material, which lead to the deterioration of its mechanical properties and a decrease in the serviceability of the coating. The physical and mechanical characteristics of the modified PBY that have been tested for wear have been studied. As can be seen from the figures in Table 2, the ductility decreases with increasing softening temperature. It is possible that this is due to oxidative dehydration reactions of naphthenoromatic compounds of bitumen with the formation of multi-ring aromatic molecules, which occur under the conditions of aging, and then their association with asphaltenes.

Table 2. The effect of the composition of the polymer-bitumen adhesive on abrasion resistance

№	Quantity of components,%			Softening tempera-ture before heating, ^{0}C	Softening tempera-ture after heating, ^{0}C
	Bitumen	SBS	MasterLife PAV-100		
1	100	0	0	47	48
2	95	0	2	39	48
3	93	4	1.5	58	64
4	90	4	2	48	54
5	85	4	3	43	49

To determine the deformation resistance of the road surface, asphalt concrete mixtures with the same granular composition with different amounts of modifier additive on the basis of 50/70 bitumen were prepared. The test results obtained during the determination of the compressive strength of asphalt concrete samples are given in Table 3.

Table 3. Compressive strength limits for polymer asphalt concrete

№	Quantity of components,%			Compressive strength, MPa	
	Bitumen	SBS	MasterLife PAV-100	0^{0}C	50^{0}C
QOST 9128-97	-	-	-	Not more than 12	Not less than 1.2
1	100			8.5	1.2
2	96	4		10	3
3	98	-	2	5	2.5
4	95.5	4	1.5	10	4
5	94	4	2	12	2.7
6	93	4	3	11	1.4

Experimental results show that the strength characteristics of PBY asphalt concrete are much higher than 50/70 bitumen-based asphalt concrete.

4.Conclusion

Thus, polymers used as modifiers in road bitumen give better results than Europrene SOL T 6302 styrene-butadiene-styrene block copolymer LG EVA EA 28400 ethylene-vinyl-acetate thermoplastic. The application of modifiers allows to obtain high-quality polymer-bitumen adhesive that meets the requirements of QOST R 52056-2003. Studies have selected the optimal composition of polymer-bitumen adhesive, which helps to improve the performance of asphalt concrete**.** In addition to the polymer-bitumen adhesive, the adhesion properties of the composition were increased by the inclusion of polyethylene polyamine, which increases adhesion.

5.References

1. Guvalov A.A., Mamedov A.D. Additions to the operational properties of asphalt concrete pavements. Current issues of strength: LXI International Conference, dedicated to the 90th anniversary of Professor M.A. Krishtala (Togliatti, September 9-13, 2019): collection of materials - Togliatti: TSU Publishing House, 2019. p. 183-184
2. Knyazev Yu.V., Budantsev V.V., Frolov V.A., Merkulov S.A. Use of polymeric materials for road modification // Young scientist. 2015. №12. p. 198 - 200
3. Guvalov A.A., Mamedov A.D. Influence of modifying additives on the properties of asphalt concrete Actual problems of strength: materials of the international scientific conference, Vitebsk, May 25-29, 2020 / ed. B.B. Rubanika. - Well done: Printing House "Victory", 2020. p.336
4. Shcherba Y.S., Kotenko N.P. Modification of petroleum bitumen with polymer additives: // Student scientific spring - 2018: materials of regional scientific and technical. conf. (competition of scientific and technical works) students, graduate students and young universities of Rostov region, Novocherkassk, 2018. p. 241 - 242.
5. Road bitumens with modifying additives [Text] / S.V.Котов, Г.В. Timofeeva, S.V. Livanova [et al.] // Chemistry and technology of fuel and oil. - 2003. № 3. p. 52–53.
6. Pat. RF 2573012. Polymer-bituminous binder / A.M. Syroezhko, V.V. Vasiliev, Yu.A. Urçeva, A.M. Gerasimov, N.V. Maydanova, Д.A. Panfilov, I.M. Дворко, O.M. Fly-suck, N.W. Lukyanov. // B.I. 20.01.2016.
7. Kudryavtseva S.V. Influence of polymer species and surface-active substances on adhesion of bitumen with mineral substrate [Text] / S.V. Kudryavtseva // Bulletin of the Kharkiv National Automobile and Road University.– 2008. №40. p. 36-39.
8. Aigul A.I. Modification of bitumen additives class PAV [Text] / A.I. Aigul, I.K. Linar // In the world of scientific discoveries.– 2010. №6.1. (12). p. 236 - 237.
9. Gohman, L.M. Application of attic polypropylene to improve the properties of bitumen and asphalt concrete [Text] / L.M. Gohman, D.S. Şemonayeva, E.N Titova // Automobile roads №8, 1990, p. 11-13

OR-IV-4

SORPTION PRECONCENTRATION OF SILVER IONS ONTO SYNTHETIC CHELATING ADSORBENT

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Abstract. Current work is dedicated to the sorption preconcentration of trace amounts of silver onto synthetic chelating polymeric adsorbent based on a copolymer of styrene with maleic anhydride containing a fragment of malonic acid dihydrazide from aqueous solutions. Adsorbent was synthesized by the polycondensation reaction. For the synthesis of adsorbent formalin was used as a crosslinking agent. The optimal conditions of the sorption process of silver ions were found: pH, contact time, initial metal concentration, ionic strength. Sorption experiments were carried out using batch systems at room temperature. The optimum pH for removal of silver ions when using synthetic chelating polymeric adsorbent modified with malonic acid dihydrazide is pH = 6. Optimal ionic strength achieved at a value of μ=0,8. The sorption capacity of the adsorbent and the percentage recovery were determined from the difference in the initial and final concentrations of silver(I) in the aqueous solution. The best elution properties toward silver ions possessed the 1,0 M HNO_3.

1.Introduction

Heavy metal ions, such as cadmium, lead, silver are among the environmental pollutants and even at low doses have negative effects on humans. Heavy metal ions become concentrated as a result of human caused activities and, accumulating in environmental objects, at a level significantly higher than the Maximum Permissible Concentration, they have a negative effect on living organisms.

Silver is a white, ductile metal occurring naturally in the pure form and in ores. Silver in trace amount is necessary for life processes. Some silver compounds are extremely photosensitive and are stable in air and water, except for tarnishing readily when exposed to sulfur compounds. [1]. On the other hand, silver is one of the heavy metal ions. The application of different treatment methods for silver ion removal from environmental objects is actual.

A lot of treatment methods proposed to recover silver, such as precipitation, extraction, cross flow microfiltration, sorption[2-22]. In the recent years, sorption due to its simplicity and reaching high sorption capacity has been widely used as an effective method for recovery of silver(I). Heavy metal poisoning is generally treated by the administration of chelating agents.

Current work is dedicated to the study of sorption preconcentration of trace amounts of silver(I) using synthetic chelating polymeric adsorbent based on a copolymer of styrene with maleic anhydride containing a fragment of malonic acid dihydrazide from aqueous solutions.

2. Experiment part

2.1.Reagents.

All of the chemicals and reagents used in the current research were of analytical grade. The standard solution of Ag(I) was obtained by dissolving an exact sample of $AgNO_3$ in distilled water. Working solutions were prepared from the standard solution by dilution with distilled water. The solution of reagent with concentration $1.0x10^{-3}$ mg L^{-1} was prepared by bidistilled water. Equilibrium concentration of silver(I) ions were determined in the liquid phase using adsorption spectrophotometry at 540 nm, pH 8.0. Adsorption studies were carried out by using $1.0x10^{-2}$ mg·L^{-1} water solution of $AgNO_3$.

The effect of pH on the adsorption of Ag(I) ions was studied at the range of pH=3-8 respectively. The pH of the buffer solutions was maintained constant using an acetic acid and ammonium hydroxide solutions respectively. The effect of ionic strength on the adsorption was studied using 2 mol L^{-1} KCl solution. Solution of 0.5 mol L^{-1} KOH was used in desorption process.

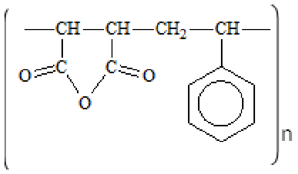

Fig. 1. Molecular structure of styrene-maleic anhydride copolymer.

2.2. Synthesis of chelating adsorbent.

Adsorbent synthesis was carried out by the known technique [23]. For each experiment 3 g of maleic anhydride styrene copolymer was measured and the corresponding quantity of amine added to a flask. Reaction proceeds in the presence of formalin at 60-70 ° C and lasts approximately 35-40 min. The reaction is carried out in sandy bath by continuous mixing. Since the reaction is carried out in aquatic environment anhydride groups of copolymer subject to hydrolysis. Because of the mutual influence of formaldehyde and amine nonstable carbonylamine is formed. The resulting carbonylamine mutually interacts with carboxyl groups of macromolecule and the amine fragment enters the macromolecule.

For removal of remaining parts of reaction product each adsorbent has been rinsed several times with distilled water. Then constant mass was dried in vacuum desiccators at 323 K, grinded and skipped through sieve with 0.14 mm of pore diameter. The resulting product was investigated by Infrared spectroscopy and then was used as the solid phase in current research. The schematic representation of considered reaction is shown on the Scheme 1.

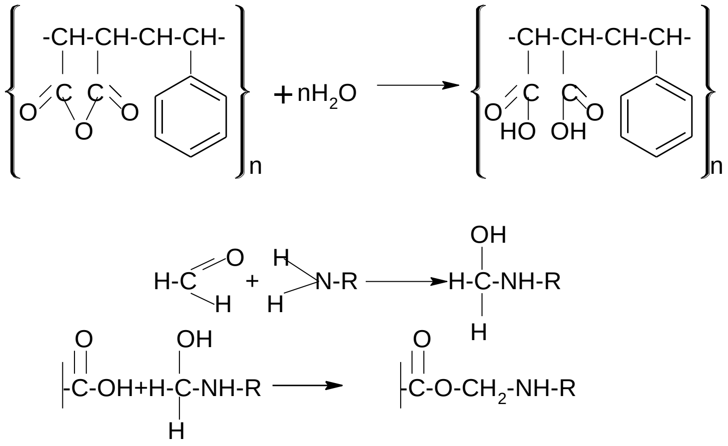

Fig. 2. The schematic representation of the polycondensation process

2.3 Equipment

Absorbances of solutions were determined using adsorption spectrophotometry. Concentrations of Ag(I) ions were determined by flame atomic absorption spectrometry using AAS-1N equipped with hollow-cathode lamps for Ag(I). Measurements were carried out in acetylene-air flame. Solutions pH values were measured using Ionomer I-130 with glass electrode. Infrared measurements of sorbent were obtained using a Varian 3600 Fourier Transform spectrometer from 400 to 4000 cm^{-1}.

3. Results and discussions

The main purpose of this study was to develop a simple, rapid, sensitive and inexpensive method for the recovery of trace amounts of silver(I) ions from aqueous media.

3.2 Influence of medium acidity

The effect of pH on removal of silver(I) ions was investigated. Sorption of silver(I) ions was carried out in static conditions from aqueous media. The mechanism of the silver(I) ions sorption is highly pH dependent. By the results of experiments, the degree of sorption passes through a maximum at pH value 6. The pH value 6 was used as the optimum pH for further studies.

3.3 Influence of contact time

The dependence of the sorption process on contact time was studied. The complete sorption of silver (I) occurs after 90 minutes. 90 minutes was chosen as a contact time for further studies .

3.4 Influence of initial Ag^+ concentration

The influence of initial metal concentration on removal of silver(I) ions was investigated. By the results of experiments it was shown, that the amount of adsorbed silver(I) ions increases with the initial concentration of Ag^+ ions and reached maximum at 80×10^{-3} mol/L. The sorption capacity of the sorbents and the percentage recovery were determined from the difference in the initial and final concentrations of silver(I) in the aqueous solution.

3.5 Influence of ionic strength

The influence of ionic strength on removal of silver(I) ions was investigated. Silver was sorbed from solutions containing 0.1-1.4 M KCl. Optimal ionic strength achieved at a value of μ=0,8.

3.6 Desorption studies.

The desorption process of silver(I) ions was carried out. Desorbing agents, such as HNO_3 and CH_3COOH with different concentrations were used for the adsorbing silver(I) ions from solid phase. The best elution properties toward silver(I) ions possessed 1 M HNO_3.

4. Conclusions

Current work is dedicated to the study of sorption preconcentration of trace amounts of silver(I) using synthetic chelating polymeric adsorbent based on a copolymer of styrene with maleic anhydride containing a fragment of malonic acid dihydrazide from aqueous solutions. The optimum pH for removal of silver(I) ions pH = 6. Optimal ionic strength achieved at a value of μ=0,8. The best elution properties toward silver(I) ions possessed 1 M HNO_3.

5.References

1. World Health Organization. Silver and silver compounds: environmental aspects.Geneva, 2002.
2. Afandiyeva, N. T. Preconcentration of silver (I) on the modified sorbent from aqueous solutions. New Materials, Compounds and Applications. 4(1), 54-60 (2020).
3. Mammadov P.R., Afandiyeva N.T., Chiragov F.M. Simple and rapid spectrophotometric determination method for trace level of silver using 2,2' -di (2,3,4- trihidroksifenilazo)bifenil. New Materials, Compounds and Applications 2(2), 123-131 (2018).
4. Celik Z., Gülfen M., Aydin A.O. Selective adsorption of silver ions from aqueous solution using polystyrene-supported trimercaptotriazine resin. Journal of Hazardous Materials. 24(12), 2166-2172(2010).
5. Jeon, C., Adsorption of silver ions from industrial wastewater using waste coffee grounds. Korean Journal of Chemical Engineering 34(2), 384-391 (2017).
6. Akgul, M., Karabakan, A., Acar, O., Yurum, Y. Removal of silver (***I***) from aqueous solutions with clinoptilolite. Microporous and Mesoporous Materials. 94(1-3), 99–104 (2006).
7. Yirikoglu, H., Gülfen, M. Selective adsorption of silver ions from aqueous solution using polystyrene-supported trimercaptotriazine resin.Separation Science and Technology. 43(2), 376-388(2008).
8. Atia, A.A., Donia, A.M., Yousif, A.M. Comparative study of the recovery of silver(I) from aqueous solutions with different chelating resins derived from glycidyl methacrylate. Journal of Applied Polymer Science. 97(3), 806-812(2005).
9. Jintakosola, T., Nitayaphat, W. Adsorption of Silver (I) From Aqueous Solution Using Chitosan/Montmorillonite Composite Beads. Materials Research. 19(5), 1114-1121(2016).
10. Lihareva, N., Dimova, L., Petrov O. and Tzvetanova, Y. Ag^+ sorption on natural and Na-exchanged clinoptilolite from Eastern Rhodopes, Bulgaria. Microporous and Mesoporous Materials. 130(1-3), 32–37(2010).
11. Guo, L., Shixing, W., Zhang, L., Hu, T., Peng, J., Cheng, S. and Fu, L. Selective Adsorption of Ag^+ on a New Cyanuric-Thiosemicarbazide Chelating Resin with High Capacity from Acid Solutions. Polymers. 9(11), 568(2017).
12. Petrova, Y.S., Pestov, A.V., Usoltseva, M.K., Neudachina, L.K. Selective adsorption of silver(I) ions over copper(II) ions on a sulfoethyl derivative of chitosan. Journal of Hazardous Materials. 299(6), 696–701(2015).
13. Jacobson, A. R., Klitzke, S., McBride, M.B., Baveye P. and Steenhuis T.S. The desorption of silver and thallium from soils in the presence of a chelating resin with thiol functional groups. Water, Air, and Soil Pollution.160(1-4), 41-54(2005).
14. Karimi M.A., Mohammadi S.Z., Mohadesi A., Hatefi-Mehrjardi A., Mazloum-Ardakani M., Sotudehnia Korani L., Askarpour Kabir A. Determination of silver(I) by flame atomic absorption spectrometry after separation/preconcentration using modified magnetite nanoparticles. Scientia Iranica.18(3), 790-796(2011).
15. Manuella L.C., Ambrósio F.de A. N., Eric S.N., Melissa G.A.V. Adsorption of silver from aqueous solution onto pre-treated bentonite clay: complete batch system evaluation. Journal of Cleaner Production. 112(1), 1112-1121(2016).
16. Conde-González, J.E., Peña-Méndeza E.M., Rybákováb S., Pasáne J. , Ruiz-Péreze C., Havel J.. Adsorption of silver nanoparticles from aqueous solution on copper-based metal organic frameworks (HKUST-1). Chemosphere. 150, 659-666(2016).
17. Praus P., Turicová M., Valásková M. Study of silver adsorption on montmorillonite. Journal of the Brazilian Chemical Society. 19(3), 549-556(2008).
18. Omri A., Benzina M. Adsorption characteristics of silver ions onto activated carbon prepared from almond shell. Desalination and water treatment. 51(10-12), 1-10(2012).
19. Syafiuddin A., Fulazzaky M.A., Salmiati S., Hong Kueh A. B., Fulazzaky M., Salim M.R. Silver nanoparticles adsorption by the synthetic and natural adsorbent materials: an exclusive review. Nanotechnology for Environmental Engineering. 5(1), (2020).
20. Hassan D.M., Farghali M.R. Adsorption of silver nanoparticles from aqueous solution by multiwalled carbon nanotubes. Adv Nanopart. 6(2), 22–32(2017).
21. Xiao-xia Zhou, Ying-jie Li, Jing-fu Liu. Highly Efficient Removal of Silver-Containing Nanoparticles in Waters by Aged Iron Oxide Magnetic Particles. ACS Sustainable Chem. Eng. 5(6), 5468–5476(2017).

PP-IV-4

STUDY OF BIOLOGICAL ACTIVITY OF N-CARBOXY-PHENYLIMIDE-2,3-DICHLOROBICYCLO- [2.2.1] HEPT-5-EN-2,3-DICARBONIC ACID.

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Abstract: Based on ortho-, meta-, and para-aminobenzoic acid, and using dichloromaleic anhydride in glacial acetic acid, N-substituted imides of dichloromaleic acid were obtained. For the synthesis of N- (ortho-meta- and para-carboxyphenyl) imide-2,3-dichlorocyclo - [2.2.1] hept-5-ene-2,3-dicarboxylic acid, N-substituted imides of dichlorormaleic acid were used as diene cyclopentadiene. The structures of synthesized adducts are confirmed by modern physicochemical methods. In order to find out whether the new adducts synthesized by us on the basis of N-substituted imides of dichloromaleic acid and cyclopentadiene possess certain practical properties, they were tested comprehensively in agriculture, and their biological activities were studied in different concentrations. The results of multiple tests showed that among the synthesized adducts N- (p - carboxyphenyl) imide - 2,3-dichlorobicyclo - [2.2.1] hept-5-ene-2,3-dicarboxylic acid has a very high fungicidal activity against verticillosis wilt cotton. Especially, it should be noted that at a concentration of 0.1% it shows a killing effect on the fungus verticillum dahlial.

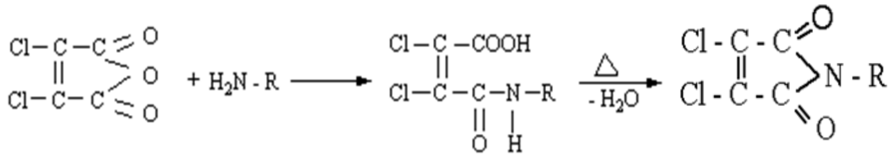
Keywords:1 aminobenzoic acid, 2imide,3 biological tests,4 fungicidal activity,5 cotton wilt, 6concentration.

1.Introduction

The problem of chemical plant protection in agriculture, protection from biodeterioration of various materials is currently gaining significant importance. Studies in these areas have revealed the peculiarity that harmful organisms, as it turned out, are adapting themselves to chemical protective equipment Therefore, the problem arises of creating new, effective biologically active compounds.. It is known that the compounds of bicyclo [2.2.1] hept and [2.2.2] oct-5-ene series possess a wide spectrum of biological and physiological effects [1–6]. On the other hand, there is a message [7] indicating the presence of pharmacological properties of the bicyclo [2.2.1] hept-5-ene compounds. They are synthesized using primary amines, dichloromaleic anhydride and cyclopentadiene and 1,3-cyclohexadiene as dienes. In our similar works [1,3,5,8-10]. devoted to the study of the reaction of diene synthesis of N-aryldichloromaleinimides with cyclopentadiene (CPD), it was shown that the obtained compounds have biological activity. In continuation of these studies, the present work was devoted to the synthesis of new mono- and bicyclic compounds based on ortho-, meta- and steam of aminobenzoic acid using dichloromaleic anhydride and cyclopentadiene (CPD) as a diene, as well as the study of their biological activity.

2.Experimental part

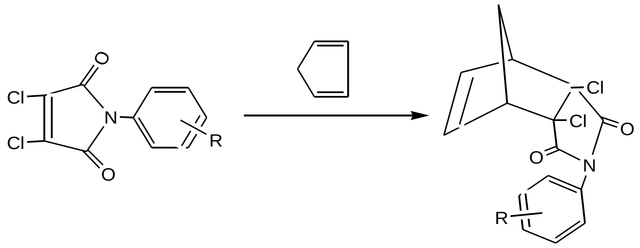
The interaction of the primary isomers of aminobenzoic acid and dichlorormaleic anhydride (DCMA) was used to synthesize N-ortho-, meta- and paracarboxyphenyl imides dichlorormaleic acid. The reaction proceeds in two stages: with the formation of an amido acid in the first stage, which under the reaction conditions further cycles to form an imide. The imide formed directly at the reaction center contains four electron withdrawing groups, which causes its high electron withdrawal. Based on this, when conducting a diene synthesis reaction with the participation of this dienophile, an N-substituted dichloromaleinimide, it was advisable to choose a diene that would exhibit an electron-donating property. We chose cyclopentadiene as such a diene. The reaction proceeds according to scheme I and II:
Scheme 1.



1 2(a-c) A 3(a-c)

R= (a), o-C_6H_4COOH; (b), м- C_6H_4COOH ; (c), п-C_6H_4COOH

Scheme -2.



3(a-c) 4 5(a-c)

R= (a), o-COOH; (b), м- COOH ; (c), п-COOH

A detailed study of this reaction and the resulting products is given in [11]. Using X-ray diffraction analysis and NMR spectroscopy, it was shown that the resulting adducts have an endo configuration[12-14]. This work presents a study of the biological activity of the synthesized compounds,N-(p-and m-carboxyphenyl) imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene- 2,3- dicarboxylic acid.

3.Results and discussion

In order to find out whether the new adducts synthesized by us on the basis of N-substituted imides of dichloromaleic acid have certain practical properties, they were tested in many ways. Since biological tests require a lot of time to carry out, we first turned to the compounds of the bicycloheptene series, believing that if the carbon-carbon double bond plays any role in determining practically useful properties, then it will manifest itself to a greater extent.

The fungicidal and bactericidal activity of the compounds was investigated by suppressing the germination of spores and mycelium on the fungi Fusarium solany (F.S), Helmintosporium satrium (H.S), Botrytis sinera (B.S) and on the bacteria Xhantomonas malvasearum (X.M). The results showed that one of the compounds has fungicidal activity (table 2).

Table 1. Fungicidal and bactericidal activity of N-meta and N-para - carboxyphenylimide compounds

Connection Name	Inhibition of spore germination.,% Concentration, 0.005 a.a.			Inhibition of mycelial growth,%, concentration, 0.003 a.a.			Inhibition of bacterial activity,%,concentration, 0.003a.a.
N-(m-Carboxyphenyl)imide-2,3-dichlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid.	65,9	85,8	–	0	30,6	-	2.1
N-(p-Carboxyphenyl)imide-2,3-dichlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid.	71,.5	87,9	–	14,9	48.6	–	22,8
TMTD - standard	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Tests of the compounds for the presence of plant growth stimulating activity of the preparations synthesized by us were carried out under laboratory conditions on wheat and cucumber seedlings. As can be seen from the obtained data (Table 3), the compounds showed stimulating activity only on wheat, and cucumber seedlings were inhibited.

Table 2. The results of biological tests of N- (m-carboxyphenyl) imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid on stimulating plant growth.

Connection Name	Dose, g / t	The length of seedlings,%	
		wheat	cucumbers
N-(m-Carboxyphenyl)imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.	1 10	108 117	85 70
Control	–	100	100

The biocidal activity of the compounds was determined using pure cultures of aerobic iron-oxidizing thionic bacteria Tnibocillus ferrooxians BKM B-458 and anaerobic sulfate-reducing bacteria Desulfovibrio acsulfuricans BKM B-1388. The test results are carried out in table. 4 and 5, respectively.

Table 3. Test results of the biocidal activity of the compounds for thionic iron-oxidizing aerobic bacteria VKM B-458

Connection Name	The concentration of the compound, wt. %				
	0.0001	0.001	0.01	0.1	1.0
N-(m-Carboxyphenyl)imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.	+	+	–	–	–
N-(p-Carboxyphenyl)imide-2,3-dichlorobicyclo - [2.2.1] hept-5-ene-2,3-dicarboxylic acid.	+	+	–	–	–

Note: "+" - growth of bacteria, "-" - lack of growth.

Table 4. Test results of compounds against sulfate-reducing aerobic bacteria VKM B-1388

Connection Name	The concentration of the compound, wt. %				
	0.0001	0.001	0.01	0.1	1.0
N-(m-Carboxyphenyl)imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.	+	+	+	–	–
N-(p-Carboxyphenyl)imide-2,3-dichlorobicyclo - [2.2.1] hept-5-ene-2,3-dicarboxylic acid.	+	+	+	–	–

Note: "+" - growth of bacteria, "-" - lack of growth.

From the data given in Tables 3 and 4, it can be seen that the studied compounds have biocidal activity against thionic and sulfate-reducing bacteria, i.e. are bactericides.

In the laboratory of the Azerbaijan Scientific Research Institute of Plant Protection, a series of synthesized adducts was tested as fungicides against verticillum cotton vilt caused by verticillum dahlial

The fungicidal properties of the compounds were studied by growing the causative agent of cotton wilt on an agarized beer wort medium in the presence of N- (p-Carboxyphenyl) imide-2,3-dichlorobicyclo [2.2.1] hept-5-en-2,3-dicarboxylic acid.

The medium with various concentrations (0.1; 0.05; 0.01% ai) of the preparations was sterilized and poured with a thin layer evenly into Petri dishes. После этого на застывщую питательную среду наносилась чистая культура возбудителя вилта verticillum dahlial, в центр чашек Петри, которые помещались в термостат, выдерживались при температуре 25-26^{0}C.

Starting from the third day after laying the experiment and then every other day, using the strip of graph paper, we measured the growth intensity of the mycelium of the fungus verticillum dahlial.

The control was Petri dishes with agar medium of beer wort without the presence of a preparation in it. The experiment was repeated three times. An analysis of the results showed that of the number of investigated compounds, only N- (p-Carboxyphenyl) imide-2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid has a high fungicidal activity against cotton verticillosis . The test results are presented in table 5.

Table 5. The results of a study of the fungicidal activity of N- (p-Carboxyphenyl) imide-2,3-dichlorobicyclo- [2.2.1] hept-5-ene-2,3-dicarboxylic acid against verticillosis cotton wilt

Experience options	Concentraton %,	Growth and development of fungus verticillum dahlial in mm for 1 month (control after 24 hours)									
		09	11	13	16	18	20	23	25	27	30
N- (p-Carboxyphenyl) imide-2,3-dichlorobicyo [2.2.1]hept-5-ene-2,3-dicarboxylic acid.	0.01	-	-	-	0.3	0.5	0.8	10	16	21	24
	0.05	-	-	-	0.3	0.5	0.8	11	17	21	24
	0.1	-	-	-	-	-	-	-	-	-	-
Control-no drug added	-	0.8	10	12	13	16	27	36	50	55	60

As can be seen from the obtained tabular data 5, the studied drug in all tested concentrations significantly inhibits growth and stops the development of the fungus verticillum dahlial. At a concentration of 0.1%, it shows a killing effect on the fungus verticillum dahlial. In this embodiment, germination of the mycelium of the fungus was not observed at all.

Also in the helminthology laboratory of the Azerbaijan Scientific Research Veterinary Institute, a number of synthesized compounds were tested as anthelmintics for fatsiol in vitro. The test results showed that N- (p-Carboxyphenyl) imide-2,3-dichlorobicyclo- [2.2.1] hept-5-ene-2,3-dicarboxylic acid has anthelmintic efficacy in vitro and for further studies as anthelmintics in It is of great interest to the body of experimental animals.

4.Conclusion

Thus, it was found that the compound N- (p-Carboxyphenyl) imide-2,3-dichlorobicyclo- [2.2.1] hept-5-en-2,3 dicarboxylic acid had a high fungicidal activity against verticillosis cotton wilt, which allows us to recommend its like a new biologically active substance.

5. References

1. Nagiyev Ya. M., Akhmedova R.M., Bagirov Sh.T., Farzaliev V.M., Hasanov A.I., Synthesis of mono- and bicyclic active compounds based on β-aminoisobutyronitrile. Azerb.chem. journ. No.3, pp. 58-66.(2005)
2. Mammadbeyli (Mammadov), E.G., Kyazimova T.G., Nagiev Y.M., Abdiev O.B., Aliev K.A. Synthesis of bicyclo [2.2.1] hept-5-enylmethyl esters of p-substituted benzoic acids.Russian Journal of orqanic Chemistry. vol.45, issue 1. pp.81-84.(2009).
3. Nagiev, Ya.M. Synthesis of New Halogen-Containing Norbornene Adducts Based on N-Substituted Imides of 2,3-Dichlorbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxylic Asids and Hexachlorocyclopentadiene. Organic Chemistry:Current Research. . Vol.7 . pp.190-193 (2018)
4. Veliev M.G., Chalabieva A.Z., Mamedova A.F. Study of the diene condensation of primary vinylacetylene and allylacetylene alcohols and their esters with polychlorocyclic dienes. Journal of Organic. Chem. , vol. 45, issue 5.pp. 668-677(2009).
5. Shakhtakhtinsky T.N., Nagiyev Y.M., Bagirov Sh.T., Adigezalov V.A., Andreeva E.I. Fungicide against verticillin cotton wilt. A.s. 1707061 .SSSR B.I. No. 48(1991).
6. Nagiev Y.M. Optimal reaction conditions for the preparation of N-m-carboxyphenylimide 2,3-dichlorobicyclo [2.2.1] hept -5-en-2,3-dicarboxylic acids Azerb.chem.journ.. No 2.pp. 129-133(2011).
7. Nagiyev Y.M., Bagirov Sh.T., Shagas G.G., Sapozhnikov Yu.E., Adigezalov V.A. Synthesis and study of the structure of N-substituted imides of dichlorormaleic acid. Azerb.chem.journ. No. 4. pp. 56-59(1986).
8. Nagiev, Ya.M. Sinthesis of N-Substituted Imides of 2,3- Dichlorobicyclo [2.2.1]hept-5-ene-2.3-dikarboxylic Asid. Russian Journal of orqanic Chemistry, 51.No.8.pp.1202-1205 (2015)
9. Chinchilla R., Farvello R.L., Galindo N., Najera S. .Asymmetric synthesis of bicyclic α-amino acids by a Diels–Alder reaction to a new chiral α,β-didehydroalanine derivative Tetrahedron: Asymmetry, vol. 10 pp. 821-825 (1999).
10. Nagiyev Y.M., Akhmedov R.M .., Gasanov A.I., Kulieva T.A., Bagirova S.Sh. Obtaining some N-substituted aromatic nitroamine adducts. Azerb.chem.journ. No. 2. pp.. 180-186.(2008).
11. NagiyevYa.M. Sinthesis of N-Substituted-2,3-Dichlorobicyclo[2.2.1] qept-5-ene-2.3- dikarboxylic Asid Imides, Russian Journal of orqanic Chemistry,, 1. No. 8.pp.469-470 (2012)
12. Nagiev Y.M., Sh.S.Nasibov, V.A. Adigezalov Conformation of ,3-Dichlorobicyclo[2.2.1]hept-5-en-2,3-dicarboxylic acid N-arylimides. Doc. AN Azerb. T. LV. VIII. No. 12. . pp. 94-96(1999).
13. Nagiyev Ya.M., ShnulinA.N., Bagirov Sh. T., Adigezalov V.A. , Mamedov I.M., Structure of N-phenylimide-endo-2,3-dichlorobicyclo- [2,2,1] -hept-5-en-2,3 -dicar boxylic acid $C_{15}H_{11}NO_2Cl_2$ (B-modification). Crystallography. Moscow. Vol. 34, issue 1. pp. 96-101(1989).
14. Nagiyev Ya.M., Shnulin A.N., Bagirov Sh. T., Adigezalov V.A. , V.I.Shilnikov, Mamedov I.M., The structure of N-phenylimide-endo-2,3-dichlorobicyclo [2,2,1] -hept-5 en2,3 dicarboxylic acid $C_{15}H_{11}NO_2CL_2$ (d-microdiffusion). Journal of Structural Chemistry, Moscow, Vol. 29, No. 2, p. 105-111(1988).

PP-IV-5

INVESTIGATION OF OBTAINING CONDITION OF TL$_3$ASS$_4$ COMPOUND IN THE AQUATIC ENVIRONMENT

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Abstract. The condition for obtaining the Tl_3AsS_4 compound was investigated on the basis of $TlNO_3$ and As_2S_5 compounds in hydrothermal conditions in the aquatic environment. It was found that Tl_3AsS_4 compound is obtained from a mixture of primary components (As_2S_5 and $TlNO_3$) in a ratio of 4:15 mol at a temperature of 80 ^{0}C in the range of pH=7-8. The individuality of the obtained Tl_3AsS_4 compound was confirmed by the RFA method and DTA, and TG analyzes were performed. The SEM results of the compound showed that the Tl_3AsS_4 sediment obtained from the solution was composed of aggregates of highly adhesive nanoparticles. The effect of pH of the medium and the amount of primary components on the yield of Tl_3AsS_4 was studied. It was found that sediments containing $(Tl_2S)_x(As_2S_3)_{1-x}$ in the solution are obtained from a mixture of primary components (As_2S_5 and $TlNO_3$) in other molar ratios.

Keywords: functional materials, interactions, solutions, sediments, chemical analysis, thermogravimetric analysis, micromorphology.

1.Introduction.

Tl_3AsS_4, $TlAsS_2$, Tl_3AsS_3, $TlAs_3S_5$, $Tl_3As_5S_{10}$, $Tl_9As_5S_{15}$, $Tl_9As_3S_{13}$, Tl_3AsS_6 and $Tl_8As_2S_9$ compounds are available in the Tl-As-S system [1,4]. These compounds and obtained glasslike alloys based on them are valuable functional materials with semiconductor, photoelectric, acousto-optical, etc. properties. In the Tl-As-S system, phase equilibrium and glass formation, as well as the physical and chemical properties of the intermediate phases, have been studied in a number of studies. The compounds and alloys in the system are mainly obtained by direct synthesis. It is known that only Tl_3AsS_4 is obtained by the interaction of Tl^+ and As^{+5} salts dissolved in solution [1]. In addition, the literature provides information on the study of micromorphology of $AgAsS_2$, Ag_3AsS_3, $CuAsS_2$ and Cu_3AsS_3 compounds obtained by hydrochemical and hydrothermal methods [2,3].

The aim was to study the interaction between $TlNO_3$ and As_2S_5 in the aquatic environment and to obtain the Tl_3AsS_4 compound individually. The article presents the results of the study of the conditions for the acquisition of Tl_3AsS_4 in the aquatic environment and some physical-chemical properties.

2.Methods and discussion of results.

According to the known methodology, as an initial component to obtain the Tl_3AsS_4 compound, the As_2S_5 compound was obtained by mixing a 0.1 M Na_3AsO_4 solution acidified with 10 N hydrochloric acid (pH=0-1) and releasing H_2S gas in a temperature range of 0-10 ^{0}C for 2 hours. The system was cooled with ice water. In this case, the following reaction occurs:

$$2Na_3AsO_4+5H_2S+6HCl \rightarrow As_2S_5+6NaCl+8H_2O \qquad (1)$$

0.35 g of As_2S_5 and 1.12 g of $TlNO_3$ were mixed to obtain Tl_3AsS_4 compound. The reaction mixture was stirred in a magnetic stirrer for 3 hours, then the precipitate was filtered, afterwhich first washed with distilled water and then with ethanol. The sediment kept in a microwave oven under hydrothermal conditions (80 ^{0}C) for 78 hours by adding ultra-clean water again to it. The pH of the condition was kept in the range of 7-8. The equation of the reaction can be summarized as follows:

$$4As_2S_5+15TlNO_3+12H_2O \rightarrow 5Tl_3AsS_4+3H_3AsO_4+15HNO_3 \qquad (2)$$

After thermal processing, the sediment was filtered, washed, and dried at 100 ^{0}C under vacuum (~10^{-1} Pa).

Obtaining the Tl_3AsS_4 compound was carried out based on the results of a number of experimental studies. The table below shows the results of 8 experiments (Table).

Table. The amount of obtained Tl_3AsS_4 sediment and passed components to the solution during the reactions.

As_2S_5, g	$TlNO_3$, g	Tl_3AsS_4 sediment, g	The amount of As^{+5} ion transferred to the solution, g
0,3500	1,1278	1,0251	0,6311
0,4011	1,2925	1,3199	0,0704

0,5002	1,6118	1,6325	0,0896
0,4922	1,5860	1,6095	0,0883
0,3944	1,2709	1,2703	0,0604
0,3539	1,1404	1,1315	0,0589
0,3098	0,9983	0,9968	0,0476
0,3321	1,0701	1,0658	0,0518

XRD Analysis.

The obtained Tl_3AsS_4 sediment was thermally processed at a temperature of 220 ^{0}C in vacuum (~10^{-2} Pa) for 2 hours and its composition was checked by X-ray analysis RFA (2D PHASER “Bruker”, CuK_α, 2θ, 20-80 degrees). It was found that the sediment consists of Tl_3AsS_4 compound and has an orthorhombic structure (Space gr.: Pnma; lattice. par.: *a=0,9268 nm, b=0,9334 nm, c=1,1123 nm,* $\alpha=\beta=\gamma=90^0$). The values of the intensity peaks in the diffractogram were well matched with the results of other studies (Fig. 1).

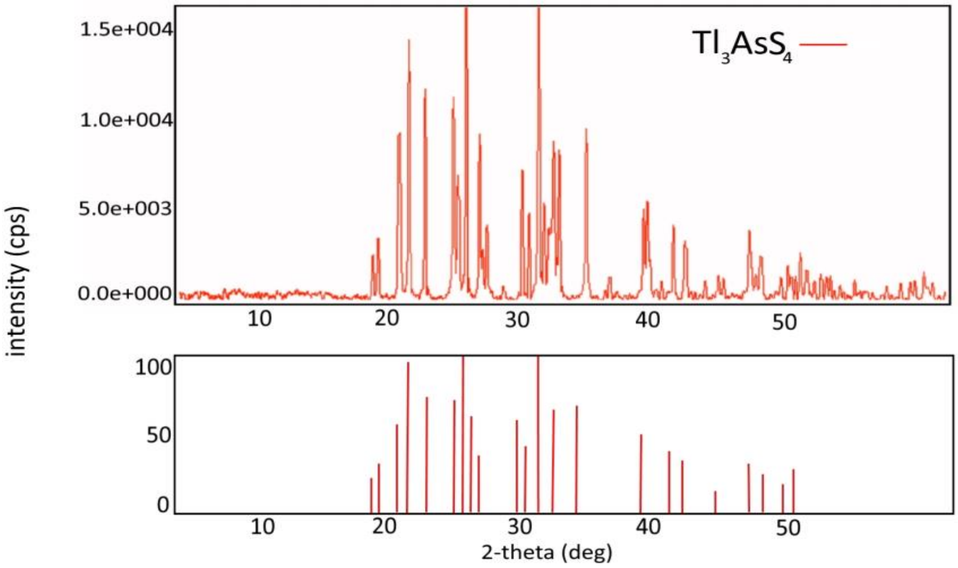
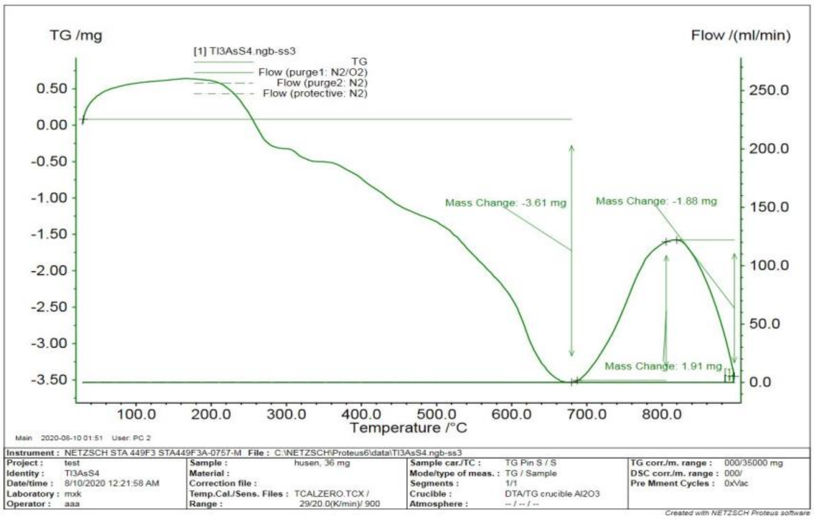


Figure 1. Difactogram of Tl_3AsS_4 compound

TG analysis.

A thermogravimetric (TG) analysis (NETZSCH STA 449F3) was performed to determine the stoichiometric composition of the obtained Tl_3AsS_4 compound (Fig. 2). The heating process was carried out in a flow of oxygen. As can be seen from the thermogravimetric curve of the compound, the decomposition of the compound begins at 180 ^{0}C. Melting of the sulfur separated from the sample occurs in the temperature range of 260-300 ^{0}C. The As_2S_3 compound formed in the temperature range of 310-360 ^{0}C melts. The exact decomposition of the Tl_3AsS_4 compound is completed at 680 ^{0}C, and the maximum mass loss in a 36 mg sample is 3.61 mg. This is well compatible with the stoichiometric composition of the Tl_3AsS_4 compound. Oxidation of decomposition products occurs when was T>680 ^{0}C and exact oxidation ends at 810 ^{0}C. 1.91 mg oxygen combine with 32.39 mg of the decomposition product. Complete decomposition of oxidation products is observed at 900 ^{0}C. After the TG analysis, the RFA results of the remaining residue showed that its main component is a Tl_3AsO_4 compound.



Instrument : NETZSCH STA 449F3 STA449F3A-0757-M File : C:\NETZSCH\Proteus6\data\Tl3AsS4.ngb-ss3

Project :	test	Sample :	husen, 36 mg	Sample car./TC :	TG Pin S / S	TG corr./m. range :	000/35000 mg
Identity :	Tl3AsS4	Material :		Mode/type of meas. :	TG / Sample	DSC corr./m. range :	000/
Date/time :	8/10/2020 12:21:58 AM	Correction file :		Segments :	1/1	Pre Mment Cycles :	0xVac
Laboratory :	mxk	Temp.Cal./Sens. Files :	TCALZERO.TCX /	Crucible :	DTA/TG crucible Al2O3		
Operator :	aaa	Range :	29/20.0(K/min)/ 900	Atmosphere :	-- / -- / --		

Figure 2. Thermogram of the compound Tl_3AsS_4

Thermal effects were observed in the DTA (pyrometer HTP-70, device Термоскан-2) curve of Tl_3AsS_4 at 265 ^{0}C and 419.8 ^{0}C. The weak thermal effect observed at 265 ^{0}C can be considered as the attenuation or polymorphic conversion temperature of Tl_3AsS_4. The thermal effect at 419.8 ^{0}C corresponds to its melting point. The reason for the relatively low melting point can be explained by the fact that the compound is in the nanoparticle form. It is known that the melting point of nanoparticles of the same substance is lower than the melting point of its monocrystals.

Scanning Electron Microscopy (SEM)

The micromorphology of the Tl_3AsS_4 compound obtained at 80 ^{0}C was studied under a HITACHI TM3000 microscope. The size and shape effects of particles in an area of 10 micrometers were determined. As can be seen from the SEM photo of the compound, the sediment from the solution is composed of aggregates of highly adhesive nanoparticles.

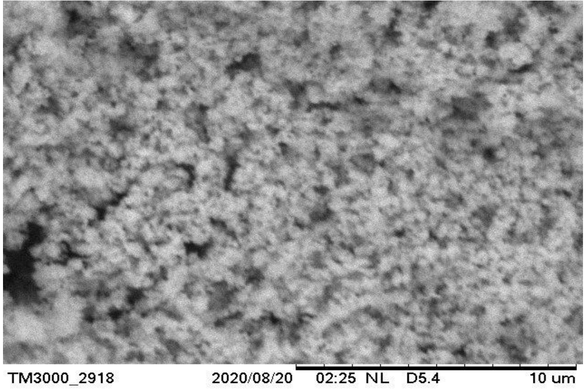


Figure 3. SEM image of Tl_3AsS_4 compound

Effect of pH of the Solution

Physical-chemical analysis methods have shown that the yield of Tl_3AsS_4 depends on the pH of the condition. Thus, there is no reaction between the primary components ($TlNO_3$ and As_2S_5) in the range of pH=1-4. The reaction occurs weakly at pH=4-7 and fasts at pH=7-8. Mixing of thio and oxysalts are obtained when was pH>8.

It was found that when was pH=7-8, depending on the amount of primary components (As_2S_5 and $TlNO_3$), $(Tl_2S)_x(As_2S_3)_{1-x}$-containing sediments are obtained in the solution. Tl_3AsS_4 is obtained from quantities taken in the appropriate ratio (4:15 mol) which is corresponding to only reaction (2).

3.Result and Conclusion.

Tl_3AsS_4 was obtained by hydrothermal method (T = 80^{0}C and pH=7-8) on the basis of $TlNO_3$ and As_2S_5 compounds and precipitation conditions were studied. The individuality of the compound was confirmed by the RFA method. It was determined by the TG analysis method that the exact decomposition of the Tl_3AsS_4 compound is completed at 680^0C. The stoichiometric composition of the compound was determined based on the decomposition and oxidation products. The SEM results showed that the Tl_3AsS_4 sediment obtained from the solution was composed of aggregates of highly adhesive nanoparticles. The effect of pH of the medium and the amount of primary components on the yield of Tl_3AsS_4 was studied.

5.References

1. Babanly M.B., Il′jasly T.M., Muradova G.V., Babanly D.M.: Tverdofaznye ravnovesija v sisteme Tl_2-As_2S_3-S i termodinamičeskie svojstva trojnyh soedinenij, Vestnik Bakinskogo Universiteta 2011, №4, c 5-12 (in Russian).
2. Gusejnov G.M. Issledovanie uslovija polučenija tetratioarsenita medi(I) gidrohimičeskim metodom. VI Mežd. Nauč. Konf. «Novye funkcional′noe materialy i vysokie tehnologii», Tivat, Černogorija – 2018, (17-21 sentjabrja), s 110-112 (in Russian).
3. Gusejnov G.M. Sulejmanova T.I.: Polučenie soedinenij $AgAsS_2$ i Ag_3AsS_3 gidrotermal′nym metodom. «Meždunarodnyj žurnal prikladnyh i fundamen-talnyh issledovanija», Moskva «Akademija estestvoznanija» 2017, №3(2), s 228-231. İSSN 1996-3955, İP-0,847 (in Russian).
4. Muradova G.V., T.M.Il′jasly, Ju.A.Jusibov, M.B.Babanly.: Fazovye ravnovesija v sistemah TlS–$TlAsS_2$ i Tl_3AsS_3–S, Azerbajdžanskij Himičeskij Žurnal, №3 2012, s 28-32 (in Russian).
5. Imanov H.A.: Investigation of conditions for obtaining arsenic(V) sulfide in aquatic environment. Nakhchivan Branch of ANAS “Scientific works” 2018, №2, p. 58-62.
6. Lazareva V.B., Kiš Z.Z. Pereš E.Ju., Semrad E.E. Složnye hal′kogenidy v sistemah $A^IB^{III}C^{VI}$. Izd. Metallurgija, 1993, s 230 (in Russian).
7. Šarlo.G.: Metody analitičeskoj himii. Kličestvennyj analiz neorganičeskih soedinenij. M., Izdatel″stvo «Himija», 1965 g, 976 s (in Russian).

PP-IV-10

THE FIREPROOF UNSATURATED POLYETHER ON BASIS OF DIBROMONORBORNENE- DICARBOXYLIC ACID

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Abstract. The synthesis of bromine-containing unsaturated polyethers on basis of anhydrides of dibromonorbornene-dicarboxylic acid, 1-chloro-2,3-propanediol and methacrylic acid was carried out. The kinetics of formation reaction of unsaturated polyether and some properties of its solutions in styrene were researched. Physical-mechanical properties of the cured polyether-styrene composites were studied. It is established the most preferable quantity of styrene in the composites.

Keywords: dibromonorbornene of dicarboxylic acid, chloropropanediol, methacrylic acid, unsaturated polyether, styrene, fire resistance.

1. Introduction

In connection with the expansion of polyether resins usage in the industry the most attention is given to resins with low inflammability. There are several well known methods for improvement of fire resistance properties of polyether resins. These are introduction of inorganic or organic additives decelerating a combustion and chemical modification by way of introduction of elements into polyether's chain which decrease inflammability [1-8]. The most widespread method of an obtaining of fireproof polyether resins is a using of bromine-containing anhydrides of dicarboxylic acids, bromination of double bond of unsaturated polyether resins or using of bromine-containing diols [9 ,10].

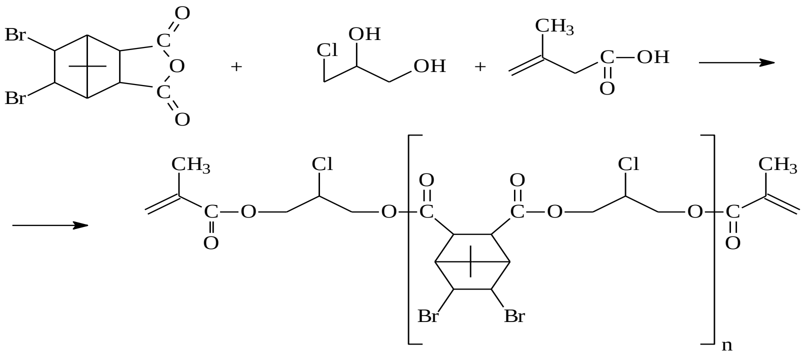
2. Method of calculation

Synthesis of methacrylate(chloropropanediol)-dibromoendomethylene tetrahydrophthalate is carried out in following way. 0,05 moles of anhydride of dibromonorbornene-dicarboxylic acid, 0,1 moles of chloropropanediol, 0,1 moles of methacrylic acid and 0,2% of p-toluene sulfonic acid are fed into the four-neck flask. P-toluene sulfonic acid is used as a catalyzer. Four-neck flask is equipped by mechanical mixer, thermometer, reflux condenser and Dean-Stark trap. Reaction mass was heated up to 180^{0}C during 3 hours in nitrogen atmosphere. Reaction course was controlled in accordance with acid number of polycondensation reaction product. The reaction was stopped at acid number 30-40 mg KOH per 1 g of resin. After completion of the process the reaction products were neutralized by 5% soda solution at room temperature. Then the mass was washed up to neutral reaction and extracted by petroleum ether. The obtained product was dried over sodium sulfate. After distillation of solution the obtained light brown resin was dried in vacuum oven at 45-50^{0}C (35-40 mm Hg) up to constant weight and was dissolved in styrene.

Fire resistance properties of specimens were researched on method of "fire-tube" according to GOST 30244-94. Compression strength of the specimens was determined according to GOST 4651-2014 on "YAD-300D" test machine. Bending strength of the specimens was determined according to GOST 4648-71 on "YAD-300D" test machine. Brinell hardness of specimens was determined according to GOST 4670-91. IR spectrums of obtained products prepared in the form of suspension in vaseline oil were taken with the help of "UR-20" spectrometer.

3. Results and discussion

The given research is devoted to development of synthesis methods and research of some laws of formation of new unsaturated polyethers containing bromine and chlorine on basis of anhydrides of 5,6-dibromonorbornene-dicarboxylic acid, 1-chloro-2,3-propanediol and methacrylic acid in accordance with the scheme shown below.



(I)

Fig.1. Unsaturated polyether synthesis.

Polycondensation of dibromonorbornene-dicarboxylic acid, 1-chloro-2,3-propanediol with methacrylic acids at molar ratio 0,5:0,5:1,1 was carried out at 140, 160 and 180^{0}C in nitrogen atmosphere. The polycondensation process began to occur at 120^{0}C. Research of the process kinetics at different temperatures showed that acid number equal to 30-40 mg KOH per 1 g of polyether is achieved at 140^{0}C during 10 hours, at 160^{0}C during 8 hours and at 180^{0}C during 3 hours. It is established that 2,5 hours is enough for practical completion of the reaction at 180^{0}C.

Kinetic curves of the reaction of anhydride of dibromonorbornene-dicarboxylic acid with 1-chloro-2,3-propanediol and methacrylic acid at 140, 160 and 180^{0}C temperatures are shown on figure 2. Dependence of completeness degree of the reaction (1/(1-P)) from time is shown on figure 3. How one can see from the figure the obtained curves have a linear character. Thus, polycondensation of blend of anhydride of dibromonorbornene-dicarboxylic acid and methacrylic acid with 1-chloro-2,3-propanediol corresponds to the reactions of the second order. The rate constants were calculated from these curves and made up correspondingly 1,18·10^{-2} g·mole^{-1}·min^{-1} at 140^{0}C, 2,14·10^{-2} g·mole^{-1}min^{-1} at 160^{0}C and 6,20·10^{-2} gmole^{-1}min^{-1}. Activation energy determined by graphical method makes up 63,1 kJmole^{-1}. (See figure 4).

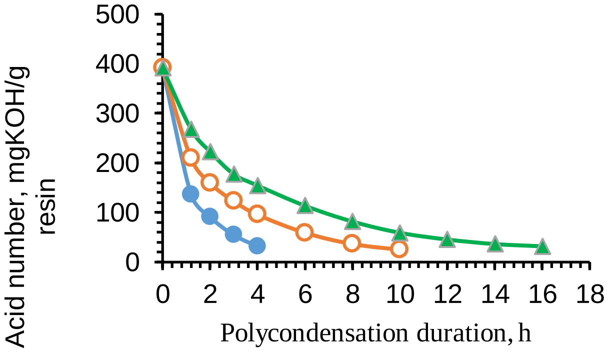


Fig.2. Kinetics curves of reaction of anhydride of dibromonorbornene-dicarboxylic acid with 1-chloro-2,3-propanediol and methacrylic acid: ●- at 140^{0}C; ○- at 160^{0}C; ▲- at 180^{0}C.

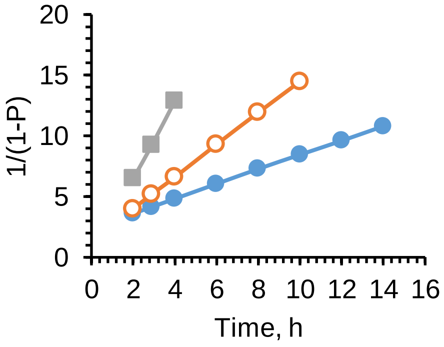


Fig.3. Dependence of polycondensation degree of 1-chloro-2,3-propanediol with methacrylic acid and anhydride of dibromonorbornene-dicarboxylic acid from reaction time: ▲- at 140^{0}C; ○- at 160^{0}C; ●- at 180^{0}C.

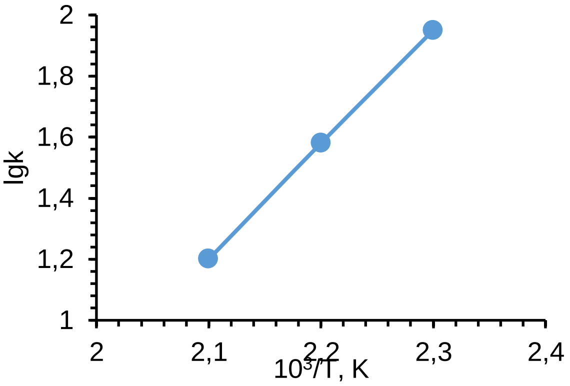


Fig.4. Dependence of rate constant (k) of polycondensation reaction of 1-chloro-2,3-propanediol with methacrylic acid and anhydride of dibromonorbornene-dicarboxylic acid from temperature.

The obtained unsaturated polyether on basis of dibromonorbornene-dicarboxylic acid, 1-chloro-2,3-propanediol and methacrylic acid is a solid black brown substance with softening point of 65-70^{0}C. Its yield makes up 90-95% from the weight of initial constituents dissolved in styrene unlimitedly.

All main absorption bands characterizing this class of compounds were discovered in IR-spectrums of unsaturated polyethers. Adsorption bands at 1715-1770 sm^{-1} (C=O) and 1645-1670 sm^{-1} (C=C) makes it possible to say about presence of ester and double bonds correspondingly in composition of unsaturated polyethers (I). Adsorption bands at 2880-2150 sm^{-1} correspond to aliphatic group “CH_2”. The bands connected with addition of end methacrylic groups appear in IR-spectrums of unsaturated polyethers (I). In particular, band at 1730 sm^{-1} characterizes stretching vibrations of carbonyl group but adsorption bands at 810, 990 and 1410 sm^{-1} characterize the deformation vibrations of “C-H” bonds at end vinyl groups. Adsorption bands at 724-748 sm^{-1} are evidence of presence of “C-Cl” and “C-Br” bonds.

The properties of styrene solution of the synthesized unsaturated polyether (I) were researched by us. Dependence of viscosity and specific weight of solution from ratio of styrene and unsaturated polyether are given in table below.

Table 1. Properties of uncured resins modified by anhydride of dibromonorbornene-dicarboxylic acid

Number	Properties	Value
1	Average molecular weight	1559
2	Density, kq/m^3	1473
3	Viscosity, cP	237
4	Acid number, mq KOH/g	35±5
5	Gelatinization time, min (At containing of 3% of hydroperoxide of methyl ethyl ketone and 8% of accelerant. Styrene content makes up 40%.)	180

A curing of unsaturated polyether (I) was carried out in the presence of an activating system (3 part by weight of methyl ethyl ketone peroxide), accelerant (8 part by weight of cobalt naphthenate) during 24 hours at 20±3^{0}C and then during 10 hours at 80^{0}C. Quantity of unreacted reagents (styrene and polyether (I)) in the cured polyether was determined in way of extraction by hot acetone during 10 hours in Soxhlet extractor. The properties of the cured styrene solutions of polyether (I) are shown in table 2. Research results of fire resistance of specimens according to the “Fire-Tube” method showed that the cured resin (I) is a self-extinguishing material.

Table 2. Physical-mechanical and other properties of the cured unsaturated polyethers (I)

Number	Properties	Value
1	Styrene content, %	40
2	Compression strength, MPa	112
3	Bending strength, MPa	37
4	Brinell hardness, kgf/mm^2	24
5	Heat resistance, ^{0}C	120
6	A time of independent burning, sec	It is extinguished
7	Weight loss, %	1,7

Thus, synthesized unsaturated polyether (I) can be used as a potting compound, binding material for laminated and pressing plastics which are characterized by satisfactory physical-mechanical and self-extinguishing properties.

4. Conclusions

1. The synthesis of bromine-containing unsaturated polyethers on basis of anhydride of dibromonorbornene-dicarboxylic acid, 1-chloro-2,3-propanediol and methacrylic acid is carried out.
1. The kinetics of formation reaction of unsaturated polyether and some properties of its solutions in styrene are researched.
2. It is established that the increasing of styrene content from 30% to 50% considerably influences polyether viscosity, while physical-mechanical properties of cured resins depend on styrene content in initial composite a little.
3. Research results of specimens fire resistance according to “fire-tube” method showed that the cured resins are self-extinguishing materials.

5.References

1. Zhanguang Huang, Wenfang Shi.: Synthesis and properties of poly(bisphenol A acryloxyethyl phosphate) as a UV curable flame retardant oligomer. European Polymer Journal. Volume 42, Issue 7, July 2006, Pages 1506-1515. doi: 10.1016/j.eurpolymj.2006.01.004
2. Anjali A.Athawale, Jyoti A.Pandit.: Chapter 1 - Unsaturated Polyester Resins, Blends, Interpenetrating Polymer Networks, Composites, and Nanocomposites: State of the Art and New Challenges. Unsaturated Polyester Resins. Fundamentals, Design, Fabrication, and Applications. 2019, Pages 1-42. doi: 10.1016/B978-0-12-816129-6.00001-6
3. Yongxia Ren, Yunsheng Dong, Yali Zhu, JingXu, YouweiYao.: Preparation, characterization, and properties of novel ultraviolet-curable and flame-retardant polyurethane acrylate. Progress in Organic Coatings. Volume 129, April 2019, Pages 309-317. doi: 10.1016/j.porgcoat.2018.11.009
4. M.Ciesielski, B.Burk, C.Heinzmann, M.Döring.: 2 - Fire-retardant high-performance epoxy-based materials. Novel Fire Retardant Polymers and Composite Materials. 2017, Pages 3-51. doi: 10.1016/B978-0-08-100136-3.00002-9
5. Y.N. Gahramanly, A.M. Mustafayev, B.N. Babanly, R.Sh. Hajiyeva, R.I. Ismailova.: Fire-proof unsaturated polyesters on the basis of anhydride of hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acid, glycerin and methacrylic acid. Chemical Problems. (1), 2018, p.51-57.
6. E.Kitzko-Valchik. A studying of self-extinguishing unsaturated polyether resins. Capsule review of industrial and new achievements. //Plastic masses. 2002. No.5, p.4-9.
7. Herman V.Boenig. Unsaturated polyesters structure and properties. Elsevier Publishing Company. Amsterdam. London. New York. 1964. P.253.
8. A.M.Mustafayev, I.A.Huseynov A.M. Garayeva and others. Comparative activity of anhydrides of norbornene-dicarboxylic acids in the reaction with ethylene glycol and methacrylic acid. IIIrd International Scientific Conference “Fine Organic Synthesis and Catalysis” devoted to 85 years anniversary of Azerbaijan State Oil Academy, Baku. 2005, p. 165.
9. R.M.Aseyeva, G.E.Zaykov. A burning of polymeric materials. Moscow: Nauka. 1981, 167 p.
10. S.G.Mustafayev, A.M.Mustafayev, I.A.Huseynov. The fireproof polybromine containing unsaturated polyethers // Processes of petrochemistry and oil refining. 2009, 10, 1(37). p. 39-41.

PP-IV-6

PREPARATION OF SPIRODIOXALANES BY CONDENSATION OF ALKYL DERIVATIVES OF CYCLOHEXANONE AND ETHYLENE GLYCOL IN THE PRESENCE OF MODIFIED FORMS OF PHOSPHOMOLYBDENUM HETEROPOLY COMPOUND

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Abstract. New representatives of spirodioxalanes were synthesized by condensation of C_5-C_7 alkyl- and cycloalkylcyclohexanones with ethylene glycol in the presence of a phosphomolybdenum heteropoly compound modified by CoBr2. The influence of various factors on the yield of target products has been studied. The synthesized spirodioxalans have a jasmine and menthol-woody aroma with various shades.

Keywords: ketone, ethylene glycol, spiroacetal, spirodioxalane, phosphomolybdenum heteropoly compound, condensation.

1.Introduction

Please note that the first paragraph of a section or subsection is not indented. The first The acetalization reaction of functionally substituted cyclic ketones with vicinal or other polyhydric (di- or trihydric) alcohols is used to protect carbonyl groups [1]. The products of the reaction - dioxaspiroalkanes containing alkyl and various functional substituents in the molecule find wide use in the perfumery and food industries [2,3], in the production of pharmaceuticals [4], solvents [5], biologically active drugs [6], etc.

Recently, information has appeared on the possibility of using 1,3-dioxalanes and their derivatives as components of motor fuels to improve their octane characteristics, increase the phase stability of alcohol-containing gasolines, and reduce the toxicity of exhaust gases [7, 8].

The synthesis of ketals is usually carried out with the participation of homogeneous catalysts of the acid type (H_3PO_4, H_2SO_4 etc.). Recently, works have appeared in which complexes containing Rh, Pd, Pt, Ce compounds [9,10] or heterogeneous catalytic systems [11,12] were used as condensation catalysts. The condensation reactions of aromatic and unsubstituted alicyclic ketones or aldehydes with ethylene glycol and glycerol have been studied more widely. There are isolated works on the synthesis of dioxaspiroalkanes based on alkyl derivatives of cyclopentanone and cyclohexanone [3,13].

This work presents the results of the condensation of C_5-C_7-alkylcyclohexanones with ethylene glycol in the presence of a phosphoromolybdenum heteropoly compound modified with cobalt (II) bromide.

2.Experimental part

The procedure for preparing a catalyst of composition $P_{0.17}Mo_{2.4}CoBr_{0.27}O_{6.8}$ and performing the experiment is similar to that described earlier in the work. [14]. The condensation reaction was carried out in a thermostated glass reactor equipped with a thermometer, magnetic stirrer, reflux condenser and Dean-Stark receiver. An alkyl or cycloalkyl derivative of cyclohexanone (0.1 mol), ethylene glycol (0.15 mol), a catalyst (0.005 mol of Mo^{n+}) and toluene (50 ml) were simultaneously loaded into the reactor as an azeotrope-forming solvent. In some experiments, benzene, octane, and o-xylene were used as a solvent.

The dependence of the yield of the target product on the ratio of the reacting components, temperature, and duration of the experiment was monitored by gas-liquid chromatography and infrared spectroscopy. In IR spectroscopic analysis, the change in the absorption band of the carbonyl group at 1730 (cm^{-1}) was taken as a criterion.

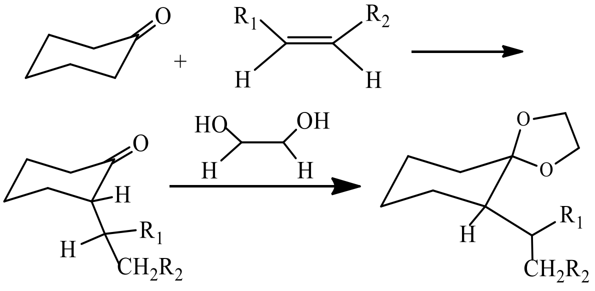
GC analysis of composition and purity of the starting reagents and acetalization products was performed using a Tsvet-500 chromatograph with a flame-ionization detector (a 2000 × 3 mm column, 5 wt % of polyethylene glycol succinate on chromosorb as a stationary phase, nitrogen as carrier gas, column temperature 160°C, injector temperature 280°C). Chromatomass spectra were recorded using a GC 7890A-

MSD 5975C Agilent Technologies instrument (column: HP5- MS, temperature program 40–280°C, helium as carrier gas)

3.Results and discussion

The literature contains information about some spirodioxalanes, in particular, cyprenal (7-tert-butyl-1,4-dioxaspiro [4,5] decane and jasmon on (2-butyl-1,4-dioxaspiro [4,4] nonane), used as part of perfume compositions [15]. The latter is characterized by the smell of jasmine.

The spiroacetals we synthesized have a jasmine and menthol-woody scent with various shades. Physicochemical and spectral data of these compounds synthesized according to Scheme 1 are given in separate examples.



Scheme 1.

where, R_1=H, R_2=n-C_3H_7 (1), n-C_4H_9 (2);
n-C_5-H_{11}(3); R_1+R_2=C_3H_6 (4);
R_1+R_2=C_4H_8 (5).

The influence of various factors on the direction of the reaction and the yield of the target products are shown in Table 1. The main reaction products are the corresponding spiroacetals (spirodioxalanes) and 1.4-dioxane, the ratio of which significantly depends on the molar ratio of the reactants and temperature (Table 1).

Table 1. Dependence of the yield of 5-pentyl-1,4-dioxaspiro [4,5] decane on the molar ratio of reagents, temperature, and duration of experiments

Initial reagents, mole		T, ⁰C	τ, h	Yield, %	
ketone	diol			spirodioxalane	1,4-dioxane
1	0,5	110	6	26,0	2,4
1	1	110	6	32,2	5,3
1	1,5	110	6	51,4	11,5
1	2	110	6	72,6	19,1
1,5	1	110	6	23,0	2,4
2	1	110	6	20,2	2,5
1	2	80	6	6,2	11,6
1	2	125	6	74,3	9,2
1	2	130	6	68,6	9,0
1	2	135	6	62,0	8,7
1	2	110	3	47,3	19,1
1	2	110	4	69,0	22,2
1	2	110	5	70,2	23,4
1	2	110	8	57,5	25,6

The synthesized compounds are characterized by the smell of jasmine and menthol-woody direction.

The synthesis of spiroacetals (spirodioxalans) is characterized by the following parameters:

4. Conclusions

5-Pentyl-1,4-dioxaspiro [4,5] decane (1) was obtained from 16.8 g of 2-pentyl-cyclohexanone and 12.4 g of ethylene glycol. Yield 14,5g (69%). T.b. 103-105°C /1,2 mmHg d_4^{20}- 0,9612, n_d^{20} -1,4634. IR-spectrum. ν, cm^{-1}: 1340,1200-1040. 650. NMR ^1H spectrum, δ, ppm.: 0,95m (3H,CH_3), 1,23-1,77m (16H, 4CH_2 cyclo and 4CH_2 alk.), 2,08m (1H, H^5, CH), 3,84-3,96 d.d. (4H, $H^{2,3}$, 2CH_2O)

5-Hexyl-1,4-dioxaspiro [4,5] decane (2) was obtained from 18.2 g of 2-hexylcyclohexanone and 12.4 g of ethylene glycol. Yield 15g (67%). T.b. 119-121°C/1,2 mmHg, d_4^{20}- 0,9612, n_d^{20}-1,4634. IR spectrum, ν, cm^{-1}: 1340, 1200-1040, 650. NMR ^1H spectrum, δ, ppm: 0,95m ($3H, CH_3$), 1,24-1,80m (18H, $4CH_2$ cyclo and $5CH_2$ alk), 2,08m (1H, H^5,CH), 3,84-3,96d.d. (4H, $H^{2,3}$, $2CH_2O$)

5-Heptyl-1,4-dioxaspiro [4,5] decane (3) was obtained from 19.6 g of 2-heptyl-cyclohexanone and 12.4 g of ethylene glycol. Yield 15,7g (66,0%), T.b. 132-134°C (1,2 mmHg., d_4^{20} -0,9582, n_d^{20} -1,4657. IR spectrum ν, cm^{-1}: 1340, 1175-1040, 650. NMR ^1H spectrum, δ, ppm.: 0,97m ($3H, CH_3$), 1,24-1,80m (20H, $4CH_2$ cyclo and $6CH_2$ alk), 2,06m (1H, H^5,CH), 3,86-3,98 d.d. (4H, $H^{2,3}$,$2CH_2O$)

5-Cyclopentyl-1,4-dioxaspiro [4,5] decane (4) was obtained from 16.6 g of 2-cyclo-pentylcyclohexanone and 12.4 g of ethylene glycol. Yield17,5g (83%). Tb.157-160°C/ 3mmHg., d_4^{20} -1,0564, n_d^{20} -1,4910. IR spectrum, ν, cm^{-1}: 1445, 1420 [δ CH_2 cyclo], 1200-1040(C-O-C). NMR ^1H spectrum, δ, ppm 1,26-1,76m (8H, $4CH_2$-spiro), 1,48м (1H, H^1, CH-cyclopentyl), 1.36-1.61 m (8H, $4CH_2$ cyclopentyl), 2,14 m (1H, H^5, CH-spiro), 3,84-3,96 d.d. (4H, $2CH_2O$)

5-cyclohexyl-1,4-dioxaspiro [4,5] decane (5) was obtained from 18 g of 2-cyclohexylcyclohexanone and 12.4 g of ethylene glycol. Yield 16,8g (75%). T.b. 149-151°C/1,2 mmHg., d_4^{20}-1,0574, n_d^{20} -1,5098. IR spectrum, ν, cm^{-1}: 1445, 1420, 1200-1040. NMR ^1H spectrum, δ, ppm: 0,85-1,64 m (10H, $5CH_2$, cyclopentyl), 1,30m (1H, H^1, CH, cyclohexyl). 1,32-1,83m (8H, $4CH_2$, spiro) 2,12m (1H, H^5, spiro), 3,84-3,96 d.d. (4H, $H^{2,3}$, $2CH_2O$)

5.References

1. Traven V.F. Organic chemistry. V.2.M .: Binom. Laboratory of knowledge. 2013.517p.
2. Voitkevich S.A. 865 aromatic substances for perfumery and household chemicals. M .: Food industry. 1994.593p.
3. Vyglazov O.G., Chuiko V.A., Izotova L.V., Vintarskaya Zh.V., Yudenko R.A. //Journal of Applied Chemistry. 2001.v.74.№11.p1829.
4. Mashkovsky M.D. Medicines. M .: Medicine-2000. Part 1.622.
5. Nedumaran.D.,Pandurangan.A.//Micropor.Mater.2013.V.169.P.25-34/doi.org/10.1021/ cr 960406n
6. Miyake H., Nakao Y., Sasaki M.//Chem.Lett. 2007. V.36, N1. P.104-105. https://doi.org/10.1246/cl.2007.104
7. Maximov A.L., Nekhaev A.I., Ramazanov D.N.//Petrol Chem.2015. V.55. N1.P.1. https://doi.org/10.1134/S0965544115010107
8. Ramazanov D.N., Dzhumbe A., Nekhaev A.I., Samoilov V.O.,Maximov A.L., Egorova E.V.// Petrol Chem. 2015. V.55. N2, P.140 https://doi.org/10.1134/S0965544115020152
9. Eshghi H., Rahimzadeh M., Saberi S.// Katal.Commun.2008.V.9.P.2460-2466.
10. Kanai S., Nagahara, Kita Y., Kamata K., Hara M.// Chem. Sci. 2017. V.8. P.3146-3153.
11. Sayama S.// Tetrahedron Lett. 2006. V.47. N24. P.4001-4005
12. Yang Z., Lei C., Zhao X., Liu R., Wei H., Ma Y., Meny S., Cao Q., Wei J., Wang X.//Chem. Select. 2017.V.2.P.9377-9386
13. Alimardanov Kh.M., Sadigov O.A., Abbasov M.F., Suleimanova E.T., Jafarova N.A., Abdullaeva M.Ya., Abbasova S.M. // Zhurn.org.chem. 2011. vol.47. issue 8. p. 1136-1143. https://doi.org/10.1134/S1070428011080069
14. . Alimardanov Kh.M., Velieva F.M., Dadashova N.R. // Journal of Applied Chem. 2018.Vol. 91, issue 11. p. 1658-1666. https://doi.org/10.1134/S1070427218110204
15. Alimardanov Kh.M., Suleymanova E.T. Chemistry of natural and synthetic fragrances. Baku, Elm. 2018.517p.

OR-IV-2

COMPARATIVE STUDY OF SORPTION OF SILVER(I) IONS ONTO SYNTHETIC CHELATING ADSORBENTS FROM AQUEOUS SOLUTIONS

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Abstract. This work is dedicated to the comparative study of sorption of trace amounts of silver(I) using synthetic chelating polymeric adsorbents modified with o-phenylenediamine, m-aminophenol and 1,2,3 triphenylguanidine from aqueous solutions. These adsorbents were synthesized by the polycondensation reaction. For the synthesis of adsorbents formalin was used as a crosslinking agent. The effect of various parameters on the sorption such as pH, initial metal concentration, contact time and ionic strength on removal of silver(I) ions were investigated. Sorption experiments were carried out using batch systems at room temperature. The optimum pH for removal of silver(I) ions when using synthetic chelating polymeric adsorbents modified with m-aminophenol and 1,2,3 triphenylguanidine is pH = 6. Optimal ionic strength achieved at a value of μ=1,0 when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine and of μ =0,6 when using synthetic chelating polymeric adsorbent modified with m-aminophenol. The sorption capacity of the sorbents and the percentage recovery were determined from the difference in the initial and final concentrations of silver(I) in the aqueous solution. The best elution properties toward silver(I) ions when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine possessed the 0,5 M HNO_3 and for adsorbent modified with m-aminophenol 1 M HNO_3.

Keywords: preconcentration, sorption, silver(I), synthetic adsorbent.

1.Introduction

The pollution of environment has been causing worldwide concern. Heavy metal ions are among the environmental pollutants and even at low doses have negative effects on humans. Compounds of some heavy metal ions can be slowly absorbed by body tissues and causes hazard to human׳s life.

Silver is one of the heavy metal ions. Silver compounds can released into environment from different sources and cause a big detrimental to human׳s life.

On the other hand, silver in trace amount is necessary for life processes. Silver is a widely used currency material. Silver and its halide salts, especially silver nitrate are widely used in photography. The major outlets are photography, the electrical and electronic industries and for domestic uses as cutlery, jewellery and mirrors.

Soluble silver(I) salts, specially $AgNO_3$ has a toxic influence and lethal effect on human׳s s in concentrations of up to 2g. Thus, the application of different treatment methods for silver ion removal from objects of environment is actual.

There are a lot of treatment methods to recover silver, such as precipitation, extraction, cross flow microfiltration,sorption[1-17]. In the recent years, sorption due to its simplicity and reaching high sorption capacity has been widely used as an effective method for recovery of silver(I).

Natural and synthetic adsorbents are used in order to recover silver ions from aqueous solutions. Synthetic absorbents are the most widely used sorbent materials.

This work is dedicated to the comparative study of sorption of trace amounts of silver(I) using three synthetic chelating polymeric adsorbents modified with o-phenylenediamine, m-aminophenol and 1,2,3 triphenylguanidine from aqueous solutions.

2. Metod

2.1.Reagents.

All of the chemicals and reagents used in the current research were of analytical grade. The standard solution of Ag(I) was obtained by dissolving an exact sample of $AgNO_3$ in distilled water. Working solutions were prepared from the standard solution by dilution with distilled water. The solution of reagent with concentration $1.0x10^{-3}$ mg L^{-1} was prepared by bidistilled water. Equilibrium concentration of silver(I) ions were determined in the liquid phase using adsorption spectrophotometry at 540 nm, pH 8.0. Adsorption studies were carried out by using $1.0x10^{-2}$ mg$\cdot L^{-1}$ water solution of $AgNO_3$.

The effect of pH on the adsorption of Ag(I) ions was studied at the range of pH=3-8 respectively. The pH of the buffer solutions was maintained constant using an acetic acid and ammonium hydroxide solutions respectively. The effect of ionic strength on the adsorption was studied using 2 mol L^{-1} KCl solution. Solution of 0.5 mol L^{-1} KOH was used in desorption process.

2.2. Synthesis of chelating adsorbent.

Adsorbent synthesis was carried out by the known technique [18]. For each experiment 3 g of maleic anhydride styrene copolymer was measured and the corresponding quantity of amine added to a flask. 1,2,3 triphenylguanidine, m-aminophenol and o-phenylenediamine were solved in water. Reaction proceeds in the presence of formalin at 333.15-343.15 K and lasts approximately 30-45 min. The reaction is carried out in sandy bath by continuous mixing. Since the reaction is carried out in aquatic environment anhydride groups of copolymer subject to hydrolysis. Because of the mutual influence of formaldehyde and amine nonstable carbonylamine is formed. The resulting carbonylamine mutually interacts with carboxyl groups of macromolecule and the amine fragment enters the macromolecule. The schematic representation of considered reaction is shown on the Scheme 1.

For removal of remaining parts of reaction product each adsorbent has been rinsed several times with distilled water. Then constant mass was dried in vacuum desiccators at 323 K, grinded and skipped through sieve with 0.14 mm of pore diameter. The resulting product was investigated by Infrared spectroscopy and then was used as the solid phase in current research. A schematic representation of the polycondensation process is shown in Fig. 1:

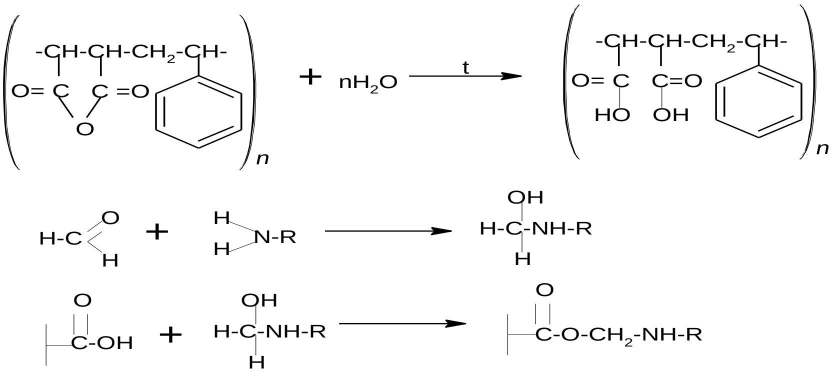

Fig.1. Scheme of polycondensation process.

2.3 Equipment

Absorbances of solutions were determined using adsorption spectrophotometry. Concentrations of Ag(I) ions were determined by flame atomic absorption spectrometry using AAS-1N equipped with hollow-cathode lamps for Ag(I). Measurements were carried out in acetylene-air flame. Solutions pH values were measured using Ionomer I-130 with glass electrode. Infrared measurements of sorbent were obtained using a Varian 3600 Fourier Transform spectrometer from 400 to 4000 cm^{-1}.

3. Results and discussions

The main purpose of this study was to develop a simple, rapid, sensitive and inexpensive method for the recovery of trace amounts of silver(I) ions from aqueous media.

3.2 Influence of medium acidity

The effect of pH on removal of silver(I) ions was investigated. Sorption of silver(I) ions was carried out in static conditions from aqueous media. By the results of experiments, the degree of sorption passes through a maximum at pH value 6 when using the sorbents, modified with 1,2,3 triphenylguanidine, m-aminophenol and pH value 6-8 when using the sorbent modified with o-phenylenediamine . It can be explained by the fact, that at lower pH, the adsorption of silver(I) ions is low. When the pH increases and reached value pH 6 the sorption sites become availables. Therefore the adsorption of silver(I) ions increases. This indicates that the mechanism of the silver(I) ions sorption is highly pH dependent. The pH value 6 was used as the optimum pH for further studies.

3.3 Influence of contact time

The effect of contact time on removal of silver(I) ions was investigated. Contact time is one of the important characteristics effecting the sorption process. The dependence of the sorption process on contact time was studied. The results of experiments shown, that sorption of Ag^+ increases with time. The complete sorption of silver (I) occurs after 90 minutes, when using a sorbent modified with o-phenylenediamine, 210 minutes, when using a sorbent modified with m-aminophenol. 150 minutes was chosen as a contact time when using a sorbent modified with 1,2,3 triphenylguanidine.

3.4 Influence of initial Ag^+ concentration

The effect of initial metal concentration on removal of silver(I) ions was investigated. Different initial Ag^+ concentrations were used in order to determine the amount of adsorbed metal by solid phase. By the results of experiments it shown, that the amount of adsorbed silver(I) ions increases with the initial concentration of Ag^+ ions and reached maximum at 60×10^{-3} mol/L when using adsorbents modified with 1,2,3 triphenylguanidine and 80×10^{-3} mol/L when using adsorbent modified with o-phenylenediamine. Further increasing of initial metal concentration doesn't significantly change the amount of adsorbed silver(I) ions. The sorption capacity of the sorbents and the percentage recovery were determined from the difference in the initial and final concentrations of silver(I) in the aqueous solution.

3.5 Influence of ionic strength

The effect of ionic strength on removal of silver(I) ions was investigated. The dependence of the sorption capacity on ionic strength of the solution was studied. Silver was sorbed from solutions containing 0.1-1.4 M KCl. Optimal ionic strength achieved at a value of $\mu=1{,}0$ when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine and of $\mu = 0{,}6$ when using synthetic chelating polymeric adsorbent modified with m-aminophenol.

3.6 Desorption studies.

At the final stage the desorption process was carried out. Desorption process allows to find out the possibility of the regeneration and reuse of the exhausted adsorbents. Desorbing agents, such as HNO_3 and CH_3COOH with different concentrations were used to find the best desorbing eluent for the adsorbed silver(I) ions from solid phase. The best elution properties toward silver(I) ions when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine possessed the 0,5 M HNO_3 and for adsorbent modified with m-aminophenol 1 M HNO_3.

4. Conclusions

Current research represents simple, rapid, sensitive and inexpensive method for the removal of silver(I) ions from aqueous solutions. The main parameters of the sorption of silver ions from aqueous solutions when using adsorbents modified with o-phenylenediamine, m-aminophenol and 1,2,3 triphenylguanidine are presented and compared. The optimum pH for removal of silver(I) ions when using synthetic chelating polymeric adsorbents modified with m-aminophenol and 1,2,3 triphenylguanidine is pH = 6. Optimal ionic strength achieved at a value of $\mu=1{,}0$ when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine and of $\mu = 0{,}6$ when using synthetic chelating polymeric adsorbent modified with m-aminophenol. The sorption capacity of the sorbents and the percentage recovery were determined from the difference in the initial and final concentrations of silver(I) in the aqueous solution. The best elution properties toward silver(I) ions when using synthetic chelating polymeric adsorbents modified with o-phenylenediamine and 1,2,3 triphenylguanidine possessed the 0,5 M HNO_3 and for adsorbent modified with m-aminophenol 1 M HNO_3.

5.References

1. Afandiyeva, N. T. Preconcentration of silver (I) on the modified sorbent from aqueous solutions. New Materials, Compounds and Applications. 4(1), 54-60 (2020).
2. Mammadov P.R., Afandiyeva N.T., Chiragov F.M. Simple and rapid spectrophotometric determination method for trace level of silver using 2,2' -di (2,3,4- trihidroksifenilazo)bifenil. New Materials, Compounds and Applications 2(2), 123-131 (2018).
3. Celik Z., Gülfen M., Aydin A.O. Selective adsorption of silver ions from aqueous solution using polystyrene-supported trimercaptotriazine resin. Journal of Hazardous Materials. 24(12), 2166-2172(2010).
4. Jeon, C., Adsorption of silver ions from industrial wastewater using waste coffee grounds. Korean Journal of Chemical Engineering 34(2), 384-391 (2017).
5. Akgul, M., Karabakan, A., Acar, O., Yurum, Y. Removal of silver (***I***) from aqueous solutions with clinoptilolite. Microporous and Mesoporous Materials. 94(1-3), 99–104 (2006).
6. Yirikoglu, H., Gülfen, M. Selective adsorption of silver ions from aqueous solution using polystyrene-supported trimercaptotriazine resin.Separation Science and Technology. 43(2), 376-388(2008).
7. Atia, A.A., Donia, A.M., Yousif, A.M. Comparative study of the recovery of silver(I) from aqueous solutions with different chelating resins derived from glycidyl methacrylate. Journal of Applied Polymer Science. 97(3), 806-812(2005).

8. Jintakosola, T., Nitayaphat, W. Adsorption of Silver (I) From Aqueous Solution Using Chitosan/Montmorillonite Composite Beads. Materials Research. 19(5), 1114-1121(2016).
9. Lihareva, N., Dimova, L., Petrov O. and Tzvetanova, Y. Ag^+ sorption on natural and Na-exchanged clinoptilolite from Eastern Rhodopes, Bulgaria. Microporous and Mesoporous Materials. 130(1-3), 32–37(2010).
10. Guo, L., Shixing, W., Zhang, L., Hu, T., Peng, J., Cheng, S. and Fu, L. Selective Adsorption of Ag^+ on a New Cyanuric-Thiosemicarbazide Chelating Resin with High Capacity from Acid Solutions. Polymers. 9(11), 568(2017).
11. Petrova, Y.S., Pestov, A.V., Usoltseva, M.K., Neudachina, L.K. Selective adsorption of silver(I) ions over copper(II) ions on a sulfoethyl derivative of chitosan. Journal of Hazardous Materials. 299(6), 696–701(2015).
12. Jacobson, A. R., Klitzke, S., McBride, M.B., Baveye P. and Steenhuis T.S. The desorption of silver and thallium from soils in the presence of a chelating resin with thiol functional groups. Water, Air, and Soil Pollution.160(1-4), 41-54(2005).
13. Karimi M.A., Mohammadi S.Z., Mohadesi A., Hatefi-Mehrjardi A., Mazloum-Ardakani M., Sotudehnia Korani L., Askarpour Kabir A. Determination of silver(I) by flame atomic absorption spectrometry after separation/preconcentration using modified magnetite nanoparticles. Scientia Iranica.18(3), 790-796(2011).
14. Manuella L.C., Ambrósio F.de A. N., Eric S.N., Melissa G.A.V. Adsorption of silver from aqueous solution onto pre-treated bentonite clay: complete batch system evaluation. Journal of Cleaner Production. 112(1), 1112-1121(2016).
15. Conde-González, J.E., Peña-Méndeza E.M., Rybákováb S., Pasáne J. , Ruiz-Péreze C., Havel J.. Adsorption of silver nanoparticles from aqueous solution on copper-based metal organic frameworks (HKUST-1). Chemosphere. 150, 659-666(2016).
16. Praus P., Turicová M., Valásková M. Study of silver adsorption on montmorillonite. Journal of the Brazilian Chemical Society. 19(3), 549-556(2008).
17. Omri A., Benzina M. Adsorption characteristics of silver ions onto activated carbon prepared from almond shell. Desalination and water treatment. 51(10-12), 1-10(2012).

PP-IV-7

IN SAMPLES DURING SORBSION OF MO (VI) IONS EFFECT OF THE MAIN MATRIX COMPONENTS ON THE DEGREE OF SEPARATION

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Abstract. A method for the determination of molybdenum (VI) ions by concentrating them with a newly synthesized sorbent has been developed. A new sorbent was synthesized by modifying the maleic anhydride styrene copolymer in the presence of m-aminophenol and formaldehyde. The resulting polymer sorbent was identified by IR spectroscopy. Formation of molybdenum with the same ligand and different ligand complexes with 2,3,4-trihydroxy-4-sulfoazonaftol reagent was studied. The sorption-photometric method includes optimal (pH-4) sorption condensation of Mo (VI) ion, desorption with $HClO_4$ (desorption rate 88%) and prihallol-based (2,3,4-trihydroxy-4-sulfoazonaphthol (R_1) Mo (VI) ion in eluate.)) includes determination by spectrophotometric method in the presence of. The method was used to study the effect of the matrix on the concentration of microns of molybdenum (VI) ions in water samples (seawater, water from oil extraction, etc.).

Keywords: Molybdenum (VI), thickening, sorption, desorption, prihallol

1.Introduction

It is known that the application of chelate-forming polymer sorbents in chemistry is expanding. This is due to the fact that it is either impossible or very difficult to directly determine the small or small amounts of different elements in complex objects. Condensation and separation with the help of chelate-forming polymer sorbents are often used as a preliminary and necessary step in the determination of elements by various chemical, physicochemical and physical methods. This step allows the separation of microelements from large volumes of solutions with a high salt background, lowering the limit of determination, and thus increases the accuracy and reliability of the method of determination. These show that very small amounts of metal ions are found in various natural and industrial objects, such as natural waters, sewage, soil, plants, food, and so on. The initial concentration is one of the most pressing issues in analytical chemistry. On the other hand, the determination of the maximum allowable concentration of heavy metal ions is also a topical analytical issue in the environmental monitoring of environmental objects. Due to the very low concentration of these elements in most objects and the serious interference effect of other matrix components, it is not possible to determine them reliably even by the most modern physical and physicochemical methods. Therefore, there is a need for initial concentration of these elements.

2.Metod

As mentioned above, one of the main thickening methods is sorption thickening. Recently, chelate-forming polymer sorbents have been widely used for this purpose.It is known from the literature that mixed-ligand complex compounds are widely used to increase the analytical parameters of complex compounds. The presented work is devoted to the separation, concentration and determination of molybdenum (VI) in the environment. In this study, the conditions of formation of MLC with various surfactants (SPCl, SPBr, STMABr), which are systematically identical to molybdenum (VI) with pyrohallol-based azo dyes (2,3,4-trihydroxy-4-sulfoazonaphthol (R_1)), were studied. and optical properties have been studied in detail. It was found that this metal ion forms intensively colored complex compounds with the proposed reagents.The experimental partIn this study, the conditions for the formation of various ligand complexes of molybdenum (VI) with pyrogallol-based azo dyes (2,3,4-trihydroxy-4-sulfoazonaphthol (R_1) with different surfactants (SPCl, SPBr, STMABr), physicochemical and optical properties have been studied in detail. It has been determined that this metal ion forms intensively colored complex compounds with the proposed reagents. It is known from the literature that mixed-bonded complex compounds are widely used to increase the analytical parameters of complex compounds [1-2].

The optimal condition of the resulting complex is pH 2 (□max-460 nm), and the maximum luminosity of the reagent is 304 nm. To determine the optimal conditions for the formation of the complex, the luminosity spectrum was derived depending on the pH of the system (pH 1-14). The figure shows the pH dependence of the complexation of molybdenum (VI) with R1.As can be seen from the figure, the optimal pH of the complex formed by molybdenum (VI) with R_1, and after pH 2 a decrease in the optical density of the complex is observed. Thus, the optimal pH of the complex shifts to an acidic environment, the value of optical density increases at the optimal pH, and hypochromic or batochrome displacement occurs at maximum light.

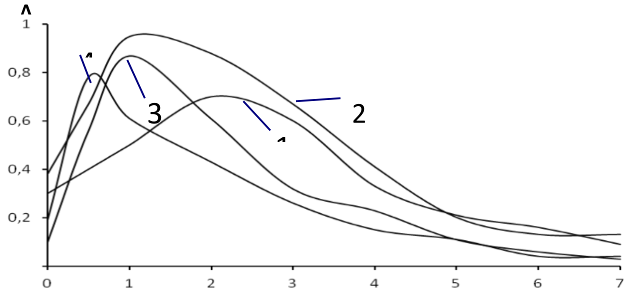
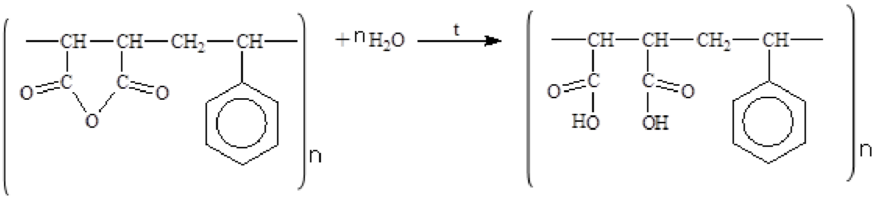
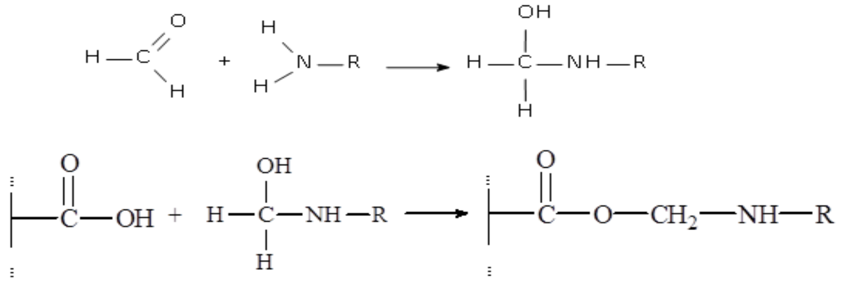


Fig. 1. The dependence of the pH of the solution on the pH of molybdenum (VI) complexes formed with or without SAS: 1-MoR1, 2-MoR1-SPCl, 3-MoR1-SPBr, 4-MoR1-STMAvr.

Azobysisobutyronitrile recrystallized in ethanol was used as an initiator. The obtained copolymer was washed with gasoline and dried to a constant weight in a drying oven at 500C. The yield of the copolymer is 95-97%. It is known in the literature [3] that maleic anhydride forms a linearly structured copolymer with styrene 1: 1 (mole ratio). The calculated amount of formaldehyde and m-aminophenol is added to the obtained copolymer. The reaction is carried out by continuous stirring in a sand bath. As the reaction takes place in an aqueous medium, the anhydride groups in the copolymer are hydrolyzed.



Due to the interaction of formaldehyde and amines in the system, unstable carbonylamine interacts with carboxyl groups in macromolecules, and the extracted amine fragment enters the macromolecule. The reactions that take place can be schematically shown as follows.



The obtained sorbent is washed several times with hot water, dried in a drying oven at 500C to a constant weight and converted to H-form by a known method [3]. 3600-3100 cm-1 in the IR spectrum of the sorbent [valence oscillations of the -OH group in the carboxyl group, as well as valence oscillations of the -NH group (3400-3200 cm-1)], 1750-1715 cm-1 (valence oscillations of the -C = O group in the carboxyl group), 1550-1530 cm-1 (C – N valence oscillations and N – H deformation oscillations), 1620-1520 cm-1 (CC valence oscillations in the benzene ring), 725-700 cm-1 (CC deformation oscillations in the benzene ring) at frequencies absorption bands are observed. Thus, the IR spectrum of the sorbent confirms its probable structure [4].

3.Results and Discussion

To prepare a solution of Mo (VI) salt (10-1) was prepared on the basis of the method known in the literature by dissolving its exact weight in water from its chemically pure (NH_4) $6Mo_7O_{24} \cdot 4H_2O)$ salt [5].

The working solutions were prepared by diluting the starting solution. KCl (pure for chemical analysis) salt solution was used to keep the ionic strength of the solution constant, and acetate-ammonia buffer (pH 3-11) and HCl (pH 1-2) were used to create the required acidity. The pH of the solution was I-130. The optical density of the products was measured on a computer-equipped spectrophotometer Lamda-40 (PERKIN ELMER) and a photocalorimeter KFK-2.

Optimal sorption and desorption conditions of molybdenum (VI) with the synthesized sorbent were determined. It has been shown that a sorbent based on maleine anhydride-styrene copolymer is characterized by low sorption capacity at low pH values and high sorption capacity in weakly acidic and neutral environments. Male anhydride-styrene copolymer-based sorbents have good kinetic properties. It does not lose its sorption properties after several (6-8 cycles) "sorption-desorption" cycles with the obtained sorbent.In water samples (seawater, water extracted during oil extraction, etc.) during the condensation of microns of molybdenum (VI) ions, the macro- and microcomponents of the matrix (Na +, K +, Mg^{2+} , Ca^{2+}, Fe (III), Al (III), Cu^{2+}, Mn^{2+} , Cl-, SO_4^{2-}-) barrier effect should be considered. To take into account the effect of these ions, different amounts of each element are added to a 50 ml solution with a concentration of molybdenum (VI) ions of 200 mg / l.

4.Conclusions

The obtained solution is concentrated and analyzed under dynamic conditions.The experimental results obtained with M1 are given in Table 1.

Table 1. The effect of Mo (VI) ions in water samples during sorption by M1 to the degree of separation of the main matrix components (flow rate 1.2 ml / min; msorb. = 100 mg)

İon	**Concentration, mcg / ml**	**Sorbent, M_1 *R*, %**
Na^+	24000	98
K^+	32000	100
Mg^{2+}	8100	96
Ca^{2+}	6200	96
Cl^-	28000	97
SO_4^{2-}	10200	100
Fe^{3+}	25	96
Al^{3+}	90	98
Mn^{2+}	55	97
Cu^{2+}	25	97

5.References

1. Aliyeva R.A, Mirzai J.I, Abdullaeva K.S.,Bahmanova F.N., Hamidov S.Z.,Ciraqov F.M. Sorption-photometric determination of molybdenum (VI) with 2,3,4-trioxy-4'-fluororazobenzene and 1,10-phenanthroline in natural waters // Journal of Factory Laboratory, 2014 № 1, p. 15-19
2. Abdullaeva KS Concentration and determination of microbicides of molybdenum (VI) complex-forming polymeric sorbent // Journal. Chemical problems, 2016, №2,
3. Akbarov O.H., Akbarov E.O. Practicum on chemistry of high-molecular compounds. Baku: Baku University, 2002, 232p.
4. Saldadze KM, Kopylova-Valova VD Complex-forming ions (complexes). M .: Chemistry, 1980, p. 336
5. Korostelev PP Preparation of solutions for chemical-analytical work. M .: Metallurgy, 1964, p.3866. Voropanova, L. A .; Gagieva, F. A. Selective extraction of molybdenum (VI) from heavy metal solutions by hydrolytic sedimentation and sorption. // Russ. (2011), RU 2428496 C1 20110910

PP-IV-9

DETERMINATION OF VANADIUM (V) BY CONCENTRATİNG İT WİTH POLYMERİC CHELATİNG SORBENTS

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Abstract. A chelating sorbent was synthesized from a modification of the maleic andhydride-styrene copolymer with m-amino phenol. Optimal conditions for the sorption of vanadium (v) by this sorbent have been studied. The results of the study showed that the maximum sorption of vanadium (v) is observed at pH 4. Desorption of sorbed metal ions under the influence of various acids was studied.

Key words: sorption, modification, vanadium, degree of extraction, desorption

1.Introduction

As we know, in order to determine the micro content of toxic metal ions in various natural and industrial facilities and remove these metal ions, recently thickening methods have been increasingly used. Synthetic and natural polymer sorbents are widely used for this purpose. It is known that the sorption properties of synthetic polymer sorbents are higher than the sorption properties of natural sorbents. Therefore, the synthesis of polymer sorbents with effective sorption properties for the determination of smaller amounts of toxic metal ions is considered relevant.

Research and analytical application of sorption properties of synthetic polymer sorbents containing chelate-forming functional analytical groups during selective concentration and separation to increase the sensitivity in the determination of micronutrients of elements is an actual issue. There is extensive information in the literature on chelate-forming ion exchangers, their synthesis, practice and theory of ion-exchange and complex-formation processes [1-6].

In the presented work, the ability of sorbent synthesized on the basis of maleic anhydride styrene copolymer to sorb vanadium (V) ions was studied and a method for its determination by concentration in natural objects was developed

2.Metod

Preparation of the used solutions. In order to prepare a solution of the salts of the vanadium (V) metal chemically pure ammonium vanadate salt was used [7]. A chemically pure KCl salt solution was used to create the required value of ionic strength in the solution. Whereas in order to create the required pH in the system ammonia-acetate buffer solutions (pH 3-11) and HCl fixative (pH 0-2) were used. The KOH solution was prepared from chemically pure potassium hydroxide and its density was determined by titration with standard HCl solution.

Devices. Concentrations of metal solutions were studied with aids of KFK-2 photo colorimeter. The pH of the solutions was determined using a PHS-25 ionomer.

Synthesis of sorbents. Radical copolymerization of maleic anhydride (c. p.) with styrene (c. p.) was carried out in benzene solution, water bath (75 – 80°C) during 140 min. Recrystallized azobisisobutyronitrile (AIBN) in ethanol was used as the initiator. The obtained copolymer was washed with benzene and dried in a drying oven at 50°C until constant weight. The yield of the copolymer is 95–97%. It is known from the literature that maleic anhydride forms a linearly structured copolymer with styrene 1:1 (mole ratio). The calculated amount of formaldehyde and m-amino phenol is added to the obtained copolymer [8]. The reaction is carried out in a sand bath, with constant stirring. As the reaction takes place in an aqueous medium, the anhydride groups in the copolymer are hydrolyzed.

As an interaction between formaldehyde and amine in the system, carbonylamin is obtained. The obtained carbonylamine interacts with the carboxyl groups in the macromolecules, and the extracted amine fragment enters the macromolecule.

3.Results and Discussion

The influence of environmental pH on sorption. The influence of environmental pH on the increaseing of concentration of metals with a chelating agent was studied. The results of the study showed that the maximum sorption of vanadium (V) is observed at pH-4

Sorbent sorption was studied under static conditions. To determine the optimal pH of the sorption, 8 beakers of the same capacity and shape are taken. An equal amount (50 mg) of sorbent is added to each beaker. The density of metal ions and the total volume of the liquid phase are kept constant in each beaker. The only variable is the environmental pH of the medium (1-8). After one day, the equilibrium concentration of the metal ion is determined by the method of atomic absorption analysis (according to the degree graph).

The influence of metal ion concentration on the sorption process. The study was performed at optimal pH. As the concentration of metal ions in the solution increases, the amount of metal sorbed increases, and at a concentration of $6 \cdot 10^{-3}$ mol/l it reaches its maximum: SC = 241 mg/g (Figure).

The influence of the ionic strength. The influence of the ionic strength on sorption has been studied. An increase in ionic strength to 0.6 has a weak effect on sorption. The next increase leads to a decrease in sorption. This is due to the fact that with increase in the ionic environment of the functional groups, the ability of metals to form complexes decreases.

Time dependence of the sorption process. The time dependence of sorption has also been studied. The results of the research showed that complete sorption of vanadium (V) occurs after 2 hours.

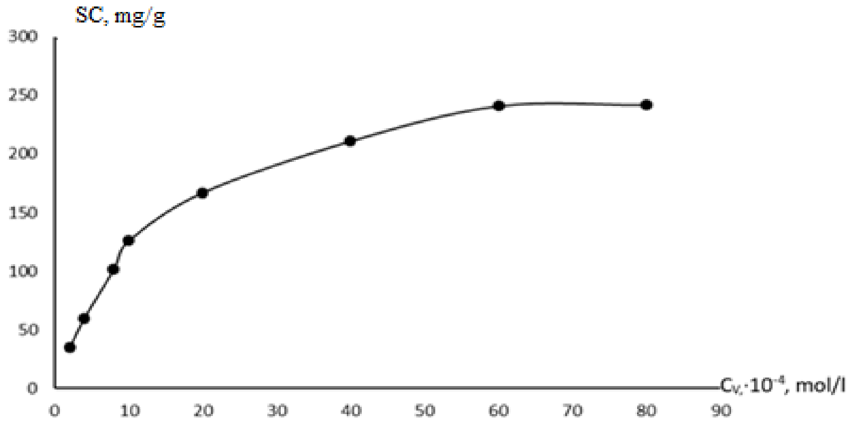

Figure. Dependence of the sorption process of vanadium (V) ion with the synthesized sorbent on the concentration of metal.

3.Desorption

The desorption of vanadium (V) from the sorbent has also been researched. For this purpose, first the optimal acid that best affects the desorption process is determined, then the optimum solubility of the optimal acid that has the maximum effect on the desorption is determined.

To determine the optimal acidity of the desorption process, the effect of different mineral acids ($HClO_4$, H_2SO_4, HNO_3, HCl) of the same concentration was studied: sorption experiments were performed by adding the same amount of metal ions and equal mass sorbent samples to round-bottomed flasks of the same capacity and shape. After the sorption process equilibrium is established, the sorbent is separated from the solution by decantation and dried. The dried sorbent samples were transferred to round-bottomed flasks, the same volume of different acids of the same concentration ($HClO_4$, H_2SO_4, HNO_3, HCl) was added on them. The optimal acidity of the desorption process is determined.

Once the optimal acidity of the desorption process is determined, its optimal concentration, which affects the maximum desorption, is determined. For this purpose, the sorbed sorbents according to the above-mentioned are transferred to the flasks, desorption experiments are carried out by changing the volume of the liquid phase and the optimal acid concentration.

The volume and concentration at which the maximum desorption takes place. The experiment showed that the best desorbent for vanadium (V) is HNO_3 acid. The table shows the results of desorption experiments.

Table. The results of desorption experiments from vanadium (V) sorbent

Acid	Concentration, mol/l	Desorption rate, %
HCl	0,5	75
	1,0	81
	2,0	89
$HClO_4$	0,5	75
	1,0	86
	2,0	92
HNO_3	0,5	81
	1,0	88
	2,0	95
H_2SO_4	0,5	79
	1,0	87
	2,0	93

4.Conclusion

The developed method is more economical, faster and more environmentally friendly..The study showed the possibility of using a matrix of a copolymer of maleic anhydride with -styrene copolymer modified with m-amino phenol for the sorption-photometric determination of vanadium (V). The sorbent used to determine the trace amounts of vanadium (V) has higher sorption properties (sorption capacity, analysis time, concentration temperature) in comparison with those known in the literature. The proposed sorbent can be reused for 7-8 cycles**.**

5.References

1. Basarghin N.N., Kutirev I.M., Chebotnikova Y.A., Qolosnitskaya V.A., Astakhova M.N., Rozovskiy Y.Q. Study of the behavior of the third component on the sorption of elements in the system chelated sorbent – element – a pair of substituted aniline. Separation and concentration in analytical chemistry. Materials of the international symposium dedicated to the anniversary of Y.A. Zolotova, Krasnodar, October 6-11., 2002, pp. 34.
2. Myasoedova G.V., Savvin S.B. Chelating sorbents. Moscow: Nauka 1984. P. 173.
3. Saldadze K.M., Kopilova-Valova V.D. Complexing ion exchangers. Moscow: Chemistry, 1980. pp. 336.
4. Aliyev E.H., Bahmanova F.N., Hamidov S.Z., Chyragov F.M. Lead (II) concentration by a chelating sorbent containing meta-phenylenediamine fragments. //Proceedings of Universities. Applied Chemistry and Biotechnology. 2020, vol.10, no.1, pp.107-113. (In Russ.) https://doi.org/10.21285/2227-2925-2020-10-1-107-113
5. Maharramov A.M., Hajiyeva S.R., Bahmanova F. N., Gamidov S. Z., Chyragov F. M. Preconcentration of Uranium(VI) on a Chelating Adsorbent Followed by Photometric Determination with 2,3,4 Trihydroxy3'Nitro4'Sulfoazobenzene // Journal of Analytical Chemistry, 2011, vol. 66, no.5, pp. 465–469 DOI: 10.1134/S1061934811050108
6. Basargyn N.N., Maharramov A.M., Hajiyeva S.R. and etc. Determination of uranium (VI) in natural waters after preliminary concentration with a sorbent containing fragments of m-amino phenol // Russ. J. An. Chem. 2013. vol. 68. no.2, pp. 136-139 [in Russian].///12
7. Korostelev P.P. Preparation of solutions for chemical analytical work. M .: Science. 1964. 261. P
8. R.A.Alieva, S.Z.Hamidov, F.M.Chiraqov. Learning of sorbtion of Zn(II) ions with chemical modified synthetic sorbent News Journal of Baku University, 2007, no.2, pp28-34

PP-IV-8

VALUATION AND STUDY OF THE ACTIVITY OF AN ESSENTIAL OIL EXTRACTED FROM A MEDICINAL PLANT MYRTLE

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Abstract. The proposed study is to assess the inhibitory effect of a common myrtus plant species on strains responsible for urinary tract infections by the application of two different techniques, hydrodistillation and extraction by Soxhlet in order to obtain better yields and good characteristics of the oil. The yields obtained by hydrodistillation and Myrtle soxhlet are respectively: 10.06 and 13.33%. The physicochemical characterizations were carried out by CGSM. The antibacterial activity of Myrtle oil against Escherichia coli was remarkable with inhibition diameters greater than 20 mm. Myrtle oil inhibits the growth of yeasts and weakens the growth of Staphylococcus aureus which is said to have a bacteriostatic effect.

Keywords: Essential oils, Common myrtus, Hydrodistillation. Soxhlet, CGSM, Antibacterial activity.

1.Introduction

In Algeria, it grows spontaneously through the Tell Atlas, the coastal regions of Algiers and Constantine, where it is known by the names of "Rihan" or "mersin" [1], [2]. An infusion of the leaves and young branches is stimulating, antiseptic, astringent and hypoglycemic and has been considered a health remedy for eczema, psoriasis, asthma, gastrointestinal disorders, urinary tract infections and diarrhea [3]. Previous studies done on the aerial parts of Myrtus have revealed the presence of several chemical compounds capable of exerting its very interesting biological effects. The leaves and flowers contain essential oils, tannins, phenolic acids and flavonoids [4], [5].

2.Materials and methods

In our study we were interested in the aerial parts of the aromatic plant which comes from the wilaya of Boumerdes of Algeria which is the myrtle and which was harvested in June. The dry Myrtle leaves are washed to remove dust and all kinds of impurities; they are then dried in an oven at a temperature of 45 ° C for 3 days, in order to remove all traces of water. (Figure 1).

Dry Myrtle Leaves Myrtle Powder

Fig.1. The sample before and after grinding.

In order to assess the influence of the extraction technique on the properties of essential oils, two methods were used, namely: Hydro-distillation and the other by an organic solvent using a Soxhlet system. The extractions were carried out on the ground dry matter using a Clevenger device. The operation took place in the organic chemistry laboratory of the Faculty of Science of the University of Boumerdes -Algeria-.

Fig. 2. Clevenger hydrodistillation setup.

The organic phase about hydrodistillation recovered in a flask is passed through a rotary evaporator in order to remove the solvent used; the latter is put under a low pressure (about 0.5 atmosphere) to reduce the boiling point of the solvent and obviously to preserve the organic phase from any thermal transformation. The organic phase thus obtained, which represents practically the essential oil of the plant, is kept in closed opaque glass bottles at a temperature of 4 to 6°C. The Soxhlet extractor is a device specially designed for the continuous extraction of liquid solid (solvent) [6], [7]. We poured into 500 mL round bottom flasks, brought to temperatures 82 and 70 ° C respectively; 400 ml of hexane serve as solvent. On the other hand, we weighed 30g of dry plant matter of myrtle leaves in cellulose cartridges. They are then introduced into the soxhlet device.The duration of myrtle extraction up to 6 hours.

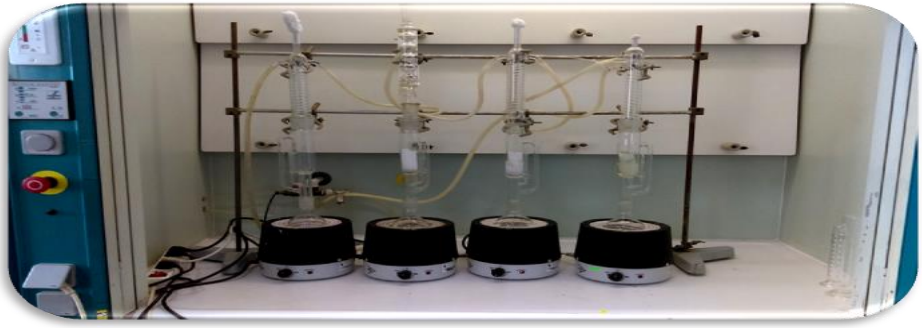


Fig.3. Soxhlet assembly

The results of the calculation expressed as a percentage of extraction yield of essential oils of Myrtle are presented in (table. 1).

Table 5. Yields of essential oils from the plant studied

	Extraction methods	
	essential oils -HD	essential oils -Soxhlet
Yield (%)		
Myrtle	10.06	13.33

It was therefore found, that the yield obtained by soxhlet is greater than that obtained by hydrodistillation. The results of the organoleptic properties are grouped in the (table. 2):

Table .2: Organoleptic properties of oils according to AFNOR [8]

Myrtle essential oils	
Organoleptic properties	
Color	Yellow orange to green
Odour	Characteristic herb
Aspect	Clear mobile liquid

Table .3: Organoleptic properties of essential oils of myrtle extracted by HD and by Soxhlet.

	Extraction methods	
Organoleptic properties	essential oils -HD	essential oils -Soxhlet
Color	Yellow orange	Green
Odour	Herbaceous	Herbaceous
Aspect	Mobile liquid	Clear liquid

(1) (2)

Fig. 4 :(1): essential oils -Soxhlet, (2): essential oils –HD

In addition, essential oils have a strong and persistent odor. Myrtle essential oil is a liquid, clear, orange-yellow (HD) to green (Soxhlet) color with a characteristic herbaceous odor. The essential oils recovered using the two HD and Soxhlet extraction methods were analyzed by gas chromatography coupled with mass spectrometry (CG/SM).

3.Experimental

The chromatograms obtained made it possible to identify and quantify the various constituents of essential oils of myrtle. The chromatogram obtained by the GCMS analysis as well as the results of the various chemical compounds grouped in (figure 5).

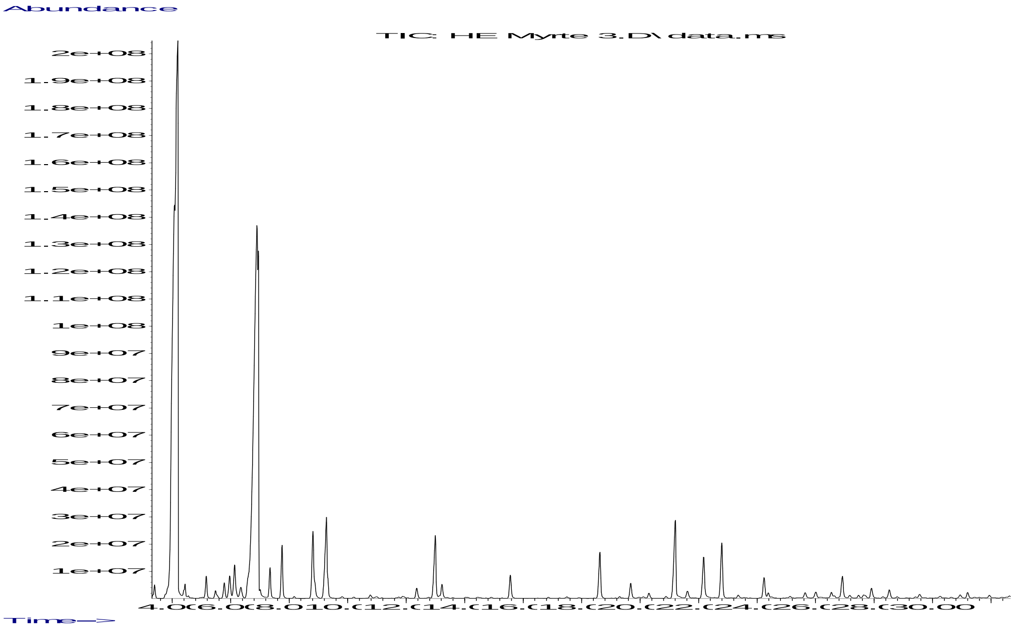


Fig. 5 Chromatogram of Myrtle HD essential oil

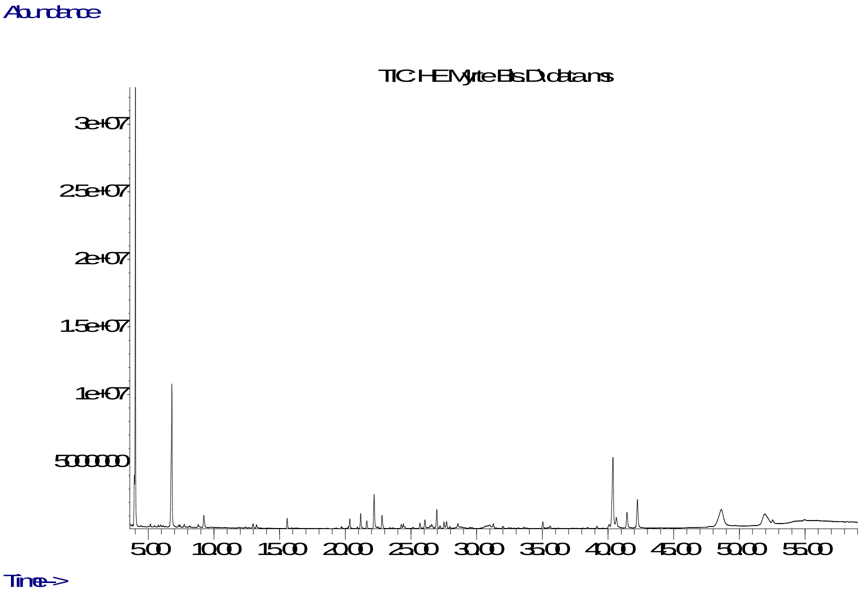


Fig .6 Chromatogram of Myrtle Soxhlet essential oil

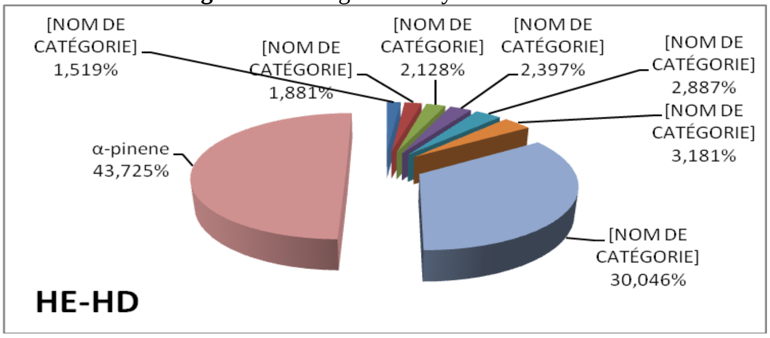


Fig. 7 Distribution in% of the main compounds of Myrtle-HD essential oil

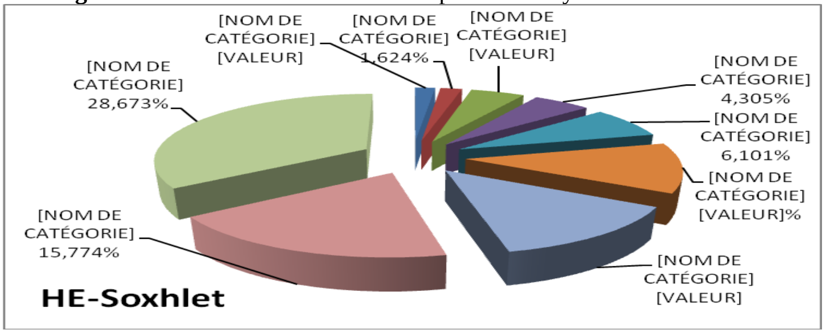
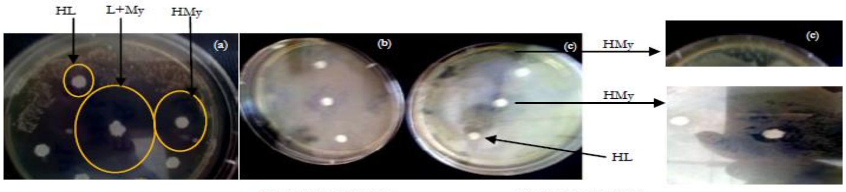
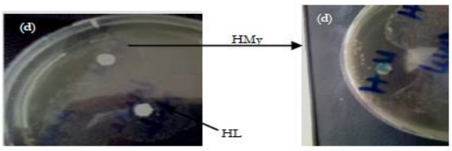


Fig .8 Distribution in% of the main compounds of HE of Myrtle-Soxhlet.

From a quantitative point of view, differences are observed in the content of the constituents identified. A-pinene and Eucalyptol are highly abundant in myrtle essential oil. From a quantitative point of view, differences are observed in the content of the constituents identified. A-pinene and Eucalyptol are highly abundant in myrtle essential oil. Terpinolene and α-terpineol which represent 2.397% and 2.128% of the essential oil of hydrodistilled myrtle do not constitute that extracted by soxhlet. Linalool is present at a rate of 3.181% in the essential oil extracted by hydrodistillation against a rate of 1.498% in that obtained by soxhlet. Limonene, Menthyl Acetate and neocurdione which represent percentages of 6.101%, 4.305%, and 9.809% respectively of the essential oil recovered by Soxhlet are not found in HD oil. Myrtenyl Acetate made up only 2,887% of HD essential oil while it reached a percentage of 11,170 in soxhlet essential oil. The Caryophyllene content was almost equivalent with 1.881% in essential oil - HD and 1.624 in soxhlet. Geranyl Acetate represents 1.519% of HD essential oil and 4.038% that of Soxhlet essential oil [9].



Escherichia coli *Pseudomonas aerugenosa* *Staphylococcus aureus*



Les levures

Fig .9 Evaluation of the antimicrobial activity of essential oils in bacterial strains.

From the results obtained, it appears that Myrtle oil has shown a strong antimicrobial activity which inhibits the growth of the microorganisms studied with different degrees of sensitivity. The antibacterial activity of Myrtle oil against Escherichia coli was remarkable with inhibition diameters greater than 20 mm. Myrtle oil is more powerful with a 100% inhibition (synergistic effect) (Figure. 9- a) [10], [11], [12]. Whereas for Pseudomonas aerugenosa, this oil had no inhibitory effect (Figure. 9- b). On the other hand, Myrtle oil inhibits the growth of yeasts and weakens the growth of Staphylococcus aureus which is said to have a bacteriostatic effect (Figure. 9- c and d) [13], [14], [15].

4.Conclusion

Whereas for Pseudomonas aerugenosa, this oil had no inhibitory effect. On the other hand, Myrtle oil inhibits the growth of yeasts and weakens the growth of Staphylococcus aureus which is said to have a bacteriostatic effect.

5.References

1. Mazari K., Bendinerad N., Benkhechi Ch et Fernandez X. Chemical composition and antim crobial activity of essential oil isolated from Algerian Juniperus phoenicea L and cupressus sempervirens. Medicinal Plant Research. 4(10): 959-964 (2010). doi: 10.5897/JMPR10.16
2. Lozniewski A., Rabaud C., Résistance aux antibiotiques, CCLIN Sud-Est juillet 2010.
3. Acar J.F., Moulin G., Rev. Sci. Tech. Off. Int. Epiz. 25, 775-792 (2006).
4. Baçer, K. H. C., & Buchbauer, G. Handbook of essential oils: science, technology, and applications. Boca Raton: CRC Press/Taylor & Francis (2010).
5. Laurent, J. Advice and uses of the most common essential oils in pharmacies, doctoral thesis. Faculty of Pharmacy of Marseille, December 15, (2017). doi: 10.2146/ajhp151043
6. Aleksic V. et Knezevic P. Antimicrobial and antioxidative activity of extracts and essential oils of Myrtus communis L. Microbiological Research, 169, 240-254, (2014). doi: 10.1016/j.micres.2013.10.003.
7 AFNOR, Collection of standards, essential oils volume 02, (Afnor Paris 2000, 661-663).
8 Aboutabl E.A., Meselhy K.M., Elkhreisy E.M., Nassar M.I. et Fawzi R. Composition and bioactivity of essential oils from leaves and fruits of Myrtus communis and Eugenia supraxillaris (Myrtaceae) Grown in Egypt. Journal of Essential Oil Bearing Plants, 14: 2, 192-200, (2011). doi: 10.1080/0972060X.2011.10643921.
9. Akin M., Aktumsek A. Nostro A. Antibacterial activity and composition of the essential oils of Eucalyptus camaldulensis Dehn. and Myrtus communis L. growing in Northern Cyprus. African Journal of Biotechnology, Vol. 9 (4), 531-535 (2010). doi: 10.5897/AJB09.1562
10 Badawy Mohamed E.I. et Abdelgaleil Samir A.M. Composition and antimicrobial activity of essential oils isolated from Egyptian plants against plant pathogenic bacteria and fungi. Industrial Crops and Products, 52 : 776– 782 (2014). doi: 10.1016/j.indcrop.2013.12.003.
11Brada M., Tabti N., Boutoumi H., Wathelet J.P. et Lognay G. Composition of the essential oil of leaves and berries of Algerian myrtle (Myrtus communis L.). Journal of Essential Oil Research, 24, No. 1, 1-3 (2012). doi: 10.1080/10412905.2012.645299.
12 Çabuk M., Eratak S., Alçicek A. et Bozkurt. M. Effects of herbal essential oil mixture as a dietary supplement on egg production in quail. The Scientific World Journal, 1-4 (2014). doi: 10.1155/2014/573470
13 Gavahian M., Farahnaky A., Javidnia K. et Majzoobi M. A novel technology for extraction of essential oil from Myrtus communis: ohmic-assisted hydrodistillation. Journal of Essential Oil Research, 25:4, 257-266 (2013). doi: 10.1080/10412905.2013.775676.
14 Kayedi M. H., Haghdoost A. A., Salehnia A. et Khamisabadi K. Evaluation of repellency effect of essential oils of Satureja khuzestanica (Carvacrol), Myrtus communis (myrtle), Lavendula officinalis and Salvia sclarea using Standard WHO repellency tests. J Arthropod-Borne Dis, 8(1): 60-68 (2014). doi: 10.7537/marslsj1301s1601.
15 Taheri A., Seyfan A., Jalalinezhad S. et Nasery F. Antibacterial effect of Myrtus communis hydro-alcoholic extract on pathogenic bacteria. Zahedan J Res Med Sci, 15(6). 19-24 (2013). doi: 10.9734/BJI/2016/28500

V. Modeling and optimization of petrochemical processes.

OR-II-1

X-RAY STUDY OF BINARY COBALT-CERIUM, MAGNESIUM-CERIUM AND NICKEL-CERIUM OXIDE CATALYSTS

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Abstract. X-ray diffraction studies of binary cerium-containing oxide catalysts active in the reaction of steam conversion of ethanol to hydrogen have been carried out. It was found that in the Co-Ce-O catalytic system, all samples contain two phases: Co_3O_4 and CeO_2. An analysis of the X-ray diffraction patterns of the system of binary Mg-Ce-O catalysts showed that individual oxides MgO and CeO_2 are formed in the samples of this system. In the catalytic system Ni-Ce-O, the formation of two phases is also observed, namely, the oxides NiO and CeO_2. It was found that in all catalytic systems the percentage ratio of the components is preserved, as evidenced by the regular change in the intensities of reflections in the diffraction patterns. The degrees of crystallinity of binary cerium containing oxide catalysts have also been calculated. It was found that an increase in the content of cobalt or nickel in the composition of binary catalysts leads to a sharp decrease in the crystallinity of the samples. The addition of magnesium oxide has practically no effect on the degree of crystallinity of the studied binary cerium containing oxide catalysts

Keywords: X-ray Phase Analysis, Binary Catalysts, Cerium Oxide.

1.Introduction

We have previously shown that ethanol is converted at a high rate into products such as acetic acid, acetaldehyde acetone, etc. on a number of binary cerium containing catalysts [1, 2]. It was shown that the direction of the ethanol conversion reaction depends on both the reaction temperature and the composition of the catalyst containing cerium-containing catalysts. This may be due to a change in the phase composition, structural and other surface properties of binary cerium containing catalysts. In this regard, in this work, we carried out an X-ray study of binary cerium-containing catalysts.

2.Experimental part

Binary cobalt-cerium, magnesium-cerium, and nickel-cerium oxide catalysts of various compositions were prepared by mixing aqueous solutions, respectively, of nitrate salts of cobalt and cerium, magnesium and cerium, nickel and cerium. The resulting mixtures were evaporated and dried at a temperature of 100°C, after which they were transferred into a porcelain dish and calcined at a temperature of 200-300°C until the complete evolution of nitrogen oxides. After that, the catalysts were calcined at a temperature of 750°C for 10 hours.

Thus, in each catalytic system Co-Ce-O, Mg-Ce-O and Ni-Ce-O, 9 samples were prepared in various ratios of components, satisfying the following conditions:

mA/nB, where A is Co, Mg and Ni; B - Ce; m, n = 1 ÷ 9; m + n = 10.

X-ray studies of the synthesized samples were carried out on an automatic powder diffractometer "D2 Phaser" from "Bruker" (CuKα-radiation, Ni-filter, $5 \leq 2\theta \geq 75°$).

3.Results and discussions

The results of X-ray diffraction studies have shown that two phases are formed in the Co-Ce-O catalytic system: Co_3O_4 and CeO_2. It was found that the formation of new chemical compounds between oxides of cobalt and cerium is not observed. Figure 1 shows the diffraction patterns of all nine Co/Ce ratios brought together. At the beginning and at the end of these diffraction patterns, oxides Co3O4 and CeO2 are also presented.

As can be seen from Figure 1, the X-ray diffraction patterns of individual cobalt and cerium oxides contain diffraction peaks characteristic of the Co_3O_4 phases (2θ = 19°, 21.1°, 27.1 °, 45°, 59.5° and 65.3°) and CeO_2 (2θ = 28.57°, 33.11°, 47.53° and 56.4°) [3,4].

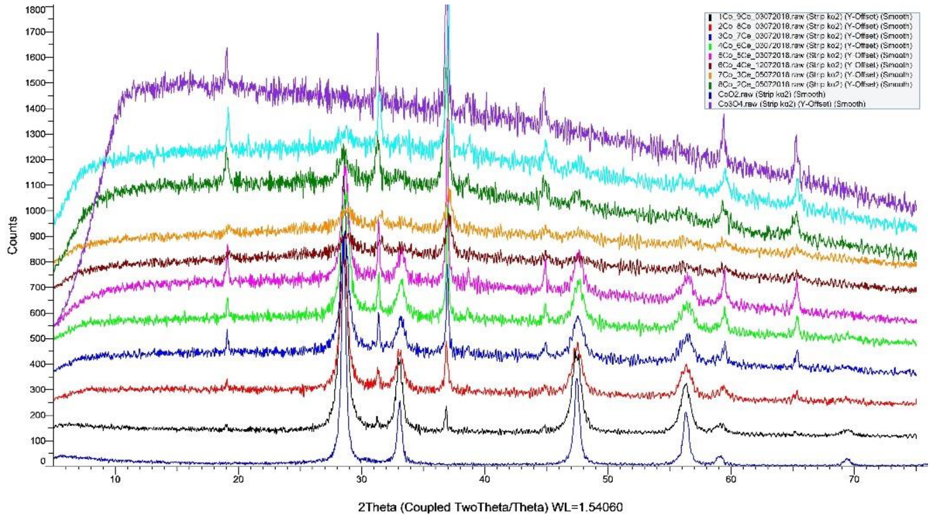

Fig. 1 Diffraction patterns of cobalt and cerium oxides, as well as all nine Co-Ce-O catalysts.

X-ray diffraction analyzes show that with an increase in the content of cobalt in the composition of the binary Co-Ce-O catalyst, the intensities of the diffraction peaks related to cobalt oxide increase, while the intensities of the diffraction peaks related to cerium oxide decrease. It is also seen from the diffraction patterns of the studied samples that, apart from the diffraction peaks related to cobalt and cerium oxide, the presence of other peaks in the diffractograms of the samples is not observed. This indicates that all the studied samples consist of two phases and in all the percentages of the components are preserved, which is evidenced by the regular change in the intensities of reflections in the diffraction patterns.

Diffraction patterns of all nine samples of the catalytic system Mg-Ce-O collected together in the figure are presented 1. Also, at the beginning and at the end of these diffraction patterns are the oxides MgO and CeO2.

As can be seen from Figure 1, the X-ray diffraction pattern of individual magnesium oxide contains diffraction peaks characteristic of the MgO phase (2θ = 36.8°, 42.9°, 58.4°, 62.2° and 74.5°) [5].

As in the previous catalytic system, with an increase in the magnesium content in the composition of the binary Mg-Ce-O catalyst, the intensities of the diffraction peaks related to magnesium oxide increase, while the intensities of the diffraction peaks related to cerium oxide decrease. Figure 2 also shows that apart from the diffraction peaks related to magnesium and cerium oxides, the presence of other peaks in the diffraction patterns of the samples is not observed. That is, the samples of the Mg-Ce-O catalytic system also contain only phases of the initial oxides of magnesium and cerium. These samples also retain the percentage of the components, which is evidenced by the regular change in the intensities of reflections in the diffraction patterns. Based on the results obtained, we can say that the formation of new phases is not observed in the Mg-Ce-O catalytic system, and only the phases of the initial oxides are present in the studied catalysts.

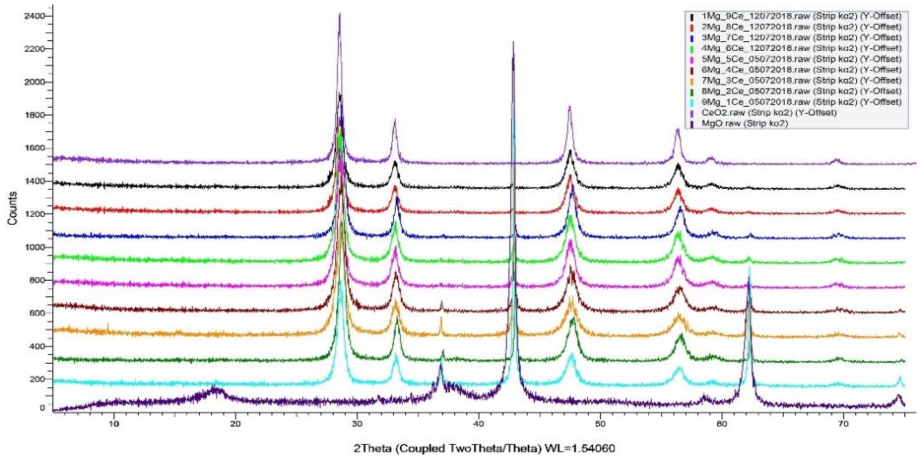

Fig. 2 Diffraction patterns of magnesium and cerium oxides, as well as all nine Mg-Ce-O catalysts.

The results of X-ray diffraction studies of all nine samples of the Ni-Ce-O catalytic system are shown in Figure 3. In addition to all nine samples of the Ni-Ce-O catalytic system, Figure 3 also shows the X-ray diffraction patterns of nickel and cerium oxides.

As can be seen from the X-ray diffraction patterns shown in Figure 3, nickel oxide has characteristic diffraction peaks, namely 2θ = 37.3°, 43.4°, 62.7° and 75.3°). The analyzes of the obtained X-ray diffraction patterns show that with an increase in the nickel content in the composition of the binary Ni-Ce-O catalyst, as in the previous catalytic systems, the intensities of the diffraction peaks related to nickel oxide increase, while the intensities of the diffraction peaks related to cerium oxide decrease. It is also seen from the diffraction patterns of the studied samples that, apart from the diffraction peaks related to cobalt and cerium oxide, the presence of other peaks in the diffractograms of the samples is not observed. This indicates that all the studied samples of the Ni-Ce-O catalytic system also consist of two phases of the initial oxides, and in all the percentages of the components are preserved, which is evidenced by the regular change in the intensities of reflections in the diffraction patterns.

Thus, we can say that two phases are formed in the Ni-Ce-O catalytic system: NiO and CeO_2, and the formation of new chemical compounds is not observed.

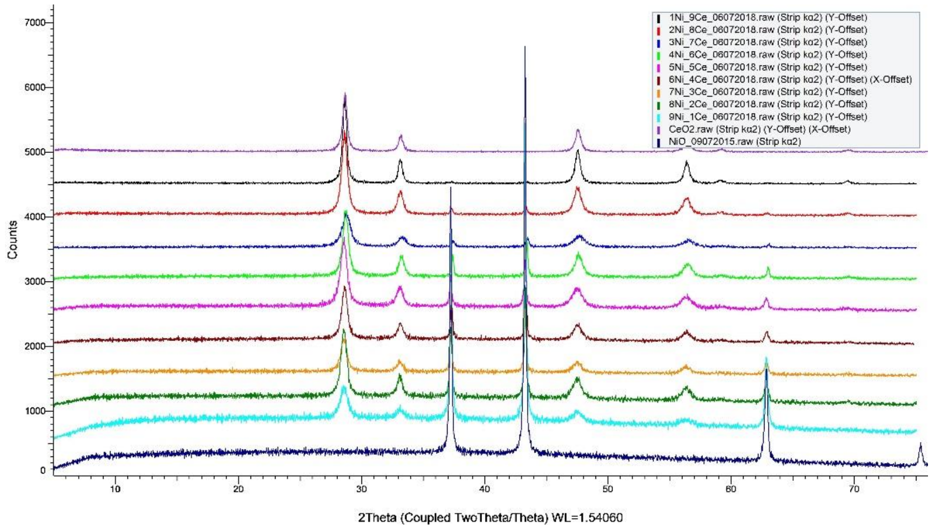

Fig. 3. Diffraction patterns of nickel and cerium oxides, as well as all nine Ni-Ce-O catalysts.

We also calculated the degree of crystallinity of all the binary cerium containing catalysts studied by us using the DIFFRAC.EVA program using the D2 Phaser device, the results of which are presented in Table 1. As can be seen from Table 1, the degree of crystallinity of the samples of the Co-Ce-O catalytic system with an increase in the cobalt content in the composition of the binary catalyst sharply decreases from 75.8% for the Co-Ce = 1-9 sample to 12.9% for the Co-Ce = 9-1 sample. The degree of crystallinity of the samples of the Ni-Ce-O catalytic system also decreases with an increase in the content of the second component of nickel in the composition of the binary catalyst, but not as sharply as in the previous samples (from 78.7% for the Ni-Ce = 1-9 sample to 27.3 % on the sample Ni-Ce = 9 1. In contrast to the previous series of catalysts, the degree of crystallinity of the catalytic system Mg-Ce-O practically does not change with a change in composition.

Table 1. Calculated degrees of crystallinity of the samples of the catalytic systems Co-Ce-O, Mg-Ce-O and Ni-Ce-O.

Catalysts	The degree of crystallinity, %								
Atomic ratio of elements	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1
Co-Ce-O	75,8	56,5	38,6	34,7	21,5	17,1	15,5	14,5	12,9
Mg-Ce-O	78,3	78,5	79,0	78,1	77,4	76,0	74,5	80	77,3
Mg-Ce-O	78,7	76,2	70,5	65,9	59,1	50,6	42,0	38,8	27,3

4. Conclusions

Binary cerium containing oxide catalysts with additions of cobalt, magnesium, and nickel consist of only two initial oxides. No chemical compound formation is observed in these catalysts. The addition of the second element to the composition of the cerium-containing catalyst leads to a decrease in the degree of crystallinity of the samples for the Co-Ce-O and Ni-Ce-O catalytic systems, while for the Mg-Ce-O catalytic system it has practically no effect.

5.References

18. Mammadova S.H., Garaybayli S.A.: The reaction of ethanol conversion over cerium copper catalysts. European Journal of Technical and Natural Sciences № 3, p.101-104 (2016).
19. Mammadova S.H., Aghayeva K.Kh.: Conversion of ethanol over binary copper containing catalysts. Chemical Problems N. 2 (18), pp.199-205 (2020).
20. Xing Liu & Charles T. Prewitt: High-temperature X-ray diffraction study of Co3O4: Transition from normal to disordered spinel. Physics and Chemistry of Minerals volume 17, pages168–172 (1990).
21. Jayakumar G., Albert Irudayaraj A., Dhayal Raj A.: Particle Size Effect on the Properties of CeriumOxide (CeO2) Nanoparticles Synthesized by Hydrothermal Method. Mechanics, Materials Science &Engineering Journal Magnolithe, 9 (1), 2017, 10.2412/mmse.3.4.481. hal-01499374.
22. Dercz G., Prusik K., Pająk L., Pielaszek R., Malinowski J.J., Pudło W.: Structure studies on nanocrystalline powder. Materials Science-Poland Vol. 27, No. 1, pp. 201-207 (2009).
23. Vikas Patil, Shailesh Pawar, Manik Chougule, Prasad Godse, Ratnakar Sakhare, Shashwati Sen, Pradeep Joshi: Effect of Annealing on Structural, Morphological, Electrical and Optical Studies of Nickel Oxide Thin Films. Journal of Surface Engineered Materials and Advanced Technology 1, p.35-41 (2011).

PP-V-1

ON A MODEL OF IDEAL DISPLACEMENT OF A CHEMICAL REACTOR

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Abstract. The issue of mathematical modeling of a chemical reactor of ideal displacement is considered, in which processes are carried out that combine chemical reactions with mass and heat transfer. Based on the law of mass conservation, a mathematical model of the chemical process is constructed, taking into account the chemical reaction. The resulting model is a differential equation in private derivatives of the order. In this model the inverse problem is set to determine the kinetic coefficient of a chemical reaction according to a given additional condition. In the beginning, the time derivative is discretized by the finite difference “back”. A solution is proposed for solving the obtained differential-difference problem. As a result, the problem is reduced to two independent differential-difference problems of the first order and a linear equation with respect to the desired kinetic coefficient. The numerical solution of these problems is determined by the finite difference method. The obtained discrete analogs are represented as an implicit difference scheme. The solution is inserted into an additional condition and the value of the desired kinetic coefficient is determined using an explicit formula.

Keywords: ideal displacement process, coefficient inverse problem, convection-reaction equation, stoichiometric coefficient, differential-difference problem, implicit scheme.

1.Introduction.

At the present time, the development of computer technology expands the possibility to use mathematical modeling in the study of the kinetics of chemical reaction’s underlying industrial processes and chemical reactor choice. It also enables the forecasting and optimization of the technological modes of industrial processes in existing productions, in conditions of changing raw material composition and productivity, as well as in the design of technological schemes for new and modernized chemical industry productions. One of the main elements of any chemical-technological system (CTS) is a chemical reactor, in which chemical processes are carried out, combining chemical reactions with mass and heat transfer, in order to produce a certain substance. Various types of reactors are used, which can be classified according to certain characteristics: the reactors can be homogeneous or heterogeneous; isothermal, adiabatic. There are periodic, continuous and semi-periodic reactors. According to the mode of movement of the reaction medium or the structure of the substance flows, the reactors are divided into reactors for ideal mixing; ideal displacement; with longitudinal mixing; with longitudinal and radial mixing and with a combined flow structure. The above classification indicates that real chemical reactors are characterized by a large number of properties, so when building a mathematical model for a chemical reactor, it is necessary to select and take into account the most important properties, as it is impossible to take into account all the properties simultaneously. The processes associated with chemical technology are very complex. Therefore, an important stage of mathematical modeling is the creation of a model that will adequately describe the process under consideration. Usually, the mathematical models of individual devices are created based on models of processes occurring in these devices, and then technological schemes are modeled that link these devices into a single technological process. Depending on the complexity of the process itself and the possibility of obtaining experimental information about its passage, the developer of mathematical models uses either a deterministic approach based on fundamental laws, or an empirical approach, which is based on the statistical processing of experimental information. Chemical and technological processes usually take place in moving flows, the hydrodynamic patterns of movement of which have a significant impact on the efficiency of chemical production. Therefore, the description of the movement of hydrodynamic flows of substances, and the use of simpler approximations of their internal structure, becomes important when compiling mathematical models of HTP.

The structure of the moving process medium is characterized by the degree to which the flow particles mix, which determines the concentration field and temperature gradients. This serves as a prerequisite for establishing some typical models of moving flows based on mixing. These are the following hydrodynamic models: perfect mixing; perfect displacement; diffusion (one - and two-parameter) models; cellular models; combined model.

2. Problem formulation and solving method.

Mathematical models of chemical reactors are based on the block principle using typical hydrodynamic models that take into account the movement of matter flows [1-3]. In accordance with the ideal displacement model, a piston flow is assumed, without mixing along the flow with a uniform distribution of the concentration of the substance in the direction perpendicular to the movement.

To construct a mathematical model of an ideal displacement reactor, we will present some element of the displacement process as a rectangular parallelepiped. According to the law of conservation of mass

$$I_{in} - I_{out} = I_{ch}. \qquad (1)$$

I_{in}, I_{out} are accordingly, the flows on the input and output sections of this element over Δt time, I_{ch} – is the change of mass over Δt time in a given element.

It is known that the flow at the input section ($x = x$) is defined by the formula

$$I_{in} = uSC\Delta t/_{x=x}.$$

S is the cross-sectional area of the device, m2.

The flow at the output section ($x = x + \Delta x$) is defined in the same way

$$I_{out} = uSC\Delta t/_{x=x+\Delta x}.$$

In steady state mode $I_{in} = I_{out}$. If the concentration changes at the entrance to the device:

$$I_{in} \neq I_{out}.$$

In the system for a certain period of time Δt there is an accumulation of matter (I_{ch}):

$$I_{ch} = CV/_{t=t+\Delta t} - CV/_{t=t}.$$

Given (1), we have

$$uSC\Delta t/_{x=x} - uSC\Delta t/_{x=x+\Delta x} = CV/_{t=t+\Delta t} - CV/_{t=t}.$$

Dividing both parts of the resulting expression by $\Delta t \cdot V$ and going to the limit at $\Delta t \to 0,\ \Delta x \to 0$, we get

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x}. \qquad (2)$$

C is concentration of the substance; t - time; u - linear flow rate; x - coordinate (length of the device).

The mathematical model of ideal displacement is a partial differential equation, since the concentration changes over time and space. This model is called a distributed parameter model.

If the mathematical model of ideal displacement takes into account the source of concentration change due W to a chemical reaction, the material balance of the reactor of ideal displacement can be written as

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} - W. \qquad (3)$$

W is the rate of chemical reaction of the substance.

If the reaction is not accompanied by volume change and isothermal process, the reactor according to the kinetic law of mass action, the rate of an elementary reaction at a given temperature is proportional to the product of the concentration of the reactants in the stoichiometric ratio:

$$W = k(t)C. \qquad (4)$$

The kinetic coefficient of the reaction $k = k(t)$ is assumed to be continuous and a bounded variable function t.

Given the expression (4) in equation (3), we get:

$$\frac{\partial C}{\partial t} + u(x,t)\frac{\partial C}{\partial x} + k(t)C = 0,$$

$$0 < x < l,\ 0 < t \le T \qquad (5)$$

Assume that the following initial and boundary conditions for equation (5) are known

$$C(x,0) = \varphi(x), \quad 0 \le x \le l, \qquad (6)$$

$$C(0,t) = \theta(t), \quad 0 \le t \le T. \qquad (7)$$

Let's assume the function $k(t)$ is also unknown. You need to restore this function by the following additional condition on the right border of the area under consideration:

$$C(l,t)=r(t), \qquad 0\le t\le T. \tag{8}$$

Function $r(t)$ is specified function.

Problem (5)-(8) belongs to the class of coefficient inverse problems [4-11]. It is assumed that the approval conditions are met:

$$\varphi(0)=\theta(0),$$
$$\varphi(l)=r(0).$$

We discretize the derivative $\frac{\partial C}{\partial t}$ with the difference "back" in equation (5) at $t_j,\ j=\overline{1,m}$ and using an explicit time approximation for the reaction operator, and implicit approximations for the convective transport operator, we write the problem (5)–(8) as follows:

$$\frac{C^j(x)-C^{j-1}(x)}{\Delta t}+u^j(x)\frac{dC^j}{dx}+k^jC^{j-1}(x)=0,$$
$$0<x<l, \tag{9}$$

$$C^j(0)=\theta^j, \tag{10}$$

$$C^j(l)=r^j, \qquad j=1,2,\dots,m, \tag{11}$$

$$C^0(x)=\varphi(x). \tag{12}$$

$k^j\approx k(t_j), \quad u^j(x)=u(x,t_j).$

Suppose that the solution of the differential-difference problem (9)–(12) on each time layer $j=1,2,\dots,m$ can be represented as

$$C^j(x)=p^j(x)+k^jw^j(x). \tag{13}$$

$w^j(x),\ p^j(x)$ - are not found functions. Substituting the ratio (13) in (9), (10) will have

$$\left[\frac{p^j(x)-C^{j-1}(x)}{\Delta t}+u^j(x)\frac{dp^j}{dx}\right]+k^j\left[\frac{w^j(x)}{\Delta t}+u^j(x)\frac{dw^j}{dx}+C^{j-1}(x)\right]=0,$$

$$p^j(0)+k^jw^j(0)=\theta^j.$$

Hence, with respect to the $p^j(x),\ w^j(x)$, we obtain the following two differential-difference tasks

$$\frac{p^j(x)-C^{j-1}(x)}{\Delta t}+u^j(x)\frac{dp^j}{dx}=0,$$
$$0<x<l, \tag{14}$$

$$p^j(0)=\theta^j, \tag{15}$$

$$\frac{w^j(x)}{\Delta t}+u^j(x)\frac{dw^j}{dx}+C^{j-1}(x)=0, \qquad 0<x<l, \tag{16}$$

$$w^j(0)=0,$$
$$j=1,2,\dots,m, \tag{17}$$
$$C^0(x)=\varphi(x).$$

Substituting (13) in the redefinition condition (11), we get

$$p^j(l)+k^jw^j(l)=r^j. \tag{18}$$

Thus, we obtain the following computational algorithm for the numerical solution of the problem (5)–(8) by definition $C^j(x),\ k^j,\ \ j=1,2,\dots,m$:

For a fixed value of the time layer j, solutions to problems (14), (15) and (16), (17) are defined, i.e. functions $p^j(x)$ and $w^j(x)$ on the segment $\lfloor 0,l \rfloor$; from the relation (18), the approximate value of the desired function $k(t)$ is determined for $t=t_j$

$$k^j = \frac{r^j - p^j(l)}{w^j(l)} .$$

The formula $C^j(x) = p^j(x) + k^j w^j(x)$ is used to determine the approximation of the desired function $C(x,t)$ $(t = t_j)$. To the next time layer the described calculation procedure is repeated.

For the numerical solution of problems (14), (15) and (16), (17), the finite difference method can be used. We introduce a uniform difference grid in the area $[0 < x < l]$ of the variable x

$$\bar{\omega}_x = \left\{ x_i = i\Delta x,\ i = \overline{0,n},\ \Delta x = l/n \right\} .$$

Discrete analogs of problems (14), (15) and (16, (17) on the grid $\bar{\omega}_x$ can be represented as an implicit difference scheme:

$$\frac{p_i^j - C_i^{j-1}}{\Delta t} + u_i^j \frac{p_i^j - p_{i-1}^j}{\Delta x} = 0 , \quad i = \overline{1, n-1} , \tag{19}$$

$$p_0^j = \theta^j , \tag{20}$$

$$\frac{w_i^j}{\Delta t} + u_i^j \frac{w_i^j - w_{i-1}^j}{\Delta x} + C_{i-1}^j = 0 , \qquad i = \overline{1, n-1} , \tag{21}$$

$$w_0^j = 0 , \quad j = 1, 2, \ldots, m , \tag{22}$$

$$C_i^0 = \varphi(x_i) , \qquad i = \overline{0, n}$$

The obtained difference problems (19), (20) and (21), (22) for each fixed value $j = 1, 2, \ldots, m$ represents a system of linear algebraic equations and the solutions of these systems are determined by explicit formulas

$$p_i^j = \frac{u_i^j \Delta t}{\Delta x + u_i^j \Delta t} p_{i-1}^j + \frac{C_i^{j-1} \Delta x}{\Delta x + u_i^j \Delta t} , \quad p_0^j = \theta^j ,$$

$$w_i^j = \frac{u_i^j \Delta t}{\Delta x + u_i^j \Delta t} w_{i-1}^j - \frac{C_{i-1}^j \Delta x \Delta t}{\Delta x + u_i^j \Delta t} , \quad w_0^j = 0 .$$

4.Conclusion.

The model is obtained in the form of a first-order partial differential equation.

A computational algorithm is proposed for solving the inverse problem of finding the stoichiometric coefficient of a chemical reaction.

5. References

1. Anderson, D.A., Tannehill, J.C., Pletcher, R.H.: Vichislitelnaya qidromexanika i teploobmen (Computational fluid mechanics and heat transfer). Mir, Moscow (1990) (in Russ.).
2. Tusheva, N.V., Moises, O.E., Mityanina, O.E., Kuzmenko, K.A.: Matematicheskoe modelirovanie ximiko-texnoloqicheskix protsesov (Mathematical modeling of chemical and technological processes). Tomsk Polytechnic University, Tomsk (2014) (in Russ.).
3. Danilov, V.G., Maslov, V.P., Volosov, K., A.: Mathematical Modeling of Heat and Mass Transfer Processes. Dordrecht, Kluwer (1995).
4. Alifanov, O.M., Artioukhine, E.A., Rumyatsev, S.V.: Extreme Methods for Solving III-Posed Problems with Applications to Inverse Heat Transfer Problems. Begell House, New York (1995).
5. Samarskii, A.A., Vabishchevich, P.N.: Numerical Methods for Solving Inverse Problems of Mathematical Physics. Walter de Gruyter, Berlin. New York (2007).
6. Yang, L., Yu, J.N., Deng, Z.C.: An inverse problem of identifying the coefficient of parabolic equation. Applied Mathematical Modeling 32(10), 1984-1995(2008).

7. Kerimov, N.B., Ismailov, M.I.: An inverse coefficient problem for the heat equation in the case of nonlocal boundary conditions. Journal of Mathematical Analysis and Application 396(2), 546-554(2012).
8. Engl, H.W., Zou, J.: A new approach to convergence rates analysis of Tikhonov regularization for parameter identification in heat conduction. Inverse Problems 16(6), 1907-1923(2000).
9. Deng, Z.C., Qian, K., Rao, X.B., Yang, L., Luo, G.W.: An inverse problem of identifying the source coefficient in a degenerate heat equation. Inverse Problems in Science and Engineering 23(3), 498-517(2015).
10. Dehghan, M., Tatari, M.: Determination of a control parameter in a one-dimensional parabolic equation using the method of radial basis functions. Math. Comp. Model. 44, 1160-1168(2006).
11. Hamzayev, H.M., Huseynzade, S.O., Qasimov, Q.Q.: A numerical method to solve identification problem for the lower coefficient and the source in the convection-reaction equation. Cybernetics and System Analysis 54(6), 134-140(2018).

OR-II-3

JOINT CONVERSION OF STRAIGHT-RUN GASOLINE AND PROPANE-BUTANE FRACTION ON Co/HZSM-5/SO_4^{2-} - ZrO_2 COMPOSITE CATALYST

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Abstract. A systematic study of the catalytic conversion of mixtures of straight-run gasoline and propane-butane fraction at 160 - 200^{0}C and atmospheric pressure on a composite catalyst 0.5%Co/ HZSM-5/SO_4^{2-} (2.0%) - ZrO_2 was carried out. The influence of certain technological parameters on the change in the catalytic properties of the 0.5%Co/ HZSM-5/SO_4^{2-} (2.0%) - ZrO_2 composite system has been studied and its performance characteristics (stability, coke formation, regeneration properties) have been studied in the process of joint conversion of straight-run gasoline and propane-butane fraction . It is shown that the contact of straight-run gasoline and propane-butane fraction with the catalyst 0.5%Co/ HZSM-5/SO_4^{2-} (2.0%) - ZrO_2 under the studied conditions leads to a change in the hydrocarbon composition, which depends on temperature, and the volumetric feed rate. It was found that varying the process conditions makes it possible to increase the conversion of the mixture components above 70% with the yield of C_5-C_6 components up to 60%, containing up to 82% skeletal isomeric high-octane components.

Keywords: straight-run gasoline, propane-butane fraction, composite catalyst, zirconium dioxide, isomerization, intermediate

1. Introduction

The current state of the production of gasoline fuels requires that they contain significant amounts of branched paraffins, which are C_5-C_6 isomeric alkanes. The main supplier of raw materials for the production of these environmentally friendly components of high-octane gasolines is the light fraction of straight-run gasoline (SRG) or natural gasoline.

Analysis of the development of the process of isomerization of n-alkanes C_5-C_6 showed its rapidly increasing competitiveness in comparison with other processes aimed at obtaining components of high-octane gasolines [1]. At the same time, the schemes of the designed and reconstructed isomerization processes are mainly equipped with a recycle of low-octane pentane and hexanes, which is associated with the need to obtain gasolines that meet increasingly stringent standards.

Modern technological schemes for the isomerization of C_5-C_6 hydrocarbon feedstock are complicated by the use of deisopentanizers (DIP); deisohexonizers (DIG) by sequential inclusion the DIP and DIG in circuit; recycling n-pentane (DP) and DIG; recycle of n-pentane and n-hexane with DIP, DIG and DP [2,3]. These technological schemes for the isomerization of hydrocarbon raw materials, aimed at increasing the octane number (ON) of the fuel, are limited by the possibility of processing only C_5-C_6 alkanes isolated from them.

On the other hand, the search for additional sources of hydrocarbon raw materials, including alternative ones, involves the involvement of associated petroleum gas in the process of obtaining fuels (gasoline). The components of the associated petroleum gas (C_3-C_4) are used as alkylating agents by involving them in the reforming process with straight-run gasolines (biforming) [4]. In this way, appears a new direction of qualified processing of oil production associated gases.

The bioforming process shows the possibility of joint processing of gaseous alkanes with heavier (liquid) alkanes. However, in connection with the unsolved problem of standardizing the content of aromatic hydrocarbons in the composition of motor gasolines, it is expedient to transfer reforming units to the process of isomerization of the gasoline fraction separated from gas condensate, the process of isoselectoforming [5]. The raw material is a mixture consisting of straight-run gasoline s.b. = 62^{0}C and C_5-C_6 fraction with end boiling point of 105^{0}C (natural gasoline). The isomerization catalyst is IP-82 (alumina-platinum fluorinated and sulfated catalyst). Currently, to increase the ON isomerization uses the improved Isomalk-2 process using sulfated zirconium dioxide SI-2 [6].

An important point is the limitation imposed on the presence of gaseous alkanes in the feedstock of the Isomalk process. However, the main disadvantage of this process is its inability to process C_{7+} alkanes. Therefore, here, too, as noted above, it is required to complicate the scheme of processing raw materials with additional technical devices for a) recycle of n-C_5; b) recycling low-octane C_6; c) recycle n-C_5 and C_6.

Hence the interrelated tasks, the solution of which is necessary for the further development of this important technology for the production of modern gasoline are arise : a) increasing the resource C_5-C_6 in hydrocarbon raw materials; b) simplification of the technology of isomerization processing of hydrocarbon raw materials containing a mixture of C_5-C_6 and C_{7+} paraffins.

The aforementioned complicated technological schemes offered by the world's leading companies such as UOP (HS-10); Axens (İP-632), Sud Chemi (Hysopar), NPP Neftekhim (Isomalk) and others allow more complete processing of C_5-C_6 alkanes but leave the assigned tasks unanswered.

Considering the above, the aim of this study was to synthesize a composite catalyst for the joint conversion of straight-run gasoline and propane - butane fraction and to study the effect of certain technological parameters (temperature, space velocity, H_2/CH ratio) on the change in the catalytic properties of this composite system.

2. Experimental part

The object of the study was a composite catalytic system, the components of which are sulfated zirconia (SZ) and cobalt-modified decationized zeolite HZSM-5. The synthesis of the catalyst was carried out according to the procedure described in [7, 8].

The composition of the synthesized composite catalyst wt.%: SZ-15; Co - 0.5; binder Al_2O_3-15; rest- HZSM-5 (0.5% Co/HZSM-5/SO^{2-}_4 (2.0%) - ZrO_2 - catalyst M-11).

Straight-run gasoline (SRG), propane-butane fraction (PBF) and their mixture in a 1: 1 ratio were used as raw materials. The composition of SRG wt%: C_4 (1), *i*-C_5(1), *n*-C_5(1,2), *i*-C_6(5), *n*-C_6(3.8), *i*-C_7-(22), *n*-C_7-(6.5) and a mixture of higher molecular weight alkanes C_{8+} (59.5); composition of PBP wt. %: up to C_2(9.1), C_3(32.4), *i*-C_4(18), *n*-C_4(26.7), *i* -C_5(7.0), *n*-C_5(6.8); composition of SRG and PBF mixture wt. %: C_2(5.0), C_3(17.8), *i* -C_4(9.9), *n*-C_4(15), *i*-C_5(4.3), *n*-C_5(4.20), *i*-C_6(3.0), *n*-C_6(2.0), *i*-C_7-(10.0), *n*-C_7-(3.0)) and a mixture of higher molecular weight alkanes C_{8+} (25.8).

The joint conversion of SRG and PBF was studied in a laboratory flow-through catalytic unit equipped with a quartz reactor. The volume of the loaded catalyst was varied within 5-10 cm^3. Before the experiment, M - 11 was reduced with hydrogen at 380^0C (2 h).

The transformation of SRG and PBP on catalyst was studied at atmospheric pressure in a hydrogen atmosphere with varying temperature, space velocity of feedstock supply, and linear velocity of hydrogen. For definiteness, in the H_2/CH ratio the calculated average molecular weight of the raw material was accepted as 80g. The transformation of the SRG : PBP mixture was characterized by the following parameters; a) conversion (consumption) of C_{4-} and C_{8+} paraffins; b) a change in the concentration (accumulation and consumption) of C_5-C_6 and i-C_7-C_7 alkanes as a result of contact with the catalyst. The reaction products were analyzed by gas chromatography using an AutoSystem XL chromatograph.

3. Results and discussion

The transformation of SRG :PBF mixture on catalyst M-11 in the temperature range 160-200^0C proceeds with the formation of both gaseous C_{4-} and liquid hydrocarbon components. As seen from fig. 1, the transformation of the mixture in the temperature range 160-200^0C is accompanied by the consumption of C_{4-} and C_{8+} paraffins and the accumulation of C_5 - C_6 and iso-C_7 - C_7 components.

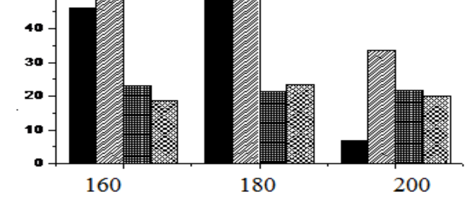

Figure: 1. Effect of temperature on the conversion of SRG + PBF on catalyst M-11.H_2/CH = 3;$WHSV_{SRG}$=2.5 h^{-1}.

Conversion: B - C_{4-}; C - C_{8+}
Accumulation: D-$\sum(C_5\text{-}C_6)$; E-$\sum(\text{i-}C_7\text{-}C_7)$

As follows from the data obtained, changes in the transformations of C_{4-} and C_{8+} components of SRG in this studied temperature range (160-200^{0}C) are complex. The C_{4-} transformation passes through a maximum at 180^{0}C, and the C_{8+} and C_{4-} conversion sharply decreases at 200^{0}C. Thus, the most optimal temperature for the joint transformation of SRG + PBP was selected 180^{0}C, and further studies were carried out at this temperature.

Table 1 shows the calculated values of the components of SRG: PBP contained in the initial mixtures of reactants. Taking into account the initial values of these components, the calculations of the conversion values (table 1) of C_{4-} and C_{8+} showed that these parameters for both components are at the level of 64-68% and only, lower contents of C_4- or C_{8+} in the converting mixture lead to an increase their conversions (77-73%). At WHSV equal to 1, the C_{8+} conversion is overestimated (73%), and at WHSV equal to 3, the C_{4-} conversion is overestimated. These data indicate the relationship between the transformations of low-molecular and high-molecular-weight components of the PSRG: PBP mixture and confirm the implementation of the process through the formation of a bimolecular intermediate of a low-molecular-weight alkane with a high-molecular one.

Table 1. Influence of the volumetric flow rate of SRG on the composition of the initial SRG: PBF mixture and their conversion on M-11 at T = 180^{0}C

WHSV_{SRG} h^{-1}	The composition of the initial mixture,wt%		Conversion, wt%	
	PBF	SRG*	C_{4-}	C_{8+}
1.0	60,8	39,2	68	73
2.0	47,7	52,3	64	65
2.5	34,2	65,8	68	68
3.0	21,1	78,9	77	68

* change in the composition of SRG components is calculated by the formula $m_i\, n_j/100\%$, where m_i is the content of the C_i component in undilutedSRG; n_j is the percentage of SRG in mixtures of SRG: PBF.

The conversion of SRG on H-zeolite/anion-modified catalysts was previously considered in [7]. A characteristic feature of this process, all other things being equal, is the formation of low molecular weight alkanes with an overestimated yield of isobutane. Taking into account this product, as well as the high content of C_5-C_6 iso-alkanes in the products of SRG conversion, it was assumed that the C_{7+} alkanes are primarily activated by their dissociative sorption on the anion-modified component and skeletal isomerization of this intermediate. As a result of the cleavage of this intermediate, transformation products of mono- and polybranched structure, as well as C_4- alkanes, are formed. It was seen from the data table. 1 that the catalysis of the transformation of the SRG : PBF mixture is not only not enriched in C_{4-} alkanes, but also actively involves them in the process. Considering this fact, as well as the similar nature of the dependence of the transformation, other things being equal, on the volumetric feed rate (WHSV) and the inability of PBF to transformations, it can be concluded that the activation of C_{7+} is primary and the involvement of low-molecular alkanes in this process is secondary. Thus, if H_2 molecules are involved in the formation of the primary intermediate, then in the process of SRG : PBF conversion, low-molecular-weight alkanes block the participation of H_2, forming a bimolecular intermediate and, therefore, suppress the unwanted cleavage of C_{7+} paraffins.

It can be seen from the data in fig. 2 that, depending on the reaction conditions, the catalyst can undergo deep deactivation.

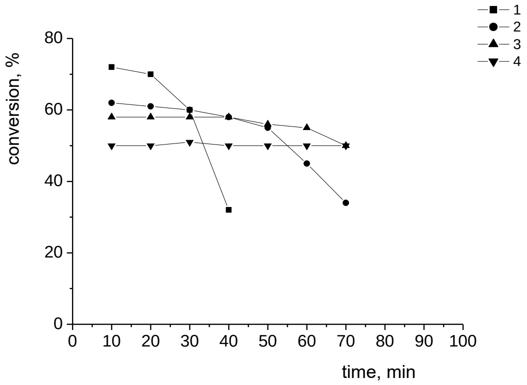

Fig 2. Influence of H_2/CH on the stability of conversion of SRG : BP (1 : 1) mixture on M-11. T = 180^{0}C; WHSV_{SRG} = 2.5 h^{-1}; GHSV_{PBF} = 500 h^{-1}. H_2/CH: 1-1; 2-2; 3-3; 4-4.

This deactivation can be facilitated by the stabilization of the bimolecular intermediate without the formation of its cleavage products and the accumulation of similar compaction products (CP) on the active surface, which have significantly higher boiling points as compared to the experimental temperature.

Table 2 shows data presenting the accumulation of CP on M-11. From these data it can be seen that during the operation of the M-11 for 1 hour, up to 1.31% of CP accumulates on it. According to fig. 2, this amount of accumulated CP corresponds to the beginning of a decrease in the activity of catalyst M-11. Further accumulation of CP on this sample by 0.10% leads to a decrease in the conversion of C_{7+} components of the reactant by more than 10%.

Table 2. Accumulation of compaction products (CP) on the composite catalyst M-11. T = 180^0C, H_2/CH = 3; WHSV = 2.5h $^{-1}$.

Catalyst	Reduction temp., ^{O}C	Time, h	CP g/g cat.	CP , %	C, g/cat	H_2,, g/cat	H/C
M-11	380	0.5	0.035	0,88	0.03	0.005	0.17
		1.0	0.052	1,31	0.045	0.007	0.16
		2.0	0.056	1,41	0.048	0.008	0.17
M-11	500	0.5	0.018	0,45	0.015	0.003	0.2
		1.0	0.027	0,67	0.023	0.004	0.17
		2.0	0.04	1,0	0.034	0.006	0.18

From the data of the elemental analysis of CP presented in table 2, it can be seen that the H/C ratio basically corresponds to the values of 0.16 - 0.18, this is within the experimental error, corresponds to the formula ($-CH_2-$) n and suggests that CP in their structure can be saturated hydrocarbons, the boiling point of which exceeds the temperature of the experiments. The products of the conversion of SRG : PBF on M-11, therefore, are not only gaseous C_{4-} and C_5-C_6 paraffins, but also CP, which are higher molecular weight hydrocarbons. However, the conversion of SRG at 140-160^0C is characterized by the absence of undesirable C_{4-} alkanes. The presence of a significant amount of C_5-C_6 branched alkanes and CP in the products shows that these intermediates undergo skeletal isomerization and cleavage (disproportionation). From the analysis of the composition of the products of the transformation of SRG at 140-160^0C it can be seen that the main hydrocarbon chain separating from the intermediates consists of four or five carbon atoms. The accumulation of C_5-C_6 products and a change in their composition is associated with the selectivity of the cleavage of the isomerized intermediate.

The presented data show that a composite catalyst consisting of the H-form of zeolite ZSM-5 and sulfated zirconium dioxide - SZ is capable of activating the low-temperature processing of SRG into C_5-C_6 alkanes with a high content of skeletal isomers. Therefore, it is of interest to consider the effect of the duration of the experiment on the functioning of this system. Figure 3 shows that the stability of the M-11 operation depends on the temperature of the catalyst treatment with hydrogen. An increase in the temperature of the hydrogen treatment of M-11 to 500^0C helps to increase the stability of functioning, but the activity of M-11 in this case decreases.

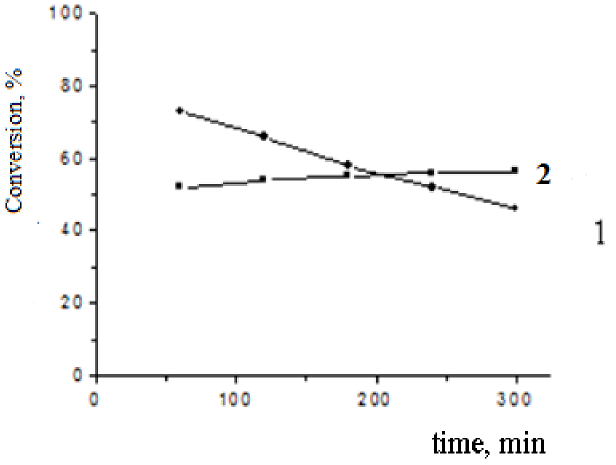

Fig. 3. Influence of the temperature of reduction of M - 11 with hydrogen on the stability of its functioning in the conversion of SRG. 1 - T_{H2} = 380^0C; 2 - T_{H2} = 500^0C

Such an effect of high-temperature, pre-treatment with hydrogen of M-11 is possibly associated with the formation of metallic cobalt and its subsequent effect on SZ, which promotes the partial reduction of this component of the catalyst system and thereby leads to a similar decrease in the activity of the catalyst.

4.Conclusion

Based on the systematic study of conversion of mixture of straight-run gasoline and butane - propane fraction at atmospheric pressure on a 0.5%Co/HZSM-5/SO_4^{2-} (2.0%) - ZrO_2 composite catalyst, the following conclusion was made:

1. It was found that, within the studied conditions, the conversion of the SRG : BF components exceeds 70% with the yield of C_5-C_6 alkanes containing up to 82% of branched high-octane components.

2. It has been shown that an increase in the H_2/CH ratio from 1.0 to 4.0 contributes to an increase in the stability of the catalyst operation from 60 to 300 minutes.

3. It was found that the cause of catalyst deactivation is the accumulation of hydrocarbons on its surface with a boiling point exceeding the reaction temperature.

4. References

1. Kapustin B.M. On new directions of oil refining and petrochemistry in Russia. In: IX Baku International Mammadaliyev Conference on Petrochemistry, pp.24-25. Baku (2016.
2. Development trends of the isomerization process in Russia and abroad. Oil and gas business. http / www.or-bus.ru.
3. Akhmetov A.F. Comparative analysis of various schemes of isomerization of pentane-hexane fraction. Oil refining and petrochemistry. **2,** 22-25 (2008).
4. Likholobov V.A., Lavrenov A.V., Tsekhanovich M.S. International application PCT/24 2006/000066, No. 2007/091912A1. Institute of Hydrocarbon Processing Problems RAS (2007).
5. Bannov P.G. Oil refining processes. Nefteximiya, Moskow (2000).
6. Shakun A. N., Fedorova M. L. New advances in the isomerization of C_5-C_6 fractions. VI International Forum "Fuel and Energy Complex of Russia", pp. 162-166. Moskow (2004).
7. Abasov S.I., Agaeva S.B., Mamedova M.T., Iskenderova A.A., Imanova A.A., Zarbaliev R.Z., Isaeva E.S., Tagiev D.B. Conversion of straight-run gasoline into C_5-C_6 alkanes on composite catalysts Co (Ni) HZSM-5/ SO_4^{2-} /ZrO_2. Journal of Applied Chemistry. **92**, 197-203 (2019).
8. Abasov S. I., Agaeva S. B., Mamedova M. T., Tagiyev D. B. Joint conversion of n-hexane and n-butane on zirconium - zeolite catalysts. Catalysis in industry. **15**, 73-78 (2015).

OR-V-6

DEPENDENCE OF OIL AND GAS TRANSPORTATION PIPELINES ON PHYSICAL AND CHEMICAL FACTORS

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Abstract. During the research, the physicochemical factors affecting the object were investigated and methods of elimination were developed:

Innovative methods of corrosion protection to increase the service life of equipment and transport pipelines, as well as a statistical method to determine the dependence of the capacity of well equipment and transport pipelines on mechanical, physical and chemical factors; complex-acting, multifunctional, thermally resistant, bactericidal type new corrosion inhibitor based on naphthenates has been developed.

Keywords: physicochemical factors, innovative methods, pipelines, corrosion inhibitor, mathematical statistical method, corrosion protection.

1. Introduction

When steel samples are immersed in a neutral salt solution, their surface corrodes. If the surface of these specimens is periodically scrubbed, the corrosion rate becomes more intense than on the untreated surface. Here the oxidized surface plays a protective role. Experiments show that the regularly cleaned surface of the steel metal, under the influence of a neutral salt solution, directs the potential of the steel in a negative direction of a few millivolts. Thus, there is a potential difference between the untreated surface of the sample and the cleaned surface. This process can be applied to the corrosion of oilfield equipment used in aggressive oil and gas systems. Given that more than 90% of wells in dry oil fields are operated by borehole depth pumps, there is a potential difference between the friction-free surface and the untreated surface during the movement of the depth pump rods on the inner surface of the pump-compressor pipes [1, 2]. As the friction on the metal surface deepens, the potential difference between the oxide layer, which plays a protective role, increases. Without friction between the pump compressor tubes and the rods, the metal surface is cleaned of the oxide layer, and a macro pair is formed between the untreated surface and the cleaned surface. The cleaned part acts as an anode function. In addition, mechanical impurities in the system (quartz sand) are involved in the corrosion (scraping or scraping) of the oxide layer in the metal. On the other hand, the equipment and lift pipes of wells operated by a submersible pump (depending on the depth of the well) operate intermittently under constant voltage.

Thus, the processes of corrosion and corrosion-erosion in well-equipment systems and transport pipelines are multifactorial. This problem is solved in the classical method by changing one parameter and keeping the remaining parameters constant. However, such an approach to the issue takes a long time. Thus, each factor requires its own set of experiments [3-8]. This is not used in studying the effects of other factors. For example, the intensity of corrosion and mechanical-corrosion erosion of wellhead equipment and transport pipelines depends on various factors: the rate of corrosion of steel, the influence of aggressive formation waters, surface tension, fluid flow rate, service life, the impact of aggressive gases, etc. depends. The effects of each of these factors have been studied separately. However, no research has been conducted to study the combined effects of these factors.

2. Experimental part

To solve the problem, a mathematical statistical method was proposed by obtaining simple analytical expressions that connect various mechanical and physicochemical factors with the main indicators of the process. A mathematical model of corrosion and mechanical corrosion is developed using the group accounting method of arguments. This method differs from other mathematical methods by its high level of correlation and low initial values. Provides a record of the impact of various factors during the process and identifies the factor that affects them the most. In general, the function of the process is as follows:

$$y = a_1 \cdot f_1(x_1,\ x_2, \dots, x_n) + a_2 \cdot f_2(x_1, x_2, \dots, x_n) + \dots + a_m \cdot f_m(x_1, x_2, \dots, x_n) \quad (1)$$

The solution of the problem of determining the dependence of the performance of pump-compressor pipes on the influence of mechanical and physicochemical factors was carried out in 2 stages. In the first stage, the process of corrosion of steel pipes in the oil and gas environment was studied, and in the second stage, the service life of pump-compressor pipes was studied.

In order to obtain a physical model of the corrosion process of steel in the form of corrosion in the oil and gas system, 2 massive initial indicators of sodium hydrocarbonate - "alkali" and calcium chloride – ‘hard’ type produced waters typical for oil fields of Azerbaijan were given. In both cases, the variable and total experimental values are n = 11 and N = 50. The actual corrosion rate in the flow of 45 grade steel metal oil and gas system was determined on a laboratory device. The velocity of the liquid in the discharge channel is determined by the following formula:

$$V = 0{,}032 \cdot \mu \cdot \sqrt{2gH} \qquad (2)$$

Here, V - the flow rate of the liquid, in m / s;

H - water manometer reading, in mm;

μ - 0.82 - coefficient of hydraulic resistance;

g - 9, 81 m / sec release emergency.

According to Kulbak's formula, the awareness of the indicators included in the array was estimated

$$j(x_j^i) = D \cdot k(x_j^i) \cdot \frac{1}{2}\left[p\left(\frac{x_j^i}{A}\right) - p\left(\frac{x_j^i}{B}\right)\right] \qquad (3)$$

where, - $D \cdot k(x_j^i)$ i in the range j - diagnostic coefficient in the sign;

$p\left(\frac{x_j^i}{A}\right)$- j - probability to fall into group A in the sign;

$p\left(\frac{x_j^i}{B}\right)$ - j - probability to fall into group B in the sign.

Calculations show that the characters included in the array are arranged in the following order according to the information:

fluid flow rate -J = 3.20;

The amount of H_2S J- = 1.65;

amount of oil - J= 1.02;

water stability - J= 0.78;

amount of chlorides J - = 0.67;

pH (environment) J- = 0.63;

minerality - J = 0.53;

oil activity - J = 0.48;

temperature - J = 0.40;

amount of bicarbonates - J = 0.21;

After processing the experimental parameters, a physical model of the corrosion process in steel was obtained:

- in the oil and gas system storing sodium hydrocarbon type water:

$$y_1 = 0{,}06441 \cdot \frac{x_9\sqrt{x_6 \cdot x_7}}{\sqrt{x_{12}}} + 1{,}564 \cdot \frac{1}{\sqrt{x_{10}}} - 0{,}1402 \cdot \frac{\sqrt{x_{11}}}{\sqrt{x_7 \cdot x_9}} - 2.611 \cdot \frac{\sqrt{x_{10}}}{x_2 \cdot \sqrt{x_7}} + \\ + 0{,}0343 \cdot \frac{\sqrt{x_1 \cdot x_3 \cdot x_8}}{x_6} - 1.142 \cdot \frac{\sqrt{x_5 \cdot x_{12}}}{x_6 \cdot \sqrt{x_9}} \qquad (4)$$

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$$y_2 = 0{,}1312 \cdot x_9 \cdot x_{12} \cdot \sqrt{x_7} + 2.6001 \cdot x_9 \cdot \sqrt{x_6} - 50{,}9 \cdot \frac{\sqrt{x_5}}{x_6 \cdot \sqrt{x_7} \cdot x_8} + 0{,}8255 \cdot \frac{1}{\sqrt{x_{10}}} - 2{,}968 \times \qquad (5) \\ \times \frac{x_9 \cdot \sqrt{x_1}}{\sqrt{x_2 \cdot x_{12}}} - 0{,}01705 \cdot x_{11} \cdot \sqrt{x_1 \cdot x_4 \cdot x_5}$$

Here: y_1 - corrosion rate of 45 grade steel in dissolved gases (H_2S, O_2 and CO_2) and oil-containing “alkaline” type formation water, g /m^2 · h;

y_2 - corrosion rate of 45 grade steel in dissolved gases (H_2S, O_2 and CO_2) and oil-containing "cod" type formation water, g / m^2 · h;

x_1 - total mineral content of produced water, kg / m^3;
x_2 - amount of sodium and potassium chloride in water kg / m^3;
x_3 - fluid flow rate, m / sec;
x_4 - amount of calcium and magnesium chlorides in water, kg / m^3;
x_5 - amount of calcium and magnesium hydrocarbons in water, kg / m^3;
x_6 - pH environment;
x_7 - amount of hydrogen sulfide in water, g / m^3;
x_8 - ambient temperature, ° C;
x_9 - fluid flow rate, m / s;
x_{10} - amount of oil in the system,%;
x_{11} - coefficient taking into account the percentage of organic acids, wetting the metal surface, in water and oil;
x_{12} - coefficient of water stability - pH of pH environment.

$$(J = pH / pH_{sat.});$$

$pH_{sat.}$ corresponds to the equilibrium state of the solvent and is determined by the following formula:

$$pH_{doy.} = pK_2 - pS_{CaCO3} - \lg[Ca^{2+}] - \lg[Q_{ümumi}] + 2{,}5\mu + 7{,}6. \quad (6)$$

Here, p is the total amount of salts in water in g / m^3;
K_2 is thermodynamically stable;
S_{CaCO3} - is a solution;
Ca^{2+} is the concentration of calcium ion in g / m^3;
Q_{total} is the total alkalinity of water – wiz q - ekv/m^3;
μ is the ionic strength of the solvent.
The obtained dependence shows a high correlation of 0.872 and 0.932, respectively.

The absolute errors of the calculated values of the corrosion rate in relation to the actual values in practice are as follows:

- $\Delta y_1 = \pm$ 0,3 g / m^2 · hour (average square error 6.4%) for produced water of sodium bicarbonate type;
- for calcium chloride type formation water$\Delta y_2 = \pm$ 0,185q/m^2 · h (average square error 3.5%).

3.Results and discussion

With the help of the obtained model, sodium bicarbonate type water (“alkaline” type) and active oil, calcium chloride type (“cod” type) produced water and low-active oil and gas system containing up to 500 g / l H_2S, 25 to 100 Under the specific operating conditions of the equipment operated in the range of °C, the liquid flow is from 0.1 to 1.0 m / sec. The corrosion rate of 45 grades of steel was calculated at the rate of 50 to 98% of the irrigation.

The corrosion rate of the medium containing sodium hydrocarbonate ("alkaline" type), the minerality and pH of which are as follows, is calculated for 4 cases:

- 50mg - eq / 100g and pH = 8.0 - 8.5; 100 mg-eq / 100g and pH = 7.5 - 8.0; 150 mg-eq / 100g and pH = 7.0–7.5; 200 mg - eq / 100g and pH = 6.5 - 7.0; (Appendix 1 - 4).

The corrosion rate for a medium containing calcium chloride (‘hard’ type) aquifers with mineral content and pH is calculated for 4 cases:

-250 mg-eq / 100g and pH = 6.2 - 6.7; 350 mg-eq / 100g and pH = 5.9 - 6.4; - 450 mg-eq / 100g and pH = 5.6 - 6.1; 550 mg-eq / 100g and pH = 5.3–5.8 (Appendix 5–8).

With the help of these tables, it is possible to accurately determine the rate of corrosion erosion in well equipment by knowing some information about the physical and chemical composition, properties, irrigation ratio and well temperature in the absence of mechanical wear and friction.

As a result, the following dependence was obtained after processing the indicators:

$$Z_1 = 229{,}1 \cdot \frac{x_{13}}{\sqrt{x_{15} \cdot x_{16} \cdot x_{18}}} + 0{,}2924 \cdot \frac{x_{14}}{x_{17} \cdot \sqrt{x_{15} \cdot x_{18}}} + 53{,}48 \cdot \frac{x_{13}}{\sqrt{Y \cdot x_{16}}} - 1285 \frac{x_{13} \cdot \sqrt{x_{18}}}{x_{14}} \tag{7}$$

$$Z_2 = 0{,}03365 \cdot \frac{x_{13}^6}{\sqrt{x_{16} \cdot x_{18}}} + 7{,}234 \cdot \frac{x_{13}^2}{x_{17} \cdot \sqrt{Y \cdot x_{17}}} - 0{,}7689 \cdot x_{13}^2 \cdot x_{16} \cdot \sqrt{x_{17} \cdot x_{18}} \tag{8}$$

Here: Z_1 and Z_2 - the service life of the pump-compressor pipe set made D of branded steel, expressed in days, in wells operated by rod and non-rod operation;

Y - g / m^2 · is the corrosion rate of 45 grades of steel, expressed in pump-compressor pipes, 45 grades of steel, installed on the well discharge line and stored for 18 ... 20 days;

The calculation by the Kulbak formula shows the curvature of the wellbore

J = 2.84; corrosion rate - 0.67;

x_{13} - pipe wall thickness, in mm;

x_{14} - is the coefficient characterizing the gap between the pump compressor pipe and the rod belt, which determines the relationship between the diameter of the pipe and the diameter of the belt;

x_{15} - m / min, which characterizes the total length of the deep-pump rod set that can pass through the pump-compressor pipes. is a parameter expressed by;

x_{16} - pump suspension depth, in m;

x_{17} - amount of mechanical mixture (quartz sand) in the product in kg / m3;

x_{18} - coefficient expressed in rad./m, which characterizes the ratio of the curvature of the wellbore to the unit depth of the well;

$$x_{18} = \Delta / l \tag{9}$$

Here: Δ - l the curvature of the wellbore in cross section, rad. l - section length, in m.

The size of D should be determined taking into account the curvature and azimuth of the body. For pipes is determined by the following formula:

$$\Delta = \sqrt{\delta_1^2 + \delta_2^2 - 2\delta_1 \cdot \delta_2 \cdot cos\Delta \cdot \beta} \tag{10}$$

Here, δ_1 - l - the curvature of the wellbore at the beginning of the interval, - l -rad; δ_2 - l - curvature of the wellbore at the end of the interval, l - rad., $\Delta \cdot \beta$ - difference in azimuths at the beginning and end of the interval, l - rad. Δ və β an inclinogram of the well (special scale).

Analysis of formulas (7) and (8) shows that the performance of pump-compressor pipes is mainly related to:

- occurrence of mechanical wear due to vibrations between the pump compressor pipes and the depth pump rods; where the curvature of the wellbore and the dynamic load (tension) in motion are taken into account.

- figurative erosion, depending on the gap between the pipes and the rods, the amount of mechanical impurities (quartz sand) in the well product;

- corrosion of pipes under stress (under pressure);

Knowing the specific technological parameters of wells and piping systems, it is possible to determine the service life of the pump-compressor pipe set, as well as pipelines, by the above method.

The performance of equipment and transport pipelines in well-assembly systems depends on the corrosion and corrosion-erosion effects of the produced well products, the erosion of the surfaces in contact with the vibrations, and many other factors.

The informative evaluation of these symptoms by the Kulbak method shows that;

- Spillage of steel metal in the oil and gas system as a result of KP depends on the flow rate of the liquid, the amount of hydrogen sulfide, carbon and oxygen gas in the well product, minerals (mainly chlorides, hydrocarbons and carbonates), ambient temperature, pH, oil surface activity, formation water stability. coefficient and so on. depends.

- The performance of the equipment in the conditions of mechanical-corrosion wear depends on the curvature of the wellbore, the rate of corrosion of the equipment material in the well product flow, the suspension depth of the lift pipes, the wall thickness, the gap between the pump compressor tubes and the rod belt, fluid removal rate and amount of mechanical impurities.

4. Conclusion

During the research, the physicochemical factors affecting the object were investigated and methods of elimination were developed:

Innovative methods of corrosion protection to increase the service life of equipment and transport pipelines, as well as a statistical method to determine the dependence of the capacity of well equipment and transport pipelines on mechanical, physical and chemical factors. Complex-acting, multifunctional, thermally resistant, bactericidal type new corrosion inhibitor based on naphthenates has been developed;

The technology of insulation of the surface of metal pipes with coatings made of non-corrosive, shock-resistant and corrosion-resistant basalt-plastic and glass-plastic materials has been developed. Possibility of application of basalt-plastic and glass-plastic materials in construction and repair of tanks and other capacities was studied;

Technologies for the production of protective belts, pump compressors and transport pipes, as well as pump rods from pure basalt-plastic and fiberglass materials in the highly corrosive oilfield environment were developed and their application together with metal pipes and rods was analyzed.

5.References

1. Abbasov E.I. On the issue of improving the performance of downhole sucker rod pumps. Collection of abstracts of the 69th international youth scientific conference. Oil and Gas - 2015, Moscow, 2015.
2. Budzulyak B.V. Self-regulation in the field of corrosion protection of oil and gas facilities. Gas industry, Moscow: 2010, No. 3, pp. 16-19.
3. Glazov N. P. Improving the effectiveness of anti-corrosion protection of steel pipelines. // Protection of metals, M .: 2001, T37, No. 5, p. 464-470.
4. Ibragimov N.G., Mutin I.I., Chernova N.V. Operation of tubing - compressor pipes with an internal polymer coating. "Oil industry" M .: 2007, pp. 82-84.
5. Ismailov G.G., Kurbanov M.M., Sadikhov R.E. Protected against corrosion of pipelines transporting high viscosity oil. International forum-competition for young scientists. The problem of subsoil use Sat, scientific gr. St. Petersburg, 2017, 19-21 April, pp. 133-135
6. Ismailov G.G., Kurbanov M.M., Sadikhov R.E. Corrosion-resistant composite basalt-plastic casing for oil wells. Oil-field business. Moscow, 2017. N8, pp. 48-50.
7. Kerimov O.M., Kurbanov M.M., Sadikhov R.E. Corrosion protection of oil tanks. The practice of anti-corrosion protection. Moscow, 2016, N4 (82). pp. 41-44.
8. Kerimov O.M., Kurbanov M.M., Sadikhov R.E. Composite-plastic sucker rods. European Applied Sciences. (Stuttgart, Germany). Section 7, Technical sciences # 8, 2016. pp. 29-31.
9. Kerimov O.M., Kurbanov M.M., Sadikhov R.E. Determination of the operability of underground equipment of oil wells, depending on the influence of mechanical and physicochemical factors. Equipment and technologies for the oil and gas complex. Moscow, 2016, No 6, pp. 45-48.
10. Novitsky V.S., Pischik L.M. Corrosion control of technological equipment. “Naukova Dumka”, Kiev: 2001, 170p.
11. Sadiqov R.E. Development of technologies for increasing the efficiency of well equipment and oil-pipe pipelines. ADNSU, Azərbaycan Ali Texniki Məktəblərinin Xəbərləri. Bakı. 2020. No. 3.
12. Taria L. Localized corrosion of stainless steel in chloride, sulfate and thiosulfate containig environments Corros. Sci., 2000, 42, No. 3, pp. 421- 441.

PP-V-4

CHLOROMALEIC ACID BISPHENYL ESTERS PRODUCTION TECHNOLOGY

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Abstract: As you can see, with the aim of rational organization of the experiment and to achieve the maximum yield of the target products, we translated the regression modeling of the process, based on the methods of planning experimental experiments. Based on the obtained regression equations, the adequacy of the proposed regression model was checked.

Key words: regression equations, dichloromaleic acid, modulation

1.Intrudaction

It is now known that the spatial structure of biologically active compounds has a decisive influence on their properties. In this regard, the search for drugs with biological activity, as well as the identification of the correlation between the activity and the structure of the synthesized compounds is an urgent problem.

2.Metod

As you know, all the proposed substances have phytotoxicity of various degrees of activity. The most toxic for seedlings were bis (2,5-dichlorophenyl ester) dichloromaleic acid, bis (3,4-dichlorophenyl ester) dichloromaleic acid and bis (2, 4, 6-trichlorophenyl ester) dichloromaleic acid.

The results of our studies of the bisphenyl esters of maleic, mono- and dichloromaleic acids synthesized by us as biologically active compounds showed that all of them mainly exhibit biological activity.

As the research results have shown, it is not always possible to make a clear correlation, since an increase in the number of chlorine atoms or nitro groups did not always lead to positive effects. The presence of these groups and atoms with a double bond in the compounds also played a role. However, some tendencies associated with an increase in the number of heteroatoms in a molecule were found.

It was also revealed that the activity of compounds largely depends on the arrangement of atoms and groups in the molecule of the substance.

For a number of years at the Institute of Catalysis and Inorganic Chemistry, original work has been carried out on the study of the preparation of bis-phenol esters of chlorine derivatives of maleic acid. Distinctive features of the processes under study are high yields of whole products with high selectivity.

3.Results and Discussion

The development of modern chemical science requires a deeper study of reactions that make it possible to create flexible and economic processes. In recent years, much attention has been removed by a new available method for obtaining chemical compounds having a number of reactive and functional groups and atoms. These compounds include polychlorinated 2,5-dihydrofurans-2, as well as aromatic bis-esters of maleic acid derivatives, which are widely used in various sectors of the national economy. Knowledge of the mechanism and study of the kinetic laws of these reactions makes it possible to more purposefully control them.

In order to obtain aromatic bis-esters of chloro derivatives of maleic acid, we first studied the interaction of dichloromaleic anhydride (DCMA) with phenols [2].

Preliminary experiments have shown that, in our case, the interaction of phenols with maleic anhydride (MA) and its chlorine derivatives gives stable β-complexes, which prevents the formation of bis-esters. The formation of these complexes was recorded with Specord UV VIS UV spectrophotometers.

The creation of an effective method for the synthesis of compounds having a number of reactive groups and atoms in the molecule, will significantly expand their application in the chemical industry: drugs, dyes, varnishes, additives to oils, intermediate products, etc.

It is known that some derivatives of both dicarboxylic acids and their analog derivatives and phenols exhibit biologically active properties.

To obtain phenyl esters of carboxylic acids, phenols often react with acid anhydrides, in contrast to alcohols, which interact with the acids themselves.

The introduction of phenols into the molecule of these compounds in order to obtain bis-phenyl esters of maleic, mono-, and dichloromaleic acids should enhance these properties. In our work, we study the reaction of interaction of polychlorinated 2,5-dihydrofuran-2 with various phenols. This produces a new group of compounds of the ether class. 5,5-dichloro, 4,5,5-trichloro and 3,4,5,5-tetrachloro-2,5-dihydrofuranones-2 ...

As you know, phenols are easily oxidized and colored in air. Therefore, they were purified by vacuum distillation or recrystallization.

The synthesis of bis-phenol esters of maleic, mono- and dichloromaleic acids was carried out by a one-step method in acetonitrile or acetone by the reaction of 5,5-dichloro, 4,5,5-trichloro and 3,4,5,5-tetrachloro-2,5-dihydrofuranones -2 with various phenols in the presence of anhydrous sodium carbonate.

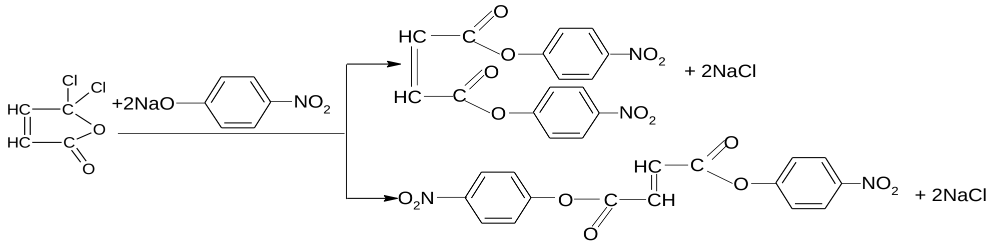
The study of the reaction of interaction of polychlorinated 2,5-dihydrofuranones-2 with phenols was carried out in a batch reactor, which is a three-necked thermostated flask, the temperature constancy of which was controlled using LATR a with an accuracy of + - 10 and controlled by a thermometer. The reactor is equipped with a high-speed stirrer and a reagent feed port. The synthesis of bis-phenyl esters of maleic acid and their chlorine derivatives was carried out as follows. Sodium carbonate and a solvent acetonitrile were loaded into the reactor with constant stirring and a given temperature, then polychlorinated 2,5-dihydrofuranones-2 were added. The phenol previously dissolved in acetonitrile is then added immediately. This moment is considered the beginning of the experiment. Stirring was continued till the end of the experiment. At the end of the reaction, the reaction mixture is poured into distilled water, where the resulting bis-phenol esters of dichloromaleic acid are precipitated. The rest of the components and reaction products are dissolved in water. Obtained target products are filtered off, washed with water, dried and determined quantitatively and qualitatively. Prelimina¬ry experiments have shown that the result of the interaction of maleic anhydride (MA) with phosphorus pentachloride (PF), on the basis of which polychlorinated 2,5-dihydrofuranones-2 are obtained, depends on three parameters: temperature, reaction time and molar ratio of the starting components (MA: PF). By varying these parameters, one or another polychlorinated 2,5-dihydrofuranone-2 can be obtained. In order to organize the experiment rationally and to achieve the maximum yield of the target products, we carried out regression modeling of the process, mainly based on the methods of planning extreme experiments. We have shown that the yield of polychlorinated 2.5-dihydrofuranones-2 depends on three variable factors: temperature (X1), contact time (X2), and the MA: PF molar ratio (X3).

The coefficients of the regression equation were calculated and, after insignificant coefficients, the corresponding dependences of the yields of bis (4-nitrophenior ether) of maleic and fumaric acids on the controlled parameters were obtained in the form of the following normalized renression equations:

$$\hat{Y}_1=42.13-13.37X_1+4.81X_3-5.48X_1^2-5.03X_2^2-4.61X_3^2$$

$$\hat{Y}_2=51.74+21.33X_1-5.76X_2+6.20X_3-3.64X_3^2$$

The reaction mechanism can be represented as follows:



The effect of temperature on the reaction was investigated in the range of 273-298K with a constant reaction time (τ = 1.6 h) and the ratio of the starting components (DCDHF: NPN = 1: 2.52). The research results are shown in Figure 1.

As can be seen from this figure, with an increase in temperature from 273 K to 276 K, the yield of the main product, bis (4-nitrophenyl ether) of maleic acid (BNPEMA), increases from 47.1% to 50.8% of the theoretically possible, and a further increase in temperature up to 298K leads to a decrease in its yield to 24.8%. The yield of bis (4-nitrophenyl ester) fumaric acid and the conversion of DCDHF are constantly increasing. The selectivity for BNPEPA is high at relatively low temperatures.

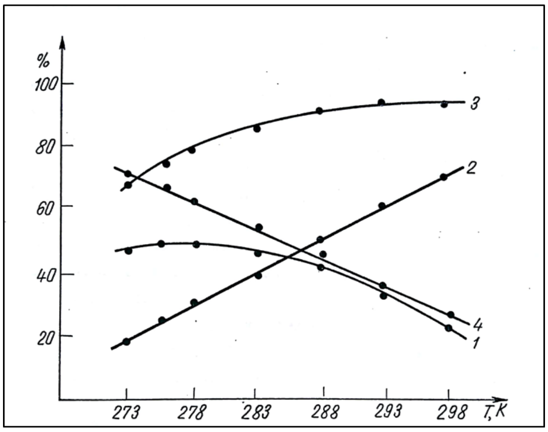


Fig: 1. Influence of temperature on the yield of the reaction products of the reaction of 5,5-dichloro-2,5-dihydrofuranone-2 with sodium 4-nitrophenolate (τ = 1.6 h; DCDHF: CPN = 1: 2.52.)

Next, we studied the influence of the reaction time on the process from τ = 0.5 h to τ = 2.5 h with the remaining optimal parameters being constant (T = 276 K; DCDHF: NFN = 1: 2.52). The research results are shown in Figure 2.

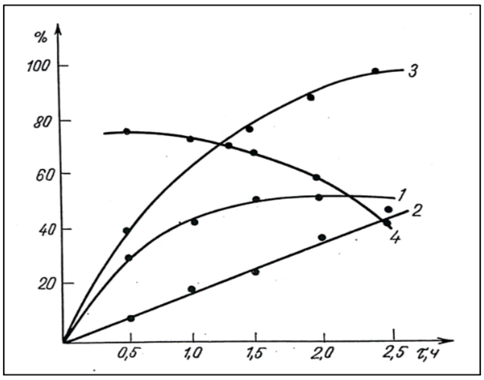


Fig. 2. Influence of the duration of the experiment on the yield of the reaction products of the reaction of 5,5-dichloro-2,5-dihydrofuranone-2 with sodium 4-nitrophenolate (T = 276 K; DCDHF: NFN = 1: 2.52).

As shown in Figure 2, a change in the reaction time from 0.5 to 1.6 h leads to an increase in the yield of the target product - BNFEMK to the maximum value (50.8%); a further increase in the reaction duration has almost no effect on the BNPEMC yield. The yield of BNFEMC constantly increases with an increase in the reaction time, while the selectivity for the target product (BNFEMC) is constantly decreasing.

The optimum temperature of 276 K was selected from the studies performed, while the yield of the target product, BNPEPA, was 50.8%, and the selectivity for it was 68% with a conversion of DCDHF of 75%.

To determine the optimal conditions for carrying out the processes of obtaining 5,5-dichloro-, 4, 5, 5-trichloro and 3,4,5,5-tetrachloro-2,5-dihydrofuranones-2, experiments were carried out on a preliminarily drawn up matrix of experiment planning. The plan of the second order was chosen, which was used as the optimal rotatable central compositional plan. The core of the design was the design of a complete n-factor experiment (Table 1).

Table 1. Complete factorial experiment in planning production polychlorinated 2,5-dihydrofuranones-2

	Tempera ture	**Contact time**	**Molar ratio MA: PF**	**Outputs**		
				DHDHF	**TCDHF**	**TeHDGF**
	X_1	**X_2**	**X_3**	**%**	**%**	**%**
1	+1	+1	+1	75,1	32,0	98,8
2	-1	+1	+1	64,0	23,5	65,0
3	+1	-1	+1	68,5	22,3	96,4
4	-1	-1	+1	59,9	18,6	57,0
5	+1	+1	-1	78,6	20,0	68,4
6	-1	+1	-1	59,7	26,4	51,0

7	+1	-1	-1	67,6	18,0	60,5
8	-1	-1	-1	58,0	15,0	44,0
9	+1,42	0	0	91,9	36,5	99,0
10	-1,42	0	0	40,3	15,5	25,3
11	0	+1,42	0	90,6	36,0	98,5
12	0	-1,42	0	67,8	11,5	60,4
13	0	0	+1,42	55,0	20,7	98,8
14	0	0	-1,42	57,0	17,7	47,0
15	0	0	0	96,7	42,0	98,9
16	0	0	0	97,8	38,0	97,0
17	0	0	0	95,4	39,9	98,9
18	0	0	0	97,6	39,5	99,3
19	0	0	0	98,9	38,8	98,4
20	0	0	0	95,9	40,0	97,4

4.Conclusions

We have developed a scientific basis for a flexible technology for the production of various polychlorinated 2.5-dihydrofuranones-2 based on MA and PP. It is shown that carrying out the reaction in a melt with constant distillation of by-products during its course leads to high yields and selectivities for the target products. Thus, it was shown that the synthesized bis-phenolic ethers exhibit biologically active properties.

5. References

1. Traven, V.F. Organic chemistry: textbook T.2 / V.F. Grass. - M: Binom. Knowledge Laboratory, 2016 .-- 520

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INTEGRATED APPROACH TO OPTIMIZE PROCESS PRODUCTION PLANNING WITH ACCOUNTING OF UTILITY SYSTEM

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Abstract. The mathematical model of integration of production planning and the energy system for the oil refining complex (ORC) is considered. It is shown that a method which takes into consideration the integration of production planning and its energy supply system allows to optimize the energy consumption of the petrochemical process and to maximize the overall profit of the ORC, in comparison with the method of sequential calculation gives credible results for organizing the effective functioning of ORC. The integrated approach, which combines the production and the utility systems, is optimized in the model of mixed integer non-linear programming using the example of ORC and, as calculations show, provides a more efficient relationship between the production and the utility units. The energy consumption model is based on the relationship of energy consumption with the operating mode of production units and their performance. The material balance of the intermediate product, such as fuel gas, fuel oil, as well as the balance of energy production and consumption by various utility are optimized considering the energy used. The effectiveness of the method has been demonstrated on the example of a real ORC.

Keywords: oil refinery complex, mathematical model, sequential approach, integrated approach, mixed integer non-linear programming.

1. Introduction

Modern enterprises pay special attention to the optimization of the technological processes due to the coordination of production in real time. Currently, there are in general four main directions which can be considered for system integration regarding the using of raw materials, energy consumption, emissions, controlling of technological processes. Taking into account any element from each direction during system integration requires knowledge of the characteristics of each of them. The implementation of the necessary integrations in this regard is carried out on the basis of methodological approaches developed for these aims, mathematical methods and optimization models [1, 2]. System integration, which takes into account the combination of separate automated processes and management tools, is directed to increase the effectiveness of functioning of the complexes, organizations, enterprises. With the automation of an increasing number of technological objects, many enterprises are faced with a situation where there are many unrelated local process control systems with different interfaces and archive formats [3, 4]. The creation of automated systems for accounting and control of material flows allows us to solve complex problems of production logistics at 2 levels:

- track the chain of movement of materials / raw materials through various production stages by introducing “control points” into the production lines (level of process control system)
- in real time mode, monitor quantitative and qualitative changes in material flows, identify inefficient technological processes, unused capacities [5, 6].

As a rule, oil refinery complexes based on functioning usually separately production and utility systems. At the same time, refineries produce not only gasoline, diesel fuel, etc., but also consume energy from the communal system — some by-products. By-products are fuel resources prepared in the form of fuel oil and fuel gas. These fuel resources can be used to maintain the continuous operation of steam generators and power generators. With this approach, the cost of fuel materials for all manufacturing enterprises will be lower than the cost of purchased. Consequently, taking into account the interaction between production systems can ensure efficient use of energy and economic profit.

In this paper the optimization of the functioning on the example of the SOCAR oil refining complex is studied and the results of two - sequential and integrated approaches are discussed.

2. Experimental part

Two types of approach - sequential and integrated - are used to optimize the operation of petrochemical complexes.

2.1. Sequential approach

The traditional optimization method for these two systems is a consistent hierarchical approach. At the initial stage of this approach, an optimal distribution of products and process flows is achieved to ensure the efficient use of raw materials. At the second stage, based on the results of production planning, the total energy requirements for processing enterprises are calculated. Meeting the requirements of utilities, at the final stage the work of utilities is optimized and fuel costs are minimized to meet the various needs of the refinery [7, 8]. In the traditional approach, production and utility systems are separated. Such a separation is the disadvantage of a consistent method, that is, when optimizing each system individually, there will be no economic benefit. As a result, the energy produced by the communal system will not be fully utilized. Therefore, there is a need for effective optimization of the integration of the two systems in the oil refining complex.

2.2 Integrated approach

Some research has been done to integrate manufacturing and utility planning and operational planning using newly developed integrated models. As a rule, oil refinery complexes based on functioning usually separately production and utility systems. At the same time, refineries produce not only gasoline, diesel fuel, etc., but also consume energy from the communal system - some by-products. By-products are fuel resources prepared in the form of fuel oil and fuel gas. These fuel resources can be used to maintain the continuous operation of steam generators and power generators. With this approach, the cost of fuel materials for all manufacturing enterprises will be lower than the cost of purchased. Consequently, taking into account the interaction between production systems can ensure efficient use of energy and economic profit. At the same time, refineries produce not only gasoline, diesel, etc., but also consume energy from the communal system - some by-products. By-products are fuel resources. These fuel resources can be used to maintain the continuous operation of steam and electricity generators. With this approach, the cost of fuel materials for all manufacturing enterprises will be lower than the cost of purchased. Consequently, considering the interaction between production systems can ensure efficient use of energy and economic profit. At the initial stage of used approach, an optimal distribution of products is achieved. At least, at the final stage of the work utilities can be optimized and for satisfy of the various needs of refineries, minimized the fuel costs [9,10]. The energy consumption model of a production unit is introduced considering the relationship of energy consumption mode of production units and their performance. The material balance of an intermediate product, as well as the balance of energy production and consumption by various utilities, is optimized taking into account the energy used [11, 12].

$$COST = \sum_{t}^{T} \sum_{j \in BOIL} \sum_{i \in FUEL} \llbracket cf_i * \left(I_{t,j,i} + \rrbracket SI_{t,j,i} \right) + \sum_{t}^{T} ELP_t * CEL \sum_{t}^{T} \sum_{J \in BOIL} XSOX_{t,j} * CSOX + \sum_{t}^{T} \sum_{J \in BOIL} XGHG_{t,j} * CGHG,$$

where t is time, i – fuels, j – units, cf_i – cost of fuel (USD/ton), $I_{t,j,i}$ - the amount of fuel i entering the boiler j and producing HP steam in the period t, $SI_{t,j,i}$ – the amount of fuel i consumed at restart phase of boiler j in the period t, ELP_t – electricity purchased from external source, CEL - electricity purchase cost, $XSOX_{t,j}$ – amount of SO_x in the boiler j in the period t, $CSOX$ - cost incurred for emissions of SO_x (USD/ton), $XGHG_{t,j}$ the amount of greenhouse gas emissions from the boiler, $CGHG$ - cost incurred for emissions of (USD/ton).

2.3. Calculation methodology

The integrated approach, which combines the production and the utility systems is optimized in the model of mixed integer non-linear programming (MINLP) using the example of ORC and, as calculations show, provides a more efficient relationship between the production unit and the utility system units. The MINLP approximation was performed using the APM MATLAB interface. This interface is a tool that makes APMonitor optimization algorithms available directly from within the MATLAB environment, enabling users to easily define mathematical programming models and solve them. The APMonitor is optimization software for mixed-integer and differential algebraic equations, allow also to transform the differential equations into a Nonlinear Programming (NLP) form. It is coupled with large-scale solvers for linear, quadratic, quadratically constrained quadratic, mixed integer linear and mixed integer nonlinear programming (LP, QP, QCQP, NLP, MILP, MINLP). For a faster solver, the "built- in" branch and bound capabilities of APOPT (Advanced Process OPTimizer) software package were used. The advantage of APOPT software package is in suitable for solving large-scale optimization problems of any of LP, QP, QCQP, NLP MILP and MINLP forms. Modes of operation include data reconciliation, real-time optimization, dynamic simulation and nonlinear predictive control.

3.Results and discussion

In all design schemes it is assumed that refineries usually consist of production and utility systems. The production system has various technological units, processes implemented in these units, which use all the raw materials for the manufacture of the final product. Each unit in the production system requires utilities provided by the utility system. The utility system uses fuel from the production system to produce steam and electricity. In this study, approaches and optimization models are used to simultaneously account for production and utility systems for decision-making in production planning. The use of mixtures of crude oils in the process of production of petroleum products is also considered. In addition, results are compared using different types of raw materials. Solutions obtained using the integrated model for crude oil mixtures provide higher returns than solutions obtained using the sequential model. In this case, the cost of the material and the price of production have a significant impact on the objective function. In the table 1 the data on the produced by SOCAR ORC and forecast for two years 2017 and 2018 are given [13,14].

Table 6. Oil refinery and production of oil derivatives in years 2017-2018, in thousands of tons [13,14]

		2018		2017	
Product	Forecast	Actual	%	Actual	%
Oil refinery - total	5911	6095.75	103.1	5810.01	104.9
Gasolines - total	1450.44	1390.27	95.9	1383.62	100.5
including petrol	1291.28	1185.64	91.8	1215.21	97.6
Oil fractions for chemistry	159.16	204.63	128.6	168.41	121.5
Jet kerosene	591.78	617.04	104.3	587.98	104.9
Diesel fuel:	1946.82	1921.78	98.7	1849.15	103.9
Light-colored products Output % of light-coloured products	3989.04 67.49	3929.09 64.46	98.5 95.5	3820.75 65.76	102.8 98.0
Liquid gas, in total	283.37	204.02	72	200.56	101.7
Treated dry gas (fuel gas)	60	53.6	89.3	60.07	89.2
Engine fuel DT	62.5	34.11	54.6	46.54	73.3
Lubricant oils	18.29	50.93	278.5	35.02	145.4
Furnace fuel oil	120.08	106.57	88.7	236.12	45.1
Oil bitumen	247.2	289.67	117.2	237.07	122.2
Oil coke	227.19	243.95	107.4	226.86	107.5

According to official information, the consumption of various types of energy in 2018 was as shown in table (2).

Table 7. Power consumption of the plant in 2018 [13, 14]

Indicators	Units of measure	Normal consumption	Actual consumption	Savings (-) Overspend (+)
Fuel	*tfe	604808	556828	-47980
Electricity power	ths kW/h	488125	414711	-73414
Thermal power	Hcal	805155	665601	-139554

To compare the proposed methods, separate calculations are done to solve the problem. The outcome presents that together with increase in productivity by 2.4%, the integrated method helps to significantly decrease utility costs. As such, these results for each of the methods are shown in table 3.

Table 8. The raw materials and products.

Raw Material (Ton/Day)	Crude Oil	MTBE	Water	Power (kW)
Sequential	16700.82	5843.96	5417.35	1139.32
Integrated	17105.85	5749.69	5360.78	1026.12

Product (Ton/Day)	Gasoline	Diesel	Kerosene	
Sequential	3808.96	5265.15	1690.52	
Integrated	3808.96	5579.75	1647.36	
Product (Ton/Day)	Fuel Oil	Fuel Gas		
Sequential	291.97	146.85		
Integrated	293.62	154.60		

Utility system operation outcomes are described in the table 4.

Table 9. The cost of utility system (ton per day)

		B1	B2	B3	B4
Fuel Oil	Sequential	340.1635	249.6544	0	0
	Integrated	340.1635	298.6802	0	0
Fuel Gas	Sequential	0	0	127.8442	60.71655
	Integrated	0	0	127.8442	55.81397
Steam Flow	Sequential	4525.457	3304.338	1508.486	686.7381
	Integrated	4525.457	3965.055	1508.486	630.9241
		T1	T2	T3	T4
Steam Flow	Sequential	3304.338	4525.457	1508.486	1508.486
	Integrated	3963.546	4525.457	1508.486	1508.486
Power (MW/Day)	Sequential	553.6142	175.7386	302.0743	59.20806
	Integrated	697.2975	175.7386	302.0743	59.20806

Refineries are a complex system that usually consists of production and utility systems. The production system has different technological units, processes implemented in these units, which use all the raw materials for the manufacture of the final product. Each unit in the production system requires utilities provided by the utility system. The utility system uses fuel from the production system to generate steam and electricity. In this study, approaches and optimization models are used to simultaneously take into account production and utility systems for decision making in production planning. The use of mixtures of crude oils in the process of production of petroleum products is also considered. The solution obtained using the integrated model is compared with the solution obtained using the sequential model. In addition, results are compared using different types of raw materials. Solutions obtained using the integrated model for crude oil mixtures provide higher returns than solutions obtained using the sequential model. In this case, the cost of the material and the price of production have a significant impact on the objective function. An approach is used that takes into account the integration of production and the energy system for the petrochemical oil refining complex and its planning. The purpose of this approach is to determine the optimal specific loads, modes and energy generation to meet the required energy for the process and aimed at maximizing the overall profit of the refinery. At a cost of 120,6 USD/ day of additional profit (1.5% improvement) at a real industrial refinery can be achieved using the integrated method compared to the sequential one. The reason is that the energy resources of intermediate products are fully utilized, and production units have more computing power in the proposed approach. An integrated approach leads to a better correspondence between the unit of production and the units of the communal system, as calculations have shown. Thus, we can conclude that in the improved model, the integration of industrial and utility systems can be used, which can be very effective in the oil refining industry to achieve favorable energy costs. An integrated method can also expand the operational capabilities of utility systems and increase the productivity of utilities and the efficient use of own fuel gas when planning the entire plant. The viability of the plant is critical and will become increasingly important in the coming decades. Higher viability costs and dynamically tight environmental laws limit the current portion to smooth out their use of viability. Such nearby utilities operating at the refinery can make useful commitments in this way, especially because of modern facilities that have high living standards. Be that as it may, it is very important to expand the capabilities of the nearby infrastructure of energy facilities at the refinery. When creating utility structures as an auxiliary unit, it is important to create a coordinated methodology that simultaneously coordinates the assembly unit and the operational organization of the utility structure. The results show that an integrated approach provides better coordination between the assembly and the healthcare system, which thus leads to a significant reduction in energy costs and material losses.

4.Conclusion

The mathematical model of integration of production planning and the energy system for the petrochemical oil refining complex is used to optimize the energy consumption of the petrochemical process and to maximize the overall profit of the ORC. It is shown that a method which takes into consideration the integration of production planning and its energy supply system, in comparison with the method of sequential calculation gives credible results for organizing the effective functioning of industrial ORC. The reason for it is that in the used approach intermediate products of energy resources are fully utilized, and production units have greater processing potential. The integrated approach, which combines the production and the utility systems is optimized in the model of mixed integer non-linear programming (MINLP) using an example of SOCAR ORC and, as calculations show, provides a more efficient relationship between the production and the utility system units. The energy consumption model of a production unit is introduced taking into account the relationship of energy consumption with the operating mode of production units and their performance. The material balance of the intermediate product, such as fuel gas and fuel oil, as well as the balance of energy production and consumption by various utility systems are optimized considering the energy used. On the example of the study of a real industrial ORC, the effectiveness of the approach being considered has been demonstrated, which leads to a sharp decrease in operating costs for the entire ORC and a significant improvement in energy conservation and reduction of emissions. We should note that this model can be used to integrate production and utilities systems and help refineries achieve lower energy costs along with higher profit. The integrated method can also help to expand the operational capabilities of the utility systems and increase the productivity of utility services and use fuel of own production efficiently when planning the effective operation of the entire oil refining complex.

5.References

1. Agha, M.H., Thery, R., Hetreux, G.,Hait A., Le Lann, J.M.: Integrated Production and utility system approach for optimizing industrial unit operations. Energy, **35**, 611-627 (2010). doi: 10.1016/j.energy.2009.10.032
2. Alhajri, I., Saif, Y., Elkamel, A. & Almansoori, A. Overall Integration of the Management of H2 and CO2 within Refinery Planning Using Rigorous Process Models. Chemical Engineering Communications, 200, 139-161, (2013). doi.org/10.1080/00986445.2012.691922
3. Shang, Z., Kokossis, A. A systematic approach to the synthesis and design of flexible site utility systems. Chemical engineering science, **60**, 4431-4451 (2005).doi: 10.1016/j.ces.2005. 03.015
4. Zhang, B.J., Hua, B. Effective MILP model for oil refinery-wide production planning and better energy utilization. Journal of Cleaner Production, **15**, 439-448. (2007). doi.org/10.1016/j.clepro.2005.08.004
5. Hao Zhao, Gang Rong, and Yiping Feng. Effective Solution Approach for Integrated Optimization Models of Refinery Production and Utility System//Ind. Eng. Chem. Res. 2015, 54, 37, 9238–9250. doi.org/10.1021/acs.iecr.5b00713
6. Demirbas, A., Bamufleh H. S. Optimization of crude oil refining products to valuable fuel blends, Petroleum Science and Technology, 35 (4), 406- 412, (2017). doi.org/10.1080/ 10916466.2016.1261162
7. Utomo F.A.P., Rosyidi C.N., Jauhari W.A. An integrated optimisation model of refinery short-term planning: a case study// Energy Systems, (2020), vol. 11, pp. 283–299. doi: 10.1007/S12667-018-0316-6
8. Klanšekc U., A comparison between MILP and MINLP approaches to optimal solution of nonlinear discrete transportation problem. Transport, (2015), vol. 30(2), pp. 135–144; doi:10.3846/16484142.2014.933361
9. Xpress MATLAB Interface Reference Manual Release 7.7 Last update 15 April, 2014. www.fico.com;
10. https://ch.mathworks.com/matlabcentral/fileexchange/45499-dynamic-optimization-with-the-apmonitor-toolbox
11. Brouer, B. D., Alvarez, F., Plum, C. E. M., Pisinger, D., & Sigurd, M. M. (2014). A Base Integer Programming Model and Benchmark Suite for Liner-Shipping Network Design. Transportation Science, 48(2), 281-312 . https://doi.org/10.1287/trsc.2013.0471
12. Joly, M., Refinery production planning and scheduling: The refining core business. Brazilian Journal of Chemical Engineering, (2012), vol. 29(2), pp.371-384 (2012). doi.org/10.1590/S0104-66322012000200017.
13.http://www.socar.az/socar/assets/documents/en/socar-annual-reports/annual_report 2018.pdf);
http://www.socar.az/socar/assets/documents/en/socar-annual-reports/annual_report 2018.
14.http://www.socar.az/socar/assets/documents/en/socar-annual reports/annual_report 2018

PP-V-3

DETERMINATION OF THE OPTIMAL MODES OF CONDUCTING A NTINUOUS PROCESS OF COPOLYMERIZATION OF BUTADIENE WITH STYRENE BY MEANS OF MATHEMATICA MODELING

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Abstract. Here are the results of studying the kinetics of the process of sad of butadiene with styrene in an emulsion in a continuous way at various dosages and modes of feeding the initial reagents. A description of the main technological features of the production of styrene-butadiene copolymer is given. The stages of building of a mathematical model of the investigated process on a periodic scale of reference are demonstrated. The main kinetic mechanism of the process was written out and the kinetic approach was applied to compile of a mathematical model. In order to simulate the copolymerization process on an industrial scale, a transition is made to the description of a continuous process and possible hydrodynamic and energy laws are taken into account. For further research of the mathematical model, numerical methods and algorithms are described, implemented in the form of a single software package. Using numerical methods and the constructed mathematical model, a series of computational experiments with different dosages of the initial reagents were carried out, which made it possible to evaluate their effect on the molecular characteristics of the synthesized polymer. The results showed that the width of the molecular weight distribution is greatly influenced not only by the change in the composition of the initial mixture, but also by the organization of a different supply of reagents. By the method of selection and empirical analysis of the results obtained, the optimal modes of supply of reagents were determined in order to obtain a polymer with specified characteristics.

Keywords: Polymer, Modeling, Rubber, Molecular Weight Distribution, Optimization.

1.Introduction

A huge part of the petrochemical products of our country is represented by various brands of synthetic rubber, which is an artificial elastomer that serves as a raw material for the production of various types of rubber. The most common is a group of products of copolymerization of butadiene-1,3 and styrene or methylstyrene, in an aqueous emulsion by a free-radical mechanism using a redox system as an initiator at a temperature of 4-10°C [1]. The regulation of the initial production parameters, technological features and the organization of a different principle of supplying reagents makes it possible to obtain a fairly wide range of products. The inability to expand the results of laboratory research to the scale of continuous production makes it difficult to conduct an empirical assessment of the quality of a polymer product. In this regard, it is of interest to select the optimal parameters of the initial loading of polymerizers and predict the properties of the resulting product on a continuous scale of production using mathematical modeling tools [2].

The technological features of production include the need for constant regulation of the chain length of the copolymer with reagents that have a strongly marked chain transfer property. Compounds of the thiol class are usually chosen as molecular weight regulators, most often tert-dodecylmercaptan [3]. To stop the chain growth when a given degree of monomer conversion (69 ÷ 85%) is reached into the last battery polymerizer, a stopper solution is fed, which stops the polymerization reaction. In addition, the resulting latex undergoes further degassing stages, the addition of an antioxidant or oil, and the liberation of rubber from the latex by the method of coagulation with acidification with sulfuric acid and the use of a triple coagulant. However by the constructing of the mathematical model, only the kinetic mechanism before the stopper is taken into account, since further stages of the production process do not affect the molecular characteristics of the resulting product.

2. Eksperment part.

Due to a rather complex kinetic mechanism and the probabilistic nature of the implementation of a particular reaction, the product of production cannot be described by one molecular weight. One of the key characteristics of the final polymer is the molecular weight distribution, which characterizes the ratio of the amounts of macromolecules of different molecular weights [4]. The final numerical characteristic of the molecular weight distribution of the product is polydispersity, for the numerical determination of which the ratio of the weight average M_w and number average M_n molecular weights is used

$$K = \frac{M_w}{M_n}. \quad (1)$$

All the more introduction of rubber products into all areas of production leads to the need to change the technology and composition of the initial mixture supplied to the first polymerizer in order to obtain a product with a given width of molecular weight distribution. One of the levers of influence on the molecular characteristics of the product is a control of the rate of the process by changing the feed of the initiating mixture, adjusting of the scheme of the regulator flow, including any change in the ratio of the supplied reagents. The description of the kinetic scheme of the production process, together with the use of mathematical research methods and their software implementation, makes it possible to create a convenient tool for organizing the selection of optimal production modes.

At the first stage of building a mathematical model, it is necessary to write down the kinetic mechanism, the filling of which can affect the molecular characteristics of the resulting product. In this case, this is an obligatory stage of initiation, as a result of which free radicals are formed, which in turn interact with butadiene M^1 and styrene M^2 molecules.

$$I \xrightarrow{k_d} R,$$

$$R + M^1 \xrightarrow{k_i^1} P_{1,0}^1,$$

$$R + M^2 \xrightarrow{k_i^2} P_{0,1}^2,$$

The stage of chain growth is also taken into account:

$$P_{n,m}^i + M^1 \xrightarrow{k_{p11}} P_{n+1,m}^i,$$

$$P_{n,m}^i + M^2 \xrightarrow{k_{p12}} P_{n,m+1}^i,$$

where $P_{n,m}$ – active ("growing") copolymer chain length $n+m$, containing n units of butadiene and m units of styrene.

Also, the kinetic mechanism should include the stages of termination of the growing chain as a result of interaction with regulator molecules S

$$P_{n,m}^i + S \xrightarrow{k_{reg}^i} Q_{n,m} + R,$$

as well as accidental termination as a result of recombination and disproportionation reactions.

$$P_{n,m}^i + P_{r,q}^j \xrightarrow{k_r^{ij}} Q_{n+r,m+q},$$

$$P_{n,m}^i + P_{r,q}^j \xrightarrow{k_d^{ij}} Q_{n,m} + Q_{r,q},$$

where $Q_{n,m}$ – inactive ("dead") copolymer chain length $n+m$, containing n units of butadiene monomer and m units of styrene.

The further construction of a mathematical model in order to solve the direct problem implies the use of various approaches. Previously, the kinetic [5,6] and statistical [7,8] approaches to solving this problem have been successfully tested. Since finding the optimal mode of conducting the production process implies multiple solutions of the direct problem and the calculation of only averaged molecular characteristics, the kinetic approach is most justified in this formulation.

On the basis of the given kinetic mechanism, a system of differential equations is written out consisting of equations of conservation of mass for the reaction system and for each of its components. Based on the numerical solution of this system, the macrokinetics of the process under consideration is simulated. In order to simulate the copolymerization process on an industrial scale, it is required to go to the description of a continuous process and take into account possible hydrodynamic and energetic laws. This requires the classification of the type of reactor according to its hydrodynamic regime and mixing method. In accordance with the described process technology, the battery for the organization of continuous production consists of series-connected polymerizers, which are reactors with a frame-type stirring device. Such an organization of reactors allows them to be classified as reactors of ideal mixing with complete and instantaneous mixing of the newly supplied mixture [9,10].

Recurrent relationships between the moments of molecular weight distribution, characteristic of a given type of reactor [9], is written in the form

$$\theta \frac{dm_j^{(k)}}{dt} = m_j^{(k-1)} - m_j^{(k)} + \theta \left(\frac{dm_j^*}{dt} \right)^{(k)}, \tag{2}$$

$$\frac{d\bar{Y}^{(k)}}{dt} = \frac{\left(\bar{Y}^{(k-1)} - \bar{Y}^{(k)} \right)}{\theta^{(k)}} + \bar{R}_y^{(k)}, \tag{3}$$

where $\theta^{(k)}$ - residence time of the reaction mixture in k -th reactor of the cascade, and the view $\bar{R}_y^{(k)}$ is determined based on the kinetic mechanism.

With considering (2)-(3) the system of differential equations describing the macrokinetics of the process under consideration takes the form

$$\left\{ \begin{aligned}
&\frac{dI^{(k)}}{dt} = \frac{I^{(k-1)} - I^{(k)}}{\theta^{(k)}} - k_i I^{(k)}, \\
&\frac{dM^{1(k)}}{dt} = \frac{M^{1(k-1)} - M^{1(k)}}{\theta^{(k)}} - k_{p11} M^{1(k)} \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{p21} M^{1(k)} \sum_{n,m=0}^{\infty} P_{n,m}^2, \\
&\frac{dM^{2(k)}}{dt} = \frac{M^{2(k-1)} - M^{2(k)}}{\theta^{(k)}} - k_{p12} M^{2(k)} \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{p22} M^{2(k)} \sum_{n,m=0}^{\infty} P_{n,m}^2, \\
&\frac{dS^{(k)}}{dt} = \frac{S^{(k-1)} - S^{(k)}}{\theta^{(k)}} - k_{reg1} S^{(k)} \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{reg2} S^{(k)} \sum_{n,m=0}^{\infty} P_{n,m}^2, \\
&\frac{d\psi_0^{Q(k)}}{dt} = \frac{\psi_0^{Q(k-1)} - \psi_0^{Q(k)}}{\theta^{(k)}} + \frac{k_{r11}}{2} \left(\psi_0^{M^1(k)} \right)^2 + k_{r12} \psi_0^{M^1(k)} \psi_0^{M^2(k)} + \frac{k_{r22}}{2} \left(\psi_0^{M^2(k)} \right)^2 + \\
&+ \left(k_{reg1} S^{(k)} + k_{d11} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d12} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_0^{M^1(k)} + \left(k_{reg2} S^{(k)} + k_{d21} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d22} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_0^{M^2(k)}, \\
&\frac{d\psi_1^{Q(k)}}{dt} = \frac{\psi_1^{Q(k-1)} - \psi_1^{Q(k)}}{\theta^{(k)}} + k_{r11} \psi_0^{M^1(k)} \psi_1^{M^1(k)} + k_{r22} \psi_0^{M^2(k)} \psi_1^{M^2(k)} + \\
&+ k_{r12} \left(\psi_0^{M^1(k)} \psi_1^{M^2(k)} + \psi_1^{M^1(k)} \psi_0^{M^2(k)} \right) + \left(k_{reg1} S^{(k)} + k_{d11} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d12} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_1^{M^1(k)} + \\
&+ \left(k_{reg2} S^{(k)} + k_{d21} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d22} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_1^{M^2(k)}, \\
&\frac{d\psi_2^{Q(k)}}{dt} = \frac{\psi_2^{Q(k-1)} - \psi_2^{Q(k)}}{\theta^{(k)}} + k_{r11} \left(\left(\psi_1^{M^1(k)} \right)^2 + \psi_0^{M^1(k)} \psi_2^{M^1(k)} \right) + k_{r22} \left(\left(\psi_1^{M^2(k)} \right)^2 + \psi_0^{M^2(k)} \psi_2^{M^2(k)} \right) + \\
&+ k_{r12} \left(\psi_0^{M^1(k)} \psi_2^{M^2(k)} + 2\psi_1^{M^1(k)} \psi_1^{M^2(k)} + \psi_2^{M^1(k)} \psi_0^{M^2(k)} \right) + \\
&+ \left(k_{reg1} S^{(k)} + k_{d11} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d12} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_2^{M^1(k)} + \left(k_{reg2} S^{(k)} + k_{d21} \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{d22} \sum_{n,m=0}^{\infty} P_{n,m}^2 \right) \psi_2^{M^2(k)}.
\end{aligned} \right. \tag{4}$$

Initial conditions for the system (4) has the form:

$$\begin{aligned}
&I(0) = I_0,\ M^1(0) = M_0^1,\ M^2(0) = M_0^2, \\
&S(0) = S_0,\ \psi_i^Q(0) = \psi_i^{M^1}(0) = \psi_i^{M^2}(0) = 0, \\
&i = 0,1,2.
\end{aligned} \tag{5}$$

The values of moments of molecular weight distribution $\psi_i^{Q(k)}, i = 0..2$ are used to find the number average and weight average molecular weights:

$$M_n^Q = \frac{\psi_1^Q}{\psi_0^Q},\ M_w^Q = \frac{\psi_2^Q}{\psi_1^Q}. \tag{6}$$

For further research of the mathematical model, represented by the system of differential equations (4)-(5), it was required to describe the numerical methods and algorithms implemented as a single software package

[11]. In order to programmatically organize the fractional feed of the initial reagents in the iterative solution of the direct problem, a variable P_1 was set that was responsible for the number of the reactor into which the next portion of the initial reagent was fed. When the initial mixture of the reactor with the number P_1 was reached, the concentration of the given reagent was increased per molar volume of the next portion. The possibility of multiple division of the initial mixture is organized in a similar way. The described scheme of fractional feed of reagents was prescribed only for the regulator, with the aim of more flexible regulation of the length of the formed macromolecules at high conversion rates.

The main task presented in this work is to calculate the conditions for conducting the copolymerization process under which the resulting product will be represented by the narrowest molecular weight distribution, while maintaining the weight average molecular weight in the range of 720 000 or more for the last polymerizer. In order to find the necessary recipe for conducting the copolymerization process, a computational experiment was carried out for various dosages and modes of supply of the initiating mixture and the regulator.

- Working volume of the polymerizer V = 10.8 m^3.
- Number of reactors - 12.
- Load on the battery by monomers in the range 3.0-3.4 t/h (butadiene - 70%, styrene - 30%).
- Dosage of initiator (pinane hydroperoxide) in the range 0.052-0.060 wt.h
- Dosage of the regulator (tert-dodecyl mercaptan) in the range 0.09-0.12 wt.h at two points of entry (into the first polymerizer and upon reaching the conversion 35%).
- Water: monomer ratio =200-220:100.

Since the volume of computational experiments performed exceeds 10^3, then we present only a part of the results obtained. Figure 1 shows the calculated dependences for three conditions of the computational experiment:

1) battery load 3.0 t/h, initiator dosage 0.052 m.h., regulator dosage 0.12 m.h. (first point – 85%, second point – 15%), water: monomers – 220:100;
2) battery load 3.0 t/h, initiator dosage 0.06 m.h., regulator dosage 0.09 m.h. (first point – 85%, second point – 15%), water: monomers – 220:100;
3) battery load 3.0 t/h, initiator dosage 0.06 m.h., regulator dosage 0.09 m.h. (first point – 50%, second point – 50%), water: monomers – 220:100;.

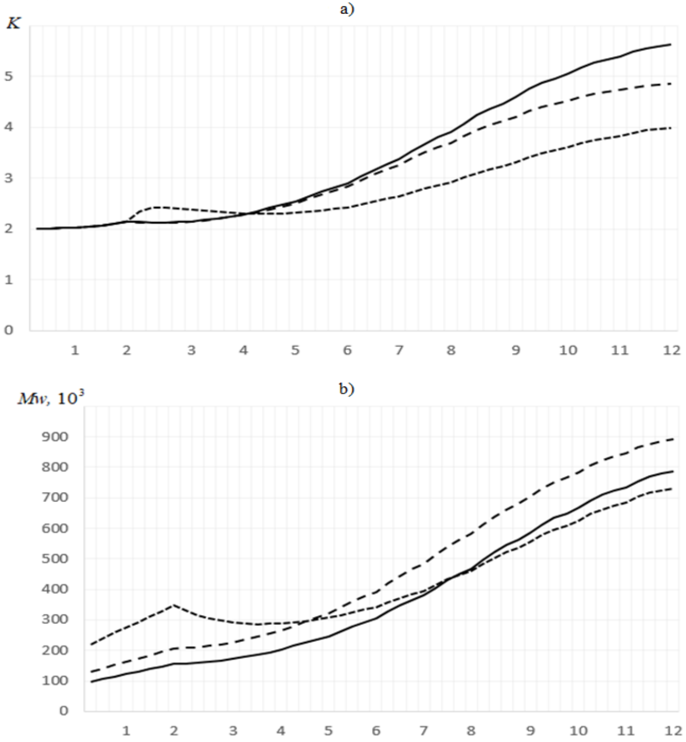

Fig. 1. Dependence of a) polydispersity b) weight-average molecular weight of the polymer product on the number of the polymerizer for various conditions of the process (solid line - condition 1; dashed line - condition 2; small dash - condition 3)

3.Results and discussion

Carrying out computational experiments with different dosages of initial reagents makes it possible to evaluate their effect on the molecular characteristics of the synthesized polymer. The obtained results demonstrate that the width of the molecular weight distribution is influenced not only by a change in the composition of the initial mixture, but also by the organization of a different supply of reagents. The results of the computational experiment for the first condition of the process demonstrate a huge effect of increasing the dosage of the regulator - a decrease in the average molecular weight along with an increase in polydispersity. A further decrease in the dosage of the regulator together with a decrease in the volume of the initiating mixture leads to a decrease in the width of the molecular weight distribution. The strongest effect on the decrease in polydispersity is exerted by a change in the regulator feed scheme and a shift of a larger volume to the second point (condition 3). However, even greater mixing of the regulator feed after a certain threshold leads to a further increase in the polydispersity value (Table 1).

Table 1. Computational results experiment for various regulator feed schemes

G charge for one battery, tons/hour	Water, m.h. / m.h.	Regulator dosage			Dosage GPP initiator, m.h.	Copolymer parameters for the latter polymerizer		
		The amount of TDM, wt.h.	1 point, %	2 point, %		M_n, 10^3	M_w, 10^3	K
3.0	220	0.09	50	50	0.052	184	730	3.98
3.0	220	0.09	40	60	0.052	183	720	3.93
3.0	220	0.09	30	70	0.052	182	730	4.01
3.0	220	0.09	20	80	0.052	180	780	4.33
3.0	220	0.09	10	90	0.052	98	480	4.89

An increase in the capacity load up to 3.4 tons per hour per cascade did not lead to the required decrease of polydispersity in the specified confidence interval for changing the reagent feed. At the same time, for the case of selection of the optimal composition of the charge in accordance with the new requirements for the product of production, this factor also has a significant role in changing the picture of the molecular weight distribution of the polymer product. In this way, the given approach with the use of mathematical research methods and their software implementation makes it possible to select the optimal modes of conducting a continuous copolymerization process for the required characteristics of the polymer product.

4.Conclusion

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5.References

1. Kirpichnikov, P., Beresnev, V., Popova, L. Album of technological schemes of the main industries of the synthetic rubber industry. L.: Chemistry (1986).
2. Mustafina, S., Miftakhov, E., Mikhailova, T. Solving the direct problem of butadiene-styrene copolymerization. International Journal of Chemical Sciences 12(2), 564-572 (2014).
3. Pat. RF 2660084 (publ. 2018). Method for producing styrene-butadiene rubber.
4. Podvalny, S.: Modeling of industrial polymerization processes. M: Chemistry (1979).
5. Miftakhov, E., Mustafina, S. Modeling and theoretical studies of the emulsion copolymerization process in a continuous way. Bulletin of the Ufa State Aviation Technical University 5(45), 98-104 (2011).
6. Zhang, M., Ray, W. Modeling of ‘living’ free-radical polymerization processes. I. Batch, semibatch, and continuous tank reactors. Journal of Applied Polymer Science 86(7), 1630–1662 (2002).
7. He, J., Li, L., Yang, Y. Monte Carlo simulation on rate enhancement of nitroxide-mediated living free-radical polymerization. Macromolecular Theory and Simulations 9(8), 463–468 (2000).
8. Al-Harthi, M., Masihullah, J., Abbasi, S., Soares, J. Dynamic Monte Carlo simulation of ATRP in a batch reactor. Macromolecular Theory and Simulations 18(6), 307–316 (2009).
9. Kafarov, V., Glebov, M.: Mathematical modeling of the main processes of chemical production. M: HigherSchool (1991).
10. Zhang, M., Ray, W. Modeling of ‘living’ free-radical polymerization processes. II: tubular reactors. Journal of Applied Polymer Science 86(5), 1047–1056 (2002).
11. Miftakhov, E., Mustafina, S. Software package for solving the direct problem of the process of emulsion copolymerization of butadiene with styrene. M.: All-Russian Scientific and Technical Information Center. №50201150588 (2011).

OR-V-3

MONTE CARLO MODELING OF A PERIODIC PROCESS OF ISOPRENE POLYMERIZATION IN A NEODYMIUM-CONTAINING CATALYTIC SYSTEM

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Abstract. This article describes an algorithm for modeling the process of isoprene polymerization in the presence of a neodymium-containing catalytic system, as well as the main aspects of the software implementation of the proposed algorithm. Solution polymerization of isoprene forms the basis of industrial production of isoprene rubber. The process of isoprene polymerization considered in the paper proceeds in a batch mode using two organoaluminium compounds – triisobutylaluminum and diisobutylaluminum hydride. A statistical approach is used to model the polymerization process. The presented approach is based on the Monte Carlo method. This method makes it possible to simulate the formation of macromolecules of the resulting polymer at the particle level, simulating at each moment of time a randomly selected reaction among all possible reactions of a given kinetic scheme of the process. The developed program based on a statistical approach makes it possible to plot the dependences of the averaged molecular characteristics of the polymer (number average and weight average molecular weights) on the monomer conversion, and, consequently, to predict and investigate the molecular weight characteristics of the polymer depending on the conditions of the production process. The article presents the results of a computational experiment, the initial data of which correspond to laboratory studies. The results of the computational experiment showed good agreement with laboratory data.

Keywords: Polymerization, Isoprene, Modeling, Monte Carlo Method, Batch process, Neodymium-based Catalyst System.

1.Introduction

Currently, the range of synthetic rubbers is quite wide. This is due to the low-quality indicators of natural rubber for the creation of industrial rubber goods. In this regard, studies of polymerization processes are of great interest both for modern science and for the world production of synthetic rubber. This area of research opens up great opportunities for studying statistical features and factors affecting processes of polymerization and allows to describe physical processes with high accuracy [1].

The production of synthetic rubbers (isoprene, butadiene, butadiene-styrene, butadiene-nitrile, etc.) is based on the processes of polymerization and polycondensation. One of the most common industrial polymeric materials is isoprene- rubber. But its production is a complex technological process carried out in the presence of catalysts of the Ziegler-Natta type. The industrial production of cis-1,4 polyisoprene in the presence of catalysts based on neodymium chloride $NdCl_3$ solvated with isopropanol has proven itself in the tire and rubber industry and in the manufacture of food products and medicine [2].

The study of this process becomes possible when constructing a mathematical model [3]. Modeling allows not only to predict the characteristics of the final product depending on the recipe and conditions of the process but also to optimize it. Consequently, an important task today is the study and modification of the qualitative indicators of polymerization products using methods of mathematical modeling.

2.Materials and methods

One of the modeling approaches used in the study of polymerization processes is the statistical approach. When using it, the growing polymer chain is simulated using random variables. Each link of the growing polymer chain is considered as a specific random process of conditional movement along the polymer molecule, while the probability of the random process is considered to be equal to the proportion of its corresponding molecules among all others in the reaction system.

The statistical approach allows an exhaustive description of the detailed structure of macromolecules in terms of several probabilistic parameters [4]. This approach to modeling polymerization processes is the basis of the Monte Carlo method. The model is a collection of particles corresponding to individual molecules or macromolecules. This allows to accumulate information about the amount, length, and composition of the resulting polymer macromolecules and at any time to obtain the actual values of the molecular characteristics of the polymerization product. It allows to observe the polymer in dynamics [5].

We use a statistical approach to modeling the batch process of solution polymerization of isoprene on the $NdCl_3$-nIPA-TIBA-PP catalytic system (IPA is isopropyl alcohol, TIBA is triisobutylaluminum, PP is piperylene). The idea of the approach is based on the method proposed in 1977 by the American physicist Gillespie [6] for studying oscillatory processes. First, it is necessary to write out the kinetic scheme of the process, which requires to know the number of types of active sites involved in the process. It may depend on the conditions and methods of preparation of the catalyst. In paper [7], the application of a modified approach was considered using a tubular turbulent apparatus with a diffuser-confuser design in the technological scheme. It showed the formation of a mono-center catalyst in the system.

It should also be noted that it is typical for neodymium-containing catalysts that, as a rule, active sites do not die during polymerization; therefore, the stage of deactivation of active sites can be excluded from the kinetic scheme.

In addition, taking into account the peculiarities of the technology of conducting an industrial polymerization process on a neodymium-containing catalytic system, two types of organoaluminum compounds can be distinguished:

1) triisobutylaluminum (TIBA), which is present initially in the catalytic complex;

2) diisobutylaluminum hydride (DIBAG), which is added separately and has a strong effect on the chain transfer process by regulating the molecular weight of macromolecules.

The kinetic scheme of isoprene polymerization in the presence of a neodymium-containing catalytic system has the form:

– chain propagation:

$$P_i + M \xrightarrow{k_p} P_{i+1},$$

– chain transfer to monomer:

$$P_i + M \xrightarrow{k_m} Q_i + P_1,$$

– chain transfer to organoaluminum compound (OAC):

$$P_i + A_1 \xrightarrow{k_{a1}} Q_i + P_1,$$

$$P_i + A_2 \xrightarrow{k_{a2}} Q_i + P_1$$

– death of active sites:

$$P_i \xrightarrow{k_d} Q_i,$$

where M – monomer, A – organoaluminum compound (A_1 – triisobutylaluminum, A_2 – diisobutylaluminum hydride), P_i – active ("growing") polymer chain of length *i*; Q_i – inactive ("dead") polymer chain of length i, $k_p, k_m, k_{a1}, k_{a2}, k_d$ – constants characterizing the reaction rate of chain propagation, transfer to monomer, transfer to organoaluminium compound and death of active sites, respectively [7].

Next, we describe the algorithm of modeling of the polymerization process using the Monte Carlo method as a sequence of steps:

Step 1. Transform the rate constants of elementary reactions:

for first-order reactions

$$\tilde{k} = k\,, \tag{1}$$

for second-order reactions

$$\tilde{k} = \frac{k}{V \cdot N_A}, \tag{2}$$

where V – reaction volume (number of molecules), N_A – Avogadro number.

Step 2. Calculate the reaction rate for every reaction:

$$R_i = \tilde{k}_i \cdot X_A \cdot X_B, \tag{3}$$

where $\tilde{k}_i$ – the rate constant of i-th reaction, in which A and B reagents are involved; X_A, X_B – concentration of reagents. By summing them, we obtain the total reaction rate:

$$R_{sum} = R_1 + R_2 + \ldots + R_n, \tag{4}$$

where n is the number of elementary reactions of the kinetic scheme of the process.

Step 3. Calculate the probability of each reaction at a given time:

$$p_i = \frac{R_i}{R_{sum}}, \quad i = 1..n. \tag{5}$$

Since these events form a complete group, it is obvious that:

$$p_1 + p_2 + \ldots + p_n = 1. \tag{6}$$

Step 4. Generate a uniformly distributed random number r on the segment from 0 to 1 and choose such value k that there is an inequality:

$$\sum_{i=1}^{k-1} p_i < r < \sum_{i=1}^{k} p_i. \tag{7}$$

Therefore, as a result of the simulation choice, the reaction under the index k should occur.

Step 5. Continuing the reasoning and repeating this process until a given value of time or conversion is reached, we will similarly algorithmize the reaction scheme.

3.Results and discussion

The authors of the article have developed an algorithm for the numerical study of the periodic process of isoprene polymerization in the presence of a neodymium-based catalytic system. The algorithm is implemented in the C ++ programming language and can be used to simulate polymerization processes in the presence of catalytic systems containing up to 4 types of active sites.

The algorithm is based on the Monte Carlo method, which works at the level of interacting particles. Monomer molecules, organoaluminum compounds are characterized only by their number, while each polymer’s macromolecule is also characterized by a number, the value of which corresponds to the number of units in the chain. All macromolecules are stored in a dynamic array, each type of active site has its own array. This allows to obtain the following information: the total number of polymer chains, the length of each chain, the number average and weight average molecular weights of the polymer, molecular weight distribution.

The simulation of the reaction currently being performed is based on a change in the total number of molecules of those reagents that are involved in it. Let's describe how the imitation process will take place, using the example of individual stages.

1. Chain propagation:
– decrease in the number of monomer molecules per unit;
– selection of a random chain in the array of active chains;
– increase in the length of the selected polymer chain by unit.

2. Chain transfer to monomer:
–decrease in the number of monomer molecules per unit;
– selection of a random chain in the array of active chains;
– adding the selected chain to the array of inactive chains;
– removing the selected chain from the array of active chains;
– adding a chain of one unit to an array of active chains.

3. Chain transfer to organoaluminum compound:
– decrease in the number of organoaluminum compound molecules per unit;
– selection of a random chain in the array of active chains;
– adding the selected chain to the array of inactive chains;
– removing the selected chain from the array of active chains;
– adding a chain of one unit to an array of active chains.

To illustrate the work of the developed program based on the proposed algorithm, a computational experiment was carried out to study the process of isoprene polymerization in the presence of a neodymium-containing catalytic system. In this case, the conditions of the process corresponding to laboratory ones were used (table 1).

Based on the experimental conditions, the molar concentrations of the reagents were obtained:
– isoprene molar concentration – 1.39 mol/L;
– diisobutylaluminum hydride molar concentration – 0.000177 mol/L;
– triisobutylaluminum molar concentration – 0.00168 mol/L;

– molar concentration of active sites – 0.00014 mol/L.

Table 10. Experimental conditions.

Catalyst concentration (*$NdCl_3$*)	0,035 mol/L
Соотношение *$NdCl_3$*/TIBA/piperylene /DFO in catalyst	1 mol/12 mol/2 mol
Catalyst dosage	1 mol *$NdCl_3$*/10000 mol of isoprene
The concentration of isoamylenes in the initial mixture	0% w.
The concentration of isoprene in the initial mixture	15,0% w.
Polymerization temperature	20ºC

It should be noted that the concentration of active sites was set in an amount of 5% of the volume of the catalyst in the molar ratio. [7].

The constructed model allows one to study the properties of the polymerization product and predict the values of the molecular characteristics of the polymer. Fig. 1 and Fig. 2 show the dependence of the number-average and weight-average molecular weights on the monomer conversion, i.e. the fraction of the conversion of monomer into the polymer, and Fig. 3 shows the dependence of the values of the polymer polydispersity index on the conversion of monomers.

The dots in the figures represent the results of a laboratory experiment for conducting a batch process of isoprene polymerization in the presence of a neodymium-containing catalytic system. The results of the statistical approach show satisfactory agreement with the results of the laboratory experiment. The relative difference between the calculated values for the number average molecular weight is no more than 13.3%, for the weight average molecular weight – no more than 2.6% (the maximum values correspond to the conversion of 78%), for the polydispersity index – no more than 9.0% (the maximum value corresponds to the conversion of 80%).

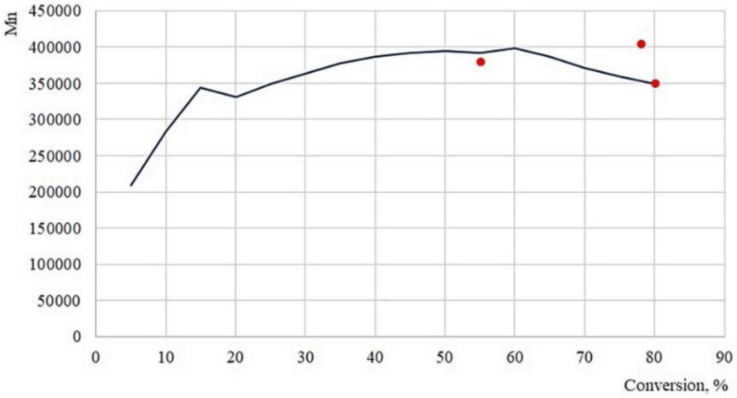

Fig.3. Dependence of the values of the number average molecular weight of the polymer from monomer conversion (dots – laboratory experiment data, line – results of computational experiment).

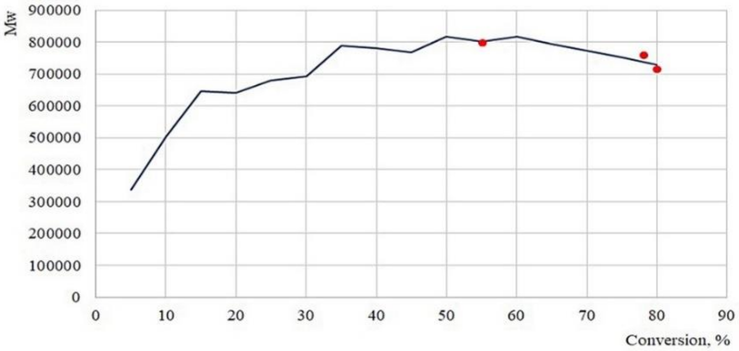

Fig.2. Dependence of the values of the weight average molecular weight of the polymer from monomer conversion (dots – laboratory experiment data, line – results of computational experiment).

The polydispersity index is determined by the ratio of the weight average and number average molecular weight. It characterizes the width of the molecular weight distribution of the resulting product [8]. The analysis of the results of the computational experiment shows that when the monomer conversion reaches 80%, the polydispersity index equals 2.1, which is typical for the model Flory distribution, while the experimental value is in the range 2.3-2.35.

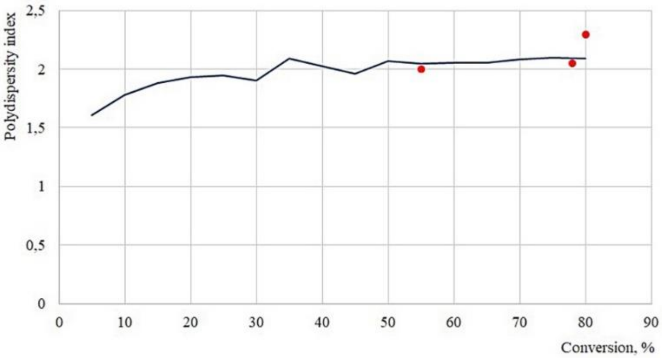

Fig.3. Dependence of the values of the polydispersity index of the polymer from monomer conversion (dots – laboratory experiment data, line – results of computational experiment).

4.Conclusion

Thus, the Monte Carlo simulation algorithm presented in this paper and the developed program allow us to study the properties of the isoprene polymerization product, flowing in a batch mode in the presence of a neodymium-containing catalytic system. Since this approach is based on the imitation of the growth of each macromolecule and tracking the processes occurring with it, it allows accumulating information on the length of the polymer chains being formed. Based on this information, it is possible to predict the dependences of the change in the main molecular characteristics of the polymer on the conversion of monomers at any time.

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5.References

1. Kirpichnikov, P.A., Beresnev, V.V., Popova L.M.: The album of technological schemes of the main industries of the synthetic rubber industry. Chemistry, Leningrad (1986).
2. Averko-Antonovich, I.Yu., Bikmullin, R.T.: Methods for studying the structure and properties of polymers. Kazan State Technological University, Kazan (2002).
3. Gartner, T.E. III, Jayaraman A.: Modeling and simulations of polymers: A Roadmap. Macromolecules 52(3), 755-786 (2019).
4. Khokhlov, A.R., Kuchanov S.I.: Lectures on Physical Chemistry of Polymers. World, Moscow (2000).
5. Mikhailova, T., Miftakhov, E., Mustafina, S.: Mathematical Simulation of the Styrene-Butadiene Rubber's Production in the Cascade of Reactors by the Monte-Carlo Method. International Journal of Chemical Sciences 14(4), 1865-1876 (2016).
6. Gillespie, D.: Exact Stochastic Simulation of Coupled Chemical Reactions. The Journal of Physical Chemistry №81(25), 2340-2361 (1977).
7. Miftakhov, E.N., Mustafina, S.A., Petrenko, V.R., Podvalnii E.S.: Modeling of a continuous process of isoprene polymerization in the presence of titanium-based catalyst systems under polycentric conditions. IOP Conf. Series. Journal of Physics: Conference Series 1479, 012073 (2020).
8. Mikhailov, V., Medvedeva, O., Mustafina, S., Mikhailova, T., Mustafina, S., Kolyazov K.: Research of Technological Properties of the Styrene-Butadiene Rubber by the Method of Mathematical Modeling. Revista San Gregorio. Special Edition-December 36, 89-100 (2019).

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RESEARCH OF THE COMPOSITION OF GASES PRODUCED IN THE CATALYTIC CRACKING PROCESS UNDER THE INFLUENCE OF MAGNETIC FIELD

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Abstract: In the conducted research was studied the intensification of catalytic cracking process by applying method of a constant magnetic field treatment of both raw materials – vacuum gasoil and mixture of VGO with 10% of atmospheric residue and catalyst - granulated OMNIKAT-210P. Variability of such indicators as process efficiency, yield and physico-chemical properties of products in case of magnetic treatment was analyzed. The effect of magnetic field influence to the yield, properties and composition of products obtained in catalytic cracking of vacuum gasoil and mixture VGO+10% AR and the advantage of atmospheric residue addition to the main feedstock is investigated and discussed. The great attention also has been paid to the change in gas products output and qualitative characteristics. As a result of experiments, it was found that during magnetization of the feedstock and catalyst of the catalytic cracking process, their structure and configuration change, which helps to increase the efficiency of the process, as well as to increase the yield and improve the quality of light petroleum products and gases in a significant amount.

Key words: catalytic cracking, light petroleum products, vacuum gasoil, catalyst, atmospheric residue, OMNIKAT-210P, gasoline fraction, wet gases, cracking gases, magnetic field, selectivity, inductivity.

1.Introduction

The current oil refining industry is characterized by excessive consumption of traditional resources of raw materials, as a result there is an inevitable shortage of suitable raw materials and a continuous increase in demand for light oil products. Therefore, finding a proper solution to the problem of heavy oil residues processing with the aim of increasing the yield of motor fuels necessary for the industry, becomes critical [1,2].

One of the main processes in the oil refining industry, with a significant share of the motor fuels production is the catalytic cracking process. The most common version of the catalytic cracking process is based on the use of a fluidized catalyst bed. The main goal of the process is to produce a high-octane gasoline component and valuable hydrocarbon gases for use as a feedstock in petrochemical synthesis [3,5].

An important aspect for providing the industry with appropriate fuel resources has the intensification of the catalytic cracking process. The process is intensified mainly by means of improving or developing new technologies, catalysts of high activity and selectivity. Nevertheless, the listed methods require large investments and do not always justify themselves in operating installations [4,5].

Recently, to intensify the process, the greatest attention attracted the use of energy and physical influences, such as electric, magnetic, electromagnetic, acoustic or vibration field. [6] In this work, we have investigated the effect of a constant magnetic field on the yield and properties of the products obtained in the process of catalytic cracking. The main goal of the study is to intensify the catalytic cracking process by pretreating the OMNIKAT-210P catalyst and raw materials with a magnetic field, thereby increasing the yield of light oil products and improving the qualitative composition of the gases obtained.

To achieve this goal, the following tasks were required to be done:

- study of the effect of a constant magnetic field on the catalytic cracking process at:

a) Preliminary magnetic treatment of the catalyst;
b) Preliminary magnetic processing of raw materials;
c) Combined pre-treatment of both catalyst and feedstock;

2.Method

For the experimental study, we took as raw materials - the fraction of vacuum gas oil 350 -500°C, atmospheric residue (AR), which is the residue from crude oil distillation process in atmospheric column, while the catalyst was granular OMNIKAT-210P. We have investigated the quality of products obtained in the process of catalytic cracking of both pure vacuum gas oil and a mixture of VGO with 10% of atmospheric residue (AR) under the influence of a magnetic field and at normal conditions. In the experiment, under the influence of a constant magnetic field with magnetic induction of 0.3 T, the samples of raw materials and catalyst were processed, both separately and together.

Tables 1, 2, 3 show the physicochemical parameters of the raw materials and catalyst used in the process, respectively.

Table 1. Physicochemical characteristics of vacuum gas oil

Indicators	Vacuum distillate
Density at 20 °C, kg/m^3	900
Fraction composition, % vol.	
I.B.P.	290
10 %	310
20 %	330
30 %	350
40 %	380
50 %	410
60 %	425
70 %	440
80 %	455
90 %	470
F.B.P.	500
Total distilled, % vol.	
up to 350 °C	7.0
up to 400 °C	45.0
up to 450 °C	86.0
up to 500 °C	98
Kinematic viscosity at 50 °C, mm^2/s	21.64
Sulphur content, % wt.	0.7
Flash point (in an open cup), °C	175
Freezing point, °C	(+)18
Acidity, mg KOH/100 ml of raw material	–
Iodine number, g J_2/100 ml of raw material	–
Coking property, % wt.	0.4
Ash content, % wt.	n/a
Content of mechanical impurities, % wt.	n/a
Water content, % wt.	0.2
Excise tar content, % wt.	10
Group hydrocarbon composition by the adsorption method,% wt.	
naphtheno-paraffin	70.7
light aromatics	9.3
medium aromatics	17.1
heavy aromatics	18.2
Resin	3.0

Table 2. Quality characteristics of atmospheric residue

Indicators	Values
Density at 20°C, kg/m^3	939.4
Fraction composition, % wt.:	
≤ 350°C	2
350-400°C	5
400-450°C	18
450-500°C	23
≥ 500°C	52
Temperature, °C:	
Initial boiling	346

Pour point	+ 22
Kinematic viscosity at 100 °C, mm^2/s	17.9
Conradson coking capacity, % wt.	5.7
Content, % wt.	
Sulphur	0.4
Ash	0.0658
Asphaltenes	2.8
Resin	10.28
Molecular mass	475
Metal content, % wt.:	
V	$8 \cdot 10^{-4}$
Ni	$13.2 \cdot 10^{-4}$
Fe	$4.0 \cdot 10^{-4}$
Cu	$0.54 \cdot 10^{-4}$
Na	$3.2 \cdot 10^{-4}$

Table 3. Qualitative characteristics of the OMNIKAT-210P catalyst

Indicators	Values
Microstructure after heat treatment at 750 ºC for 5 hours, μm	150-180
Average particle size, μ	65-70
Average pore diameter, mm	0.4-0.45
Bulk density, g/ml	0.61-0.65
Chemical composition, % wt:	
Si	15.41
Al	11.7
Ti	1.08
Fe	0.711
V	0.402
S	0.199
Cl	0.196
K	0.154
Mn	0.069
Cr	0.057
Ba	0.026
Sr	0.015
Zr	0.009
Pb	0.009
Zn	0.006
Ni	0.04
Co	0.003
Nb	0.002
Bi	0.001
Sn	0.001
Rn	0.001

The experiments were carried out at 500°C and a feed rate of 1 h^{-1} in a laboratory setup shown in Fig. 1.

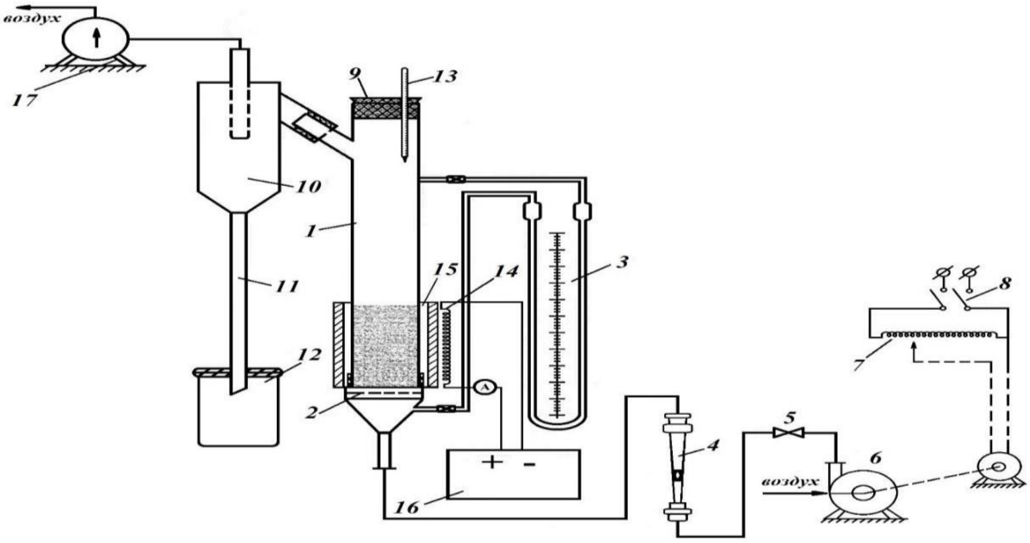

Fig. 1. Schematic illustration of a laboratory setup for studying the effect of a magnetic field on the catalytic cracking process: 1 - reactor, 2 - metal mesh, 3 - differential pressure gauge, 4 - rotameter, 5 - control valve, 6 - air fan, 7 - autotransformer, 8 - potentiometer, 9 - plug, 10 - cyclone, 11 - riser, 12 - storage container, 13 - thermometer, 14 – magnetic coil, 15 - magnet wire (core), 16 - regulated power supply, 17 - gas meter

Before start-up, the unit is purged with nitrogen, which is preliminarily passed through a reactor with copper shavings placed in a furnace to remove oxygen. The reactor 1 of the setup is made of quartz, the volume of the reaction zone is 30 cm^3, and the inner diameter is 30 mm. The automatic control system and autotransformer 7 provided the required process temperature. The experiments were carried out at a temperature of 460-510°C. The raw mixture was fed into the reaction zone using a special liquid pump.

The volumetric feed rate was 1 h^{-1}. Initially prepared granular catalyst Omnikat-210P in a volume of 15-20 cm^3 (the average diameter of the granules was 2 mm) was placed in a quartz reactor, preliminarily loading a quartz packing in a volume of 1 – 2 cm^3 into the lower part, a quartz packing in a volume of 2 – 3 cm^3 was also placed on top of the catalyst. The average diameter of the quartz contact granules was 2 mm.

Further, the reactor with the catalyst was placed in a cylindrical quartz furnace 2, while the process temperature was controlled by thermocouples at three points: the lower, middle, and upper layers of the catalyst. The temperature was measured using a chromel-copel thermocouple, which was placed in the thermocouple pocket of the reactor. In the reactor the operating temperature was gradually achieved by using temperature controller.

If it was necessary to work in a magnetic field, the reactor together with the stove was placed between the poles of an electromagnet 15 with a magnetic induction of 0.3 T, while the flux of magnetic induction was regulated by changing the direct current from the rectifier 16.

When the set temperature was reached, the raw material, preheated in the evaporator, in the vapor-liquid state, was fed from the container into the reactor 1 using a liquid pump. The autotransformer regulates the evaporator temperature, and the reaction temperature is read from the ratiometer.

The reaction of catalytic cracking is carried out in the reactor at given operating parameters: temperature and volumetric feed rate. The reaction products from the reaction zone enter the condensation-refrigeration system. After condensation, the catalyzate is sent to the receiver, and the hydrocarbon gases, having passed the gas meter, are discharged into the atmosphere, with a preliminary gas sample taken for analysis.

After the completion of the experiment, the reactor is purged with air at a temperature of 600°C to implement the oxidative regeneration of the catalyst.

3.Results and discussion

Tables 4 and 5 show the experiment results of the catalytic cracking process under the influence of a constant magnetic field, both on the feedstock and on the OMNIKAT-210P catalyst. Analyzing the output data given in the tables, it follows that by adding 10% of atmospheric residue to the vacuum gas oil, it became possible to increase the yield of light fuels by 7%. This is probably due to the presence of polycondensed (phenanthrene and naphthalene) aromatic hydrocarbons in the composition of atmospheric residue. The above mentioned hydrocarbons can be classified as special activator additives that affect the formation of oil dispersed systems, as well as their properties and phase transitions.

The explanation for the increase in the yield of products of the catalytic cracking process with the addition of 10% of atmospheric residue to vacuum gas oil is the high adsorption capacity of the hydrocarbons included in the composition of atmospheric residue, which are chemisorbed on the catalyst surface at a rate and play the role of initiators of the carbonium ions formation, i.e. are initiators of cracking. Additionally, this initiation effect can be explained by the fact that the flow of thermal reactions intensifies with the increase in weight of the raw material.

Table 4. Effect of magnetic field on the process of catalytic cracking of pure vacuum gas oil

Indicators	**VGO at normal conditions**	**Magnetic treatment (0,3 T)**		
		feedstock (-) catalyst (+)	**feedstock (+) catalyst (-)**	**feedstock (+) catalyst (+)**
Taken:				
Vacuum Gasoil	100	100	100	100
Obtained, % wt.				
Gaseous products	14.8	10.1	10.4	13.8
Liquid products, including	80.0	85.0	83.5	81.0
Fraction I.B.P.-190 °C	32.3	40.5	41.7	35
Fraction 190-350 °C	21.4	23.7	22.3	19.2
Fraction above 350 °C	26.3	20.8	24.0	26.8
Coke	3.2	3.0	3.0	3.2
Losses	2.0	1.9	2.0	2.0
The sum of light fractions	53.7	64.2	64.0	54.2
Conversion	73.7	79.2	79.0	71.2

Note: (+) - processed by magnetic field; (-) - not processed by magnetic field

Table 5. Effect of magnetic field on the process of catalytic cracking of the VGO + 10% AR mixture

Indicators, % wt.	**Feedstock: VGO + 10 % AR at normal conditions**	**Magnetic treatment (0,3 T)**		
		feedstock (-) catalyst (+)	**feedstock (+) catalyst (-)**	**feedstock (+) catalyst (+)**
Obtained, %				
Gas products	17.5	4.6	4.5	17.8
Liquid products, including	77.2	90.3	89.7	76.9
Fraction I.B.P.-190 °C	29.3	26.8	26.6	28.6
Fraction 190-350 °C	35.1	55.3	55.1	36.2
Fraction above 350 °C	12.8	8.2	8.0	12.1
Coke	3.3	3.0	3.2	3.2
Losses	2.0	2.1	2.6	2.1
Total:	100	100	100	100
Conversion	87.2	91.8	91.7	88.4
The sum of light products	64.4	82.1	81.7	64.8

Note: (+) - processed by magnetic field; (-) –not processed by magnetic field

As can be seen from the data given in tables 4 and 5, the best results for the yield of light petroleum products (gasoline and diesel fractions) were obtained when processing with the influence of magnetic field only the catalyst: for cracking of VGO, the yield increased by 10.5%, and for cracking the mixture of VGO + 10% AR - by 17.7% wt. The yield of gases obtained in the cracking process under the influence of MF decreases by about 4.7%.

However, the qualitative composition of the catalytic cracking products obtained by processing under the influence of MF has greatly improved. According to the data given in table 6, when comparing the quality properties of catalytic cracking products carried out both under the influence of a magnetic field and at normal conditions, a decrease in the sulfur content in the composition of the desired products is mainly observed, the octane number of the gasoline fraction increased up to 83 points, in the composition of the obtained gases the content of valuable PPF and BBF increased up to 45.0% and 37.6%, respectively.

Table 6. Comparison of the qualitative charachteristics of products of VGO catalytic cracking under the influence of a magnetic field and at normal conditions

Product properties	**Under the influence of MF**	**At normal conditions**
Gasoline		
Density at 20 °C, kg/m^3	732.8	744.5
Sulphur content, %wt.	0.9	0.11
Octane number	83	81
PPF		
Propylene	45.0	43.2
C_4 %wt.	7.0	6.5
Sulphur content, % wt.	0.018	0.02
BBF		
C_3, %wt.	4.8	3.6
C_4,%wt.	37.6	29.9
C_5 and above, %wt.	3.2	2.8
Sulphur content , %wt.	0.016	0.02
Dry gas		
Sulphur, %vol.	0.7	1.0
C_3 and C_4, % wt.	8	10
CO	0.30	0.32

Additionally, on the spectrophotometer "SPECORD M40" in the region of 30000-10000 cm^{-1} were recorded electronic spectrum of diffuse reflection of the catalyst original sample and the sample treated with MF.

The spectra of the treated and initial catalyst have significant differences between themselves. Consequently, against the background of broad absorption, an absorption band has been observed at 25,500 and 20,000 cm^{-1}. The observed absorption bands in the spectra of the treated catalyst at 25500 and 20000 cm^{-1} can be characterized with absorption by Fe^{2+} and Fe^{3+} ions in octahedral coordination.

By considering the above mentioned, we can conclude that in our case, there is a possibility of Fe^{3+} ions presence in the system, in some cases with absorption bands coinciding with the Fe^{2+} bands, or masked by more intense background absorption.

Based on the performed spectral studies, it turns out that after treatment of the catalyst with a magnetic field, the Fe^{2+} and Fe^{3+} ions are stabilized in the system in octahedral coordination.

The effect of a MF with magnetic induction of 0.3 T on the dispersion and structure of petroleum feedstock - vacuum gas oil and its mixture with atmospheric residue - was also studied using dynamic light scattering (DLS) and UV spectroscopy. According to the data given in table 7, it can be seen that in the samples of a mixture of VGO with atmospheric residue without influence of magnetic field, the size of the determined particles ranges from 36.9 to 5541.7 nm.

Table 7. Particle size for initial (-) and magnetically treated (+) samples of atmospheric residue and its mixtures with VGO in solutions of hexane and toluene

Designation	Median, Nm	Mode, Nm	Geo mean, nm	Geo var., nm^2	Dif. Coef., m^2/s	q, %
AR (-) : hexane	639.5	624.7	740.5	1.17	$2.12\ 10^{-12}$	25
AR (-) : toluene	1.3	1.1	1.4	1.05	$1.21 \cdot 10^{-9}$	30
AR (+) : hexane	474.3	472.9	575.4	1.3179	$2.89 \cdot 10^{-12}$	16

AR (+) : toluene	1.3	1.1	1.4	1.05	$1.21\cdot10^{-9}$	55
VGO + AR (-) : hexane	37.7	36.9	38.6	1.07	$3.59\cdot10^{-11}$	30
VGO + AR (-) : hexane, in 10 min.	5541.7	«—»	5540.0	1.00	$2.45\cdot10^{-13}$	110
VGO + AR (+) : hexane, in 30 min.	1.1	1.1	1.2	1.004	$1.20\cdot10^{-9}$	55

The magnetic effect on the raw material leads to the dispersion of particles up to 1.2 nm and this state of the system remains stable over time. UV studies have shown that the bands observed in the spectrum characterize π-π transitions in the asphaltene structure, and the changes in the samples subjected to the influence of magnetic field (shift to longer wavelengths) are due to the fragmentation of clusters of asphaltene structures. Due to the fragmentation of asphaltene clusters, a decrease in the viscosity of atmospheric residue is achieved, so that it is liquefied in vacuum gas oil, consequently, makes it possible to reduce the temperature of the catalytic cracking process by 50°C, reaching 450°C.

Table 8. Comparison of composition of the wet gas obtained in the catalytic cracking process under the influence of a magnetic field and at normal conditions

Fluid Catalytic Cracking Unit №55 of Heydar Aliyev Oil Refinery		According to carried out research	
At normal conditions		Under the influence of magnetic field	
Designation	Volume %	Designation	Volume %
Hydrogen	3.1	Hydrogen	31.2
Oxygen	0.4	Oxygen	1.5
Nitrogen	0.3	Nitrogen	15.2
Methane	5.7	Methane	1.7
CO	0.6	CO	38.0
CO_2	1.1	CO_2	0.3
H_2S	0.6	H_2S	0.2
Ethylene	4.7	Ethylene	0.9
Ethane	2.7	Ethane	2.0
Propylene	15.2	Propylene	2.2
Propane	5.9	Propane	1.3
Isobutane	16.2	Isobutane	1.2
Isobutylene	4.6	Isobutylene	1.0
Normal butane	6.6	Normal butane	0.5
Tertiary butane	5.7	Tertiary butane	0.7
Stabilized buthylene	4.7	Stabilized buthylene	0.5
3- methyl buthene-1	0.4	3-methyl buthene-1	0.0
Isopenthane	11.9	Isopenthane	1.1
2-methyl buthene-1	2.2	2-methyl buthene-1	0.1
Normal penthane	5.8	Normal penthane	0.2
2-methyl buthene-2	1.6	2-methyl buthene-2	0.2
Density at 20°C	1.521	Density at 20°C	1.261

Table 8 shows a comparison of qualitative characteristics of the wet gas obtained both in the catalytic cracking unit № 55 at the Heydar Aliyev Oil Refinery and in the process of catalytic cracking carried out by us under the influence of constant MF. Based on the data presented, it is quite noticeable that a decrease in the amount of such components as CO_2, H_2S and an increase in the nitrogen content take place when the process is carried out with the influence of a constant magnetic field. For wet gas, a decrease in the content of acidic components in its composition is a great advantage, which makes it possible to reduce the risk of corrosion of the process apparatus.

4.Conclusion

In conclusion, on the basis of the carried out research, we found that by applying the constant magnetic field to the catalytic cracking process, the overall efficiency of the process, yield and quality of desired products considerably increase. The most adequate results were obtained by preliminary magnetic treatment of only the catalyst due to the provision of a high yield of light oil products (gasoline and diesel fractions) and an improvement in the qualitative parameters of the obtained gas fractions, thereby making it possible to significantly increase the efficiency of the process.

NOTE

The magnetic resonance characteristics of the observed EPR signals are given in table 9.

Table 9. Magnetic resonance characteristics of studied samples of gasoil and atmospheric residue mixtures

Percentage ratio of components «gasoil / atmospheric residue»	Organic radical						VO^{2+}			
	ΔH (0,1 mW)	ΔH (100 mW)	G (0,1 mW)	g (100 mW)	I, × 10^{17}, spin/g	A/Ao	ΔH (0,1 mW)	ΔH (100 mW)	I, × 10^{17}, spin/g	A/Ao
100/0	No signal									
95/5	7,5	7,8	2,0030	2,0031	4,8	4,4	9,6	10,5	0,55	8,8
85/15	7,5	7,8	2,0030	2,0032	9,7	4,2	9,6	10,5	1,1	9,8
0/100	7,2	7,3	2,0029	2,0032	17,0	5,3	9,9	11,3	5,1	13,9
After magnetic treatment										
95/5	7,4	7,9	2,0030	2,0032	18,8	5,3	9,8	10,7	3,1	10,7
85/15	7,4	7,9	2,0029	2,0032	20,0	5,1	10,9	10,7	4,4	15,2
0/100	7,2	7,3	2,0030	2,0032	20,0	4,9	9,5	11,9	4,9	11,5

Note. A /Ao - the ratio of the intensities of the signals recorded at the powers of 0.1 and 100 mW applied to the sample from the klystron.

In the initial samples of vacuum gas oil, the EPR signal is not recorded, which indicates the absence of polynuclear aromatic structures. In the sample, the feedstock + atmospheric residue, a rather strong signal of organic paramagnetic centers (PMC) is recorded, the parameters of which indicate that it is mainly due to hydrocarbon aromatic polyconjugation systems.

In addition to the singlet signal of organic PMCs, a weakly saturated microwave power (high value of the parameter A/A_0) 8-component signal of vanadyl ions VO^{2+}, caused by the hyperfine interaction of the unpaired electron magnetic moment with the magnetic moment of the nucleus ^{51}V is also recorded in the feedstock. The anomalously high intensity of the hyperfine structure component m=1/2, located in lower fields compared to the signal of organic PMCs, indicates that it is due to vanadyl porphyrin structures typical for heavy oil. Since some of them are "associated" with aromatic layers of organic matter in oil, the behavior of the EPR spectrum of vanadyl was also analyzed. The addition of 15-20% atmospheric residue into the feedstock leads to an increase in the concentration of organic PMCs, which indicates a molecular tightening of polyconjugated systems.

In this case, there is also a moderate increase in the recorded intensity of the spectrum of vanadyl ions (in terms of atmospheric residue), which can be explained by a change in the relaxation characteristics of their unpaired electron due to the transformation of the effective sizes of vanadyl porphyrin complexes.

5.Reference

1. Khalafova I.A., Aliyeva N.T., Aboul-Fotouh T.M. Intensification of catalytic cracking process //Azerbaijan Chemical Journal 2010, №1. P.161-165
2. Kapustin V.M., Gureev A.A. Technology of oil refining Volume 2 Destructive processes. M.: Kolos. 2007. P.334
3. Khalafova I.A., Yusif-zadeh A.A. The influence of magnetic field on hydrodynamics of "boiling layer" of catalytic cracking's industrial catalyst //Bulletin of Science and Education 2018, № 3(39). P.6-12
4. Letzie U. "Improvement of catalytic cracking process for the production of clean fuels" //Oil and Gas Technologies 2005. №6. P.52
5. Khalafova I.A., Huseynova A.D., Adjamov K.Y., Poladov F.M. The use of a constant magnetic field to intensify the catalytic cracking process// Oil refining and petrochemistry 2012, №6. P.20-21
6. Khalafova I.A., Huseynova A.Dj., Mirzoyeva L.M., Akhundov E.A., Poladov F.M. Cracking of vacuum distillation in the mixture with fuel oil on microspheric catalyst DA-250 // Transactions of Azerbaijan Institutes of Technology 2012, №2. P. 31-34

PP-V-7

DETERMINATION OF THE DYNAMIC ACTIVITY OF ADSORBENTS FOR THE PURPOSE OF COMPUTER MODELING

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Abstract: based on the results of the experiment, the analysis of various adsorbents for the adsorption of CO_2, H_2S and NO_2 from natural gas showed that it is advisable to use NaX zeolite. Synthetic zeolite of the NaX brand selectively extracts the above components simultaneously. The dynamic activity of adsorbents is the main indicator that determines the size of adsorbents and the time of the adsorption cycle.

Key words: adsorption, zeolite NaX, dynamic activity, adsorbent, sorption capacity, adsorbents.

1. Introduction.

It is known that natural gas can be purified from H_2S, CO_2 and NO_2 by adsorption or absorption. The most optimal sorption method for cleaning natural gas from H_2S, CO_2 and NO_2 is adsorption treatment. Adsorbents for $C0_2$ are activated carbon and zeolites, and for H_2S — only zeolites. This method simplifies the design of the cleaning system, since no special equipment is required for the regeneration of the adsorbent, which can be carried out with purified natural gas heated in a heat exchanger. The disadvantage of this method is the additional consumption of natural gas for the regeneration of adsorbents [1].

When removing $C0_2$ and H_2S from natural gas by absorption, mono- and diethanolamines with high absorption capacity are used. However, their application requires the introduction of additional complex equipment into the cleaning system related to the absorption of impurities contained in natural gas and the regeneration of absorbents with heat supply [2].

Gas preparation, as well as gas purification by adsorption method, has been widely used in practice and has a number of advantages. These are high environmental indicators, large drying depth, low specific adsorbent consumption, and good operating characteristics of plants [3].

General advantages of adsorption methods of gas purification:

1) deep cleaning of gases from toxic impurities;

2) comparative ease of regeneration of these impurities with their conversion into a commercial product or return to production.

The use of continuous cleaning methods in a moving adsorbent requires high-strength industrial sorbents, the development of which for most processes has not yet been completed. The absorption capacity of an adsorbent under operating conditions is considered to be its working or dynamic activity. Dynamic activity is always lower than static and depends on the operating conditions of the adsorbent. The dynamic activity of adsorbents is the main indicator that determines the size of the adsorbents and the time of the sorption cycle. To purify gases from H_2S, CO_2 and NO_2, zeolites are mainly used.

In computer simulations, the adsorption isotherms and the exact numerical value of the dynamic activity are particularly important.

The works [1, 2] show the possibility of isolation of H_2S, SO_2 and NO_2 from natural gases on NaX zeolites. It is known that the nature of NaX zeolite, its multiplicity relative to raw materials, and the isotherm of natural gas adsorption have a great influence on the results of H_2S, SO_2, and NO_2 adsorption.

However, the study of the thermal stability of zeolite adsorbents is important, which allows you to evaluate the thermal stability while determining the moisture content and some other characteristics of the adsorbent.

2. Experimental setup

This experimental material is devoted to the study of the adsorption under dynamic conditions of H_2S, SO_2 and NO_2 from natural gases and the determination of their adsorption isotherm, as well as their dynamic activity [5].

The characteristics of the adsorbent (NaX zeolite samples) are shown in table 1.

Table 1. Adsorption properties of NaX adsorbents

Indices	Samples		
	1	2	3
Density, g/cm^3	0,785	0,770	0,747

Granulation (mm), %			
2,7 – 2,0	33,2	34,0	31,6
2,0 – 1,5	63,7	62,8	63,8
1,5 – 1,0	3,1	3,2	4,6
Content, %			
ashes	7,4	7,1	7,9
kalia	0,20	0,26	0,27
sulfur	0,46	0, 47	0,67
Pore volume, cm^3/g			
$V_{ми}$	0,28	0,32	0,33
$V_{ме}$	0,11	0,13	0,12
$V_{ма}$	0,28	0,31	0,35
$V_{\sum}$	0,67	0,76	0, 80
The structural constants			
W_o cm^3/g	0,29	0,33	0,35
$B \cdot 10^6$ (for benzene)	0,44	0,54	0,54

Adsorption allows almost complete removal of polluting components from the gas mixture and makes it possible to perform deep gas cleaning. This explains the increasing use of adsorption methods for gas separation and purification in environmental protection where other methods are not effective enough.

Adsorbents used in waste gas treatment systems must meet the following requirements: have a high adsorption capacity when absorbing components, have a low concentration in gas mixtures, have high selectivity, have high mechanical strength, have the ability to regenerate and have a low cost.

Experiments on adsorption were carried out according to the following method. NaX zeolite attachments were activated in a muffle furnace at 673K for 2 hours, then cooled in a desiccator. The process of natural gas purification using synthetic zeolites was studied on a model flow-type installation. Natural gas from the common collector was fed to the adsorption column, which is a cylindrical device with a total height of 1250 and a diameter of 100 mm (volume of 10 liters). Figure 1 shows the experimental setup diagram.

Adsorption cleaning methods are based on the absorption of impurities by solids with a developed surface - adsorbents. The absorbed molecules are held on the surface of solids by Van- der-Waals forces (physical adsorption).

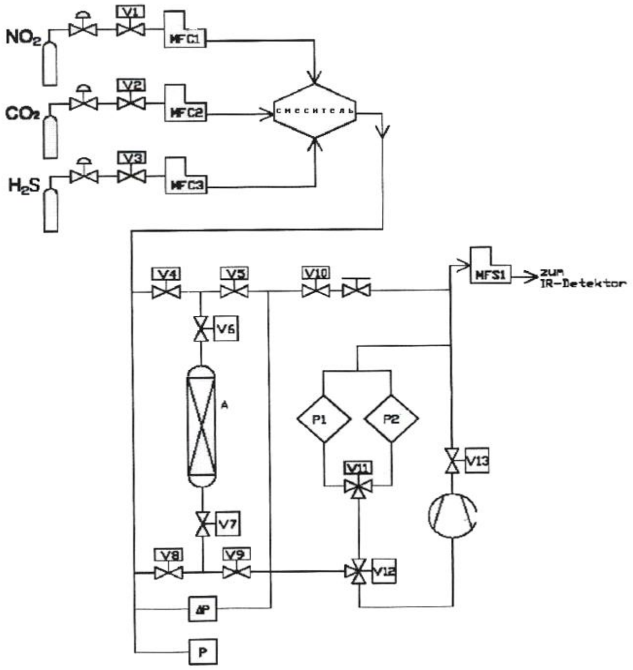

Fig. 1. Experimental setup diagram

3. Discussion and results

Based on the results of the analysis, the dynamic activity of the NaX adsorbent was calculated using the formula [4]:

$$A_д=C_0W\tau/h \qquad (1)$$

where C_0- the initial concentration of H_2S, CO_2, and NO_2 in solution, g/100g; W– speed of gas flow, m/s; τ - time protective action of the adsorbent, h - is the height of the adsorbent layer, m.

We have studied the adsorption isotherms of CO_2, H_2S and NO_2 on adsorbents-activated carbon SCT and zeolite NaX.

The adsorption isotherms are determined on NaX zeolite. The feasibility of Using NaX zeolite for adsorption of CO_2, H_2S and NO_2 has been established.

The adsorption isotherms are quantitatively described by Langmuir equations.

The dynamic adsorption capacity of the absorber is less than its equilibrium adsorption capacity, because under operating conditions, with a short contact of the solid and gas phases, the adsorption equilibrium can not be established:

$$a_д = a_\infty \eta, \qquad (2)$$

where η – the degree of utilization of the equilibrium (statistical) adsorption capacity.

Under the following conditions of the adsorption process: the height of the adsorbent layer H_a = 0.6...0.75 m; w = 0.3-0.5 m/s; $C_0 = (1\text{-}17) \cdot 10^{-3}$ kg/m^3 the degree of use of the equilibrium adsorption capacity n takes values from 0.85 to 0.9.

Thus, the stock ratio is the inverse of the degree of use the equilibrium adsorption capacity has the form:

$$k_з = \frac{1}{\eta} = \frac{a_\infty}{a_д} \qquad (3)$$

and varies between 1.12 and 1.25.

Dynamic sorption capacity (activity) $a_д$ – the amount of adsorbent absorbed by the sorbent layer until it appears behind the layer (slip), kg/m^2.

$$a_д = C_0 \cdot w \cdot \tau_з, \qquad (4)$$

where C_0 – the initial concentration of the adsorbent in the gas flow, kg m^3; w – the speed of the gas flow, m/s; $\tau_з$ - the time of the protective action of the adsorbent layer is determined by the Shilov equation:

$$\tau_з = k_з (H_a - h_a);\ k_з \cdot h_a = \tau_0;\ \tau_з = k_з \cdot H_a - \tau_0;\quad k_з = \frac{a_\infty}{w \cdot C_0}, \quad (5)$$

where $k_з$ – coefficient of the protective action of the layer of adsorbent, which expresses the travel time of the front of sorption per unit height of the absorber layer, s/m; h_a – the height of the unused layer of adsorbent in a dynamic experience, m; $\tau_з$ - the time the protective action of the layer of adsorbent, s. This is the time elapsed from the beginning of passing the vapor-gas mixture through the adsorbent layer to the moment when the adsorbent appears behind the adsorbent layer.

Table 2. Values of static and dynamic activity of adsorbents activated carbon SCT and zeolite NaX

Adsorbents	Activated carbon SCT			Zeolite NaX		
components	H_2S	CO_2	NO_2	H_2S	CO_2	NO_2
Static activity , g/100g	9.88	7.63	6.96	12.27	10.51	9.75
Dynamic activity, g/100g	7.02	5.24	4.73	9.89	8.34	7.81

4. Conclusions

The analysis of various adsorbents for the adsorption of CO_2, H_2S and NO_2 from natural gas has shown that it is advisable to use NaX zeolite. In computer simulations, the adsorption isotherms and the exact numerical value of the dynamic activity are particularly important. The dynamic activity of adsorbents is the main indicator that determines the size of the adsorbers and the time of the adsorption cycle [6].

5.References

1. Indra Perdana, Derek Creaser et.al. A comparison of NO_x adsorption on Na, H and BaZSM-5 films // Applied Catalysis, v.72, pp.82-91, (2007).
2. Youssef Belmabkhout, Rodrigo Serna-Guerrero, Abdel Hamid Sayari. Adsorption of CO_2 from dry gases MCM-41 silica at ambient temperature and high pressure 1: Pure CO_2 adsorption Chemical Engineering Science 64, 3721-3728, (2009).
3. Keltsev N.V. Basics of adsorption technology. Moscow, p.592, (1984).
4. Bystrov G.A., Galperin V.M., Titov B.P. Neutralization and utilization of waste in the production of plastics. l. Chemistry, p.139, (1982).
5. Bayramova A.S., Yusubov F.V., Babaev R.K. Investigation of the process of adsorption of H_2O, CO_2 and NO_2 from natural gas for the purpose of computer modeling // Austrian Journal of Technical and Natural Sciences, № 5-6, May June, Austria, Vienna, pp.123-127, (2015).
6. Yusubov F.V., Bayramova A.S. Analysis of operating modes of industrial adsorbers. Journal "Chemical and oil and gas engineering", Moscow, №5, pp.15-18, (2019).

OR-V-2

MODELING AND OPTIMIZATION OF THE ADSORPTION PROCESS FOR SEPARATING GAS MIXTURES

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Abstract. The process of adsorption separation of gas mixtures (CO_2, CH_4 and C_2H_6) was investigated. The adsorption isotherm of the process of adsorption separation of gas mixtures has been studied. Also, the output curves of the process of adsorption separation of gas mixtures were obtained. Synthetic zeolite CaA and natural zeolite-cliniptilolite (Ai-Dag deposits, Azerbaijan) were used as adsorbents. It was found that the isotherm for both of these adsorbents corresponds to the Langmuir type. From the gas mixture on the CaA zeolite, the components are adsorbed by the amount of CO_2 - 5.1 mmol / g, CH_4 - 0.5 mmol / g and C_2H_6 - 2.9 mmol / g at a pressure of 1 bar. From the gas mixture, the components on natural clinoptilolite are adsorbed by the amount of CO_2 - 4.7 mmol / g, CH_4 - 0.51 mmol / g, and C_2H_6 - 2.6 mmol / g at a pressure of 1 bar. The nature of the curves for all components of the gas mixture is the same. Consequently, the output curves of adsorption on CaA zeolite and on natural clinoptilolite at a gas flow rate of 15 cm / min were determined. The obtained isotherms and output curves of adsorption of gas mixtures show that for the adsorption separation of components (CO_2, CH_4, C_2H_6), it is better to use synthetic CaA zeolite. Modeling and optimization of the process of adsorption separation of gas mixtures (CO_2, CH_4 and C_2H_6) have been carried out.

Key words: gas mixtures, separation, adsorption, modeling, optimization

1. Introduction.

It is known that the emission of carbon dioxide contributes to the global warming of our planet. Therefore, it has now become a actual topic for many scientists and engineers around the world. Reducing CO_2 emissions requires new technologies to alleviate climate change. In particular, the separation of carbon dioxide from gas mixtures is a particularly important aspect of various industrial plants from an environmental and economic point of view. The methods of adsorptive separation of gas mixtures are based on physical adsorption and are considered as promising methods for the separation of gas mixtures [1].

The present work is devoted to modeling and optimization of the adsorption process for separation of gas mixtures (CO_2, CH_4 and C_2H_6). In scientific works [2-6], the characteristics of some adsorbents for the process of adsorption separation of gas mixtures separately CO_2, CO, H_2S, CH_4, C_2H_2, C_2H_6, C_3H_8, etc. have been investigated. The adsorption capacity, adsorption isotherms and the output curve are also studied. Various scavengers have been investigated to study CO_2 adsorption by pressure modulation. A comparison between these materials weredone based on the following criteria: adsorption equilibrium, regenerative capacity and aging. First, the adsorption of pure CO_2 wastested. The adsorption equilibrium was determined in the temperature range (0–75 °C) and the pressure range (0.4–8 bar) [7–10].

However, not yet sufficiently investigated and in some cases there is no information about the adsorption of various aspects of the separation of gas mixtures (CO_2, CH_4 and C_2H_6).

2. Experimental setup.

Sorption isotherms were measured on an automatic weighing adsorption apparatus (Rubotherm). As an absorber, a sample (about 50 mg) was placed in a sample tube and dried for 6 hours at 400 °C to remove residual solvent molecules prior to measurement. CO_2 (99.99%), CH_4 (99.99%) and C_2H_6 (99.99%) were used for all adsorption isotherm experiments and the output curve and temperatures were controlled with a water bath (297.5 K). Synthetic CaA zeolites and natural zeolite cliniptilolite (Ai-Dag deposits) were used as adsorbents. The characteristics of the adsorbents are given [1] and tab. 1. Their comparative analyzes were carried out. Used triple model gas mixtures: CO_2- 33.33%, CH_4- 33.33% and C_2H_6- 50% vol. The experiments were carried out at a temperature of 297.5 K and a pressure of 1 bar.

The experimental setup is shown in Fig. 1. On an experimental setup, a mixture of CO_2 / CH_4 / C_2H_6 gases were passed through a fixed bed of CaA zeolite, natural clinoptilolite, and then the concentration of these components was easured with a weight adsorption apparatus (Rubotherm).

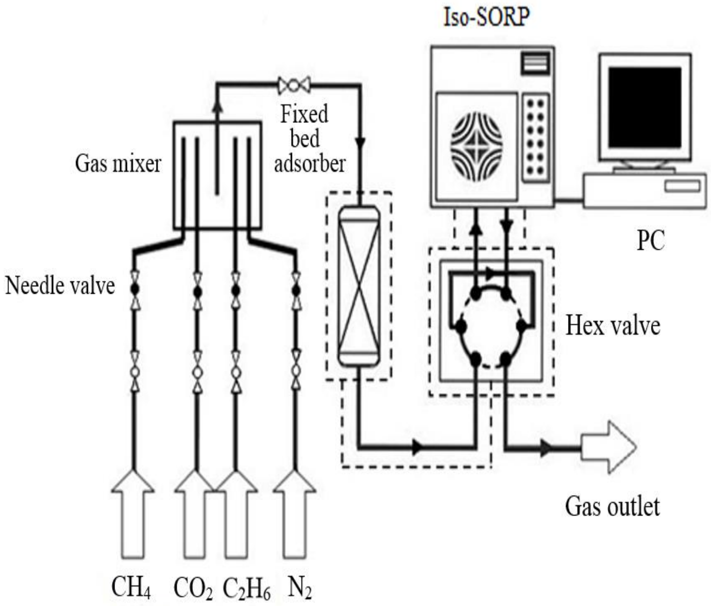


Fig. 1. Experimental setup diagram

Table 1. Characteristics of the synthetic zeolite CaA

Index	CaA
Bulk density, g / cm^3	0,75-0,80
Mass fraction of the fraction, 1.6-3.2 mm,	96,7
Crushing strength, kg / mm^2, kg / granule	2,0-2,5
Diameter of granules, mm	1,6-3,2
Dynamic capacity for water vapor, mg / cm^3, not less than benzene, mg / cm^3	120-130 50-55
Pore size, Aº	5

The experiments were carried out on the installation under dynamic conditions. Before the experiment, zeolites were dried in a muffle furnace at 400^0C for 6 hours in the presence of air. The temperature was maintained with an accuracy of 0.10 ° C using ultrathermostats.

3. Discussion and results

Figure 2 shows the adsorption isotherm of gas mixtures (CO_2, CH_4, C_2H_6) on the CaA adsorbent. As presented from Fig. 2, the isotherm corresponds to the Langmuir type. From the gas mixture, the components are adsorbed by the amount of CO_2 - 5.1 mmol / g, CH_4 - 0.57 mmol/g and C_2H_6 - 2.9 mmol/g at a pressure of 1 bar. Figure 3 shows the isotherm of adsorption of gas mixtures (CO_2, CH_4, C_2H_6) on an adsorbent - natural clinoptilolite. As can be seen, from Fig. 3 the isotherm corresponds to the Langmuir type.

From the gas mixture, the components are adsorbed by the amount of CO_2 - 4.7 mmol/g, CH_4 - 0.51 mmol/g and C_2H_6 - 2.6 mmol/g at a pressure of 1 bar. The nature of the curves for all components of the gas mixture is the same. The steepest slope is obtained for the CO_2 component. From the experimentally obtained adsorption isotherms it can be observed that the CaA zeolite, in comparison with natural clinoptilolite, exhibits a greater absorption capacity.

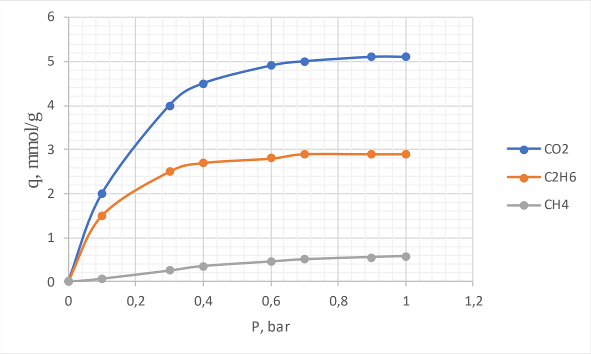


Fig. 2 Isotherm of adsorption of CO_2 / CH_4 / C_2H_6 on CaA zeolite

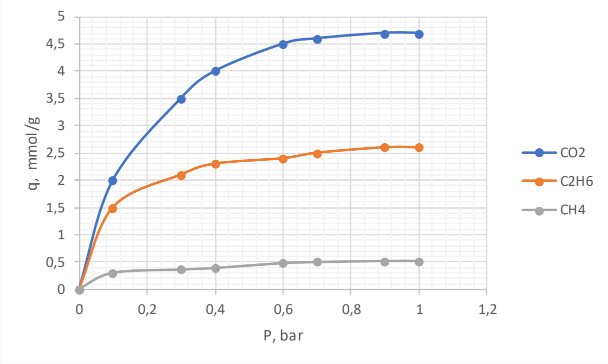


Fig. 3 Isotherm of adsorption of CO_2 / CH_4 / C_2H_6 on natural clinoptilolite

Hence, the adsorption output curves are determined. Figure 4 shows the output curve of the adsorption of gas mixtures (CO2, CH4, C2H6) on the CaA zeolite. As can be seen from Fig. 4, a high steepness of the curves was obtained for the CH4 component at a gas flow rate of 15 cm/min. Adsorption equilibrium started at 8 min for all components completed within 10 min. The whole process took approximately 10 minutes. Convex curves were obtained for the components CH4, C2H6, while for the component CO2 the curves were obtained in the S-shape. At the same time, the output curve of adsorption of gas mixtures (CO2, CH4, C2H6) on natural clinoptilolite obtained at a gas flow rate of 15 cm/min. As can be seen from Fig. 5, all curves were obtained in the S-shape. Adsorption equilibrium started at 10 min for all components completed within 12 min. The whole process took approximately 12 minutes. The obtained isotherms and output curves of adsorption of gas mixtures show that for the adsorption separation of components (CO_2, CH_4, C_2H_6), it is better to use the synthetic CaA zeolite.

It is known that Azerbaijan has rich deposits of natural clinoptilolite and synthetic zeolites are not produced. For this reason, in the future, after modification, natural clinoptilolites can be successfully used for the adsorptive separation of components (CO_2, CH_4, C_2H_6). This will give us economic benefits.

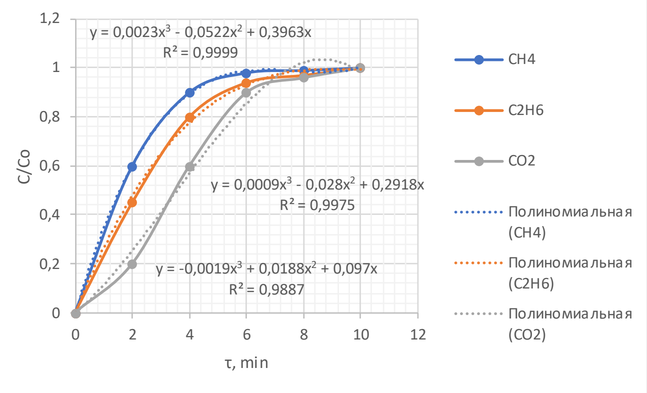


Fig. 4 Output curve of CO_2 / CH_4 / C_2H_6 adsorption on CaA zeolite at layer length 100 cm.

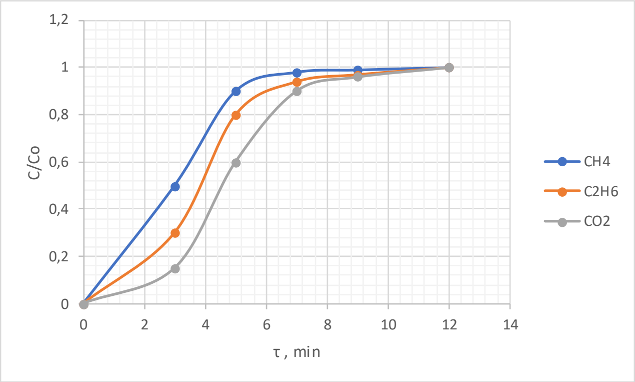


Fig. 5 Output curve of CO_2 / CH_4 / C_2H_6 adsorption on natural clinoptilolite, with a bed length of 100 cm.

A mathematical model of the adsorption process has been developed [11]. The mathematical model of the process contains the following equations: the equationof equilibrium of the absorbed substance;

$$\frac{\partial(c+a)}{\partial t} + \upsilon\frac{\partial c}{\partial x} = D_e\frac{\partial^2 c}{\partial x^2} , \qquad (1)$$

kinetic equation of the adsorption process;

$$\frac{\partial a}{\partial t} = \beta[c - c(a)], \qquad (2)$$

Initial and boundary conditions;

$$x = 0;\ c = c_0;\ \alpha = \alpha_0;\ \ t = 0;\ \ c = 0;\ \ \alpha = 0; \qquad (3)$$

as well as the Langmuir isotherm equation

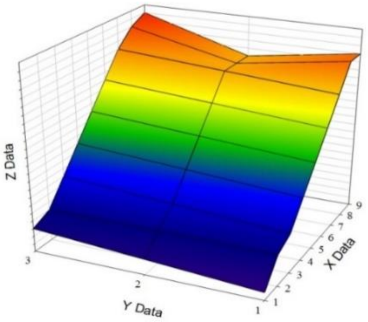
$$a = \frac{a_\infty \cdot b \cdot c}{1 + b \cdot c} \qquad (4)$$

where x is the variable height of the adsorption layer; t is the adsorption time; ɑ is the concentration of the substance absorbed in the solid phase (adsorbate); c is the concentration of the component that must be absorbed in the moving phase (adsorptive); ɑo and co - initial concentrations of adsorbate and adsorbent, respectively. - linear flow rate, β - total rate constant of external and internal diffusion; b is the constant of the Langmuir equation, - ɑ∞ equilibrium value of the adsorbate in the adsorbent. From the experimentally obtained adsorption isotherms, it can be seen that the CaA zeolite, in comparison with natural clinoptilolite, exhibits a higher absorptive capacity.

Consequently, the effect of the pressure drop in the adsorbent layer and the initial concentration of the adsorptive on the adsorbate concentration for the adsorption separation of components (CO_2, CH_4, C_2H_6) has been studied. As seen from Fig. 6 and 7, the pressure drop in the adsorbent bed and the initial concentration of the adsorptive sufficiently affects the concentration of the adsorbate at the outlet of the adsorber. Optimization was carried out by the modified Hook-Jeeves method. The following optimal process parameters were found: adsorption time - 11 min, adsorption temperature - 23 °C, pressure 0.92 bar, length of the fixed bed of adsorbent 94 cm. Equations of the output curves were obtained based on experimental data.

$Y = 0.0023 \cdot X^3 - 0.0522 \cdot X^2 + 0.3963 \cdot X$; $R^2 = 0.9999$ для компонента CH_4 (5)
$Y = 0.0009 \cdot X^3 - 0.028 \cdot X^2 + 0.2918 \cdot X$; $R^2 = 0.9975$для компонента C_2H_6 (6)
$Y = 0.0019 \cdot X^3 - 0.0188 \cdot X^2 + 0.097 \cdot X$; $R^2 = 0.9887$ для компонента CO_2 (7)

Equations (1) - (4), together with equations (5) - (7), will form a complete mathematical model of the process of adsorption separation of gas mixtures (CO_2, CH_4 and C_2H_6). The constructed mathematical model can be used with optimal process control.



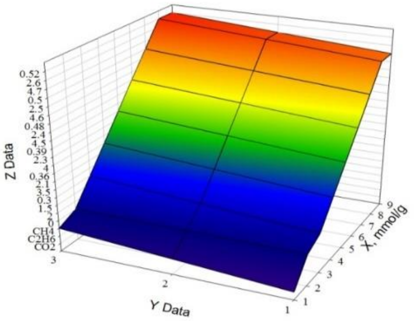
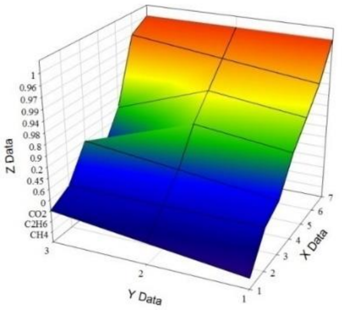


Fig. 6-a Dependence of the adsorbate concentration on the pressure drop of the CaA adsorbent bed X Data - CO_2, У Data- CH_4, Z Data- C_2H_6

Fig. 6-c Dependence of the adsorbate concentration on the pressure drop of the natural clinoptilolite laye X Data - CO_2, У Data- CH_4, Z Data- C_2H_6



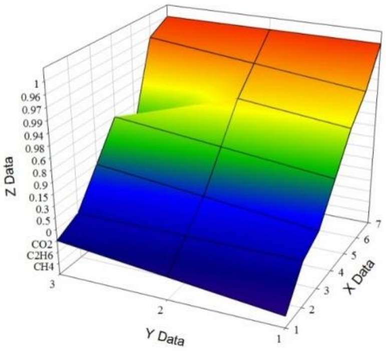


Fig. 7-a Dependence of the adsorbate concentration on the initial concentration of the adsorptive on the CaA adsorbent X Data - CO_2, У Data- CH_4, Z Data- C_2H_6

Fig. 7-c Dependence of the adsorbate concentration on the initial concentration of the adsorptive on natural clinoptilolite X Data - CO_2, У Data- CH_4, Z Data- C_2H_6

5.References

1. Yusubov F.V., Ibragimov Ch.Sh. Adsorption separation of gas mixtures in a fixed bed of adsorbent. Journal "Chemistry and technology of fuels and oils", No. 3, pp. 27-30 (2018).
2. Nikifirov I.A. Adsorption methods in ecology. Saratov State University, 48 p. (2011).
3. Shin-ichiro Noro, Rika Ochi , Yasutaka Inubushi , Kazuya Kubo , Takayoshi Nakamura , S.-i. Noro et al.CH_4/CO_2 and CH_4/C_2H_6 gas separation using a flexible onedimensional copper(II) porous coordination polymer / Microporous and Mesoporous Materials 216, 92-96 (2015).
4. Liao, P.-Q. et al. Monodentate hydroxide as a super strong yet reversible active site for CO_2 capture from high-humidity flue gas. Energy Environ. Sci. 8, 1011–1016 (2015).
5. Rajamani Krishna Highlighting the Influence of Thermodynamic Coupling on Kinetic Separations with Microporous Crystalline Materials . ACS Omega 4, 3409−3419, (2019).
6. Denysenko, D., Grzywa, M., Jelic, J., Reuter, K. & Volkmer, D. Scorpionate-type coordination in MFU-4l metal–organic frameworks: small-molecule binding and activation upon the thermally activated formation of open metal sites. Angew. Chem. Int. Ed. 53, 5832–5836 (2014).
7. Yusubov F.V., Bayramova A.S. Modeling heat and mass transfer during the adsorption of gas mixtures in the transition mode. "Journal of Engineering Physics and Thermophesics".vol. 92, No. 1, vol. 92, p. 120-127*(in Russian)* (2019).
8. Böhme, U. et al. Ethene/ethane and propene/propane separation via the olefin and paraffin selective metal–organic framework adsorbents CPO-27 and ZIF-8. Langmuir 29, 8592–8600 (2013).
9. Zhang, Y. et al. Highly selective adsorption of ethylene over ethane in a MOF featuring the combination of open metal site and p-complexation. Chem. Commun. 51, 2714–2717 (2015).
10. Pires, J., Pinto, M. L. Saini, V. K. Ethane selective IRMOF-8 and its significance in ethane–ethylene separation by adsorption. ACS Appl. Mater. Interfaces 6, 12093–12099 (2014).
11. Yusubov F.V., R.K. Babaev, E.A. Mamedov Optimization of adsorption processes in the oil and gas industry. Journal "Chemistry and technology of fuels and oils". Moscow, 2012, p. 48-51. (in Russian) (2012).

OR-V-4

DEVELOPMENT OF A COMBINED ALGORITHM TO FIND THE OPTIMAL CONTROL IN THE REACTOR CASCADE

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Abstract. The paper presents the task of chemical process optimization in the reactor cascade and considers a combined algorithm for solving the optimization task. The kinetic model of the process with variable reaction volume on the basis of law of active masses is given. The combined algorithm is based on the Lagrangian and Newton methods.

Keywords: reactor cascade, optimal control task, penalty method, Newton method.

1.Introduction

The methodology of the catalytic modeling is a clear sequence presented in detail in numerous works by Academician G.K. Boreskov and Corresponding Member of the Russian Academy of Sciences M.G. Slinko, as well as foreign scientists N.A. Amundson and R. Aris. They correspond to the general scheme of mathematical modeling formulated by Academician A.A. Samarsky.

Nowadays, the possibilities to increase the reactor productivity by increasing its size have been practically exhausted; in this connection, the task of intensification of catalytic processes at the expense of new methods of their maintenance, i.e., implementation of optimal control is set. A considerable number of works by G.K. Boreskov, M.G. Slinko, K. Denbig, A.I. Boyarinov, V.V. Kafarov, G.M. Ostrovsky, Y.M. Volin, V.I. Bykov, S.I. Spivak and other have been devoted to the development of methods for optimization of catalytic processes/

While solving the task of catalytic process optimization it is necessary to perform two stages: first, analysis of the kinetic model and determination of process limit values; second, technological optimization is carried out by selection of optimal structural and operating parameters of reactors.

2.Metod

2.1Kinetic model

Any chemical reaction is represented as $\boldsymbol{\sum_{i=1}^{m} \nu_{ij} X_i = 0,\ j = \overline{1,n}}$, where $\boldsymbol{X_i}$ - substances involved in the reaction, $\boldsymbol{\nu_{ij}}$ - stoichiometric coefficient at component $\boldsymbol{X_i}$ in j-th stage, n - number of elementary stages, m - number of substances involved in the reaction [1]. The speed of a single stage, expressed through the concentration of the i-th component C_i by a ratio of $N_i=VC_i$ (V – mixture volume), make a note of:

$$w_i = \frac{1}{V_p}\frac{VdC_i + C_i dV}{dt}, \tag{1}$$

where V_p is the volume of the reactor. If the volume of the reaction mixture is substantially unchanged during the chemical reaction ($dV \approx 0$) then $V_p = V$ and expression (1) takes the form:

$$w_i = \frac{dC_i}{dt}, \tag{2}$$

It often turns out that the value of dC_i/dt is related not only to the number of acts of chemical transformation, but also to the law by which the system volume changes. At the same time, this change can be made in an arbitrary way. For example, during the reaction in a cylinder with a movable wall (piston) the system volume can be arbitrarily changed out of any connection with chemical transformations taking place in the system. On the other hand, in practice, gas reactions with variable volume have to be faced when the number of molecules in the reaction changes and the system pressure is kept constant. Therefore, when developing a mathematical description of a complex process, it is necessary to take into account the change in the number of molecules in the reaction mixture in the course of chemical reactions. To determine whether there is such a change in the course of reactions, a matrix of stoichiometric coefficients is constructed, the elements of which are the stoichiometric coefficients v_{ij} of substances involved in reactions. According to the matrix, the components of the vector δ_i are found:

$$\delta_j = \sum_{i=1}^{m} v_{ij}\,,\ \ j = \overline{1,n}.$$

If at least one of the vector δ_i components is different from zero, the reaction will proceed with the change in the number of molecules (or reaction volume).

According to the law of mass preservation, the total material balance for the variant when the total concentration $C = \sum C_i$ c changes in time has the form:

$$\frac{dC_i}{dt} = \sum_{j=1}^{n} v_{ij} r_j\,, \quad i = \overline{1,m}, \tag{3}$$

where r_j is the reaction rate *j*, written out according to the law of the acting masses.

Let us pass to (3) concentrations of substances in mole fractions and complement the system with the condition for normalizing the components of the reaction medium:

$$\sum_{i=1}^{m} x_i = 1. \tag{4}$$

The initial molar density of the reaction medium C_0 is constant at all temperatures. Then rewrite system (3) in the form:

$$\begin{gathered} \frac{dx_i}{dt} = \frac{F_i - x_i F_n}{N}, \qquad F_i = \sum_{j=1}^{n} v_{ij} W_j, \\ \frac{dN}{dt} = F_n, \;\; F_n = \sum_{i=1}^{m} \delta_i W_i, \end{gathered} \tag{5}$$

where $N = C/C_0$ is the relative change in the number of moles of the reaction medium, $W_j = r_j/C_0$ are the reduced rates of chemical reactions, $j = \overline{1,n}$ with the initial conditions:

$$x_i(0) = x_i^0, \;\; i = \overline{1,m}, \quad N(0) = 1. \tag{6}$$

The resulting system of equations (5) with initial conditions (6) is a kinetic model of a complex (multi-stage) reaction, taking into account the change in the number of moles during its implementation [3] - [5].

The next stage of modeling is calculation of material and heat balance of the process in the reactor.

2.2.Modeling of an ideal bath mixing reactor

The Ideal Mixing Reactor (IMS) of periodic action is simultaneously loaded with all kinds of initial substances or their mixture and after a certain time required to achieve a given degree of completion of the process the production mixture is unloaded. The RIS operation is a periodically recurring cycle. Periodical processes are used as an integral part in the chain of operations and in such reactors, as a rule, low-tonnage processes are carried out.

As equations of IMS material balance we use the kinetic model of reaction (5)-(6).

Thermal balance equation has the form

$$\begin{gathered} C_p \frac{dT}{dt} = \sum_{j=1}^{n} Q_j W_j(x, T) + \frac{\alpha_x S_x}{C_0}(T_x - T), \\ G_x C_x \frac{dT_x}{dt} = \alpha_x S_x (T - T_x), \end{gathered} \tag{7}$$

with start conditions

$$T(0) = T^0, \quad T_x(0) = T_x^0, \tag{8}$$

where *T* and T_x- reaction and refrigerant temperatures; C_p - molar heat capacity of the reaction mixture; Q_j - thermal effects of reactions; α_x- heat transfer coefficient; S_x - specific heat transfer; C_x - refrigerant capacity; G_x - molar flow of refrigerant.

2.3.Modeling of the ideal displacement reactor

When developing a mathematical description of the process in a tube reactor, we will also consider a system of material and thermal balance equations.

The equations of material balance on the basis of kinetic model (5)-(6) have the following form

$$\begin{gathered} \frac{1}{S}\frac{dx_i}{dl} = \frac{F_i - x_i F_N}{\bar{N}}, \;\; F_i = \frac{1}{\vartheta C_0}\sum_{j=1}^{n} v_{ij} r_j, \quad i = \overline{1,m}, \\ \frac{1}{S}\frac{d\bar{N}}{dl} = F_N, \;\; F_N = \frac{1}{\vartheta C_0}\sum_{j=1}^{n} \delta_j r_j, \end{gathered} \tag{9}$$

where S - cross-sectional area; $x_i= N_i/N$. $N=\sum N_i$- total molar reaction mixture consumption $(N(0)=N_0)$; $N_i=\vartheta C_i$ - molar i-flow; ϑ - volume feed rate; l - reactor length; $\overline{N}=N/N_0$ - relative velocity of reaction flow.

Thermal balance of the displacement reactor is described by equations

$$\begin{aligned} \frac{C_pN}{S}\frac{dT}{dl}&=\sum_{j=1}^{n}Q_j\frac{r_j}{\vartheta C_0}+\frac{\alpha_xS_x}{C_0}(T_x-T), \\ \frac{G_xC_x}{S}\frac{dT_x}{dl}&=\alpha_xS_x(T-T_x), \end{aligned} \tag{10}$$

where G_x - molar refrigerant feed rate.

The system of equations (9)-(10) is supplemented by initial conditions

$$at\ l=0:\ x_i=x_i^0,\ i=\overline{1,m},\ \overline{N}=N^0,\ T=T^0,\ T_x=T_x^0. \tag{11}$$

2.4.Construction of a reactor cascade model

For further investigation we will move on to dimensionless variables and introduce additional upper indexation by reactor sequence. At that time, the material balance of the system in the j-core is represented by the following equations

$$\begin{aligned} &\frac{dx_i^j}{d\varepsilon^j}=f_i^j\,(x,T), \qquad i=\overline{1,m+1}, 0\le\varepsilon^j\le 1, \\ &\frac{dT^j}{d\varepsilon^j}=f_{m+2}^j(x,T,T_x), \\ &\frac{dT_x^j}{d\varepsilon^j}=f_{m+3}^j(x,T,T_x), \qquad j=\overline{1,R}. \end{aligned} \tag{12}$$

where the right side $\boldsymbol{f_i^j}$ of the reactor depends on the reactor type; $\boldsymbol{x_i^j}$ is a molar fraction of i-th reagent in j-core; ; $\boldsymbol{x_{m+1}^j}$ is relative change in the number of reactive medium molecules in the j reactor; $\boldsymbol{\varepsilon^j}$ – residence time in j-core for the ideal mixing reactor or length-on j-core for the ideal displacement reactor (dissipated); $\boldsymbol{T^j}, \boldsymbol{T_x^j}$ - temperature of reaction mixture and refrigerant in j reactor; R - reactor cascade size.

The system (12) closes the boundary conditions

$$\begin{aligned} x_i^1(0)&=x_i^0, \quad T^1(0)=T^0, \\ x_i^{j+1}(0)&=x_i^j(1), \quad T^{j+1}(0)=T^j(1), \end{aligned} \tag{13}$$

it is shown here that the output data of one reactor is the input for the next reactor. Thus, the mathematical model of the process in the cascade of reactors is presented as a system of equations **(12)-(13).**

3. Results and discussion

3.1.Theoretical optimization

At the stage of theoretical optimization, the temperature of the reaction mixture Tj is accepted as a control variable, and at the stage of technological optimization various parameters can be selected, in particular, the temperature of the refrigerant Tj_x. So, the controlled process described by the system of usual-venous differential equations with initial conditions of

$$\frac{dx}{dt}=f(x(t),u(t),t),$$

$$x(t_0)=x^0,$$

defined on time interval $\tau=[t_0,t_1]$, where t – independee variable, $x(t)$ – n- phase vector, $u(t)$ – control variable vector. Initial phase vector $x(t_0)=x^0$ is set.

Control parameters and phase variables can be subject to various restrictions based on technological or economic criteria. The task of optimal control with free right end of trajectory consists in search of vector-function $u(t)$ satisfying the constraints and delivering minimum to the function. $I_0(u)=\varphi_0(x(t_1))$. In the task of optimal management with terminal restrictions, there are also restrictions of the following kind $I_j(u)=\varphi_j(x(t_1))=(\le)0,\ j=\overline{1,m}.$ In the task of optimal control with phase limitations on the system trajectory there are phase limitations of inequality type $I_j(u)=g_j(x(t),u(t),t)\le 0,\ j=\overline{m+1,mt}.$ All functions $\varphi_j(x(t_1)),\ j=\overline{0,m}$ and $g_j(x(t),u(t),t),\ j=\overline{m+1,mt},$ are assumed to be continuously differentiable for all arguments.

The tasks of optimal management with phase limitations of the non-availability type have always been more time consuming and difficult to solve. The possibilities of the methods, which have been well studied theoretically, differ significantly in terms of accuracy, reliability and efficiency. The method of external penalty functions, despite many criticisms, has a number of attractive theoretical properties and can be very useful at the initial stages of calculations. The methods of the modified La Grange functions are much more precise and may differ in the absence of good initial approximations. The areas of convergence of Newtonian methods are even smaller, but with good approximations they allow to obtain highly accurate solutions. Thus, it is natural to use a combination of methods whose aggregate properties exceed the capabilities of each method separately.

3.2.Method of external penalty features

To preserve the continuity property of the second derivative, cubic penalty functions are used in tasks with terminal constraints. Penalty for violation of restrictions $g(x,u,t)\le 0$ is an addition to the target functionality of the subcomponent

$$\int_{t_0}^{t_1}\left\{\begin{matrix} g^3(x,u,t), & g(x,u,t)>0 \\ 0, & g(x,u,t)\le 0 \end{matrix}\right\}dt,$$

obtained by increasing the number of phase variables:

$$\dot{x}_{n+1}=\left\{\begin{matrix} g^3(x,u,t), & g(x,u,t)>0 \\ 0, & g(x,u,t)\le 0 \end{matrix}\right\},\quad x_{n+1}(t_0)=0.$$

Then the total functionality has the form $I(u)=I_0(u)+s\cdot x_{n+1}(t_1),$ where *s* is a penalty factor.

3.3.Method of modified Lagrange functionality

For the first time such design in the tasks of optimal control was proposed in the works of F.L. Chernousko. It is introduced into consideration the functionality of the

$$L(u,\lambda,s)=I_0(u)+\int_{t_0}^{t_1}\left[\frac{1}{2s}\left(\max\{0,\lambda(t)+s\cdot g(x,u,t)\}^2-\lambda^2(t)\right)\right]dt,$$

where $\lambda(t)$ – Lagrange multipliers (double variables), *s* – penalty factor. It should be noted that the penalty factor in this method has a different meaning than for the method of external penalty functions, as it is not a means of achieving the accuracy of the solution, but the regularization factor, which gives the property of quasi-monotonicity of the convergence process by the dual variables.

On the basis of a combination of these methods for the task of optimal control, we obtain an initial approximation to run the algorithm of the Newton method.

4.Conclusions

The problems of creating an accurate mathematical formulation of the problem of optimal management and finding an effective way to solve the problem remain relevant. Due to the rigidity of kinetic model equation systems, many optimization methods diverge and do not allow finding a solution. The use of combined algorithms facilitates the solution of this problem and also reduces the computational time of the optimal control task.

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5.References

1. Mikhailova T, Mustafina S, Mikhailov V, Podvalnyi S 2020 Application of computer simulation by the Monte Carlo method to the study of compositional heterogeneity of the product of copolymerization (IOP Conf. Series: Journal of Physics: Conf. Series 1479) doi:10.1088/1742-6596/1479/1/012073
2. Hamidullina Z, Ismagilova A, Spivak S 2020 Analysis of informativity of kinetic parameters of complex chemical reactions (Herald of Tver State University. Series: Chemistry) № 1 (39) PP. 70-80.
3. Ziganshina F, Akhmetyanova A, Ismagilova A, Hursan S, Akhmerov A 2018 Theoretical-graphic method for determination of homodynamic reactions for cyclic chemical compounds (Management systems and information technology) № 4 (74). C. 72-77.
4. Medvedeva O, Mustafina Sofia, Mikhailov V, Mikhailova T, Mustafina Svetlana 2018 Application of Monte Carlo Method in the Construction of Copolymerization Process Modeling Algorithm for the Continuous Mode in the Reactors Cascade (Proceedings of IEEE East-West Design & Test Symposium) PP. 209-212.
5. Mikhailova T, Miftakhov E, Mustafina S 2017 Study of the chain transfer agent's effect on the butadiene-styrene copolymer's properties based on the Monte-Carlo method (CEUR Workshop Proceedings. Proceedings of the Mathematical Modeling Session at the International Conference Information Technology and Nanotechnology vol. 1904) PP. 289-292.
6. Mustafina S, Mikhailova T, Mustafin T 2015 Optimal parameters of the α-methylstyrene oligomerization reaction in the presence of a zeolite catalyst (International Journal of Chemical Sciences) 13(2) PP. 1071-1075.
7. Stepashina E V 2012 The formation of a mathematical model of catalytic processes with a variable reaction volume on the basis of the graph-theoretic approach (Bulletin of the Tomsk Polytechnic University vol 320) № 3 pp 31-36.
8. Stepashina E.V 2010 The problem of modelling catalytic processes with varying reaction volume and the properties of solutions (Math society magazine) №3 (12) pp 122-128.
9. Karamova A 2009 Mathematical Modeling and Numerical Investigation of Catalytic Processes in the Reactor Cascade (in Russian): Dis. ...Cand. of Physics and Mathematics. 02.00.04, 05.13.18 (Ufa: Bashkir State University) p 127
10. Karamova A, Mustafina S and Spivak S 2008 Algorithm for solving the task of optimization of the process with variable reaction volume in the reactor cascade (Ufa: Vestnik of Bashkir University) pp 855-859

OR-V-1

IDENTIFICATION OF THE GRAVITATIONAL DEPOSITION MODEL OF A SINGLE WATER DROP IN OIL

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Abstract. The process of gravitational sedimentation of a single spherical water droplet resting in an oil reservoir is considered. To describe this process, a mathematical model is proposed that takes into account the actions of the gravity force of the drop, the buoyancy force of Archimedes, the force of the added mass and the resistance force of oil. Within the framework of the proposed model, the problem is posed of identifying the drag coefficient according to an additionally specified condition relative to the droplet velocity at a certain fixed point of the reservoir. To solve the problem, an analytical solution to the model is determined and the resulting solution is substituted into an additional condition. As a result, the identification problem is reduced to a nonlinear transcendental equation for the desired drag coefficient. A simple iteration method is used to numerically solve the obtained equation. Based on the proposed computational algorithm, numerical experiments were carried out for model data.

Keywords: gravitational settling, fluid drag force, drag coefficient.

1.Introduction

It is known that oil extracted from the bowels of the earth is not a pure product, but includes various side components: water from reservoirs, salt, oil gas, mechanical impurities, etc., which affect the quality of raw materials and the operation of the production and technological process. In order for the oil produced from oil wells to be allowed to be processed further, it is necessary to purify it from various kinds of impurities. Chemical, physicochemical, and physicomechanical methods are used to remove water from liquid hydrocarbons [1]. Mostly chemical methods are used to remove dissolved water. These methods are based on chemical reactions that occur between the water contained in hydrocarbons and a chemical reagent introduced into them, which reacts with water to form a compound insoluble in the hydrocarbon phase. Physicochemical methods are based on the ability of some substances, which are adsorbents, to bind water molecules in the hydrocarbon phase in an emulsified and dissolved state. Physicomechanical methods include methods of separation of emulsions in force fields: in a centrifugal field; in an electric field; in a gravitational field. Gravity settling is considered the most common method of physical and mechanical dehydration of oil. Two types of sedimentation modes are used - periodic and continuous, which are respectively carried out in sedimentation tanks of periodic and continuous action. Batch tanks are usually cylindrical tanks. The crude oil to be dewatered is introduced into the reservoir via a distribution pipe. The oil is kept in the tank for a certain time. During the aging process, a compound of water droplets is formed and larger and heavier water droplets under the influence of gravity (gravity) settle to the bottom and accumulate in the form of a layer of produced water. The oil is then collected at the top of the reservoir. The settling is carried out when the processed oil is stationary.

It should be noted that for effective control of oil dehydration processes by gravitational sedimentation in reservoirs, it is very important to build a mathematical model of gravitational sedimentation of individual water droplets in oil. The creation of this model allows us to assess the influence of various factors on the efficiency of the sedimentation tanks.

2. Problem formulation and solving method

Let us consider the process of gravitational settling of a spherical incompressible drop of water at rest in an oil reservoir. We will take the point of origin of the water drop in oil as the reference point and direct the coordinate axis vertically downward.

Suppose water droplets are forced by gravity force P directed vertically downwards

$$P = m_w g ,$$

buoyancy force of Archimedes F_A , directed vertically upwards

$$F_A = -m_w g \frac{\rho_o}{\rho_w},$$

the force of the added mass F_D equal to half of the oil mass in the volume of the drop, directed vertically upwards

$$F_D = -\frac{2}{3}\pi R^3 \rho_o \frac{du}{dt}$$

and the oil resistance force F_τ, described by Newton's quadratic law of resistance, depending both on the properties of oil and on the speed and shape of the drop, also directed vertically upwards

$$F_\tau = -\frac{C}{2} s_w \rho_o u^2,$$

$u = u(t,z)$ - the rate of gravitational sedimentation of the drop, ρ_w-density of a drop, g -free fall acceleration, $m_w = \frac{4}{3}\pi R^3 \rho_w$ - mass of the drop, ρ_o - the density of the oil resting in the reservoir, $s_w = \pi R^2$ - maximum drop of cross-sectional area, C - dimensionless coefficient of resistance, depending on the mode of movement, R - radius of a drop , g - acceleration of gravity.

Then, according to Newton's second law, the mathematical model of the gravitational sedimentation of a drop in the reservoir can be represented as

$$m_w \frac{du}{dt} = m_w g - m_w g \frac{\rho_o}{\rho_w} - \frac{2}{3}\pi R^3 \rho_o \frac{du}{dt} - \frac{C}{2} s_w \rho_o u^2$$

or

$$\frac{du}{dt} = \beta - C\lambda u^2, \qquad (1)$$

Which $\beta = \frac{4g(\rho_w - \rho_o)}{4\rho_w + 2\rho_o}$, $\lambda = \frac{3\rho_o}{2R(4\rho_w + 2\rho_o)}$.

Taking into account the ratio

$$\frac{du}{dt} = \frac{du}{dz}\frac{dz}{dt} = u\frac{du}{dz},$$

we transform equation (1). As a result, we will have

$$u\frac{du}{dz} = \beta - C\lambda u^2. \qquad (2)$$

Suppose that the following initial condition is given for equation (2)

$$u\big|_{z=0} = 0. \qquad (3)$$

Obviously, when setting the parameters C, ρ_w, ρ_o, R solving equation (2), taking into account the initial condition (3), we can find the dependence of the drop sedimentation rate on the coordinate z.

However, it is necessary to note a very important circumstance regarding the drag coefficient C. It is generally accepted that the drag coefficient depends on the value of the Reynolds criterion Re [2–4]. In order to choose the value of the drag coefficient, you must first know the value of the Reynolds criterion. However, due to the fact that the formula for calculating the Reynolds criterion includes an unknown function - the rate of sedimentation of a drop $u(t,z)$, it is not possible to calculate the value of the Reynolds criterion and, therefore, the drag coefficient. Suppose that the drag coefficient C is unknown, and instead of this, the droplet velocity at some fixed points in the reservoir is assumed to be given

$$u\big|_{z=h} = v. \qquad (4)$$

Thus, the identification problem is to determine a function $u(t,z)$ and a coefficient C that satisfy equation (2) and conditions (3), (4). To solve the target identification problem (2) - (4), we first find an analytical solution to equation (2) that satisfies the initial condition (3). Equation (2) is a differential equation with separable variables and its solution, taking into account condition (3), is written in the form

$$u(t,z)=\sqrt{\frac{\beta(1-e^{-2C\lambda z})}{C\lambda}}\,. \tag{5}$$

The solution of equation (2), presented in the form (5), substituting into the additional condition (4), we obtain the following nonlinear transcendental equation for the drag coefficient C

$$C\lambda v^2=\beta(1-e^{-2C\lambda z})\,. \tag{6}$$

In view of the nonlinearity of equation (6), it is not possible to find its analytical solution. For the numerical solution of equation (6), one can use the simple iteration method [5].

Thus, having determined the droplet velocity at a certain fixed point $z=h$, by direct measurement in the reservoir, it is possible to find the value of the drag coefficient from the solution of equation (6).

3. Results of numerical calculations

On the basis of the proposed computational algorithm, numerical calculations were carried out for the model data. The results of numerical calculations carried out for the case of $\rho_w =$ 1000 кг/м^3, $R=$0.005; 0.02; 0.05 м , $\rho_o =$ 900 кг/м^3, are presented in the table.

Numerical calculations show that as the droplet velocity increases at a fixed point in the reservoir, the drag coefficient decreases. However, the opposite picture is observed with increasing droplet size: as the droplet radius increases, the drag coefficient increases. The analysis of the results obtained shows that by fixing the droplet velocity at a certain point in the reservoir, it is possible to find the value of the drag coefficient using the proposed algorithm. The proposed computational algorithm can be used to study the processes of oil dehydration by gravity sedimentation.

Table 1. Results of a numerical experiment

v ,m/s	Calculated value C		
	$R=$0.005 m	$R=$0.02 m	$R=$0.05 m
0.25	0.2322	0.9291	2.3229
0.50	0.0580	0.2322	0.5807
0.75	0.0257	0.1031	0.2579
1.00	0.0142	0.0569	0.1424
1.25	0.0084	0.0336	0.0840
1.50	0.0047	0.0189	0.0473
1.75	0.0021	0.0084	0.0211
2.00	0.0001	0.0003	0.0009

4.Conclusion

1. The paper proposes a mathematical model of the process of gravitational deposition of a single spherical drop of water at rest in the oil reservoir.
2. The proposed model is based on a computational algorithm for identifying the drag coefficient according to an additionally specified condition relative to the rate of gravitational deposition of a drop at a certain fixed point of the reservoir.

5.References

1. Planovskiy A.N., Nikolaev P.I.: Processes and devices of chemical and petrochemical technology. Khimiya, Moscow (1987) (in Russ.).
2. Bürger, R. & Wendland, W. L.: Sedimentation and suspension flows: Historical perspective and some recent developments. Journal of Engineering Mathematics 41(2), 101–116 (2001).
3. Vodop'yanov I. S., Petrov A. G., Shunderyuk M. M.: Unsteady sedimentation of a spherical solid particle in a viscous fluid. Fluid Dynamics 45(2), 254-263 (2010).
4. Dorgan A. J. and Loth E. Efficient calculation of the history force at finite Reynolds numbers. Int. J. Multiphase Flow 33(8), 833–848 (2007).
5. Kalitkin N. N.: Numerical methods. BHV-Petersburg, Saint Petersburg (2011) (in Russ.).

VI. Industrial ecology.

OR-V-5

MODELING OF CRUDE OIL - SURFACTANT INTERACTION BASED ON THE DATA OF DYNAMIC LIGHT SCATTERING STUDY

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Abstract. The presented work presents the results of a study of the effect of a surfactant (surfactant) on crude oil by the method of dynamic light scattering (DLS) in combination with measurements of viscosity and density, a mathematical description of this interaction. The effect of surfactants on crude oil is considered as a process aimed at maintaining the stability of oil by changing the particle size distribution, which occurs with a decrease in the average particle size of the colloidal system. The method of boundary functions with asymptotic approximation for solving singularly perturbed equations with a small parameter was used to simulate the process of interaction between a surfactant and an oil colloidal system. The change in the distribution of particles of a colloidal system under the action of a surfactant on it is presented as an ensemble of parallel identical processes in specified intervals of particle size, in which the same process takes place with its own initial conditions. The calculation results are presented in the form of distribution curves in dependence on the time of exposure to surfactants on the oil colloidal system.

Key words: oil, colloid, stability, surfactant, particle distribution density, asymptotic modeling method

1. Introduction

When transporting oil from the well to the collection point and further along the main oil pipeline, especially in the autumn-winter period, complications arise caused by the deposition of asphaltene-resinous-paraffin substances on the inner surface of oil pipelines. The accumulation of these sediments leads to a significant decrease in the flow area of the oil pipeline, at which the transportation of the produced oil is possible at a higher pressure. An increase in pressure in the oil pipeline leads to an increase in pres-sure at the well head, which reduces production, as well as the destruction of a worn-out pipeline, leading to oil spills, polluting the environment. [1,2]. To maintain stability with a given dispersion, surfactants of various nature are introduced into the oil environment. By this, by reducing the hydrodynamic resistance, the process of oil transportation through pipelines is optimized [3-5]. The paper presents the results of a study of the effect of surfactants on crude oil by the method of dynamic light scattering in combination with measurements of viscosity and density and a mathematical description of this effect.

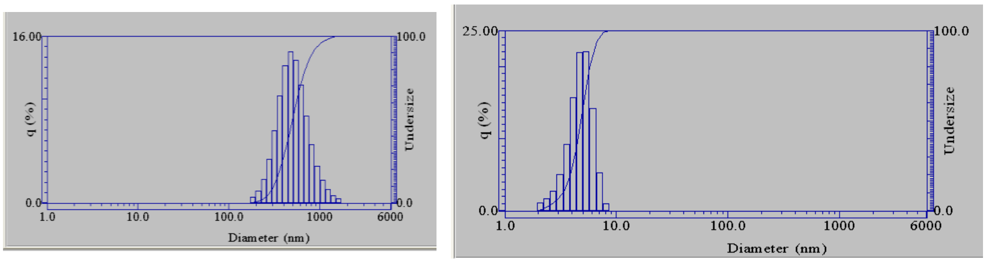
2. Experiment and its results

Samples of dehydrated oils from the Neftchala, Alat-Deniz and Bulla-Deniz fields were studied as objects of research.. Table 1 shows the values of a number of physicochemical characteristics of the studied oils.

Table 1. Physicochemical characteristics of the investigated series of oils

Oil *	Kinematic viscosity, sSt	Pour point, °C	Density, g/cm^3	Oil composition,%		
				Heavy paraffins	Asphaltene	Resins
Нефтчала	196.53	-34	0,9124	0,33	2,14	18,85
Алят-дениз	185,0	+19	0,8687	10,0 -15,0	0,3 –1,2	3,2 - 9,0
Булла-дениз,	22,0	+13	0,840	14,0	0,24	13,35

* Before measurements, all oil samples were dehydrated to a residual water content of 0.3% (by weight).



a) b)

Fig. 1. Histograms of DRS for a mixture of oils from the Alat-Deniz and Bulla-Deniz fields before and after the addition of **SNPKh**-2005 additive in an amount of 0.001 wt% at a temperature of 20 °C.

3.Results and discussion

As can be seen from the above Fig. 1, the effect of surfactants on the oil system results in a change in the particle size distribution density of the colloidal system. The study of the dependence of the DRS histograms on the time of exposure to the surfactant on the oil colloid shows that the process with the precipitation of ARPD in the sediment is significantly slowed down in the presence of the surfactant and during a long fire the quasi-equilibrium state of the oil colloidal system is maintained.

The quasi-equilibrium state of the oil colloidal system, established under the influence of surfactants, can be represented in a simplified form by a combination of the following transitions::

$$A+B \underset{K2}{\overset{K1}{\rightleftarrows}} R, \quad (1) \qquad\qquad R \xrightarrow{k_3} D \quad (2)$$

Here A - colloidal particles of oil, B - molecules of surfactant introduced into the oil colloid; R-complexes of petroleum colloid particles with surfactants. Crushing the aggregate into fragments under the influence of surfactants, i.e. fragmentation and "capture" of fragmentation products by surfactant molecules slows down the process of their settling. Scheme (2) displays the process of breaking stability, when aggregates A, sticking together, grow to such a size D that they settle on the surface of the pipeline. The coefficients k1, k2 are the constants of the transitions of the initial state A to the state R after interaction with the surfactant, k3 is the constant of the transition of A to D.

The process observed for an oil colloidal system is considered by us as an ensemble of parallel processes in given intervals of particle size, within which the same process X (t) proceeds with the corresponding initial conditions, which are described by the same equations of motion, but have different initial microstates x. In general, the structure of the ensemble is determined by the density function ρ (x), so that ρ (x) dx represents the number of sample systems that have initial microstates belonging to the volume element dx. The set of sampled values X consists of all possible microstates x. The adopted approach allows us to take the measured distribution Px as the initial condition of the Cauchy problem and calculate the final state of the particles (size) of the oil liquid. For the mathematical description of the process, the following basic provisions are adopted:

1. There is homogeneity, pair interactions and invariability of the type of oil colloid particles in time.
2. Particles of oil colloid and surfactant particles are uniformly distributed in the reaction zone and there is no diffusion.
3. The number of particles changes (increases or decreases) in a continuous manner, and the function describing the number is a continuously differentiable function.
4. The total mass of aggregating and crushing particles of the oil colloid does not change and retains its original value, i.e. there is no loss of mass.
5. The fragments of particles formed during fragmentation are able to stick together again with other fragments or with the initial aggregates, increasing their size;
6. The sedimentation rate of the aggregates is greater than the sedimentation rate of the debris particles; fragmentation inhibits the settling of a suspension of fragments of aggregated particles;
7. Other additional factors affecting the dynamics of aggregation and fragmentation are not taken into account, since they significantly complicate the structure of the forecast model and calculations based on it.
8. Interaction of surfactant with oil colloid leads to a decrease in surface tension and fragmentation of particles of oil colloid.

9. The total mass of particles is unchanged, only the number of particles, the size and size of their surface change.

To simulate the observed process, an asymptotic method for solving singularly perturbed equations was used - the method of boundary functions [5,6]. The method under consideration allows one to find approximate solutions of singularly perturbed problems in the form of series with an asymptotic approximation in parameter. As a small parameter, we used the values associated with the rate constants of the above reactions.

Small parameters in the equations are taken as perturbations, the initial differential equations are unperturbed, and the extended equations are singularly perturbed equations. The essence of the asymptotic approximation is that the approximation is attained immediately for all t from the interval $0 \le t \le T$ and the inequality $\left| x_\mu(t) - \bar{x}(t) \right| < c\mu^k$ holds. Therefore, the result is an asymptotic approximation with an accuracy of the order of μ. The system of differential equations, corresponding to the above schemes (1) and (2), describing the rate of change in the surface area of particles, contains a small parameter at the derivative, and with a known form of asymptotic expansion, the solution in this parameter has the following form:

$$\mu \frac{dS_{Ai}(t)}{dt} = -k_1 m S_{Ai}^2 - k_2 S_{Rj} + \mu k_3 S_D \;,$$

$$\frac{dS_{Rj}(t)}{dt} = k_1 S_{Ai}^2 - k_2 S_{Rj}\,, \quad 0 \le t \le T \qquad (3)$$

provided: t = 0 $S_{Ai} = S_{Ai}^0\,,\; S_{Rj} = S_{Rj}^0\;,\; i = \overline{1, \mathrm{N}}\,,\; j = \overline{1, \mathrm{M}}\,,$ (4)

Here μ> 0 is a small parameter; S_A(t), S_R(t) -vector functions of dimensions *n* and *m*.

The system of two differential equations (3) with respect to the sought-for surface areas $S_A(t)$, $S_R(t)$, $S_D(t)$ is a kinetic model of the process under consideration. Introducing vector functions we have: $z = (S_A^2,\, S_R)^T$ and the matrix $A = \begin{pmatrix} -mk_1 & k_2 \\ mk_1 & -k_2 \end{pmatrix}$.

In vector form (3) will take the form:

$$\mu \frac{dz}{dt} = A(t) + \mu\, f(t)\,, \;, \qquad (5)$$

$$z(0, \mu) = z^0 \text{, where } z^0 = (S_A^0,\, S_R^0)^T. \qquad (6)$$

For μ = 0, system (7) is expressed: $A(t)\,\bar{z} = 0$ (7)

The determinant det A(t) = mk$_1$k$_2$ - mk$_1$k$_2$ = 0 has eigenvalues λ = (λ$_1$, λ$_2$) the matrix A (t). $\lambda_1 = 0$, and equation (7) is a family of solutions. It is given by the formula $\bar{z}(t) = a(t)\, e_1(t)$, where $e_1(t) = (k_2,\, mk_1)^T$ is the eigenvector A (t) corresponding to $\lambda_1 = 0$, *a*(t) is an arbitrary scalar function on which the solution of the degenerate equation (7) depends. The value λ_2 of the matrix *A*(*t*) has the form $\lambda_2(t) = (k_2 - mk_1)$ and the corresponding eigenvector $e_2(t) = (-1,\, 1).^T$ For system (3), there is a solution and in obtaining its asymptotics we use the solution of the degenerate system [5,8]:

$$F(S_A, S_R) = -k_1 m S_{Ai}^2 \_ k_2 S_{Rj} + \mu k_3 S_{D_\upsilon} = 0,$$

$$f(S_A, S_R) = \frac{dS_i^R(t)}{dt} = k_1 S_{Ai}^2 - k_2 S_{Rj}\,, \qquad (8)$$

where $0 \le t \le T$,, $S_A^0(0) = S_{Ai}^0\,,\quad S_{Rj}^0(0) = S_{Rj}^0$ (9)

The functions *F*(S_A, S_R, *t*), *f*(S_A, S_R, *t*) are continuous and differentiable in the domain *D*. The equation *F*(S_A, S_R, *t*) = 0 has an isolated root relative to S_A. The solution to the problem system exists for t> 0 and as t → + ∞, tend to the rest point $S_{Ai}^0 = \chi(S_K^0,\, 0)$ of the domain D. Under these conditions, there is a unique solution ($S_A(t,\mu)$, $S_R(t,\mu)$) of problem (5), for which an asymptotic expansion in a small parameter is valid [5]:

$$Z(t,\mu)=\sum_{k=0}^{1}\mu^k(\bar{S}_i(t,\mu)+\Pi_\kappa S_i(\tau,\mu)),\quad i=S_A,S_S, \qquad (10)$$

and the assessment takes place: $\left\|\bar{Z}(t,\mu)-S^C(\tau,\mu)\right\|\le c_n\mu^k$. Here τ = t/μ. In expressions (9), (10) means ($S_A(t,\mu)$, $S_R(t,\mu)$) in the aggregate Vi = ($S_{Ai}(t,\mu)$, $S_{Ri}(t,\mu)$), i =0,1 are functions of the regular part of the asymptotics, $\Pi_k(t)$ = ($\Pi_k S_A(t)$, $\Pi_k S_R(t)$) - functions of the boundary layer.

$$\mathrm{S}^{\mathrm{C}}(t,\mu)=\sum_{k=0}^{1}\mu^k(\bar{S}_k(t,\mu)+\Pi_\kappa S_k(\tau,\mu)), \qquad (11)$$

Since the solution of the problem A_μ. is a vector-function, then by we mean $\bar{z}(t)$ some required component from $\bar{Z}(t,\mu)$. Asymptotic approximation with respect to the pa-rameter μ for a solution $\bar{z}_\mu(t)$ n the domain D if for all t from this subdomain at once the estimate $\bar{Z}(t,\mu)-S^C(\tau,\mu)\to 0$ holds as $\mu\to 0$. If for sufficiently small μ and for all t from D the inequality holds, where c and k are some given positive numbers, then $\bar{Z}(t,\mu)$ it is an asymptotic approximation for $\bar{z}(t)$ in the subdomain D with an accuracy of the order of μ^k. In this case, to achieve this accuracy Δ_N, each of the functions of the approximate solution is calculated with an accuracy, k = 0.1, ... N. [6]

This approach allows us to efficiently construct this approximation by solving simpler problems than the original problem A_μ. The constant S^C in (11) depends on n and does not depend on μ. To obtain a numerical solution to problem (5), the function is calculated with accuracy:

$$\mathrm{S}_{\mathrm{N}}^{\mathrm{Ch}}(t,\mu)=\sum_{k=0}^{1}\mu^k(\bar{S}_\kappa^h(t,\mu)+\Pi_k^h S_\kappa^h(\tau,\mu)),\quad 0\le t\le T, \qquad (12)$$

The function $\bar{\mathrm{Z}}_{\mathrm{N}}^{\mathrm{h}}(\mathrm{t},\mu)-\mathrm{S}_{\mathrm{N}}^{\mathrm{Ch}}(t,\mu)$ thus const ructed will be uniform in μ on the entire segment from [0;T] by numerical approximation of the solution of problem (5).

At each step of integration, the parallel solution of the equations formed above for each selected range of particle sizes with the corresponding initial conditions will make it possible to numerically obtain changes in the particle distribution. This leads to the need to solve a system of q·(g + l) non-linear differential equations, where g- is the number of differential equations determined by the method, q- is the number of selected ranges of constancy of oil particle sizes.

The $S_D(t)$ function is related to the amount of the settling part of the adsorbate. As indicated above, this amount is directly related to the size and concentration of the fragmented adsorbate. The $S_D(t)$ function is determined by integrating the last equation (5): $S_D(t,\mu)=S_A^0+\int_0^t S_A(t,\mu)\,ds$.

Substituting its asymptotics instead of $S_A(t,\mu)$, we can find the asymptotics of the function $S_D(t,\mu)$. However, it is conditional, since the model does not take into account changes in the density of particles and the medium, which is important for assessing deposition. According to reaction (3), the concentration of S_A decreases, which indicates the fragmentation of aggregates.

The problem under consideration was numerically solved by the Runge-Kutta method of the 4th order. The grid step does not depend on μ and is chosen from the condition of the required accuracy $c_n\mu^k$. Solving problem (1) by this method led to the need to solve a system of g·(m + l) nonlinear differential equations, where g is the number of selected ranges of particles with the same dimension. In the course of the implementation of the numerical method, the main computational costs fell on the calculation of boundary functions. For small μ, this system is rigid [8]. For too small μ, this system is ill-conditioned. As a result, the iterative method for solving the system is unstable to computational errors, it requires a very accurate setting of the initial approximations. The conditions for its applicability of the method are the conditions for the existence of an asymptotic expansion of a certain type for the solution of problem (3). The method does not require any additional restrictions on the coefficients of differential equations and on the initial conditions [9, 10].

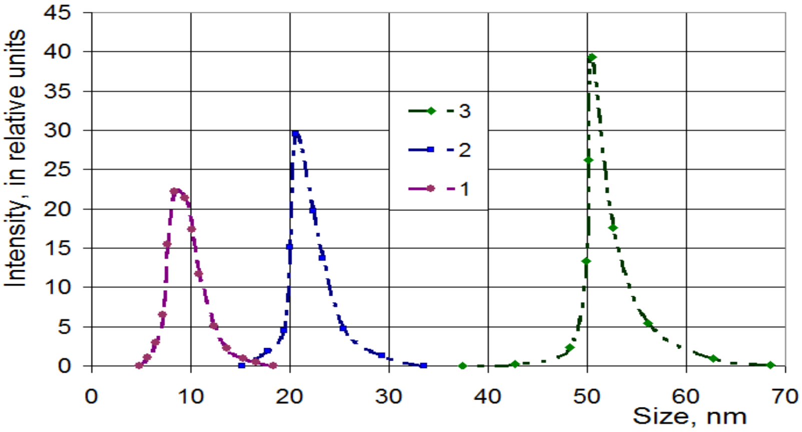


Fig. 2. Dependence of the distribution of particles in the oil colloidal system when exposed to surfactants after: 3 - 2, 2 - 15 and 1 - 20 minutes.

4. Conclusion

The methodology for modeling the boundary function method is described in detail in the literature. In the article, in describing the phase variables of the model, the surface area of the particles was used, which made it possible to bypass the specific feature of the process: at the same concentration, the particles can have different size values, which did not allow using the law of mass action in its traditional form. Another feature is the application of this method to describe the change in the particle size distribution density under the influence of surfactants. In the boundary expansion, the number of terms was limited to two, since an increase in the number of terms significantly increases the computational time. As a result of solving the process model, which is an ensemble of equations, describing changes in the system of poly-sized particles with different initial conditions, it will be possible to determine the change in the average value of the distribution density of the sizes of oil particles and calculate the amount of surfactants required for this

5.References

1 Frittelli, J., Parfomak, P.W., Ramseur, J.L., Andrews, A., Pirog, R. and Ratner, M., 2014. U.S. rail transportation of crude oil: Background and issues for Congress. Congressional Research Service, Report R43390, 25 p.

2 Graziano,M., Gunther,P., and Lema,E., 2017. The Economic Impact of Crude Oil Transportation in the Great Lakes-St. Lawrence Region: A Preliminary Study, available from https://www.glc.org/work/oil-transportation/publications/

3 Kumar S., Mahto V. Use of a Novel Surfactant To Prepare Oil-in-Water Emulsion of an Indian Heavy Crude Oil for Pipeline Transportation.// Energy & Fuels 2017, 31 (11), 12010-12020. DOI: 10.1021 / acs.energyfuels.7b02437

4 Djemiat, D. E., Safri, A., Benmounah, A., Safi, B. (2015). Rheological behavior of an Algerian crude oil containing Sodium Dodecyl Benzene Sulfonate (SDBS) as a surfactant: Flow test and study in dynamic mode. Journal of Petroleum Science and Engineering, 133, 184-191. DOI: 10.1016 / j.petrol.2015.05.012

5 Rzayev Yu.R.,Suleimanova S.A., Ismailov E.G., Shukurov R.K. Investigation of the incompatibility of oils when mixed.Azerbaijan Oil Industry.2018,No.10,pp.37-42.

6 Vasilyeva A.B., Butuzov V.F. Asymptotic methods in the theory of singular perturbations: Nauchn.-Teor. manual.- M.: Higher school., 1990.-208 p.: ill. (Actual problems of applied and computational mathematics.)

7] Petukhova N.Yu. A system of differential equations with a small parameter: numerical solution based on asymptotic representations /// Proceedings of higher educational institutions. Volga region. Physics and mathematics. - 2017.- No.2(42).-S.3-17. DOI 10.21685 / 2072-3040-2017-2-1

8 Hayer, E. Solution of ordinary differential equations. Rigid and differential algebraic problems / E. Hayer, G. Wanner. – M. : Mir, 1999 .-- 685 p.

9 Berezin, BI Using asymptotic expansions to construct numerical algorithms forsolving singularly perturbed boundary value problems /B.I.Berezin and N.Yu.Petu-khova // Fundamental and Applied Mathematics. -1996.- T. 9,No. 4.-P.1187–1194.

10 Doolan E. Uniform numerical methods for solving problems with a boundary layer / E. Doolan, J. Miller, W. Shilders. - M.: Mir, 1983 .-- 200 p.

1 Olkhovskaya V.A., Zinoviev A.M. Influence of structural phase changes on filtration of high-viscosity oil // Ashirovskie readings: Sat. Proceedings of the International Scientific and Practical Conference.-Samara, Samar. state tech. un-t, 2012. - pp. 160–165.

2 Bibik E.E. Directory. Kinetics of coagulation and structuring. Access mode: http://chemanalytica.com/book/novyy_spravochnik_khimika_i_tekhnologa/08_elektrodnye_protsessy_khimicheskaya_kinetika_i_diffuziya_kolloidnaya_khimiya / 5025
3 Rzayev Yu.R., Suleimanova S.A., Ismailov E.G., Shukurov R.K. Investigation of incompatibility of oils during their mixing. Azerbaijan Oil Industry. 2018, No. 10, pp. 37-42.
4 Vasilyeva A.B., Butuzov V.F. Asymptotic methods in the theory of singular perturbations: Nauchn.-Teor. manual.- M.: Higher school., 1990.-208 p.: ill. (Actual problems of applied and computational mathematics.) Doi: 10.17759
5 Berezin BI Using asymptotic expansions to construct numerical algorithms for solving singularly perturbed boundary value problems /B. I. Berezin and N. Yu. Petukhova // Fundamental and Applied Mathematics. -1996. - T. 9, No. 4. - P. 1187–1194.
6 Petukhova N.Yu. A system of differential equations with a small parameter: numerical solution based on asymptotic representations /// Proceedings of higher educational institutions. Volga region. Physics and mathematics. - 2017. - No. 2 (42). - S. 3-17. DOI 10.21685 / 2072-3040-2017-2-1
7 Hayer, E. Solution of ordinary differential equations. Hard and Differential -algebraic problems / E. Hayer, G. Wanner. – M. : World, 1999. - 685 p.
8 Doolan E. Uniform numerical methods for solving problems with a boundary layer / E. Doolan, J. Miller, W. Shilders. - M.: Mir, 1983 .-- 200 p.

OR-VI-1

CHARACTERISTICS AND MORPHOGENETIC DIAGNOSIS OF ALLUVIAL MEADOW-FOREST SOILS FORMED IN SHAMKIRCHAY VALLEY

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Abstract: The use of modern technologies and technologies, global climate change, arid regions, and rapid desertification processes once again prove the relevance of land conservation. All direct anthropogenic and natural processes in the world have led to the degradation, salinization, erosion and destruction of this resource. Azerbaijan is not one of the richest countries in terms of land resources. There are 0.12 hectares of land per capita in the country. However, if we take into account that 41.8% of the total land resources of the republic (86.6 thousand km^2) are subject to varying degrees of salinization, and 37.4% to varying degrees of erosion [1,2,3,4].

The article provides information on research conducted on alluvial meadow-forest (All) lands formed in the territories of the Shamkirchay reservoir in the administrative districts of Shamkir and Samukh. In the research area there is a subtype of clay alluvial meadow-forest (Allgl) of this type of soil. In general, the subtype extends over an area of 558.76 ha and covers an area of 557.98 ha in the Shamkir district and 0.78 ha in the Samukh district. Land plots were laid in both areas. In this article siol profile analyzes the morphological description of 4 section in characteristic places, research the current state of diagnostic indicators, agrochemical features. The results of these analysis, analyzes in tables and explanations. The main statistical analysis indicators were humus, total nitrogen, phosphorus and potassium, granulometric composition (fractions of sand, dust, silt and clay), soil's acid reaction (pH) and carbonate content ($CaCO_3$) [4,5,6,7,8].

Keywords: alluvial meadow-forest soils, humus layer, fertility parameters, soil profile, soil acid reaction, morphological description, granulometric composition, soil diagnostics.

1.Introduction

Alluvial meadow-forest lands are widespread in the country, mainly in the Ganikh-Ayrichay valley, under the Tagai forests on the right and left banks of the Kura River, in the Guba-Khachmaz massif. As the source of the Shamkir River is the Kur River, these soils are spread in the study area at an altitude of 150-200 meters above sea level - 558.76 hectares.

Preliminary information about these soils was given in the late XVIII century, early XIX century in the works of Russian soil scientist VV Dokuchayev. According to him, this type of soil is forest soil, located under the forest floor and has a light gray soil layer. These soils are gradually replaced by bluish-dark clay sediments after 46 cm. After V.V. Dokuchayev, V.P. Smirnov-Loginov and V.V. Akimtsev called these soils as "Tagai soils". However, the great Azerbaijani scientist H.A. Aliyev, who conducted research with a large expedition, denied the name "Tagai" and called these soils as "Alluvial meadow-forest". As the main argument, H.A. Aliyev took into account the alluvial activity of rivers in the process of soil formation and the decisive role of surface and ground waters formed as a result of its influence in the formation of forest plants.

In the area of our study (on the right and left banks of the Shamkir River) there is a clayey alluvial meadow-forest subtype of alluvial meadow-forest soils. The main reason for the formation of these soils was the periodic change of course and alluvial sediments.

As mentioned above, in the study of alluvial meadow-forest soils H.A. Aliyev, V.V. Dokuchayev, V.P. Smirnov-Loginov, V.V. Akimtsev, M.M. Sibirtsev, M.P. Babayev, V.H. Hasanov, Ch.M .Jafarova, G.Sh.Mammadov, K A.Alakbarov, V.R. Volobuyev, M.E. Salayev, A.M. Shikhlinsky, A.N. Izyumov and other scientists played a great role [7,8,9,10].

2.Research material and methodology

The material for the study was studied in 2 parts - theoretical and practical. The first part analyzes the results of long-term complex research on the classification, nomenclature and diagnosis of soils in Azerbaijan. In the practical part, the soil profiles taken by us were analyzed on the basis of modern methods currently used in world practice and the results were obtained. The soil type and subtype given in the article have been adapted to international land names, and a soil map has been compiled based on the WRB and ArcGIS program. During the research, soil horizons were indexed, and the genetic characteristics of the soils were adjusted to the correlation of the WRB system with the main indicators of the land classifications of Azerbaijan.

The purpose and objectives of the research: The main purpose of the study is to conduct soil-ecological research on alluvial meadow-forest soils formed on the right and left banks of Shamkirchay in Shamkir and Samukh regions, study of subtype, study of natural and anthropogenic factors, and regulation of fertility indicators in these lands, study of morphogenetic diagnostics.

Object and method of research: Alluvial meadow-forest soils cover the local area in the study area. The soil profiles analyzed in the characteristic places in the article were carried out in 2018-2019 on predefined routes in Shamkir and Samukh districts. All profiles in the district were determined on the basis of modern methods and tools (determined by geographical coordinates). The geographical coordinates of the soil samples were determined using the Garmin GPS map 62s (Table 1). The article highlights the analysis of 4 soil profiles by subtype, soil thickness, layers are determined by profile. Among the diagnostic indicators, granulometric composition, soil color, structure, hardness and a number of morphological features were noted. The required procedures were carried out on the basis of the methods submitted to the laboratories of "Soil Reclamation" (soil analysis) of the Institute of Soil Science and Agrochemistry of the Azerbaijan National Academy of Sciences and “Soil Agroecology and Bonitization” laboratories [8,9,10].

During field research, total humus in the soil was determined by I.M. Tyurin method, general nitrogen by Keyldahl method and carbonates were studied with calcimeter device. In the form of $CaCO_3$ was analyzed by the titration method, total phosphorus (P) and total potassium (K) by ICP-MS (agilent) device, and the granulometric composition, which is one of the leading factors,by N.A. Kaczynski’s method.

Table 1. List of profiles of the alluvial meadow-forest soils located in the characteristic places in the field of research (determination by geographical coordinates)

№	Number of section	X coordinate (east lenght)	Y coordinate (north width)
Alluvial-meadow-forest (All)			
1	**Section 85**	**$46^{0}\ 17^{/}\ 25{,}312^{//}$E**	**$40^{0}\ 54^{/}\ 5{,}952^{//}$N**
2	**Section 126**	**$46^{0}\ 13^{/}\ 22{,}718^{//}$ E**	**$40^{0}\ 55^{/}\ 15{,}017^{//}$N**
3	**Section 127**	**$46^{0}\ 13^{/}\ 59{,}804^{//}$ E**	**$40^{0}\ 54^{/}\ 47{,}858^{//}$N**
4	**Section 128**	**$46^{0}\ 15^{/}\ 1{,}748^{//}$ E**	**$40^{0}\ 54^{/}\ 38{,}121^{//}$N**

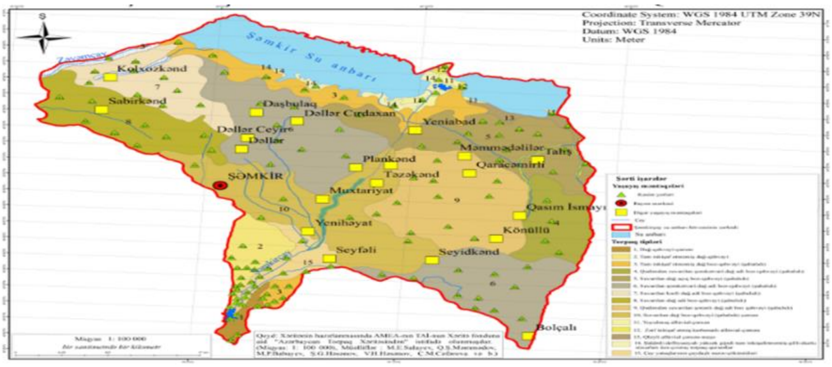
In the field studies, general humus in soil has been studied by the I.M Tyurin’s method, total nitrogen – kjeldahl method, carbonates - calcimeter. $CaCO_3$ form has been analyzed by titration method, total phosphorus (P) and total potassium (K) – by the ICP-MS (agilent) device and one of the most important factors is the granulometric composition - by N.A. Kachinski’s method. The cations absorbed to determine soil absorption capacity have been determined by D. Ivanov method, hygroscopic moisture has been determined by thermal method (the soil was dried at x 0,5 ° C) and soil reaction of the soil has been determined in pH meters (1:5) in aqueous solution. As well as, the ammoniacal absorption from nitrogen forms has been analyzed by the Konyev method, the ammoniacal water solubility has been analyzed by Nesler method and nitrates have been analyzed by the method of Grandval and Lajoux. The accuracy of the results have been determined using the mathematical statistical method (B.A. Dospekhov) [9,10]. The sections placed in the characteristic areas and analyzed in the article are shown in Map 1.

3.Analysis of the obtained results

D.V. Dobrovolsky conducted the first fundamental research on the genesis, diagnosis and classification of alluvial soils. He considered that river valleys and their predominantly hydrophore part, as a completely special type of landscape, were the youngest and most dynamic areas of the earth, strongly influenced by geological and biological factors, with very variable soil formation conditions and complex soil structure. In the hydrophore of Shamkirchay, there are both young and completely new lands (riverbed blocks, water ponds- stagnant water), as well as lands with zonal soil formation features, free from the conditions of the hydrophore regime. From the results of our comparative-geographical research, it was determined that clayey alluvial meadow soils cover the main part of the Shamkirchay submarine, as well as in the central part of the inflow cones. Soil areas are usually dominated by smooth and micro-depressions of the terrain. Soil-forming rocks In the Shamkirchay valley, alluvial sediments with clayey-clayey and sandy-rocky carbonate are predominant.

The soils of the study area in Shamkir and Samukh districts (characteristics of soil divisions and types) are mainly included in the “accumulative carbonate division”. These lands have been actively used in agriculture since ancient times. Accumulative relief forms in the form of water-erosion are predominant. Depending on the relief conditions, alluvial meadow-forest soils of different morphogenetic profiles are found.

Map 1. Profiles in characteristic places in alluvial meadow-forest soils existing in the research area



In general, on the basis of many studies, it was determined that, as in other areas of the country, the presence of a buried humus layer in the genetic profile of alluvial meadow-forest soils formed in Shamkir and Samukh regions (AUhg = 0.8-2.0 m). These morphogenetic features can be clearly observed in the profile of soil № 126 in the forest area on the southern shore of the Shamkir reservoir in the Shamkir region. The profile is determined by geographical coordinates. The X coordinate (eastern length) of the section is **46^0 13$^/$ 22,718$^{//}$ E**, and the Y coordinate (northern latitude) is **40^0 55$^/$ 15,017$^{//}$N** (Table 1). The relief of the area consists of micro-depressions and its soil-forming rocks consist of glay sandy-clayey low-carbonate alluvial sediments. Vegetation consists mainly of poplar and willow liana-plain-tagai forests. Shrubs and meadows are visible on the floor under the forest. The level of weakly mineralized groundwater fluctuates between 1.5-2.0 meters.

AO (0-2 cm) - there is a weakly fragmented forest substrate, consisting mainly of a mixture of forest sedges and grasses.

AU$_{ca}$ (2-16) - It has a grayish-brown thick accumulative humus layer, dusty clayey, fine-grained-nutty structure; rich in soft semi-deciduous plant remains and fringed grass roots. Optimal biological processing and small insect traces are clearly visible. Low humidity, clear transition. It does not boil under the influence of HCl.

A/B$_{ca}$ (16-30) - mainly grayish, dusty clayey. It has thin layers of clay and a soft nutty structure. Small tree roots and half-rotten plant remains are found. It is gradual, not clearly structured. Sometimes it is possible to come across worm routes. It is sharply transitioned. It does not boil under the influence of HCl.

B/Cgca (30-58) - It is light gray, slightly sandy-clayey. It does not have a clear structure. Soft, large tree roots are found. There are poorly selected brown rust spots. Moist, sharp transition. Boils weakly under the influence of HCl.

AUgca (58-86) – It has a dark gray buried layer of humus. It is clayey-loamy. It has a broken granular structure. Soft, large tree roots are found. Blue-brown rust spots with signs of gleysol are clearly visible. It is moist and the transition is sharp. Boils weakly under the influence of HCl.

Clgca (86-119) – It is light gray; sandy, slightly clayey. It is unstructured. It is scattered and soft, sparse tree roots are found. Occasionally brown-rusty clay layers are formed. Humidity is increasing. The transition is sharp. Boils weakly under the influence of HCl. Traces of groundwater are noticeable.

AU^h_gca (119-145) - It has a layer of buried humus with a dark gray-brown tint. It is clayey-loamy. The damaged grain is in the form of small lumps. It is soft and has large tree roots. It is formed in the form of clearly distinguished bluish-brown, brown-rust spots. Signs of gleysol are noticeable. It is very humid. The transition is sharp. Boils weakly under the influence of HCl. Groundwater is found.

Cllgca (145-169) – It has a light-gray, sandy structure; It is rich in carbonate alluvial sediments. Signs of weak gleysol are noticeable. There are thin layers of clay. Groundwater is found.

As can be seen from the morphological description of the soil profile № 126, in gleysol alluvial meadow-forest soils, there are different processes in different genetic layers. However, in general, the soil profile in each layer is poorly developed. It is characterized by a layer of humus and a complex granulometric composition under the semi-decomposed forest floor. The carbonates are washed from the top layer and spread to the bottom layers. A layer of humus buried in the middle and deep layers is found. Due to the effect of HCl on the lower layers, the boiling increases and the dry residue begins to appear.

Table 2 analyzes the main diagnostic indicators of land plots on alluvial meadow-forest soil type in Shamkir and Samukh regions on 4 profiles (Profile № 85, Profile № 126, Profile № 127, Profile №128).

Profile № 85: The profile is defined by geographical coordinates. The X coordinate (eastern length) of the section is **46^0 17$^/$ 25,312$^{//}$E**, and the Y coordinate (northern latitude) is **40^0 54$^/$ 5,952$^{//}$N** (Table 1). The profile consists of 3 tiers. The thickness of the humus layer along the profile is 3.74-0.79%. According to humus, nitrogen is 0.269-0.166%. Hygroscopic humidity is 6.48-5.34%; according to CO_2, $CaCO_3$ is 11.83-

7.98%, total of absorbed bases 31.01-18.47 mg-eq, the pH fluctuates between 7.2-8.2. The percentage of granulometric content less than <0.001 mm varies between 8.79-19.37%, and the percentage less than <0.01 mm varies between 24.13-41.08%. Granulometric analysis also shows that these soils are mainly light, medium and heavy loamy. Although the dry residue is not taken into account in the upper layers, it has been determined towards the lower layers. Phosphorus is 14.38-30.15 mg / kg, and metabolic potassium is 264-462 mg / kg (Table 2).

The soil **profile № 126** placed in the territory of Shamkir region was also determined by geographical coordinates. The X coordinate (eastern length) of the section is **46^{0} $13^{/}$ $22,718^{//}$ E**, and the Y coordinate (northern latitude) is **40^{0} $55^{/}$ $15.017^{//}$N** (Table 1). The profile also consists of 3 tiers. The thickness of the humus layer along the profile is 3.46-0.89 %. According to humus, nitrogen is 0.268-0.098%. Hygroscopic humidity is 6.47-5.52 %; according to CO_2, $CaCO_3$ is 12.73-7.71 %, total of absorbed bases 31.32-13.86 mg - eq,

Table 2. Analysis of the main diagnostic indicators of alluvial meadow-forest soil type land profiles in Shamkir and Samukh regions

№ section	Depth, cm	Humus %	Nitrogen %	Hyg. humidity	$CaCO_3$ % due CO_2	SAB, mg-ekv	pH	Granulometric composition, %	
								<0,001 mm	<0,01 mm
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
85	AO 0-2	Weakly fragmented forest substrate							
	AU_{ca} 2-17	3.74	0.269	5.63	9.83	30.16	7.2	12.56	36.54
	A/B_{ca} 17-31	1.47	0.127	5.34	10.21	25.31	7.7	11.36	32.90
	B/Cgca 31-52	1.18	0.109	6.19	11.83	23.72	7.9	13.20	24.13
	AUgca 52-83	2.09	0,166	6.30	8.33	31.01	7.3	11.16	39.02
	Clgca 83-127	0.87	Not.an	5.37	11.26	18.47	7.9	8,79	28.02
	$AU^{h}_{g}ca$ 127-159	3.05	-----	6.48	7.98	28.67	7.4	19.37	41.08
	Cllgca 159-198	0.79	-----	5.77	11.54	19.34	8.2	9.74	24.86
126	AO 0-2	Weakly fragmented forest substrate							
	AU_{ca} 2-16	3.46	0.251	6.15	8.62	31.32	7.2	16.44	54.21
	A/B_{ca} 16-30	1.94	0.156	6.47	11.06	29.78	7.2	15,35	63.47
	B/Cgca 30-58	1.02	0.098	6.22	12.39	25.37	7.6	18.37	42.84
	AUgca 58-86	2.73	0.268	5.54	8.94	26.44	6.7	14.32	59.16
	Clgca 86-119	0.97	Not.an	6.29	12.73	13.86	7.4	7.11	38.07
	$AU^{h}_{g}ca$ 119-145	3.14	-----	6.18	7.71	24.04	6.9	18.46	66.82
	Cllgca 145-169	0.89	-----	5.52	10.31	17.59	7.3	9.78	37.88
127	AO 0-2	Weakly fragmented forest substrate							
	AU_{ca} 2-15	3.84	0.275	6.94	10.35	33.42	7.5	16.91	63.18
	A/B_{ca} 15-29	1.93	0.156	6.51	12.37	31.93	7.5	17.28	61.73
	B/Cgca 29-51	0.98	0.096	6.43	13.26	27.11	7.7	10.17	59.69
	AUgca 51-78	3.42	0,249	6.41	8.25	23.53	7.4	15.73	57.32
	Clgca 78-116	0.95	Not.an	5.71	12.35	15.06	7.8	11.73	48.21
	$AU^{h}_{g}ca$ 116-139	2.34	-----	5.74	9.77	26.17	7.5	18.67	67.18
	Cllgca 139-157	0.79	-----	6.37	11.57	16.15	7.9	8.84	37.58
128	AO 0-2	Weakly fragmented forest substrate							
	AU_{ca} 2-17	4.06	0.289	5.99	8.36	32.91	7.1	18.34	58.37
	A/B_{ca} 17-32	2.61	0.198	6.16	10.25	30.05	7.3	19.51	59.63
	B/Cgca 32-49	1.19	0.109	5.83	10.84	31.52	7.3	10.44	52.88
	AUgca 49-83	4.41	0,311	6.48	6.89	27.44	6.8	18.07	59.16
	Clgca 83-120	1.13	Not.an	6.31	10.53	14.84	7.0	9.96	46.42
	$AU^{h}_{g}ca$ 120-144	3.02	-----	6.43	8.57	24.04	6.8	17.17	58.91
	Cllgca 144-172	0.88	-----	5.92	12.04	15.59	7.1	10.41	45.48

the pH fluctuates between 6.7-7.6. The percentage of granulometric content less than <0.001 mm varies between 7.11-18.46 %, and the percentage less than <0.01 mm varies between 37.88-66.82 %. The dry residue has been determined towards the lower layers. Phosphorus is 11.44-32.44 mg / kg, and metabolic potassium is 327-449 mg / kg (Table 2).

The soil **profile № 127** placed in the territory of Samukh region: The X coordinate (eastern length) of the section is **46^0 $13^{/}$ $59.804^{//}$ E**, and the Y coordinate (northern latitude) is **40^0 $54^{/}$ $47.858^{//}$N** (Table 1). The profile also consists of 3 tiers. The thickness of the humus layer along the profile is 3.84-0.79 %. According to humus, nitrogen is 0.275-0.096 %. Hygroscopic humidity is 6.94-5.71 %; according to CO_2, $CaCO_3$ is 13,26-8,25 %, total of absorbed bases 33,42-16,15 mg-eq, the pH fluctuates between 7,5-7,9. The percentage of granulometric content less than <0.001 mm varies between 8.84-18.67 %, and the percentage less than <0.01 mm varies between 45.48-59.63 %. The dry residue has not been determined. Phosphorus is 9.46-32.66 mg / kg, and metabolic potassium is 282-378 mg / kg.

The soil **profile № 128** placed in the territory of Samukh region was also determined by geographical coordinates. The X coordinate (eastern length) of the section is **46^0 $15^{/}$ $1.748^{//}$ E**, and the Y coordinate (northern latitude) is **40^0 $54^{/}$ $38.121^{//}$N** (Table 1). The profile consists of 3 tiers. The thickness of the humus layer along the profile is 4.06-0.88 %. According to humus, nitrogen is 0.311-0.109 %. Hygroscopic humidity is 6.48-5.83 %; according to CO_2, $CaCO_3$ is 12.04-8.36 %, total of absorbed bases 32.91-14,84 mg-eq, the pH fluctuates between 7.3-6,8. The percentage of granulometric content less than <0.001 mm varies between 9.96-19.51 %, and the percentage less than <0.01 mm varies between 45.48-59.63 %. Granulometric analysis also shows that these soils are mainly light and medium clayey. The dry residue has not been determined. Phosphorus is 16.27-32.58 mg / kg, and metabolic potassium is 238-358 mg / kg (Table 2).

4. Conculusion

1. The results of large-scale soil-ecological surveys conducted in 2018-2019 on alluvial meadow-forest lands formed in the territory of Shamkir and Samukh regions are reflected in the article. Based on the results of chemical analysis of soil samples taken, the main physicochemical and nutrient elements in the soil have been analyzed by modern methods.
2. Complex features of granulometric composition in the genetic profiles of gleysol alluvial meadow-forest soils have been identified in the study area; The presence of a layer of humus at a depth of 80 cm to 2 meters, sometimes the soil profile has 2 or 3 tiers, and other processes, morphogenetic indicators have been identified.
3. Table 2 analyzes the analysis of diagnostic indicators of fertility parameters of profiles placed in characteristic places, the morphological analysis of some profiles have been analyzed. The presented soil profiles are also shown on map 1.
4. The article studies the diagnostic indicators of alluvial meadow-forest soils with new methodologies, analyzes the occurring ecological processes and obtains consistent results. Thus, humus, nitrogen, hygroscopic humidity, CaCO3 according to CO2, total absorbed bases, pH-environment of the area, granulometric composition in 2 forms (<0.001 mm and <0.01 mm), dry residue on AO, AUca, A / Bca, B / Cgca, AUgca, Clgca, AUhgca, Cllgca profiles have been studied (Table 2). It is also clear from the morphological description of the various soil profiles placed in the research area as a result of field-soil and chamber laboratory researches that, there are differences between AUa-thickness of humus layer,% of nitrogen, formation, depth and hardening of illuvial carbonate Bca-layer, their structural aggregates, granulometric composition, hygroscopic moisture and other morpho-diagnostic features in different micro-relief forms and economic areas.

5.References

1. State Standard of the Republic of Azerbaijan. Soil quality - laboratory methods for determining the microbiological respiration of the soil. AZS ISO, Baku, 2013.
2. Babaev M.P., Ch.M.Jafarova, Hasanov V.H. - Modern classification of Azerbaijan soils. Baku, “Elm”, 2011, pg.360.
3. Babaev M.P., Hasanov V.H., Ch.M.Jafarova, Huseynova S.M. – Morphogenetic diagnostics, nomenclature and classification of Azerbaijan soils. Baku, “Elm”, 2011, pg.452.
4. Ministry of Agriculture of Azerbaijan. State Land Management Project Institute - Report on the soil cover and effective use of Shamkir region. Ganja 1972. 187 pages.
5. Mammadov G.Sh. - Socio-economic and environmental bases of efficient use of Azerbaijan's soil resources. Baku, "Elm", 2007, 854 pages.
6. Sadiq M.N., Mammadov E.E. - Characteristics of the relationship between physical and chemical and fertility indicators of agricultural soils in the mountainous zone. Collection of scientific works devoted to the 110th anniversary of Hasan Aliyev "Soil Science and Agrochemistry", Volume 23 No. 1-2, 2018, pp. 130-136.
7. Sadigov R.A. - Influence of erosion processes on fertility parameters of soils in the cultivation area of the northeast slope of the Lesser Caucasus. Philosophy doctoral thesis manuscript. Baku 2013. 167 pages.

8. Sadigov R.A. - The influence of the “Main Canals” of the New Shamkirchay Reservoir on the soil and environmental conditions of the basin. International research journals "Successes in modern science and education", "Successes of modern science" SUCCESSES OF MODERN SCIENCE. Included in the Higher Attestation Commission (No. 862), Agris, RSCI No. 12, T.11, 2016.
9. Sadigov R.A. - A brief overview of soil-water and geological surveys in the Shamkirchay reservoir basin and the methodology and technology of field operations using the VEP (Vertical Electric Probing) method. Journal of Scientific Works of AzSUU No. 1. 2018, p. 54-61.
10. Sadigov R.A. - Investigation of erosion processes in the mountain-brown soils of the New Shamkirchay reservoir. Collection of scientific works dedicated to the 110th anniversary of Hasan Aliyev "Soil Science and Agrochemistry", Volume 23 No. 1-2, 2018, p. 259-262.

OR-VI-3

ECOLOGICAL ANALYSIS OF THE CURRENT STATE OF TRANSPORT SECTOR IN AZERBAIJAN

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Abstract: This article discusses the growth of the number of cars and great damage they cause to the environment and our ecology using the official statistics of the last 30 years. Since 1990, vehicles that have been used in the countries where they are produced and have expired or are about to expire have been brought to our newly independent country. Examples of such cars are cars made in neighbouring Russia, in Europe and in Asia. Currently, 82% of the country's total number of cars consists of cars with a service life of more than 10 years, cars with an interval of 5-10 years make up 14.9% of the car fleet, and only 3.27% of the country's total number of cars are cars with a service life of up to 5 years. 40.5% of vehicles in our country are cars made in neighboring Russia, and 16.97% are Mercedes cars. Mr. President has approved the State Program of Azerbaijan Republic on Road Safety for 2019-2023. The goal of the program is to dispose of cars with a service life of 10 years and more than 10 years and to increase the number of newly produced cars in the country. After the implementation of the program, the ecology of our country will be protected, as cars will be put into operation under the standards in the country. The activity of other modes of transport in the development of our country is undeniable, I also touched upon these modes of transport in the article [1,2,3,4,5,6].

Keywords: Transport sector, ecological analysis, recycling, old cars, environmental safety

1.Introduction

Ensuring high socio-economic indicators and activities of many industrial enterprises located in our country, especially in large industrial cities, requires a well-developed transport system that meets global trends. Insufficient development of the transport system creates significant limitations for the development of other industries and is one of the factors that can negatively affect the development of their competitiveness [3,4,5,7].

At the same time, despite the prioritisation of development of the transport system in the region, the density of intercity and international roads in the northern, western and southern directions of the country, limited traffic capacity of the roads, insufficient application of international technical rules and requirements remain one of the most pressing issues today. In some cases, these lead to environmental problems. Expansion of roads, destruction of roadside greenery and the modernization of highways are inevitable [5,6,7,8].

Problem and Investigation for solutions: There are some problems in the modernization of existing industrial parks for vehicles in our country that do not meet the standards. Exploring possible solutions is one of the priorities of our research. According to the official statistics for 2019, the number of vehicles in our country is 1,398,824. Vehicles up to the last 5 years account for 3.27% of the country's total number of cars (45,383 units). Vehicles with an interval of 5-10 years make up 14.9% of the country's total number of cars (207,392 units), and those operated for more than 10 years make up 81.78% of the country's total number of cars (1,135,021 units). It is clear from the statistics that most of the vehicles used in the country have a highly negative impact on the environment. Most of these cars were imported to our country in the early 1990s and were brought to our country shortly after they were used in the countries where they were produced [3,6,7,8,9].

40.5% of the country's total number of cars are Russian-made (Moskvich, Vaz 06, Vaz 07, Volga, etc.) and 16.97% are German-made Mercedes cars. According to the statistics of the last 20 years, Table 1 shows that in 2000, the most used foreign cars in Azerbaijan were cars made in neighbouring Russia, CIS-made cars and German-made Mercedes rank the second and the third place respectively. In 2005, Russian-made cars are again the most used foreign cars in Azerbaijan, followed by German cars and CIS cars consequently. In 2010 and 2015, Russian-made cars still rank first place and followed by German Mercedes cars. However, Hyundai cars replaced CIS-made cars in the third place. Nowadays, these three brand cars still dominate in the country's car usage with increasing number. Since 2010, the car industry experienced a slight decrease in the number of Russian-made cars and a significant increase in the number of Mercedes and Hyundai model cars. In 2019, Russian-made cars, Mercedes and Hyundai model cars numbered 483,738, 202,664 and 72,847 respectively [8,9,10].

In some cases, the use of obsolete and physically obsolete vehicles reduces traffic safety and harms the environment. After a while, the cars brought to Baku are sent to the regions and operated there, causing great damage to the ecology of our country. These processes ultimately harm human health and lead to the deterioration of the transport system in the region. To normalize the environmental situation in our country, it is necessary not only to use new vehicles but also to organize the utilization (recycling) of obsolete and substandard vehicles. Theoretical research is needed to substantiate the urgency and modernity of the problem, to determine the organizational scheme and methodological support for the evaluation of the performance of the vehicle recycling system, created as a special infrastructure within the industry.

The urgency of the problem is reflected in the "State Program of Azerbaijan Republic on Road Safety for 2019-2023" approved by the decree of President Ilham Aliyev. According to the State Program, to achieve the set goal, in 2019-2020, the Cabinet of Ministers together with the Ministry of Economy, the Ministry of Internal Affairs, the Ministry of Transport, Communications and High Technologies, the Ministry of Taxes, the State Customs Committee should ensure the development and implementation of a vehicle utilization program to improve road safety in Azerbaijan, to ameliorate the ecological situation, to ensure the removal of obsolete, technically unsafe and environmentally unfit vehicles from circulation in terms of improving and stimulating local car production. As in other developed countries, the transport sector, which is the most important component of Azerbaijan's production and social infrastructure, occupies a special place in the country's agricultural complex, provides links between remote economic facilities, creates a material basis for foreign economic relations [7,8,9,10,11].

Since the beginning of the XXI century, interest in the transport sector in the Republic of Azerbaijan has sharply increased. Renovation of roads, construction of a transport network in line with modern world infrastructure (construction of a new era of transport and logistics companies), increasing the import of new transport standards are considered important factors in the development of this sector. In 2018, according to the World Bank’s International Logistics Performance Indicator, the Republic of Azerbaijan ranked 123rd out of 167 countries for.

In the face of the globalization of economic processes, the maximum realization of the country's transport and logistics potential and making it a strong economic source, increasing the number of local representatives of transport services in the world market and strengthening the country's role in international transport corridors are the main priorities of the Azerbaijani economy. Azerbaijan occupies one of the leading positions at the crossroads of Europe and Asia due to its unique geographical position and is considered the centre of the region from north to south and from east to west. For our country, the Eurasian transit route is one of the most promising issues in today's conditions. According to the statistics of 2019, the length of roads in our country was 19,336 km, and 1,793,000 passengers and 154,000 tons of cargo were transported by this means of transport [9,10,11].

The development of railway transport in our country is still in progress. The total length of the existing railways is 3302 km. According to the statistics of 2018, the operating length of roads is 2133 km, the length of highway is about 1169 km. In 2018, 13,954 tons of cargo and 2,841 passengers were transported by rail. The share of air transport in Azerbaijan is growing day by day. According to official statistics for 2018, 2,399 passengers and 208,000 tons of cargo were transported by air. Pipeline transport, which is considered to be one of the other transport sectors and the most important for the economy and the most environmentally friendly mode of transport, is a leading force for the economy of our country. According to the latest official statistics, the length of pipeline transport in the country is 5,438 km. 1523 km of the pipelines are oil pipelines and 3915 km of pipelines are used for gas transportation. 45,241 tons of oil and 16,911 tons of gas were transported. Water transport through the Caspian Sea also continues to develop. In recent years, the Sea Port has been relocated from Baku Bay to Alat Port, which meets new modern international standards. The Sea Port proves once again that Azerbaijan will play a major role not only in the region but also in strengthening the economies of East and West. According to official statistics for 2018, 82 million tons of cargo and 15.7 thousand passengers were transported by water. The Azerbaijan Caspian Shipping Company has 50 ships in reserve to ensure large and small cabotage in the Caspian Sea [10,11].

The most used mode of transport in Baku is road transport. According to official statistics for 2018, the number of vehicles in Baku is 648,275. At the end of 2019, the total length of paved roads was 11,818 km, which is 61.1% of the total length of roads. This is higher than the average level for Azerbaijan. One of the biggest challenges is that the capacity and carrying capacity of roads in Baku are not sufficient to provide the existing traffic flow, so the development and modernization of roads should be one of the key tasks in the long-term strategy of Baku. The average age of road transport in Azerbaijan excels the level of European countries. The physical and mental deterioration of cars not only affects traffic safety but also affects the environment and road conditions. Fleet renewal is an urgent question for Azerbaijan. According to official statistics for 2019, 1,135,000 (81.78%) cars have been in use in our country for more than 10 years. With the increase in service life, the cost of repairs and maintenance of vehicles increases. It is necessary to allocate financial assistance to this sector to renew the vehicle fleet. It is almost impossible for private transport owners to do that.

It is necessary to take complex measures to solve the situation and priority areas should be selected. Thus, it is important to allocate state support for the disposal of expired and unusable vehicles in the Republic of Azerbaijan. In the face of the reduction in the budget and investment in the transport industry, the tasks the transport sector of the country has in this context, require large expenditures. Therefore, for the development of the transport complex in the Republic of Azerbaijan, it is necessary to determine the direction of certain modes of transport, taking into account a unified system of priorities, prospects for the development of transport-related industry and social and environmental problems in the region.

Table 1. The number of cars by brands

Car companies	**The amount of production by years**					
	2000	**2005**	**2010**	**2015**	**2018**	**2019**
Total	332,02	479,44	815,683	1,129,596	1,170,672	1,193,907
Russian-made cars	301,06	382,69	499,858	490,315	484,553	483,738
CIS-made cars	10,645	8,962	5,469	52,798	56,595	57,733
BMW	2,421	6,697	17,375	24,945	26,167	26,892
Opel	707	1,579	19,125	42,641	44,037	45,071
Mercedes	4,653	32,226	109,176	192,685	199,016	202,664
Ford	1,059	1,961	3,962	8,218	9,897	10,826
Reno	1,592	2,716	2,659	4,678	7,483	10,288
Toyota	909	4,368	23,949	46,777	50,797	53,152
Nissan	1,252	5,506	18,007	32,525	33,245	33,666
Daewoo	2,334	5,128	7,245	10,719	10,770	10,749
KIA	625	1,609	10,305	30,745	34,186	36,368
Hyundai	-	6,080	31,028	61,477	68,179	72,847
Azsamand	-	-	3,701	3,386	3,451	3,515
Tofash	664	5,945	7,137	6,317	6,233	6,210

Table 2 shows the statistics of the number of cars in our country and regions for the last 30 years. The statistics show that in 1990 there were 398,761 cars in the country. That year (1990) the first place in the country in terms of cars was taken by Baku city and surrounding settlements with 116,030 cars, the second place was taken by Aran economic region with 81,533 cars, and the third place was taken by Ganja-Gazakh economic region with 48,663 cars. For the same year (1990), the lowest number of cars was 12,196 in Sumgayit and 3,132 in the Yukhari Karabakh economic region. Compared to these figures, in 2000 (after 10 years) the number of cars in the country was 438,626. Over 10 years, the number of cars in the country increased by 39,865 and accounted for 9.1% of all cars in the country. 145,998 cars were registered in Baku and surrounding settlements, and 2,730 in Yukhari Karabakh economic region. These figures reached 982,000 cars in the country in 2010. There was a more than the twofold increase that year. In 2010, Baku and surrounding settlements ranked the first place with 598,000 cars, and the lowest result was 3,230 cars in Yukhari Karabakh economic region. In 2019, the number of cars in the country increased by 416,000 to 1,398,000. In 2019, the number of cars in Baku and surrounding settlements increased by 35,135 (5.5%) to 633,267. The lowest result was registered in Kalbajar-Lachin economic region with 24,666 cars. In 2019, 155,404 cars were registered in the Ganja-Gazakh economic region, 190,965 cars in the Aran economic region. These economic regions crossed the border of 100,000 after Baku.

Table 2. The number of cars by regions

By regions	**The number of cars by year**				
	1990	**2000**	**2010**	**2015**	**2019**
Country	398,76	438,62	982,55	1,322,61	1,398,82
Baku city	116,03	145,99	598,13	728,70	633,267
Absheron	18,08	21,20	33,40	60,430	72,442
Sumqayit	12,19	14,76	23,52	40,888	47,044
Ganja-Gazakh	48,66	63,34	90,92	130,102	155,404

Ganja city	13,83	17,89	34,53	43,498	45,579
Shaki-Zaqatala	22,84	25,55	29,67	47,705	61,474
Lankaran	26,89	33,26	46,06	60,145	76,579
Guba-Khachmaz	16,41	18,62	23,65	37,180	53,329
Aran region	81,53	80,70	95,40	140,149	190,965
Yukhari Karabakh	3,13	2,73	3,23	42,364	61,617
Kalbacar-Lachin	-	-	-	15,573	24,666
Dakhlik Shirvan	13,21	13,68	12,33	20,845	29,953
Nakhchivan	15,54	18,25	24,99	39,411	39,128
Occupied regions	36,40	15,25	24,74	-	-

Table 3 provides the monitoring of the number of private cars per 100 households in the country over the past 20 years. While there were 19 cars per 100 families in the country in 2000, in 2010, 2015 and 2019 it was 40 cars, 52 cars, 54 cars respectively.

Table 3. Number of private cars per 100 families

	2000	**2010**	**2015**	**2018**	**2019**
Country	19	40	52	53	54
Baku (including districts)	25	101	114	98	95
Absheron region	18	17	33	38	40
Khizi region	11	11	17	26	28
Sumqayit city	18	27	48	52	54
Ganja city	23	47	55	57	57
Shaki city	19	20	34	38	39
Calilabad region	27	27	35	42	44
Guba region	17	18	29	38	41
Barda region	23	22	37	47	51
Fuzuli region	-	-	31	42	46
Gubadli region	-	-	26	36	41
Akhsu region	25	17	33	42	45
Nakhchivan Autonomic Rep.	13	15	25	25	25

According to the number of cars per 100 families in 2000, Jalilabad region with 27 cars took first place, and Khizi region with 11 cars took last place. In 2005, the first place was taken by Baku with 52 cars, and the last place was taken by Khizi region with 11 cars. Since 2005 Baku has been on the top of the list and reached to 95 cars which are less than previous year's results. Khizi ranked the last place until 2018 and reached 24 cars. In 2018 and 2019, the last place was taken by Nakhchivan Autonomous Republic with 25 cars.

4.Conclusion

1. According to statistics for the last 30 years, the number of vehicles in the country has increased 4 times. The four-fold increase in the number of vehicles in the country has increased the damage to the environment and the atmosphere by four times. In the last 30 years, the number of vehicles increased 4 times in Absheron economic region, 6 times in Baku city and surroundings, 4 times in Sumgayit city, 3 times in Ganja-Gazakh economic region, 3.5 times in Ganja city, 3 times in Sheki-Zagatala region, 3 times in Lankaran economic region, 3 times in Guba-Khachmaz economic region, 2.5 times in Aran economic region, 20 times in Yukhari Karabakh economic region, 1.5 times in Kalbajar-Lachin economic region, 2 times in Dakhlik Shirvan economic region and Nakhchivan Autonomous Republic.
2. 82% of the vehicles in our country are more than 10 years old. Currently, the cars are manufactured under Euro 5 (6) standards. This means the reduction of toxic and carcinogenic gases released into the environment. Since cars older than 10 years are not manufactured under these standards and have been in operation for more than 10 years, they cause significant damage to the environment and the atmosphere. It is mandatory to dispose of such cars and replace used cars with new ones.
3. Because European cars meet Euro 4 and Euro 5 standards, they emit less waste and are better quality cars, but cars made in Russia and the CIS pollute the environment more because they cause more negative effects and emit carcinogens. In the future, it is more appropriate to reduce the number of cars made in Russia and the CIS and increase the number of cars made in Europe and Asia.

5.References

1. Mammadov.R.M.-Geography of the Republic of Azerbaijan. III volume, Baku, 2015, pp.199-214.
2. Ministry of Ecology and Natural Resources of Azerbaijan-Information on the state of the environment and the work done in Azerbaijan between 2008-2012", Baku, 2013, pp.32-34.
3. Bayramov. Sh., Zeynalova.F.-Hazard to Ozone and Ozone Hazard, Baku, 2011, p.107.
4. Ecological security. Sumgait. Bilik, 2013, SSU, p.184.
5. Aliev F.Q, Badalov A.B., Guseinov E.M., Aliev F.F.-Ecology, Textbook, Baku, "Elm", 2012, p.828.
6. Ahmadov Sh.A., Muradov N.M.-Ecology. The pollution of Atmosphere, Baku, 2008, p.82
7. Ahmadov.Sh.A. , Xalilova.A.A.-Global ecology, ATU, Baku, 2015.
8. Hamidov M.M.-The Constructive Security of Automobiles, Textbook, 2012, p.183.
9. Hasanova A.A.-Ecology of Azerbaijani cities, Monoqrafiya, Baku,2008
10. Xalilova.A.A., Allazov. M.R.-Recycling of industrial waste, ATU, Baku,2013.
11. Ismayılov.C.-General Ecology, Baku, 2013, p.176.

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ANALYSIS OF THE INTERNATIONAL LEGAL STATUS OF THE CASPIAN SEA

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Annotation: The Caspian Sea is a closed body of water that has no connection with the world's oceans. The Caspian Sea is a basin rich in flora and fauna as well as natural resources. The issue of determining the legal status of this closed basin, which plays an important role in connecting the two continents, is still an unresolved issue [1,2,3,5,7].

In general, the problem of the legal status of the Caspian Sea is a very controversial and complex process, so the stages for the analysis of Azerbaijan's position in the development of this process are reflected in the article. The share of natural resources of the Caspian Sea among the countries of the Caspian region is shown in the description given in the article. The article analyzes issues related to determining the international legal status of the Caspian Sea, considers the positions of the Caspian littoral states. Special attention is paid to geopolitical processes in the Caspian region and the policy of countries outside the region [1,2,4].

Key words: Caspian Sea, international legal status, analysis, closed basin, fauna and flora, geopolitical division.

1.Introduction

In the 1990s, the collapse of one of the world's two superpowers, the USSR, created a number of independent states in the South Caucasus and Central Asia. In this regard, geopolitical activity in the West began to develop rapidly, the issue of radical reconsideration of many problems in the Eurasian space was raised, as well as the struggle for a reconsideration of geopolitical issues related to the Caspian region. In particular, the problem of determining the international status of the Caspian Sea between Russia, Azerbaijan, Iran, Turkmenistan and Kazakhstan has caused heated debates [3,4,5,6,7].

Only in the law on the state border of the USSR adopted in 1982, the USSR unilaterally approved the Astara-Hasangulu line as the state border. The Iranian side did not express its official reaction to this decision and in the published maps (for example, the geological map of Iran) the Caspian Sea was shown on the Astara-Hasangulu line. Thus, Iran was forced to reconcile with the situation and did not take any official steps to change the situation. As a result, 88% of the Caspian Sea remained under the control of the USSR and 12% under the control of the Iranian side.

On the eve of the collapse of the USSR, it should be noted that the middle line (as the water border), which formed the basis of the sectoral division, was adopted as the administrative-territorial border between the allied republics. However, the emergence of new independent states in the Caspian region has radically changed the political situation here. The main reason for this was the growing interest of both the Caspian littoral states and the world's major countries in the rich hydrocarbon resources in the region; First of all, the discovery of promising oil and gas fields in the shelf zones of Azerbaijan and Kazakhstan resulted in the inflow of large amounts of capital from other countries to these regions [6,7,8,9,10,11,12].

2.Analyses and discussions

In general, the problem of the legal status of the Caspian Sea is a very controversial and complex process, so to analyze the position of Azerbaijan in the development of this process, it is necessary to divide it into three stages: [10,11,12].

- The first stage covers 1992-1994. This stage ends with the study of the problem, the discussion of the legal status of the Caspian Sea in bilateral and multilateral meetings and the formation of a conceptual position of Azerbaijan in solving the problem and the signing of the "Treaty of the Century".
- The second stage covers 1995-1998. This stage is characterized by a clear definition of the positions of the littoral states on the status issue and the intensification of bilateral and multilateral meetings and Turkmenistan's territorial claims against Azerbaijan in the Caspian Sea.
- The third stage lasts from 1999 to the present. This stage is also marked by the achievement of bilateral agreements on the legal status of the Caspian Sea. It is characterized by a complete change in Russia's position on the legal status of the Caspian Sea and the signing of bilateral and trilateral agreements between Azerbaijan and Kazakhstan and Russia [10,11,12].

The development of promising oil and gas fields in the Caspian Sea, the use of biological resources, the development of transport and the growing environmental problems made it necessary for the countries of the region to draw up a general convention on the legal status of the Caspian Sea. A special working group with the participation of representatives of the Caspian littoral states has been set up to draft such a convention. This reflects the importance of the issue in question for the Caspian littoral states. Although the numerous meetings of the working group in each of the Caspian littoral states have led to a convergence of positions, but this has not yet led to a full understanding [7,8,9,10].

In order to determine the legal status of the Caspian Sea, a general agreement must first be reached as to whether this body of water is a "sea" or a "lake". It is unfortunate that some Caspian littoral states, based on their geopolitical and economic interests, still ignore the norms of international law and put various pressures on the countries of the region to accept the status to their advantage.

In 1998, the Russian side ended the four-year blockade of the Volga transport routes in the direction of Azerbaijan. Russia's and Iranian-backed proposals to divide the coast into 10, 15 and even 45-mile territorial water zones have not been accepted by other Caspian littoral states. Otherwise, it is clear that the remaining water area and its natural resources would be considered common. Given that the main oil and gas reserves are located in the shelf zones of Azerbaijan, Kazakhstan and Turkmenistan, then Russia and Iran have overlapping interests in this matter [5,8,10,12].

Despite the apparent change in Russia's policy on the status of the Caspian Sea, in essence, they managed to protect their interests by correctly assessing the real situation. This is primarily due to the signing of relevant agreements with Kazakhstan in 1998 and Azerbaijan in 2002 on the division of the Caspian Sea.

Azerbaijan is the only country in the Caspian region that has been pursuing a consistent policy on the legal status of the Caspian Sea since 1993 in accordance with international law. The legal status of the sea requires official confirmation by the Caspian littoral states that it is a lake. According to the scientific classification accepted in the world of geography, it is called a "water basin with no natural access to the world's oceans". Surprisingly, some Caspian littoral states denied such an undeniable fact and intended to shape the legal status of the Caspian Sea in accordance with their interests, giving it a closed sea, inland water basin and other names. Subsequent processes have shown that these attempts have failed.

The transformation of the Caspian Sea into a center of international cooperation in 1999-2000, the growing development of cooperation with the world, as well as the realization of the West-East energy corridor, the restoration of the Great Silk Road have further increased the importance of the Caspian Sea. Leading in this direction, the influence of Azerbaijan on the geopolitical situation in the region was very strong. The restoration of the Great Silk Road at the initiative of the country in 1999 and the adoption of the Baku-Tbilisi-Ceyhan main export pipeline as an official means of transporting oil at the OSCE Istanbul Summit on November 18 had a positive impact on determining the Caspian regime based on mutual respect [12].

During the meeting of Russian President Vladimir Putin with President of the Republic of Azerbaijan Heydar Aliyev, who paid an official visit to Azerbaijan on January 9, 2001, the political situation in the Caucasus, international conflicts, as well as the settlement of the Caspian Sea status were discussed. The "Baku Declaration" signed at that time was the beginning of a special stage in resolving the status of the Caspian Sea due to its historical significance. It was clear from this concept that the Russian Federation took a constructive position in its proposals on the Caspian Sea, where it put forward concrete proposals to bring the principles of cooperation in line with Azerbaijan's position. This was the result of many years of hard work by Azerbaijani diplomacy at the beginning of the 21st century. Of the more than 20 official documents signed, the Baku Declaration, which reflects the views of both countries on the Caspian Sea, was of particular importance. According to the articles of the document, the closeness of the positions of the two countries on the status of the Caspian Sea was officially declared, the disagreement was to some extent put an end and in principle it was the first and only document that laid the foundation for the idea of division into national sectors [4,7,9].

The middle line of the Caspian Sea In 2002, it was agreed that Azerbaijan and Russia would divide the bottom of the Caspian Sea into sectors in accordance with the principle of the middle line. This agreement should be considered the first successful step towards solving a very important and complex problem, such as the division of the Caspian Sea into sectors. As Azerbaijan borders all four Caspian littoral states at sea, it is especially important to accept the legal status of the Caspian Sea on a compromise basis. Unfortunately, Azerbaijan has to agree on its position on this issue with each of the neighboring countries at sea. There is no other state in the Caspian region in such a situation [2,3,5,6,8,10].

The position of the Kazakh side in solving the problem of the legal status of the Caspian Sea largely coincides with the position of the Azerbaijani side. The Kazakh side is most interested in the division of the Caspian Sea on the principle of the middle line. Because in this case, the share of Kazakhstan in the Caspian Sea is more than any other country - 29%. Kazakhstan is the only country that has demarcated its offshore sectors with all three Caspian littoral states and has signed agreements with Azerbaijan, Russia and Turkmenistan. The demarcation of the middle sea line has forced Kazakhstan to create a navy to protect its sector and territorial waters. As mentioned above, the Iranian side in most cases does not compromise on the issue of the legal status of the Caspian Sea. However, Russia's signing of agreements with Kazakhstan and Azerbaijan on the division of the seabed into sectors has resulted in Iran being left alone in this matter.

Figure 1. If Caspian was a sea or lake status of the Caspian Sea

In recent years, the Iranian side has proposed to divide the Caspian Sea into five equal parts. Other Caspian littoral states disagree. In this case, Turkmenistan is "losing" its promising fields in the South Caspian Sea. The Iranian side, realizing the absurdity of its proposal, is consciously making such claims. The goal is to get enough concessions from future compromises. It is almost impossible to solve the principle of "20% of the sea should be allocated to each Caspian littoral state" proposed by the Iranian side, both methodologically and technically. Because the constant change in sea level and the significant indentation of the coastline make it impossible to find a focal point in the water area for the even distribution of the basin.

Of course, in order to achieve progress in the legal status of the Caspian Sea, the Iranian side must build its policy in accordance with reality and the current situation. Thus, if Turkmenistan reaches an agreement with other Caspian littoral states on this issue, the Iranian side may remain isolated. The Third Summit of the Caspian littoral states held in Baku on November 18, 2010 was not only about bringing together the countries of the region and the division of the Caspian Sea, but also about issues of mutual interest such as maritime security, the five-party economic cooperation formula, protection of ecology and biological resources. was considered an important event.

During the meeting, the presidents signed an agreement on security cooperation in the Caspian Sea and adopted a joint declaration. The agreement states that security in the Caspian Sea is the exclusive right of the Caspian littoral states. The parties adopted this document based on the norms and principles of international law, including the principles of independence, sovereignty, territorial integrity, inviolability of borders, non-use of force and non-interference in the affairs of others, enshrined in the UN Charter. The document provides for cooperation in the fight against terrorism, organized crime, arms, drugs, smuggling of weapons of mass destruction, the fight against poaching, as well as joint rescue operations. The parties intend to cooperate in other areas, except for the military aspect of security. It is also noted that "nothing in this agreement determines the legal status of the Caspian Sea." The presidents attending the Baku meeting stressed the importance of maintaining the recent progress in the process of determining the legal status. President of Azerbaijan Ilham Aliyev stated that the agreement reached between Russia, Azerbaijan and Kazakhstan should be an example for other countries in the basin. The Azerbaijani side considers it necessary to take these agreements as a basis and conduct negotiations on the final status in accordance with this practice.

Protocols to the Framework Convention for the Protection of the Marine Environment of the Caspian Sea were also agreed at the Baku summit. These documents will help prevent environmental degradation of the sea. As it is known, the main bioresource of the Caspian Sea is sturgeon. Countries in the region have long been considering a moratorium on their hunting. Finally, the issue was resolved at this meeting. The Presidents of Azerbaijan, Russia, Kazakhstan, Turkmenistan and Iran reaffirmed their intention to continue working on the Convention on the Legal Status of the Caspian Sea in the Joint Declaration adopted at the end of the third summit in Baku.

Speaking at the 4th Caspian Summit in Astrakhan, Russia on September 29, 2014, President of the Republic of Azerbaijan Ilham Aliyev expressed his country's satisfaction with the results and agreements reached and expressed hope for the solution of unresolved issues. It should be noted that President Aliyev's speech was very mild and diplomatic, and he spoke about the latest processes and prospects in the Caspian Sea, without making any specific statements on the military presence of non-states in the Caspian Sea, the Trans-Caspian Pipeline and the territorial dispute with Turkmenistan.

There are several important points in the final declaration of the Astrakhan summit of the Caspian states:

I. Non-use of force and threats;
II. Ensuring a stable balance of armaments;
III. The inadmissibility of the military presence of non-Caspian states.

The fourth and sixth points are in the interests of Russia and Iran. The Convention on the Legal Status of the Caspian Sea was signed at the 5th Summit of the Caspian littoral states in Aktau, Kazakhstan. Following the 5th Caspian Summit, Ilham Aliyev, Vladimir Putin, Nursultan Nazarbayev, Hassan Rouhani and Gurbanguly Berdimuhamedov signed a document defining the legal status of the Caspian Sea. Among the main issues discussed in the press release, the heads of state noted the legal status of the Caspian Sea, cooperation in the field of economy, transport, ecology and protection of biological resources in the Caspian region, security in the region and globally. The signing of the Caspian Convention coincided with the International Caspian Day on August 12. Bilateral and multilateral meetings of the littoral states on the Convention on the Legal Status of the Caspian Sea since 1992 have come to their logical conclusion, because so far each state has approached the legal status of the Caspian Sea differently, based on national interests.

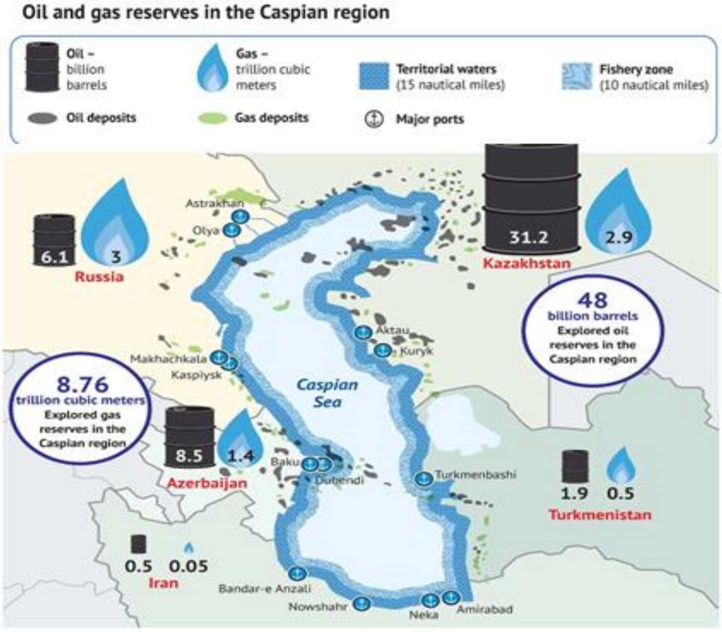

Figure 2. Convention on the Legal Status of the Caspian Sea

For many years, the Azerbaijani side has proposed a fair division of the Caspian Sea within the framework of international law and the principle of "win-win", but certain artificial obstacles did not allow to reach an agreement on the final status. Work on the document has been underway since 1996. On May 14, 2003, in Astana, Azerbaijan, Russia and Kazakhstan signed a tripartite agreement on the "division of the Caspian seabed into national sectors in the middle line, the common use of the water surface" and the parties signed a final agreement on the division of the Caspian seabed. The draft convention was finally agreed at a meeting of the Foreign Ministers of the Caspian littoral states on December 4-5, 2017 in Moscow. According to the Convention, the Caspian littoral states exercise sovereignty, sovereign rights, exclusive rights and jurisdictions.

The Convention can also be described as the "Constitution of the Caspian Sea." According to the signed convention, the Caspian Sea is neither a sea nor a lake. This is a novelty in the history of the world's seas. It is impossible to call the Caspian Sea the sea because it has no access to the oceans. At the same time, in terms of water capacity and geography, the Caspian Sea is not. It was agreed that the Caspian Sea will consist of inland waters, territorial waters, fishing zones and common space. Coastal states will have national sovereignty, provided that they do not exceed 15 nautical miles in territorial waters. In addition, in fishing zones within 10 miles, coastal states acquire exclusive rights within their borders. The rest of the sea area is put into general use.

The convention also does not prevent the passage of pipelines from the seabed. This issue was also interesting for Azerbaijan and Turkmenistan in terms of the construction of the Trans-Caspian gas pipeline. The document clearly states that any country can build any pipeline with the consent of the state through which the pipeline passes. That is, we are not talking about any general agreement. However, a protocol on the environmental impact of Caspian projects could provide Russia and Iran with an additional means of blocking such projects in the future. One of the important points of the Convention is to prevent foreign countries from gaining access to the Caspian Sea. The Convention contains a provision on the inadmissibility of the participation of the armed forces of third countries (ie non-Caspian states) in the Caspian Sea. Therefore, "the Caspian littoral states will not hand over their territories to any other state acting against the contracting states and for other military activities.

3.Result

1. It is considered expedient to follow the following proposals and recommendations to solve the problem of the legal status of the Caspian Sea: the status of the Caspian Sea should be accepted as an international lake, and its legal regime should be determined on the basis of the principle of division into national sectors along the middle line; a certain system of norms should be developed in order to regulate various aspects related to the use of the Caspian Sea; in this case, the interests of the Caspian littoral states, existing international practice and international law must be taken into account; the Caspian littoral states must take real steps to solve the problem, demonstrating a strong political will; to this end, it should strengthen its activities through high-level meetings; the consistent efforts of the Azerbaijani leadership to determine the status of the Caspian Sea are to be applauded; Azerbaijani diplomacy should expand political and humanitarian relations with the foreign ministers of the Caspian littoral states; there is a serious need to join the efforts of the Caspian littoral states in the field of Caspian ecology; there is a serious need for the Caspian littoral states to comply with international law in the use of Caspian resources; it is important that Azerbaijan and other Caspian littoral countries pay serious attention to people's diplomacy in protecting the Caspian Sea. In general, the problem of the legal status of the Caspian Sea is one of the factors affecting the current international situation in the Caspian littoral states.

2. In this regard, the solution of the problem of the status of the Caspian Sea is of great international importance in the context of the current geopolitical situation of the states. The growing demand for energy resources in the world market, such as oil and natural gas, the participation of world countries in transregional projects related to the exploitation and transportation of these resources, the security of export pipelines show the need to resolve the legal status of the Caspian Sea. The settlement of disputes in the Caspian region, the formation of a security environment and the establishment of stability will have a positive impact on the economic development of the Caspian countries, as well as the expansion of opportunities for countries seeking to strengthen cooperation in the joint use of energy resources.

4.References

1. Darabadi P.-The Caucasus and the Caspian in world history and geopolitics of the XXI century. Moscow 2010
2. Hasanov S.-The issue of the status of the Caspian Sea in interstate relations. Baku, Science 2002.
3. Aliyev A.-Caspian policy of the littoral states. Baku, History and its problems, №1 2009.
4. Suleymanov A.-The problem of regional security in the principle of division of the Caspian into national sectors. Baku 2011.
5. Suleymanov A., Mammadov K.-Different approaches to the security problem in the Caspian region. Baku University News 2010, Socio-political sciences series №2.
6. Ramazanova E. The Caspian Sea: Legal Challenges of Delimitation between Littoral States. University of Tromso, fall 2012.
7. http://www.21yyte.org/assets/uploads/files/187-202%20ertan.PDF
8. http://journal.yasar.edu.tr/wpcontent/uploads/2012/10/26_Sayi_1_makale_Cenk-Sevim
9. http://www.21yuzyildergisi.com/assets/uploads/files/67.pd
10. http://www.eia.gov/countries/regions-topics.cfm?fips=CSR
11. http://newtimes.az/ru/geopolitics/3086
12. www.kremlin.ru,www.russianconcil.ru,news agencies

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RESOURCE AND ENERGY EFFICIENCY CRITERIA OF RECYCLING TECHNOGENIC MATERIALS AND THEIR QUALITY ASSESSMENT

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Abstract: A methodology of FABA quality assessment from the viewpoint of an object for processing and recycling is offered based on an analytic study of an accumulation of patented technologic solutions. The practicability of using such methodology is rationalized. Examples of resource saving technologies are given, which have undergone semi-industrial and experimental industrial approbation. The reasons of practicability of extensive involution of technogenic waste present in artificial waste pile-ups, which contaminate the environment, into processing and utilization are explained. It is noted that resource efficiency characterizes the system of resource saving from the viewpoint of the degree of waste utilization and the quality of production obtained (while minimizing costs and environmental risks).

Criteria of resource efficiency of waste and secondary raw materials recycling are outlined: degree of waste utilization, technologic indicators of the processes used, characteristics of new products, specific energy consumption. Resource efficiency assessment is provided using the example of FABA utilization. Fundamental principles of FABA processing and utilization are given, as well as ways of improving their quality when used as a secondary raw material.

Keywords: technology, waste management, secondary raw materials

1. Introduction

Maximum reduction of the amount of landfilled unprocessed waste is one of the main tasks of resource saving.

Resource saving strategy sets the priority approach of maximally reducing materials expenditure and their secondary reuse.

Resource efficiency is a characteristic of the resource saving system from a viewpoint of degree of waste utilization and quality of the resulting product (while minimizing costs and environmental risks). Degree of waste utilization is the amount of resources for secondary material use obtained from waste, quantified as percentage of the total amount of generated waste of this type. Quality of the resulting product is determined by specific indicators of its industrial use [1].

The choice of a resource saving technology is determined by its technological indicators, characteristics of raw materials and final products, environmental soundness of the process and costs minimization. These technologic indicators are used to generally determine resource efficiency of solving the problem of waste and secondary raw materials use and recycling.

Technological criteria, which are a combination of the main process parameters examined below (α, β, ε, γ), correlate according to the formula $\gamma\beta=\alpha\varepsilon$, where the target function is extraction $\varepsilon = \frac{\gamma\beta}{\alpha}$ (on the condition that the content of useful component β in the final product must fulfill the requirements of the subsequent stage of waste utilization).

These technological criteria of resource efficiency of waste and secondary raw materials processing are:

- degree of waste utilization, %;

- technological indicators of the applicable processes (such as benefication, metallurgy, chemical treatment etc.): fraction of the target component in the raw material (α, %); extraction (ε, %); content (β, %); yield (γ, %);
- (if the product is used in construction industry) constructional and technical properties of the final product: compressive strength ($\delta_{compression}$, MPa); flexural strength ($\delta_{flexural}$, MPa); freezing tolerance (F, cycles); thermal conductivity (λ, $W{\cdot}K^{-1}{\cdot}m^{-2}$); water absorption (W, %);
- (for paper and pulp recycling industry) paper-forming properties of waste pulp and paper: breaking length, m; bursting strength, kPa;
- specific energy consumption, kWh/t (for raw materials, products).

2. Metod

Below the resource efficiency of a technology for power plant coal combustion (by)products – fly and bottom ash (FABA) is assessed.

Wherein a FABA technology is a combination of methods (operations) of FABA treatment in order to improve their quality as a secondary raw material (i.e. composition and fineness stabilization, extraction of useful components, removal of undesired components) with subsequent processing and utilization of enriched products (compliant with the requirements of resource saving as well as legal and technical documentation).

Many methods of FABA processing and utilization are available.

The most potential method of large-scale use of FABA given that it is thermally treated and can't be incinerated (and contains reactive oxides of calcium, silicon and aluminum, has low thermal conductivity) is therefore in the construction industry (this has been practiced since the 1930s) and in road construction. At the same time FABA is a potent source of new products. One ton of FABA can contain up to 90 kg of iron, 160 kg of aluminum, 10-30 kg of magnesium, 1-3 kg of titanium, 1 kg of rare metals [3].

In order to improve the quality of FABA as a secondary raw material, methods of enrichment have to be used. A technologic possibility (and economic feasibility) has been proved for FABA separation via benefication methods into magnetic fraction (yield is 5-10%mass., iron content 35-50%, germanium 10 g/ton, 80% fineness –0,1+0,05 mm), light fraction which contains microbeads (yield is 2%, density 0.3-0.5 $g{\cdot}cm^{-3}$) and non-magnetic fraction (yield is 90%, 70% fineness –0,05 mm) which is a raw material for construction industry (and other industry branches) [4].

The main technologic indicators which characterize the process of benefication (separation) are *extraction*, *content* and *yield.* They allow to evaluate the efficiency of a given technology and compare it to the other technologic processes dedicated to solving similar tasks.

Extraction Ɛ of the component into the separation product is a ratio of the mass of the component in the separation product to the mass of the component in the initial raw material.

Content β of the component in the separation product is a ratio of the mass of the component in the separation product to the mass of the separation product.

Yield γ of the separation product is a ratio of the mass of the separation product to the mass of the initial raw material.

Indicators of separation are usually expressed in percentages (less commonly in decimal quantities).

Products and half-products (waste fractions) obtained after separation (of FABA in particular) must be compliant with the applicable valid standards and requirements of a specific manufacturing process to which they will be sent.

To examine a specific example .

One ton of FABA is sent for separation. The material is transported on the conveyor belt with suspended magnetic separator installed above it.

One ton of FABA contains 5% of iron (50 kg).

As a result of magnetic separation magnetic fraction in the amount of 25 kg is obtained; represented by ferrous metals (20 kg) and impurities (5 kg).

Determination of indicators of separation:

$$\text{Ɛ}=\frac{20\,kg}{50\,kg}\,\text{x}100\%=40\%;\ \beta=\frac{20\,kg}{25\,kg}\,\text{x}100\%=80\%;\ \gamma=\frac{25\,kg}{1000\,kg}\,\text{x}100\%=2.5\%.$$

The numeric values of technologic indicators allow to make conclusions about efficiency of the separation process (whether these indicators are good or bad).

Extraction: the indicator value of 40% was achieved with the maximum possible of 100%. Large losses of ferrous metals which are left in the non-magnetic fraction indicate that single-step magnetic separation is insufficient, at least one more step is required (introducing one more separator into the processing scheme).

Content: 80% is a high indicator, but according to the applicable Russian state standard (GOST) the content of iron in magnetic fraction for municipal waste benefication has to be not less than 97% (therefore secondary cleaning is required).

Yield: 2.5% is an acceptable indicator which shows that a part of iron compounds was separated from the main bulk of waste (yield of magnetic separation tailings is 100%-2,5%=97,5%; and in case of FABA processing these tailings are an optimized product which can be used in construction industry).

Since FABA is a multicomponent system, the most important indicator is comprehensiveness of raw material usage.

The indicator of the comprehensiveness of FABA usage is a number of components which are extracted into quality products.

3. Results and Discussion

Rational and comprehensive processing of FABA ensures extraction and obtaining of resource valuable components and materials, as well as compliance with valid and applicable norms of secondary raw material utilization.

According to the research by the Kuzbass State Technical University and the Thermal Physics Institute of the Siberian Branch of the Russian Academy of Sciences, using non-magnetic (ferrous metals removed) fraction of FABA allows to lower the cement consumption by 30%. Using FABA in cement manufacturing without removing ferrous compounds leads to a decrease of mechanic and technologic indicators of cement, an increase of setting time [5].

Another unfavorable impurity of FABA is unburned carbon. Different technologic of unburned carbon removal from FABA (flotation, gravitation etc.) are compared using the following technologic indicators: yield of coal concentrate (usually ~20%) and its carbon content (usually 70-80%); coal content in tailings no more than 5%. A technology with higher indicators is chosen.

In order to compare the technologies of enriched FABA utilization in construction industry and road construction (such as manufacturing of concrete, cement, binders, cement clinker etc.) constructional and technical properties of the final products are examined: strength characteristics, normalized water content, flowing property, non-consolidation etc (basic quality indicators of the resulting products) [6].

Using FABA for purification of slightly contaminated discharge water is possible (fly ash – a part of FABA – has adsorptive properties). The quality of purification is assessed by the changes in composition of discharge water from the viewpoint of lowering the content of various contaminants [7].

Another proven way of using FABA is manufacturing of granulated fertilizers (which improves the productive capacity of acidic soil). At the same time soil chalking with an ameliorant derived from waste can be viewed as environmental and resource saving technology since its usage allows to lower the consumption of nitrogenous and phosphorous fertilizers.

As can be seen from the above, technologies are compared taking into account the specifics of the branch usage of the final products.

Regardless of the type of waste which is being processed, the raw materials composition in the feed of a thermal process must be optimized by the criteria of energy saving and environmental safety:

- thermal utilization of waste should be performed for enriched combustible fraction with specific fineness (determined by a given process) and calorific capacity which don’t contain resource valuable and dangerous components (spent dry galvanic elements, expired mercury-containing devices etc.);
- calorific capacity of a mixture of wastes (like solid municipal waste) which is to be incinerated is in the range of 2000-3000 kcal/kg (which ensures that the process is stable and autogenic);
- unburned carbon content in slug is not more than 0.3% (requirements for unburned carbon content);
- slug hazard class not lower that IV.

Main ways of improving energy efficiency of waste processing:

- completeness of waste combustion (unburned carbon yield minimization);
- sound preparation of waste for thermal processing (i.e., briquetting, ballast removing etc.);
- extraction of unburned carbon from ash (its briquetting and use as fuel);
- fullness of heat recovery for heat generated in thermal processing of waste:

  - for instance, through heat of molten slug during processing of dusty metallurgy waste into clean metallized ingots;
  - through obtaining more efficient energy carriers, for instance in a so called "adiabatic" process of waste gasification;
- energy saving through improving the main manufacturing technology:
  - tin sulfide sublimation is low in power consumption and can be applied as a technology of extracting tin from low metal content smelter slugs;
  - 30% of energy can be saved using a technology of processing industrial waste into hydraulic binders based on special physical treatment and using efficient chemical additives;
  - technology of extracting nanoparticles of carbon from carbonaceous material is low in power consumption (due to using a feedstock of waste which has undergone high energy treatment during the process of aluminum electrolysis);
- crushing spent tires with addition of rubber devulcanizer.

Introducing such wastes into the industrial cycle is largely tied to their resources, composition, degree of technological usage and readiness of waste for processing and utilization, the demand of obtaining new products [8].

Based on the foregoing, the scientific approach for implementing policy in resource saving and resource efficiency is based on determination of cause-effect relationships between regular waste generation (meaning their properties, quantity and quality) and practicability of their recycling and utilization (considering priorities for investment). Systems of waste management are created in order to protect the environment and ensure rational use of natural resources (taking into account one of the basic principles: it is preferable to conserve the energy contained in waste by using it as a secondary raw material as opposed to incinerating it and utilizing the energy generated by that) [9].

Introducing large-tonnage wastes into the industrial cycle requires valid and reliable information about not only the available resources, but also the quality of the secondary raw materials and possible methods of their processing and utilization, which in turn necessitates organized testing of storages and landfills of technogenic materials and conducting large-scale experimental research (similar to new mineral deposits), which is a complex and laborious task, which takes time and resources to be completed. (Assessment of the resources available in mineral deposits is done in conjunction with examination of their enrichability, that is, their ability to be processed using existing technologies).

In order to save time and reduce costs, as well as to increase comprehensiveness and reliability of research a methodology of technogenic waste quality assessment and their possible utilization methods was suggested, based on analytic study of an accumulation of patented technologic solutions, which are dedicated to recycling technogenic raw materials generated as a result of processing mineral deposits and derivatives thereof (in a chain of manufacturing various products which have lost their consumer properties with time) [2,6].

To justify the viability of applying such methodology:

- patented technologic solutions are obtained experimentally using actual samples of industrial waste, thus identifying not only the possibilities of using a given technology, but also precising the composition of wastes as objects of recycling;
- experiments can be regarded as crosscutting: they are conducted by various researchers and solve different tasks;
- patented technologies of secondary raw materials reuse are resource saving solutions and therefore can be viewed as innovative offers;
- in case the conducted experiments were successful on a larger scale (i.e., semi-industrial) the technology can be recommended for practical implementation and used as a starting point for engineering.

Below is a list of new resource saving technologies which have been tested on semi-industrial and experimentally industrial scales:

- technology of recycling finely dispersed wastes of electrolytic aluminum manufacturing containing carbon and fluorine (millions of tons of such waste are accumulated on slimy landfills);
- technology of recycling dusts of secondary lead and paste of lead batteries;
- technology of combined processing of cuprous slug and copper anode slime;
- technology of steel smelter slug and ferrous sulphate disposal (derived from regeneration of spent etching medium);
- technology of extracting magnetic fraction from FABA;
- technology of FABA's complex recycling, extraction of valuable components and unburned carbon;

- technology of pyrite cynder recycling;
- technology of phosphogypsum recycling (combined with extracting valuable components, incl. rare earth metals);
- technology of obtaining high strength artificial gypsum stone.

Analysis of patented technologic solutions indicates that technogenic fields of large tonnage waste in the Russian Federation have been practically studied and considered to be serviceable. All approbated technologic solutions can be assumed to be resource efficient. Therefore, the problem of waste, stemming from the methods of its solving, is refocused to be a problem of secondary raw materials as a part of the resource saving issue. It is extremely important that introducing many types of secondary raw materials into the industrial cycle is based on using experimentally tested technologic solutions and that technologic and investment risks are reduced to the minimum.

On the whole, extracting valuable components from raw materials with subsequent utilization of the remaining part in the construction industry is basically a rational solution of the resource saving and improving resource efficiency problems (strategic planning).

4. Conclusions

Based on the foregoing, the analytic study of an accumulation of patented resource saving solutions of various technological tasks, which is used in this paper, is an effective method to evaluate quality of technogenic raw materials and its readiness for introduction into the industrial cycle. This approach is also the most informative and well-grounded method of evaluating the soundness of concepts of solving the problem of secondary raw materials and creating applicable market conditions to recycle and use waste in a given region, to minimize environmental and investment risks, and it can also be used as a method for expert assessment in determining environmental and economic efficiency and practicability of recycling technogenic raw materials, and in implementation of sound environmental industrial policy.

Practicability of extensive involution into processing and utilization of large tonnage waste as technogenic raw materials concentrated in artificial waste landfills which contaminate the environment, is explained by the following reasons:

- the necessity of solving the problem of waste is dictated by the regulatory documents;
- environmental requirements (there is approximately 2 billion tons of FABA, over 3 billion tons of ore-mining and smelting waste and other wastes which contaminate the environment are accumulated in the Russian Federation; the formation of landfills is associated with withdrawal of land from beneficial use); environmental problems in and of themselves do not pose an interest to the market, but at the same time a part of a new product’s competitiveness is related to its environmental characteristics (eco-efficiency);
- FABA and slugs are finely crushed thermally processed and incombustible product (they contain reactive calcium, silicon and aluminum oxides, possess low thermal conductivity); the properties of many wastes determine their potential usefulness for the construction industry and road construction;
- many wastes contain valuable components (compounds of iron, microbeads, rare and rare earth metals, precious metals, etc.).

Actions to be taken on a state level:

- legal requirement that all enterprises must maintain records of waste management and provide data on it to authorities;
- state support of marketing products which contain secondary raw materials;
- placing restrictions on using primary raw materials or products therefrom, if similar materials or products using secondary raw materials are available;
- preferential taxation of enterprises which perform activities of waste management;
- discounted fares on transportation of raw materials obtained from waste;
- soft loans for the purposes of creating the infrastructure of waste utilization.

Unfortunately, as of now such large tonnage wastes as FABA and phosphogypsum are mainly practically used only for manufacturing construction and road materials, significantly less commonly as agrochemicals and almost never as raw materials for extraction of valuable components, especially metals (incl. those which are strategically important).

The analysis of an accumulation of patented technologic solutions proves that FABA and phosphogypsum, which generate large landfills, can be reused, and characterizes their broad technologic possibilities as object of processing.

5.References

1. Ivankov S. I., Skobelev K. D., Shubov L. Ya., Doronkina I. G. Systematization of multi-tonnage waste and patented technologies for their utilization and processing / Scientific and technical aspects of environmental protection. 2020. No. 1. C. 2-118. DOI: 10.25791/esip.02.2020.1138
2. Shubov L. Ya., Skobelev K. D., Ivankov S. I., Doronkina I. G. Analytical assessment of ash and slag waste as technogenic raw materials (to substantiate environmental industrial policy)/ Ecology of industrial production. 2018. no. 3 (103). Pp. 15-23;
3. Koltsov, V.B., Sevrukova, E.A., Slesarev, S.A. The allocation of gallium from a multicomponent eutectic in the disposal of technological waste recycle/ Proceedings of the 2017 IEEE Russia Section Young Researchers in Electrical and Electronic Engineering Conference, ElConRus 2017. DOI: 10.1109/EIConRus.2017.7910765
4. Palod R., Deo S.V., Ramtekkar G.D. Utilization of waste from steel and iron industry as replacement of cement in mortars/ Journal of Material Cycles and Waste Management. 2019, 21(6), pp.1361-1375. DOI: 10.1007/S10163-019-00889-3
5. Marvila M.T., Alexandre J., de Azevedo A.R.G., Zanelato E.B. Evaluation of the use of marble waste in hydrated lime cement mortar based/ Journal of Material Cycles and Waste Management. 2019. 21(5), pp.1250-1261. DOI:10.1007/ S10163-019-00878-6
6. Shubov L. Ya., Skobelev K. D., Doronkina I. G., Zagorskaya D. A. Comparison of ash and slag waste processing technologies. The indicators of the comparison/ Ecology of industrial production. 2019. No. 4 (108). Pp. 6-12.
7. Zhang J., Wang L., Halden R.U., Kannan K. Polyethylene Terephthalate and Polycarbonate Microplastics in Sewage Sludge Collected from the United States/ Environmental Science and Technology Letters, 2019, 6(11), pp.650-655. DOI.10.1021/acs.estlett.9b00601
8. Pu Y., Wu G., Tang B., Xu L., Wang B. Structural features of global recycling trade networks and dynamic evolution patterns/ Resources, Conservation and Recycling, 2019, 151. DOI: 10.1016/j.resconrec.2019.104445.
9. Li, J., Sun, Y., Zhang, X., Guan, X. Weak magnetic field enables high selectivity of zerovalent iron toward metalloid oxyanions under aerobic conditions/ Journal of Hazardous Materials. 2020. *DOI:* 10.1016/j.jhazmat.2020.123330

PP-VI-4

THE RESEARCH OF BITUMEN-POLYMER COMPOSITES

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Abstract: The article is dedicated to obtaining of bitumen-polymer wastes based composites and the study of their properties. The amount of polymer wastes generated separately in different countries of the world is leading to a global environmental disaster. One of the directions of efficient treatment of polymer-based wastes is the development of composition of composite materials having high operational properties and production technologies on the base of them. Namely, from this point of view, the study of various compositions and production technologies of bitumen-polymer-based composites having high operational properties not only is of both scientific and applied importance, but also creates conditions for solving environmental problems. For this purpose, Baku 85/25 bitumen has been modified with different types of polypropylene waste and as a result of the research, it was determined that the addition of 2.6 k.h. polypropylene waste to bitumen under optimal conditions improves the properties of bitumen, significantly reduces the penetration rate of modified bitumen and increases the softening temperature. This is explained by the fact that polypropylene macromolecules play the role of reinforcement for the components of modified bitumen by increasing their abrasion resistance to various influences and improve the physical-mechanical and operational properties of the composite material.

Keywords: bitumen, polypropylene waste, penetration, ecology

1.Introduction

During the production processes of synthetic rubber, rubber-based products and polymers, as well as after the use and exploitation of rubber and polymer-based consumer goods, due to removal from operation (decommissioning) according to their purpose, waste masses of large amounts and types accumulate not only on the earth surface, but also in the sea and ocean basins, giving the message of environmental disaster of our time. Therefore, one of the most important issues in the forthcoming emergency is to expand and accelerate research being carried out in the direction of efficient treatment processes and technologies to minimize this growing waste. One of the efficient treatment directions of polymer-based wastes is the development of the composition of composite materials having high operational properties and production technologies on base of them. The addition of a certain amount of polymers with different macromolecular structures to each other gives new properties to the obtained material. It was determined by the research that the addition of small amounts of PE to polypropylene (PP) increases its sustainability to freezing and impact [2,3], as well as resistance to oxidation [4]. Moreover, the addition of PP to PE increases the mechanical strength and solidity [5] and resistance to high temperature of the obtained composite [6]. These properties allow obtaining of new bitumen-based composites with high operational properties using PE and PP-based wastes.

Oil-based bitumen is mainly used as a binder in the composition of composites. Binding properties differ in various brands of bitumen. These differences are evident in the modification of different brands of bitumen. The strength rate to breaking characterizing the physical and mechanical properties of BND 60/90 and BND 60/130 brands of bitumens obtained using different methods and the composites obtained from modification in the presence of rosin under the same conditions, increases linearly to BND 60/130 when it exceeds the maximum to BND 60/90 [7]. This means that each brand of bitumen can be modified to meet the requirements of the utilization area in accordance of its purpose. Given that oil-based bitumen is a basic component in the preparation of composites, mainly used in the laying of asphalt-concrete road pavements, a simple solution to the problems that arise during operation is its simple modification by various techniques. The purpose is that such optimal properties as creating a solid coating layer of hydrocarbon components of bitumen on the surface of stone-sand materials, reducing surface deformation from the effects of high temperatures and tonnage transportation (increasing the contact strength of moving machines and mechanisms with the road surface), the formation of cracks, direct holes at low temperatures (this subsequently causes water to migrate to the lower layers and the layer to collapse), increasing the service life of the coating layers are not possible without modification. In the submitted material, Baku 85/25 brand bitumen was modified with various types of polypropylene waste.

2.Experimental part

A new bitumen production process with a project capacity of 400,000 tons/year based on Biturox technology has been launched in our country. The plant mainly produces EN 40/60 brand of bitumen. It is known that BNK 40/180 and BNS 90/10 brand bitumens for construction purposes are widely used for roofing in the relevant production processes. The research used Baku 85/25 brand of bitumen with the properties given in Table 1, and polypropylene waste as a modifier. The PP with a linear structure produced on an industrial scale has a molecular weight of M-60-200 mm, a density of 900-910 kg/m^3, a melting point of 165-170^{0}C and a softening temperature of 75^{0}C. Experimentally, samples of the polymer-bitumen composition were prepared as follows. The polypropylene waste taken in the first stage was intensively mixed with bitumen in the reactor at 180^{0}C for 20 minutes after swelling in CCI4 for 1.5 hours. A number of bitumen compositions were prepared by this method. The softening temperature of the obtained bitumen compositions, the penetration depth of the needle at 25°C and its elongation at 25 ° C were determined according to State Standard-33142-2014, State Standard-33136-2014 and State Standard-33138, respectively.

Table 1. Properties of “Baku 85/25” brand bitumen

The name of indicators	Indicators
Penetration, 25^{0}C	121
Softening temperature, ^{0}C	51
Elongation, mm	811
Elasticity, %	-

3.The obtained results and their discussion

Information on the composition of the bitumen of Baku 85/25 brand modified with polypropylene waste is given in Table 2, and the physical and mechanical properties are given in Table 3.

Table 2. The compound of compositions

Names of components / Code of mixtures	Amount of components, mass h.			
	1	2	3	4
Bitumen “Baku 85/25”	100	100	100	100
Polypropylene waste	0	2	4	6

Table 3. Physical and mechanical properties of compositions

Names of components / Code of mixtures	Amount of components, mass h.			
	1	2	3	4
Penetration, 25^{0}C	121	94	41	28
Softening temperature, ^{0}C	51	64	89	92
Stretching, mm	811	230	163	160
Elasticity, %	-	73	88	82

These researches, in addition to a direct solution to essentially the intended purpose, are no less important and provide unexaggerated services in solving global environmental problems created by our time. After production wastes, generated as a result of the development of the production and processing of polymer materials, operation and use of products prepared on their basis, the creation of recycling technologies, creating conditions for their purposeful use play its positive and important role in solving modern environmental problems, and is also economically viable in terms of efficient use of hydrocarbon resources.

Due to the presence of large amount of polymer materials, including polypropylene waste, among modern household waste, their use as recyclable raw materials is also of great importance. Polypropylene waste is usually collected directly during production processes in the form of obsolete products obtained from polypropylene. From this point of view, based on the results of the conducted experiments (Table 3), it can be said that the properties of Baku 85/25 bitumen significantly improve when 2-6 k.h. of polypropylene waste is added to it. Thus, the penetration indicators of modified bitumen significantly decrease, and its softening temperature increases. These indicators confirm that polypropylene macromolecules are evenly distributed in the bitumen environment due to the used technology. Given that the macromolecule of PP is a branched methyl group in the hydrocarbon chain (Figure 1), it consists of three main isomers - isotactic (PPi), syndiotactic (PPs) and atactic (PPa), depending on the configuration of the macromolecule [1].

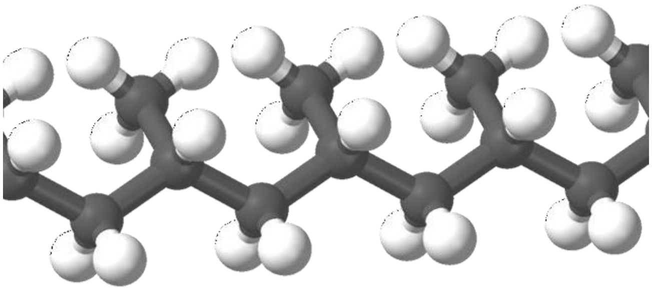

Figure-1. Structure of PP macromolecule (iPP)

As a result of the research (Table 3), it was determined that the addition of 2.6 k.h of polypropylene waste to Baku 85/25 brand bitumen improves the properties of bitumen, significantly reduces the penetration indicators of modified bitumen, and increases the softening temperature.

4.Conclusion

This is explained by the fact that polypropylene macromolecules play the role of reinforcement for the components of modified bitumen by increasing their abrasion resistance to various influences and improve their physical-mechanical and operational properties. The results of the research can be explained by the fact that polypropylene macromolecules with different isostructures are evenly distributed in the bitumen environment due to the used technology, and the migration of bitumen components to the bottoms formed by methyl isomers of PP leads to the formation of segmental crystal layers.

5.References

1. Karian, H.G. Handbook of Polypropylene and Polypropylene Composites, Revised and Expanded [Текст] / ed. H.G. Karian – Boca Raton: CRC Press, 2003, 576 p.
2. Blom, H.P. Polymer. – 1998. – №39. – P.4011-4022.
3. Tai, C. M. J. Polymer Testing. – 2000. – Vol. 19, №2. – P. 143-145.
4. Shibryaeva, L. S. Thermal Oxidation of Polymer Blends. Leiden, Boston: VSP, 2006. – 248 p.
5. Jose, S. Eur. Polym. J. – 2004. – Vol. 40, №9. –P. 2105-2115.
6. Utracki, L. A. Commercial polymer blends. London: Chapman and Hall, 1998. – 658 p.
7. Vasileva E.O., Evdokimova N.G., Egorova N.A. The science. Technology. Production - 2017. Applied science as a tool for the development of petrochemical industries, May 10-26, 2017.
8. D. S. Mamed Hasan-zade, A. I. Babaev, A. G. Ismailov, S. V. Yusifova / Patent, Certificate №350, “Industrial Property” monthly official bulletin, № 6, Baku-2019.
9. Abdullin A.I. Bulletin of Kazan Technological University 2011, no. 19, p. 205-207.
10. D.S.Mamed Hasan-zade, A.I. Babaev, K.S.Gasanov. "Oil refining and petrochemistry", Moscow, No. 8, 2019

OR-VI-4

ACID-FREE METHOD FOR OBTAINING ORGANOMINERAL FERTILIZER

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Abstract: A comprehensive analysis of the state and development of technologies for obtaining single-component and complex fertilizers, as well as their agrochemical efficiency, was studied. Despite a large number of new promising developments in the NPK fertilizer technology, the most significant drawbacks of their main types remain unchanged: in the technology of nitrogen fertilizers-a high rate of their dissolution; in the phosphoric technology – the acidifying effect of superphosphates and a significant negative impact on the environment (esterification of reservoirs, along with nitrogen), in the potash technology – the predominant release and use of KCI.

Key words: organomineral fertilizers, meliorant, phonolite, superphosphate, geothermal water.

1. Introduction

When using household waste, it should be taken into account that they contain a large number of microorganisms, the bulk of which is a bacterial group, including mesophilic and thermophilic bacteria. Therefore, when using raw household waste to prepare fertilizers applied to the soil, they should be neutralized.

The purpose of the invention is to expand the raw material base of organic waste used, improve the quality of fertilizer by introducing trace elements and eliminating pathogenic microflora using local natural resources at no additional cost [1, 2].

The problem is solved by the proposed method for obtaining organomineral fertilizer, in which geothermal water containing 10-15% H_2S is added to the crushed solid household waste, having a temperature of 55-75^{0}C, the mixture is mixed with crushed phonolite, the resulting mixture is kept in a furnace at a temperature of 100-110^{0}C for 1.5-2 hours, and then the resulting mass is neutralized with a shell to a pH of 6.5-7.5.

The novelty of the invention is that solid waste is used as a source of nutrients, and as an additional source of potassium, phonolite is used, which is an available natural substance, and the elimination of pathogenic microflora is carried out by geothermal waters containing hydrogen sulfide [3].

2. Experimental part

Municipal solid waste is a source of $N_{com.}$, P_2O_5 and K_2O. The use of phonolite will increase the content of such an important element as potassium in the fertilizer, and treatment with geothermal waters having a temperature of 55-75^{0}C eliminates pathogenic microflora without spending additional energy [4].

Solid household waste of the following composition, mass, is used as organic mass. %:

Paper and cardon	**20 – 30**
Food waste	**5 – 45**
Tree	**1 – 4**
Metal	**1,5 – 4,5**
Textiles	**4 – 7**
Bones	**0,8 – 2,0**
Glass	**3 – 10**
Leather and rubber	**4 – 7**
Stones	**1 – 3**
Polymer materials	**1,5 – 5**
Etc	other

Solid household waste has the following chemical composition, % dry weight: organic matter- 55-73; $N_{com.}$ nitrogen-0.7-1.7; P_2O_5 phosphorus- 0.5-0.7; K_2O potassium- 0.3-0.7; CaO calcium-3.9-5.6; H_2S sulfur-0.2-0.3; carbon-28-34. Moisture content, % total weight of 32-48; pH of 6.5-7.5.

The used phonolite from the Lerik region of Azerbaijan has the following chemical composition by mass %: **SiO_2 – 59,79; TiO_2 – 0,85; Al_2O_3 – 16,98; Fe_2O_3 – 3,25; FeO – 2,76; MnO – 0,09; MgO – 2,51; CaO – 1,69; Na_2O – 1,93; K_2O – 9,6; P_2O_5 – 0,55.**

The used geothermal waters of the Lerik region of Azerbaijan contain up to 28-31% H_2S.

To neutralize the resulting compost, a shell plant of the Lerik region of Azerbaijan was used, which has the following composition, mass %: **CaO – 51-97; MgO – 1,33; CO_2 – 38-48; Al_2O_3 – 2,0; Fe_2O_3 – 0,3; K_2O – 1,2; N_2O – 0,5.**

Crushed household waste is placed in a 600-800 ml container. Then, in order to neutralize microorganisms from solid household waste, geothermal water is added from the well at a temperature of $55-75^0$C. After 10-15 min. the mixture is introduced when mixing crushed phonolite in an amount that provides the required content of trace elements. The resulting mass is kept in the oven at $100-110^0$C for 1.5-2.0 hours.

To the resulting mass, which has a pH of 4.0-4.5, gradually add the crushed shell, bringing the pH to 6.5-7.0. The resulting organomineral fertilizer is granulated according to a well-known method [5].

3. Results and discussion

Solid household waste has the following chemical composition, % dry mass: Organic matter-56-73; $N_{com.}$-0,7-1,7; P_2O_5 phosphorus- 0,5-0,7; K_2O potassium-0,3-0,7; SiO_2 sulfur- 0,2-0,3; CaO calcium-3,9 – 5,6; carbon- 28-34. Moisture content, % total weight 32 – 48, pH-6.5 – 7.5.

The used phonolite from the Lerik region of Azerbaijan has the following chemical composition, mass., % SiO_2-59,79; TiO_2-0,85; AI_2O_3-16,98; Fe_2O_3-3,25; FeO-2,76; MnO-0,09; MgO-2,51; CaO-1,69; Na_2O-1,93; K_2O-9,6.

The used geothermal waters of the Lerik region of Azerbaijan contain up to 28-31% H_2S.

To neutralize the resulting compost, a shell plant of the Lerik region of Azerbaijan was used, which has the following composition, mass. %:

CaO-51 – 97; MgO-1,33; $CO_2$38 – 48; AI_2O_3-2,0; Fe_2O_3-0,3; K_2O-1,2; N_2O-0,5.

The method is performed as follows:

Crushed solid household waste is placed in a container with a volume of 600–800 ml. Then, in order to neutralize microorganisms from solid household waste, geothermal water is added from the well at a temperature of $55-75^0$C. After 10 – 15 minutes. the mixture is introduced when mixing crushed phonolite in an amount that provides the required content of trace elements. The resulting mass is kept in the oven at $100-110^0$C for 1.5-2 hours.

To the resulting mass, which has a pH of up to 4 – 4.5, gradually add crushed shell, bringing the pH to 6.5 – 7.0. the Resulting organomineral fertilizer is granulated according to a well-known method [6].

Methods of research in a container placed 100g. crushed solid household waste to which add 5ml of geothermal water, in which the concentration of hydrogen sulfide is brought to 15%. In 10 minutes. to this mixture, add 15 grams of crushed monolithic rock. After that, the container is placed in the oven and kept at a temperature of 100^0C for 1.5 hours.

The obtained powdery organic-mineral fertilizer contains, by mass. % : $N_{com.}$-0.51; P_2O_5-0.40; K_2O-5.5; H_2O-11.3; MgO-1.6; organic matter: SiO-16.5; CaO-17.33; AI_2O_3-9.4; Na_2O-0.86, other oxides – 2.0.

The resulting powdered fertilizer with ph4 is neutralized by adding 2.4 g. shell, bringing the pH to 6.5.

After granulation, the resulting fertilizer has the following composition, mass%: $N_{com.}$ – - 0.50; P_2O_5-0.44; K_2O-6.6; H_2O-2.7; MgO-1.67; organic matter-38.2; SiO_2-17.9; CaO-18.97; AI_2O_3 – 9.8; Na_2O – 0.92, other oxides – 2.3. Mechanical strength of granules- 21kgs/sm^2.

From what has been written, it can be seen that during the experiments, the amount of geothermal water was 1-5 ml. The amount of phonolite used was 1 gram. The results of the analysis are shown in the table and graph. The table shows that solid household waste that we use always remains stable. The amount of geothermal water was 1-7ml H_2S, while the amount of geothermal water was 0% no matter how much in the geothermal water.

According to the digestibility of phosphates (by their solubility), phosphorus-containing fertilizers are classified as follows:

- - water-soluble P_2O_5rot. (as an impurity H_3PO_4);
- digestible P_2O_5ass. (partially soluble in citric acid solution);
- insoluble P_2O_5com. (aluminosilicates that are not soluble in weak acids).

Water-soluble phosphates are currently prohibited from being used as fertilizers (since they lead to esterification of reservoirs). Low-water-soluble phosphates of industrial superphosphates are CA **$Ca(H_2PO_4)_2 \cdot H_2O$** (solubility – 1.8 g/100g of H_2O) and $CaHPO_4$ – "precipitate" (solubility – 0.02 g/100g of H_2O).

Assimilable phosphates in termofosfatnaya very diverse: salts of calcium and magnesium **($CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, $MgHPO_4$, $MgHPO_4 \cdot 2H_2O$); radanites [$CaNaPO_4$, $CaNa_4(PO_4)_2$, $CaKPO_4$]; α-$Ca_3(PO_4)_2$, $Ca_4P_2O_9$, half of which are hard-to-digest forms of phosphates (poorly soluble in citric acid).**

Difficult to digest phosphates of fused magnesium phosphates do not allow them to be used as fertilizers, so they are used only as feed-grade fluorinated phosphates **[7]**.

The method of obtaining organomineral fertilizers from phosphates and brown coal by shifting them (~1: 2 mass.) does not require energy consumption, but the product can be called a fertilizer only conditionally (P_2O_5ass. ~2%, P_2O_5com. ~9%) [8].

The most promising methods can be considered activation and heat-alkali treatment. At the same time, we should immediately note the main disadvantages of these methods: during mechanical activation, the share of digested phosphates remains relatively low, and high energy consumption is required during heat treatment.

4. Conclusions

Taking into account the above, the review highlights the most promising areas of development of mineral fertilizers technology.

In the technology of nitrogen fertilizers, it is necessary to develop methods for obtaining prolonged nitrogen and complex nitrogen-containing fertilizers.

5.References

1. Margalis F.G., Ukanyants T.T. Production of complex fertilizers. Ed. "Chemistry", pp.117-128, (1996).
2. Ukanyants T.T. / / Agrochemistry, № 5, p.146, (1989).
3. Fersman A.E. Our Apatite and phosphorite. Moscow, (1986).
4. Posin M.E., Kopylev B.A., Alosmanov M.S. Technology of mineral salts. Ed. "Chemistry", Leningrad, P.81, (1989).
5. Kononov A.V. Sterlin V.N., Evdokimova L. I. Fundamentals of complex fertilizer technology. Moscow, "Chemistry", P.307, (1988).
6. M.A. Menkovsky, L.N. Shvakhsman. Physical and colloidal chemistry. Moscow: "CHEMISTRY", P.208, (1976).
7. Posin M.E. Technology of mineral salts. Ed. L., "Chemistry", P.1326-1327, (1991).
8. Karmashov V. F. Chemical processing of phosphorites. pp.300, (1983).

PP-VI-5

RESEARCH OF THE PROCESS OF Cl - ANIONING OF MINERALIZED WATER OF A WIDE CLASS

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Abstract: Technological parameters of Cl-anioning process of different types of mineral waters in AH-31 and AB-17 anion exchange resins widely used in chemical desalination plants have been determined. 8-120 m^3/m^3) and desulphurization rate (98-99%) can be achieved. These anion exchange resins have been identified. It was found that by pre-acidification of water it is possible to increase the ion-exchange capacity of AH-31 anion exchange resin by SO$_4^{2-}$ ions by 40-50%. Appropriate formulas for analytical determination of technological parameters of AH-31 anion exchange resin, ion-exchange capacity and residual concentration of SO$_4^{2-}$ ions were obtained depending on the ionic composition of water, pH, processing and regeneration conditions [1,2,3].

Keywords: brackish, ground, stratal, saline waters, anionites AN-31 and AV-17, exchange capacity of anionite

1.Introduction

The presented article is devoted to the study of the regimes and conditions of Cl – anionization of natural saline waters of a wide class, covering the main types of sea and brackish underground (ground, well, stratal, etc.) waters. The subject of research was natural saline waters with a salinity of 2 to 35 g / l, which are of greatest interest from the point of view of their use instead of fresh water in heat power engineering, oil production, petrochemistry and other industries. The content of sulfate ions can range from 5-10 to 73-80 mEq / l, chlorides - from 20-30 to 300-400 mEq / l, and bicarbonates - from 2-3 to 7-8 mEq [1,2].

2.Experimental part of research

The specific research objectives were:

- an experimental study of the features and basic laws of the process of Cl - anionization of the class of waters under consideration on the AB-17 and AN-31 anion exchangers with the determination of rational areas of their application;
- selection and justification of models for calculating technological parameters of the Cl - anionization process: exchange capacity of the anionite and the residual content of ions;
- development of conditions for the regeneration of anionite, excluding the fallout of carbonate and sulfate deposits when using own concentrates of aninated waters;
- development of technological schemes for Cl - anionization of saline waters using ion exchange filters of standard designs;
- development of a method for calculating Cl-anion exchange filters and technological schemes based on the selected or specially developed models.

The combination of these tasks is the basis of the Cl-anionization technology. The procedure for solving the problem of choosing and justifying models for calculating the Cl-anionization process included:

- analysis of known models;
- substantiation of the nature and content of the main studies aimed at improving the model or developing a new model that most fully corresponds to the conditions of Cl - anionization of waters of the class under consideration;
- performance of relevant analytical and experimental studies.

Experimental studies on Cl-anionation with equilibrium mining of ion exchangers were carried out on dynamic columns with d = 20 mm at a layer height of 40 cm. 31 and AV-17 in conditions of nonequilibrium depletion and regeneration. When developing an experimental-statistical model of the Cl-anionization process, the need for which was justified by analyzing existing models. The experiments were carried out on columns with a layer height of 1.5 m. This eliminated the need to take into account the influence on the process parameters of such an important factor as the height of the ion exchanger layer. Research on softening saline waters / 2 / showed that the height of the ion exchanger layer has the most significant effect on the process parameters in the range from 0.5 to 1.5 m. Therefore, for a reliable transfer of laboratory research results to industrial filters, experiments should be carried out at a layer height not less than 1.5 m.

In any case, the layout of the experimental stand included a dynamic column, containers for source water, wash water, and treated water, as well as communication lines (Fig. 1). The filter piping is made in such a way as to provide the possibility of organizing both direct-flow and counter-flow regeneration. To organize countercurrent regeneration, the "clamping" of the ion-exchange layer was ensured by installing a sponge over the layer of ion-exchange resin.

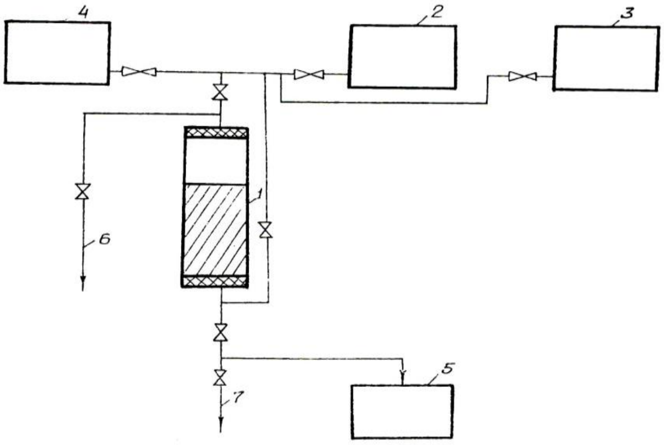

Fig. 1. Scheme of the experimental stand
1 - dynamic column; 2-5 - capacity; 6.7 - throw line

The research methodology for the development of conditions for the regeneration of the anion exchanger with its own concentrates of anionized water included two directions: the study of the capabilities of the advanced regeneration technology (reuse of the spent regeneration solution) and the development of regeneration modes that exclude the precipitation of $CaCO_3$ and $CaSO_4$ in the anion exchanger. In the first case, two-stage regenerations were carried out using, at the first stage, a NaCl + Na_2SO_4 mixture with a total concentration of 4 to 7% and with additional regeneration of the anionite with a 10% NaCl solution. In the second case, the modes of anionization with acidification of the initial water and regeneration solution were studied.

At the stage of experimental studies, the scope of chemical control included the determination of chlorides, sulfates, bicarbonates, calcium and magnesium in the source water. During processing, chlorides, bicarbonates and sulfates were determined in samples with a volume of 0.2 to 0.5 liters, depending on specific conditions. The bulk of the work was carried out on model solutions. Chemical analyzes were carried out according to the methods [2,3].

The following were determined as the output indicators of the process:

- residual content of sulfates and bicarbonates, according to chemical analyzes;
- exchange capacity of the anion exchanger, according to the formula:

$$E = \frac{Q\left(C^{out}_{SO_4^2} - C^{rem}_{SO_4^{2-}}\right)}{V_{AH}}, \quad g - eq/m^3 \qquad (1)$$

where Q is the amount of treated water, l; $C^{out}_{SO_4^2}$ - and $C^{rem}_{SO_4^{2-}}$ - initial and residual concentration of sulfates in water, g-eq/m^3; V_{AH} - loading volume of anionite, l.

The exchange capacity of the anionite for bicarbonate ions was determined by formulas similar to (1).

In a number of cases, the specific production of anionite was also determined as an output parameter of the process. amount of treated water 1m^3 of anion exchanger, q:

$$q = Q/V, \; m^3/m^3 \qquad (2)$$

The study of the process of Cl – anionization of a wide class of mineralized waters AN-31 and AV-17, first of all, to assess the anti-warp effect, then it was important to determine the total exchange capacities of ion exchangers when working on pure solutions of sodium sulfates.

Table 1 shows the results of experiments in which both sorption and regeneration were carried out under conditions close to equilibrium. The concentration of sulfates varied from 5 mg-eq/l to 70, which covered the entire spectrum of the studied waters. The table also shows the data obtained in comparable conditions on the AN-31 and AV-17 by the authors of the work [4].

The data obtained indicate high values of the total exchange capacities of anion exchangers in the absence of an anti-warp effect. In the investigated region of variation of the concentrations SO_4^{2-} the total exchange capacity for AV-17 is 1400^{+}_{-} + g-eq/m^3 and is in good agreement with the data [4]. The capacity of the AN-31 is slightly higher than that of the AV-17. It is reached 1700 g-eq/m^3. Moreover, in contrast to AV-17, there is a slight increase in the exchange capacity with an increase in the concentration of sulfate ions.

Table 1. Results of experiments to determine the total exchange capacity during sorption of SO_4^{2-}, Cl –form AN-31 and AV-17, g-eq/m^3

Consentration SO_4^{2-} mq-eq/l	AH-31	AB-17*
5	1440	$\frac{1400}{-}$
10	1480	$\frac{1400}{1450}$
30	1550	$\frac{1460}{1420}$
50	1580	$\frac{1500}{1490}$
70	1650	$\frac{1450}{-}$

* - the denominator contains data [4].

4. Results

The influence of the counter-ionic effect (chloride concentration) on the technological parameters of the Cl-anionization of saline waters on the investigated anionite can be judged from the results of the experiments. The experiments were carried out according to a direct-flow regeneration scheme. The specific salt consumption was taken as 200 kg/m^3. Salt water was captured from ground (brackish) salt content slightly more than 1 g/l to ocean water with a salinity content of 35-40 g/l.

When choosing the starting point (Ccl = CSO_4 = 9 mg-eq/l), we proceeded from the availability of reliable data for this water in studies. From the results of the experiments, it follows that the presence of chlorides and an amount comparable to sulfates for both brands of anionites leads to a decrease in the exchange capacity by about 30% of the total, but in absolute values, rather high indicators are achieved - 1010-1160 g-eq/m^3. threefold to 27 mg-eq/l leads to a decrease in the working exchange capacity of AN-31 to 750 g-eq/m^3, and AV-17 - 540 g-eq/m^3. Thus, the influence of counterions is more strongly susceptible to AV-17.

5.References

1. Feyziev G.K. Highly efficient water softening and demineralization methods. - M.: Energoatomizdat, 1998.192s.
2. Dadasheva T.I. Improvement of the technology of ion-exchange softening and additional softening of sea waters in desalination schemes and waste-free complex processing. Author's abstract. dissertation cond. engineering sciences. Baku, 1992, 24p.
3. Kostrikin Yu.M. Instructions for the analysis of water, steam and sediments in the thermal power industry. Publishing house M. "Energy", 1967, 192s.
4. Potapova N.V. Development of a method for chlorine-anionization in water purification schemes at thermal power plants.: Avtoref. dissertation cond. engineering sciences. Moscow, 1990, 20s.

OR-VI-2

ANALYSIS OF SEDIMENTATION TECHNOLOGIES FOR A MIXTURE OF GYPSUM AND MAGNESIUM HYDROXIDE IN HIGHLY MINERALIZED WATER TREATMENT SCHEMES

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Abstract. The article presents the results of studies of the unit for clarification of spent regeneration solutions of Na - cation exchange filters in the schemes of low-waste technology for softening seawater. The effect of the doses of coagulant, flocculants and the rate of stirring of the solution on the intensity of precipitation of the gypsum-magnesia mixture was studied. The kinetics of sediment compaction is investigated and the properties of the contact mixture are considered. Investigations of the sedimentation process and the influence of a number of factors on its sedimentation properties are given and the optimal parameters of their changes are determined.

Key words: processed regeneration solutions, gypsum-magnesia mixture, coagulant, flocculants, precipitation process.

1.Introduction

Primorsky regions (Absheron peninsula) experience a shortage of fresh water, the consumption of which by industry exceeds its consumption to meet the sanitary and hygienic demands of the population. Under these conditions, one of the solutions is to replace fresh water with sea water. One of the largest consumers of fresh water is thermal power plants, which use it after demineralization or deep softening as an additive in the heat cycle. The most expedient and economical method of using sea water at thermal power plants is thermal distillation with preliminary Na-cation exchange softening [1]. However, with ion-exchange softening of seawater, a large amount of highly mineralized wastewater is formed, the discharge of which into the sea is prohibited, and utilization by known methods is economically inexpedient, since the cost of wastewater treatment is higher than the cost of preparing the water itself [3]. Several variants of technological schemes have been developed, including units for clarification, Na-cationization, thermal concentration and salt separation. Regeneration of the cation exchanger is carried out by the purge water of the evaporators operating on softened sea water. Of all the units, the least studied unit was the clarification unit for spent regeneration solutions of Na-cation exchange filters, which predetermined the research. Analysis of the available data [1-3] shows that, in general, studies of the sedimentation process were carried out on natural and saline waste waters, characterized by high bicarbonate hardness. In this case, in the clarifier during the liming process, a mixture of magnesium hydroxide and calcium carbonate precipitates. Sea water has a low bicarbonate hardness (3-4 mEq / l), but a high concentration of sulphate ions (65-70 mEq / l). Therefore, when liming the spent regeneration solutions in the clarifier, the gypsum-magnesia mixture will precipitate.

2.Experimental part

The spent regeneration solutions of Na-cation exchange filters are supersaturated with respect to calcium sulphate. There are two options for treating the regeneration solution, depending on the specific conditions. First, before liming, the supersaturation on gypsum is first removed and the second - the regeneration solution is lime directly. To prepare an imitation of the lime mortar, the flow chart for the steady state was calculated using the method of successive approximation. The main parameters of the water treatment equipment were earlier determined [1].

For the first option, the following composition of the imitation solution was prepared (meq / l): Ca^{2+} - 20; Mg^{2+} - 290; Na^{+} - 1133; SO_4^{2-} - 448; Cl^{-} - 1133. Liming was carried out with 6% lime milk, the dose of which corresponded to the concentration of the magnesium ion. Coagulation was carried out with sulfuric acid iron due to the high alkalinity of the lime solution. The coagulant dose ranged from 100 to 800 mg/l. To intensify the process of flocculation, a flocculants, polyacrylamide (PAA), was introduced into the solution, the dose of which varied from 1 to 3 mg per 100 mg of suspended solids.

Analysis of the results obtained shows that the best results were obtained at a stirring speed of 60 rpm. When the flocculants dose was increased threefold, the sediment compaction rate practically did not change. When the coagulant dose was doubled, the sediment compaction rate increased by 20%.

For the second option, a simulated solution was prepared (meq / l): Ca2 + - 161; Mg2 + - 287; SO42- -448; CI- - 1133. The interval of variation of the doses of coagulant and flocculants corresponded to previous studies, and the speed of stirring the solution, as optimal, corresponded to 60 rpm.

As in previous studies, only coagulation of the solution has little effect on the kinetics of sediment compaction. The sediment compaction rate increases when only PAA is introduced into the test solution. Analysis of the combined effect of the coagulant and flocculants on the kinetics of sediment compaction shows the advisability of introducing PAA after intensive mixing of the limed and coagulated solution.

Along with the study of the kinetics of compaction formed in the sludge clarifier, the properties of the contact medium are considered according to the well-known method [3]. Were calculated: the rate of sedimentation of the suspension - Vs; constrained sedimentation rate - V0; volumetric concentration of solid particles in the suspended layer - C0; the speed of free sedimentation of the suspension - Vr; suspension density - γ0. The results of the studies are presented in the table. Similarly, an increase in the density of the sediment is observed, since the proportion of gypsum in the treated solution in the first case is greater than in the second and the density of gypsum is significantly higher than the density of magnesium hydroxide. The absence of PAA reduces the sedimentation rate by an order of magnitude. On the contrary, the refusal to coagulate the solution (6) both in terms of the sedimentation rate and its density gives the same results as in the case of the simultaneous introduction of a coagulant and a flocculants (4). An increase in the temperature of the solution to 60 ° C increases the rate of compaction of the sediment and has almost no effect on the change in its density (7).

3. Results and discussion

Thus, the studies of the sedimentation process carried out under static conditions and the influence of a number of factors on its sedimentation properties made it possible to determine the significance of the factors and the optimal parameters of their change.

Table1. Results of calculating the properties of the contact medium

№	Treated water quality					Sludge properties					
	$Ж_{treated}$	$Ж_{ca}$	$Ж_{Mg}$	Щ	pH	V_c mm/sec	C_o mm/mm	V_o mm/sec	V_r mm/sec	$\gamma_{\circ}$ g/l	$H_{кон}$ mm
1	90	90	0	3.5	11.1	0,023	0,303	0,016	0,074	0,029	163
2	100	100	5	2	9.8	0,028	0,350	0,018	0,177	0,096	130
3	115	115	0	4.6	11.5	0,053	0,555	0,024	0,787	0,051	220
4	100	95	5	2	9.7	0,109	0,447	0,073	0,402	0,110	110
5	100	95	5	0.5	9.8	0,008	0,836	0,001	0,005	0,020	291
6	110	105	5	1.0	9.7	0,098	0,300	0,068	0,311	0,109	110
7	110	100	10	1.5	9.2	0,123	0,289	0,087	0,371	0,089	110

Note: №. 1-3 - with preliminary gypsum deposition; №. 4-7-co-precipitation of gypsum with magnesium hydroxide; №. 3 - the dose of lime 7.2 mg / l; № 1,2,4,5,6,7 - dose of lime 6.6 mg / l; №. 6 - without coagulant; №. 1,2,3,4,5,7 - FeSO4 - 400 mg / l; №. 5 - without PAA; № 1,2,3,4,6,7 - dose of PAA 1 mg / 100 mg of suspended solids; №. 7 - temperature 60oC; № 1,2,3,4,5,6 - temperature 25 ° C.

5.References

1. Abdullaev K.M , Feyziev G.K, Agamaliev M.M “Review of the technology of mineralized water testing”/ Problems of energetics. 2010, № 1, P.3-27. Baku.
2. Agamaliyev M.M, Mammadbeyova R.H, Ahmadova C.A. “Technology of water treatment by membrane methods”. ASOIU, BAKU, 2017, 624 p.
3. Hasanov A.A, Mammadova F.M, Salimova N.A “Wastewater treatment” ASOIU, Baku,Textbook,2017, 310p.

OR-VI-5

THE RESULTS OF INDUSTRIAL TESTS OF NANOECOTECHNOLOGİES IN THE PRACTICE OF PRIMARY PREPARATION OF OIL

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Abstract. The article contains the following questions: leading companies and scientists in this direction; literature review conclusions; the philosophy a carrying out of industrial tests of nanoecotechnologies in the practice of primary preparation of oil (PPO); the oilfield objects for carrying out experimental-industrial tests (EIT); basic requirements to demulsifiers for the implementation of nanoecotechnologies at the practice of PPO; experimental part; results of EIT and discussions; scientific novelty; conclusions and economic efficiency on the results of EIT of nanoecotechnologies using nanodemulsifiers "IKHLAS" in the practice of PPO.

Keywords: nanoecotechnologies, desuspensifier and desuspensification, intramolecular and intermolecular surface activity.

1.Introduction

At each oil field, the produced fluid (oil + water + gas + mechanical impurities), is separated from the gas in the shop of primary preparation and pumping of oil (ShPPPO) then subjected to thermochemical treatment to remove water, salts and mechanical impurities within existing standards. There after commercial oil is transported to refineries, and the produced formation water is utilizated of in reservoir pressure maintenance system (RPMS) with the concentration of oil in water (Cn) not more than 50 mg/dm3 [8, 14]. Reverse demulsifiers, which have been proposed for treating formation water from oil, have not been confirmed by results of EIT and introductions. In recent years, some new brands of the latest generation demulsifiers have appeared on the world market: marks “DEMTROL” (“Dow” company, USA); marks “DMO” (“Baker Hughes”, USA); marks “Condem” (“Champion Technologies, Inc”, USA); marks “Randem” (company “Rauan Nalko”, USA-Kazakhstan); marks “Kemelix” (“Croda oil and gas” company, England); marks F-929, F-940, R-11, X-2647 (companies “Toho Chemical Industry Co., Ltd”; “Iskra Industry” and others, Japan); marks “Dissolvan” (“Hoechst”, “Basf”, “Clariant”, Almatıneftexim”, Germany); demulsifiers of the company “Auby” France; demulsifiers of Shanghai Trustin Chemical Co., Ltd, Qingdao Aurora Chemical Co., Ltd, Shanghai Jianying Chemical Co., Ltd. and others. China; marks “SNPX” (“NİİNeftepromxim” company, former “Soyuzneftepromxim” company, Russia); marks “Flek” (Flek company, Russia); liquid-crystalline nano-demulsifier “TND” (Tyumen State University, Russia); marks “Khazar” ("IPChP" NAS of Azerbaijan); marks “Alkan” ("IPChP" NAS of Azerbaijan); marks “ND” (Research and Design Institute Oil and Gas, SOCAR.

Helped in this case an analytical analysis of the scientific works of some scientists (V.M.Abbasov, A.I. Gasanov, S.M. Abbaszade, E.Sh. Abdullaev, F.S.Ismailov, B.A. Suleymanov, H.F.Miralamov, Q.Q.İsmayılov, G.I. Kelbaliyev, S.R.Resulov, D.N.Levchenko, G.N. Pozdnishev, A.A. Abramzon, A.I. Rusanov, I.N. Evdokimov, T.A.Fedushak, S.Axmadi, F.M.Xutoryanskiy N.Y.Bashkirseva, O.Y.Sladovskaya, V.Garstein, U.Muller, Ch.Deghenhard, D.N.Mingazov, B.T.Mullaev, L.P.Semihina, B.R.Faxrutdinov, R.F. Hamidullin, H.Abdurahman, R.Cato, Y.Fu, C. Gabriel, B.Marie, A.Mosayebi, V.Ramesh, E.H.Diyarov, J.Wu, G. Yin, F.Wang, C. Carsten and others) in the field of development, research and implementation of demulsifiers in the conditions of primary preparation of oil, which allowed to determine the purpose and objectives of the work. The work was fulfilled out on the basis of the scientific and technical cooperation agreement between Azerbaijan State Oil and Industry University and the “International Oil Services Kazakhstan” LLP.

2.Conclusions of the literature review on the direction

We consider it appropriate in the article to present the conclusions of the literature review on the direction:

- At the world level, the founder of nanotechnology in oil production is Academician A.Kh. Mirzadzhanzade [9];

- For the first time, the “ND-1/4” nanodemulsifier developed by scientists at Research and Design Institute of Oil and Gas SOCAR in 2012 successfully passed experimental-industrial tests (EIT) at the “Zhetybai” field of the Republic of Kazakhstan for maximum extraction of commercial oil from a hard destroy water-oil emulsions (HDWOE) [4];
- The development and large-scale use of nanoecotechnologies capable of processing oil nanocolloids [HDWOE; a hard to destroy water-oil suspensions (HDWOS); trap oil; barn oil; bottom sediments of technology and commercial tanks; oil sludge; polymer containing oil emulsions; oil with viscoelastic properties or oil with structural - reological properties [5] etc.], formed in primary oil preparation technologies is one of the priority areas of modern oil-field nanotechnology;
- Information about the emulsifying properties of HDWOE in relation to reverse and direct emulsions was not found;
- No data were found on the use of demulsifiers that can destroy both reverse, direct and middle emulsions (or HDWOE);
- For the first time, TND liquid crystalline nanodemulsifier was developed, however, there is no supporting information about the widespread use of this reagent [13];
- Currently, the number of surfactant demulsifiers in the world market exceeds thousands of industrial designs such as oxyalkylene block copolymers based on polyhydric alcohols, amines, polyamines, phenol-formaldehydes resins and epoxies resins. But the question of how surfactant demulsifiers differ from conventional surfactants remains open.
- In accordance with the concepts of emulsion - emulsifier - demulsifier - demulsification, no information on the concepts of "desuspensifier" and "desuspensification" was found in terms of completeness of the concepts of suspension - suspensifier. These concepts are new and important for applied colloid chemistry in terms of new properties of matter and new phenomena;
- Intramolecular and intermolecular surface-activity concepts have not been identified for surfactants of demulsifiers;
- For inorganic substances (Na and K metals), scientists at the University of Edinburgh have discovered a liquid-crystalline hybrid state of matter [7], but no such discovery has been identified for surfactants;
- For the active components of demulsifiers, questions of the correlation relationships of the type property – structure – optimal effects also has been a little studied;
- The property-structure relationships for n-aliphatic alcohols, as solvents have not been sufficiently studied;
- Have not been identified colloid-chemical concepts that can differentiate between micelleformation and clusterformation;
- The main achievements in the nanocolloidal states of asphaltenes and resins in the composition of oil emulsions, against the background of conflicting views of other scientists, belong to I.Evdokimov and his employees, besides recently they have a scientifically based criticism regarding the phase inversion existing mechanism for the destruction of oil emulsions using demulsifiers [1, 2];
- Negatives from oil nanocolloids such as visco-elastic systems (VES) at the PPO and ways to overcome them have not been studied enough;
- The results of the analysis of the data available in the literature found that nanocolloids in the composition of crude oil, being the reasons for the increase in the strength of all types of oil emulsions, create nanoenergies barriers in a dispersion medium that can to lower the possibilities of actions of conventional demulsifiers;
- Model research work carried out by Azerbaijani scientists on the formation and decomposition of oil emulsions is one of the priorities of issues of the direction [6];
- There is no information on polynanostructural, multifunctional and universal nanodemulsifiers that will be represented in the future as the latest generation of demulsifiers, which may open the way for further research on the most important priority issues of oil-field nanotechnology.

3. Experimental part

3.1 Research methods

Laboratory and experimental-industrial tests carried out on all fields used methods for determination of water, chloride salts and mechanical impurities in oil and oil concentrations in formation water. Determination of water concentration in oil implemented out on the apparatus Dean-Stark to according of State

Standard (GOST) 2477-2014. Determination of chloride salts in oil was carried out on the basis of State Standard 21534-76. Determination of mechanical impurities in oil was performed in accordance with State Standard 10577-78 by gravimetric method. The method for determining the concentration of oil in formation water is based on the Sectoral Standard 39-225-88 (or 39-133-81) [14]. The method is based on the determination of the optical density (D) by extracting the oil from water with an organic solvent in a spectrophotometer (Spectrophotometer PE-5300VI, St. Petersburg, Russia). Usually are Installed dependence curve of optical density on the oil concentration Cn, often expressed in a straight line for each field oil.

3.2 Research objects

The objects for industrial nanotechnology in the practice of PPO: were some oil fields of the Republic of Kazakhstan in accordance with the agreement on cooperation between the Azerbaijan State University of Oil and Industry and “International Oil Services Kazakhstan”:

"Zhetybai" field (JSC "Mangistaumunaigas", National Company "KazMunaiGas"). The field is located 85 km south-east of sity Aktau. The field has been in exploitation since 1967. The field is at a late stage of exploitation. Annual oil production: ~1.3 million tons. Oil reserves amount to 345 million tons. Well depth up to 1700-2400 m. Oil has: a water cut rate of ~72%, a density of 850-860 kg/m3, and a freezing point of 31oC. Oil contain: paraffins 17-25%; resins 4.5-15.5%; asphaltenes 0.9-3.4%. The PPO is carried out by thermo-chemical method at 65-75oC using “Randem-19” demulsifier (“Rauan-Nalko” Kazakhstan-USA company) with a specific consumption (Sc) of 200 g/t. The PPO technology carried out in ShPPPO, and it is accompanied by the formation of oil nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of process and commercial tanks; oil sludge; ARPD; polymer containing oil emulsions; oil with viscoelastic properties, etc. Formation water (oil concentration Co≈ 600-1400 mg/dm3) does not meet the requirements of the RPMS (not more than 50 mg/dm3);

“Tenge Oil & Gas” LLP (local private oil field). The field is located 150 km south-east of sity Aktau. The field was discovered since 1964, the history of the exploitation of present wells according to the field begins from 2000. Annual oil production: ~137 000 tons. Well depth up to 2450 m. Oil has a water cut rate of ~0-63% (0% corresponds to new wells; for highly resistant oil emulsions 22-25%; for unstable oil emulsions up to 63%), a density of 840-850 kg/m3, a freezing point of 32oC, kinematic viscosity at 50°C 14.2 mm2/s (or cSt). Oil contain: paraffins 17-25%; resins up to 15.2%; asphaltenes up to 3.4%. The PPO is carried out by thermo-chemical method at 82-86oC using “Dissolvan V 5748” demulsifier (“Almatyneftekhim A” LLP Kazakhstan-Germany company) with a Sc up to 200 g/t. The PPO technology carried out in ShPPPO and it is accompanied by the formation of petroleum nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of technology and commercial tanks; oil sludge; ARPD; oil with viscoelastic properties, etc.). Formation water (Co≈830 mg/dm3) does not meet the requirements of the RPMS;

“Phystech II” JSC (local private oil field). The field is located 185 km from Aktau to the north, near the “Buzachi” and “Karazhanbas” oilfields. The field was discovered since 1984, The field began to function since 2005. Oil reserves are 18 million tons. Annual oil production: ~157 000 tons. Well depth up to 548-659 m. Oil has a water cut rate of ~48%, a density of 940 kg/m3, in physical properties and chemical composition are close to the oils of the “Karazhanbas” field. Dynamic viscosity at 50°C 38.2 mPa·s (or cP – santi puaz). Oil contain: paraffins up to 1.6%; resins up to 19%; asphaltenes up to 3.9%. The PPO is carried out by thermo-chemical method at 65-75oC using “SNPX-4315D” demulsifier (Russia) with Sc=221 g/t. The PPO technology carried out in ShPPPO, and it is accompanied by the formation of petroleum nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of technology and commercial tanks; oil with viscoelastic properties, etc.). Formation water (Co≈335 mg/dm3) does not meet the requirements of the RPMS;

“Akkulka” field of “TetisAralGas” LLP (private oil field of the Great Britain). The field is located 450 km from Atyrau to the east. The field began to function since 2003. The field is more characteristic of gas reserves. Therefore, there is only one oil well in exploitation. Annual oil production: ~255440 tons. Oil reserves amount to 4.3 million tons. Well depth up to 500 m. Oil has: a water cut rate of ~63%; density is 804 kg/m3; the temperature of the oil at the wellhead is about 74°C. The oil emulsion is unstable, therefore for oil preparation technology is not necessary for additional heating of the emulsion. The PPO is carried out by chemical method using “DMO-86520” demulsifier (“Baker Hughes”, USA) with Sc up to 69.6 g/t. The PPO technology carried out in ShPPPO, and it is accompanied by the formation of oil nanocolloids of type paraffin deposits with mechanical impurities. As an inhibitor of paraffin deposition is used PAO - 85327 (produced in Great Britain). Formation water (Co≈99 mg/dm3) does not meet the requirements of the RPMS;

OGPM "Zhaikmunaigas" ("EmbaMunaiGas" JSC National Company "KazMunaiGas"). The oilfields of OGPM (oil and gas production management) "Zhaikmunaigas" are located 170 km south-west of Atyrau. The "Zhaikmunaigas" oilfields have a history of over 120 years. It was here, in the Atyrau region at the "Karashungul" field, in 1899 that the first oil fountain shot up. This was the starting point for the formation of the Kazakhstan oil and gas industry. OGPM "Zhaikmunaigas" was organized in 1973. Annual oil production: ~0.9 million tons. The residual recoverable oil reserves at the "EMG" ("EmbaMunaiGas") fields as of 01.01.2020 determined to 86.2 million tons. Well depth up to 850-1000 m. Oil has a water cut rate up to ~91%, a density up to 840-892 kg/m3. Oil contain: paraffins up to 1.75%; resins up to 11.8-13.7%; asphaltenes up to 0.85%. The PPO is carried out by thermo-chemical method using "Dissolvan-4795, 4397" with Sc=246 g/t in the ShPPPO for oil "S.Balgimbayev" (at T≈25oC, i.e. without heating, - cold demulsification) and Sc=41.2 g/t for on a mixture of oil from other fields (at T≈60oC, i.e. with heating). The PPO technology carried out in ShPPPO, and it is accompanied by the formation of oil nanocolloids (bottom sediments of technology and commercial tanks based on HDWOS; polymer containing oil emulsions; oil with viscoelastic properties; gas hydrates, etc.). Formation water (Co≈220 mg/dm3) does not meet the requirements of the RPMS;

OGPM "Dossormunaigas" ("EmbaMunaiGas" JSC National Company "KazMunaiGas"). The oilfields of OGPM "Dossormunaigas" are located 100-130 km east of Atyrau on the territory of Makat district of Atyrau region. OGPM "Dossormunaigas" was organized in 1911. OGPM "Dossormunaigas" JSC includes three fields: "Karsag", "Botakhan" and "Bayshonas". Annual oil production: ~152 000 tons. The residual recoverable oil reserves at the oilfields of OGPM "Dossormunaigas" determined to 10 million tons. Well depth up to 135-850 m. Oil has a water cut rate up to ~85%, a density up to 840-870 kg/m3. Oil contain: paraffins up to 0.17-2.19%; resins up to 9-52%; asphaltenes practically absent. Formation water salinity up to 130-254 g/dm3. The PPO is carried out by thermo-chemical method using "Dissolvan-4795" demulsifier with Sc=193.2 g/t in the ShPPPO "Karsak" (at T≈60-65oC) and Sc=51.6 g/t for of oil "Botakhan" field (at T≈40oC). The PPO technology carried out in ShPPPO, and it is accompanied by the formation of petroleum nanocolloids (bottom sediments of technology and commercial tanks based on HDWOS; polymer containing oil emulsions; oil with viscoelastic properties (especially on the "Botakhan" field), etc.) therefore there are problems. Formation water (Co≈73 mg/dm3) does not meet the requirements of the RPMS;

4. Results of eıt and dıscussıons

4.1 The philosophy a carrying out of industrial tests

The purpose of the experimental industrial tests (EIT) - identification of the effectiveness of industrial nanoecotechnologies with the use of "IKHLAS" nanodemulsifiers brands in the practice primary prepartation of oil (PPO), in comparison with basic demulsifiers. Naturally, that the purpose of the EIT is the main priority, however, during the EIT is not excluded the achievement also of results incidental effects that are related to the unique properties and potential capabilities of the test object, in this case "IKHLAS" nanodemulsifiers. During laboratory tests (bottle tests), it is difficult to record the incidental effects associated with the processing of oil nanocolloids [HDWOE; HDWOS; trap oil; granary oil; bottom sediments of technology and commercial tanks; oil sludge; polymer containing oil emulsions; asphaltene-resinous paraffin deposits (ARPD) oil with viscoelastic properties, etc.], which are potential sources of deterioration of PPO technology, environmental pollution, as well as the loss of valuable hydrocarbon components. Therefore, as experience with EIT shows, incidental effects cannot be prescribed also in EIT programs. They can be taken into account only during the EIT, when they appear. Manifestations of some side effects, sometimes even exceeding the value of the goal of the EIT, which have signs of scientific novelty, as well as an elements of scientific discovery, are of particular interest to science and industry.

4.2 The EIT results for some oil fields

"Zhetybai" field (JSC "Mangistaumunaigas", National Company "KazMunaiGas"). During 03.11.2014-03.12.2014, were held the EIT of nanoecotechnologies in the "Zhetybai" field with the help of "IKHLAS-1" brand nanodemulsifier selected on the basis of laboratory test results. As shown in table 1, the polyfunctional "IKHLAS-1" provides high quality commercial oils and formation waters by highly breaking reverse and direct emulsions in the PPO conditions. As follows from table, the efficiency (E) of "IKHLAS-1" in all technological, ecological and economic positions is much higher than the efficiency of the demulsifier "Randem-2219".

Table.EIT results of nanodemulsifier “IKHLAS”-1 in comparison with the basic demulsifier “Randem-2219”

Parameters	“Randem-2219”	“IKHLAS-1”	E, times
specific consumption of the demulsifier, g/t	204	160-178	1.2-1.3
minimum and maximum concentration of chloride salts in running samples VST №13, mg/dm^3	41-460	12-151	3-3.4
minimum and maximum concentration of water in running samples VST №13, %	0.12-1.2	0.03-0.27	2.2-4
dominant concentration of chloride salts in control oil, mg/dm^3	45-703	28-45	1.5-15.6
the average daily consumption of Volga river water, m^3	777	595	1.3
number of cases that do not meet the standards in the 1-month control analysis	26	1	26
average oil concentration in the waste water, mg/dm^3	600-1400	30-50	20-28
HDWOE formation volume, m^3/day	100	0	many

It is known that natural oil emulsions can have a fourfold nanostructure [nanomicellar structure of a dispersion medium; nanoscale fractions of a dispersed phase; nanoscale molecular adsorption layers (MAL) or protective shells or "armor" shells, from a scientific point of view, MAL will be more correct; nanosized particles of organic (based on paraffins, ceresins and etc.) and inorganic (clay, iron sulfide, salts, and particles of formation rocks and etc.) origin inside the MAL. Thus, in our opinion, there are certain nanosized molecular barriers for demulsifiers in oil emulsions. Therefore, we have introduced the corresponding requirement for demulsifiers: the demulsifiers should have the properties of nanodemulsifiers with a polynanostructure. In this direction, the results of the EIT were positive. The results of the EIT of the “IKHLAS-1” nanodemulsifier at the “Zhetybay” field compared to the base demulsifier “Randem-2219”: the specific consumption of the demulsifier is reduced by 21.6%; dominant concentrations of formation water and chloride salts are reduced by 2.1 and 12.3 times, respectively; the oil concentration in the formation water is reduced by 25 times from ~1000 to ~40 mg/dm3. During the EIT, in contrast to the basic technology, were not discovered the formation of characteristic oil nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of process and commercial tanks; oil sludge; ARPD; polymer containing oil emulsions; oil with viscoelastic properties, etc.). The “IKHLAS-1” nanodemulsifier was recommended for implementation at the “Zhetybay” field [3].

“Tenge Oil & Gas”. During 11.05.17-05.06.17, were held the EIT of nanoecotechnologies in the “Tenge Oil & Gas” field with the help of “IKHLAS-1” brand nanodemulsifier. The technology of PPO in the “Tenge Oil & Gas” field is carried out at the GP-2 and GU-1 places. Therefore, the results of the EIT were considered in singly:

GP-2 place (EIT for a period of 11.05.17-26.05.17). The oil prepared during the base technology in QP-2 was at the level corresponding to group 3 (water up to 1%; chloride salts up to 900 mg/dm3 concentration; and mechanical mixtures up to 0.05%) and on the basis of the existing contract, between“Tenge Oil & Gas” and “OMG” AC was handed over to ShPPPO in the “Uzen” field for final preparation. The results of EIT on record residual concentrations of water (0.06%) and chloride salts (10.5 mg/dm3) for the first time to confirm the high level of effectiveness of the “IKHLAS-1” nanodemulsifier on GP-2.

GU-1 place (EIT for a period of 27.05.17-05.06.17). Oil preparation at GU-1, it is a two-stage process: The first stage is completed with a capacity of V2 (~40 m3); the second stage covers the commercial tanks VST-1,2 (100 m3). Finally, the commercial oil is transported by autotankers (40 m3) to the oil delivery point (ODP 8 km), where it is delivered and filled into horizontal tanks (100 m3) and then after settling surrenders to “KazTransOil”. The EIT results: for samples V2 [on concentration of water (%) and chloride salts (mg/dm3)] - the efficiency of “IKHLAS-1” nanodemulsifier is 14 and 18 times higher than the “Dissolvan V 5748”, respectively. Experiments samples from V2 on the Dean-Stark showed that the residual water content in the oil was 0.0% and for the “Dissolvan V 5748” is 3.2%. These figures confirm that the “IKHLAS-1” nanodemulsifier is operating at a higher level in the “Tenge Oil & Gas” field. The relatively high concentration of chloride salts in commercial oil was first explained by the intense adsorption of chloride salts on the surface of nano- and micro-sized paraffin particles present in highly paraffinic oils. Therefore, it is recommended to strictly follow the technology of desalination with fresh water. The Co is reduced by 18 times, from ~830 to ~46 mg/dm3. During the EIT, in contrast to the basic technology, were not discovered the formation of characteristic oil nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of technology and commercial tanks; oil sludge; ARPD; oil with viscoelastic properties, etc.). Therefore, “IKHLAS-1” has the properties a strong demulsifier - desuspensifier - inhibitor for oil nanocolloids. Since 2018, the "IKHLAS-1" nanoecotechnology is successfully implemented in the practice of the PPO of the “Tenge Oil & Gas” field with Sc=170 g/t.

“Phystech II” JSC oil field. The EIT were conducted in the period 12.04.17-17.04.17. The oil initially produced at the "Phystech II" JSC complex is transferred to the nearby “Arman” field on the basis of an existing contract in order to be fully processed to commercial crude oil quality. Oil is transported by autotankers. In horizontal cylindrical tanks (100 m3), bottom sediments are formed consisting of a mixture of HDWOE, HDWOS, and each time these bottom sediments are returned to the initial stage of preparation technology, the demulsifier has a relatively high temperature, and oil quality indicators are not enough. On the other hand, produced water contains oil with a concentration of 200-470 mg/dm3. All these arguments are factors that negatively affect the profitability of PPO within the base technology (“SNPX-4315D” base demulsifier). Comparative results during of EIT: reduction of oil preparation temperature from 65-75oC to 60-70oC; reduction of specific consumption of demulsifier from 221 g/t to 70 g/t; oil settling time is reduced from 40-60 minutes to 40-45 minutes, (or the upper limit by 25% (Fig.1); inhibition of bottom-up sediments of HDWOE and HDWOS mixtures during EIT and application "IKHLAS-1" its confirms its as a highly efficient polyfunctional reagent (demulsifier-desuspensifier- inhibitor, as scientific novelty) of with respect to the corresponding oil colloids. The amount of residual water in oil samples in the "Phystech II" JSC laboratory is determined in a Russian-made VSN-L apparatus in the mode of up to 60% water content in oil (Fig.2).

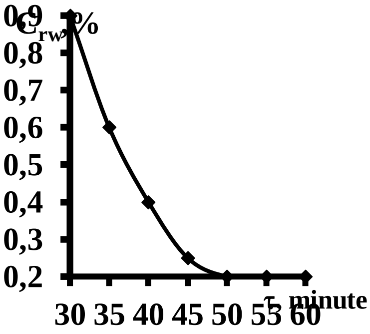

Fig.1. Dependence of residual on settling time

Fig.2. The residual concentration water in the water in (Crw) oil il during EIT of "IKHLAS-1" (Sc = 99 g/t)

During the EIT, in contrast to the basic technology, were not discovered the formation of characteristic oil nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of technology and commercial tanks; oil with viscoelastic properties, etc.). Since 2018, the "IKHLAS-1" nanoecotechnology has been successfully implemented in the practice of the PPO of the "Phystech II" JSC field.

“Akkulka” oil field of “TetisAralGas” LLP (private oil field of the Great Britain). The EIT were conducted in the period 14.08.17-26.08.17. Oil in the “Akkulka” field is produced only from the AKD-01 well. The average fluid temperature at the wellhead has been 74oC. Water-oil emulsion refers to unstable emulsions. The reason is both the chemical composition and the low density of oil. Concentrations of residual water and chloride salts at the end of demulsification for base technology has been Crw = 0%; Crchs = 285.8 mg/dm3 respectively. The PPO is carried out in groups of facilities (GF) in the “Akkulka” field. The main objects of GF: dose block of demulsifier (DBD); oil and gas separator (OGS), which is the primary indicator of demulsifier efficiency. At this facility, the emulsion disintegration and the volume of water transferred to the water tank (WT) must be maximal; two tanks VST-700 and VST-600 with volumes of 700 m3 and 600 m3. One of these tanks is technological and the other commercial. Filling of auto oil tankers intended for transportation of commercial oil to the point of delivery is carried out on a special site. The quality of oil and water in the samples is monitored in the laboratory of the GF. Comparative results during of EIT: Dominant concentration intervals of chloride salts in commercial oil for demulsifiers "DMO-86520", "IKHLAS-1" 201-300 mg/dm3 and 100-150 mg/dm3; the maximum concentration is 407 mg/dm3 and 151 mg/dm3; Xs for "IKHLAS-1" (up to 33.7 g/t) is 2 times less than for "DMO-86520" (up to 69.6 g/t); the oil concentration in the composition of formation water is reduced by 3.5 times, from ~99 to ~28 mg/dm3. An inhibitor of paraffin deposition “PAO – 85327” (produced in Great Britain) precipitates, creates problems in dosage, does not provide the required effect against paraffin deposition, therefore the PPO system contains petroleum nanocolloids based on a mixture of paraffin with mechanical impurities. During the EIT and the introduction of "IKHLAS-1", the dosage of “PAO – 85327” was suspended, there were no problems with petroleum nanocolloids based on a mixture of paraffin with mechanical impurities (as a potential source of environmental pollution). Consequently, "IKHLAS-1" has shown the properties of a highly effective demulsifier and paraffin inhibitor. This is the first time a similar effect has been observed in the practice of PPO. Since October 2017, the "IKHLAS-1" nanoecotechnology is successfully implemented in the practice of the PPO of the “Akkulka” field.

OGPM "Zhaikmunaigas" ("EmbaMunaiGas” JSC National Company "KazMunaiGas"). The EIT of “IKHLAS-1, 2” nanodemulsifiers were conducted in the period 06.01.18-25.01.18. Jaikmunaygaz OGPD has 7 oilfields on its balance sheet (“YZK”; “YVK”; “YVN”; “Janatalap”; “Gran”; “Zaburunye”; “S.Balgimbayev”). The oil to enter the ShPPPO from these fields passes of preparation is takes singly in two versions: 1) oil from “S.Balgimbayev” field without heating; 2) mixture of oil of the other 6 fields with heating. Comparative results during of EIT: The basic demulsifiers “Dissolvan-4795, 4397”, in contrast to “IKHLAS-1, 2”, precipitate in the capacity and create problems during dosage and thereby significantly was reduced the effectiveness of demulsification; in both variants of PPO, the daily consumptions of demulsifier were reduced from 89.94 kg to 44.97 kg (twice); during the test period EIT, due to the gas factor unlike the base technology, viscous-elastic systems (VES) are not formed and hydrate formation (HF) is not observed in “YVK”, “YZK”, “Gran” fields; for the first time, VES was named colloidal barns due to its ability to absorb oil, gas, water and mechanical mixtures; for the first time, “IKHLAS-1, 2” demonstrated highly effective demulsifier-destructor-inhibitor properties against petroleum nanocolloids such as VES and hydrate; since the formation of VES and HF are completely different phenomena, the solution of relevant problems with the same reagent (“IKHLAS”) is “know-how” [14]; the efficiency of “IKHLAS-1” for oil dehydration at the "Gran" field was 9 times higher; in Fig. 3 are presents comparative diagrams for the dominant concentration intervals of chloride salts in crude oil, which reflect the advantage of nanodemulsifiers "IKHLAS-1, 2"; the concentration of oil in formation water (Cn) was 8.8 times less (on average, the Cn decreased from 220 mg/dm3 to 25 mg/dm3); during the EIT, in contrast to the basic technology, were not discovered the formation of characteristic oil nanocolloids (bottom sediments of technology and commercial tanks based on HDWOS; polymer containing oil emulsions; oil with viscoelastic properties; gas hydrates, etc.). Since 01.07.19 the "IKHLAS-1, 2" nanoecotechnologies were been successfully implemented in the practice of the PPO of the “Jaikmunaygaz” OGPD.

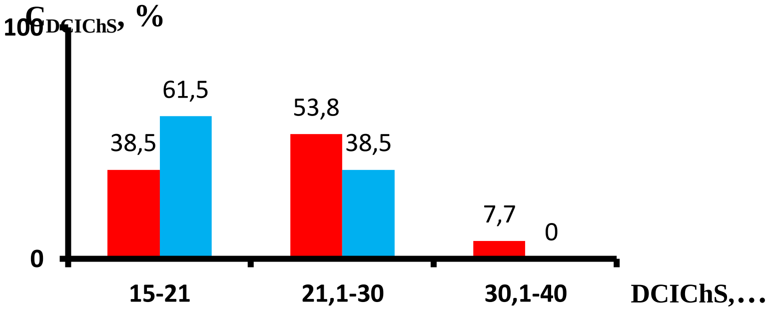

Fig.3. Dominant concentration interval of chloride salts (CDCIChS) in commercial oil: red - “Dissolvan-4795, 4397”; blue - “IKHLAS-1, 2”

OGPM “Dossormunaigas” ("EmbaMunaiGas” JSC National Company "KazMunaiGas"). The EIT were conducted in the period 02.02.2019-12.02.2019. OGPM “Dossormunaigas” has 3 fields: "Karsak" "Botakhan" and "Bayshonas". The daily production for these fields is 326 t, 80 t, 10 t, respectively. The preparation time of "Botakhan" oil is 4 hours (basic technology: Sc=51.6 g/t; T≈60-65oC), and the preparation time of "Karsak" and "Bayshonas" oil mixtures is 6-8 hours (basic technology: Sc=193.2 g/t; T≈40oC). Thus, the daily preparation of oil is intermittent, in two stages. As "Botakhan" oil is a VES, the oil in the field is processed with a demulsifier, and then transported to ShPPPO. Comparative results during of EIT: the basic demulsifiers “Dissolvan-4795”, in contrast to “IKHLAS-1”, precipitate in the capacity and create problems during dosage and thereby significantly was reduced the effectiveness of demulsification; the Sc for a mixture of oils was reduced by 1.7-2.2 times, and at the “Botakhan” field by 1.24 times; the efficiency of “IKHLAS-1” nanodemulsifier is 3 times higher on the concentration of residual water, and the efficiency is up to 8 mg/dm3 on the concentration of residual salts in the oil (from VST №10 and 12 commercial tanks); the concentration of oil in formation water is 73 mg/dm3 for the base demulsifier, 29 mg/dm3 for “IKHLAS-1”, and the efficiency is 2.5 times higher; during the EIT, in contrast to the basic technology, were not discovered the formation of characteristic oil nanocolloids [bottom sediments of technology and commercial tanks, based on HDWOS; polymer containing oil emulsions; oil with viscoelastic properties (especially on the “Botakhan” field), etc.]. Since 01.07.19 the "IKHLAS-1" nanoecotechnologies has been successfully implemented in the practice of the PPO of the “Dossormunaigas” OGPD.

4.3 Some requirements to demulsifiers and scientific novelty

To ensure high efficiency of the implementation of nanoecotechnology at the practice of PPO, demulsifiers, in our opinion, should meet the following basic requirements (in abbreviated form):

∨ The surface pressure for nanodemulsifiers should be at least 40-42 mJ/m2 [10];

∨ In order to ensure high efficiency of the thermo-chemical method in the process of demulsification of all types of oil emulsions and corresponding oil nanocolloids, finding nanodemulsifiers in the liquid crystal hybrid aggregative states of a substance are the most expedient [11];

∨ The demulsifiers used to ensure the most effective destruction of oil emulsions and other oil nanocolloids under PPO conditions should have the properties of nanodemulsifiers with a polynanostructure;

∨ The most suitable solvents for nanodemulsifiers are critical nanoemulsions with synergistic effect;

∨ The demulsifier with the solvent should not give a visco-elastic systems;

∨ Molecules of the active phases of nanodemulsifiers should easily overcome of nanostructured barriers in the dispersion medium and in the dispersed phase of oil emulsions;

∨ Surfactants only with intramolecular surface-activity can be highly effective demulsifiers for oil emulsions;

∨ Nanodemulsifiers can also perform the function of a nanodesuspensifier (the term “desuspensifier” is used for the first time) for treating bottom sediments consisting of a mixture of HDWOE and HDWOS;

∨ Nanodemulsifiers can also perform the function as an inhibitor and a solvent of visco-elastic systems and of gas hydrates in the condition PPO;

∨ The latest generation of demulsifiers must have properties polynanostructural, intramolecular and intermolecular synergy, multifunctional and universal nanodemulsifiers.

Scientific novelty:

- For the first time, the formation water was utilization into RPMS without additional for the treatment;
- For the first time in oil-field practice, the “IKHLAS” nanodemulsifiers has served as both a highly effective demulsifiers and a highly effective inhibitors for oil nanocolloids;
- Experimentally established a previously unknown property of demulsifiers for the destruction of water-oil and oil-water emulsions, which consists in the fact that when interacting with oil suspensions, a new property appears, the so-called "desuspensifier" [the term "desuspensifier" was first introduced into colloidal chemistry; project of promising scientific discovery (PPSD)] [12];
- Experimentally established the previously unknown phenomenon desuspensification of suspension, which consists in the fact that the interaction of desuspensifiers with suspensions leads to the phenomenon of desuspensification (the term "desuspensification" was first introduced by us into colloidal chemistry; PPSD);
- An experimentally was established unknown previously property of surfactants, which consists in the fact that for them a visual interphase and volume accumulation of liquid crystals is observed, as a sign of the existence of a hybrid liquid-crystalline state of surface-active substances (PPSD);
- Theoretically established, a previously unknown property for surfactants, which consists in the that, there is intramolecular surface activity, (this issue is considered for the first time) which determines the difference between demulsifiers and other surfactants, i.e. highly effective demulsifiers must have intramolecular activity (PPSD);
- Theoretically established, a previously unknown property for surfactants, which consists in the that there is intermolecular surface activity, due to which micellization phenomena for colloidal surfactants and cluster formation occur for non-colloidal surfactants (PPSD);
- The intramolecular and intermolecular surface activity, in our opinion, can be expressed using the value of the distribution coefficient in hydrocarbon liquid - water systems;
- For the first time in the history of oil production, in the examples of the fields of the RK, have been achieved a colossal economic, technological and environmental development of oil preparation and delivery systems due to nanoecotechnologies using the “IKHLAS” brand of nanodemulsifiers;

- The relatively high concentration of chloride salts in commercial oil was first explained by the intense adsorption of chloride salts on the surface of nano- and micro-sized paraffin particles present in highly paraffinic oils.

5.Conclusıons

In general, during the EIT of nanoecotechnology in the practice of primary preparation of oil, in the above oilfields, in contrast to the basic technologies, the necessary qualities of marketable oil and formation water for reservoir pressure maintenance systems were provided, and also absent the forming of technologically, environmentally and economically problematic oil nanocolloids (HDWOE; HDWOS; trap oil; barn oil; bottom sediments of technological and commercial tanks; polymer-containing oil emulsions; ARPD; oil with viscoelastic properties; gas hydrates, etc.), as resulting in, was achieved high efficiency for multifunctional reagents “IKHLAS” with a polynanostructure: demulsifiers – desuspensifiers – depressants - inhibitors of oil nanocolloids, ARPD, corrosion, saltdeposits, etc. Actual and expected annual economic efficiency from the use of “IKHLAS” nanodemulsifiers on abovelisted oil fields are 359 825 $ and 2 517 187 $, respectively (there is a supporting document).

5.References

1. Evdokimov, I., Fesan, A., Kronin, A., Losev, A.: Common of “Rag” Layers in Water-in-Crude Oil Emulsions with Different Stability. Possible Presence of Spontaneous Emulsification. Journal of Dispersion Science and Technology, vol. 37 (11), pp. 1535-1543 (2016). doi: org/10.1080/01932691.2015.1116081
2. Evdokimov, I., Fesan, A., Losev, A. New Answers to the Optical Interrogation of Asphaltenes. Monomers and Primary Aggregates from Steady State Fluorescence Studies. Energy & Fuels, vol. 30 (6), pp.4494-4503 (2016). doi:org/10.1021/acs.energyfuels.6b00027
3. Gasanov, A., Dashdiyeva, T., Dashdiyev, R.: Evaluation of novel nanodemulsifier based on colloidal and non-colloidal surfactants for the removal of hydrocarbons from wastewater. Journal of water chemistry and technology, vol. 41 (6), pp. 377-383 (2019). doi: springer.com/article/10.3103/S1063455X19060067
4. Ismayilov, F., Aga-zade, A., Dashdieva, N., Dashdiev, R.: On the results of industrial testing of the nanodemulsifier ND-1/4 on demulsification of a hard destroy water-oil emulsions of the Zhetybai field. Azerbaijan Oil Industry. No1, pp.39-45 (2015). (in Russian).
5. Ismayilov, G., Izbazarov, E., Adygezolava B., Khalilov R. Study of influence of demulsifiers on complex in rheology oil dehydration kinetics. Perm Journal of Petroleum and Mining Engineering, vol. 16 (2), pp..138-147 (2017). (in Russian). doi: 10.15593/2224-9923/2017.2.4
6. Kelbaliev, G., Rasulov, S., Mustafaeva, G.: Modeling the phenomena of coalescence of drops in the processes of separation of oil emulsions. Chemistry and Technology of Fuels and Oils. 2 (606), 12-16 (2018). (in Russian). doi: springerprofessional.de/en/modeling-of-phenomena-of-drop-coalescence-in-oil-emulsion-breaki/15896552
7. Kennedy, Sh.: Bizarre new state of matter is both liquid and solid (2019.04.10) https://mysteriousuniverse.org/2019/04/bizarre-new-state-of-matter-is-both-liquid-and-solid/, last accessed 2020.08.05.
8. Miralamov, H., Ismayilov, G.: Transportation of oil and gas by pipelines. OGSRPI, Baku: (2010). (in Azerbaijan).
9. Mirzadzhanzade, A., Maharramov, A., Nagiyev, F.: On the development of nanotechnology in oil production. Azerbaijan Oil Industry. 10, 51-65 (2005). (in Russian).
10. Nugmanov, A., Dashdiyeva, T.: Surface pressure is one of the main criteria for evaluating the effectiveness of nanodemulsifiers for destruction of reverse and direct emulsions. International Journal of Innovative Research in Science, Engineering and Technology, vol. 8(1), pp. 234-242 (2019). doi:10.15680/IJIRSET.20190801043
11. Nugmanov, A., Gasanov, A., Dashdiyeva, T.: New hybrid aggregat state of some organic substances and their prospects in oil-field nanotechnology. International Journal of Multidisciplinary Research and Modern Education, vol. 5 (1), pp. 149-161 (2019). doi: 10.5281/zenodo.3242737
12. Nugmanov, A., Izbasarov, A., Dashdiyeva, T. and others: Demulsifier for the destruction of water-oil and oil-water emulsions / Pat. 30960, RK, "International Oil Services Kazakhstan LLP", publ. 2016.03.15. (in Russian).
13. Semikhina, L.: A method of improving the quality of separation of water-oil emulsions using nano-demulsifiers / Pat. RU2413754C1, RF, Tyumen State University, publ. 2011. 03.10. (in Russian).
14. SST 39-225-88. Water for injection into oil reservoirs. Quality requirements. (in Russian). doi: gostrf.com/normadata/1/4293836/4293836522

PP-VI-7

INVESTIGATION OF THE PHOSPHORIC – MAGNESIUM SOLUTIONS EFFECT IN INCREASING THE VALUE OF MOBILE PHOSPHORUS IN SOIL

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Abstract. In connection with the collapse of industrial production of fertilizers in the Republic of Azerbaijan, the need for fertilizers, especially those containing phosphorus, has increased. The investigations were carried out to solve this problem showed that the introduction of phosphate-magnesium compounds into the soil during irrigation, which is available in sufficient quantities in the region, contributes to an increase in the content of exchangeable phosphorus in the soil.

It has been established that when magnesium-containing compounds are used, the amount of mobile phosphorus in the soil increases and satisfies the need of plants for it, and also contributes to its enrichment with many nutrients, and prevents the accumulation of harmful heavy metals in the soil.

Therefore, there are no environmental hazards in the soil and in the cultivated crops. And this is of great ecological and economic importance for our lands.

Keywords: mobile phosphorus, phosphate-magnesium compound, meadow soils, gray-brown soils, nutrients

1. Introduction

At the present moment, the urgent problem of the agricultural industry is its economy. Ecologists in order to solve these problems carry out comprehensive scientific and technical research in this direction.

For the introduction of intensive technologies, increased soil fertility is required. Various fertilizers can contain basic plant nutrients that improve the physical, chemical and biological properties of the soil and provide increased yields.

On the territory of the Azerbaijan Republic, the need for phosphorus fertilizers has always been great, and the production of this fertilizer will be constrained due to the limited resources of phosphorus-containing raw materials in this region. And the purchase of a significant amount of phosphorus fertilizers from foreign countries to meet the need is ineffective from an economic point of view.

In connection with the determination of new raw material bases for the production of fertilizers, taking into account the restoration of degraded lands, improving soil fertility and increasing the productivity of agricultural crops, the need to develop recommendations for the development of mineral resources and man-made waste in our region in this direction determine the scientific and practical significance and the relevance of research.

2. Experimental part

Numerous investigations have shown that phosphorus nutrition of plants proceeds more intensively when using other nutrients, in particular magnesium. Soil scientists V.G. Mamedova and others have experimentally proved that the introduction of magnesium into the soil against the background of mineral fertilizers, along with the creation of water-resistant aggregates, reduces both its filtration and its permeability [1].

It has been proven that as a result of the introduction of phosphorus fertilizers into the soil, enriched with magnesium, diphosphates or silicones are formed, which are easily assimilated by plants [2].

The researchers also point out that magnesium-containing ore is one of the most developing breeds. Depending on the amount of minerals in the ore, it is divided into several types [3,4].

These include chrysotile, chrysotile antigorite, antigorite, talc-chrysotile, bastide. Among them in the Caucasus widely.

Taking into account the above, the influence of magnesium-containing raw materials, which is available in large quantities in our region, on the amount of mobile (exchangeable) phosphorus in the soil has been studied.

3. Results and discussions

For research, we used magnesium-containing ore, the chemical composition of which is shown in Table 1.

Table 1. Chemical composition of magnesium-containing raw materials

№	Component	Content,% mass
1	SiO_2	38,65
2	Al_2O_3	9,5
3	Fe_2O_3	5,33
4	FeO	2,41
5	MnO	0,09
6	MgO	29,12
7	CaO	0,82
8	Na_2O	1,06
9	K_2O	0,45
10	H_2O	1,57
11	SO_3	11,00
	Total	100,00

As can be seen from Table 1, there are no elements harmful to soil and plants in the chemical composition of the ore, and its introduction into the soil during irrigation can contribute to its enrichment with many nutrients.

Waste from livestock farming was used as a source of phosphorus, which contains 58-62% mineral-$Ca_3(PO_4)_2$ and 26-30% organic matter.

To determine the effect of phosphorus-magnesium solutions obtained by the developed technology, agrochemical studies were carried out in regions where the lack of mobile phosphorus is especially revealed.

The experiments were carried out on the Kur-Araz lowland in the Belasuvar region on light gray-brown and meadow soils.

A small amount of mobile phosphorus in them required the introduction of 120-160 kg / ha for cotton, and 100-120 kg / ha of phosphorus fertilizers for winter wheat.

The cultivated crops were watered at a moisture coefficient of 0.25-0.30.

In laboratory conditions, the content of Ca, Mg and mobile phosphorus in the soil was determined by conventional methods.

The results of analyzes of the soils of the experimental plots are presented in Table 2.

Table 2. Agrochemical parameters of soils of experimental plots

Experimental plots	Humus,% mg/kg	Nitrogen total.,%	P_2O_5, mg/kg	K_2O,	$CaCO_3$,%
Grey earthly meadow	1,96	0,16	14,50	109	11,5
Grey brown	2,92	0,22	20,85	326	13, 4

During the period of the experiments, magnesium and phosphorus-magnesium solutions obtained by the developed technology were added for comparison in both areas.

The conditions of the experiments and the results obtained are presented in Table 3.

Table 3. The amount of mobile phosphorus in gray - earthly-meadow soil for winter wheat, mg / kg

Num-ber of ex-peri-ence	Scheme of experiments	Repetition				P_2O_5 Average, mq/kq
		I	II	III	IV	
1	Inspection	12,52	13,91	13,25	13,08	13,19
2	100 q of soil + magnesium containing solution	16,21	17,56	15,89	15,97	16,40
3	100 q of soil+ phosphorus-magnesium solution	25,86	26,42	25,92	26,79	26,25

Table 4. The amount of mobile phosphorus in gray – earthly -meadow soil under cotton, mg / kg

Number of experience	Scheme of experiments	Repetition				P_2O_5 Average, mq/kq
		I	II	III	IV	
1	Inspection	14,23	13,92	14,56	15,01	14,43
2	100 q of soil + magnesium containing solution	16,95	16,09	15,59	16,48	16,28
3	100 q of soil+ phosphorus-magnesium solution	26,93	27,51	28,02	27,38	27,46

Table .5. The amount of mobile phosphorus in gray-brown soils for winter wheat, mg / kg

Num-ber of experience	Scheme of experiments	Repetitio				P_2O_5 Average, mq/kq
		I	II	III	IV	
1	Inspection	21,00	19,85	23,15	22,00	21,50
2	100 q of soil + magnesium containing solution	23,02	22,82	21,89	22,98	22,68
3	100 q of soil+ phosphorus-magnesium solution	33,85	33,55	32,96	33,80	33,54

Table 6. The amount of mobile phosphorus in gray-brown soils for cotton, mg / kg

Number of experience	Scheme of experiment s	Repetition				P_2O_5 Average, mq/kq
		I	II	III	IV	
1	Inspection	22,25	23,21	21,75	23,71	22,73
2	100 q of soil + magnesium containing solution	23,45	23,95	22,80	24,60	23,70
3	100 q of soil+ phosphorus-magnesium solution	37,55	36,00	35,55	37,10	36,55

As follows from the data given in table. 3-6, the introduction of a magnesium solution into the soil during irrigation contributes to an increase in the content of mobile phosphorus in the soil, moreover, in comparison with grey - earthly-meadow soils, in gray-brown soils where wheat and cotton were cultivated, the value of mobile phosphorus is higher. So, in the control variant on gray-meadow soil, the value of mobile phosphorus for wheat was 13.19 mg / kg, for cotton - 13.43 mg / kg of soil, and on gray-brown soil, respectively, for wheat - 21.50 mg / kg, for cotton - 22.73 mg / kg of soil.

In the variants of application of magnesium and phosphorus-magnesium solutions on grey - earthly -meadow soil under wheat, these values increased and varied, respectively, within 16.40-26.25 mg / kg, and under cotton 16.28-27.46 mg / kg of soil. By applying the same solutions to gray-brown soils, an even greater increase in these values was observed, which, respectively, were 22.68-33.64 mg / kg for wheat, and 23.70-36.55 mg / kg of soil for cotton.

In addition, it should be noted that the introduction of only magnesium into the soil during irrigation contributes to an increase in the amount of calcium and magnesium cations in it within 12-15%, which plays a large role in increasing the content of mobile (exchangeable) phosphorus in the soil. Its main effectiveness is the prevention of phosphorus transition when applied to the soil into a form that is difficult to assimilate for plants, therefore, with a large demand for phosphorus fertilizers, the efficiency of magnesium use increases.

4. Conclusions

The possibility of using magnesium-containing compounds to increase the content of (exchangeable) mobile phosphorus in the soil has been investigated.

There are no elements harmful to the soil and plants in the chemical composition of magnesium-containing compounds, and its introduction into the soil prevents the accumulation of many harmful heavy metals in it, therefore it is effective from an ecological point of view.

The results of the hold investigations showed that the introduction of phosphorus-magnesium solutions during irrigation, the value of (exchange) mobile phosphorus in the soil increases and fully satisfies the need of the soil and plants in it. This makes it possible to abandon the traditional phosphate fertilizer-superphosphate, the creation of a production technology or delivery requires significant costs at the moment. Given the country's high demand for this fertilizer, this is of great importance from an economic point of view.

5.References.

11. . Mamedova B.G. The role of magnesium raw materials in improving the water-physical and chemical properties of irrigated grey earthly-meadow soils of the Shirvan veld. Journal "Agrarian Science", No. 1-2, 1997, pp. 99-102.
12. .Gurbanova Z.R. Change of phosphorus regime in gray-brown soils under the influence of irrigation "Agro EcoInfo" 2019№2 (36) .8s.
13. Mamedova B.G. Mekhtiev G.D. Salmanov S.M. The influence of serpentinite on the ecology of the soil environment. Proceedings of the Institute of Soil Science and Agrochemistry, Volume 21, No. 1, Baku, “Elm”, 2013, pp. 144-147
14. Qashqai M.A. Natural resources of the Azerbaijan SSR, Baku, Azerneshr, 1960.
15. Gurbanova ZR Ibragimova S.M. and others. Industrial tests of the superphosphate production process using non-traditional raw materials. Fertility magazine No. 1 2009 p.25-27.
16. Gurbanova Z.R. The importance of magnesium in the soil-plant and the problem of the production of magnesium-containing fertilizers. Azerbaijan National Academy of Sciences. Ganja branch. Collection. Izvestiya. Ganja, 2018, No. 1 (75) P.159-164.

PP-VII-7

HISTORICAL ROLE OF THE ECOLOGICAL COGNITION IN HUMAN'S SCIENTIFIC ACTIVITY

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Abstract. In the scientific development stages of philosophy, the human problem was investigated not only by particular philosophers, but also by the philosophical trends and philosophical schools. In the 21st century, efforts are being made to link the richness of the human spirituality with culture, science and education. As a science, philosophy emphasizes the importance of creativity in the essence of human. This, in turn, involves creativity as a reference to universal values.

The creation of artificial human beings and the presence of artificial intelligence through the use of new scientific techniques and technologies in order to avoid unnecessary scientific provisions on the humanity present great prospects for further work, philosophical research and study.

Keywords: Human Existence, Scientific-Philosophical Study of Human, Philosophical Analysis of Human Spirituality, Ecological Cognition, Philosophical Trend

1.Introduction

Philosophy examines the origin of the human, essence, nature, relationship of nature and society, existence of personality, his social status, his personal identity, his personality and then his transformation into historical personality. There are also other disciplines that investigate the human. Philosophy attains a certain interpretation within the framework of the philosophical worldview by summarizing the results of these sciences. When we look at the functions of this science, it becomes clear that in any case the human problem has not lost its relevance nowadays as it was in ancient times. First of all, it is noteworthy that from the time of its inception, the human became the area of interest for all scientists. As long as mysterious aspects of human issues dominate, research in this area will not be stopped in the future. On the other hand, human beings are insistent on self-knowledge and understanding. The main reason for this is the meaning of human life. As long as a person cannot understand himself or the world around him, the meaning of his existence will not matter at all. As a result, a human will not have the incentive to enrich his spirituality. This means that the long history of the human race will have no meaning. Innovations in this field by philosophers and other experts suggest that human beings are more important to the social environment where they live as biological beings and play a vital role in human life. This, in turn, encourages people to make the most and maximize their mission. The main point of this question is what criterias compile meaning of life.

2.Metod

The human existence in philosophers' views regards human problem, along with the importance of developing the knowledge of people in this area, determine what are the priority issues for the development of other sciences.

2.1 Before the acknowledgement of philosophy as a science and including modern times, the human:

1. As the most organized and supreme subject of nature,
2. As a mystical being in mythology,
3. As a result of the influence of supernatural forces in religious views,
4. As it is a living species from other planets in modern times,

-opinions are formed from considerations, science and other sources.

Today, the issues in these areas do not lose their relevance. Research has led us to the conclusion that man, as a living species known to science, has undergone some evolutionary changes on the planet Earth and is a highly organized being that we know today. From ancient times to modern times, philosophers have taken a unique approach to this issue. When philosophy first emerged as a science, the main issue of philosophy was the relation of matter to spirituality, the soul to being, the matter to consciousness, and the physics to the psyche, but in modern times the main issue of philosophy is the human factor. Since everything that exists in the environment is perceived by human beings, our existence is possible only through human beings. It happens when a person perceives the world around him. From this point of view, the subject of philosophy compiles the human, the world, and at the same time human's place in this world.

2.2 Scientific-philosophical study of human

Scientific-philosophical study of human in the modern era, the human is studied through the prism of ecological consciousness. We can already state that these two issues actualize the philosophy of ecological cognition. Philosophers have focused their attention on the historically formal parameters of cognition. At present, the relationship between the living image and objects&events in the surrounding world is relevant in ecological cognition. Within the framework of the possibilities of ecological cognition, the human has regulated his actions with the world around him. We see this in the philosophers' choice of topics that are appropriate for each period of time.

The ancient Greek philosopher Diagen, a follower of the school of atomism, said he was looking for a human with a lamp in his hand [1]. By this he meant that the Roman Empire had made so many invasions that they traded human slaves in the occupied territories as booty as well. Pratagor, one of the founders of the Sophist school, claimed that the human is the criterion of all that exists and the measure of everything [2]. They considered the human to be an ecological part of the nature.

In the system of slavery, only free people were considered as humans. Of course, slaves were not considered as human beings there. Therefore, in ancient philosophy, Plato (known to the Turks as Aflatun), a prominent representative of the classical period, referred to slaves as animal species. His famous student Aristotle (known to the Turks as Arastun) said that " the human is a political animal and a slave is a talking tool" [3].

Epicurus believed that the main purpose of philosophy should be to ensure the happiness of the human, to create training for him to achieve happiness. First of all, this training can bring happiness by freeing a person from the fear of death.

It should be pointed out that the ideas of the ancient Greek philosophers about the human were formed and developed in connection with a specific historical period, the requirements of society.

2.3 Philosophical analysis of human spirituality

In the philosophical analysis of human spirituality in Islamic philosophy of the Middle Ages, the human played a key role in the interpretation of all events. Islamic philosophers point out that there are two main directions that define a person's spiritual image:

1. Self-knowledge
2. Understanding the society.

Islamic philosophy claims that the human is related to the material as a body and to the spiritual as a soul. The material (I.e the body) is temporary, and the spiritual (soul) is eternal.

Along with Islamic philosophy, theologians in the West in the Middle Ages paid special attention to the human problem. In Christianity, unlike in Islam, you must first understand God in order to understand yourself.

2.4 Ecological cognition

Ecological cognition studies compared to the Middle Ages, in the New Age has significantly changed the role of the human in the world. Philosophers of this period F. Bacon, T. Hobbes, B. Spinoza included human to the system of natural relations and considered him as the object of cognition. They deemed it important to study the human from a biological and socio-ethical aspects.

Rene Descartes, contemplating about the essence of the human in his mind and intellect, wrote: " I think, therefore I am" [4].

Eighteenth-Century French representatives of the Enlightenment: J.J. Russo (1712-1778), P. Holbax (1723-1789), K.A. Helvetius (1715-1771), Denis Diderot (1713-1784), Julien Lametri (1709-1751) and others focused more on the problems of human and society. They showed that the human is born free, but is not free. Freedom is possible on the basis of a "public contract". They explained the human from a naturalistic and mechanistic point of view. In the Middle Ages, the powerful peasants were not considered semi-privileged according to the ideas and laws of that time. Some New Age ideologists, on the other hand, deemed that real humans are only those who owned private property. Bentham, a nineteenth-century English sociologist, wrote that it is a form of personal property that makes us human. As with the creation of private property, the human gave up nomadic lifestyle. A human who created his property on the land created a feeling of love for his descendants and homeland. Pre-Hegel classical philosophy envisioned the human as a rational, regulated, law-abiding system. The parts of this system were arranged harmoniously, and the full self can be understood objectively with the help of practical intelligence. The study of the human as a concrete being, the explanation of his essence from both an idealist and a materialist point of view, dates back to the 19th century. Therefore, this period has special importance in the history of philosophy. Representatives of classical German philosophy, George Hegel, interpreted the human problem from the standpoint of idealism, and Ludwig Feuerbach from the standpoint of anthropology. In Hegel's philosophy, the essence of the human is formulated as a "substance-subject". According to him, substance (meaning the primary cause) is the inner essence of human. A substance is a moving subject [5].

L. Feuerbach did not separate human from nature and considered him as a concrete being.

In the middle of the 19th century, the Danish thinker S. Kierkegaard developed Hegel's doctrine of the "concrete" existence of the human against the idea of abstract human. The central category of this teaching, Existence (being alive), is the only active beginning. However, by "existence" S. Kierkegaard did not mean the social activity of human, but the religious and ethical world of a separate human being isolated from society.

He considered existence as a sphere beyond the mind control of the individual's emotions and feelings.

The German philosopher F. Nietzsche also created a whole doctrine about human. He considered the human willpower to be the beginning of all his activities and actions. This is an instinctive, irrational beginning of aspiration for power, and all human actions, feelings, and thoughts obey this instinct. According to him, there is no objective law, no regularity in nature and society. The only principle of this world is aspiration for power. The main conclusion drawn from Nietzsche's philosophy is that "human must become a wild animal and surrender to the will of instincts."

Arthur Schopenhauer, like Friedrich Nietzsche, accepted will and instinct as the main condition, the beginning. He claimed that man is like a wild animal, as animal life is full of suffering, so human life is full of suffering as well, often dependent on chance.

Friedrich Nietzsche's views were continued in a more moderate form by Henri Bergson, a representative of intuitionism. He showed that human consciousness has two aspects: intuition and mind. According to Bergson, the mind is incapable of comprehending life, and can only be done by intuition. The source of life is "absolute consciousness," that is, God. God is the eternal life and freedom [5].

Marxism interpreted human as a social being determined by the economic, social, and cultural conditions of the society in which he was "located."

Among human doctrines, personalism is particularly noteworthy. Personalism is a philosophical-idealist school of thought that considers the personality as the primary creative reality and the most valuable spiritual wealth. According to personalism, the world is a manifestation of God, who is the highest persona (personality was of two kinds: 1-persona and 2- personalitas; persona is a person who embodies individual qualities; personalitas is a person who embodies public qualities). This philosophical school of thought was more widespread in the United States, France and Russia. B. Bowen (1847-1910), H. Kerr (1857-1931), E. Munye (1905-1950) Fleuring, Brightman, Berdyaev and so on were the representatives of this thought. Brightman writes that all reality - nature and spirit - has a common origin, which is the consciousness of the individual. According to personalists, personality acts as a special and temporary carrier of God. God can implement his power only through the human. Therefore, all personalities and their freedom depend on God. The personalists believed that the liberation of society did not mean the liberation of the human. On the contrary, the development of mankind results in the enslavement of the human. They saw the development of technology as the cause of all human misery.

2.5 The philosophical trend

The philosophical trend neotomism was thoroughly studied by its representative I. Kiles regards the human’s cognition problem. According to him, the human body is created naturally and obeys the laws of nature, and his heart and soul are created by God, which is why he is immortal. According to Neotomists, human's main goal should be reuniting with God. Only God can eliminate people's tiredness, suffering, and emptiness in their hearts.

There are a number of other views on humans' position in life, lifestyle, and people management. For example, representatives of the biological philosophical school of thought E. Bogardus and R. Williams claim that humans' position in life, development, lifestyle and etc. depend on genes, i.e. hereditary traits. Those with good genes only become active and skillful.

Representatives of the psychological school of thought G. Gilbert, B. Skinner, E. Fromm, on the other hand, believe that all this depends on the psychological qualities of the human [6].

A comprehensive explanation of the human problem requires the detection of its social nature, the analysis of the motives that determine consciousness and activity, a detailed study of various historical forms of lifestyle, and an in-depth study of the causes of biological tendencies in it.

In order to learn the true nature of human, it is necessary to consider him in public, because human is a product of society, and society is the sum of the connections and relationships of individuals. It is impossible to imagine a person outside of these connections and relationships - public relations. The essence of human is not an abstract thing belonging to an individual, it is a set of public relations.

Phenomenology, which claims to be an integrator of the human sciences, is about the body and mind problem. For instance, according to Husserl, the founder of phenomenology, the human body is characterized as restorable, and the spiritual world (spirit) of human as irreversible. A characteristic of the soul is the inalterability and its impossibility to return to its former state (otherwise it would be possible to turn the elderly’s psyche into the child's psyche). Husserl understands human as the union of matter and spiritual, the union of body and soul. He considers the essence of human as a spiritual and physical being, which has an important influence to the cultural system as a whole.

The existentialist Sartre, who was always profoundly cognizing the necessity of human's "philosophical" freedom, distinguished three aspects of this freedom: human's metaphysical freedom was to realize his absolute freedom and to fight against everything that limited it; freedom of the art, that is, relieving communication with other people through artworks and alluring them into that atmosphere of freedom; political and social freedom of the oppressed people.

According to the postmodern philosophers, in order to understand the existing social norms, human has to stay away from that norms for some period of time, as the social norms are better understood when they are observed distantly.

4. Conclusion

In philosophy, the human problem helps everyone to know themselves a little better. Human, as we know him, has the most complex structure of all living things. So, this topic, which examines human from different perspectives, is relevant for the science spheres. In this regard, the proposed research is a definite attempt for self-knowledge for any person. It is known that human and the world are a miracle.

Philosophy, as a fundamental science, increases research in this area, both for world science and for human himself. He is interested in cognizing the world as deeply as possible. As a result, it is clear that the ideas offered by science today are not enough to recognize human. So, there is a problem that is important for science. The solution to this problem must now be analyzed in the human-ecological consciousness-ecological cognition context, passing through the human-consciousness-cognition prism. The opinion of L. Feuerbach, a representative of German classical philosophy, draws attention - in his logic, the substance of human's creation is irrelevant. More important than substance is the life itself lived by human over time. That is, it is expedient to develop the value criterion determined by science. The laws of society are based on individual or personal interests. It would be expedient to pay attention to their working mechanism. Today's reality (Covid-19 pandemic) forces us to change our attitude towards the human and his ecology. The reason can be understood on the basis of the process that takes place in any issue.

5.References

1. A., M., Tagiyev: Philosophy (textbook). "Zardabi LLC", page 384. Baku (2012)
2. Hajiyev Zeynaddin Jamal oglu: Philosophy. Textbook for universities. ''Turan Evi" Publishing House, page 488. Baku (2012)
3. ANTHOLOGY OF THE WORLD PHILOSOPHY in four volumes, volume 1, Antiquity and medieval philosophy part 1, Publishing house "Thought". Moscow (1968)
4. Yusif Rustamov: Fundamentals of Philosophy, "Nurlar" Publishing House, page 504. Baku (2007)
5. Agayar Shukurov: "Philosophy" II edition (textbook for universities), Electronic book YYSQ - e-publication of the National Virtual Library, N 69 (2011), page 471, Baku (2011) http://www.kitabxana.net/
6. M.B Zeynalov: History of Philosophy (Western Philosophy), page 544. Textbook for universities. – Baku, "Azerbaijan" publishing house (2000)

PP-VI-8

PHOTOCHEMİCAL TRANSFORMATİON OF OİL FRACTİON UNDER UV RADİATİON

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Abstract. Photochemical transformations in the oil fraction of crude oil from the Dubendinsky oil terminal have been studied by IR and UV spectroscopy. It was found that the maximum absorption values in the region 3000-2900 cm^{-1} initially decrease depending on the radiation time, and then increase at times greater than 60 minutes, while the maximum Abs values in the region 2900-2800 cm^{-1} decrease depending on exposure time. There is a monotonic decrease in the maximum value of Abs in the region of 1600-1400 cm^{-1} with an increase in the irradiation time. A similar dependence is also observed in the range 1400-1300 cm^{-1}. A slight decrease in the absorption maximum Abs with increasing irradiation time is observed for the 800-600 cm^{-1} bands. In the UV absorption spectra of the oil fraction, a broad band was identified with a maximum at about 260 nm, the intensity of which weakly depends on the duration of irradiation. This band is characteristic of UV absorption spectra of monocyclic aromatic hydrocarbons. Some peaks in the 220-240 nm region are probably associated with mono- and bicyclic aromatic compounds. The peaks observed at shorter wavelengths (200–220 nm) are probably related to alkanes and cycloalkanes.

Keywords: Oil fraction, UV irradiation, IR spectra, UV spectra, absorption.

1.Introduction.

Photochemical transformations of crude oil under the influence of UV radiation and sunlight play an important role in its degradation in the environment [1, 2]. Since crude oil has a complex structure, some of the components that make up the fraction undergo direct photolysis. Mainly the UV region absorbs aromatic and polycyclic aromatic compounds, as well as some oxygen-containing components. A number of studies have investigated the effect of UV radiation on asphaltenes and resins [3-5]. It was found that during the photolysis of aliphatic and liquid paraffins in the presence of asphaltenes and resins, sensitized decomposition of hydrocarbons occurs. We have previously studied the effect of UV radiation on the chemical decomposition of crude oil by UV and IR spectroscopy [6]. It is shown that under the action of UV irradiation, the absorption bands change depending on the intensity of the incident light. To understand the mechanism of the ongoing photochemical processes, it seems appropriate to study the effect of UV light on individual fractions of crude oil.

The aim of this work is to study the effect of UV radiation on the oil fraction of crude oil by IR and UV spectroscopy.

2.Method.

Crude oil from the Dubandi oil terminal was used, the characteristics of which are: density, kg / m^3 (866 (20 ° C), 867 (25 ° C), 864 (37.8 ° C),) Kinematic viscosity, cCT (18.147 (25 ° C), 11.342 (37.8 ° C), 7.56 (50 ° C)).

The separation of the oil fraction was carried out according to the GOST 11858 standard. The oil sample was thoroughly mixed for 5 minutes. Then, normal hexane (1: 5) was added to the sample flask and the solution was moved for an additional 1 hour and kept in the dark at room temperature for 24 hours to isolate asphaltene. Then the solution is filtered from thick filter paper and washed with filter paper with n-heptane.

The composition of the sludge consists of carbene-carbide and asphaltene. Hydrocarbons and tar remain in the filter. To determine the oil fraction, silica gel (4: 1) is added to the filter and stirred for 2 hours and filtered, and the filter is washed with n-heptane. Thus, the oil remains in the filtrate and the resin falls into the silica gel. The oil content was 52%.

The photolysis process was carried out under static conditions at room temperature in a quartz cell with a width of 1 mm and a volume of 450 μL, using the full spectrum of a PRK-4 mercury lamp lamp. The radiation flux was measured by the formation of CO from acetone and was $\Phi = 2 \times 10^{15}$ quanta / sec.

The lamp radiation consists of resonance lines having the following relative intensities: 546.1 nm (71.75%), 435.8 nm (62.4%), 404.7 / 7.8 nm (35.9%), 365,0 / 6.3 nm (100%), 312.6 / 3.2 nm (68.0%), 302.2 / 2.6 nm (31.2%), 296.7 nm (14.3 %), 280.4 nm (10.3%), 265.2 nm (23.4%), 253.7 nm (26.1%), 248.3 nm (10.5%).

UV spectra were recorded in a quartz cell with a volume of 4 ml (a = 10 mm, b = 10 mm, h=40 mm) on a VARİAN SCAN-50 spectrophotometer (UV Visible spectrophotometer) with a wavelength of λ = 200-400 nm. Since the spectra were recorded with a concentrated sample, the absorption bands were wide and the oil and tar fractions were diluted 1600 and 3500 times with dichloromethane and the absorption spectra in Fig. 2 refer to diluted samples.

3.Results and Discussion

IR spectra were recorded on a Varian 640 IR spectrometer in the range of 400-3400 cm-1, which are shown in Figure 1.

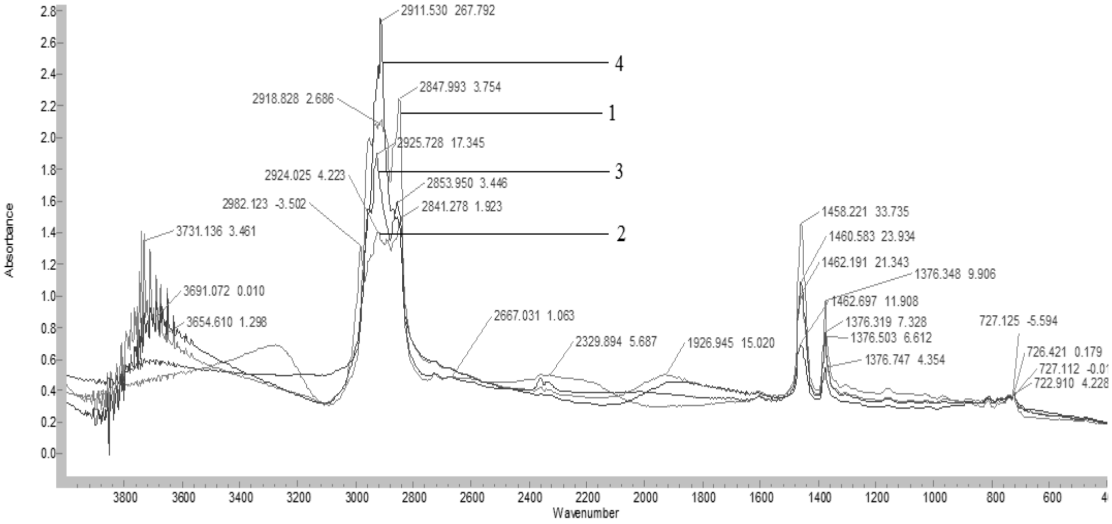

Figure 1. Infrared absorption bands of the oil fraction samples at different times of UV irradiation. 1 _ original; 2_20 minutes; 3 _60 min; 4 _90 minutes

The absorption bands observed in oil fractions include vibrations of C - H bonds in saturated (700-800, 1380, 1470, 2800-3000 cm^{-1}) and aromatic (700-900, 3050 cm^{-1}) structures, C = C bonds in aromatic nuclei (1610 cm^{-1}), C = C groups (1680, 1710 cm^{-1}), C-O and O-H bonds in ethers, alcohols and phenols (1050, 1150, 1230 cm^{-1}) and O-H groups participating in the formation of hydrogen bonds (3000-3500 cm^{-1}) [4].

As can be seen from the figure, in the region of approximately 2800-3100 cm-1 there are several intense peaks corresponding to stretching vibrations of CH_3- and -CH_2- groups, and peaks corresponding to bending vibrations of CH alkyl groups in the region of 1300-1500 cm^{-1}. The spectrum of the initial samples shows a broad band with a maximum at 3300 cm^{-1} and 2300 cm^{-1}. In the irradiated samples, a broad band with a maximum at 1900 cm^{-1} and a weak band with a maximum at 700 cm^{-1} are observed.

As shown in the table, the maximum values of absorption Abs in the region of 3000-2900 cm^{-1} initially decrease depending on the radiation time, and then increase at times greater than 60 minutes, while the maximum values of Abs in the region of 2900-2800 cm^{-1} decrease. depending on the exposure time. There is a monotonic decrease in the maximum value of Abs in the range 1600-1400 cm^{-1} with an increase in the irradiation time. A similar dependence is also observed in the range 1400-1300 cm^{-1}. A weak decrease in the absorption maximum Abs with increasing irradiation time is observed for the 800-600 cm^{-1} bands.

Our research has shown that the main constituent of crude oil is polycyclic aromatic hydrocarbons (PAHs), which are approximately 8.2 wt%. Monocyclic aromatic hydrocarbons (MAH) and n-alkanes are 0.01 and 0.52 wt%, respectively [4]. It is natural to assume that the bulk of UV radiation is absorbed by PAH molecules.

As shown in [2], PAH molecules have triplet excited levels of the order of 3.5 eV, and in the case of the presence of two quantum processes, the energy absorbed by PAH molecules can be transferred to alkane molecules, which leads to a decrease in the corresponding alkane bands, which is observed in the IR spectra of irradiated samples.

Figure 2 shows the UV absorption spectra, which reflect the structural changes in the oil fraction under the influence of ultraviolet radiation. The observed peaks in the spectrum cover the region of 200–260 nm.

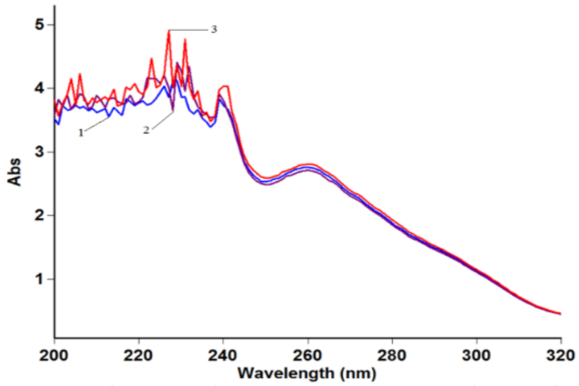

Figure 2. Absorption spectra of products formed during photolysis of the oil fraction under the influence of UV radiation. (1 - initial, 2 - 20 minutes, 3 - 60 minutes).

The intensity of the broad band with a maximum at about 260 nm weakly depends on the radiation duration. This band is observed in UV absorption spectra of monocyclic aromatic hydrocarbons and the extinction coefficients of aromatic compounds such as benzene, toluene, o, m, p-xylene, butylbenzene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene with a maximum absorption band of about 260 nm, is in the range 200-700 l/mol·cm. Several absorption peaks are observed in the 200-240 nm range. Some of these peaks (220-240 nm) are likely associated with mono- and bicyclic aromatic compounds. The peaks observed at shorter wavelengths (200–220 nm) are probably related to alkanes and cycloalkanes. With an increase in the radiation duration, an increase in the intensity and a shift of the peaks observed in this region are observed. It should be noted that some of the peaks observed at 200-220 nm correspond to the absorption band of dichloromethane used as a solvent. A weak change in the band intensity at 260 nm and an increase in the band intensity observed at 220–240 nm can be associated with the transfer of energy from aromatic compounds to alkane and cycloalkane molecules.

4.Conclusion

The results show that the use of IR and UV spectroscopy allows the monitoring of chemical changes in the oil fraction of crude oil when exposed to UV radiation. It was found that the photolysis of the oil fraction changes the absorption of functional groups responsible for the decomposition of saturated hydrocarbons, which is associated with the transfer of radiation energy from PAH molecules to them.

5.References

1. E. M. Fathalla. // Degradation of Crude Oil in the Environment: Toxicity Arising Through Photochemical Oxidation in the Aqueous Phase Egypt. 2007. P. 13
2. Земенкова М.Ю, Шалай В.В, Земенков Ю.Д, Щерба В.Е / Мониторинг эксплуатционных свойств нефти и нефтепродуктов при воздействии солнечной радиации // Современные проблемы науки и образования. – 2015. –№ 2 (часть 3), URL: http://www.science-education.ru/ru/article/view?id=23579
3. М.А.Наджафова. // Сенсибилизированная генерация свободных радикалов и их гибель при фотооблучении тяжелых нефтяных остатков. Автореф. дис. док. хим. наук. Баку., 2009
4. Ч.К.Салманова. // Фотоокисление компонентов тяжелых нефтяных остатков и их антиокислительные свойства. Автореф. дис. док. хим. наук. Баку., 2011
5. Ф.И.Самедова., М.Ф.Мир-Бабаев. // Высокомолекулярные гетероатомные соединения нефтей Азербайджана. Баку. 1992 г. С. 7.
6. Т.С.Идрисов., М.А.Курбанов., У.А.Кулиева. // Исследование фотолиза сырой нефти под воздействием УФ лучей УФ и ИК спектроскопических методом. Химические проблемы. 2017. № 3. С. 276.

PP-VI-9

DEPOSITION OF CHEMICAL BALLASTS IN "UNDESIRABLE"OIL MIXTURES

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Abstract. In the article it was studied the precipitation kinetics of various ballasts (resins, asphaltenes and paraffins, as well as water, salts and mechanical mixtures) in "undesirable" mixtures of oils. It was found that the bulk of all ballasts precipitate within 8-10 hours. Studies have shown that, depending on the chemical composition of oils, their formation of "undesirable" mixtures can also occur in the intensive deposition of various ballasts.

Keywords: oil mixing, physical and chemical properties, mechanical mixtures, ballast deposition, asphaltenes.

1. Introduction

As it is known, the construction of transportation networks and the location of production areas do not allow the transportation of oil from the field to the points of consumption with the initial quality indicators. The existing networks of in-field and main oil pipelines can technologically transport oil only in the form of mixtures. However, there are specific problems arising from the mixing of different types of crude oil. One of the main problems is the "undesirable" mixing of oils, which leads to contamination of equipment (pipelines, tanks, heat exchangers, furnaces, rectification columns, etc.), and sometimes a complete shutdown.

2. Research method

The results of research show that one of the reasons that make the mixing of different types of crude oils "undesirable" is the presence of organic solids in the form of precipitated asphaltenes. It is known that asphaltenes are soluble in aromatic compounds such as toluene, but not in paraffinic compounds such as n-pentane. The main problem with the presence of asphaltenes in various crude oils is that asphaltenes are often separated from these mixtures in the form of sediments. As long as there is a need to create practical and cost-effective means and methods for mixing different types of oils, these problems remain unresolved. Recent research suggests that nonlinear deviations (errors) in the quality of mixtures of different types of oils from existing ideal oil models are most likely due to the structural transformation of oil nanophases [1-3]. "Undesirable" manifestations of asphaltenes in oil mixtures are possible at concentrations corresponding to the boundaries of the nanophases.

3. Results and discussion of the problem.

The existing various models of the processes under consideration do not yet allow to predict the changes in the quality of the oil mixtures used with the accuracy necessary for engineering calculations. Therefore, there is a need to add and improve criteria to assess the "undesirable" as well as the "optimal" concentration of asphaltene and other high-molecular chemical compounds, taking into account the interaction of individual components in transported oil mixtures. In order to study the effect of mixing of different types of oils on their rheological and physicochemical properties, oil samples of different fields and their mixtures were studied in the laboratory [4,5]. Physico-chemical properties of the tested crude oil of the Bulla (BO) and Garachukhur (GO) fields of Azerbaijan, as well as research methods are shown in Table 1. As can be seen from Table 1, the BO and GO oil samples differ in their rheological and physicochemical properties. In the example of BO and GO oils, it was determined that, regardless of the mixing sequence [4.5], there are nonlinear deviations in the quality of the mixture. Anomalies of quality indicators are also evident in the oil mixtures (“GO” + “BO”) and (“BO” + “GO”). Anomalous changes in physicochemical parameters occur in a mixture ("GO" + "BO") of mass fractions in the ratio of 0.42: 0.58.

Then, the sedimentation kinetics of different ballasts under standard conditions in the above-mentioned mixtures of “GO” and “BO” oils (42-58%) was studied. For this purpose, immediately after the preparation of each mixture, it was kept to settle at a temperature of 20 ^{0}C and the amount of ballasts deposited in it was determined every hour in accordance with the relevant standards. The results of hourly measurements to determine the amount of RAP (resin-asphaltene-paraffin), mechanical mixtures, water and salt ballasts in the GO:BO (42-58%) oil mixture are shown in Table 2. Table 2 also shows the total amount of deposits of ballasts that accumulated during the day. Based on the data in Table 2, the time dependence of the amount of deposits of ballasts (RAP + mechanical mixtures, water and salts) was established. The dependences reflecting the sedimentation kinetics of ballasts in oil mixtures are shown in the figure. As can be seen from the figure, most of all ballasts set down within 8-10 hours. Also, the amount of sediment increases intensively for up to 8 hours, and then begins to decrease sharply. After 10 hours, the deposition process slows down and is practically over.

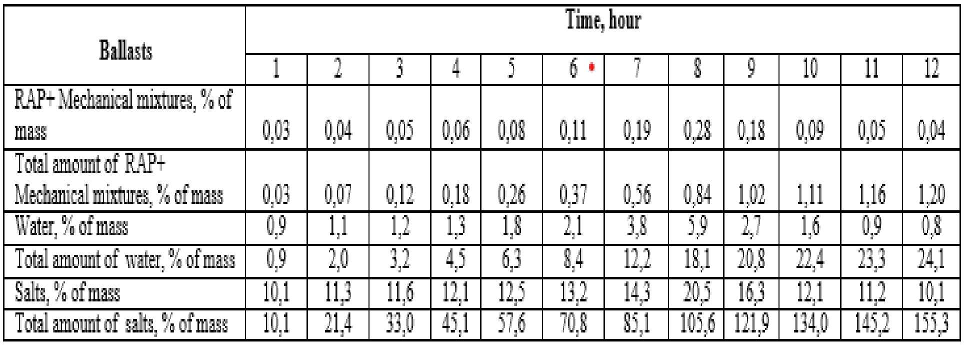
4. Conclusion

Thus, our research has shown that, depending on the chemical composition of different oils, the formation of "undesirable" in the mixture can also be manifested by the intensive deposition of various ballasts, which can lead to contamination of facilities and, in some cases, may result in the shutdown of technological oil storage and transportation pipelines.

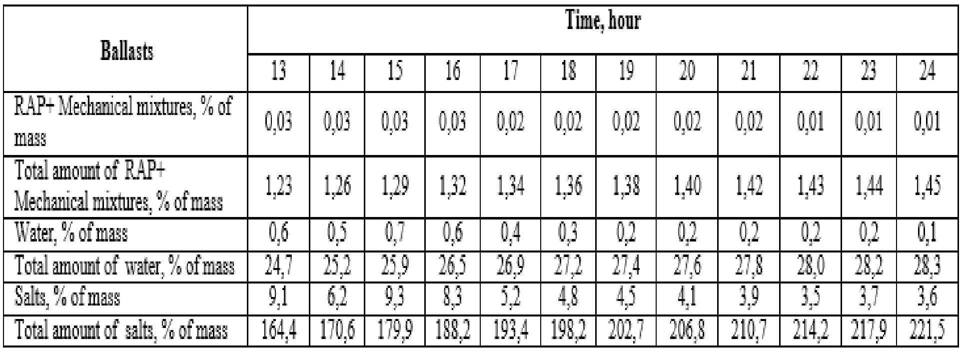
Table 1. Physico-chemical indicators of crude oil from Bulla (BN) and Garachukhur (GN) fields of Azerbaijan

Indicators	**Crude oils**		Research methods
	BO	GO	
Density at 20^0 C, kq/m^3	973,4	914,7	AUSS 3900
Kinematic viscosity at 20^0 C, sSt.	15,76	6,41	AUSS 33
Resin, % of mass	10,27	13,28	Chromatograph
Asphaltenes, % of mass	0,23	0,64	AUSS 11858
Paraffins, % of mass	13,34	2,53	AUSS 11851
Saturated vapour pressure, kPa	16,2	9,7	AUSS 1756
Set point, °C	+9	+3	AUSS 20287
Mechanical mixtures, % of mass	5,72	6,42	AUSS 6370
Salts, mq/l	480,6	530,3	AUSS 21534
The amount of water, % of mass	43,2	56,4	AUSS 2477

Table 2. Sedimentation kinetics of ballasts in GO: BO (42:58%) mixtures at t=20 ^{0}C



Ballasts	Time, hour											
	1	2	3	4	5	6	7	8	9	10	11	12
RAP+ Mechanical mixtures, % of mass	0,03	0,04	0,05	0,06	0,08	0,11	0,19	0,28	0,18	0,09	0,05	0,04
Total amount of RAP+ Mechanical mixtures, % of mass	0,03	0,07	0,12	0,18	0,26	0,37	0,56	0,84	1,02	1,11	1,16	1,20
Water, % of mass	0,9	1,1	1,2	1,3	1,8	2,1	3,8	5,9	2,7	1,6	0,9	0,8
Total amount of water, % of mass	0,9	2,0	3,2	4,5	6,3	8,4	12,2	18,1	20,8	22,4	23,3	24,1
Salts, % of mass	10,1	11,3	11,6	12,1	12,5	13,2	14,3	20,5	16,3	12,1	11,2	10,1
Total amount of salts, % of mass	10,1	21,4	33,0	45,1	57,6	70,8	85,1	105,6	121,9	134,0	145,2	155,3



Ballasts	Time, hour											
	13	14	15	16	17	18	19	20	21	22	23	24
RAP+ Mechanical mixtures, % of mass	0,03	0,03	0,03	0,03	0,02	0,02	0,02	0,02	0,02	0,01	0,01	0,01
Total amount of RAP+ Mechanical mixtures, % of mass	1,23	1,26	1,29	1,32	1,34	1,36	1,38	1,40	1,42	1,43	1,44	1,45
Water, % of mass	0,6	0,5	0,7	0,6	0,4	0,3	0,2	0,2	0,2	0,2	0,2	0,1
Total amount of water, % of mass	24,7	25,2	25,9	26,5	26,9	27,2	27,4	27,6	27,8	28,0	28,2	28,3
Salts, % of mass	9,1	6,2	9,3	8,3	5,2	4,8	4,5	4,1	3,9	3,5	3,7	3,6
Total amount of salts, % of mass	164,4	170,6	179,9	188,2	193,4	198,2	202,7	206,8	210,7	214,2	217,9	221,5

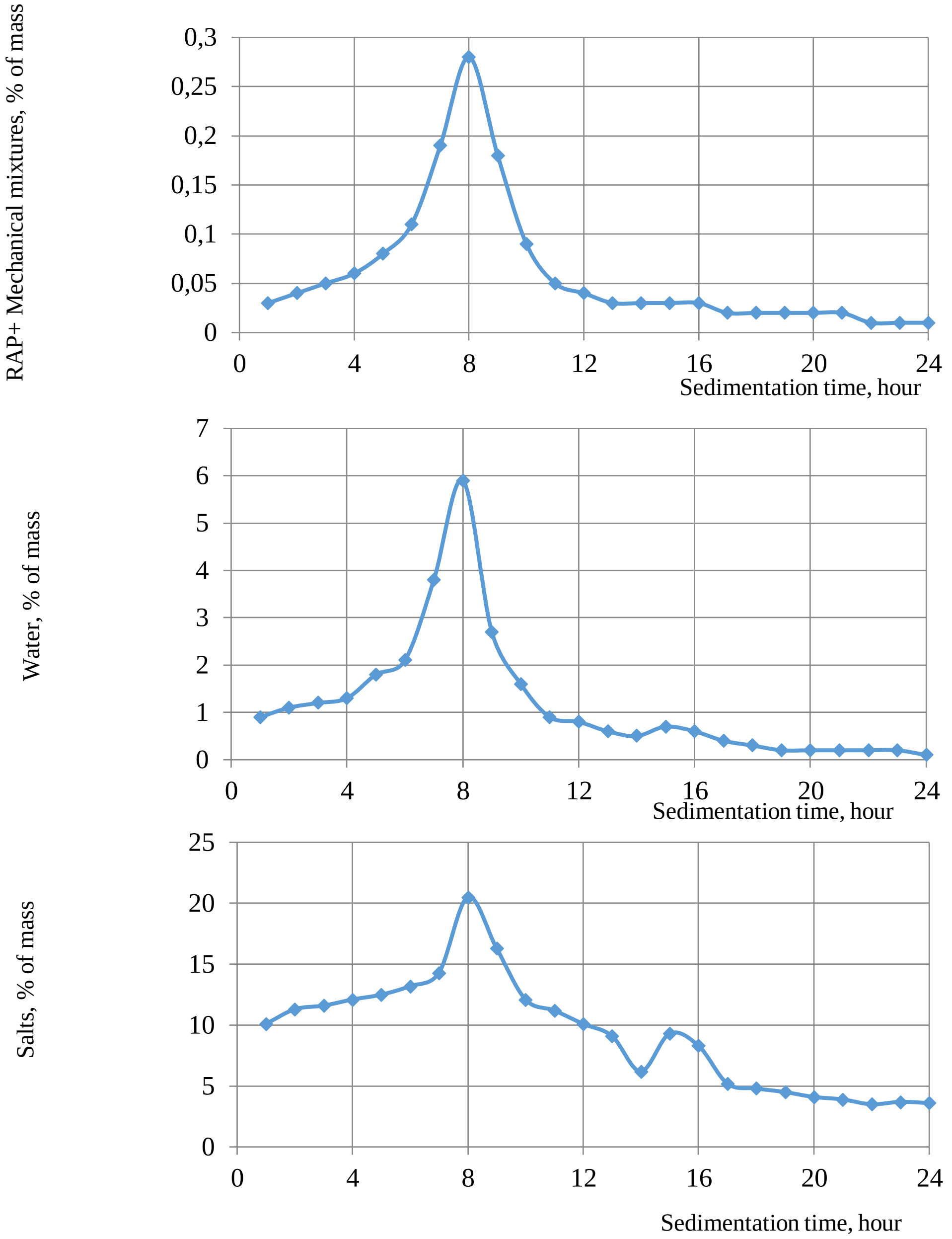


Fig. Sedimentation kinetics of ballasts in GO: BO (42:58%) mixtures at t=20 ^{0}C

5.References

1. Evdokimov I.N. Nanotechnology for controlling the properties of natural oil and gas fluids. M: MAKS-Press, 364 p.(2010)
2. Evdokimov I.N., Losev A.P. Features of the analysis of associative hydrocarbon media. Applicability of refractometric methods // Chemistry and technology of fuel and oils, 2007, № 2, p.38-41
3. Evdokimov I.N., Losev A.P. Inversion problem in oil-water field emulsions. Traditional concepts and their experimental substantiation // Drilling and oil, 2010, № 3, p.16-17
4. Nurmamedova R.G., Ismayilov G.G. On the change in the quality indicators of oils during their mixing // BULLETIN of the Kazakh-British Technical University № 1 (24), 2013, p.19-27
5. Ismayilov G.G., Serkebaeva B.S., Adygezalova M.V. On some problems of infield treatment of oil and water// Bulletin of the Higher Technical Educational Institutions of Azerbaijan Vol. 18, № 1, 2016, p.29-38

PP-VI-10

A QUALITY OF INFORMATION IN THE SAFETY DATA SHEETS FOR CHEMICAL PRODUCTS

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Abstract. According to the Strategy for the development of chemical and petrochemical industry during the period up to 2030 [10], it is planned to increase the volume of production of the most important types of chemical products, as well as to meet a growing need of the internal market in chemicals and new materials. The introduction of new products to the market for the industry will also mean the receipt of new safety data sheets (SDS). In this paper, main mistakes in the preparation of safety data sheets for chemical products were analyzed by the experts of the CIS Center. The article is addressed to managers and employees of industrial enterprises who make decisions on the preparation of safety data sheets.

Keywords: SDS, Chemical Safety, Responsible Care, Safety Data Sheet

1.Introduction

General requirements for the compilation of safety data sheets

According to the technical regulations of the Eurasian Economic Union "On the safety of chemical products" (TR EAEU 041/2017), the safety data sheet for chemical products is a document of the established form containing information on the hazardous properties of chemical products, data on the organization that puts products on the market, hazard warning measures and requirements to ensure the safe handling of chemical products. The safety data sheet should be included in the accompanying documentation for chemical products when delivered. SDS can be compiled by a manufacturer or a person authorized by the manufacturer, an importer of chemical products, who releases it into circulation in the customs territory of the Union. A copy of the safety data sheet must be provided free of charge on paper or electronic media upon customers or any interested persons request [1].

SDS should be compiled for all types of chemicals and mixtures, except for those excluded from the scope of GOST 30333 “Safety data sheet for chemical products. General requirements”, for example, medical products, perfumery and cosmetics, food products and others. Primarily, the safety data sheet must be prepared by an expert who has basic knowledge in chemistry, occupational health, medicine, logistics and environmental protection. SDS should be drawn up in Russian language, however, if there are appropriate requirements in the legislation on the territory where the chemical product is being delivered, SDS may be drawn up in its state language(s).

The information in the passport must be stated correctly, clearly and concisely for the perception of the user of any level of educational background. For instance, the use of such phrases as: "does not pose a danger", "does not have a harmful effect", "safe" or "non-toxic" can complicate perception of a user and therefore be misleading [1,2,3].

What it should be paid attention to

Despite the seeming, at first glance, simplicity, not everyone manages to draw up the safety data sheet that meets all the rules and standards. Most commonly, about 40% of safety data sheets received by CIS Center for initial verification are being returned to the compiler for revision.

The drafting instructions for the SDS currently are regulated by GOST 30333 [2].

The compiler of the safety data sheet, first of all, needs to determine what substances are included in the product and in what quantitative ratio. It is important to provide the composition of the product in mass fractions of percent up to 100%, and it is necessary to take into account absolutely all the components included in the composition, the percentage of which is greater than or equal to 0.1%, since according to the GHS (globally harmonized system of classification and labeling of chemicals) [4], the available data on the hazardous long-term effects of exposure to the substance may testify in favor of a particular hazard classification. Examples of such hazards are carcinogenicity, mutagenicity, reproductive toxicity, sensitizing effects by inhalation and skin contact. Therefore, the composition of the finished product, specified as accurately as possible, allows to provide an adequate hazard assessment, classification and filling out the corresponding sections of the SDS.

The most difficult part of the compilation is the hazard identification section (section 2), since it requires additional training in the field of hazard classification and the choice of warning label elements, as well as the availability of reliable information about the hazards of products, and in particular, its components. A mandatory requirement for the competent compilation of this section is understanding the GHS [4]. Undoubtedly, it is easier to classify a chemical product consisting of just one substance, since the substances themselves have been studied in detail and there is enough information on them to determine each type of hazard. The difficulties are caused by new, insufficiently studied substances, or mixtures of substances for which an information is difficult to find or is simply not available. In this case, it is necessary to conduct tests to determine certain physicochemical, toxicological, ecotoxicological indicators, otherwise there is a risk of incorrect assessment of the hazardous properties of the product to which the manufacturer (or an authorized representative acting on behalf of the manufacturer) exposes the consumer.

Correct classification allows the user of the safety data sheet to be informed about the presence of a particular hazard. The absence or ignorance of data on hazardous factors can lead to errors when working with products, which entails the wrong selection of workers' protection equipment, lack of necessary knowledge and training, incorrect selection of materials and equipment, and also leads to violation of waste disposal rules. This non-compliance can lead not only to work-related injuries, but also to adverse consequences [7].

In addition to the main criteria for hazard classification, there are exceptions to the rules or already predefined classifications for specific substances, such as methanol, ethylene glycol, hydrofluoric acid, sulfuric acid, formaldehyde and others. Changes may affect, among other things, transport classification. So, for example, until 2012, ethylene glycol (ethylene glycol antifreezes) was on the list of dangerous goods, with UN number 2810 ORGANIC TOXIC LIQUID, N.O.S., hazard class 6.1 and a pictogram "Toxic", but was excluded from list, and today is not a dangerous cargo, despite the abundant data on the toxicity of this substance [5].

The next most difficult section to compile is the 14th section on transport information, because the data in this section are directly related to classification and labeling. This section obliges to have the necessary knowledge of the current rules for the carriage of dangerous goods for each mode of transport, as well as general instructions for the carriage of goods – UN Recommendations [6]. Transport and warning labeling must be consistent with each other. Experience shows that the incorrect selection of the UN number, which does not reflect the presence of the existing danger, can lead to additional inspections by transport or customs services, and in the worst case, to the seizure of incorrectly labeled cargo [8]. According to the Novorossiysk Commercial Sea Port, in the absence of completed shipping documents (which include a safety data sheet), the port has the right to impose penalties on the customer, for example, for the occupation of access roads by railway wagons in the amount of $ 11 for every hour of downtime [9]. Therefore, the noncorrespondence of sections 2 and 14 of the SDS can lead to additional unforeseen expenses.

Section 4 also causes difficulties – a description of symptoms, especially for mixed products, because these data are not available in open sources and in the absence of tests, the compiler must independently determine the type of product exposure. So, in case of incorrect filling of this section, a consumer may underestimate the hazardous exposure and neglect safety measures or protective equipment, which can lead to injuries. In addition, the description of incorrect symptoms of poisoning lead to inaccurate first aid measures, which, if an injury occurs, can only make the situation worse.

As practice shows, in the 5th section of the safety data sheet (fire hazard) information is often indicated in a way that does not correspond to the characteristics of the product. For example, for a 50% solution of methyl alcohol, a compiler indicates the absence of fire hazard properties. This difficulty in most cases is associated with the reluctance of the organizations to conduct additional tests for new products. However, incorrect information in this section may lead to a worsening of the emergency situation and lack of proper safety measures when working with the products. The emergency team will simply not be aware of the hazardous behavior of a product. Some substances during thermal destruction form toxic combustion products, some have a list of prohibited extinguishing agents, as well as other specifics. So, if a fire occurs near the tanks of sulfuric acid, it is forbidden to use water for extinguishing, since their mixing causes an exothermic reaction with the release of a large amount of heat, which can lead to an explosion.

Section 11 (information on toxicity) and 12 (information on environmental impact) are also difficult to compile, since usually the data is of a narrow nature and is intended for experts. Particular difficulties arise when calculating acute toxicity indicators for the effects on the body and ecotoxicity for mixed products, since for this it is necessary to refer to standards and calculation methods that require additional knowledge. At the same time, the availability of accurate values of toxicity indicators and information on the hazardous properties of products is mandatory for correct hazard classification.

The quality of compiling a safety data sheet depends directly on the specialist engaged in its development. It is important to understand that a safety data sheet is a document that requires knowledge in various fields of science and appropriate training. Forced involvement of employees with no experience in the preparation of safety data sheets leads to a protracted registration process and disruptions in the submission of the document.

Safety data sheet to export

It should be noted that not only Russian SDS, but also international SDS may contain incorrect information.

The expert council of the European Chemicals Agency carried out research work aimed to analyze the quality of SDS. The results of the evaluation of 4500 SDS showed that about 50% of the tested SDS contained invalid data. At the same time, sections 1, 2, 3, 8 and 15 caused a particular difficulty in compiling an SDS.

The main problem in section 1 was the lack of detailed data on the use and restrictions on the use of chemical products. Incorrect indication of the concentration ranges of the components in the mixture, information about which should be given in Section 3, almost always led to incorrect product classification and its labeling in Section 2. This happens due to the fact that SDS compilers do not pay attention to the compatibility of data in the text of the document, which leads to complete disagreement of the sections. Also, in some cases, the classification was completely absent.

The lack of data on the parameters of the working area subject to mandatory control (maximum permissible concentrations of harmful substances) or the inaccuracy of information provided on control measures, including technical measures and information on personal protective equipment, is a common mistake when developing section 8.

There was also a lack of information on physicochemical, toxicological and ecotoxicological properties without explaining the reasons for the lack of information, as should be indicated in sections 9, 11 and 12. In cases where information is not provided at all or there are errors in the SDS, this leads to unforeseen consequences not only for users, but also for all participants in the supply chain [12,13].

Ways to solve the problem of inaccurate data in safety data sheets

The volume of shipped chemicals and chemical products of our own production in Russia in 2018 reached 2,742,593 million rubles, in 2019 - 3,265,833 million rubles [14]. According to the Strategy for the development of chemical and petrochemical industry during the period up to 2030 [10], it is planned to increase the volume of production of the most important types of chemical products, high-quality socially-oriented products, as well as to meet the growing needs of the domestic market for chemicals and new materials, and to expand the range of products.

It is also worth mentioning the preparation for the entry into force of the EAEU TR 041/2017, which regulates the availability of a safety data sheet when passing the registration procedure for chemical products. Changing market conditions and legislation lead to the fact that the manufacturer (or the person authorized by the manufacturer), the importer of chemical products, releasing chemical products into circulation in the customs territory of the Union, will have to draw up a safety data sheet. At the same time, the course towards import substitution adopted by Russia will lead to an expansion of the range of chemicals produced in the country, and it will be necessary to prepare safety data sheets for all newly introduced substances to the market [15].

Thus, the preparation of safety data sheets is an important area of work, which in the near future will become more and more relevant for chemical enterprises. However, the current form of regulation in the world does not provide a verification of SDS, which is used by unscrupulous organizations and does not always provide reliable information not only about the composition of the product, but also about the dangers it poses.

In Russia, however, the safety data sheet is checked by an expert organization. This measure has long proven itself and justified the assigned obligations. So on the territory of the Russian Federation for more than 25 years, safety data sheets have always been checked. Any company can send its SDS for verification and its entry into the register in order to be sure of the correctness of the information in the SDS, as well as to confirm its openness to the consumers.

Also, an important step towards a reliable assessment of the hazard of products is to conduct physical, chemical and toxicological tests for industrial chemical products. This measure allows to assess the degree of danger of products without referring to publicly available data, which often are focused on well-studied substances or groups of substances that are similar in chemical composition and action.

However, if the manufacturer does not have the resources to conduct a research, it is possible to assess the degree of danger by resorting to informational data sources: research materials, reference books, domestic and international databases. In this case, the effect of the product should be assessed according to the most dangerous option. In this situation, the personal responsibility of the manufacturer and his interest in the protection of human health and environmental objects are important.

4.Conclusion

A safety data sheet for chemical products is a widely recognized and effective mean of communicating the dangers of chemical products and is intended to transmit data to downstream consumers on the properties of substances and their mixtures and on measures to prevent these hazardous properties. It is necessary to treat the preparation of the safety data sheet as responsibly as possible, because the information it contains is often one of the main sources of safety in the workplace. It should be noted that according to the GHS, a SDS must be drawn up by a specialist with a sufficient level of professional training. However, as practice shows, this recommendation is neglected, which often leads to numerous errors in the content of sections of the passport. Inaccurate data can cause the development of fatal consequences in production during the use and transportation of chemical products. It is possible to avoid mistakes in the preparation of documentation if there is a well-formed expert community. Reliable data in the SDS will reduce the risks of inappropriate handling and injury in the workplace, as well as the initiation of litigations.

Legend

The GHS is a globally agreed system of hazard classifications and labeling of chemical products.

TR EAEU 041/2017 **-** technical regulations of the Eurasian Economic Union "On the safety of chemical products."

PB RF **-** safety data sheet for chemical products of the Russian Federation.

SDS **-** safety data sheet, chemical safety data sheet for export.

5.References

1. Technical Regulations of the Eurasian Economic Union "On the safety of chemical products" (TR EAEU 041/2017), adopted by the decision of the Council of the Eurasian Economic Commission dated March 3, 2017 No. 19.
2.GOST 30333-2007. Safety data sheet for chemical products. General requirements; 2009, - Moscow: Standartinform, 2008 - 7.
3. P 50.1.102-2014 Preparation and execution of the Safety Data Sheet for chemical products; 2015, Moscow: Standartinform, 2015 .- 30.
4. Globally Harmonized System of Hazard Classifications and Labeling of Chemicals (GHS). // United Nations Organization. - 8 revised edition. New York and Geneva, 2019.
5. Minutes of the fifty-sixth meeting of the Council for Railway Transport of the Member States of the Commonwealth (part 70), May 17-18, 2012. - Moscow, 2012.
6. Recommendations for the transport of dangerous goods. Model Rules // United Nations Organization. - 21 revised editions. New York and Geneva, ST / SG / AC.10 / 1 / Rev.21, 2019.
7. Vinogradova E.N., Lyashik A.M., Reshetar O.A. Safety data sheet for chemical products in Russia within the framework of the implementation of the UN-GHS recommendations. Differences and national characteristics // Chemical Safety, 2019, 266-276.
8. Skobelev D. O., Vinogradova E. N., Reshetar O. A., Pleshivtseva T.S., Accompanying documentation for the transport of dangerous goods // Chemical Safety, 2018. No. 1, 244 - 251.
9. Novorossiysk Commercial Sea Port: Official site. - URL: www.nmtp.info// (Date of access: 18.06.2019).
10. GARANT.RU. Information and legal portal. - URL: http://www.garant.ru/ (Date of access: 01.02.2020).
11. Lebedev A.D., Lyubinskaya T.S. Improving the efficiency of access to information on the dangers of chemical products based on the safety data sheets of chemical products of the Russian Federation and the CIS // Quality and Life, 2019. No. 4 (24). 88-92.
12. Orlova AM, Druzhinina NA, "Dangerous" safety data sheets // Competence. 2019. No. 6. 36-39.
13. Report on Improvement of Quality of SDS // WG “Joint initiative ECHA Forum - ECHA ASOs on Improvement of the quality of SDS” Version (1.0 - 16.05.2019), May 2019. - Helsinki, 2019. DOI: 10.2823 / 005933.
14. Industrial production in Russia. 2019: Statistical collection / Rosstat. - P 81 M., 2019, 286.
15. Ivanov V.P. The influence of the magic of import substitution on the chemistry of results // Chemical Industry Today, 2020 №1.

OR-VI-6

USE OF WALNUT SHELL WASTE AS A SORBENT

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Abstract. The environment polluted by various compounds, including petroleum products, forces us to look for new available sorbents for their purification. An effective plant raw material as adsorbents with high sorption characteristics can be quantitatively large waste from the production of walnuts. In this work, a carbon-containing material from walnut shells (WGO) was obtained, subjected to carbonization and acid treatment, with the prospect of using it in wastewater treatment processes. Carbonization was carried out in a muffle furnace with air access for 2 hours in crucibles. The optimal temperature regime for firing walnut shells is chosen - 400 ° C. To improve the sorption properties, the obtained samples were activated with acids.

Key words: sorbents, carbon-containing materials, walnut shells, carbonization, sorption characteristics, filtration.

1.Introduction

There are many minerals in our Azerbaijan Republic. For many years, oil was the main raw material, and therefore, due attention was not paid to other natural resources. And the natural resources of Azerbaijan are diverse. So, for example, in addition to oil, there is gas, shale, peat, brown coal. And in Naftalan, medicinal oil is produced. Ore minerals (iron, aluminum, gold, silver, molybdenum ores) should also be noted. Nonmetallic useful minerals occupy a leading place in mineral resources. This is rock salt, gypsum, bentonite clay.

Azerbaijan began to stand out in other areas as well. At the present stage, when oil prices are constantly changing and mainly downward, it is necessary to look for and develop new sources of income to replenish the budget. One of them is walnut growing. From ancient times on the territory of Azerbaijan (Gabala, Zagatala, Baku) there were valuable walnut forest plantations. And today Azerbaijani products - walnuts - are in demand. Walnut is a very valuable food product, high-calorie, healthy from the point of view of medicine. The development of this raw material base has one drawback: a sufficient amount of waste in the form of shells accumulates in the processes of walnut production. It becomes necessary to dispose of it in order to obtain the necessary and useful products. From such products it is possible to obtain a sorbent - activated carbon, which can be effectively used for the purification of oily waters.

The number of pollution sources is increasing every time, but one of the most widespread and very effective is oil and oil products. Water is used in large quantities, and it is already as waste water is a source of pollution in all areas of the environment [1]. Getting into a reservoir, these oil-contaminated wastewater has a lower density compared to water and is very poorly soluble in it. For example, for gasoline solubility in water does not exceed 20-30 mg / dm3, for kerosene fraction 70-90 mg / dm3, and for heavy oil residues - 0 [2]. To prevent the process of stopping metabolism, it is necessary to purify wastewater to the specified standards: MPC of oil and oil products in water, depending on further use, ranges from 0.05 mg / dm3 to 0.1-0.3 mg / dm3 [3,4].

A huge number of the declared methods of purification of oily wastewater can be divided into mechanical, physicochemical, electrochemical and biological [5]. Biological treatment is used to purify organic pollutants [6]. The sorption method is one of the most promising. When cleaning wastewater from oil impurities, the most effective method is assumed to be sorption.

The main issue when using this method is the selection of sorbents. Sorbents for wastewater treatment from oil and oil products differ in composition; they can be made from natural or synthetic materials. For example, walnut-growing wastes can be used as raw materials, especially since the territories of walnut forests in Azerbaijan are very large. But the question arises in what form they can be used. In the initial state, the use of these waste plant materials is technically difficult. In the production of activated carbons, the main condition for the selected raw materials is the invariability of the chemical composition and structure. Naturally, the most correct way to solve this issue would be to determine the processing parameters of walnut shells in order to use them as activated carbons. There are works in which technological development of plant raw material wastes is proposed in order to improve sorption properties [7,8]. The commonality of these technologies lies in two stages: carbonation and activation. For optimal performance of the mode of the carbonization process, stable maintenance of the final temperature, time and speed of the process is required [9]. It is the carbonization process that creates the characteristic porosity, which can increase the sorption capacity of the surface. However, due to the fact that this process depends on many factors and there is no possibility of obtaining a predetermined porosity of coal, it is necessary to select the conditions for carbonization by means of ongoing research. The second stage is activation. Activation is used to improve the structure of the adsorbent. Activation is the final stage, it is carried out to clean the surface of the raw material, to increase the number, nature and volume of pores. The process is carried out at high temperatures and in the presence of some oxidizing compound. It can be oxygen, water vapor and CO2. Activation is carried out after carbonization, where the initial change in the porosity of the raw material begins. And already at the second stage, under the influence of high temperatures, various chemical reactions occur on the surface of the raw material, but the original structure, channels, pores are not destroyed. Both of these stages make it possible to modify the properties of the resulting active carbons.

2.Experimental part

Walnut shells were taken as the object of research. The choice fell on SGO due to the hardness of the shell, the absence of harmful impurities, with a natural porosity consisting of 5-10% silicon oxide and 80-90% carbon (by weight).

For all studies, 500 g of walnut shells were taken. This mass was left for 24 hours at room temperature to dry. A preliminary study of the elemental composition of CGO in order to confirm the possibility of using it as a raw material for the production of activated carbon has established that its shell is suitable. From the total amount of the shell, a part was taken, which was crushed to particles less than 0.20 mm. Table 1 shows data on the elemental composition of raw materials.

Table 1. Elemental composition of raw materials

Raw	Elemental composition mass.%				
	C	H	N	S	O
СГО	50,01	6,25	0,45	0,09	42,0

Table 2. Chemical composition of walnut shell ash,%

Сырьё	Зола	CaO	MgO	K_2O	P_2O_5	Fe_2O_3
СГО	1,64	0,84	0,12	0,20	0,02	3,84

Further, another fraction of 1-3 mm was prepared to determine such parameters as: bulk density, yield and moisture of the shell.

Table 3. Physical characteristics of raw materials

raw	Bulk density, g / dm3	Output,%	Humidity,%
СГ0	612	86.0	11.0

For subsequent experiments, we took a fraction of 2.5-7 mm, dried at a temperature of 1050C. The carbonization process was carried out as follows: four crucibles with 100 grams of shells were placed in a muffle furnace with air access, the temperature change was from 200 to 800 ° C for two hours.

Carbonation is used to increase the carbon content, release with the simultaneous removal of volatile components and, importantly, increase the porosity and surface. All these processes are necessary for the next stage - activation. Chemical activation to obtain active carbons from the walnut shell with a certain modification was used 10% sulfuric acid, and to obtain oxidized carbons, they acted with nitric acid. The carbon content increases with an increase in the firing temperature, and at the same time the amount of oxygen and air decreases. The study of the process shows that with a duration of heat treatment at a temperature of 8000C and a time of 2 hours is impractical. Already at a temperature of 400-5000C and a time of 60 minutes, a decrease in carbon in active coals of SGO begins.

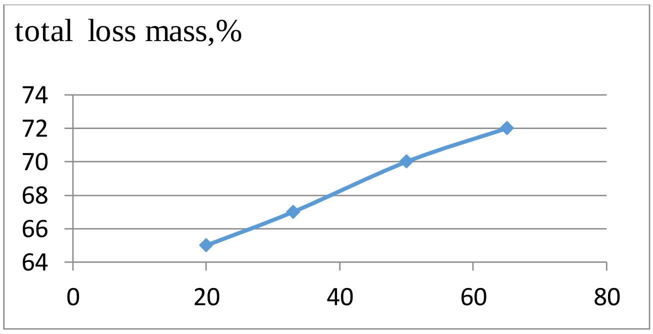

Figure: 1. Dependence of the mass loss of CGO on temperature during carbonization

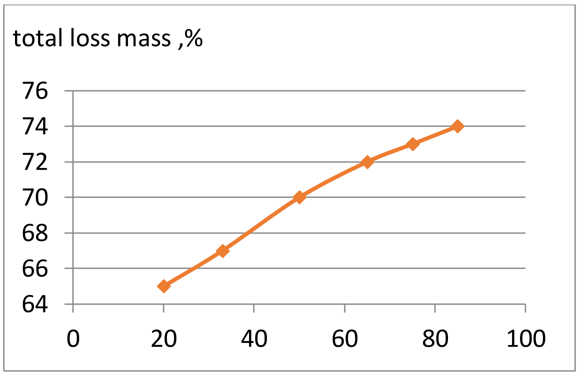

Figure: 2. Duration of heat treatment at 6000C, min.

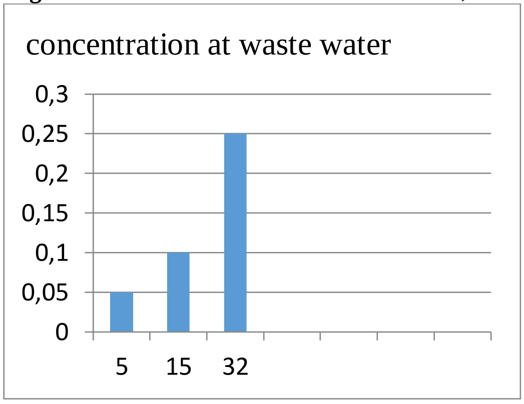

Figure: 3. Dependence of the carbonization temperature on the total mass loss of the CGO

Table 4. Elemental composition of SGO (initial and carbonated),%

example	C	O	H	Mg	Si	K	Ca
Initial SGO	50,54	42,5	6,25	0,16	0,60	0,80	1,62
Carbonated SGO	81,11	12,89	1,98	0,57	0,59	1,72	3,71

Closer to 8000C, the change in mass stabilizes. At this temperature, the final combustion of carbon takes place, and this is already almost the white ash of SGO. To select the most efficient activated carbon from the CGO, it is necessary to find out under what conditions the greatest amount of carbon is formed. It will also allow you to find out the sorption capacity, i.e. the maximum amount of sorbate absorption by a unit of sorbent mass. It was found that the oil capacity of the selected sample is 4.1 g of oil, i.e. 1 g of sorbent absorbs such an amount within an hour. After carbonization of the walnut shell, it acquired a good mechanical strength and high absorption capacity. Their use for the purification of oily waters by filtration through a fixed bed of adsorbent is effective. For this, we prepared model test solutions. The finished oil product, diesel fuel, was taken as an oil impurity. It is known that oil products in wastewater can be in different states. In the process of sedimentation, the so-called free oil products are removed, then flotation removes the bound ones and finely dispersed concentration of 20 mg / l remains in the water. And this requires the process of adsorption and filtration. The laboratory unit included an adsorption and filtration process for more efficient separation of oil impurities from wastewater. This interaction of the two processes makes it possible to reduce the amount of impurities to 92%. Diesel fuel was mixed with distilled water, then suspended petroleum products were separated using a mechanical stirrer. Then we defended, while waiting for the separation of the aqueous and hydrocarbon phases. The initial concentration of diesel fuel in water was determined by the gravimetric method. A glass column with a height of 50 cm and a diameter of 3 cm was used, the height of the loading layer of the selected sorbent was 20 cm; the model solution passed by gravity from top to bottom through the fixed bed. 22.5 mg / l diesel fuel was added to the model solution. The prepared solution began to be investigated on the effect of wastewater treatment from oil pollution on the transmission rate. The following figures were chosen: 6; 15 and 32 ml / min. As seen from Fig. 4, the degree of purification from oil impurities depends on the transmission rate.

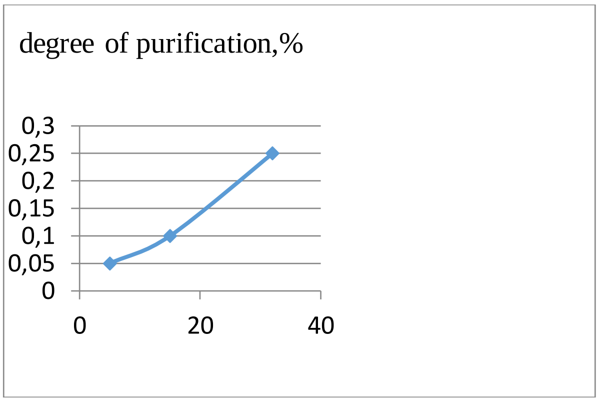

Fig. 4. Dependence of the degree of purification from oil impurities on the transmission rate

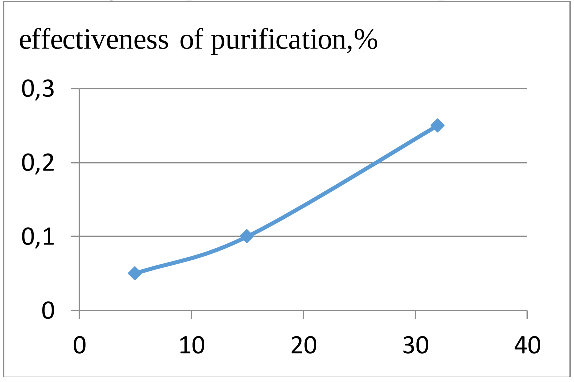

Fig. 5. Dependence of the cleaning efficiency on the height of the sorbent layer

The results obtained show that the degree of purification depends both on the height of the adsorbent bed and on the transmission rate. An important role in cleaning is played by the rate of filtration due to the fact that the time of contact of waste water with an adsorbent can be very small, seconds, therefore it is necessary that during this period of time the water is purified from oil products.

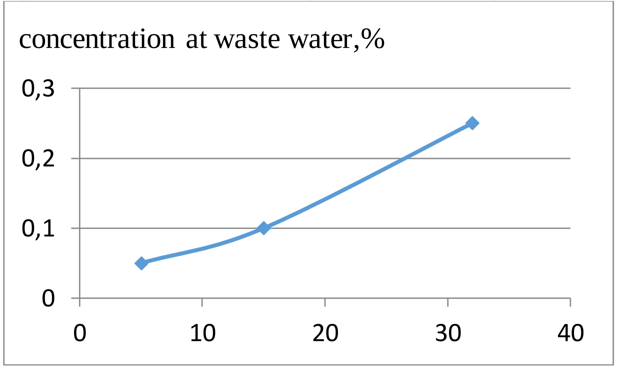

Fig. 6. Change in concentration in waste water depending on filtration rate

From all the above results, the effectiveness of carbonized walnut shells as a sorbent for use in the process of purifying wastewater from oil impurities has been established.

4.Conclusions

1. A natural environmentally friendly sorbent based on walnut shells has been proposed.
2. The study of the carbonization process shows that the duration of heat treatment at a temperature of 800 0 C and a time of 2 hours is impractical. At this temperature, the final combustion of carbon takes place, and white ash of SGO is formed.
3. Analysis of studies showed that the maximum sorption is achieved when using a sorbent obtained at 400 ° C in the interval of 30 minutes.
4. It has been established that the degree of water purification from oil impurities depends on the filtration rate of the solution being purified.
5. The performed studies have established that the oil capacity of the proposed sample is 4.1 g of oil and it can be used for the purification of oily waters and the degree of purification can be 92%.

5.References

1. Tsupikova N.A. Osobennosti normativov otsenki kachestva vod prirodnikh vodnikh obyektov v RF I ES. [Features of standards for assessing the quality of water in natural water bodies in the Russian Federation and the EU]. Vestnik Rossiyckogo universiteta drujbi narodov. Seriya: Ekologiya i bezopasnost jiznideyatelnosti 1, 65-77 (2016) (in Russ.).
2. Chuikin A.V., Grigoriev S.V., Velikov A.A. Opredeleniye neftyanikh zagryazneniy v vodnikh obraztsakh s ispolzovaniem khromatografii v parakh vodi[Determination of oil contaminants in water samples using chromatography in water vapor]. Neftekhimiya. Izdatelstvo: Rossiyskaya akademiya Nauk 46(1), 65-69 (2006) (in Russ.).
3. Prikaz Rosribalovstva ot 18.01.2010 № 20 “Ob utverjdenii normativov kachestva void vodnikh obyektov ribakhozyaystvennogo znacheniya, v tom chisle normativov predelno dopustimikh kontsentrasiy vrednikh veshestv v vodakh vodnikh obyektov ribakhozyaystvennogo znacheniya”. Zaregistrirovano v Minyuste RF 9 fevralya 2010 g. № 16326.Order of the Federal Agency for Fishery of January 18, 2010 No. 20 ["On approval water quality standards for fishery water bodies, including standards for maximum permissible concentrations of hazardous substances in the waters of fishery water bodies ”. Registered with the Ministry of Justice of the Russian Federation on February 9, 2010 No. 16326] (in Russ.).
4. Yu.N. Zhenikhov, V.N. Ivanov. Organizatsya gosudarstvennogo ekologicheskogo kontrolya [Organization of state environmental control. Tutorial]. Uchebnoe posobie. Tver: TGTU (2010) (in Russ.).
5. Privalova N.M, Dvadnenko M.V, Nekrasova A.A, Popova O.S, Privalov D.M. Issledovaniye metodov ochistki vod ot zagryazneniy neftyu i nefteproduktami[Study of methods of water purification from oil and oil products pollution]. Politematicheskiy setevoy elektronniy nauchniy jurnal Kubanskogo gosudarstvennogo agrarnogo universiteta 113, 307-316 (2015) (in Russ.).
6. Serebrennikova M.K., Tudvaseva M.S., Kuyukina M.S. Biologicheskie sposobi ochistki neftezagryaznennikh stochnikh vod (obzor)[Biological methods of purification of oil-contaminated wastewater (review)]. Vestnik Permskogo universiteta.Seriya Biologiya. Izdatelstvo: Permskiy gosudarstvenniy natsionalniy issledovatelskiy universitet 1,15-30 (2015) (in Russ.).
7. Valiullina V.N., Zabolotskikh V.V. Ispolzovaniye rastitelnikh otkhodov v proizvodstve sorbtsionnikh filtrov[Use of vegetable waste in the production of sorption filters]. Selskokhozyaystvenniy jurnal,2(7),273-276 (2014) (in Russ.).
8. Yamansarova E.T., Gromyko N.V., Abdullin M.I., Kukovinets O.S., Zvorygina O.B. Issledovaniye sorbtsionnikh svoystv materialov na osnove rastitelnogo sirya po otnosheniyu neftyanim zagryazneniyam void [Investigation of the sorption properties of materials based on vegetable raw materials in relation to oil pollution of water]. Vestnik Bashkirskogo universiteta 20(4),1209-1212 (2015) (in Russ.).
9. Vezentsev A.I., Nguyen Hoay T'yau, Gabruk N.G, Oleinikova I.I, Shuteeva T.A Polucheniye uglerodsoderjashikh sorbtsionnikh materialov iz vtorichnogo rastitelnogo sirya[Obtaining carbon-containing sorption materials from secondary plant materials]. Nauchnie vedomosti Belgorodskogo gosudarstvennogo universiteta. Seriya: Estestvennie nauki 40(18),15-20 (2017) (in Russ.).

PP-VI-11

ON THE ISSUE OF RATIONAL PROCESSING OF HEAVY PYROLYSIS RESIN

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Abstract. The dependence of the productivity and composition of heavy pyrolysis resin on hydrocarbon reserves and process conditions has been investigated. As for the additional products containing valuable hydrocarbons as the target product and the combination of their composition and technological pyrolysis regime, it is shown that along with the maximum productivity of low molecular weight heavy olefins, it is possible to achieve significant productivity and qualitative changes in heavy pyrolysis resin. Heavy pyrolysis resins are high-modulus carbon fibers designed to produce high-quality graphite electrodes, high-activated carbon black, various structural carbon materials that allow the production of graphite for nuclear reactors and needle coke, such as abrasive additives, binders, impregnators and fiber-forming tops. can be used in production.

Keywords: technological mode, pyrolysis, heavy resin, olefins, ethylene, propylene, naphthalene, gasoline, aromatic hydrocarbons..

1.Introduction

One of the urgent problems of modern oil refining is the need to deepen oil refining and develop the rational use of oil residues. However, modern petrochemistry has long been not content with oil refining waste (1) and, for the successful, independent functioning of its main branch, organic synthesis (2), a pyrolysis process (3) was developed, around which modern petrochemical complexes are based.

Since the pyrolysis process currently provides raw materials for petrochemical processes, much attention is paid to the development of this process, and the development of methods for improving the process through the rational use of production waste is an urgent task. It is known that the waste of the pyrolysis process is a heavy resin, which has not yet found qualified use.

Published works (4-6) present the results of research works devoted to the rational use of heavy pyrolysis resin.

2. Experimental part

This paper presents the results of a study of the possibility of using heavy pyrolysis resin as a raw material for the production of bitumen.

In (5), the results of a study of the possibility of obtaining bitumen based on heavy resins obtained in the process of pyrolysis with the supply of 10 and 50 wt% to the pyrolysis reaction zone are presented. It was found that at a temperature of thermo-oxidative compaction with oxygen in the air of the oxidation process of 2500C and the supply of water vapor in the pyrolysis process of 10 and 50% of the mass, duration of 10% of hours, on the basis of each sample of heavy resin, bitumen with softening temperatures of 28-670C can be obtained that meet the requirements of GOST 9812-74 for insulating or the requirements of GOST6617-76 for construction bitumen.

Since at present at the Sumgait EP-300 plant, low-octane gasoline is used as a raw material and the supply of water vapor is 20% of the mass for the raw material, we took a sample of the heavy pyrolysis resin, the characteristics of which are given in Table 1

Table 1. Physicochemical parameters of heavy pyrolysis resin

Name	Indicators
Density kg/m^3	1024
Coking, %	11,8
Ash content, % masses.	0,04
Fractional composition:	
Temperature, nK^{0}C	203
10% for, Temperature ^{0}C	221
50% for, Temperature ^{0}C	293
65% for , Temperature ^{0}C	325
Hydrocarbon composition% mass:	
paraffin-naphthenic	3,0

aromatic tar asphaltenes carbenes and carbides	63,2 11,7 15,4 0,4
Flash point, ^{0}C	115
Conditional viscosity, for 50^{0}C for 100^{0}C	 4,86 1,62

The sample taken of the heavy pyrolysis resin was subjected to the process of thermo-oxidative compaction in a laboratory setup at temperatures of 230-2600 ^{0}C, an air flow rate of 1.0-2.0 l/min/kg of raw material and duration - until a product of bituminous consistency was obtained.

The results of the process of thermo-oxidative compaction of heavy pyrolysis resin are summarized in Table 2.

Table 2

Oxidation mode				Material balance,% mass	
Raw materials	Temperature, ^{0}C	Duration, hour	Consumption, 1.0 air, l/min,	Oxidized resin yield	Softening point, ^{0}C
Heavy resin pyrolysis	220	10	1,0 2,0	95,7 95,2	Fluid
	240	10	1,0 2,0	92,3 92,8	24 28
	250	10 15	1,0 2,0	91,7 91,3	40 48

From the data in Table 2, it can be seen that as a result of the thermal-oxidative compaction of the heavy pyrolysis resin at temperatures of 2300°C, the air flow rate is 1.0-2.0 l/min/ kg of raw material, with a duration of 10 parts, the obtained II samples do not meet the requirements of GOSTs for such an indicator of bitumen as softening temperature. However, with an increase in temperature to 2500°C, a product with a softening temperature of 28-300°C was obtained.

With a further increase in the duration of oxidation to 15 hours, a product with a softening point of 510°C is obtained. The quality indicators of bitumen obtained as a result of the oxidation of heavy pyrolysis tar were compared with the requirements of GOST 6617-76 for petroleum and GOST 9812-74 for petroleum bitumens. The results are summarized in Table 3.

Table 3

Name indicators	Bitumen				
	GOST 9812-74		GOST 6617-76		Heavy resin pyrolysis
	BNN-III	BNN-III	BN 50/50	BN 70/30	Heavy resin pyrolysis
Softening point, ˚C	24	63	50	70	28-51
penetration at 250˚C, not less	4	3	4	3	6-4

Thus, our studies have shown the possibility of rational use of the waste of the pyrolysis process - heavy resin, by expanding the raw material base for the production of bitumen.

4.Conclusion

During the study, we learned that the hydrocarbon composition, physical and chemical properties of heavy pyrolysis resin in industrial pyrolysis plants vary depending on the type of raw material, the technological mode of the process and the consumption of highly heated water vapor. The analysis showed that the quality of pyrolysis by-products changes even when some raw materials are processed. In this case, the dominant factor in the pyrolysis process is the technological regime.

5.References

1. Dumskiy Y.V., Cherednekova G.F., Dumskiy S.Y. New processes for the use of by products of pyrolysis of hydrocarbons, News of Volgograd State Technical University, 2014, №1, p.80-82.
2. Sadigov F.M., Mageramov Z.Y, Gadjiev G.N., Guseinov N.A., Geydarli I.I., Gasanzade G.G. - Research of ways of extraction of naphthalene from heavy resin pyrolysis, Abstracts of the Baku International Mammadaliyev Conference, Baku, 2016.p,137.
3. Solodova N.L., Abdullin A.I., Hydrocarbon pyrolysis. -Kazan: p2007-239.
4. Zohrabov E.R., Salimova N.A., Adzhamov K.K. - Obtaining pitch from heavy pyrolysis resin, AOCh, BAKU, 2000, No. 4 p35-37.
5. Akarsh Verma, Laxmi Budiyal, M.R. Sanjay, Suchart Siengchin, Polymer engineering and science, volume 59, issue 10, p2041-2059.

PP-VI-6

MATHEMATICAL MODELING OF MOTION OF THE SOLID PARTICLES IN THE FILTER-COALESCER WASTEWATER TREATMENT

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Abstract. The article describes the method of calculation of the motion of particles in the filter-coalescer wastewater treatment, based on the mathematical description of the motion of the cleaning fluid and the particles in the channel coagulator. It is found that fine particles in the coagulator moving in a stream so that the process of consolidation and coalescence to occur at specific sites in the gap between the cones, with little flow velocity vector changes direction and magnitude that the process provides an efficient aggregation of particles. The length of this section should be sufficient to ensure that the bulk of the particles reached a critical size. This allows the particles to migrate subsequent channel sections coagulator holding particles in the flow, and eliminating such deposition of particles on the internal surfaces of the device even when moving within the annular gap. There scheme of electromagnetic filter of coagulator, two-dimensional scheme of the magnetic coagulator, scheme of epure of speed vectors in the canal of coaguator and scheme of particles interaction in the canal of coagulator are given too.

Keywords: Wastewater Treatment, Coagulant, Mathematical Model Of The Particle, Solid Particles, The Computational Experiment.

1. Introduction

The treatment of discharged water at machine-building enterprise which contains considerable quantity of metal chips and used lubricating-cooling fluid (LCF) is pertaining to great technical difficulties as the emulsions differ with resistance and week biological oxidability of mineral oil, they take the mechanical, physico-chemical and biological cleaning methods very hard. In most cases the operation waste water form low-concentration suspension containing fine particles with dimensions of 0.1-15 micrometer. It may be said that the wastewater of many enterprises forms aggregative stable system [1-6].

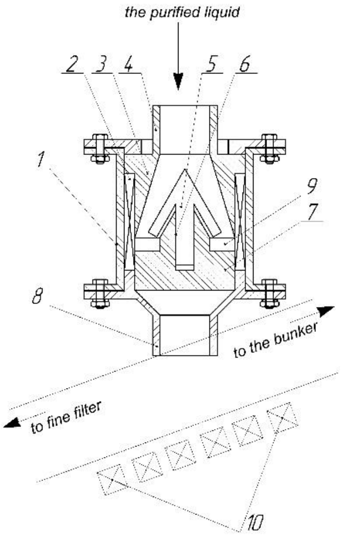
The particles with dimensions of 0.1-5 micrometer and less filtrate with little to no and remaining in suspension state are taken by water flow to extended distance, they are deposited on the internal surface of the aggregates, and it has a negative impact on their working capacity.

However, it is known that in the process of filtration out of wastewater the particles with dimensions of 5-10 micrometer and more are extracted quite easy, that is why the aggregation (enlarging) of the small particles to such dimensions let to manage the process of particles filtration and to fully exclude the settlement of hard deposits on the internal surface of the aggregates in case of right organization of cleaned liquid flow.

There are three methods of aggregation development: electrolytic coagulation, flocculation with hydrophobizated reagents, and flocculation with polymers. For ferromagnetic particles, there are methods of magnetical coagulation [7-10]. The deficiency of majority of the facilities used for coagulation based on prior art is polishing of the internal surfaces because of the settlement of fine particles in the dimensions of 0,3–5 micrometer.

It is necessary to project the machinery, which provides the process of coagulation with the help of modern instrumental facilities, which use the mathematic models of motion of both small and large particles in the flow of cleaned liquid. Such approach allows determining the optimal parameter of the facility providing the effective conduct of process of small particles aggregation. For his reason the issues of mathematical modeling of particles motion, investigation and elaboration of self-cleaning methods of the internal surfaces come to the fore and are important today [11-14].

The paper considers the coagulator, which allows effective magnetizing of the particles and their coagulation in the ramjet mode. For decrease of the particles settlement process on the internal surface of coagulator it is suggested to use the vertical scheme of wastewater flow with the changing speed and flow direction.



Pic 1. Scheme of electromagnetic filter of coagulator

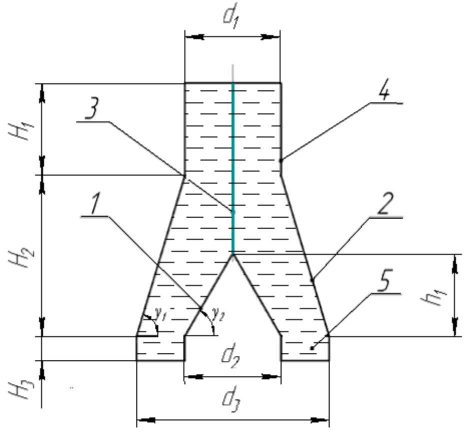
The scheme of coagulator is shown on pic.1. The concerned equipment consists of: main body 1; magnetic field generator 2, inner magnetic circuit submerged in the main body 5, made in the forms of cone with tail 6, which has possibility of central axial movement in reference to the main body and cylindro-wedge member 7, which is situated with the split in relation to outside cone 3; inlet branch 4; grooves 9 slotted in the cylindrical belt of the parts 7 for the liquid flow to the outlet fitting 8; electromagnet system 10.

The equipment is working as follows: the cleaned liquid enters the inlet branch 4, then it goes to the cone backlash of the magnetic circuit of the coagulator, formed by cones 3 and 5. Here the magnification of the particles and their aggregation take place.

Then the liquid containing the large particles flows to the outlet fitting through the grooves 9. After that the separation of the large particles takes place on the magnetic separator and liquid enters the filter of fine purification.

2. Method

On the basis of this model it is planned to create the instrumental facilities of coagulator projectors with the vertical flow of liquid and to receive the recommendations on optimal parameter choice of coagulator. On Pic.2 there is show the scheme of coagulator canal in the in two-dimensional formulation. Also there are shown all dimensions determining the duct geometry of the coagulator, these particular dimensions determine the character of flow motion and the speed in the point of particle location $\overline{V_i} = (V_x, V_y, V_z)^T$, which is the managing effect of the particles flow process in the coagulator canal.



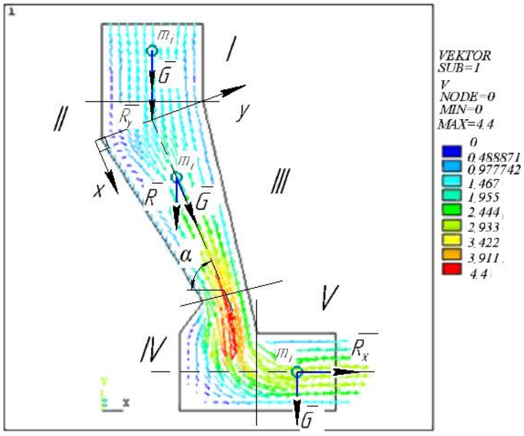
Pic.2. Two-dimensional scheme of the magnetic coagulator
1- Internal cone, 2 – external cone, 3 - reference axis, 4 - inlet fitting, 5 - outlet fitting

3. Results and discussion

For determination of the flow speed the finite-element method was used, which was realized in ANSYS package. Such method of speed determination allows to find the speed of water in any point of cutset of coagulator. For task there were formed the boundary conditions which are determined by duct geometry of coagulator.

3.1. Liquid motion simulation

As the result of modeling the epures of speed vectors are received and the margins of velocity conditions of liquid flow in the canal (see pic.3), on which there is shown the scheme of distribution of velocity vector of the flow points, received by the calculation method.



Pic.3. Epure of speed vectors in the canal of coaguator

Let us consider the flow of fluid on the different parts of coagulator. Let us split the canal section of coagulator into five sections. In Section I the flow speed to the length of inlet branch changes with little to no, and in cross-sectional view in the area of boundary layer it is equal to 0,5 m/s, and in the flow center - 1.5 m/s. In Section II the flow deflection takes place, herewith the form of liquid distribution epure becomes unsymmetrical, but the best speed value on the module scarcely changes, the trajectory of particles here is curvilinear, in these sections in liquid, the fine particles with dimensions of d_i prevail. Further in Section III the stricture takes place, and this causes the growth of flow speed in the flow center from the value of 1,5 m/s up to 4,5 m/s, the calculations show that in this section the uniformly accelerated motion of the liquid takes place. In this section the process of particles aggregation takes place, their size grows up to D_i, but the fine particles with dimensions of d_i also can remain. In Section IV the flow deflection of the liquid through 90^0 takes place, the motion takes places by curvilinear trajectory, the area bordered upon the internal surface of the outlet fitting, where the speed decreases nearly to zero level is seen well. The speed in the flow center which is 4,4 m/s at the start of the section decreases almost to the level of 3 m/s, the uniformly retarded motion of the liquid takes place. In section V the flow goes almost regularly with the speed of 3 m/s in the center. The received velocity fields allows researching the particles motion in the flow on the different sections of the motion. The epure of velocity distribution over a cross section is presented in the form of differential equation.

Equation of curve:

$$V_x = a_1 + a_2 \cdot x + a_3 \cdot x^2$$

The points the curve has to path through:

$$A = [L, 0]$$

$$M = [L \cdot (1 - \cos(\gamma)), L \cdot \sin(\gamma)]$$

$$D = [c, d]$$

3.2. Моделирование движения частиц в канале

In Pic.4. the scheme of particles interaction in the canal of coagulator is presented. Let us consider that each particle is influenced by the force of hydrodynamic resistance determined by the differential speed of the water flow in the place of particle location and particle's own speed, weight force, buoyancy force, and force of magnetic action on a particle. Differential equations of particles motion in the canal in the projection of reference axis are presented as following:

$$m_i \cdot \frac{d\dot{x}_i}{dt} = R^R{}_{xi} + F_{mxi}$$

$$m_i \cdot \frac{d\dot{y}_i}{dt} = m_i g - F_{ai} + R^R_{yi} + F_{myi}$$

$$R^R{}_{xi} = cS\rho\left(V_{xi} - \dot{x}_i\right) | V_{xi} - \dot{x}_i | / 2$$

$$R^R{}_{y_i} = cS\rho\left(V_{y_i} - \dot{y}_i\right) | V_{y_i} - \dot{y}_i | / 2$$

We will determine the forces bringing about the aggregation of particles by the formulas:

$$Fmx_{i,j} = \frac{r_{i,j}}{k_{i,j} + (x_j - x_i)^2 + (y_j - y_i)^2} \cdot \frac{x_j - x_i}{\sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}}$$

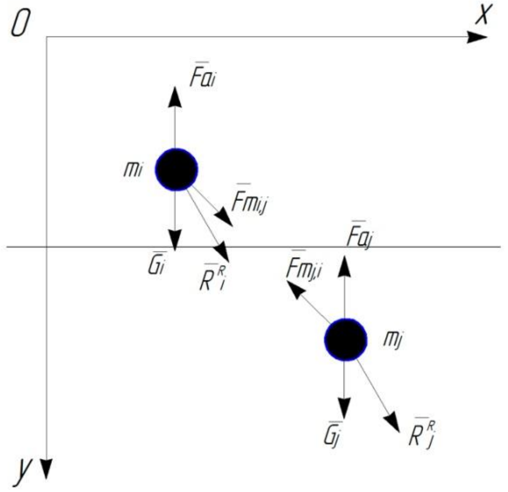
$$Fmy_{i,j} = \frac{r_{i,j}}{k_{i,j} + (x_j - x_i)^2 + (y_j - y_i)^2} \cdot \frac{y_j - y_i}{\sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}}$$

in which r, κ - are the magnetic interaction figures.

If $(R_i+R_j)2 = \delta_{i,j}{}^2$, in which $\delta_{i,j}{}^2$ is squared distance between the particles, then the contact between particles attended by sticking and aggregating takes place. Further on they move together. The equation of such movement is written as:

$$(m_i + m_j)\frac{d\bar{v}_i}{dt} = \bar{R}_i^R + \bar{G}_i + \bar{F}_{ai}$$

Aggregate composed of two particles can join some more particles to itself, or can leave the canal.



Pic. 4. Scheme of particles interaction in the canal of coagulator

For determination of the initial rate of the particles in the 3rd section the flat motion of the liquid in the canal of the coagulator was researched in the 2nd section.

3.3. Results of the modelling

Let us consider that the appearance of a particle in any point at the start of section III of the canal takes place by accident. The size of fine particles changes by the normal law. Modeling the movement of n-particles entering the 3rd section we can study the process of large particles formation in the process of coagulation.

Further on the calculations were conducted for the following parameters

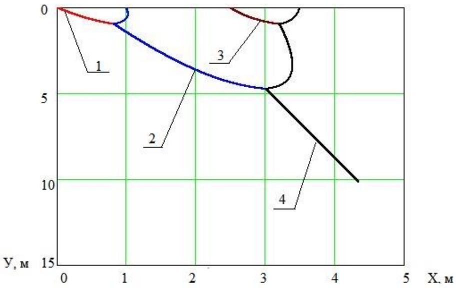
$\mu_{1i}=225$, $\mu_{2i}=15$ и $r_{ij}=3\cdot10^{-11}$

Let us integrate the differential equation for entry conditions:

$x_1=0 \quad x_1=1 \quad x_1=2.5 \quad x_1=3.5$

$y_1=0 \quad y_1=0 \quad y_1=0 \quad y_1=0$

After integration we will receive the functions indicated in pic. 5



Pic. 5. Particles trajectory

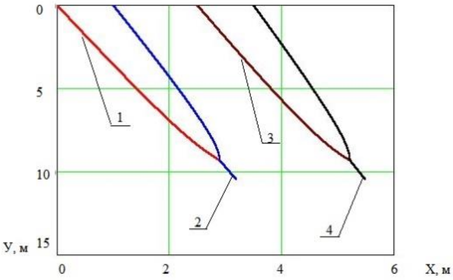
$1-y_1(x_1),\ 2-y_2(x_2),\ 3-y_3(x_3),\ 4-y_4(x_4)$

Let us integrate the differential equation for changed parameters $\mu_{2i}=1$ ***u*** $r_{ij}=2\cdot10^{-12}$ ***and entry conditions:***

$x_1=0 \quad x_1=1 \quad x_1=2.5 \quad x_1=3.5$

$y_1=0 \quad y_1=0 \quad y_1=0 \quad y_1=0$

After integration we will receive the functions indicated in pic. 6



Pic. 6. Particles trajectory

$1-y_1(x_1),\ 2-y_2(x_2),\ 3-y_3(x_3),\ 4-y_4(x_4)$

The analysis of these functions shows that the type of particles motion essentially depends on the parameters μ_{2i}, r_{ij}, k, which determine the forces of particles interaction, and also the size of the particles m_i. You can clearly see the process of particles motion in canal, their sticking and aggregates motion. As the value μ_{2i}, r_{ij} decreases, the distance on which the sticking process takes place increases, and this allows to relate with the magnet field parameters and geometrical dimensions of the canal of coagulator.

4. Conclusion

There is suggested the method of calculation of the particles motion process in the coagulator in the process of effluents treatment, based on the math description of the cleaned liquid and the particles motion in the canal of coagulator.

It is determined that in the coagulator the fine particles move in the flow such as the sticking and enlarging process takes place on the special areas in the backlash clearance between the cones, herewith the speed vector of the flow vary its direction and value only slightly, and this provides the effective process of aggregation of the particles. The length of this area must be enough to let the basis weight of the particles reach the critical size $S=10^{-10}$. This allows to transfer the particles on the further areas of the canal of coagulator holding the particles in the flow and excluding the settlement of such particles on the internal surfaces of the equipment even during the motion inside the circular clearance.

In such a way, the liquid with large aggregates transfers to the zone of magnetic separation and filter. The analysis of the received data allows to make changes into construction of the cone circular coagulation and to length the working surface of magnetic gap, and by this to improve the filter-coagulator set in the complex on effluents treatment. The experimental researches confirmed the received theoretical results.

5.References

1. Ibrahimov N.G., Khafizov A.R., Shaydakov V.V. and etc. Complications in petroleum production, Ufa: Monography, 2003. 302 p. (in Russian).
2. Shaydakov V.V. Development of technical features for petroleum production in complicated conditions. Dissertation on competitioner of academic degree of D.Sc. in engineering. Ufa, 2004. 336 p. (in Russian).
3. Yascun S.F., Safarov D.I. Mischenko V.Y., Loktionova O.G. Vibration machines and technologies. Baku, Elm, 2004, 408 p. (in Russian).
4. Safarov D.I., Yascun S.F. Vibraton technological processes of effluents treatment. Baku, Elm, 2004, 358 p. (in Russian).
5. Hasanov M.M., Ragulin V.V., Mikhaylov A.G., Shaydakov V.V., Nikitin R.V., Laptev A.B., Knazev V.N., Prsiyancev M.N. Perolium production in complicated conditions.– M: Nedra, 2000, 653 p. (in Russian).
6. Inushin N.V., Kashtanova L.E., Laptev A.B., Mugtabarov F.K., Khaydarov F.R., Khalitov D.M., Shaydakov V.V. Magnetic treatment of the industrial liquids - Ufa: State publishing house of the scientific technical literature ‘Reaktive’, -2000.-58 p. (in Russian).
7. Inushin N.V., Ishemguzhin E.I., Kashtanova L.E., Laptev A.B., Maximochkin V.I., Khaydarov F.R., Shaydakov V.V Apparatus for magnetic treatment of liquids. - M: 000 ‘Nedra-Businesscenter’, -2001.-144 c. (in Russian).
8. Patent № 69859 RF, MPK C 02 F 1/48 Coagulation device for ferromagnetic particles of fluids and gases / Shaydakov V.V., Musayev M.V., Chernova K.V., Poletayeva O.Y., Shaydakov E.V.; ‘Engineering company ‘Inkomp-neft’ LLC. - № 2007136705/22; stated on 03.10. 07; published on 10.01.2008 // Bul. 2008. № 1. p. 13. Electronic academic periodical ‘Petroleum Engineering’, 2011, № 4 http://www.ogbus.ru 113 4. (in Russian).
9. Shaydakov V.V., Urmancheev V.V., Poletayeva O.Y., Balapanov D.M., Musayev V.M., Shaydakov E.V. Coagulation of mechanical admixtures in liquid flow // Petroleum engineering. 2009. № 9. p. 53-55 (in Russian).
10. Khurshudov A.G., Zalyaliyev M.A., Plechev A.V. Nikiforov S.Y. Prevention of barium sulfate scale buildup by magnetic fluid conditioning // Development and exploitation of oilfield, 1995. -N5.- p.56-58. (in Russian).
11. Khasanov M.M., Ragulin V.V., Mikhaylov A.G., Shaydakov V.V., Nikitin R.V., Laptev A.B., Knazyev V.N. Influence of magnetic field on carbonate scale buildup at wells // Electronic academic periodical ‘Petroleum Engineering’. 2002. №2. (in Russian).
12. Mirzajanzadeh A.Kh., Khasanov M.M., Bakhtizin R.N. Etudes on modeling complex systems of petroleum production. Non-linearity, nonequilibrium, indefiniteness: monograph. UGNTU. Ufa: Petroleum Engineering, 2009. 431 p. (in Russian).
13. Bakhtizin R.N., Panakhov G.M., Guseynov V.G. Rheological flow phenomena of liquids with filling materials // Electronic academic periodical ‘Petroleum Engineering’. 2015. №1. C.178-200. URL: http://ogbus.ru/issues/1_2015/ogbus 1 2015. p.178-200. (in Russian).
14. Safarov D.I., Yemelyanova O.V., Loktionova O.G. Modelling of pollution particles motion process in liquid flow. News of the South-West State University. 2012. № 4-2 (43). C. 225-227 (in Russian).
15. Loktionova O.G., Safarov D.I., Yemelyanova O.V. Research of the particle motion in liquid flow during effluents treatment. News of the South-West State University. Series: Technics and technologies. 2012. № 2-1. p. 163-172. (in Russian).

VII. Stages of development of petrochemical industry.

OR-VII-1

THE HİSTORY OF AZERBAİJAN’S OİL İNDUSTRY (İN THE EARLY XIX-XX CENTURY)

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Abstract. The article is about the history of the Azerbaijani oil industry, the information of Masudi, Marco Polo, Adam Oleari, the instructions of Peter I on Baku oil during the occupation of the Caspian littoral territories by invading the territory of Azerbaijan in 1722-1723, the important role of the oil factor in the Russian occupation of Northern Azerbaijan in 1801-1828, the transfer of oil wells belonging to the Baku khan to the tsar’s treasury.

It was also discussed about the tsarist government which completed the military-political conquest of northern Azerbaijan, facing great difficulties in appropriating this country economically in the first 30 years of the XIX century, after the reform period (60s years of the XIX century) impact of Russia’s growing oil industry on growing oil demand on Azerbaijan’s oil industry, severe impact of the economic crisis in Russia and in Europe on the Baku oil industry in the early 80s years of the XIX century, during the second half of the 1980s, the impact of industrial growth on the development of the oil industry during the second half of the 80s.

Talking about the open and close competition between local and foreign companies for the acquisition of oil fields during the study, extremely hesitant and contradictory attitude of the Russian authorities to this process, the entry of Azerbaijani oil into world politics, the re-emergence of the oil issue on the eve and during the World War I, the struggle between Great Britain, the USA, France, Germany and the Ottoman Empire for new sources of oil during the war it was concluded that oil has become a key factor in victory in the war. If the warring parties had more energy sources and used them more efficiently, there would be no doubt that victory would be in those bloc countries.

Keywords: Azerbaijani oil industry, XIX-XX centuries, Great Britain, Russian invasion, Ottoman, Germany, struggle against Azerbaijan oil

1. Introduction

Azerbaijani oil has historically been in the interest of foreign countries. From the beginning of the XIX century Russia has taken the path of occupation to seize Azerbaijani oil and unfortunately, this was eventually achieved. Northern Azerbaijan was occupied by Russia. Beginning in the late XIX century, Azerbaijani oil began to attract the attention of European big companies.Since the beginning of the XX century, the struggle for Azerbaijani oil has intensified. During the First World war, this struggle changed from an intercompany struggle to an interstate. Even a lot of statesmen, politicians, military figures and researchers linked the fate of the victory to Azerbaijani oil. During the First World War, Azerbaijani oil was able to influence world politics. So, the historical problem of the Azerbaijani oil industry is scientifically actual.

The history of Azerbaijan’s oil industry is very old. One is found information dating back to the first centuries AD about Baku oil. The famous arabian historian of the X century Masudi wrote about black and white oil. Italian traveller Marco Polo of the XIII century reported about Baku oil. Adam Oleary, a famous German traveller who travelled the shores of the Caspian Sea in 1636, wrote that we had seen with our own eyes that large quantities of special oil were extracted and transported in carts for sale. [29 p 477]

At the beginning of the XVIII century undergoing extensive invasions the Russian Empire attaches great importance to Baku and the shores of the Caspian Sea. In 1722-1723, Russia invaded Azerbaijan and seized the Caspian coast through open military intervention. At that time, Peter I ordered the commander-in-chief of the Russian military forces in the region, General Matyushkin, to send or bring as much oil as possible from Baku. [15 p 604]

The Russians, who captured Baku in the summer of 1723, declared all the treasury and proceeds to the tsarist treasury. The Russian treasury received up to 50 thousand manat a year from Azerbaijani oil sources.[9 p 48]

The oil factor along with political and military factors also played an important role in the Russian occupation of Northern Azerbaijan in 1801-1828. After the occupation of Baku khanate by Russia, oil wells belonging to Baku khan were transferred to the tsar’s treasury. According to some Russian-language sources, the annual income of the khan’s treasury from these oil wells reached 1.000.000 manats (70.000 roubles in Russian currency). [19 p 104]

Padjitnov, one of the researchers of the Azerbaijani oil industry, basing on different archival materials, came to the conclusion that as soon as the Baku Khanate was captured, the oil wells became the property of the Russian state. After occupation Russia's colonial authorities tried to make as much money as possible from the newly occupied territories, but it was difficult to find concrete ways to achieve this goal. In the first 30 years of the XIX century, completing the military-political conquest of Northern Azerbaijan the tsarist government faced great difficulties in economically appropriating this land. In the post-reform period (sixty years of the XIX century), as a result of the growing demand for liquid fuels in Russia's growing industry and the gradual penetration of Azerbaijani oil into Russia's domestic markets, oil production in Baku expanded rapidly from the early 1960s to 6-7 years from 377 thousand poods, it reached 1.73 million pods. There were already 17 oil refineries in the Baku region in 1867. [27 p 280]

In the early 1980s the economic crisis including Russia that engulfed Europe struck a blow to all sectors of the Baku oil industry in the middle of this year. Drilling and production were extremely limited, trying to escape the huge reserves of extremely cheap oil the industrialists burned it, dumped it into the sea and lakes. [23 p 18] In 1886 H.Z.Tagiyev was forced to offer oil free(without money) to oil buyers after the strong oil spills that hit his Bibiheybat field and flooded the surrounding fields. [21 p 77]

But during the second half of the 1980s the recession was first replaced by a revival and then by an industrial boom, demand for oil and the price of oil rose as a result of the expansion of transport and the transition to oil. Oil production compared to 1983 increased 4-5 times in 1891. The scale of technical equipment of the mines was also expanding, the perfection of the applied equipment was increasing.

If there was only one company that produced more than a poods of oil in the early 80s of the XIX century in Baku more than 10 million poods, eight such companies produced two-thirds of the oil. The level of concentration in the oil refining sector was higher. In 1980 only 9 percent of refineries produced 75 percent (51 million poods) of oil products. [22 p 10-11]

From the end of the XIX century Azerbaijani oil began to play an important role in international relations. Azerbaijani oil entered world politics with the boom of the well drilled in Balakhani. The interest of foreign oil companies in Baku has increased, the investment of different countries in the oil industry has increased. During the World War I the oil problem came up again. The period of the World War I plays an important role in the struggle for Azerbaijani oil. Military operations were also carried out for oil during the war. Oil was a major factor influencing the foreign policy of the participating states during this period.

The United Kingdom understood the importance of oil much earlier than other countries during this period. One of the main directions of his foreign policy was to capture oil basins that the United States has not seized yet. Winston Churchill said that first of all, we must create oil reserves in our country, then we must gain the right to buy raw oil at a low price, and the last we must have control over oil sources. [20 p 50] 45% of the British fleet worked with oil at the beginning of the World War I. Then the transition to oil refining of other ships was accelerated at the request of the Ministry of the Navy. [12 p 30-31 British capital and companies operating in Baku played an important role in this affair. They began to aspire more to the Baku oil region. There were 11 British enterprises which capital was 39.4 mln roubles in Baku in 1902. In 1893-1903 47 mln roubles of 63.6 million roubles invested by the British fell to the share of Baku oil region. [13 p 32-36] There were already 50 British enterprises which capital were 293.3 million roubles in 1910-1913 in different oil regions of Russia.[6 p 46]. During the World War I two giant military-political blocks, the Entente and the Alliance of the Three and the geopolitical struggle in the Middle East between Soviet Russia were gaining control over the Caspian region. The key to his geopolitical success was to take over Baku, the largest industrial center in the Caucasus, which supplied more than 95 percent of Russia's oil. [5 p 75] The main cause of tension between Britain and the USA was the issue of Mosul oil and Azerbaijan oil. [2 p 9]

In the late of XIX century and the early of XX century Azerbaijan was the first in the world in oil production. The reason for the rapid increase in oil production in Azerbaijan is due to the extremely rich oil fields, the availability of cheap labor and the introduction of technical innovations. Bashkir historian Valiahmedova writes that oil was an important factor in the struggle for oil in the sharp international conflicts and eventually led to the World War I. [28 p 16] The British oil expert V.Ch.Childs expressed the huge role of Azerbaijani oil in international relations during the World War I so: " If there was not Baku oil, the events of 1914-1921 would not have been the same as the events in the Middle East. [1 p 58] During that period the basis of the USA oil policy was the struggle for sales markets. At the beginning of the XX century american capital was very weak in the Azerbaijani oil industry. But the USA's interest for Azerbaijani oil increased during World War I. There was no oil products center in

France at the beginning of the World War I. So in connection with the supply of oil the country appealed to the Royal Dutch, especially Standard Oil.[10 p 17] French capital in the person of Rothschild penetrated Azerbaijan in the 80s of the XX century.

German capital was interested in owning Azerbaijani oil through the Nobel Brothers. The relations of the company expanded with German capital at the beginning of the XX century. The German corporation company owned 40 percent of Nobel's shares. At the same time, the German capital had a connection with the Lionozov Oil Production Company in Baku. Some of Western European companies united against Standard Oil during this period. Germany played one of the important places in the transportation of Baku oil in 1910.[18p83] Germany had already won third place in this field on the eve of the World War I. If in 1986 oil products transported from Baku to Germany accounted for 12% of total transportation, in 1903 this pointer reached 17.9%. Germany was in the third place due to the demand for Baku oil among European countries. Soon the British and French pushed Germany into the background. The demand for Baku oil has also increased in the Ottoman state. Ottoman Turkey has become an important market for Baku's oil products since the late of the XIX century. It should be noted that since 1895 kerosene exported from Baku to Turkey was 585890 poods, while in 1897 this figure reached 4.618.791 poods. [1 p 60]

In 1914 Russia extracted 67020 thousand barrels or 16.4 percent, in 1915 68548 thousand barrels or 14.3 percent, in 1917 69960 thousand barrels or 13.8 percent of world oil. [16 p 80-81] For example, in 1913 only 561,3 million poods oil was extracted. 467 million poods fell to the share of Baku oil region. It is known that if in 1901 there were 83 companies engaging in the transportation of oil from Baku, in 1915 their number was 43. The number of companies selling oil about 10 million poods was 32 in 1901 and 31 in 1915. The number of companies selling oil more than 10 million poods was 11 in 1901 and 12 in 1915. So, in a short period of time, 50 percent of medium and small enterprises selling oil have gone out of business. Twelve big companies concentrated 90 percent of oil sales. The largest trade organization was the Nobel Brothers Society. It shared about 27 percent of the oil extracted from Baku. The second largest Caspian-Black sea society accounted for 10.5 percent of Baku's oil production.[24 p 169]

400.000 tons of oil shipped annually to European ports on the eve of the war by rail and pipeline between Baku and the Black Sea. Oil production fell by a total of 40 percent between 1914-1918 Although Baku oil was declining, 4/5 of Russia's oil still fell to the Baku region.[18 p 21] In 1913 270.1 million poods oil, in 1914 244.6 million poods oil, in 1915 319.7 million poods oil, in 1916 337.1 million poods, in 1917 281.5 million poods oil was transported from Baku via the Volga.[24p172] Both the tsarist government and the oil industry bourgeoisie were unable to see in advance the economic shocks of the World War I.[7p14]

Noting the impact of economic factors on international relations Miryagub Mehdizadeh wrote that the largest of these factors is undoubtedly oil. Oil is also the biggest force behind the success of the general war. The only driving force behind many vehicles as railways, military equipment, tanks, cars, planes is petroleum products such as oil and gasoline. The most natural answer to the politicians' question consisted of this sentence: "Whoever has the world's oil resources, the victory is definitely his".[2 p 8] The February revolution in Russia completely changed the socio-political and social situation of the empire. The Bolshevik coup strengthened the movement for autonomy and independence of the colonized peoples in Russia. The Bolsheviks began to seize Azerbaijan shortly after the coup contrary to the principles they proclaimed. The analysis shows that the main purpose of the occupation of Azerbaijan was to own oil. As a result, Baku was occupied by the Bolsheviks. Violent establishment of Bolshevik government in Baku, threat of oil ownership met with resistance of Azerbaijan national forces. After the establishment of the Baku People's Commissariat during the first three months 1.5 million tons of oil were sent to Russia. [3 p 93] The nationalization carried out by the Bolsheviks began to worry foreign companies with capital in the Baku oil industry.

The warring states after the collapse of the Russian Empire began to aspire to Baku, a major source of fuel that could play a main role in the fate of the war and account for 83 percent of Russia's oil production.Oil has become a main factor in victory in the war. If the warning parties had more energy sources and used them more efficiently, there would be no doubt that victory would be in those bloc countries. Bolshevik Russia, together with its Russian allies, used Azerbaijani oil against the German bloc for common purposes. The withdrawal of the new Russian government from the war created favorable conditions for the attack of German and Ottoman armies in the direction of the South Caucasus. [24 p 125] The situation did not satisfy both bloc states. When Russia announced its withdrawal from the bloc of its former allies, the Alliance took more decisive action. Baku oil and the geopolitical position of Azerbaijan became more important.

The United Kingdom was trying to acquire the strategically important Caspian Sea, primarily Azerbaijan oil. The seizure of Azerbaijani oil had a special place in the foreign policy of the British government. British magnates were particularly interested in the Baku oil industry and considered it a great blessing. British authors E.Q.Davenport and Sydney R.Cook write that Baku was the basis not only for the development and distribution of oil resources in the Caucasus, but also in Northern Iran and Turkestan. The English magazine "Middle East" in 1918 wrote: There is no other country as Baku to its oil in the world. Baku is the largest oil center in the world. If oil is a kingdom, Baku is its throne." [26 p 115]

General Dansterville elaborated on the essence of the British policy of acquiring Azerbaijani oil so: "The capture of Baku can give us the following results: closing the enemy's access to oil reserves and its doors to Central Asia. The seizure of oil reserves would have disrupted trains on the South Caucasus Railway, which was largely dependent on Baku's oil resources. Baku is very important. Every risk taken to obtain it would be justified."[11 p 14]

The importance of the Azerbaijani oil factor has moved the British government in this direction. The British government decided to send an army to Baku in December 1917 But the British were unable to attack Baku.

At the same time Germany became more active in the struggle for Azerbaijani oil. The main reasons for this activity of Germany were as follows: at the beginning of the war, when the Germans could not get the Mesopotamian oil from the British, Romanian oil did not fully meet their needs, they began to pay special attention to Azerbaijani oil. As a result of the revolution Russia's withdrawal from the war created favorable conditions for the German bloc countries, especially the Ottoman Empire, in the South Caucasus.

The occupation of Baku was of great economic, political and military significance for Germany. Getting Baku oil will provide Germany with raw materials, remove it from the blockade of the Allies, allow the population of German colonies living in the South Caucasus to enter the Alaman army units.

Accessing new sources of oil remained a main problem for the British Empire during the war. On the eve of October 1917 the British owned Baku oil industry supplied 60-70 percent of all Baku oil.[25 p 11] The British Minister of War Milne told the British Army Command in Mesopotamia that the Royal Government attached great importance to the establishment of permanent control over the Caspian Sea. [17 p 83]

The states fighting for Azerbaijani oil considered all the means they used acceptable. The American researcher Louis Fischer writes it is necessary to understand that it is easy to take big risks getting Baku's oil lands. [14 p 12]

Russia did not intend to give Baku to anyone although it did not have enough power. Only Baku oil could save Russia from economic decline as a result of the World War I and the Bolshevik coup. [1 p 21]

Russia's withdrawal from the war raised the issue of the Ottoman state's struggle for Azerbaijani oil. Azerbaijani oil began to play an important role in international relations again from the end of 1917. The intensification of the struggle for oil was due to the socio-political situation in Baku. The Turkish historian writes that Soviet government was afraid of implementing the principles of "the Declaration of the Rights of the Russian People's" in the Caucasus. This would lead to the loss of oil in the Caucasus and Baku.[4 p 479]

The Allies wanted to prevent the Bolsheviks from owning Baku oil, spread Bolshevism in the region and seize Baku oil by helping the newly formed South Caucasus Commissariat. Baku oil could play a key role in the Allies' victory in the war. According to the US government, Bolshevism will gain and strengthen by seizing oil in the South Caucasus. Russia's withdrawal from the war would strengthen the Germany bloc countries.

After the beginning of Brest-Litovsky peace between Russia and Germany the policy of the Allies on Baku oil has become even clearer. The end of December 1917-the beginning of January 1918 the official circles of the Allies began to make open statements about establishing relations with Caucasian governments and assisting patriotic forces in the region.This situation allowed the Ottoman Empire to gain an advantage on the Caucasus front. From the beginning of 1918 the Ottoman Empire began to pursue an active policy towards Azerbaijan. At that time, the Germans involved the Turks in a military operation against the British and wanted to own Baku and Baku oil themselves. Although the Turkish attack met the general military goals of the Allies, the Germans opposed it in their own interests. At the same time, the British took action to prevent the Germans and Turks from owning Baku oil. The local population did not like the British, but mainly the Turks. During this time the Baku oil region mainly met the needs of Russia. In Baku in January 1918 18.5 million poods oil, in February 15.9 million poods oil, in March 12.5 million poods oil, in April 12.8 million poods oil was extracted. [8 p 1-3]

The genocide against Turks and Muslims in March and the conflict of interests of the states with claims in the region first of all encouraged the Ottoman Empire to take more active action for AzerbaijanThe USA also followed the Turkish attack on Baku and tried to prevent it. During the Turkish attacks, the press reported that Batumi was a very important city for Turkey. Because the pipelines of Baku, a famous oil center on the shores of the Caspian Sea pass through this city. Baku’s big oil trade will come under Turkish control with the capture of Batumi.

Although Germany tried to separate the South Caucasus from Russia, it was jealous that it was carried out under the control of the Ottoman state. Because Baku oil played an important role in Germany’s plans for Azerbaijan.

So getting new cheap sources, gaining a favorable market had a special place in the oil policy of foreign countries in the early XIX-XX centuries. Special attention was paid to Azerbaijan in this policy.

-The struggle between the great powers in the South Caucasus was mainly for Baku oil from November 1917 to May 1918. The Allies took measures to seize Baku oil as soon as the talks between Russia and the German bloc countries began in Brest-Litovsk. According to the signed documents, the annexation of the South Caucasus to the British sphere of influence was announced. But at that time the British did not have large opportunities to acquire Baku oil.

-Azerbaijan’s liberation from colonial slavery establishment of the republic, the socio-political outcome of the World War I for the people of Azerbaijan was a historical event. Azerbaijani oil had become a main condition for victory by the end of the war. Baku oil began to play an important role in international relations even after the proclamation of the Azerbaijan Democratic Republic. The Azerbaijani oil factor played an important role in some issues as the Batum treaty signed between the Ottomans and Azerbaijan, the Ottoman-Azerbaijani-Georgian agreement on oil exports between Baku and Batumi, the USA special interest in Azerbaijani oil, the invitation of the British to Azerbaijan and the acquisition of Baku oil, Russian-German talks on Baku oil, Baku oil due to Turkish-German contradictions and so on. There was a fundamental change in the position of Baku oil in international relations after the defeat of the Ottomans and the Treaty of Mudros. The struggle of the Allies for Azerbaijani oil has intensified.

5.References

In Azerbaijani and Turkish

1. Gasimov M. Azerbaijan policy of the great powers during the World War I (1914-1918). In 3 parts. I part. Baku: Kanun, 2000, p. 58
2. Mehdizade M. Petroleum in international politics. Baku, Azerneshr, 1994, p.9
3. Suleymanov M. Oil millionaire. Baku: Azerbaijan Publishing House, 1996, p.93
4. Kurat A.N. Turkey and Russia. Turkish-Russian relations from the end of the XVII century to the war of liberation(1798-1919). Ankara;1970, 479

In Russian

5. Aliyev I. Azerbaijan Caspian oil. M.; Izvestia, 2003, p 75
6. Akhundov B.Y. Baku oil industry’s mono-political capital before revolution. M.; Stsekzidat, 1959 p 46
7. Aliyarov S.S. Oil monopolies in Azerbaijan during the World War I. Baku:izd. AQU,1974, p. 14
8. Baku oil industry at the third half of the 1918. Magazine. “Oil works”, 1918, 27 maya, №9-10, p. 1-3
9. Butkov M.Q. Materials for new history of Caucasus, Kn I.-Spb, 1869, p48
10. Delezi F. Oil.Trans. of frants. I.Markels and Kh. Rit. M.; New Moscow, 1923, p 17
11. Denstervil L. British imperalism in Baku and Iran. 1917-1918 Memories Trans.from Eng. B. Rudenis. Tbilisi: Soviet Caucasus, 1925, p. 14
12. Devenport E.Q., Sydney R.Kuk. Oil issues and english-american relations. Trans. of eng.A.F.Speranskovo. M.:Izd. Military news, 1925, p 30-31, 130
13. Eventov L. Foreign capital in oil Russia. M.L.:Izd. Planning economy, 1925, p 32-36
14. Fisher L. Imperialism oil. Oil international war. Trans.american press .St. Volskovo. M.L,:Qosizdat, 1927, p 12
15. Komarov V. Persian war 1722-1725 years. Russian news, t.68. 1869, p 604
16. Kodzishevskiy E.A. Russian oil in the world market.M: izd. BSNX,1924, p. 80-81
17. Lavrov S.B. English policy in Caucasus and Middle Asia 1917-1919. Magazine , “Historical questions”, M.;1979, №, p. 83

18. Lespanol de lya Trameri P. World War for oil. Trans.from frants. L.Tumermana. M.;Izd. Military news, 1925, p. 83-85
19. Mamedov A. (1800-1872 years)-Historian Markist, Kn 4, 1936, p.104 Azerbaijan oil industry after the abolish of the ransom system
20. Merkis F. Black blood, Per.s.nem. Predsl.N.A.Simonia. M.: 1978, p 50
21. MKNPR. 1883-1914 years. p. 77
22. Nardova V.A. The beginning of the Russian oil monopoly. 1880-1890 years.L. 1974, p 10-11
23. Overview of the Baku province for 1888, p. 18
24. Pajitnov K.A. Essays about the history of Baku oil discovery (from the late XVII to Great October Revolution), M., L.: State scientific and technical oil industry and alpine literature., 1940, p. 172
25. Pavlovich Mikh World oil war. M.:Young guard, 1923, p. 11
26. Seyers K., Kan A. A secret war against the Russian Empire. M.: state press of foreign literature. 1947, p. 115
27. Sumbatzadeh A.S. Azerbaijan industry in the XIX century. p.280
28. Valiakhmedova Q.H. The struggle of the great powers and oil companies for Iranian oil (1921-1918-years.). Candidate of Historical Sciences Ekaterinburg, Uralsky University, 1999, p. 16
29. Oleari A. Description of the trip to Moscow and description of the trip from Moscow to Iran and back. -Spb, 1906, p.477

PP-VII-2

SUPERPHOSPHATE PLANT İN THE 70-80s OF THE XX CENTURY

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Abstract. The article discusses the achievements of Sumgayit Superphosphates in the 70-80s of the XX century, improving the quality of labor productivity, adherence to the economy mode and timely fulfillment of commitments. At the same time, chemists who put forward rationalization proposals have managed to improve the quality and reduce the cost of production.

As a result of the exchange of experience of chemists with other Republics of the Union, the intensity of production has significantly improved, the annual output has increased, and serious shortcomings in production have been eliminated. During the Soviet regime, in order to increase production, contracts, agreements and commitments were made between workshops, brigades, shifts and individual chemists on the socialism race. It was mentioned that the products produced at the plant are exported to Georgia, the North Caucasus and the Central Asian Republics.

Keywords: Superphosphate plant, fertilizer production, chemical industry, rationalization proposals, plans and commitments

1.Introduction

The Superphosphate plant occupies one of the significant place in Sumgayit chemical enterprises. This plant has played an important role in the development of agriculture and increasing productivity. In the 70s and 80s, production increased even more and met the needs of the Union Republics along with domestic demand.

In the 70s and 80s of the 20th century, Sumgayit Superphosphates were successful in all areas of the economy. They managed to increase labor productivity by more than 20 percent against the plan, improve quality, and save a lot of money. At the same time, they made a doubled commitment and fulfilled both with honor, sending more than 80,000 tons of "soil vitamins" to agriculture in addition to the plan. In general, the staff of the enterprise prepared more than 750,000 tons of valuable fertilizers in the decisive year and sent them to the state and collective farm fields. [25]

Over the years, most of the substances on Mendeleev's schedule began to be produced in Sumgayit. Numerous chemical plants were located in a small area. [23 p17]

Workers of the superphosphate workshop prepared 199,000 tons of soil "vitamin" instead of 185,000 tons in three months. According to the commitment, it is planned to produce 12,000 tons of products a year in addition to the plan. However, instead of 12,000 tons per year, 14,000 tons of additional fertilizer was produced in three months. If the annual commitment is compared to the three-month work, 754 tons of anatit instead of 75 tons, 10,650 hectocalories of heat energy instead of 3,750 hectocalories, and 21,881 kilowatt-hours of electricity instead of 12,500 kilowatt-hours were saved during that period. Our chemists have submitted 26 rationalization proposals in three months. Of these, 14 were licensed for production. [27]

The staff of the superphosphate workshop produced 263.5 thousand tons of mineral fertilizers in four months, exceeding its annual socialist commitment. [22]

In a simple superphosphate workshop, the raw material transfer scheme is the most complex process. The current structure of this scheme has not been able to meet demand for a long time. Specialists brought the simplest form of the scheme from the Kedainiai chemical plant in the Baltics, and the intensity of production has significantly improved. The previous scheme in 1973 alone caused 1,300 hours of idle time in the superphosphate plant's chambers. As a result, apatite passed through a number of carriers before entering the cells, contaminating the apparatus and causing great losses. On the other hand, it was necessary to maintain a common line to stop any equipment. The new scheme eliminated the tires, elevators and transporters in the system. The dosing that replaced them ensured that the raw material was fed directly from the hopper to the mixer. [10]

As a result, 9 technicians were transferred to another field, the annual output increased by 50,000 tons, and a number of spare parts were no longer needed. Carrying out the process in an optimal mode accelerated the process of separation of fluorine gas, eliminated serious shortcomings in the process of its conversion into acid and its transfer to the fluorine-aluminum shop. Special attention is paid to the study of best practices in the sulfuric acid workshop, which supplies the enterprise with raw materials. If last year 51 proposals on the scientific organization of labor were implemented at the plant, most of it falls on the share of the workshop. Taking advantage of the achievements of best practices, the workshop team has been operating at project capacity since april, improving its technical and economic performance from month to month. [10]

The extremely gratifying results achieved by the workers of the "Fertility Factory" in the decisive third year of the ninth five-year plan are well known to all. They took an active part in the All-Union Socialist race last year (1972) and signed the first victory report in our city. It is also 1 month and ten days ahead of time. [9] From the beginning of october 1974, the staff of the Superphosphate Plant prepared 591,300 tons of high-quality fertilizers as well as 1 month ten days early. This is 36,470 tons more than the plan for that period. At the same time, the collective plans to produce 6,000 tons more fertilizer than in the control figures of the ninth five-year plan for 1975 and to increase the total volume of production to 810,000 tons. New sulfuric acid and granular superphosphate production was planned for the fourth quarter of next year (1975). [24]

The superphosphates of the "Fertility Factory" fulfilled the 10-month plan in 9 and a half months. During that period, they sold "soil vitamin" worth about 1 million manat to collective and state farm fields at the expense of the obligation. Superphosphate producers adopted a tense and reciprocal plan for 1975, undertook to increase annual superphosphate production to 810,000 tons. [8] In the first half of 1975, superphosphates provided 115 percent of the production plan and 111.4 percent of the sales order. Supphosphate producers have managed to significantly increase sales compared to the same period last year (1974). The volume of production increased by 14.9%, sales - by 11.3%. In general, 1 million 780 thousand manat worth of products were supplied during this period, more than 1 million 224 thousand manat worth of soil "vitamins" were sent to customers. The plant itself had 17,700 tons of superphosphate fertilizer left. [12]

The granular superphosphate workshop of the superphosphate plant fulfilled the plan by 127.9 percent in the first half of 1975. In addition to the plan, tons of products were produced and sent to rural workers. The team also worked effectively in July. The plan was implemented by 12 percent. The chemists worked productively in the first decade of august. The plan was fulfilled by 175 percent. [21]

The superphosphates worked hard in the final year of the ninth century. September was successful for the workers of the granular superphosphate plant. The monthly plan was fulfilled by 180 percent. [7]

Unlike the eighth five-year plan, from the first year of the ninth five-year plan, contracts and commitments were made between the workshops, brigades, shifts, and individual chemists concerning the socialist race. The products produced at the plant were exported to Georgia, Armenia, the North Caucasus, the Central Asian Republics and rural areas of Azerbaijan. New lines were launched in simple superphosphate and sulfuric acid workshops. If in 1971 the "Fertility Factory" produced a total of 12 million 286 thousand manat, in 1874 this figure reached 24 million 87 thousand manat. In 1974 alone, 4,781,000 manat worth of goods were produced due to liabilities. In the final year, 109,847 tons of granular superphosphate and 41,783 tons of microelemented granular superphosphate were produced. 809,000 tons of simple superphosphate were prepared and sent to rural workers. In 1971, 447,344 tons of products were produced in the simple superphosphate workshop. A year later, this figure reached 583,000 tons. In 1973, 711,821 tons of "vitamin" were produced. In 1972, instead of 700,000 tons, 810,000 tons of high-quality products were produced. If 62.6% of the annual plan was fulfilled in the first year of the five-year plan, 115.7% of the plan was provided in the fourth year of the five-year plan.

In the ninth five-year plan, labor productivity increased significantly and the cost of fertilizer produced was reduced. In 1974, labor productivity increased by 68 percent compared to 1972. Compared to the eight months of 1973, the cost of production during the same period in 1974 was reduced by 9.2 percent. Due to the reduction of cost alone, the company received an additional income of 260,000 manats. The acquisition of better quality micronutrient simple and granular superphosphate can be considered an important achievement of the ninth five-year plan. If in 1972 141 rationalization proposals were applied to production and 212 thousand manats of income was received, in 1974 the number of rationalizers was increased to 202, and the income increased almost 6 times and amounted to one million 194 thousand manats. In 1974, production increased by 55 percent compared to 1972. [11]

In the final year of the ninth five-year plan alone, the staff of the Superphosphate Plant delivered 30,300 tons of superphosphate fertilizer to the country in addition to the plan. This was 10,000 tons more than what was envisaged in the accepted socialist commitment. In 1975, 48,442 tons of granular fertilizers were delivered to customers in addition to the plan. Workers of the plant planned to increase production by 24 percent in 1976 and sell fertilizers worth 680,000 manat. At that time, it is planned to produce 15,000 tons of simple, 10,000 tons of granular and 5,000 tons of microelement fertilizers. It was intended to reduce the cost of commodity products by 0,1 percent for the plan of the current year. To solve this problem, it was planned to save 70 tons of apatite, dozens of tons of sulfuric acid, 500,000 kilowatt-hours of electricity and 400 tons of conventional fuel. In addition, it is planned to build aluminum workshops, put into operation two production lines in the existing granular superphosphate workshop, and increase productivity by 25 percent that year. [4]

The Sumgayit superphosphates made the following socialist commitments for 1976:

- To fulfill the plan on gross output by december 25, to increase the volume of production by 24.9% compared to last year, to produce goods worth 680,000 manat in addition to the plan, to increase labor productivity by 5% compared to 1975;

-increase the quality of products, reduce the cost of marketable products by 0.5%, save 150 tons of sulfuric acid, 70 tons of apatite, 50 tons of sulfur, 600,000 kilowatt-hours of electricity, 40 tons of conventional fuel;

- to take economic benefit of about 500 manats from the implementation of rationalization proposals, application of new techniques and scientific organization of labor; [19]

The first quarter was productive for the staff of the superphosphate plant. The state plan and socialist commitments were observed in all workshops of the plant. Due to the commitment, 12,500 tons of simple superphosphate, 9,169 tons of granular superphosphate, hundreds of tons of sulfuric acid and fluorinated aluminum were produced. In a simple superphosphate workshop, the amount of phosphate anhydride in the finished product was increased from 18 to 19.5 percent by increasing the rotation speed and power of the reaction chamber. The launch of a drying drum in the Futor aluminum shop doubled productivity and also allowed to release the quality of the purchased product as the first type. During the first three months of 1976, chemists saved 40 tons of sulfuric acid, 50,000 kilowatt hours of electricity, 15 tons of anatite, hundreds of meters of filter material, brought more than 50,000 manat to the enterprise due to technological innovations. By the end of the tenth five-year plan period, chemists had set a goal of increasing fertilizer production to 1.2 million tons per year. [26]

Workers of the superphosphate team achieved high results in 1976. Chemists produced products worth 6 million 490 thousand manat, of which 5 million 717 thousand manat were sold. As a result, the plant sent 37,000 tons of simple, 115,000 tons of granular superphosphate fertilizers to collective and state farms of the Transcaucasian and Central Asian republics. The superphosphate plant started producing sulphate and was delivered to the project capacity 6 months ahead of schedule. Acid products were exported to Ukraine, Kazakhstan and other republics. By september 1976, 264,763,000 tons of high-quality products had been produced and send to customers at the granular superphosphate plant. In 1977, it was planned to create a second granular superphosphate complex at the plant, which would be launched next year and produce 700,000 tons of products together with the previous plant. Thus, by the end of the tenth five-year plan, it was planned to increase the production of granular fertilizers at the superphosphate plant to 1.1 million tons, and the production of simple superphosphate fertilizers to 1.2 million tons.

Great attention was paid to the application of rationalization proposals in creating an abundance of products, increasing the efficiency of work and further improving the quality of products. Thus, 160 proposals applied to production in 1976 saved the state more than 220,000 manat. The collective made high socialist commitments for 1977. According to this commitment, it was planned to produce 850,000 tons of simple, 320,000 tons of granular fertilizers, produce product worth 10 million manat and send 38 million manat worth of products to customers. It was planned to increase labor productivity by 6 percent, to produce additional products worth 1 million manat, to produce 30,000 tons of simple fertilizers, 5,000 tons of granular fertilizers and 1,500 tons of sulfuric acid. [3]

During the first four months of 1976, the Superphosphate Plant's Sulfuric Acid Workshop No. 2 delivered an additional 10,103 tons of high-quality sulfuric acid. As a result, the team worked more efficiently in April, producing 4% of the total plan and sending it to customers. [15]

During the days of october 20, 1977 the chemists of the superphosphate plant produced 4,700,000 tons of mineral fertilizers as a result of the commitment. During the same period, more than 2,000 tons of products were produced in the sulfuric acid workshop No. 2 in addition to the plan. Abundant and high-quality products were also produced in the plant's fluorinated aluminum shop. About 3,000 tons of additional products were produced at the shop during this period. In general, the company's chemists sold more than 130,000 manat worth of products during the 20 days of october. [14]

Simple superphosphates increased productivity by 4.2 percent compared to the same period in 1977. The victory of the chemists of the granular superphosphate plant was even more gratifying. The shop's chemists increased production by 29.9 percent compared to last year. The staff of the fluorinated aluminum shop also coped with the task and fulfilled the half-year plan by 106.5 percent. [6]

By the end of 1978, the chemists of the superphosphate plant had undertaken to produce 1,300 tons of simple, 500 tons of granular superphosphate fertilizer, 40 tons of aluminum fluoride, 500 tons of sulfuric acid and more than 100,000 manat worth of products in addition to commitments. Upon completion of the expansion of the existing simple superphosphate plant with an annual capacity of 800,000 tons, it was planned to increase the production of mineral fertilizers by another 360,000 tons. [13]

Since the beginning of 1979, 114,000 simple and 118,000 granular fertilizers have been produced and sent to customers. The second granular superphosphate was created on the territory of the plant, the existing facilities were reconstructed. After the commissioning of the complex in 1980, the company planned to increase the production of granular fertilizers to one million one hundred thousand tons. The bureau of inventors and rationalizers of the plant carried out useful measures. The innovators are expected to submit 160 proposals in 1979 and achieve an economic benefit of 235,000 manat. Within four months 37 proposals licensed for various areas of production allowed to save 50,000 manat. [5]

In 1988, the staff of the superphosphate plant made the following socialist commitments:

- to produce 4,370 tons of sulfuric acid in addition to the plan;
- to deliver another 3 tons of fluorinated aluminum in addition to the previous obligation;
- to produce and sell products worth 150,000 manat in addition to the plan;
-Save 900,000 kilowatt-hours of electricity, 1,000 hectocalories of heat energy, 600 tons of conventional fuel;
- increase labor productivity by 2.1 percent;
- commissioning of oleum lead and ensuring its design capacity one month ahead of schedule;
-To provide equipment to the recreation area in the Yashma area of the Caspian Sea. [18]

The superphosphates of the "Fertility Factory" have honorably completed the tenth five-year plan, providing agriculture with high-quality mineral fertilizers. They completed the tenth five-year plan in november 1980. The sales plan was implemented earlier - on september 10. 33,190 tons more fertilizers were sent to the agricultural workers of the republic than planned. However, according to the commitment made in the eleventh five-year plan, in 1985 it was planned to increase the production of mineral fertilizers to 150-155 million tons in in conventional units. Of this, 36-37 million tons had to be fertilizers containing 100 percent nutrients. Superphosphate producers undertook to produce 5,670,000 tons of simple superphosphate, including 2,580,000 tons of granular superphosphate in the eleventh five-year plan. In order to cope with this program, it is planned to implement a number of scientific and technical measures aimed at the production of abundant and high-quality fertilizers, increase production and launch new workshops to improve product quality. It is planned to launch a second superphosphate plant with a project capacity of 700,000 tons, which will significantly increase production at the enterprise. The production technology of a new type of fertilizer, which is richer in microelements, has already been developed. [17]

During the first three years of 1981, the chemists of the superphosphate plant fulfilled the order for the total product by 102.4 percent, and for sales by 101 percent. Granular superphosphate producers, which fulfilled the three-month plan by 111.8 percent, sent 10,138 tons more than planned, and ordinary superphosphate producers delivered 4,690 tons more than expected. Sulfuric acid producers have supplied additional products in the amount of 2.5 percent of the plan. The staff of the granular superphosphate workshop worked better and managed to increase production by 10.3 percent compared to the same period last year. [1]

The chemists of the superphosphate workshop complied with the five-month plan on labor productivity by 104.8 percent through comprehensive use of internal resources and labor resources, working time, power of equipment and other advanced means. The staff of the plant set a goal to reach the plan level of the first year of 1981 on june 25. The five-month specified figures are as follows: production plan 104.4 percent, sales order 102.1 percent. As a result, 771,000 manat worth of agricultural products were supplied, of which product worth 361 thousand manat were sent to customers. During this period, ordinary superphosphates collected 6,752 tons of soil "vitamin", sulfuric acid suppliers collected 6,026 tons of raw materials, and granular superphosphates worked at the planned level. [2] The staff of the sulfuric acid plant No. 1 of the Superphosphate plant provided the state plan for the first year of the eleventh five-year plan well ahead of schedule. They finished last year with 806,000 tons of products instead of 800,000, fulfilled the plan by 105.5 percent, and delivered 6,000 tons of sulfuric acid due to the obligation. Increasiung labor productivity, improving product quality, strengthening the savings regime and etc. indicators were satisfactory.

The chemists made the following commitments for 1982:

-implement the state plan for 1982 by the end of december;
-deliver 1000 tons of sulfuric acid in addition to the plan;

-implement important organizational and technical measures, many rationalization proposals, reduce the cost of production by 0.2% due to savings in raw materials and supplies;

-save on important materials - 40 tons of sulfur, 800 hectocalories of steam, 165,000 kilowatt-hours of electricity, 800 tons of conventional fuel;

- increase labor productivity by 4.5 percent compared to the plan;

-implement 20 rationalization proposals with an economic benefit of 55,000 manat. [20]

During the eleventh five-year plan period, one of the important tasks was to increase the volume of production in the chemical and petrochemical industry by 30-33 percent and increase labor productivity by 28.3 percent. On may 25, the chemists of the "Fertility Factory" produced a total of 437,000 manat in addition to the five-month plan, 1 million 164 thousand manat of products and 250 tons of soil products sent to customers. In the first quarter, enterprises of the chemical industry produced more than 10 times more mineral fertilizers, more than 7 times more sulfanol, and more than 2.5 times more synthetic detergents. [16]

As a result of the research, it can be concluded that the Superphosphate Plant has made a significant profit due to cost savings, rationalization proposals and the introduction of new technologies. However, these revenues were directed in the interests of the Central Government.

5.References

1. Aghayev H. Product with quality mark. Socialist Sumgayit. April 4, (1981)
2. Aghayev H. Potential force. Socialist Sumgayit. June 9, (1981)
3. Aghayev H. In the labor shift of superphosphates. Socialist Sumgayit. March 12, (1977)
4. Aghayev N. In the face of responsible responsibilities. Socialist Sumgayit. January 15, (1976)
5. Aghayev N For the abundance of fertilizers. Socialist Sumgayit. May 24, (1974).
6. Aghayev N. Zarbaji in the labor shift. Socialist Sumgayit. July 6, (1978).
7. Five-year plan is ready. Socialist Sumgayit. October 9, (1975).
8. The decisive stage. Socialist Sumgayit. October 26, (1974).
9. To increase the efficiency of social production. Socialist Sumgayit. July 18, (1974)
10. Address of best practice: Superphosphate plant. Socialist Sumgayit. July 13, (1974)
11. Mammadov E. Malikov G. Confident steps of superphosphates. Socialist Sumgayit. October 21, (1975).
12. Nasirov M. Our team is a beacon. Socialist Sumgayit. July 22, (1975).
13. Rafiyev J. New constructions of superphosphate plant. Socialist Sumgayit. August 15, (1978).
14. Rzayev F. News from the Chemical Union. Socialist Sumgayit. October 22, (1977).
15. Rzayev F. Tested criterion. Socialist Sumgayit. May 26, (1977).
16. An important area of industry. Socialist Sumgayit. May 28, (1983).
17. Sardarli R. Fertilizer means blessing. Socialist Sumgayit. January 10, (1980).
18. Socialist commitments. Socialist Sumgayit. August 26, (1980).
19. Socialist commitments. Socialist Sumgayit. January 29, (1976).
20. Socialist commitments. Socialist Sumgayit. January 5, (1982).
21. Socialist Sumgayit. August 15, (1975).
22. Socialist Sumgayit. May 18, (1974).
23. Sumgayit magazine. № 4. p.17. (2014).
24. New plan of interaction of superphosphates. Socialist Sumgayit. October 1, (1974).
25. New commitment of superphosphates. Socialist Sumgayit. January 12, (1974).
26. Tapdigli R. Quality and economy. Socialist Sumgayit. April 15,(1976).
27. Raise the race flag high. Socialist Sumgayit. May 2, (1974).

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STRATEGIC ROLE OF SUMGAYIT IN THE DEVELOPMENT OF PETROCHEMICAL INDUSTRY OF AZERBAIJAN

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Abstract. The article discusses the strategic role of Sumgayit in the development of petrochemical industry of Azerbaijan. The evolution and development of the petrochemical industry in Azerbaijan taking into account the development of the oil industry is analyzed. Objective prerequisites of formation and development of petrochemical oil refineries are considered. The arguments of construction of petrochemical plants in Sumgayit on oil products processing and their expediency are presented. Construction of large chemical and petrochemical enterprises - Sumgayit Synthetic Plant, Chemical Plant, Superphosphate Plant and large petrochemical plant ‘Organic Synthesis’ is chronologically considered. The period of intensive development of the petrochemical industry of Azerbaijan in Sumgayit Industrial Center in 1970-1980 is especially analyzed. The historical role and merits of the national leader Heydar Aliyev on modernization and development of petrochemical enterprises and, in general, petrochemical industry are revealed. Heydar Aliyev's efforts to plan and bring to a completion the construction of the unique petrochemical complex ‘EP-300’ which are still considered the leading processing plant in this industry, are considered in detail. The development of the petrochemical industry in the period after the restoration of independence is analyzed. The main historical events and work on updating the capacities of this industry in modern conditions are given. The economic efficiency of new large plants built in Sumgayit Chemical Industrial Park is described. A number of proposals to strengthen the capacity of Azerbaijan's petrochemical industry in the near future are made then.

Keywords: The Petrochemical Industry Of Azerbaijan, The Strategic Role Of Sumgayit, The ‘Synthetic Rubber’ Plant, The ‘Organic Synthesis’ Plant, The Ep- 300 Plant, The Sumgayit Chemical Industrial Park.

1. Introduction

The remarkable thing is that in spite of intensification of petroleum industry development since the 2nd part of the 20th century in relation to petroleum production on Absheron peninsular, the long term effect of this development process on the other area of the peninsular and also the territory of Sumgayit was not observed. Thus, the enterprices of raw material producion were opened mainly in Baku. Inspite of the fact that in future years Sumgayit became famous as town of chemists, the construction of industry enterprises had been just begun before Sumgayit was awarded the status of city. The foundation of the chemical and petrochemical industry in Azerbaijan dates back to the 60-70s of the 19th century, and this was directly related to construction of petroleum production enterprises. As late as at the end of the 19th century the prodution of sulphuric acid and caustic soda existed in the plants in Baku. Alongside with this, besides production of sulphuric acid there were plants of the other chemical entrpries including the production of soda and sodium alkaline. In the end of the 20th century the soda plants in Baku were among the largest enterprises in Russia in accordance to their production power and number of workers. In the beginning of the 20th century nitrogen and chloride acids, iron sulfate and chalcanthite used in the agriculture, surrogate of soap for soap and textile factories were manufactured in Baku [1]. At those periods of time the acativity on the name of Sumgayit was not encountered, and there is limited information about these territories, the population, and their fields of activity. Before Azerbaijan was invaded by the USSR, gasoline and toluene plants were also operating in Baku. Said otherwise the network of chemistry enterprices was already formed, and there would be a time when the center of gravity of the chemical and petrochemical industry falls on Sumgayit, and we will return to all this further. In terms of natural-geographical territory and conditions.

As far back as 1934 the planning and preparation workd for construction of heat and power station on this territory began. For this purpose a special committee from Heavy Industry Commissariat of USSR came to Baku, and the main purpose of this committee was to choose the most appropriate places for cnstruction of heat and power production and chemistry enterprises. As the other issues of that period such strategic decisions were taken only in Moscow, and in 1935 on the board meeting of Heavy Industry Commissariat in Moscow the area nearby Sumgayit station was chose as the most appropriate as we have mentioned before. Here the construction of chemistry industry enterprises, including heat and power station was in contemplation. The engineers who came from Leningrad took efforts to different options of Sumgayit city and its industrial enterprises construction.

2. Method

Base economic methods such as analysis, synthesis, comparison, generalization and systematization of the evolution and development of the petrochemical industry in Azerbaijan are used in the preparation of the article. Consists of systematic and comparative analysis, methodological approaches and ways to diversify non-oil industry and increase its export potential in Azerbaijan.

3. Results and discussion

However, since the outbreak of World War II, the construction of chemical and petrochemical plants in Sumgayit has been postponed for an indefinite period. The remarkable thing is that in spite of the continued Great Patriotic War since 1944 the reconstruction of incompleted industry enterprises, including the regeneration of the creation processes here, formation of the social-economical infrastucture processes had been started again. For this purpose 'Transcaucasia industry-construction' complex of enterprises was formed in Sumgayit in 1944, and the strategic tasks of this complex were acceleration of the construction works, preparation of the industry enterprices for operation, and also provision of contruction of the social-ecomonic objects required for population, contruction of the residential area. Namely at this period in 1945 the first head plan of Sumgayit was prepared, and alongside with it in 1948 the plan of the industry zone was prepared and accepted. In the same year when the Great Patriotic War ended in May 1945 the first chemisty enterprise – the chemistry plant - was put in place, and the production of caustic soda was started here. In 1947-1948 years The Construction complex of enterprises No 1 was formed in Sumgayit, at the same time the 'Rubber Construction complex of enterprises' was organized for more planned construction of 'Synthetic rubber' plant. Since 1952 the development processes of the 'Synthetic rubber' plant began to accelerate. The scientific technical inquiries conducted at that period on buying the new products at chemisty enterprises were directed on finding implementation in production, and at that period the chemistry enterprises in Sumgayit were very active. In 1952 synthetic ethanol was produced in Sumgayit 'Synthetic rubber' plant for the first time in Soviet Union. It is interesting fact that the scientists and experts of the developed countries could not believe and were very surprised by the successful activity of rubber production at that period, the development of thier technologies, and producing of this product in Sumgayit [2]. Ethylbenzene production at the plant was planned on September 1956, and at the same year the derivation of butadiene from butane was started, and in 1960 the production was put in place. The monometer which is of strategical importance for the economics of the former USSR, and the workshops producing butadiene-styrene rubber were put in place in 1957. On September 25, 1957 the production of butadiene by the use of styrene and ethanol was started. Thus for the first time in the former USSR the production of butadiene-styrene rubber of non-plant origin took place in Sumgayit 'Synthetic rubber' plant in 1957, and being a major event it gave a powerful impetus to the social-economic development of Sumgayit during those years [3]. 'Rapid development of the 'Synthetic Rubber'plant in Sumgayit stimulated the development of the other plants also, and in 1962 the 'Superphosphate' plant, in 1966 the Additives plant began their activity. The creation of 'Superphosphate' plant and the decision about its construction in Sumgayit was taken by the Chemistry Ministry of USSR in 1948, and the edict on it was issued in 1956. The main purpose of construction of this plant was to provide the production of sulfuric acid, oleum and accumulative acid and phosphate fertilizer. The first sulfuric acid workshop was commissioned in January 1962 at the plant, which was built in 1958. The annual production of a simple superphosphate workshop put in place in 1963 was 720 thousand tonnes, and the annual production of granular superphosphate workshop was 314 tones. This plant was considered to be one of the largest chemical factories not only in our republic, but also in the former USSR and Europe, and alongside with production of 40 types of products here, they were exported to 200 cities of the former union and several foreign countries. The main production facilities were put in place in 1967-69. For example, the propylene concentrating plant with annual capacity of 16 thousand tonnes was commissioned in 1967, nitrogen-oxygen workshop – in 1967, ethoxyline resin workshop with annual capacity of 8 thousand tonnes – in 1968, chloromethyl oxirane production with annual capacity of 24 thousand tonnes – in 1968, pyrolysis and gas fractionation workshops with annual capacity of 60 thousand tonnes – in 1968, high-pressure polyethylene workshop with annual capacity of 24 thousand tonnes was commissioned in 1969 [3, s.96]. In the process of industrial potential formation in Sumgayit the historical role also belongs to another large chemical enterprise which was previously functioning as former Sumgayit chemistry industrial complex which had been acting as 'Organic Syntethis' Production Association till 1994. Thus, in 1960s the constructon of Sumgayit chemistry industrial complex played special role in development of chemistry industry in Azerbaijan. In 1963 the Gas fractionation factory set was put in place in the framework of construction of this plant in Sumgayit. In 1964 the catalytic rifting of gasoline, and in 1967 propylene concentrator was put into operation. In 1969 the ‘EP-60’ complex was put in place, and production of high-pressure polyethylene was started [4]. All these had a significant impact on strengthening of Sumgayit as an industrial center and the growth of its potential. One of the remarkable events in the history of this plant is related to costruction of ‘Polimer-120’. The purpose of the facility put in place in 1988 was mainly connected with processing of ethylene gas – the main product of ‘EP-300’ facility, and as we have mentioned before the production of strategic product polyethylene was implemnted at this facility, and till today the facility continues its operation. Polyethylene products can be considered as one of the chemical industries and products with the strongest export potential in Azerbaijan. Production of high pressure polyethylene consisted of "Polymer-120" factory set and synthesis workshop No.9. But as the result of modernization processes oconducted during last years the synthesis workshop No.9 was taken out of service. The general project power of "Polymer-120" factory set is 120 thousand tonnes, it consists of two manufacturing lines with 60 thousand tonnes project power each.

The plants constructed in a planned manner one after another in the former USSR and joined the administrative and economic mechanism of the super government in a whole and the construction processes of ‘EP-300’ factory set which is one of the largest chemistry and petroleum chemistry complexes formed as the result of these plants activity and located in Sumgayit fell within this period. It should be noted that in order to preserve historical objectivity, the planning and construction of a unique factory set ‘EP-300’ on the area of the ‘Synthetic Rubber’ plant was realized even if it was very hard, it was possible directly due to great leader Heydar Aliyev’s hard work, consistent policy and constant care. Thus, in the mid-1970s Heydar Aliyev came to ‘Synthetic Rubber’ plant, walked the area of current ‘EP-300’ factory sent step-by-step, and on the site gave the necessary tasks to the authorized persons on the construction plans and projects of the future huge set. Later at the period when the Ministry of Petroleum Chemistry Industry of USSR discouraged the construction of this unique factory set on the area of ‘Synthetic rubber’ plant, Heydar Aliyev inviting the authorized representatives from Moscow to Azerbaijan, proved the possibility of projection and construction of this unique object on the territory of ‘Synthetic rubber’ plant. Thus, at late 1970s the projection of this huge set was finished, and in the early 1980s the foundation for its construction was laid. Later in spite of many difficulties, obstacles, especially issues caused by the reconstruction processes which stimulated the Soviet Dissolution, the construction of ‘EP-300’ factory set was finished. By putting this set in place the industrial potential of Sumgayit significantly increased, and until now the strategic role of the city in strengthening as an industrial center was possible thanks to that facility. As the result of putting in place of the ‘EP-300’ factory set several irrational sets and productions were closed and the production structure considerably expanded. Putting in place of this factory set made possible the development of ‘Synthetic rubber’ and ‘Organic Synthesis’ plants and transfer it on the next level, and made possible the production of the more effective chemistry and petroleum chemistry products. The factory set also had a multiplier effect, the buying of large amounts of raw materials played a key role in formation of the production enterprises network in Sumgayit and other regions of the republic. For the sake of objectivity, it should be noted that the national leader Heydar Aliyev played historical role in formation and rapid development of Sumgayit industrial centre effectively using the resources of such a large state as the USSR for the welfare and future of his nation [5]. In 1970 upon the direct initiative of the national leader Heydar Aliyev the special program on development of ‘Superphosphate’ plant was prepared and executed. Constructing and putting in place the productions of two more new sulfuric acids for the short period of time, the first production volume of this product was 690 thousand tonnes, and the annual production volume of fertilizers production was increased from 720 thousand tonnes to 1.2 thousand tonnes [6, s.76]. In 1969-82s 17 new production objects were put in place at the ‘Organic Synthesis’ plant in Sumgayit. Thanks to these new modern productions, the enterprise achieved really great growth in those days. In 1980s the high-productive modern technology equipment producing granular phosphorus fertilizers was put in place at Sumgayit ‘Superphosphate’ plant for the first time in Transcaucasia [7, p.8-9].

The remarkable thing is that, in the period after restoration of independence of Azerbaijan with the aim of development of management system of the chemistry industry ‘Azerkimya’ State Company was created in 1992 and was operating in Sumgayit [8]. The company embodied all the chemistry and petroleum-chemistry enterprises of the republic such as Baku tyre works, Rubber-technical products, Iodine-Bromine, Pharmaceuticals plants, Chemistry plants of Sumgayit, ‘Synthetic rubber’, ‘Organic Synthesis’, ‘Superphosphate’, ‘Household chemistry’, Mechanical repair plants, ‘Azerizolit’, ‘Rubber technical products’, ‘Fibers’, ‘Regenerat’ in Mingechevir, ‘Iodine-bromine’ in Neftchala, ‘Plastic mass’ production in Salyan, and also ‘Olefins’ Scientific-Research and ‘Azerkimya’ State Project Development Institutions [9].

In the mid-1990s in Sumgait it was necessary to ensure the efficiency and productivity of existing petrochemical plants and auxiliary materials, including with industrial steam [10]. Taking this into consideration to provide the stable operation of chemistry enterprises in Sumgayit, first of all, to achieve high pressure steam supply of ‘EP-300’ factory set there was need in a new facility, and such kind of set was put in place in April 2001. The main purpose of Steam Generator Complex constructed and commissioned by Japan companies ‘Nichimen Corporation’ and ‘Chioda’ was to provide ‘Ethylene-Polyethylene’ plant with 110 and 16 atmospheric steam in whole, partial electricity power. The other chemical and etc. Enterprises use the steam and electric power produced in this factory set. Using two boilerhouse work basing on the project power, it is possible to produce 480 tonnes of steam per an hour, and also 180 tonnes of 110 atmospheric vapor and 300 tonnes of 16 atmospheric vapor. Especially as the result of putting in place of this facilty, since 2001 the chemistry industry and in Sumgayit at a whole, regeneration of industrial potential, the processess of modernization and development were quite intensified. Alongside with these, in 1990-2010 at the chemistry and petroleum-chemistry enterprises which were the basis of industrial potential in Sumgayit production of the most products was fully stopped, only the activity of chemistry and petroleum-chemistry facilities operating on the account of raw material received from oil refining on the country area were relatively stable, there has been no decrease in the volume of production in these areas, and these facilities mainly operate at ‘Ethylene-Polyethylene’ plant in Sumgayit.

In accordance with the Order about ‘Improvement of management mechanisms in petroleum-chemistry industry’ by the President of Azerbaijan Republic dated after April 2, 2010 ‘Azerkimya’ State Company was gave under the remit of SOCAR [11]. The target for ‘Azerkimya’ PA for 2015-2019 was modernization of the existent production, provision of the newly constructed Polypropylene and Polyethylene productions with the required amount and quality raw material, and increase of efficiency of ‘EP-300’ production.

The production capacity of the two facilities of ‘SOCAR Polymer’ located on the area of Sumgayit Chemical Industrial Park is 180 thousand tonnes for polypropylene and 120 thousand tonnes of polyethylene. This plant was already put in place and the informafion about this will be given further [12]. The main production activity of ‘Azertechnoline’ LLC located at Sumgayit Chemical Industrial Park was production of steel pipes, and the industrial processes organized here meet the world standards. The plant has 3 production lines and the annual production power is 200 thousand tonnes. Carbamide plant of the enterprise is 40 hectare, the annual gas consumption is 435 million m^3, and the annual product production power was 1200 tonnes of ammoniac, 2000 tonnes of carbamide. The average annual production volume is expected to be approximately 650-660 thousand tonnes. As well as meeting the internal demand in this strategical product n the country, it will be also exported to Turkey and other countries of the world [13]. 9th time on July 18, 2018 the head of state participated in the opening ceremony of propylene plant constructed in the framework of ‘SOCAR Polymer’ project at Sumgayit Chemical Industrial Park with president of Italy Sergio Matterella. The Propylene plant with the general investment of 816 million USD and expense of 768 million USD is a historical event in modernization and strengthening of industrial potential of Sumgayit. The whole ammount of the income at the production period of the plant is forecasted to be 6,3 billion USD. Another advantage of this plant is its multiplicative nature, thus, 19 types of polypropylene and 12 high-grade polyethylene products manufactured at the plant, as well as raw materials [14].

With the construction of new facilities and large plants, the strategic role of the Sumgait Industrial Center began to be strengthened at a more intensive pace in the development of Azerbaijan’s petrochemical industry.

4. Conclusion

Thus, in the development of Azerbaijan’s petrochemical industry, the Sumgait Industrial Center and its enterprises have played a historical role and these positions need to be strengthened in the near future. For this, there are considerable reserves and we consider it possible to implement the following projects and build new petrochemical facilities:

1) Synthetic Rubber Plant played a historical role in Sumgayit’s formation and development, but this plant is not functioning at the moment, it was closed for objective reasons, thus Sumgayit Synthetic

Rubber Plant was among the objects that Adolf Hitler planned to occupy according to his 'Barbarossa' plan and even Khayo Eylers was appointed as director, these historical factors should be considered, surely it is impossible to restore the former rubber factory, but instead it is possible to produce rubber and tirea from semi-finished products based on crude oil, there are necessary technologies in this field, and our specialists know this, at the same Chinese companies are interested in the construction of a tire plant in the Chemical Industrial Park in Sumgayit, in this regard, it is advisable to establish a rubber and tire production complex with Chinese companies, and, in determining the name of this enterprise, the revival of the name 'Synthetic Rubber' in any form could be regarded as a great consideration for the history of Sumgayit.

2) Sumgayit produces isopropyl alcohol, which is in constant demand in the world market and there are only a few plants in the world that produce this product. At present, this production is part of the 'Ethylene-Polyethylene' plant in Sumgayit, most of the equipments of the plant are old, although it has been modernized and renovated many times, the Sumgayit Izopropyl Alcohol plant should be built on the basis of new technologies.

3) Polyester resin was produced tt the closed at proper time 'Organic Synthesis' plant in Sumgayit, it was also a history of the industrial development of Sumgayit but now this production has been abolished, in the future, as the refining of oil and the raw material base for the chemical products expanded, the construction of the 'Sumgayit Polyethylene Resins' plant would be fair and efficient. The purchase of this product would have the potential to produce raw materials for furniture in our country.

4) There was a large butadiene production complex at the closed at proper time 'Synthesis Rubber' plant in Sumgayit, but again this production was abolished for objective reasons, butadiene also meant raw material for the production of rubber and was extracted from the processing of side products from the 'EP-300' facility. The restoration of this production is not considered, but the construction of 'Sumgayit Butadiene Plant' based on modern technology may be considered in the future when oil refining and the raw material base is strengthened, and the products extracted from this plant may be directed for use in the previously offered rubber and tire plant, or exported, thus and the demand for this product remains high in the global market.

5) It is known that oil and gas raw materials in Azerbaijan allow the development of chemical and petrochemical industries. Establishment of modern processing facilities based on oil and gas raw materials is a base for the creation of other competitive, export-oriented chemical and petrochemical enterprises, and several of them were included in these proposals, but every time the issue of raw materials comes up as an important factor. From this point of view, taking into account that the existing 'EP-300' is already obsolete for many parameters and no matter how much the 'EP-300' is upgraded, it may cause difficulties in meeting the objectives of economic development in Azerbaijan and copping with the issues of several times industrial potential increase in Sumgayit. With all of this in mind, the construction of the 'EP-400' facility in Sumgayit and, consequently, a serious leap in the development of the chemical and petrochemical sector in our country should be considered. Putting this complex in place and effective use of the existent potential, establishment of new production enterprises could give an impetus to increase the annual export only at chemical and petrochemical sector in Sumgayit up to 2-3 billion USD level and would have a powerful multiplier effect on the development of the non-oil sector in the country and etc.

5.References

1. Aliyev Sh.T. Stages of development, existing problems and perspectives of chemical and petrochemical complex // "Economy and life" journal, № 7-8, Baku, 2004, P.61-70 (in Azerbaijani).
2. Romanenko P.G. Introduction of new technology in the chemical industry. (In the book "From the Experience of Fighting for Technological Progress"). Leningrad, 1952, p. 120 (in Russian).
3. Shirkhan Salimov, Ramal Aliyev. History of establishment and development of Sumgayit city chemical industry. Monograph. Sumgayit: SSU Publishing House, 2016, 154 p., P.107 (in Azerbaijani).
4. Scheme of development and deployment of productive forces of the Republic of Azerbaijan for the period up to 2000. Volume 2, Baku, 1982, 556 s. (in Russian).
5. Aliyev Sh.T. Assessment and reconstruction of the chemical and petrochemical complex of Azerbaijan. Baku, "Science and education", 2012. - 156 p. (in Azerbaijani).
6. Ismayilov E.V. Reconstruction of production areas of the enterprise, ways to increase production / Proceedings of the conference "Socio-economic development of Sumgayit: current problems and prospects." 2008, 130 p. (in Azerbaijani).
7. Sadigov F.M. Heydar Aliyev and the chemical industry of Azerbaijan. Baku - "Azerbaijan" publishing house, 2003, 144 p. (in Azerbaijani).

8. Aliyev Sh.T. Sumgayit industrial center: use of existing potential and modernization priorities. Baku, “Science and education”, 2012. - 196 p.(in Azerbaijani).
9. Aliyev Sh.T. Modern aspects and directions of development of petrochemical complex in Azerbaijan // “Audit” journal, 2016, №3, P. 41-45. (in Azerbaijani).
10. Support programme for the industrial regeneration of the Sumgayit region of Azerbaijan. United Nations Industrial Development Organization. Vienna, March, 1996, 112 p.
11. Order of the President of the Republic of Azerbaijan on improving management mechanisms in the petrochemical industry. Baku, April 2, 2010. (in Azerbaijani).
12. Ilham Aliyev attended the opening of a technical equipment plant in Sumgayit. October 25, 2015. - https://president.az/articles/16482 (in Azerbaijani).
13. Ilham Aliyev attended the opening of the SOCAR urea plant in Sumgayit. January 16, 2019.- https://president.az/articles/31534 (in Azerbaijani).
14. Ilham Aliyev and Italian President Sergio Mattarella attended the opening of a polypropylene plant built within the SOCAR Polymer project in the Sumgayit Chemical Industrial Park. July 18, 2018.- https://president.az/articles/29502 (in Azerbaijani).

OR-VII-2

STAGES OF DEVELOPMENT OF PETROCHEMICAL INDUSTRY

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Abstract. The petrochemical industry of the Republic of Azerbaijan, being one of the main segments of the country's economy, plays a special role in shaping the path of long-term and sustainable development. The essence of the article presented on the strategic development of the petrochemical industry of our country is the general strategic policy line reflected in this sector in a certain period. This article reflects the history of the petrochemical industry, the current situation, development trends and the goals for the development of this area.

Keywords: industry, petrochemical industry, chemical industry, development of industry in Azerbaijan, history of industry in Azerbaijan

1. Introduction

The foundation of the petrochemical industry in Azerbaijan has been laid in the 60s and 70s of the 19th century and has directly related to the development of the oil refining industry. The chemical industry, which was still a new industry area at that time, has undergone a long and complicated progress since the end of the 19th century.

In 1859, the first oil refinery (plant) has been built in Baku. In 1863, Javad Malikov has built a kerosene plant in Baku and has the first in the world used refrigerators in the oil refining process. In 1867, there were 15 oil refineries.

The manufacture of chemical products has been extremely developed uneven and one-sided. The existing chemical plants have been restored in 1920-28 and began to be equipped with modern equipment. In 1926-30, for the first time in the former USSR, methods for obtaining iodine from boreholes have been prepared, and as a result, the Neftchala iodine-bromine (1931), Surakhani (1931) and Ramana (1932) iodine plants have been put into operation. Thus, the foundation of the iodine-bromine industry was laid. The opening of the Bina channel soot factory in 1934 and the Garadagh soot factory in 1939 led to the establishment and development of the soot industry.

During the Second World War, the chemical industry has provided the front line with the requisite products. In 1944, the Baku Iodine Plant has been established on the basis of the Surakhani and Ramana iodine plants. Construction of a chemical plant in Sumgait has begun in 1943. In 1945, the first product of caustic soda has been obtained at the plant, and in 1979, a production association has been established on the basis of the plant.

Due to the outbreak of World War II, the construction work in Sumgait has been suspended. Since 1945, heavy industrial enterprises - Chemical, Pipe-Rolling, and Synthetic-Rubber, Aluminum, and Superphosphate plants have been put into operation in Sumgait. The Chemical Plant, considered the largest petrochemical enterprise in Europe at that time, has been put into operation in 1966.

Heydar Aliyev - after the genius came to power, thanks to his will and determination, a major turning point in the reconstruction and modernization of the chemical industry of Azerbaijan had commenced. Since Heydar Aliyev attached special importance to the role of the chemical complex in the Azerbaijani economy, with his wisdom, determination and perseverance he had managed to make special government decisions at that time governing bodies of the USSR for the development of major reforms in Azerbaijan's oil extraction and petrochemical industries. In 1971, Heydar Aliyev, who carefully studied the critical issues facing the chemical industry in the country, first of all, laid the foundation for the concept of development of the chemical industry by organizing the creation of a program to modernize the industry in all technical, economic and social terms. Due to his outstanding reputation in the former Soviet Union, his principled position, his daily work supervision, as well as his high demand for the timely construction and commissioning of enterprises, the reconstruction of oil refineries and chemical plants has become the reality of the period.

Pic. 1. Speech by Heydar Aliyev.

With the persistence from the union leadership, Heydar Aliyev would demand the improvement of Azerbaijan's chemical and petrochemical structures, the abolition of obsolete and staled production facilities, the creation of modern, heavy-toned, waste-free enterprises, at the same time, making crucial decisions that paved the way for the construction of technical and nature protection enterprises. (Pic.1) In order to fully implement the concept, development program of chemistry, authored by the great leader, a large amount of capital was allocated with his personal suggestion and insistence from the former all-union fund.

In the 1970s and 1980s, petrochemical plants have operated at full capacity and have exported products to almost every part of the former USSR. As a result of this economic growth, Sumgait has become one of the largest cities in Azerbaijan.

In 1981, the construction of the EP-300 complex, which produces ethylene and propylene, valuable products of petrochemistry, with modern, heavy-duty, waste-free technology, high production capacity, was launched in Sumgait. The complex was planned to utilize hydrocarbon raw materials off of oil refineries of the republic. It should be noted that the launch of such a complex, based on the latest and advanced technology, was a great event for that period, even within the dimensions of the scale of the USSR. By the virtue of EP-300 plant, the Ethylene-Polyethylene plant currently produces high-quality polyethylene, which is in great demand in the global market, and at present this plant plays the role of a major supplier of raw materials for the overall development of the chemical complex in our country.

At that period of time, along with EP-300, as a technological follow-up of thereof, foundation of the Polymir-120 complex for the production of polyethylene has been laid. These unique complexes were especially valuable and rather convenient as the raw materials for the primary unit EP-300 were obtained not from overseas, but directly from hydrocarbon products manufactured at oil refineries of the republic.

In 1992, the central state structure of the chemical industry of Azerbaijan - "Azerkimya" State Company was established. The company encompasses versatile chemical and petrochemical enterprises of the republic - Baku Tires, Rubber-technical products, Iodine-bromine, Household chemical, Superphosphate, Mechanical-repair, Mingachevir "Azerizolit", Rubber-technical products, Glass fibers, Regenerate, Neftchala Iodine bromine, plastic processing of Salyan, as well as Scientific-Research “Olefins” and “Azerikimya” State Designing Institutions. These enterprises produced chemical productions, such as polyethylene, propylene oxide, propylene, polyester resin, technical and absolute isopropyl alcohol, caustic soda, liquid chlorine, chloride and sulfuric acid, etc.

In 2001, massive and unique thermal-energy complex - Steam-Generator, which plays a decisive role in the future development of the chemical industry, which fully and completely supplies Sumgait chemical enterprises with stable electricity and high-pressure steam was launched. The steam-generator unit was built at the Ethylene-Polyethylene plant with a state-guaranteed loan from the EKSIM Bank of Japan construction of which began back in August 1998. After the commissioning of this unit, the cost of electricity and thermal energy consumed by the enterprises of Azerkimya State Company, and ultimately the final products manufactured has fallen significantly. This led to introduction of the produce to the global markets at a competitive price, and accrual of profit by many companies.

“Azerkimya” Production Association has been established within SOCAR by the Decree “On amendments and additions to the Decree of the President of the Republic of Azerbaijan No. 844 dated

January 24, 2003" On improvement of the structure of the State Oil Company of the Republic of Azerbaijan "signed on April 22, 2010."

Reconstruction works have commenced at the EP-300 unit of the Ethylene-Polyethylene plant, which is part of the structure of Azerkimya PU. During the reconstruction, replacement of obsolete equipment with state-of-the-art equipment, modernization of the the control and measurement system of the technological process and enhancement of the project capacity were amongst the planned activities.

It should be noted that the creation of fertile investment conditions in Azerbaijan, the protection of investments by the state expands the domestic market, gives a rise to opportunities for domestic consumption and export of products.

Modernization and improvement of the structure of the petrochemical industry, diversification of the non-oil industry and surge of its share in the economy, as well as export potential, expansion of competitive production, science and innovation, efficient use of energy, high value added, establishment of knowledge economy, training of qualified personnel for new production areas is one of the main priorities of development of Azerbaijan's industry.

Recent radical reforms and large-scale construction work in all sectors of the country's economy have led to the short-term modernization and strengthening of the capacity of production areas and infrastructure. The political and economic policy successfully pursued by President Ilham Aliyev has increased the international prestige of our country, ensured its socio-economic development, at the same time, turned the Republic of Azerbaijan into the most dynamically developing country in the world, being an attractive country for foreign investors. With regards to the rapid development of all sectors of the economy, the growing demand for petrochemical products, as well as meeting the needs of the population of these products are the main factors characterizing the need for the development of this sector.

The existing enterprises of the petrochemical industry in the Republic of Azerbaijan are as follows:

Oil Refinery named after Heydar Aliyev. The Heydar Aliyev Oil Refinery has been established by the order of the former USSR Ministry of Oil Industry dated July 29, 1953. (Pic.2)

Pic. 2. Oil Refinery named after Heydar Aliyev.

ED-AV-6 for oil refining at the plant (year of commissioning - 1976), high technological forces, such as catalytic reforming plant (1980), gradual coking plant (1986), catalytic cracking plant (1993) operate.

The catalytic cracking unit for the production of high-octane components of gasoline, has been built and commissioned in 1993, has improved the quality of gasoline and diesel fuel produced in conjunction with the catalytic reforming unit, which was commissioned in 1980.

In 2016, the modernization and reconstruction of the plant began and a number of contracts were concluded for the development. As part of the ongoing reconstruction and modernization of the plant, rise of 7.5 tons per annum of processing capacity of the plant, and production of top quality of oil products that meet Euro 5 standards are have been planned. Reconstruction will increase the country's export potential and the profitability of the oil refinery, as well as provide a stable supply of raw materials to Azerkimya PU. As a result of the project, it is expected to optimize the operating costs of the oil refinery, as well as improve the environmental situation in Baku.

SOCAR Polymer. SOCAR Polymer (Pic.3) has been established on July 16, 2013 to strengthen the country's chemical industry. The main purpose of SOCAR Polymer is to make the most of the gas extracted during oil refining operations and set up a basis for small and medium-sized enterprises engaged in the processing of plastic materials. The company's production enterprises consist of polypropylene and plants producing high-density polyethylene. These plants have been built in the Sumgait Chemical Industrial Park.

Pic. 3. SOCAR Polymer.

Carbamide plant. The carbamide plant (Pic.4) was commissioned in early 2019. The plant, which is a total area of 39.27 hectares, is located in Sumgait.

Pic. 4. Carbamide plant.

The carbamide is a colorless chemical. İt dissolves quickly in water. It contains 46.4% nitrogen. İt is mainly used as fertilizer in agriculture, including livestock, chemical industry, medicine, etc.

The plant, primary raw material of which is a natural gas, consists of ammonia, liquid and granular urea. The plant produces 1200 tons of ammonia and 2000 tons of urea per day.

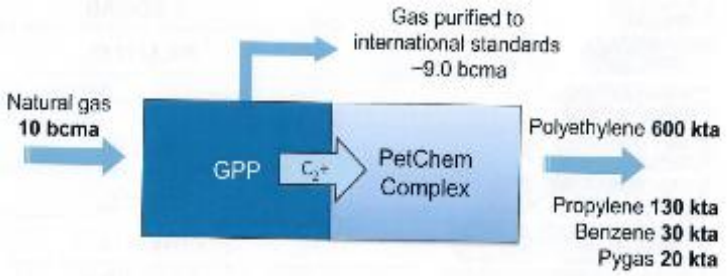
Methanol plant. The first and only Methanol plant (Pic.5) in the Caucasus, located in the Garadagh district of Baku, has been commissioned in 2013 and is the first gas-chemical production enterprise in the country.

Pic. 5. Methanol plant.

Methanol, one of the main products of the gas chemical industry, is a clear colored petrochemical liquid that is usually obtained from natural gas and can be broken down naturally. Methanol, an important intermediate chemical product in the world industry, is used in the furniture industry to make synthetic fibers for laminate, artificial leather and textiles, acetic acid, recycled plastics, household paints and adhesives, and even medicines such as ASA (acetylsalicylic acid). It is used as a chemical reagent, as a fuel for domestic heating systems and kitchens, as well as an efficient transport fuel. Methanol is also used to produce fuel components that, when added to gasoline, burns fuel cleaner and reduces emissions into the environment. Therefore, the production of methanol is considered the cleanest and most ecologically harmless process in the chemical industry, because any waste is not thrown into the atmosphere or water bodies during its production.

Methyl alcohol produced at the methanol plant with a purity of 99.98% is "A" branded methanol, which is the purest methanol product manufactured in the world.

SOCAR GPC project. The new gas processing plant intended for construction in Sangachal will include a Gas Processing Plant, a Steam Cracking Plant and a Polyethylene Plant. Construction of the plant, with an annual production capacity of 10 billion cubic meters of gas, is expected to begin in 2022.
The structure (Pic.6) of the plant will be as follows:



Pic. 6. The structure of SOCAR GPC project.

The recent rise in demand for petrochemical products globally, the gradual removal of obsolete technologies (equipment and plants) from production and their replacement with new ones, environmental protection, and failure to modernize the infrastructure of the petrochemical industry can be considered as one of the key factors to achieving enduring and sustainable development.

Production of science-intensive and high-tech, competitive and export-oriented petrochemical products that meet global standards, production of new petrochemical goods that meet modern requirements in a bid to get rid of the dependence on imports, adherence of the quality of these products to modern requirements and fully meet domestic demand are the main goals in the development of the industry.

5.References

1. http://minenergy.gov.az/az/neft/neft-senayesinin-inkisaf-tarixi
2. http://www.socar.az/socar/az/company/organization/azerikimya-production-union
3. http://socar.az/socar/az/company/organization/heydar-aliyev-oil-refinery
4. http://socar.az/socar/az/company/organization/carbamide-plant
5. https://www.stp.az/karbamid-zavodu
6. http://socar.az/socar/az/company/organization/socar-methanol-plant
7. http://www.e-senaye.az/index.php?action=company_detail&company_id=276
8. http://elmtehsil.com/elm-ve-heyat/azerbaycanin-neft-kimya-senayesi/106
9. http://www.socargpc.az/en/project

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«DEVELOPMENT STAGES AND FEATURES OF THE OIL İNDUSTRY İN AZERBAİJAN»

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Abstract. Oil has existed since ancient times and plays an important role in the formation and development of civilization. If we turn to history, we will see in the 9th-11th centuries the state of Media located in the south-west of South Azerbaijan and Iran, and the Medes, who called the burning substance from the earth's crust “nafata”. Later the word “nafat” was replaced by the word “oil”, meaning “filtered”.

Knowing that the first oil well in the world was drilled in Baku and the oil industry was formed here, the article will use “Azerbaijani oil” instead of the epithet “world oil industry”.

It is known that energy plays a key role in social development, which is manifested in the growth of labour productivity in society and quantitatively and qualitatively characterizes the development of human society. It is not only a manufacturer of products that meet any specific needs of society, but also a key factor in the development of the social sphere, improving the quality of life of the population. All this poses new challenges for the global oil industry and their solutions.

The global energy sector is currently undergoing reconstruction, which means that the structure of this sector will change radically in the next ten years. First, this will apply to all industries, and the goal will be to turn “the face” of global industry, including the energy sector, towards consumers. In addition, this will take place throughout the entire "technological chain", that is, in the energy sector, and in different areas and among different regions of the world.

Keywords: oil, industry, production, companies, factors, global, energy, economy, technologies, development, parametrs, market.

1.Introduction

In the 7th-6th centuries BC, there was important information about the existence of oil on the territory of our country. The concept of "Land of Fire" is associated with the natural appearance of oil and gas resources here. Opinions about the existence of oil in Azerbaijan are reflected in the works of the Arab geographer Al-Masoudi, the Italian traveler Marco Polo, the German traveler E. Kempfer and the French scientistSerevak [2, p. 19].

The first mechanized oil well in Azerbaijan was drilled in 1848, but the beginning of industrial oil production is considered to be 1872 year. Drilling and production of wells after that began: in 1859 in the United States, in 1893 in Indonesia, in 1909 in Iran, in 1934 in Kuwait, in 1938 in Saudi Arabia, in 1956 in Algeria and Nigeria, in 1961 year in Western Siberia, In 1969 in the North Sea, etc. It should be noted that the first drilled and operated offshore oil wells were also carried out in Baku.

After 1872, oil statistics began to be kept. Specialized companies began to appear for its exploration, development and production. All this led to the formation of a class of entrepreneurs in the oil industry, which led to the emergence of various forms of joint-stock cooperation. It is known that in 1873, 12 companies were engaged in oil production in the Absheron region of Azerbaijan, and at the end of the century - 61 companies. Research shows that in the 19th century, oil production began in various regions of the world, including Peru, Romania, on the shores of the Sea of Azov, on the Taman Peninsula, in the Kuban River valley, in Grozny and others.

2.Metod

One of the main factors determining the country's oil industry is its oil reserves, which are the basis of all possible investments. The Middle East is known to be hegemonic in terms of oil reserves. However, unless new sources of energy are found in the near futurethe entire world will soon become dependent on oil from the Middle East.

According to the prominent oil scientist, academician Azad Mirzadzhanzadeh, reserves in the Middle East, which determine the development of the oil industry, are 1.72 times higher than in all regions of the world [1, p. 53].

The transition of the global energy industry to a new way of working is determined by three main parameters: globalization, new technologies and sustainable development. All this, in contrast to the traditional approach, brings the end consumer of energy resources to the fore. Thus, globalization implies close interaction of the economies of different countries. And therefore, the economic development of one specific country separately from the world economy is impossible.

In the context of globalization, any changes in the economy of this or that country will affect the economic development of other countries of the world. In the context of globalization, the producer-consumer or consumer-producer chain ensures that information reaches each other as soon as possible.

The second most important factor in the global energy market is new technologies. Thus, the activity of "electronic business" in the world determines the rapid development of new equipment and technologies in competitive industries.

Although the concept of sustainable development is new, it has taken its rightful place in the development of the world economy. Sustainable development is, in short, examining past problems from a new perspective. Sustainable development characterizes the economic development of the economy, region and country in various parameters.

It should be noted that in today's international market, the energy sector, like other industries, is experiencing its own "crisis". At the same time, the entire global economy, as well as individual industries, face uncertainty. These include: how long will the high (low) price of oil remain? ; how long will the effects of the oil and electricity price spikes last? ; how will energy producers and consumers cope with persistent energy demand and a sudden drop in oil prices?

Thus, the words "energy crisis" and "lack of energy resources" that existed in the seventies of the last century began to appear again, and this situation manifested itself in the 19-20s of the twenty-first century. Naturally, other things being equal, this is determined not only by local conflicts, but also by the pace of development of the world economy.

A.A. Konoplyanik notes [3, p. 89]: "The ultimate goal of the development of the energy market is the formation of a financial and energy space based on the principles of a single game, fair competition, non-discrimination, interchangeability and mutual benefit. While the pace and scope of some of them is different, the basic laws apply to all".

According to current projections, global energy consumption will grow by 45% over the next 20 years. According to these forecasts, in 2025 the demand for oil in the world economy may increase by 35 million barrels per day, or 42%, and demand for gas - by 1.7 trillion m3, or 60%. According to experts, the situation in the global energy market is characterized by the following:

- a sharp increase in the demand for energy resources of the developing countries of Asia, since they account for up to 45% of the world demand for oil
- demand for gas in Europe in 2020 will be 60-70% due to imports; the gap between consumption and production is expected to widen in developed countries as a whole
- limitation of additional forces in oil production, lack of forces for oil refining and transport
- asymmetry of information, which is the fifth factor of production, i.e. its absence in the world oil market.

The existence of globalization in the world highlights the problem of energy security. In this sense, the countries of the world are taking preventive measures to ensure energy security and eliminate number of possible cataclysms:

- strong offer of traditional energy sources for sustainable development and sustainability of the world economy
- improving the efficiency of the use of energy resources and protecting the environment
- development and use of new energy sources to enter the world energy market.

In the era of globalization, Azerbaijan is actively involved in solving the problem of energy security in the world energy market by attracting new oil and gas fields. As mentioned above, the first oil well was drilled in Azerbaijan and put into commercial production. Take all of these into account, below we will consider the evolution of the oil industry in Azerbaijan.

The formation of the history of oil in Azerbaijan can be conditionally divided into the following stages:

- 1. The period from 1848 to 1871
- 2. The period from 1872 to 1901
- 3. The period from 1902 to 1917
- 4. The period from 1920 to 1927
- 5. The period from 1928 to 1940
- 6. The period from 1941 to 1945
- 7. The period until 1946-1970
- 8. The period from 1971 to 1991

- 9.The period from 1992 to 1994
- 10. From 1994 to the present, i.e. stage of implementation of the "New Oil Strategy".

We noted that the first oil well in Baku was drilled in 1848, and from that time until 1871 it has been characterized as a period of industrial drilling. This period is characterized as the beginning of the oil industry in Russia (and in Azerbaijan as part of it). This period is characterized by a small volume of oil production and primitive technologies for the development of oil fields. At the beginning of this period, oil production was 8.9 thousand tons, and in 1871 - 25.6 thousand tons. During this period, capitalism began to develop in Russia, new industries appeared, and the produced oil could not satisfy all needs. During this period, the purchase of land plots hindered the development of the oil industry. Under pressure from other industrialists, the Imperial Russia abolished the buyout system and opened a new stage in the development of the oil industry.

A new stage in the prosperous development of the oil industry in Russia (Azerbaijan) began in 1872-1901. This period is characterized by massive mechanized drilling of oil wells, the use of new technologies in the oil industry. In those years, the design of the deep well pump was developed. Research shows that in 1872 Russia produced 27,000 tons of oil, of which 26,000 tons, or 96.3%, came from Azerbaijan. At the end of this stage, that is, in 1901, 11.937 million tons of oil were produced, including Azerbaijan's share of 10.979 million tons or 92%. During this period, the United States produced 10.237 million tons of oil, which is less than 1.7 million tons, that was produced in Russia, and 0.742 million tons less than was produced in Azerbaijan. The development of the oil industry during this period led to the development of the oil refining industry and changed the technological stage of this industry. Thus, there was a transition from oil distillation to continuous technological processes, which was a very serious step for this period. During this period, the following were implemented: drilling of oil wells in different parts of the Absheron Peninsula, the development of industrial entrepreneurship, the arrival of various businessmen from all over the world to Baku to work in this area.

The next stage, 1902-1917 characterized by stagnation in the Russian oil industry. During this period, the inflow of foreign capital into the oil industry begins. The concentration of production is gaining new momentum. The largest oil companies in the world, the Nobel Brothers Partnership, Shell and Standard Oil own large amounts of oil resources. At the beginning of World WarThe First, these three companies accounted for 51.6% of all oil production and 75% of oil sales. The superiority of these companies has led to a constant rise in the prices of oil and petroleum products. An artificial shortage of oil began to be created in the country, which was explained by the depletion of fields. Foreign companies were not interested in implementing technical and technological innovations in the oil industry. In addition, they deliberately cut back on drilling without isolating oil reservoirs, all of which resulted in rapid waterlogging.

During this period, Azerbaijan was the main oil-producing region. So, in 1902, Russia produced 11.621 million tons of oil, and Azerbaijan's share was 10.504 million tons, or 90.4%, in 1917 this figure, respectively, amounted to 8.8 million tons and 6.6 million tons (or 75%). At that time, the organization of oil exploration in the Ural region of Russia was rejected by foreign oil companies, which was characterized by a rapid decline in oil production in the country. Pre-revolutionary Russia produced 10.281 million tons of oil in 1913, including 7.799 million tons (or 75.9%) of oil in Azerbaijan, which was three times less than at the same time in the United States. The volume of oil production in Russia in 1917 amounted to 8.8 million tons, including 6.646 million tons (or 75.5%) in Azerbaijan, in the same year there was a revolution, and in 1918 the first Democratic Republic of Azerbaijan was founded, which was soon overthrown by Russia and its the Dashnaksvassals, and the Soviet government was established in Azerbaijan in 1920, and the entire oil industry was nationalized.

After the nationalization of the oil industry, issues such as the restoration of destroyed oil fields, an increase in production, an increase in the production of oil products, and regulation of the export of oil products were raised and resolved.

From the first years of nationalization, the reconstruction of the drilling and production process was carried out, and the massive use of rotary drilling was carried out. There was a startfor: sealing during oil production, the use of deep pumps instead of a sludger, measures in the field of collection and transportation of associated gas, the transition from steam engines to electric motors in the fields, etc.

The subsequent development of the oil industry, i.e. 1928–1940 characterized by the complexity of the assigned tasks. New industries began to emerge in the country, and the pace of transportchanged. All of this started to increasethe demand for oil and petroleum products, so in 1930-1932 demand in the domestic market increased by 4 million tons, or 36.5%. During this period, the oil industry not only satisfied the country's demand for oil products, but also significantly expanded its exports, and the amount of oil and oil products increased by 1.3 million tons, or 27%. In terms of growth rates, the oil industry was ahead of other industries. During this period, exploration and production drilling began to develop intensively, new reserves were discovered and put into operation. As a result, in 1931, oil production in Russia reached 22.392 million tons (13.153 million tons or 58.7% in Azerbaijan). The volumes of oil production and processing were converging, while the depth of oil refining increased. The geography of the oil industry expanded, for the first time the oil refining industry was located far from the place of production (Tuapse, Batumi, Kherson, etc.). These plants were mainly intended for production of export products. At the end of this period, that is, in 1940, the volume of oil production in Russia was 31.121 million tons, and in Azerbaijan - 22.176 million tons, or 71.3%.

In the 30s of the last century, there was a transition in Azerbaijan to improve production methods in oil fields and oil refineries. Thus, during drilling, a transition was made from the percussion method to the rotation method, from the traction method and compressor operation to the submersible pump method.

At the initiative of Azerbaijani oil scientists, the economic issues of pumping and compressor operation of wells in oil fields, a feasibility study for transferring low-productivity wells to a deep pumping method of operation, and determining the economic efficiency of mechanized methods of oil and gas production were resolved.

During World War II, that is, 1941-1945, the problems and conditions facing the oil industry changed radically. Although oil was already produced in the Urals at the beginning of the war, oil production there accounted for 12% of total production. In the first year of the war, that is, in 1941, Russia produced 33.00 million tons of oil, where at that time the share of Azerbaijan was the highest, that is, 23.54 million tons or 71.3%. The war set new rules for the development of the oil industry, which began to take shape in more remote parts of the country. This led to a decrease in production in the country, so in 1942 Russia produced 22.0 million tons of oil, which was 66.7% less than in the previous year.

At the same time, production in Azerbaijan decreased to 15.7 million tons, which is 7.84 million tons or 33.3% less than in the previous year. During this period, production steadily decreased, and in 1945 Russia produced 19.436 million tons of oil, where Azerbaijan's share was 11.07 million tons or 57.0%.

Academician Azad Mirzadzhanzadeh notes (1, p. 3) that during the war, four out of every five aircraft, tanks and cars worked with the products of the Baku oil refineries. However, this activity of Azerbaijan did not receive any acknowledgement in the former Soviet Union.

The development of the oil industry in 1946-1970 suggests that in 1949 the goal was set to produce 35.4 million tons of oil, and in 1950 this figure was already reached to 37.878 million tons. During this period, factories producing products for the war began to produce equipment for the reconstruction of the oil industry.

The process of developing new oil regions (Tatarstan, Central Asia, etc.) began.

Over the years, the volume of discovered reserves increased 2.5 times, and production - by 87%. In 1970, oil production in the oil industry increased by 352.574 million tons or 330.828 million tons (16.2 times) compared to 1946. The volume of production in Azerbaijan amounted to 20.187 million tons in 1970, compared to 1946, this increase amounted to 8.253 million tons or 69.2%. This increase was mainly due to the discovery and commissioning of new fields. It is important to note that in 1948, for the first time in Azerbaijan, the exploitation of the legendary "Oil Rocks" (NeftDaşları) in the open sea became a historical moment in the development of the oil industry.

After World War II, the problem of profitable exploitation of watered reservoirs in oil fields that were at their final stage of development came to the fore. Older fields that have been in production for many years had large residual oil reserves. Therefore, the problem of determining the economic limit for the development of these resources was also solved.

Since the early 50s of the last century, artificial stimulation methods have been developed to maintain reservoir pressure and increase production. Studies have shown that the presence of one injection and at least two production wells in a row in a water-driven mode was economically feasible. The relationship between production and the well network was studied, and it was decided to reduce the cost of production. Then the method was used to reflect the characteristics of oil deposits, that is, layering, tectonic faults, etc. We proposed a methodological approach to the development of oil and gas fields and its feasibility study based on international experience.

The further development of the oil industry in Azerbaijan coincides with the first coming to power of Heydar Aliyev (1971-1991). During the first reign of Heydar Aliyev, serious attention was paid to all sectors, but at the same time, special attention was paid to the oil industry. Firstly, this industry was one of the traditional in Azerbaijan, and secondly, it was necessary to develop the oil industry in the sea. As a result of the natural depletion of onshore production in Azerbaijan and the development of offshore fields, production fell from 20.187 million tons in 1970 to 11.545 million tons in 1983. This situation persisted until the last years of the existence of the Soviet Union. Thus, the volume of production in 1991 fell to 9.749 million tons.

The processes taking place in the Soviet Union, the nationwide movement that laid the foundation for the year of the dream of freedom, led to the creation of the legal successor of the Azerbaijan Democratic Republic, the independent Azerbaijan Republic. In the first years of independence, both internal strife and the aggression of Armenia against our territorial integrity created many problems.

Problems, including the loss of traditional markets after the collapse of the former Soviet Union, weakening of economic ties between republics, incompetent governance, and so on, continued to increase. All of this negatively affected the activities of certain industries, including the oil industry, and eventually led to the decline of some of them. Thus, the activities of oil-machine-building factories, fulfilling 75-80% of the needs during the times of the former Soviet Union, as well as exporting oilfield equipment to foreign countries, were paralyzed. The activation of internal and external forces, the incompetence of the authorities created an unbearable situation in the country, threatened the existence of an independent Azerbaijan Republic. It was at this moment that the national leader Heydar Aliyev, who came to power for the second time at the insistence of the people, faced the dilemma "death or life". On the one hand, internal disagreements, on the other, outside interference, and thirdly, industrial enterprises, which practically ceased to exist, demanded a quick and correct solution from Mr. Aliyev. The decision of the man who led the republic for many years was not long in coming. And Heydar Aliyev decided to start with the oil industry.

Why the oil industry? In our opinion, firstly, this industry was more or less active, secondly, the infrastructure was preserved in it, thirdly, highly qualified specialists were concentrated in this industry, and fourthly, the products of this industry could be exported. We noted above that special attention should be paid to the development of offshore fields in Azerbaijan, since these fields had large oil reserves that could be extracted. However, we did not have the right equipment for working in deep sea areas. Taking this into account, Heydar Aliyev invited foreign oil companies to come to Azerbaijan, and, first of all, the legislative base for their normal functioning in the republic was strengthened.

After all this, the “Contract of the Century” was signed in 1994, and the “New Oil Strategy” was launched in Azerbaijan, the founder and architect of which was the national leader Heydar Aliyev. The consortium consisted of companies from different countries: the USA, Great Britain, Norway, Turkey and others with a total investment of $ 80 billion. For ensuring the normal work of foreign investors, the Law "On Investment Activity" was adopted, which contains many benefits and incentives.

Today Azerbaijan has turned from a country that received investments into a country that invests; SOCAR has offices in various countries. Azerbaijan implements world-class oil projects: Baku-Tbilisi-Ceyhan; Baku-Tbilisi-Erzurum; TANAP, TAP, where gas produced within the Shah Deniz-2 project will be supplied to the European market.

4.Conclusion

Against the background of the energy security of the countries of the world, the participation of Turkey and Azerbaijan in global projects is highly valued, and new ways in this direction are being explored.

5.References

1. Mirzadzhanzadeh A.H., Sultanov Ch.A., “Etudes of Azerbaijan's oil concept”, Baku, 1994, 100p.
2. Hacizadeh E.M., “Model of economic development in oil and gas production”,Baku, Elm, 2002, 472p.
3. Konoplanik A.A., “Russia in the Emerging Eurasian Energy Space: Issues of Competitiveness”, OOO “Nester Academic Publisher”, 2003, 592p

OR-VII-3

ACHIEVEMENTS OF THE SCIENTIFIC SCHOOL MEMBER OF THE ACADEMY OF SCIENCES OF THE REPUBLIC OF BASHKORTOSTAN D.L. RAKHMANKULOV IN THE FIELD OF CHEMISTRY AND TECHNOLOGY OF CYCLIC ACETALS

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Abstract. The paper presents some achievements of the scientific school in the chemistry and technology of cyclic acetals and their heteroanalogues, founded by member of the Academy of Sciences of the Republic of Bashkortostan D.L. Rakhmankulov at the Ufa State Petroleum Technological University (USPTU).Cyclic acetals and their heterocyclic analogues are multifunctional reagents.They actively use at various stages of obtaining complex organic structures, including biologically active compounds and preparations.In addition, reagents based on them are used as corrosion inhibitors for metals, additives to fuels and lubricating oils, plasticizers of resins and polymers, solvents, components of paints and varnishes, therefore, research in the field of obtaining compounds of these structural classes remains relevant.

Keywords: Cyclic acetals, D.L. Rakhmankulov, 1,3-dioxacycloalkanes.

Member of the Academy of Sciences of the Republic of Bashkortostan DilyusLutfullichRakhmankulov founded scientific schools at USPTU on the chemistry and technology of cyclic acetals and their heteroanalogues, on the development of corrosion inhibitors for oil field equipment and on the history of science and technology [1-4].Below are some of the most significant research results carried out in the unique scientific school of D.L. Rakhmankulov in 1970 on the chemistry of cyclic acetals and their heteroanalogues.The research results of D.L. Rakhmankulov and the staff of the scientific school formed the basis of numerous scientific articles, monographs, dissertations.The analysis of these studies makes it possible to assess the significance of the research carried out and to determine the directions that will be of scientific and practical interest.

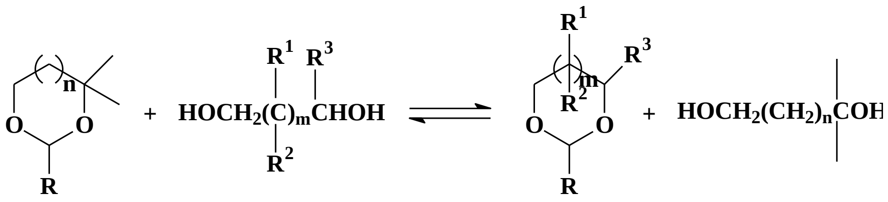
The conversion products of cyclic acetals and their heteroanalogues have a variety of practically valuable properties and can be used as initiators of polymerization, plasticizers of polymeric materials, components of paint coatings, metal corrosion inhibitors and biologically active compounds of various functionalities.

First of all, the scientific school developed methods for obtaining1,3-dioxacycloalkanes on the basis of available petrochemical feedstock, studied the possibilities of their improvement and intensification. One of the famous methods for the preparation of 1,3-dioxacycloalkanes is the Prince reaction, in which olefins interact with carbonyl compounds.A great contribution to the study and expansion of the possibilities of using this reaction was made by M.G. Safarov, N.E. Maksimova, E.A. Kantor et al.

However, the Prince reaction does not allow to obtain a wide range of 1,3-dioxacycloalkanes with different numbers of carbon atoms in the ring; therefore, acetalization of 1,2-, 1,3-, 1,4-diols and other polyhydroxy compounds is a universal method for the synthesis of 1,3-dioxacycloalkanes in the presence of acid catalysts.Other methods have been developed for the preparation of cyclic acetals and their analogues.

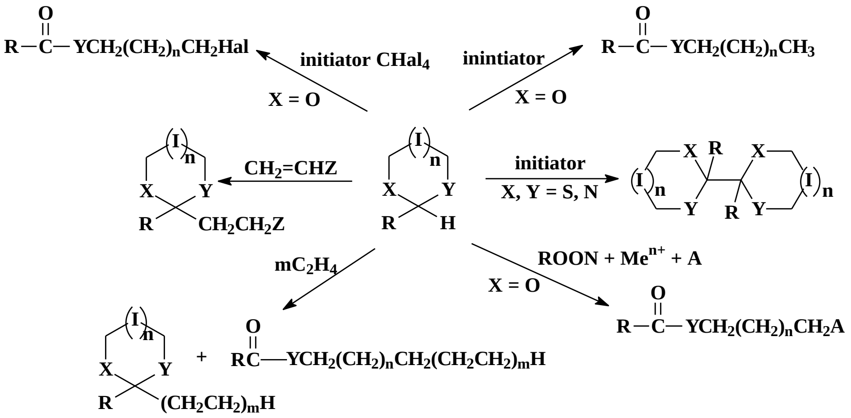
A wide range of studies on the mechanism of alcoholysis, esterolysis, transacetylation, the interaction of 1,3-dioxacycloalkanes with amines and thiols and other heterolyticreactions of 1,3-dioxacycloalkanes was carried out by O.B. Chalova, R.S. Musavirov, N.A. Romanov, I.M. Brudnik and other students and colleagues of D.L. Rakhmankulov.

Thus, the transacetylation of 1,3-dioxacyclanes with di-, tri- and tetra-alcohols is a method of introducing substituents into the fourth, fifth, sixth position of the ring and changing the number of units in the cycle:



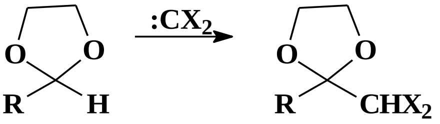
R = H, Alk; R^1, R^2, R^3 = H, CH_3, OH, CH_2OH; m, n = 0, 1, 2

Research in the field of radical and ion-radical reactions of 1,3-diheteroanalogues of cycloalkanes and related compounds, carried out by a team led by V.V. Zorin, made it possible to carry out the transformation of various compounds directly through the carbon-hydrogen bond.It was found that N- and S-containing heteroanalogues of cyclic acetals in the presence of radical initiators are able to selectively transform into thioethers, acid amides, their halogen derivatives, telomersand adducts of cyclic and linear structures:



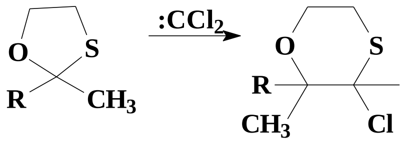
The preparation of halogenated cyclic acetals and their heteroanalogues should be considered separately.Conversion of 1,3-diheteroanalogues of cycloalkanesunder the action of dihalogencarbenes in the scientific school ofD.L. Rakhmankulov was studied by O.G. Safiev, A.A. Vildanov, O. G. Orazov, Z.A. Ayupova, D.V. Nazarov, T.F. Tkachenko, V.A. Saprygin and others.

It was found that dihalogeno- and phenylhalogenocarbenes are selectively introduce into activated C-H-bonds of 1,3-dioxacycloalkanes, forming the corresponding 2- or 4-dihalomethyl- or phenylhalomethyl-1,3-dioxacycloalkanes:



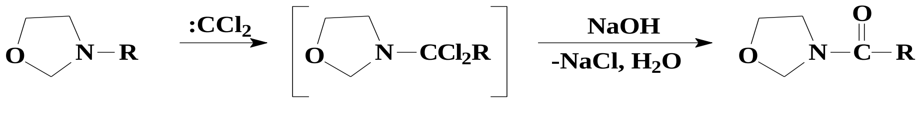
X = Cl, Br; R = Alk, Ph, Ar

The mechanism of the reactions of N- and S-containing heteroanalogues with halogencarbenes differs from the reactions of 1,3-dioxacycloalkanes.Thus, the reaction of 2,2-disubstituted 1,3-oxathiolanes with dichlorocarbene leads to the formation of six-membered cyclic dichlorinated derivatives of 1,4-oxathiane:

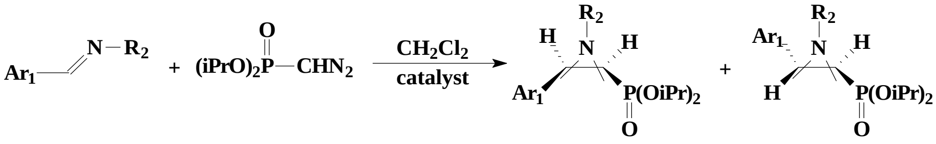


R = CH_3, C_2H_5, C_4H_9, C_6H_5

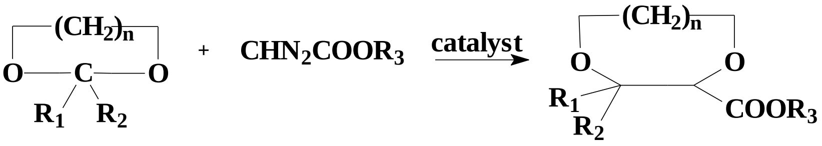
Based on N-alkyl-1,3-oxazolidines, the corresponding N-acyl-1,3-oxazolidines were obtained:



D.L. Rakhmankulov attached great importance to interaction with scientific centers in our country and abroad.Thus, together with the research groups of the Universities of Perugia and Ferrara (Italy) and the University of Bonn (Germany), studies were carried out on the stereoselective preparation of individual isomers in the series of polysubstitutedaziridines by adding phosphorylcarbene to imines (N.G. Kuznetsova):

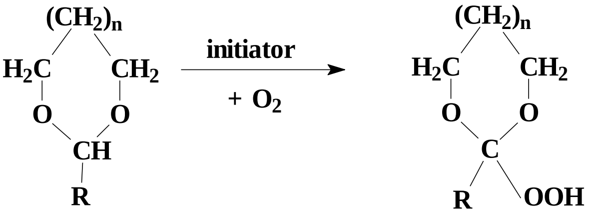


Together with colleagues from the Institute of Organic Chemistry of the Ufa Scientific Center of the Russian Academy of Sciences (V.A.Dokichev, V.V.Shereshovets, N.N.Kabalnova, O.S.Vostrikova, R.M.Sultanova), the reactions of oxidation, reduction of 1,3- dioxacycloalkanes and interaction carbenes with 1,3-dioxacycloalkanes have been investigated.So, the study of the interaction of cyclic acetals with diazocarbonyl compounds in the presence of salts of mixed-valencemetals made it possible to establish the rules of the introduction of alkoxycarbonylcarbenes into the carbon-oxygen bonds of the cycloacetal fragment:

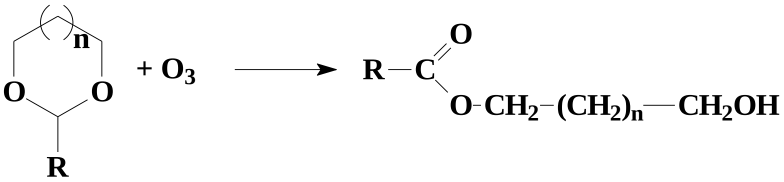


$n=0,1,2$; R_1, $R_2=H$, Alk, Ar; $R_3=Alk$, Ar

The radical-chain liquid-phase oxidation of cyclic acetals obeys the rules known for hydrocarbons. Dialkoxyalkyl radicals, being carbon-centered, easily react with molecular oxygen, that leads to the formation of the corresponding hydroperoxides:



In ozone oxidation reactions, almost the only product is the corresponding monoester:



In addition to the above, the scientific school studied the reactions of acetals and orthoesters with organosiliconecompounds, with organic compounds of aluminum and magnesium, as well as photochemical reactions of linear acetals and heteroanalogues.

The studies carried out made it possible to develop affordable methods for obtaining cyclic acetals and their derivatives, as well as methods for intensifying these transformations using ultrasound and microwave radiation [5]. These studies are of scientific and practical importance.

A detailed analysis of the research results of the scientific school of D.L. Rakhmankulov, devoted to the chemistry of homolytic, heterolytic and other reactions of cyclic acetals and their analogues, was carried out in the monograph [6].

5.References

1. Vil'danov, F.Sh., Zlotskij, S.S., Latypova, F.N., Mazitov, R.M., Shavshukova, S.Ju., Udalova, E.A.: D.L. Rakhmankulov is an authenticscholars and organizer of science and education. Inter, Ufa (2008).
2. Shavshukova, S. Yu., Vikhareva, I.N., Udalova, E.A.: Perspectives of cyclic acetals chemistry. Bashkir chemical

journal 16 (2), 123-131 (2009).
3. Mamlieva, A.V., Mikhaylova, N.N., Latypova, F.N., Udalova, E.A.: General methods for the synthesis of cyclic acetals. History and pedagogy of natural science 4, 25-27 (2018).
4. Shavshukova, S. Yu., Udalova, E.A., Mikhailova, N.N.: To the 80th anniversary of the scientist: D.L. Rakhmankulov’s scientific heritage. History of Science and Engineering 11, 42-47 (2019).
5. Shavshukova, S. Yu.: Experience of using microwave radiation in organic synthesis. In: Organic synthesis and petrochemistry at USPTU. Results and perspectives, pp. 337. Bashkir encyclopedia, Ufa (2018).
6. Vil'danov, F.Sh., Chanyshev, R.R., Latypova, F.N., Zlotskij, S.S.: The chemistry of acetals and their analogues in the studies of the scientific school of D.L. Rakhmankulov. Gilem, Ufa (2015).

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ON OIL PRODUCTION IN AZERBAIJAN IN THE LATE MIDDLE AGES

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Abstract.In modern times, the petrochemical industry of Azerbaijan is one of the most technologically advanced industries in the country. In fact, this sector, which is the basis of the country's economy, has come a long way, consisting of several stages. Among these stages, the last medieval period, which covers the XVI-XIX centuries, has a special place. Compared to previous periods, in the XVI-XVII centuries there was a strong increase in oil production in the Absheron Peninsula, the main center of oil production in Azerbaijan.

The oil produced was exported to neighboring countries in addition to meeting local demand. During this period, a lot of information can be found in the sources about the export of Azerbaijani oil to Iran, Turkey, Russia and Western European countries. There has also been some progress in oil extraction and refining. Baku residents dug oil wells with their backs and ashes, strengthening them with stone masonry and wooden poles. The extracted oil underwent several stages of refining.

Dark brown crude oil was processed twice in large earthenware pots to produce a transparent product, such as alcohol. Such products were mostly used in the lighting of houses and in the treatment of various diseases. The finished oil was packed in leather bundles and transported to warehouses in different parts of Absheron, from where it was sent to various places by ships and caravans of camels. However, the deep decline in economic life in Azerbaijan and neighboring countries in the 18th century as a result of increased internal strife and wars led to a decrease in demand for oil and a sharp decline in its production.

Keywords: black oil, white oil, well, production, warehouse, processing, growth, export

1.Introduction

Oil, one of the main resources of Azerbaijan, was in the region during the Middle Ages and attracted the interest of almost all merchants, travelers and diplomats. In their travel notes, diaries, memoirs and diplomatic correspondence, they provided valuable information on the areas of oil extraction, refining, sale and application in Absheron. Based on this information, in the presented article aims to study the state of oil production in Azerbaijan during the last Middle Ages.

2.Method.

Empirical, theoretical, qualitative, quantitative, multi-method, longitudinal, cross-sectional study, case study methods were used in the study.

3.Results and discussion.

Using methods determined the process of the oil industry in Absheron particularly, and in Azerbaijan in generally only in the 60s and 70s of the XIX century to enter a new, faster, systematic stage of development.

Although the history of oil production in Azerbaijan dates back to antiquity, more detailed information about its large-scale production rebounded to the early Middle Ages. Speaking about the natural resources of Azerbaijan, the 7th century Albanian historian Moisey Kalankatuklu emphasizes the extraction of oil and salt in the regions on the banks of the Kura River [2,s.16-17]. In the following centuries, oil production in Absheron became more widespread and its income was one of the most important sources of revenue for the state treasury. During the reign of the Arab Caliphate, Absheron's high oil revenues allowed it to maintain a military garrison that protected the northern borders of the caliphate from attacks by nomadic tribes. Yagut al-Hamawi, an Arab author who lived in the late twelfth and early thirteenth centuries, wrote about Baku: "There is a very large source of oil there. His daily income is a thousand dirhams. There is another source nearby, from which ... white oil flows like a flood day and night without knowing it. His income is the same as in the previous source." [17, s. 15].

Marco Polo (1254-1324), a famous Venetian merchant and traveler who visited Azerbaijan in the late 13th century, also provides interesting information about Absheron oil. He wrote, "There is a source of oil on the Georgian border, and this oil is so plentiful - that can be loaded on hundreds of ships. It cannot be eaten, but it can be burned or smeared on the body or on itchy camels. They come from far away to buy this oil and burn it all over the country." The Venetian merchant, who described a large oil fountain coming out of the ground independently, stated that "This fountain erupts so much oil in an hour that it can fill hundreds of ships." [14, s.56].

Although medieval authors spoke with great admiration about Baku oil, specific information about its production volume can be found only in the work of the prominent 15th-century Azerbaijani geographer

Abdurrashid Bakuvi. According to him, the daily oil production in Absheron was 200 camels [3, s.89]. If we take into account that each camel's load is 18-20 poods (16,4 kq), then we can determine that about 1,314,000 - 1,560,000 poods of oil is extracted in Absheron every year.

European and Eastern travelers who visited Azerbaijan in the late Middle Ages provide more detailed information about oil production in Absheron. It is clear from these data that in the 16th and 17th centuries, there were 500 wells producing white and black oil in 7 oil fields around Baku. The oil flowing from these wells formed 'oil lakes' in nearby pits. The collected oil was stuffed into goat skins and sold to merchants. Sources report that the extracted oil is transported to different regions of the country and abroad by caravans with 400-500 cargo animals each. [5, s.224-225]. The extraction, protection and sale of oil were carried out under the supervision of a special chief appointed by the judge. Great attention was paid to the protection of oil wells and lakes. Knowing that it was very difficult to put out a fire, the judges worked hard to protect the oil wells and lakes with special guards, creating a large stockpile of sand nearby to put out the fire. [5, s.224-225].

The information of the German traveler Engelbert Kempfer, who visited Baku in January 1683 about the oil production in Absheron, is of great interest. Kempfer, who visited the oil fields in Balakhani, Ramana Surakhani and Binagadi villages, writes that he saw 2 producing and 8 discarded white oil wells in Surakhani village. Wells up to 80 feet [80 m] deep were drilled through the ridge and the mouths were secured with stones. According to him, solid clay soil wells could be drilled to any depth without any reinforcement work, and this did not endanger the lives of workers. However, given the characteristics of the Absheron lands, such a situation would be possible only in relation to shallow wells. Oil flowed from one of these wells, which was larger in width and length, day and night. In general, based on Kempfer's data, it can be concluded that 600,000 poods of oil were extracted annually in Absheron. The annual income of the Shah's treasury from oil production was 7,000 tomans. [13, s.41-44]

The rise in Azerbaijan's oil industry in the 16th and 17th centuries was replaced by a sharp decline in the early 18th century. The decline in sales markets due to the economic crisis that engulfed the Safavid state of Azerbaijan, the occupation and division of Azerbaijan by Ottoman Turkey and Russia played a key role in this issue. It is clear from the information of the Russian military in the 1920s that at that time there were only 70 wells and 30 warehouses left in and around Baku. Revenues from the sale of oil also declined sharply in 1728 to a total of 2,000 tomans. [16, s.426]. The traveler I.Y. Lerkh, who visited Azerbaijan twice in the 30s and 40s of the 18th century, shows that the number of oil wells in Balakhini has halved compared to the previous four. [15, s.84].

After the collapse of Nadir Shah Afshar's empire in 1747, the establishment of independent khanates in Azerbaijan created relatively favorable conditions for the development of the oil industry, as well as other sectors of the economy.

The oil fields, once owned by the Shah's government, became the property of the Baku khans, who accepted the patronage of the Guba khanate, a more powerful feudal state. The relative slowdown in foreign attacks and civil wars has led to a gradual increase in oil production. S.Q. Qmelin, a member of the Russian Academy of Sciences, who traveled to Absheron in 1770 to describe oil wells, wrote that in the present-day Bayil area, which the Russians called the 'Shah Bazaar' at the time, there was a circular and dug perpendicular to the ground. There are more than 70 oil wells with a depth of two sajen (2.13 m). Oil extracted from these wells is stored in a nearby warehouse. However, because Bayil oil lags behind Absheron oil in quality, it was sent only to Salyan. S.G. Gmelin also provides valuable information on the selling prices of white and black oil produced in Absheron. According to him, 15 pounds of black oil was sold for 5 kopecks with the money of the khanate, while 8 pounds of kerosene was sold for 30 kopecks. [9, s.73].

In the conditions of relative stability in the country in the late 18th and early 19th centuries, oil production in Absheron developed, albeit slowly. Of course, oil production during this period fell at least three times compared to the XVII century. However, the attempts of the Baku khans to get the maximum income from oil production led to a certain growth trend in this area. According to S.G. Gomelin, Baku khans earned 40,000-50,000 manats a year from oil production and sales. [9, s.73].

One of the sources compiled in the first years of the XIX century provides a lot of factual material reflecting the real situation of the oil industry in Baku. It is clear from this material that "oil is extracted in the Absheron Peninsula in three types: greenish liquid, black solid and white. The first type using in lighting trade is more important, so they produce more." [12, s.109].

The increase in demand for oil in the country and in foreign markets has led to a gradual increase in the number of oil wells and the expansion of oil production areas. It is clear from the information given in the "Table on the condition of oil wells and oil storage depots" compiled during the Russian occupation of the Baku Khanate in 1806 that there were 121 oil wells in Absheron. 82 of these wells were located in

Balakhani, which has long been the main center of oil production in Absheron, 15 in Surakhani, 17 in Bibiheybat, and 5 in Binagadi. [1, v.20-22; 7, s.6-11]. As can be seen, the number of oil wells has increased several times compared to the 20s and 30s of the XVIII century.

The increase in the number of oil fields and wells was accompanied by an increase in the volume of oil produced. It is clear from official documents compiled during this period that Absheron produced 260,000 pounds of black and 2,500 pounds of white oil a year. The daily sales of crude oil were 37 halvars [4, s.81]. If we take into account that each halvar is equal to 19 poods (pood equal to16,3 kq), we will see that 700 poods of oil is sold daily in the Baku khanate, and 255,500 poods during the year. These figures once again confirm that most of the oil produced in Abshron was exported to other regions of Azerbaijan and neighboring countries.

As mentioned earlier, during the last Middle Ages, the oil fields of Absheron were first owned by the Safavid Shahs, and from the middle of the XVIII century by the Baku Khans. In addition, there were wells belonging to individuals and the foundation of Bibiheybat Mausoleum. While privately owned wells were taxed to the state treasury, the proceeds from the wells belonging to Bibiheybat Mausoleum remained entirely in the mausoleum itself. [5, s.230]. Nevertheless, the judges of Baku had no difficulty in paying 7,000 tumens a year to the royal treasury for the proceeds of the sale of oil. [5, s.229].

In the second half of the XVIII century and the beginning of the XIX century, oil production and sales in Absheron were completely under the control of the Baku khans. S.G. Gmelin wrote that “no one could take oil without the knowledge of the official appointed by the khan.” He says he saw a clay plaque with the khan’s name on the white oil well, which was covered with stones [19, s.72-73]. According to I.T. Drenyakin, a Russian army officer who marched on Azerbaijan in 1796, “each batman was paid one abbasy or 20 kopecks with the khanate’s money for the land determined by the khan for each batman (8 kq) of oil.” [10, s.162].

A comparison of the available sources shows that during the last Middle Ages, which spanned a period of about 300 years, there was no such change in the technique of drilling oil wells, as well as in the refining and storage of oil. During all this time, the main tool used in drilling oil wells was the back and ashtray. The population of the villages near the mines was engaged in drilling oil wells, discharging the extracted oil into nearby pits, and filling the skins with refined oil and transporting it to the city's warehouses. Kempfer, who witnessed the extraction of oil in the village of Surakhani, wrote that each of the 32 wells operating here was serviced by a worker from the village, and that he received only 7-8 abbasy a month for his hard work [13, s.43-44].

Drilling of oil wells was carried out taking into account the characteristics of the Absheron soil. In the seventeenth century, no work was done to strengthen the walls of wells drilled to any depth. E. Kempfer explains this by the fact that the wells drilled in the clayey Absheron soil are not in danger of collapsing. However, the materials of the German traveler of the khanate period show that he made a mistake in this matter. Thus, at the beginning of the 19th century, all wells registered in Absheron were reinforced with stone or wooden beams. Undoubtedly, landslides caused the wells to fill and workers to die. Taking into account these factors, the oilmen dug the wells perpendicular to the ground, taking them wide from above.

I.Lerkh states that the depth of one of the oil wells drilled in Lokbatan reached 90 sajens (1 sajen = 2.13 m) [15, s.84]. As the well deepened, it narrowed. However, in order to prevent landslides, the contraction was not gradual, but a sharp protrusion. The part of the well, both before and after the protrusion, was reinforced with stone masonry or wooden beams. At the beginning of the 19th century, 13 of the 82 wells operating in Balakhani village had stone and 18 had wooden supports. The remaining wells were reinforced with stone masonry at the top and wooden supports at the bottom [1, v.20-22].

The oil from the production wells underwent a multi-stage refining process. In most cases, the oil was extracted from the wells through leather bundles and first collected in special pits dug nearby to remove impurities, primarily water [11, s.27].

Oil from high-yielding wells was pumped to nearby wells through special channels. Refined oil was transported to storage facilities in each mining area. Kempfer writes that one of such warehouses he came across in Surakhani was 17 steps long and 7 steps wide. Stairs were built at both ends of the shallow, attic-covered warehouse. Workers entering the warehouse through these stairs loaded the stored oil into leather carts and loaded them on carts and transported them to stone warehouses near the castle walls in Baku [13, s.43-44]. During the khanates, there were 32 such warehouses in Absheron.

In the late 18th and early 19th centuries, S. Bronevsky, a traveler who spoke about oil production at the Shah Bazaar in Bayil and Pirallahi Island, wrote: “White oil springs are located 18 versts north of Baku. Pits have been dug for easy collection of oil and removal of extraneous particles, and oil flows here from boiling springs through specially drawn troughs. The number of such pits in both mines is quite large, but the white oil accumulates in only one pit. The latter, which is very clean, is sold at a high price and is mainly used for lighting and medicine." [8, s.405]. Indeed, at the beginning of the 19th century, every pood of black oil was sold for 70-80 kopecks with the money of the khanate, while every pood of white oil was sold for 3 manats. [4, s.81].

There are facts confirming that Baku residents are able to process the produced oil. Russian travelers I.Y. Lerkh and S.G. Gomelin, who visited Azerbaijan in the XVIII century, give more detailed information about it. Lerch wrote, "Oil does not burn quickly, it is dark brown. But when it leaves, it turns light yellow. White oil is a bit turbid, but when separated it becomes transparent like alcohol and ignites quickly." [15, s.85]. Large-capacity pottery, which the Russians called 'cubes', was used to separate the oil. After boiling the white oil twice in such pots, a very dark and colorless new product was obtained, which was mostly used as a medicine. [9, s.71].

From ancient times the oil was used for various purposes, first of all for lighting. The use of oil as the main means of lighting in Azerbaijan and neighboring countries in the late Middle Ages is confirmed by the travelogues of many travelers who visited Absheron at different times. In the middle of the 17th century, the Turkish traveler Evliya Chalabi wrote that in almost all settlements of Azerbaijan, houses were lit with oil-filled lamps. [18 s.183]. Oil was also considered the best way to illuminate buildings where silkworms were fed. M.F. Biberstein, a traveler who visited Absheron in the late 18th century, wrote that "the oil produced here is mostly sold in Gilan, because silkworm breeders in this region are convinced that oil is the only substance from which silkworms can be used to light buildings and harm worms." [6, s.15]. Throughout the late Middle Ages, this issue played an important role in sending a large part of Absheron oil to Iran, where silk production was widespread.

In the late Middle Ages, black oil was also used as a fuel to heat homes and baths. I. Lerkh wrote that the locals stayed under the sun, collected black oil from the soil, turned it into a circle, and then loaded it on carts and sold it in the city and far away. Lerch also spoke about the great therapeutic value of Absheron oil, noting that it was used against ringworm, skin diseases, convulsions, scurvy, rheumatism and other diseases [15, s.29].

4.Conclusion

As can be seen, the development of the oil industry in Absheron during the last Middle Ages was closely linked with the military-political conditions established in Azerbaijan. Reaching a high level of development in the second half of the 17th century, the industry was in deep decline in the 18th century due to the destructive effects of almost continuous wars, and production fell by at least three times. Despite some revival that began in the late 18th century, the oil industry in Absheron entered a new, faster stage of development only in the 1960s and 1970s.

5.References

1. Azərbaycan Dövlət Tarix Arxivi. f.24, siy.1, iş 390
2. Moisey Kalankatuklu. Albaniya tarixi. Müqəddimə, tərcümə, qeyd və şərhlər akademik . Z.Bünyadovundur. Bakı, 1993
3. Абд ар-Рашид ал-Бакуви. Китаб Талхис ал-асар ва аджаиб ал-малик ал каххар. Перевод З.М.Буниятова. М., 1971
4. Акты Кавказской Археографической Комиссии. т. IV, Тифлис, 1869, док. 95
5. Ашубейли С.Б. История города Баку. (период средневековья). Баку, 1992
6. Биберштейн М.Ф. Описание провинций, расположенных на левом берегу Каспийского моря, лежащего между реками Терек и Куры. //НА ИИ НАН Азербайджана. инв.466
7. Брилинский А. Краткий исторический и статистический обзор ручной добычи нефти. Баку, 1915
8. Броневский С.Б. Новейшая географическая и историческая известия о Кавказе. т.I, М., 1823
9. Гмелин С.Г. Путешествие по России для исследования всех трех царств природы. ч.3, СПб., 1785
10. Дренякин И.Т. Описание Ширвана. //История, география и этнография Дагестана. (Архивные материалы), М., 1958
11. Искендерова М.С. Бакинское ханство. Баку, 1999
12. Каспийская торговля. //Библиотека для чтения. т. 8, СПб., 1834
13. Кемпфер Э. Красота чужих стран. Перевод с латинского М.А.Байбаковой. //НА ИИ НАН Азербайджана. фонд 1, опис 2, инв. 5091,
14. Книга Марко Поло. Перевод И.П.Минаева. М., 1955
15. 15.Лерх И.Я. Сведения о втором путешествии в Персии, совершенном в 1745-1747 гг. Перевод с немецкого М.М.Абезгуза. // НА ИИ НАН Азербайджана. инв. 486
16. Соймонов Ф.И. Описание Каспийского моря и чинененных на оном российских завоеваний, как часть истории Государя императора Петра Великого. СПб., 1763
17. Якут ал-Хамави. Географический словарь. Перевод с арабского П.К.Жузе. //НА ИИ НАН Азербайджана. инв. 504
18. Эвлия Челеби. Книга путешествий (Извлечения из сочиения турецкого путешественника XVII века). вып.3, М., 1983

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CHANGES İN THE OİL İNDUSTRY OF THE AZERBAİJAN SSR İN 1921-1927

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Absrtact.The article reflects the changes that took place in the oil industry of Azerbaijan in the period up to 1927 compared to 1920 and 1921. Initially, the situation in the oil industry remained tense. Many skilled workers left their enterprises and moved to the countryside due to food shortages and general economic disarray. Lack of workers in enterprises was one of the main problems. On june 15, 1921, a special decision was made at a meeting of the Labor and Defense Council of the RSFSR (LDC) to study ways to restore the Baku oil industry and prepare measures. In 1924, work was in progress to provide the Azerbaijani oil industry with new, modern equipment. Among the work done in this direction, first of all, it should be noted the application of drilling rigs in the oil industry. The application of new technology in the drilling of oil wells was also a key factor in ensuring the rapid growth of the oil industry. It should be noted that despite the progress in the oil industry of Azerbaijan in the period from 1929 to 1927 compared to the beginning of 1920, it had not yet reached the pace of development before the First World War.

Keywords; oil industry, RSFSR, drilling, new economic policy, Azerbaijan Oil Committee

1.Introduction

After the establishment of Soviet power in Azerbaijan in the early 1920s, the situation in the oil industry remained tense, as in some areas. Its interest in the development of the oil industry, which was vital for the Soviet government, which saw Baku as its main source of fuel, led to the development of this sector. The application of new methods and technologies in the drilling of oil wells created a special basis for the development of this field. As a result of the development of the oil industry, there was a need to technically restructure mechanical engineering, one of the most important branches of heavy industry.

Initially, after the nationalization, crisis in the oil industry of Azerbaijan became more widespread and deep. For example, if in april 1920 17.2 million pounds of oil were extracted, in june this figure fell to 14.9 million pounds, and in september to 10.8 million pounds. Refining fell to 4.8 million pounds in september from 6.9 million pounds in june. The decline was so obvious that even Soviet statisticians had to admit that "nationalization not only did not live up to its expectations, but the oil industry, which continued to exist, seemed to be on the verge of collapse" [12, p.458]. The situation was similar in oil refining. If in june 1920, 6.9 million pounds of oil products were processed, in july of that year this figure was 7.9 million pounds, and in september 4.8 million pounds [10, p.23]. The recession continued in full force in 1921. In general, production decreased by 7.3 million pounds from march 1920 to september 1921 [18, p.25].

Many qualified workers left their enterprises and moved to the countryside due to food shortages and general economic disarray. The number of oil industry workers decreased from 52,000 in 1916 to 23,000 in 1921. This decrease was releated primarily to the workers leaving the mines due to mass starvation in the early days of the Soviet government [25, p. 47-49].

At that time, Azerbaijan was a leading link of primary importance in the fuel supply system of the RSFSR. As it is known, during the Azerbaijan Democratic Republic, the national government was not able to establish normal economic and trade relations with the main consumer of Baku oil - Soviet Russia. For this reason, the warehouses in Baku were full of oil and oil products. Immediately after the announcement of the Soviet government, free transportation of oil to Russia began: from april 30 to may 2, 12 ships full of oil (1239,000 pounds) were sent from the port of Baku to Astrakhan [2, p.25]. 15 million pounds of oil products were sent from Baku to Russia in may, and 24 million pounds in june [6, p.438]. In general, during the navigation season of 1920, 160 million pounds (2.6 million tons) of oil were exported to the RSFSR [17, p.96]. Serebrovsky A.P, chairman of the Azerbaijan Oil Committee, assessed the extraordinary vital importance of Azerbaijani oil for Soviet Russia at the city-wide conference of the Baku branch of the Azerbaijani Communist (Bolshevik) Party: “By the end of 1919, our reserves were exhausted. For example, all of Russia had about 5 million pounds of oil reserves, several million pounds of coal, half a million pounds of cotton ... Textile factories operated at only 5% of their productivity, most other enterprises were shut down ... Only in late 1919 Russia proletariat captured the outskirts of Russia (we are talking about Ukraine, Turkestan and other national regions) and obtained their raw materials ... Baku can supply up to

150 million pounds of oil this year (actually 160 million pounds) ... Azerbaijan is a collaborator and friend of the Soviet Republic of Russia. By supplying Russia with fuel, the economic lever can be decisively turned to the benefit of the proletariat.

The fact that Serebrovsky was appointed chairman of Azerneft, created by the center to manage the nationalized oil industry, was further evidence that the "independence" of Soviet Azerbaijan was nothing but an illusion. As Narimanov wrote, Serebrovsky, who had "royal" powers, created a kind of "monarchy" and did not report to the Azerbaijani government. The situation reached the point that “when an Azerbaijani peasant burnt splinter for the lack of kerosene, when an Azerbaijani citizen saw that kerosene was sold cheaper in Tbilissi (Georgia) than in Ganja, you are forced to hear reproach to the perpetrators of these and accusations of colonialism”[8, p.440]. By the end of 1920, a considerable amount, 9.9 million tons of Azerbaijani oil was transported to Russia from Baku [10, p.23]. M.A.Rasulzadeh writes in his book “Azerbaijan Republic” that oil, the real wealth of Azerbaijan, is completely monopolized by Russia and only a part of it is given to the Azerbaijani government for export to the Iranian and Turkish markets to meet domestic needs [9, p. 74].

The new economic policy required the restructuring of the oil industry. On september 1, 1921**,** “Azerneftcom” became an independent Azerneft Trust, subordinated to the National Economic Council of the RSFSR and transferred to the account of the farm. By the way, it should be noted that immediately after the Sovietization, the oil industry, although formally subordinated to the National Economic Council of Azerbaijan, was under the direct control of the center. The actual situation was established legally with the above-mentioned decision and the Russian government (note that the USSR had not yet been formed at that time) became the real owner of Azerbaijani oil. A very small part of the oil produced in the republic was used to meet the needs of Azerbaijan. For example, out of 2.495 million tons of oil extracted in the 1921/22 economic year, only 4.6% (113.6 million tons) was allocated to the oil fund of the republic [3, p.6]. Although the demand for oil and oil products in Azerbaijan was 3246815 pounds, 290.2 million pounds of 304.2 million pounds of oil produced during the nationalization period were sent to Russia [10, p.57]. Only after the appeals of the Central Executive Committee of Azerbaijan [22, p.16] in 1923 the volume of oil allocated for Azerbaijan was increased to 10%.

A similar situation was observed in cotton growing: in march 1923, the Azerbaijan Cotton Committee and the General Cotton Committee of the USSR jointly established the "Russian-Azerbaijani Cotton Company" [20, p.26]. The main goal of the ruling center was to turn Azerbaijan into one of its cotton bases in order to provide the Russian textile industry with cheap raw materials.

However, the oil industry continued to decline in 1921. Although some progress was made in the oil industry in early 1921 thanks to some improvements in the share of oil workers and some other measures, in the summer, as we have noted, the situation worsened again: in july, drilling and oil production fell to a critical level. As the statisticians of that time noted, " it would be wrong to rely only on the “creative enthusiasm” of hungry, naked workers in the absence of the most necessary materials and transport, and in the general decline of labor discipline"[12, p.459]. The most unfortunate situation arose during the excavations. In general, the following regularity was observed in the oil industry: oil production was proportional to the regular drilling of new wells and the deepening of old ones. In this regard, if the total drilling depth in 1920 was 2,861 sazhens, in 1921 it dropped to 2,278 sazhens. Drilling did not reach such a low level even in the early 80s of the XIX century. On the eve of the war (in 1913) the drilling depth reached 76,000 sazhens [13, p. 39].

In june 1921, an award was given to workers to stimulate drilling [18, p.20]. On june 15, 1921, a special decision was made at a meeting of the Labor and Defense Council of the RSFSR to study ways to restore the Baku oil industry and prepare measures. In accordance with this decision, a special commission of the Labor and Defense Council headed by Smilgan arrived in Baku in august. The following tasks were set before him: 1) Provision of oil workers with wages, food, clothing and footwear in the amount of the subsistence minimum; 2) Improving the provision of the oil industry with financial resources, technical materials and transport; 3) Replacement of collegiality with unified management [12, p.459].

In the middle and second half of 1921, the party and state bodies of Azerbaijan raised salaries, increased bread rations, and expanded the distribution of clothing and natural rewards. These measures helped to stabilize the number of workers. The exacerbation of the food crisis in Baku in march 1921 led to a further decline in productivity in oil production in the next few months [12, p. 459].

The transition to a new economic policy raises the issue of leasing or concession of enterprises that require capital investment and do not operate. The oil, textile and fishing industries were among them.

In such a situation, the government of the RSFSR approved the concessions of some oil districts of Baku and Grozny on february 1, 1921. In a letter to A. Serebrovsky on april 2, 1921 Lenin wrote: "It is highly desirable that 1/4 (perhaps even 2/4) of Baku be given to concessionaires" [7, p.218]. N.Narimanov, who supported the concession of part of the oil industry enterprises and mines to foreign investors, believed that this measure would allow to obtain new equipment, which is extremely necessary for the development of the oil industry [16, p.107-108]. However, the idea of Lenin's concessions of oil fields to foreign companies was opposed by the Baku oilmen and the Council of Trade Unions of Azerbaijan (in our opinion, as well as the Baku party organization) and ultimately did not happen [4, p.91-92]. In his speech at the First All-Azerbaijani Congress of Soviets in may 1921, N.Narimanov stated that we must take everything necessary from the bourgeoisie and learn. We are talking about concessions in the sense that we must give the entire oil-bearing territory to the British, Belgians, the Dutch, or do not want to give the Bibiheybat area to foreign capitalists. In this way, we find a way to revive and restore the cemetery. If we can use the help of the bourgeoisie to restore our industry and strengthen our power in 3-4 years, we will tear down the concession agreement, a piece of paper [11, p.57]. It should be noted that despite the serious efforts of the British “Royal-Dutch” and the American “Standard Oil", the Soviet state did not allow these companies to concession oil fields [15, p.66].

Forced to agree with this dictation of the center, N. Narimanov stated in the Supreme Economic Council on january 2, 1922 that the granting of concessions should be carried out only with the consent of the central authorities [24, p.4]. This fact clearly showed who the real owner of Azerbaijani oil was.

It should be noted that foreign companies themselves showed special interest in the Azerbaijani oil industry. At an international conference in Genoa in 1922, Western oil monopolists tried to show their desire to find a way to it by demanding the return of Azerbaijani oil fields to former oil companies. However, N. Narimanov, who was included in the Soviet delegation to the conference as a representative of the Azerbaijani SSR, was told by the Baku Soviet on february 14, 1922, " Considering that at the Genoa Conference the international bourgeoisie will try to put pressure on the working masses of the Soviet republics in order to enslave and plunder them economically, Baku Soviet instructs you to put the Soviet Union, in the person of the united Soviet representation, relying on the working masses and the worker-peasant Red army against the united front of the imperialist powers [4, p.97]. By the way, the representative of the Azerbaijani political emigration A. Topchubashov also took part in the conference. Although N.Narimanov was in favor of partial concessions to foreigners, A.Topchubashov was against any concessions with the Soviet government. Researchers of the Azerbaijani oil industry prof. Sh. Salimov writes that the Soviet state's refusal to pay its former debts and its support for the partial concession of oil fields was in fact aimed at splitting the front of Western countries [10, p.122].

After the transformation of the Azerbaijani Oil Committee into an independent Azerneft Trust in september 1921, significant progress was made in strengthening the oil industry organizationally and economically, and in improving its material and technical base. Granting Azerneft some independence in foreign trade was also a factor in improving its supply. Thus, “Azerneft” Trust has acquired the right to initiate economic activities, purchase the necessary materials, exchange goods, and sell some of the products as it sees fit. The slogan "Self-preservation" became the basis of the trust's economic activities. Wage equality was abolished; a tariff was included, which determined the payment based on the final result of the work done. The government has given “Azerneft” significant freedom in foreign trade operations to exchange oil and kerosene for equipment abroad. A special trading apparatus - “Azerneftsyndicate” was established under Azerneft to trade oil products in Europe, South Caucasus, Central Asia, Middle East (Iran, Turkey, Afghanistan) [21, p. 4-5].

Only since the end of 1921 has it been possible to prevent the decline in oil production. As a result, if in 1920-1921 the economic year 2456 thousand tons of oil was produced, in 1921-1922 this figure was 2945 thousand tons. This increase was primarily due to the introduction of the method of traction in the extraction of oil (extraction of oil from the well with a bailer- S.M.). On the other hand, the increase was due to the drilling of new oil wells. If 1316 wells were put into operation in the 1920-1921 economic year, the number of wells commissioned in the 1921-1922 economic year increased by 296 more than the previous year and amounted to 1612. The number of wells drilled in 1922 reached 7068 [2, p.47].

Increasing investment in the oil industry helped to stop the decline in this area. Thus, if in the 1920-1921 economic year 13.8 thousand tons of gasoline, 91.6 thousand tons of lubricating oil, 31.8 other oil products were purchased, in 1921-1922, 20.5 thousand tons of gasoline, 134.1 thousand tons of lubricating oil, 165.7 thousand tons of various oil products were obtained, respectively [2, p.37].

As a result of the search for new oil fields in Absheron in 1922, rich oil fields were discovered in Kirmaki and Kirmekialti layers in Balakhani-Sabunchu region [4, p.98].

The transition from recession to its recovery began in various spheres of economic life with the measures taken. But it was still too early to talk about any development. As D. Bunyadzadeh wrote, “The rapid development of the oil industry in Azerbaijan began in 1923-1924. From this time, the oil production system was fundamentally changed, a deep pump was applied instead of the obsolete well, and closed operation of wells began [5, p.32-33]. In the economic year of 1922-1923, 1160 tons of oil was extracted from 3 wells with deep pumping. In the economic year of 1923-1924, the number of wells using the deep pumping method reached 87, and 32,646 tons of oil was extracted from these wells [2, p.43].

In 1924, work continued to provide the Azerbaijani oil industry with new, modern equipment. Among the work done in this direction, first of all, it should be noted the application of drilling rigs in the oil industry. In the 1923-1924 economic year, 27,105 meters of the 7,0098-meter drilling in the Baku mines were the share of the drilling method.

Oil production is growing rapidly: if 2.945 million tons of oil were extracted in the 1921-1922 economic year, 3.485 million tons in 1922-1923, 4.125 million tons in 1923-1924, and 4.663 million tons in 1924-1925 oil were extracted [19, p.207].

The revival in oil production was also accompanied by positive changes in the field of oil refining. However, despite the positive changes in the field of oil refining in 1921-1926, it did not reach the pre-war level, the volume of refined oil in 1926 was only 77.7% of the 1913 figure [2, p.47]

The revival in Azerbaijan's oil industry has led to an increase in the number of workers here. However, this increase was mainly due to workers from Russia and Ukraine. Despite the policy of "localization", (“indigenization”) the training of national qualified workers was unsatisfactory. For example, if in 1921, 4151 Azerbaijanis worked in the oil industry (2972 of them were workers), in 1925 their number reached 5271 (4504 workers) (these figures do not include the number of workers from Iran, the absolute majority of whom are Azerbaijanis) [23, p. 76-77].

One of the reasons for this situation was the administrative-command policy of the Center's executives, as well as the head of “Azerneft” A.P. Serebrovsky. Narimanov, who had always struggled with Serebrovsky, wrote: "If you look at the staff of Neftkom and Baksovet now, the impartial observer is horrified. Local muslim engineers and intellectuals are trading, and these enterprises are filled with russians, armenians and jews ”[8, p.440]. According to the information Narimanov referred to, only 1192 Russian children were enrolled in factory apprenticeship schools, while 1192 russian children studied in factory-plant apprenticeship schools, only 26 Azerbaijanis received vocational training[8, p.453]. As a result of the activities of such figures as Narimanov, in 1924 it was possible to increase the number of azerbaijani youth studying in factory-plant apprenticeship schools to 40% [4, p.119].

The application of new technology in the drilling of oil wells was also a key factor in ensuring the rapid growth of the oil industry. Already in the economic year 1924-1925, half of the drilling work was carried out by twist drilling. Thus, 67,140 meters (55 percent) of the 122023 meters of drilling done at that time were carried out by twist drilling. As a result, it was possible to exceed the level of 1913 in the drilling of wells in the 1925-1926 economic year. If in 1913 drilling was carried out at a depth of 171774 meters, in 1925-1926 this figure reached 202985 meters (128270 meters, of which 63.3 percent fell to the share of drilling) [2, p.43-44].

The main reason for the increase in the number of drilling operations was the use of deep pumps and compressors (air, steam, gas compression machine - S.M.). Of the 2,257 wells in operation in 1925, 797 were wells where these methods were applied [2, p.45].

Despite significant investment in the oil industry, it was not possible to achieve the desired results in this area. Thus, as a result of the electrification of oil fields, until 1925, 65% of “Azneft” union drilling rigs were powered by electricity. The foundation of oil engineering was laid. One of the measures taken to develop the oil industry was the commissioning of the Schmidt plant. 5.514 million tons of oil were produced in 1926/27, which was 75% of the production in 1913 [19, p.207]. By the way, the oil industry was able to exceed the production of 1913 (7.35 million tons) only in 1928/29 (8.363 million tons) [14, p.32]. Drilling in 1925/26 exceeded the level of 1913 by 23% [23, p.28-29]. In september 1926, the number of oil wells reached 2,692, of which 1,549 were deep pumps and 145 were compressors. By the fall of 1926, daily oil production exceeded 1 million pounds. For comparison, if in october 1924 the average daily oil production was 787,000 pounds, in august 1926 this figure reached 1,051,000 pounds, an increase of 20.5 percent. In 1925-1926, 8 million pounds of gasoline and 10 million pounds of lubricating oil were produced [2, p.45-47].

The training of nationally skilled workers in the oil industry was still unsatisfactory. In 1926, 4411 people (3708 workers) and in 1927, 4468 people (3955 workers) worked in this field (these figures do not include the number of workers from Iran, the absolute majority of whom are azerbaijanis). In percentage terms, the share of local azerbaijanis fell from 17.9% in 1921 to 10.6% in 1926. The number of Iranian azerbaijanis remained stable - 20%. The share of Russian workers increased and reached 55% in the early 1930s [23, p.76-77].

References:

In Azerbaijani

1. ANAS TİEA, work 1829
2. ANAS TİEA, work 2404
3. SAAR, f.411, p.5, work 123
4. History of Azerbaijan. In seven volumes. Volume VI (April 1920 - June 1941). Baku: Elm, p. 568, (2008)
5. Bunyadzade D. Ten years on the path to socialism. Baku: Azerneshr, p.64 (1930)
6. Ibrahimov Z.V. Lenin and the victory of the socialist revolution in Azerbaijan. Baku: Azerbaijan State Publishing House, p.528, (1970).
7. Lenin V.İ. About Azerbaijan. Baku: Azerbaijan State Publishing House, p.396(1970)
8. Narimanov N. Selected works. Baku: Lider, p.496.(2004)
9. Rasulzadeh M.A .The Republic of Azerbaijan. Transliterator of Arabic graphics, author of notes and dictionary Asif Rustamov. Baku, Science,. 116 pages.(1990)
10. Salimov Sh.D. Azerbaijani oil in international relations (1920-1922). Baku, Baku University Publishing House, p.160 (2005)
11. Samedov K., V.I Lenin on concessions. Scientific Works of the Azerbaijan Institute of National Economy, Baku:, №1, p.53-59 (1970)

In Russian

12. Azerbaijan desktop calendar 1924-1925. Baku: Publication of a special section at AzCIC, p. 536.(1926)
13. The weight of the Caucasus. Tbilisi, p.490 (1923)
14. Twelve years of the Azerbaijan SSR. Statistical collection. Baku: Azerneshr, p.118 (1940)
15. Dilbazov A.K. Transition to a new economic policy in Azerbaijan and its specifics (to the 50th anniversary of the NEP). Scientific notes of the Institute of National Economy named after D. Buniatzade, Baku:, №2, p. 59-67 (1971)
16. Dilbazov A.K. Formation of socialist industry of Azerbaijan. M .: Higher School, p.160 (1976)
17. History of the USSR from ancient times to our days. In 12 volumes. T. VIII. M .: Nauka, p.726. (1967)
18. Review of the Azerbaijani oil industry for five years of nationalization. Baku: Second Gostipography Azpoligraftrest VSNH, p.182.(1925)
19. Review of the activities of the government for 1925 and 1926. Report to the V All-Azerbaijani Congress of Soviets. Baku: Sovnarkom and VES Departments Publishing House, , p.408.(1927)
20. Report to the III All-Azerbaijani Congress of Soviets in 1922-1923. Baku: Sovnarkom Publishing House, Ch. I., p.53 .; Ch. II.p. 328 (1923)
21. Polonskiy L. NEP in Azerbaijan // Literary Azerbaijan, №1, p.3-9 (1990)
22. Minutes of the third session of the plenum of the Azerbaijan Central Executive Committee of the Soviets of Rab., Cross., Krasnoarm. and the Sailor. Deputies (March 3-5, 1922). Baku: AzTsIK Publishing House, p.71. (1922)
23. Fifteen years of the Azerbaijani oil industry (1920-1935). A brief statistical directory. Baku-Moscow: Nefteizdat, p.80. (1935)
24. Creation and strengthening of the dictatorship of the proletariat in Azerbaijan (thematic collection of scientific works), Baku:, p.80. (1988)
25. Tokarzhevsky E.A. Essays on the history of Soviet Azerbaijan during the period of transition to world work on the restoration of the national economy (1921-1925). Baku: AN Azerbaijan Publishing House. SSR, , p.212. (1956)

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PHENOMENOLOGY OF OIL AND ITS FEATURES IN THE ART OF AZERBAIJAN

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Abstract. The article considers the phenomenology of oil through the segments of the philosophy of culture, which by their origin and essence are closely related to the episteme of the world perception. Azerbaijani oil is a special page for our country, its historical past, modernity and future. In the XXI century, the idea of harmonious co-evolution of nature and society is gaining more and more popularity. The harmonious combination of natural resources and cultural values of the country is the philosophy of modern Azerbaijan, which is building the mechanism for distributing the natural resources for the purpose of social security of the population. Such strategy makes possible to shape a secure future for the nation. After all, oil is not only fuel, but also energy, life, the generator of the wheel of history, a kind of engine of progress in industrial society. Oil not only provides the daily life, but is also a starting point for understanding what our society will be like in the future.

The article considers the phenomenology of oil in the aspect of Azerbaijani art. The works of art of Azerbaijani authors testify to the heroes-workers of the oil industry, whose generalized images inspired many outstanding composers, artists, sculptors to create the works of deep philosophical sound. The artistic factor, to some extent present in them, contributes to a deeper phenomenological approach when reflecting the oil theme. Thanks to spiritual carriers, such as music, fine arts, cinematography, the images and names of the first well drillers and creators of oil fields have forever remained in the history of Azerbaijan.

Key words: the phenomenology of oil, Azerbaijani oil, oil in musical reflection, oil in the cinematography, oil in the visual arts.

1.Introduction

Topicality of the research topic is that, oil itself has a huge impact on the life of the society. Oil becomes the object of consciousness, more and more penetrating into human thinking. That is its phenomenon. Oil is becoming the independent substance for study. For Azerbaijan, as the oil-producing country, oil is one of its symbols, and therefore its phenomenon is projected onto other strata of life, including culture and art.

The novelty of the problem «Phenomenology of oil and its features in the art of Azerbaijan», is as follows:

- the phenomenology of oil is presented as the primary direction not only in the national framework, but also in the spatial survey of the post – soviet states;
- for the first time, the phenomenon of oil was considered in the aspect of Azerbaijani art;
- for the first time, there was made the attempt to generalize the artistic character on the basis of works of various types of Azerbaijani art.

2. Methods

Historical, logical, the method of systems analysis, as well as the methods of generalization, analysis and synthesis.

3.Discussion

The phenomenology, being one of the directions of modern Western philosophy, is presented through the scientific developments of such scientists as E. Husserl, M. Heidegger, E. Levinas, M. Merleau-Ponty and others. The distinctive feature of phenomenology is that, it is of a methodological nature, in other words, in fact, phenomenology is not just one of the philosophical trends, but it is the very methodology itself that was proposed by E. Husserl and M. Heidegger. Thanks to the works of these philosophers, phenomenology, as a whole, poured into a worldwide movement, and such a substance as oil turned into an object of comprehensive, dialectical study, which laid the foundation of science. Husserl was the first, who presented a methodically reflected view of the naturalistic theory of knowledge, which served as the impetus for the transcendental turn, which included the Descartes and Kantian curve at once, having in mind that, the meaning of transcendental reduction consists of two components: negative and positive. If the first hinders the transition of the main epistemological problem from the philosophical (phenomenological) dimension to the scientific one, then the second keeps the philosophical dimension of the problem in its purity open [1]. Moreover, Husserl analyzed the stages of the complex, polyphonic, creative process of transcending in art [2]. His student Heidegger went further, he refused the language of intellect, consciousness, experience and, etc. However, at the same time, he considered the phenomenology with new openness, new receptivity, and the sense of unity with the world [3]. Levinas expanded the concepts of living embodiment and more refined technique for suspending the conceptualization to reveal the experiences as they arise [4]. Sartre introduced an ethical dimension to what has traditionally been an epistemological project [5**]**. Merleau-Ponty made the important contributions to the philosophy of art, history, management of natural resources and politics, which played an important role in the spreading of phenomenology [6**].**

Thanks to the works of the mentioned scientists in the philosophical science included such direction as the phenomenology of oil. On the one hand, oil is the welfare, but on the other hand, it harms the environment, which stipulates the search for its alternative. The nationwide leader of the Azerbaijani people Heydar Aliyev, starting the project «Contract of the Century» (2004 year), understood that it was the necessary stage in the economic breakthrough of Azerbaijan.

"Pumped out of nature and became, as a part, endowed with great importance for the world economy, geopolitics, social relations and political institutions, oil is acquiring its autonomous agency (if not to say “subjectivity”). Turning into a fetishized object of human desire, extracted with the help of technological operations, oil has a counter effect on a person. It would seem, that being the product of an active invasion of technology into the passive matter of nature, oil is capable of overturning subject-object relations, depriving a person of critical rationality and turning him into a hostage of his own passion / desire. The concept of "resource curse" despite of its metamorphism reflects well an unconscious supposition about the true relationship between oil and human beings"[7]. Here is another characteristic of oil: "Oil awakens the extraordinary emotions and passions, as oil is above all a colossal temptation. This is a promise of easy and crazy money, wealth and strength, happiness and power"[7].

In connection with the phenomenology of oil in a philosophical sense, the formulation of this problem itself, it should be better to highlight some sources that gave impetus to the understanding of oil. First of all, this is the book by Daniel Yergin “Oil output. The world history of the struggle for oil, money and power” (1990) for which he received the Pulitzer Prize [7]. The translation of the English title of the book «Prize» as output into Russian reveals the vision of oil as a phenomenon in the best possible way. The word "output", as we know, has two meanings in Russian. One of them is extraction, pumping out from the depths, and the other meaning is welfare, property, prize, reward, in other words, its ultimate outcome is the acquisition of power. The double-natured name of the Russian translation «output» very well reflects the essence of oil. In particular, D. Yergin made oil the subject of independent study and gave it the «status» of a phenomenon.

The phenomenology of oil in a philosophical sense has, based on stated in his book, three main aspects:

1) the progressive development of the capitalist formation and entrepreneurial activity; the dominance of the company «Standard Oil» in oil industry of the USA; the expansion from handcrafted oil production to technological progress in the local and the international economy of the XX century.

Throughout the history, contracts have been concluded between individual oil
industrialists, large corporations and the countries.

However, by that time, oil had already won public recognition and became the most important source of energy. In the XX century it radically changed the life.

2) oil is associated with politics and power. This was confirmed by the First and Second World Wars. Certainly, Hitler was interested in the oil of Caucasus. Nevertheless, due to the oil advantage the USA, Germany and Japan ended in a fiasco.

During the Cold War, the USSR and the USA fought for oil domination. The Suez crisis in the 50s was also driven by oil. In the 70s, the struggle for oil became a global problem. Oil has also become «a bone of contention» and the cause of the war in the Persian Gulf.

However, oil continues to maintain its high commodity position; it is the decisive point in the national strategies and the international policies.

3) transformation of the world into a «hydrocarbonic society». Today people are so dependent on oil that they do not fully realize its enormous impact. Nevertheless, someday, perhaps in the near future they will have to take a decisive step towards switching to alternative energies, because, the «black gold» is losing its value [8,].

The phenomenology of oil receives the independent study and disclosure of the problem at the conference in St. Petersburg, in 2018, which was namely held under the name «Phenomenology of oil». At this forum, researchers from different countries (Russia, Italy, Germany, Serbia), the representatives of the world of art - artists, sculptors, as well as philosophers, writers, philologists and political scientists took part in an interdisciplinary discussion of oil. The phenomenon of oil was presented in the aspect of philosophical analysis through the prism of the humanities, and the reflection of oil in art was also considered. At the conference was emphasized that, oil has become an object of worship for various social groups, and religious confessions [9]. It should be mentioned that, the topic of this article to a certain extent was formed under the influence of familiarization with the materials of this conference, because for Azerbaijan as an oil-producing country, one of the symbols is oil.

It should be noted that, in the XX century, the demand for oil determined the supply, respectively, the growing dependence on it was noted positively and symbolized the progress. In the context of the struggle for state independence, the Republic of Azerbaijan made a qualitative breakthrough to such extent that it was called the economic miracle. Here, of course, oil played the main role. The oil reserves of the Absheron Peninsula in the world dimension are one of the richest and most ancient. The ancient Greek historian Plutarch testified that the soldiers of Alexander the Great used oil brought from Absheron for lighting at night [10]. Oil was transported in wineskins or pottery vessels. Since then, the process of its extraction from the bowels of the earth and the Caspian Sea, as well as the transportation of raw materials, has changed significantly: the manual labor was replaced by modern mechanized installations; instead of pottery vessels and other containers, the pipelines were built to transport oil to the European countries.

In the aspect of the topic of the phenomenology of oil, it is impossible not to mention 2020 year. The pandemic, which touched precisely the human factor – the most vulnerable - struck down on all existing stereotypes, all hierarchies, it has significantly shaken the hegemony of oil, at least for the moment. There has been a big reassessment of values, but it is naturally impossible to realize this and see further prospects for how this will all develop; only time can show it. The Covid-19 pandemic, which has catastrophically collapsed global energy demand, extremely aggravated the already inexorably growing global overproduction of oil [11]. Most countries were not ready for such a sudden collapse and, not knowing what anti-crisis measures to take, suffered huge financial losses, while countries with developed economies, quickly navigating in the environment of pandemic continued along the path of decarbonization, in other words they refused of the fossil fuels. «The Stone Age ended not because of a shortage of stones, but simply it had to give the way to the new technologies» [11]. This associative parallel, even in an ironic form, depicts a very uncertain future of oil ...

The perception of Azerbaijan as the oil producer has become so deeply rooted in the world and in the mentality of the Azerbaijani people itself that it has integrated into the culture and become a part of life. Oil seemed to flow into the cultural space, turning into an independent substance, condensing in itself the historical energy, various ethical values and the ideological meanings. The artistic attributes of oil are present even in the design of a number of architectural structures in Baku. In particular, one of the striking examples is the building of the Central Bank of the Republic of Azerbaijan, which is located in the center of Baku, on one of the main streets – Rashid Behbudov street. Here, we can talk about the color layout, since it was built of golden glass and black alcapon, i.e. there are two colors here - black and gold, symbolizing the image of oil as «black gold» and, which is very important, this is the building of the Central Bank of Azerbaijan. It is also symbolic that behind the building is located the Azerbaijan State University of Oil and Industry – the talent foundry of the world's best oil specialists. Facing the building there is a sculpture with a raised hand of Heydar Aliyev, pointing the way forward to great achievements, to the harmony of nature and art. Another very interesting example, a more modern interpretation of the use of oil themes, can serve the installations with the participation of oil rigs, which are located in the park in front of the building of the new Palace of Water Sports. It really smells of fuel oil here and the pumps run into the well! It is impossible to imagine the Absheron landscape without oil derricks, which are spread like clusters along the entire coast… The whole history of oil began precisely from these rigs, from the time when there was so much oil that, the rigs were placed right on the ground and they pumped oil. And, therefore, in the 50s - 60s, this Absheron landscape with an abundance of oil-derricks was very familiar and symbolic.

Thanks to the spiritual media - music, painting, sculpture, etc., the images of the first well drillers, creators of oil fields have forever entered the history of Azerbaijan. The art community has dedicated and dedicate their works to them, the heroes of oil industry. During the silent film years, the famous photographer A. M. Michonne shot the newsreels «The Fire of the Oil Fountain at Bibi-Heybat» (1898) and «The Oil Fountain at Balakhany» (1898). The plot of these newsreels is about the hard everyday-life of oil workers, about sabotage at oil wells, about the heroic work of drillers and oil producers. The first demonstration of the «The Oil Fountain at Balakhany» took place on August 2, 1998. It is remarkable that, that based on this date, by the order of the President of the Republic of Azerbaijan Heydar Aliyev (December 18, 2000), August 2 was declared the Day of Azerbaijani Cinema. In 1916, the joint-stock company «Pirone» released the film based on the novel of the same name by the writer Ibragim bey Musabekov «The Kingdom of Oil and Millions». In the film is shown Baku at the beginning of the XX century, the life of Baku millionaires and the life of workers who earn their daily bread by hard labor in the oil fields. By the way, the shooting of this film was sponsored by oil industrialists [12]. In 1923, the documentary film “The Fire at the Surakhani Oil Fields” was shot. I would especially like to mention the documentaries "The Novel about the Caspian Oil Workers" (1953) and "Conquerors of the Sea" (1953). This film dilogy was directed by the famous filmmaker, one of the most famous documentary filmmakers of the XX century, Roman Carmen, which is about the life and extraordinary friendship of oil workers, about their heroic deed, every day "subduing" the sea weaves, producing oil in harsh conditions. R. Carmen is the author of such films as "The Great Patriotic War *," The Nuremberg Trials "and many others. As it is known, art as a form of reflection of reality carries the factor of artistry. The documentaries also carry the artistic message to one or another degree. In these films of Roman Carmen, the romantic feeling on the one hand (the romanticism of glorifying the labor of oil workers), and the maritime theme on the other hand, are very characteristic and they create the artistic mood of the films.

In 2015, on the occasion of the 70th Victory over Nazi Germany, with the support of the Heydar Aliyev Foundation, was shot the documentary film “Target is Baku. How Hitler lost the war”. The film was shot by the Baku Media Center and the famous French documentary film company “Clarke Costelle & Co” (CC & C). the project was directed by the producer, film director Arzu Aliyeva. The film states the fact that, during the war years, more than 70 percent of oil and 80 percent of gasoline consumed in the Soviet Union fell to the share of Azerbaijan [13]. At the same time, the company «Clarke Costelle & Co» (CC&C) released another film «Apocalypse: The Second World War», in which the battle for oil takes place as the main storyline.

The next type of art that gets involved in the orbit of “oil” influence is music. At first glance, it might seem that what could be the intersection points of seemingly incompatible things - oil and music? No, we are not talking about creating a piece of music like the famous "Bolero" by Ravel, which the composer, as it is known, wrote under the influence of a visit to a steel mill. Here, very interesting deep aspects of another plan arise. There are connections of a different nature between music and oil. The first aspect is historical. When the oil boom began, the large oil owners invested not only in education and enlightenment, but also in art - they built the Opera House, began to invite the musicians, artists, singers, etc. the European musical culture penetrated intensively in Azerbaijan.

One of the many reasons for this process was oil, which changed Baku into an important industrial city, multinational in appearance, which in its turn led to the emergence of typical attributes of European musical art here. However, at that time in Azerbaijan it existed in isolation from the national musical culture. The broad Azerbaijani public circles did not perceive the classical samples of European composer's creativity. The fusion of two musical cultures different in systemic qualities was carried out by the coryphеus of Azerbaijani musical creativity - Uzeyir Hajibeyov. The appearance of this outstanding Azerbaijani composer was prepared by many historical factors. One of them, of course, not directly, but indirectly, was the active development of the oil industry in Azerbaijan, which contributed to the creation of conditions for the assimilation of professional European music in Azerbaijan [14].

The second aspect is associated with the musical creativity, which, to one or another degree, has in its content a reflection of the theme related to oil. Consequently, at the end of the 1920s and early in 1930s, U. Hajibeyov and M. Magomayev wrote the first Azerbaijani mass songs, including songs about oil. Later, the songs about oil workers were created by T. Kuliev and A. Rzayev. Music for two documentaries dedicated to oil workers was written by K. Karayev - "The Novel about the Caspian Oil workers" and "Conquerors of the Sea Weaves". Oil workers are the heroes of the film "My Favorite Song" (or Bakhtiyar), the music for which was written by Tofig Kuliev. The ballet of Tofig Bakikhanov "Caspian Ballad" is dedicated to Azerbaijani oil workers [14]. It is especially important to emphasize that the oil theme so inspired K. Karaev, so penetrated into his consciousness that years later, when he comprehended this problem in a purely musical aspect related to the development of folk music in composer's work, he was struck by a deep analogy of the connection between folklore and oil deposits.

If we already make comparisons, then, most likely, folk music can be likened to oil deposits, which are located in the earth in the form of layers located from the surface at different depths» [15]. And further K. Karaev continues to deepen this analogy: “Some 70-80 years ago in Absheron,” he argued, “it was enough to dig a well several meters long, and it quickly filled with oil ... People, in pursuit of profit, predatorily squander the upper, the most accessible to them layers. Oil began to go deeper, the upper layers were depleted, and now it can be produced only with the help of sophisticated technical devices. The situation is similar with folk music. Let's think about it, are not we getting it too easily, aren't we too mercilessly using the upper, easily accessible layers, isn't it time for us to think about the fact that folk music is really inexhaustible, but its main wealth is not only on the surface, but lies much deeper than we suppose and that it's time for us to get to them, armed with the necessary technical devices" [15]. By technical adaptations K. Karayev meant modern means of musical expression, which are not always quickly assimilated, not only by a wide audience, but even by professional musicians. Certainly, in order to do this, one must be a virtuoso, a foremost worker. In this respect, the statement of the outstanding Azerbaijani scientist A. Kh. Mirzadzhanzadeh is characteristic: "To reject new forms of writing, like everything new, only on the basis of what is perceived by an "average" person is not enough, of course, it is not correct. What is perceived today by the "eminent" representatives or the "elite", tomorrow will be perceived by the "average" person [16]. Azad Mirzajanzadeh is famous not only for being an outstanding corypheus of Azerbaijani oil and gas science, academician, oil worker, teacher, he is a man of encyclopedic knowledge, an unusually all-round mind, deeply versed in art and, in particular, a fine connoisseur of music. For example, the following phrase belongs to him: «Try to express music in any other form, - writes A. Kh. Mirzadzhanzadeh - Music does not convey the meaning of speech, but it is, to a much more powerful degree than speech, capable of conveying the tone of speech intonations» [16]. It is important to note that, Academician A. Mirzadzhanzadeh is the author of the manual "Introduction to the specialty", envisaged for students of technical universities. It is significant that he writes this manual through the prism of the humanities, literature and art, i.e. thus demonstrates that for the students of technical universities, future engineers and young technical specialists, the humanitarization of their thinking is very relevant and important. In his manual "Introduction to the specialty", he also quotes Kara Karayev about musical folklore, talks about the greatest cultural wealth of the Azerbaijani nation, which is subject to deep respect.

The third aspect is oil and charity. Very often it is the oil companies that sponsor music festivals, concerts, in addition, oil companies often sponsor talented children, their studies, etc. I would especially like to emphasize that the oil company "LUKOIL" financed the creation of films about the outstanding composer Kara Karaev and the famous conductor Niyazi.

The topic of oil also finds an interesting disclosure in the fine arts of Azerbaijan. The National Art Museum of Azerbaijan has collected the expositions of different times for future generations [17]. Not only music, but also works of art display the heroes -oil workers, whose individual and generalized images inspired many outstanding artists to create masterpieces of fine art. As the head of the Department of International Relations and Museum Innovations of the National Museum of Arts A. Melikova notes, the first "sketches" that have been preserved on postcards of the XIX - early XX centuries were made in the prerevolutionary years by foreigners who came to Baku on various occasions. Thus, the British artist W. Simpson and the French photographer A, Michonne, being in Baku, photographed the oil fields in Surakhani and the hard work of the workers. A prominent Russian painter and graphic artist A. Ostroumova-Lebedeva, while being in Baku, during the First World War, painted a number of oil-related pictures. Among them we can note: "Bibi-Heybat" and "Oil platforms of Baku" and many others, reminding the sketches from nature. Currently, both paintings are not in Azerbaijan: one of them is in the Tretyakov Gallery, and the other is in the Art Museum of Estonia, in the Kadriorg Palace [18].

It should be especially emphasized that, the above-mentioned plots of the paintings cover the period when Azerbaijan ranked first place in the world in oil production. At that time, in some fields (Balakhani, Ateshgah-Shubany, Lokbatan), the daily oil production rate reached 16-20 tons. The famous well №1 in the Surakhany field produced 35 tons. of white oil. In the Ganja region of Azerbaijan, Naftalan medicinal oil, which has no analogue in the world, was produced. In Bibiheybat, 18-30 meters from the coast, for the first time in the world, oil was extracted from a hand-drilled well in the sea. Later, oil and gas field Neft Dashlary was explored in the Caspian Sea.

Already in the Soviet period, when a whole pleiad of Azerbaijani artists, having received their education in higher educational institutions in Moscow, Leningrad and Tbilisi, returned to Azerbaijan, and they immediately joined an active creative search. Furthermore, in the Azerbaijani fine arts, the next national stage of development began with the priority of the oil line. As a result, appeared the beautiful paintings by artists - S. Salamzadeh "A team of young oil drillers", "Baku" by T. Taghiyev. "Industrial Landscape "," Hills "by L. Feyzullaeva," Oil Rocks "by K. Khanlarov," Trestle "by B. Mirzazadeh," Oil Rocks "by N. Ismayilov. In continuation of the series "Oil Rocks" M. Rahmanzadeh presented the graphic work "Our Guests", which depicts foreign representatives in the process of showing them a picture of a unique offshore oil field, symbolizing the national landmark of Azerbaijan. Then oil was a strategic resource for the huge Soviet power. The maestro of landscape painting, Sattar Bahlulzadeh, glorifying the living, realistic beauty of nature, brought concentration to the oil theme on the one hand and reverent, respectful attitude on the other. The artist devoted many paintings to the oil fields of the Absheron Peninsula. The canvases of our famous contemporaries - T. Javadov, N. Gasimov, M. Abdullayev, who also repeatedly refer to the oil theme, breathe realism.

Tair Salakhov. "The Shift is Over". 1957.[19]

Tahir Salakhov. Triptych "Land of Fires", 2007 (one of parts). [20]

It should especially be noted that the picture of the outstanding artist Tahir Salakhov "The Shift is Over". According to T. Salakhov himself, while painting the picture, the portraits of heroes-sailors flashed in his head - Mikhail Kaverochkin, drowned in a whirlpool of waves, fearless sailors – explorers from the boat "Sergey Chvanov", who gave their lives for the benefit of their native Azerbaijan [18]. In 2007, a new testimony to the large-scale personality of T. Salakhov appeared, his last work - the famous six-meter triptych "Land of Fires", in which the artist skillfully realized his idea of showing the past and present of the Azerbaijani people. One of the parts of the painting depicts a modern, powerful drilling rig equipped with the latest technology.

After breakup of the USSR, the modernist, postmodern and other trends and styles sounded in the visual arts, opening the new, bright pages of our modernity. The oil strategy of the century further emphasized the priority of "black gold" and inspired the honored artists to new creativity. Consequently, there appeared the installations by I. Eldarova, mosaic by K. Alieva, neon painting by F. Alekperov, as well as canvases painted in oil. The author of the unique technique of painting with oil is Sabir Chopuroghlu. He uses in his works instead of oil paints, watercolors, etc. directly the oil itself. His paintings are of interest all over the world. There is the painting "Caspian Symphony" among them which was awarded with the 1st degree Diploma [21]. This picture is filled with a philosophical meaning about the relationship between man and nature. After all, in fact, life is the same canvas that we paint ourselves.

Sabir Chopuroglu. "Caspian Symphony". 2006. [22]

4.Conclusive statement

The phenomenology of oil, presented in the aspect of Azerbaijani art, reveals associative parallels of the process of extracting "black gold" with the process of creating folk art - music, fine arts, etc. Extracting minerals from nature's pantries, we empty the upper layers, the pyramid of values subsides, goes deep, one has to use sophisticated techniques to extract the treasures of creativity or nature.

In the national framework and in the spatial survey of the post-Soviet states, the phenomenology of oil is a primary direction and is of great interest in the aspect of dialectical philosophy. Thus, the study of various works of art in Azerbaijan, representing its various types, is evidence of the generalization of the artistic order of this philosophical theme. The additional generalization carried out in the works of art of Azerbaijan is predetermined by the priority symbolic factor of oil and the State Strategic Policy of Harmonious Development in order to form a new cultural world and careful use of natural resources.

According to the President of Azerbaijan Ilham Aliyev: "... We managed to direct the revenues from oil to the development of the non-oil sector. We have managed to invest large investments in human capital" [23].

5. References

1. Savin A. Transcendentalism and Historicity in Husserl's Phenomenology. Khanty-Mansiysk: Yugorsk State University Publishing House, 2008, 210 p./ https: /eng. iph. ras.ru /eng_savin.htm
2. Regina-Nino Kurg. Edmund Husserl’s Theory of Image Consciousness, Aesthetic Consciousness, and Art/ https://core.ac.uk/download/pdf/ 43660823.pdf, 137 p.
3. Phenomenology.Martin Heidegger /https://science. jrank.org/pages/10640/
4. Emmanuel Levinas. Stanford Encyclopedia of Philosophy/ First published Sun Jul 23, 2006; substantive revision Wed Aug 7, 2019. / https://plato. stanford.edu/entries/levinas/
5. Jean-Paul Sartre. Stanford Encyclopedia of Philosophy / First published Thu Apr 22, 2004; substantive revision Mon Dec 5, 2011. /https://plato.stanford.edu/entries/sartre/
6. Maurice Merleau-Ponty**.** Stanfor**d** Encyclopedi**a** of Philosophy/ Firs**t** publishe**d** Wed Sep 14, 2016. / https://plato.stanford.edu/entries/merleau-ponty
7. Husserl E.Phenomenology of oil/Zh/K Intelros "Emergency reserve". №125, 2019, p.3-5 /, https://www.nlobooks.ru/magazines/neprikosnovennyy_zapas/126_nz_4_2019/article/21699/
8. Ergin D. Production/World history of the struggle for oil, money and power/Translated from English. M.: Alpina Publisher, 2018, 944 p.
9. Materials of conference on topic of Phenomenology of Oil, St. Petersburg, 17-18 May, 2018. : https://spbu.ru/news-events/calendar/fenomenologiya-nefti
10. Mir-Babayev M.Yu. First oil fields in Azerbaijan (wells) / Azerbaijan oil industry -2008.-№9.-P.72-75
11. Gurkov. A. “Black Oil Loses its Value” Comments: “Coronavirus sharply approached the end of the oil century. 11.04.2020. https://www.dw.com/ru/%D0%BA%D0%BE%D0%BC%D0%BC%D0%B5%D0%BD%D1%82%D0%B0%D1%80%D0%B8%D0%B9-%D0%BA%D0%BE%D1%80%D0%BE%D0%BD%D0%B0%D0%B2%D0%B8%D1%80%D1%83%D1%81-%D1%80%D0%B5%D0%B7%D0%BA%D0%BE-%D0%BF%D1%80%D0%B8%D0%B1%D0%BB%D0%B8%D0%B7%D0%B8%D0%BB-%D0%BA%D0%BE%D0%BD%D0%B5%D1%86-%D0%BD%D0%B5%D1%84%D1%82%D1%8F%D0%BD%D0%BE%D0%B3%D0%BE-%D0%B2%D0%B5%D0%BA%D0%B0/a-53096277
12. Azerbaijani cinema. Presidential Library / http: //www.preslib. az / ru / news_XxfGw.php)

13. The presentation of the film “Target - Baku. How Hitler Lost the War for Oil "/Worker of Baku. May 5, 2015, p.9
14. Mamedova K. Oil and Music/National Academy of Sciences of Azerbaijan. Institute of Philosophy and Law. Department of Environmental Problems of Philosophy. Collection of scientific articles. Ecology, philosophy, culture. Issue 13, Baku: Muterchim, 1997, 133- 135 p.
15. Karaev K. In the battle for the truth of life / Soviet culture. January 28, 1969
16. Mirzadzhanzadeh A.Kh. Introduction to the specialty. Baku, 1987, 241, 219-220 pp.
17. Melikova A. The topic of oil in the modern world fine arts / abstract dis. Baku, 2016
18. Mikeladze G. Oil etudes / Black gold in the fine arts of Azerbaijan. Property / Caspian, 2016, January 9, pp.16-17
19. https://www.trend.az/life/socium/2067622.html
20. https://www.trend.az/life/socium/2067622.html
21. Mikeladze G. Oil Paintings. Caspian, 23 January 2016, pp. 18-19
22. https://www.calvertjournal.com/articles/show/9625/sabir-chopuroglu-the-azerbaijani-artist-painting-with-crude-oil
23. Akhundova E. Ilham Aliyev. Portrait of the President against the Background of Changes, ROSSPEN (Russian Political Encyclopedia), Moscow, 2016, 173 p.)

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HISTORY OF PRODUCTION OF ENERGY RESOURCES IN AZERBAIJAN

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Abstract. In the second half of the 19th century, in 1872, industrial oil production began in Azerbaijan. The work done in the field of oil production in Baku during this period soon introduced him to the world as an oil center. It is known historically that war and peace are the result of the terrible struggle of the world's great powers to seize territories rich in raw materials. The military-political events that took place in the first period of the oil industry of Azerbaijan – the second half of the XIX century – the beginning of the XX century confirm the so-called 1914-1918 years of the First World War.

The widespread use of gas in Azerbaijan dates back to the beginning of the second half of the 19th century. In 1859, natural gas was used as fuel to produce steam at a small plant in Surakhani. In 1902, gas erupted from a well drilled in this area.

Azerbaijan's rich oil and gas fields were known to oil companies here, and this fact did not escape the attention of war supporters. Investments in the oil industry and its technical development make Baku a center of international importance.

Keywords: oil, natural gas, industry,

1.Introduction

From the 1970s onwards, foreign capital began to flow into the Baku oil industry, which included primarily French, Germans, and British. The biggest advantage belonged to the British. At the beginning of the 20th century, 12 large British companies were engaged in oil production in Baku. What was the reason for such intensive intervention of British capital in the Baku oil industry? This was not determined only by the demand for Baku oil. According to historical documents, Tsarist Russia used Baku oil not only economically, but also in its foreign policy. Thus, tsarism tried to neutralize the anti-Russian position in England. During 1874-1899, the number of foreign investments in the oil industry of Azerbaijan reached 29. The first foreign company based on foreign capital was established in Baku by the Nobel Brothers. These brothers were very talented inventors, skilled financiers and business people. The Nobel brothers opened the first oil refineries in Baku in 1873, and in 1878 they commissioned the world's first oil tanker, the Zoroastrian (Zoroastrian), in the Caspian Sea. The new technique required a technically advanced specialist. By paying high salaries, the Nobel brothers were able to invite talented scientists, engineers and economists to the company. [1]

2.Results

Along with foreign companies, Azerbaijani national and Russian companies also wanted to develop oil fields in the Caspian Sea, but this was not technically possible at that time. In 1872, only 0.1% of the capital invested in oil produced and sold fell to the share of the national capital of Azerbaijan. This was due to the capital invested by H.Z.Tagiyev and A.M.Nagiyev. During this year, H.Z.Tagiyev's enterprise was among the oil enterprises of Azerbaijan. Although the company produced 10 million pounds of oil in the 1980s, that figure was 20 million pounds in 1893 and 32 million pounds in 1896. Along with H.Z.Tagiyev, there were Azerbaijani oil industrialists interested in oil production, such as A.S.Abdullayev, A.M.Nagiyev, A.M.Mukhtarov and I.Hajinski. In 1913-1915, 46-48 enterprises (29%) out of 165 oil enterprises belonged to Azerbaijani shareholders. In 1880, 39 of the owners of 100 oil and gas plants and 150 oil factories in Baku were Azerbaijanis. The abolition of the lease system has also had positive results in the field of transport. Transportation of oil from the fields was one of the most important problems of the oil industry. During these years, the cost of transporting oil was about twice as expensive as crude oil production. In other words, although the price of crude oil in the field was 3 kopecks, its transportation cost 5 kopecks. The high cost of transportation necessitated the construction of pipelines between the mines and refineries.

In 1901, Azerbaijan produced 11.5 million tons of oil, covering 52% of the world's oil production. This was a world record that year. In 1901, the number of wells drilled increased from 9 to 1,740. Between 1872 and 1913, Baku's oil production accounted for 95-97% of all oil production in Russia and more than half of global production. At the beginning of the century there was a strong decline. There were many reasons for this. These included the depletion of oil reserves, overproduction, outdated drilling and refining technology, low-cost oil products, and extremely high taxes. As a result, between 1899 and 1901, oil production in the Baku region, which was 8-12 million tons, decreased to 5-7 million tons in 1903-1917, and to 2.6 million tons in 1918. After this period, there was a decline in oil production in Baku. In 1903, oil production decreased to 596.8 million pounds. The crisis did not go unnoticed by oil refineries. In total, in 1903, only 79 oil refineries continued to operate. The effects of the crisis were not limited to the production of lubricants. As a result, there was an increase in exports of oil products.

In general, the number of foreign companies in Azerbaijan in 1916 was more than 100. Foreign companies controlled more than half of refined oil - 75 percent of all oil trade. In 1917, an increase in oil production was expected. However, 3.376 million tons of oil were produced in 1918 and 3.690 million tons in 1919, which was less than normal for Azerbaijan and was only half the value of oil produced in 1916.

Azerbaijan's rich oil reserves have not escaped the attention of war supporters. Because on the eve of World War I, Azerbaijan was second only to the United States in world oil production. Thus, it provided 95% of Russia's oil production. Investments in the oil industry and its technological development made Baku a center of international importance. In 1911-1914, Azerbaijan produced 38 million tons of oil. Britain, France, Germany, Russia and the United States, all involved in the war, were in a hurry to find world oil reserves. As a result of the research, it was revealed that Azerbaijan's oil reserves are greater than those of huge oil reserves such as Mexico and Iran, and not less than those of the United States. As the years passed, Europe, which was at peace, not only made the most of its oil potential, but also became increasingly aware of its strategic power.

Azerbaijan's gas industry has undergone a great development during its 170-year history. This history is closely connected with the history of oil production in Azerbaijan. Extensive use of gas in Azerbaijan dates back to the last century. In 1859, natural gas was used as fuel to produce steam at a small plant in Surakhani. In 1902, a well drilled in this area created a gas fountain. This well with a daily flow of 57,000 cubic meters led to the establishment of the first gas transportation system in Azerbaijan. In 1907, Azerbaijan produced 130 million cubic meters of gas. As oil and gas production develops in the country, the use of gas energy has become more widespread. Already in 1950-60, production reached 6 billion cubic meters, and as a result, the republic's industry, utilities, power plants have switched to a system of using this type of energy. The development of the gas industry has affected all other sectors of the economy. In 1982, Azerbaijan produced a record amount of 14.9 billion cubic meters of gas. In 1990-91, the gas consumption of the republic reached a peak – 17 billion cubic meters, of which 5.5 billion cubic meters were spent by the energy complex of the republic, power plants. At present, the existing gas network of the republic has large-scale transit opportunities. [2]

It is one of the most suitable regions for Azerbaijan in terms of gas reserves. The existence of rich gas reserves here led to the establishment of the Azerbaijani gas industry and a single gas network in the middle of the century. However, the economic revival has increased the demand for natural gas here, and at certain times our republic has met the need for this energy carrier by purchasing additional fuel from the unified gas system of the Soviet Union. Due to the collapse of the Union, our country had to meet its demand for natural gas from domestic sources. In the 1990s, the country's gas production (5,589.5 thousand cubic meters in 1998) was below its needs. Expansion of exploitation of new oil and gas fields, efficient use of existing resources have recently solved this problem, and Azerbaijan has become a gas exporter.

Beginning in 1969, the oil and gas industry, like all sectors of the economy of the Azerbaijan SSR, entered a period of high dynamic development. This stage coincides with the first period of national leader Heydar Aliyev's leadership of the Azerbaijan SSR. During this period, a new stage in the history of the development of the oil and gas industry of the Azerbaijani SSR, especially offshore oil production, began. In 1970, the Caspian Oil Production Association was established and the USSR Ministry of Oil Industry commissioned Azerbaijani oil workers to carry out geological exploration, drilling, development, exploitation and other work in all sectors of the Caspian Sea, taking into account the experience of Azerbaijani oil workers in the Caspian Sea. [3]

The increase in offshore oil and gas production was already associated with oil and gas fields at greater depths. Exploration of rich oil and gas fields in the deeper areas of the sea as a result of the acquisition of "Khazar" type self-propelled barges for geological exploration in the depths of 70 m, and later "Shelf" type semi-submersible drilling rigs, which allowed to work in the depths of 200 m. As a result, 8 new oil and gas fields were discovered compared to the end of the 1960s, oil reserves were doubled and gas reserves were tripled. In 1975, the total oil and gas production was 27.1 million tons (conventional fuel). In the 1980s, the number of floating drilling rigs reached 11, and as a result of their use, fields with rich oil reserves, which now make up the bulk of Azerbaijani oil and lie at a depth of 80-350 m, were discovered (Gunashli, Chirag and Azeri).

It was on the initiative and under the leadership of Heydar Aliyev that for the first time in Azerbaijan, a special program for oil refining was developed and launched. According to this program, factories with new equipment and technology were created, new facilities were built. At the same time, the reconstruction of oil refineries began. During this period, in order to build the "Deep Sea Foundations" plant in the Azerbaijan SSR, in Baku, then in the USSR 450 mln. It was possible to obtain such permission from Moscow to allocate US dollars as a result of Heydar Aliyev's great efforts. Construction of the plant began in 1978, and in 1989 the plant was commissioned.

The collapse of the USSR, the restoration of state independence and the modern stage of development of the oil and gas industry, which covers the recent history of the Republic of Azerbaijan, are characterized by the emergence of the "New Oil Strategy". The State Oil Company of Azerbaijan (SOCAR) and a consortium of foreign oil companies (Azerbaijan International Operating Company - AIOC) have signed the Production Sharing Agreement for 1994-2024, dubbed the "Contract of the Century". With the new agreement signed on September 14, 2017, the development of the Azeri-Chirag-Guneshli oil field has been extended until 2050. The new agreement provides for the gradual payment of $ 3.6 billion in bonuses by foreign investors to Azerbaijan and an increase in SOCAR's share from 11.6% to 25%. This agreement lays the foundation for a new stage in the development of the oil industry in Azerbaijan.

Gas is produced onshore and offshore in the Republic of Azerbaijan. For many years, gas was produced onshore in the country, but now this ratio has sharply changed in favor of offshore fields. Over the past three years, the Republic of Azerbaijan has produced 5.6-5.9 billion tons of oil annually at sea and 0.2-0.3 billion tons on land. cubic meters of gas are produced. To date, 445.2 billion manat have been spent in Azerbaijan. cubic meters of gas was produced, of which 320.1 billion. cubic meters were extracted at sea. Gas is now being produced offshore under the Contract of the Century. [9] According to the data, in 1998 alone, more than 200 million cubic meters of gas were extracted from the Chirag platform. As a result of the search, oil and gas condensate fields were discovered in the "Ashrafi" and "Karabakh" fields in the Azerbaijani sector of the Caspian Sea. Production from the Shah Deniz field, one of the richest gas and condensate fields in the world, began in December 2006. As of April 1, 2010, 18.8 billion cubic meters of gas was extracted from this field. By 2015, the Shah Deniz field is expected to produce about 20 billion cubic meters of gas a year. At present, the problems of gas transportation in the Caspian region have become urgent. In this regard, many companies are interested in implementing the Trans-Caspian pipeline project.

The development of the oil and gas industry has played a major role in strengthening the economy of the Republic of Azerbaijan and establishing economic and political relations with the leading countries of the world. This "black gold" extracted from the depths of the earth has caused the people many sufferings and occupations over the years. And only after Azerbaijan gained independence, the oil and gas industry, which became more of a political factor than an economic one, forced the world to keep pace with the independent Azerbaijani state. Azerbaijani oil has gained its true value and was given to the people. Along with the successes achieved in the field of oil, knowledge and experience in the history of oil, oil production and refining have been formed in the national science of Azerbaijan.

During more than 170 years, 67 oil and gas fields were discovered in the Republic of Azerbaijan during the years of industrial oil and gas production. Currently, 55 of them are in operation. In general, 1365.5 million tons of oil was extracted from the ground, 430 million tons of oil and 443.8 billion cubic meters of gas were extracted from offshore fields. At present, more than 95% of Azerbaijani oil is extracted from the sea. In 2010 alone, the Republic of Azerbaijan produced 52 million tons of oil and more than 16 billion cubic meters of natural gas. This figure is 1.9 million tons of oil and 1.8 billion cubic meters of gas for the first quarter of 2020. At present, more than 2 million tons of oil is extracted from onshore fields in Azerbaijan. [8]

4.Conclusion

Oil and gas production in the Republic of Azerbaijan is an important part of national income. The main task of the Azerbaijani state is to ensure that oil, which is the greatest heritage of the people, serves to improve its welfare. For this purpose, social programs and projects have been adopted in a number of areas to increase the socio-economic and cultural welfare of the people. The most important issues are the creation of many jobs, the creation of social infrastructure, increasing attention to science, education and health, increasing salaries and pensions, etc. designed. Of course, our state, unfortunately, has not forgotten that we are still in an unjust war. The Azerbaijani government is also focusing on increasing military spending, treating Karabakh war veterans, increasing the benefits of war veterans and martyrs' families, providing them with housing, increasing their pensions, and improving the living conditions of refugees and IDPs. Another important direction is the strengthening of the Azerbaijani Diaspora in the world, the adoption of programs aimed at expanding cultural and economic ties with friendly countries in order to succeed in the world "information war". From this point of view, it is important to study this important area, analyze it properly and use it in the next strategies. For the first time, national leader Heydar Aliyev recommended the development and importance of such topics as Azerbaijani oil, its history, development of the oil industry, the place of oil in world politics.

5.Reference

1. Aliyev Jamal. From the history of development of the oil industry in Azerbaijan. Baku: 1960.
2. Azerbaijan's oil and gas pipeline system. Azerbaijan Oil Industry Information and Resource Center. Baku: 2006.
3. Ismayilov Israfil. Azerbaijani oil in the XX century. Baku: 2007.
4. Encyclopedia of the Azerbaijan Democratic Republic, in two volumes. Volume II. Baku: "Lider Publishing House", 2004.
5. State Oil Company of the Republic of Azerbaijan. official website www.socar.az
6. Ministry of Industry and Energy of the Republic of Azerbaijan. official website www.mie.gov.az.
7. British Petreloum (BP) official website www.bp.com
8. http://regulator.gov.az/az/history/neft-qaz
9.https://az.wikipedia.org/wiki/Az%C9%99rbaycanda_t%C9%99bii_qaz

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PARTICIPATION OF STATE OIL COMPANY IN IMPLEMENTING OIL STRATEGY OF THE REPUBLIC OF AZERBAIJAN
(1994-2019)

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Abstract. The article is dedicated to the history of SOCAR's participation in the development and implementation of the national oil strategy of Azerbaijan. The author was able to shed light on SOCAR's participation in the implementation of the national oil strategy based on facts, citing official government documents, scientific literature, and media materials. The article states in detail its contribution to the strengthening of the country's international position and the improvement of its socio-economic situation during the implementation of the national oil strategy.

Keywords: Caspian oil, Contract of the Century, SOCAR, TRACECA, TANAP, TAP

1.Introduction

Since the early period of the restoration of state independence, the Republic of Azerbaijan has faced the consequences of economic and political mess inherited from the Soviet Empire. The country has suffered from a serious political and economic crisis, significantly declined production, low productivity, and more problems [1]. Besides, the Armenian-Azerbaijani Nagorno-Karabakh conflict, the violation of the country's territorial integrity, refugee, and IDP problem aggravated the political crisis.

2.Results

On October 18t, 1991, Azerbaijan chose a state model based on democracy, national equality of all citizens, liberal economy, and political pluralism by regaining its independence. The national leader of the Azerbaijani people, Heydar Aliyev, who returned to power in 1993, launched energy diplomacy which was the beginning of national oil strategy [2]. New Oil Strategy is the result of his political activity.

The oil diplomacy of Azerbaijan had been developed by the national leader Heydar Aliyev. From the early years of the restoration of state independence, Azerbaijan has brought the output of Caspian oil reserves to the fore. Thus, since January 1989, Western companies have shown great interest in the Caspian oil of the Republic of Azerbaijan, because the exploitation of onshore oil wells was not as productive as it used to be. As a result of geological exploration and research work carried out in the Caspian Sea sector of the Republic of Azerbaijan in the early 1990s, promising oil fields were discovered [3].

Recognizing the geopolitical importance of the oil factor in international relations, the Azerbaijani administration highlighted the issue of active use of "energy diplomacy" in solving vital issues for the people. The establishment of new diplomatic and economic relations with the United States and the West was one of the most important directions of this strategy. The Republic of Turkey was the main regional partner of the Republic of Azerbaijan. "The Contract of the Century" was signed on September 20, 1994, after the maintenance of mutual relations with the Russian Federation and other neighboring countries. "The Contract of the Century" was the most important step in launching a national oil strategy, signed by 11 major oil companies from 8 countries, including SOCAR. This agreement increased the confidence of the world community in Azerbaijan and ensured the flow of the world's largest oil companies to the Caspian region [4].

"The Contract of the Century" was of utmost importance in strengthening the position of the Republic of Azerbaijan in the international arena. The national oil strategy created by the national leader Heydar Aliyev included the principles of "open door" and "balanced policy". All states interested in the region were involved in cooperation. The oil strategy was meant to ensure a close corporation with the countries in the region by taking their interests into account and creating a balance.

Highlighting the importance of the contract for our country, national leader of the Republic of Azerbaijan Heydar Aliyev stated: "Since 1994, Azerbaijan has been implementing its new oil strategy, and the main principle of this strategy is to effectively use Azerbaijan's rich natural resources, including oil and gas for the welfare of the people" [5]. The signing of the contract opened a new stage in the life, economy and especially the oil industry of the Republic of Azerbaijan [6]. One of the main directions of the strategy was the transport of Azerbaijani oil to world markets. The long-term protection of Azerbaijan's interests in this field, the development of large-scale international economic cooperation, increasing oil production in the region, and in the meantime, ensuring peace, stability, and security are important issues for our state [7].

However, this strategy does not end with the signing of the "Contract of the Century" but enters a new phase. Back in April 1995, US officials, First Deputy Secretary of Energy Minister W.White and Congressman G. Laughlin paid an official visit to our country and met with President Heydar Aliyev [8]. The official visit of the President of the Republic of Azerbaijan Heydar Aliyev to the USA in the summer of 1997 was the next step towards the development of political and economic cooperation between Azerbaijan and the United States. During the visit, The President of the Republic of Azerbaijan met US President W.Clinton, Vice President A. Gore, Secretary of State M. Albright, Secretary of Energy F. Pena, Secretary of Defense W. Cohen, Secretary of the Treasury R. Rubin, Secretary of Commerce W. Daly, members of the US Congress and discussed issues of bilateral cooperation, regional security, and cooperation in the economic sphere.

Along with the American direction, cooperation with Great Britain, France and the Federal Republic of Germany also played an important role in the foreign policy of the Republic of Azerbaijan. On July 19-24, 1998, the President of the Republic of Azerbaijan paid another official visit to the United Kingdom and held official meetings with Queen Elizabeth II, the Prime Minister, and the Ministers of Finance and Defense. The parties signed a "Joint Declaration of Friendship and Cooperation between the President of the Republic of Azerbaijan and the Prime Ministers of the United Kingdom and Northern Ireland". According to the document, "Joint Declaration of Friendship and Cooperation" of February 23, 1994, was the basis for current bilateral relations. Besides, it aimed to deepen existing areas of cooperation and lay the groundwork for "action in new areas".

As a result of reached agreements and signed contracts during foreign trips, “Exxon”, “Mobil”, “Moncrief”, “Chevron”, “Arco”, “Conoco”, “Occidental Petroleum”, “Texaco”, “Frontier”, “Union Texas Petroleum” and other giant companies became partners in Azerbaijan's energy projects.

The financial resources required for the implementation of the domestic and foreign policy concepts of the Republic of Azerbaijan were provided by the income from the sale of Caspian oil. It is noteworthy that Caspian oil, along with being a source of national income of Azerbaijan, also plays the role of a political factor determining the situation in the region and the international arena. Azerbaijan uses oil diplomacy to implement its foreign policy strategy. It is the Caspian oil that attracts large foreign investors to sponsor various industries in the Republic of Azerbaijan.

The main obstacle in this direction was the issue of determining the legal status of the Caspian Sea. Not only Azerbaijan but also other countries with interests in the region were aware of the importance of the Caspian's energy resources. The usage of Caspian's energy resources is not only an economic phenomenon but also an important tool for achieving Azerbaijan's political security and territorial integrity. Heydar Aliyev's deep intellect and political will again played a great role in resolving this issue. The agreement with the Russian Federation and the Republic of Kazakhstan on the principles of the legal status of the Caspian Sea increased its international reputation and significantly strengthened its political position.

The "Contract of the Century" later led to the signing of 20 more agreements and thus the investment of more than 60 billion in our country, creating a political and economic basis [9]. One of the most important components of the new oil strategy was the idea of building the Baku-Tbilisi-Ceyhan main export pipeline and making it a reality. The realization of this idea is the biggest step taken in the foreign policy and economic development of Azerbaijan. According to the TRACECA program, the development of air, water, cargo, road, and rail transport has accelerated. The passage of the Trans-Caspian gas pipeline through the territory of the Republic of Azerbaijan and the export of Turkmen gas and Kazakh oil to world markets has brought great economic and political benefits to the Republic of Azerbaijan and increased the country's geostrategic importance [10].

Implementing a successful foreign policy strategy in parallel with the new oil strategy, the Republic of Azerbaijan has been actively developing relations with the European Union since 1994. In 1996, President of the Republic of Azerbaijan Heydar Aliyev signed a cooperation agreement prepared by the European Union. According to the program European Union was supposed to provide material and technical assistance to the Republic of Azerbaijan in the implementation of structural reforms aimed at strengthening the market economy and the execution of infrastructural projects.

During the period between 1993-2004, the European Union provided financial and technical assistance to the Republic of Azerbaijan, allocated € 100 million for structural reforms and technical restoration projects within the framework of emergency and humanitarian assistance programs. The European Union's INOGATE, ECHO, and other programs finance several important projects in our country.

The contribution of the oil strategy to our country and the region is that the Republic of Azerbaijan became the first state to master the huge energy potential of the Caspian Sea and form a new economic model for the development of the region as a result of this policy. Furthermore, the Republic of Azerbaijan became a country that granted the expansion of international political and trade relations between Europe and Asia. In addition, it has become an important state in the region by implementing INOGATE, TRACECA, and other major projects in the development of the Caucasian transport corridor [11]. The construction of the TANAP and TAP pipelines, which would transport Azerbaijani gas to Europe, further increased transit capacity in the region.

During the implementation of the oil strategy, the Azerbaijani state proved to be the full owner of its natural resources and began equal and mutually beneficial cooperation with foreign partners. This cooperation has paved the way for the oil strategy based on the efficient use of energy resources and the distribution of profits, as well as for the economic development of the non-oil sector. This has had a significant impact on the solution of many social issues, the reduction of the unemployment rate, the establishment of a stable political system, and its integration in the international political and economic spheres. The increase in strategic foreign exchange reserves and budget funds has had a positive effect on overcoming certain threats to macroeconomic stability [12]. Thus, the end of the XX-beginning of the XXI century led to the formation and strengthening of the national statehood of Azerbaijan. The establishment of a diversified export oil and gas pipeline system has opened up prospects for ensuring the country's energy independence, providing Europe and other remote regions with high-quality resources, and creating real opportunities for Azerbaijan as a stable transit corridor for transporting energy produced in the Caspian countries [13]. Thanks to the oil strategy, existing offices were re-equipped, modern western technology was applied, and a stronger and more mobile infrastructure was created.

In November 1997, the report on primary oil under the framework of “The Contract of the Century” was a significant milestone in the implementation of Azerbaijan's national oil strategy.

In 1996, the Republic of Azerbaijan signed an agreement with the Russian Federation and the Republic of Georgia on the transportation of primary oil from the Azeri-Chirag-Gunashli reserves through the territory of these countries. In November 1997, the Northern Pipeline was made available for exploitation, and the transportation of Azerbaijani oil to Novorossiysk began. This was another great success of the national oil strategy. In April 1999, the western route Baku-Supsa, which connects the Caspian Sea with the Black Sea through Georgian territory, was launched. On April 17, 1999, the Baku-Supsa pipeline and the Supsa terminal on the Black Sea coast were put into operation.

The Ankara Declaration on the construction of the Baku-Tbilisi-Ceyhan (BTC) Main Export Pipeline signed between the Republic of Azerbaijan, the Republic of Turkey, and the Republic of Georgia in 1998 is considered to be an important step in the implementation of this major project. The United States and Kazakhstan have also joined the agreement. On November 18, 1999, within the framework of the OSCE Summit in Istanbul, the Presidents of the Republic of Azerbaijan, Georgia and the Republic of Turkey signed an agreement on the transportation of crude oil via the Baku-Tbilisi-Ceyhan pipeline, the main export pipeline. Many noted the necessary geopolitical importance of this route. In any case, on September 18, 2002, the foundation stone of the $ 3 billion Main Export Pipeline (MEP) was laid near Baku. More than $ 4 billion would be spent on the construction of the BTC pipeline in the future, which was planned to transport 50 million tons of oil. On May 28, 2006, the first Azerbaijani oil was transported through the Ceyhan terminal. Thanks to the BTC, the Main Export Pipeline (MEP), has solved the problem of transporting oil through the Bosporus and Dardanelles through large tankers. BTC costs were $ 2.58 per barrel and the northern Novorossiysk pipeline was $ 3.6 per barrel. By signing the agreement between Kazakhstan and Azerbaijan on June 16, 2006, on Kazakhstan's accession to the BTC system, the issue of efficient filling of the pipeline with oil was also resolved. At the end of 2006, the Baku-Tbilisi-Erzurum gas pipeline was put into operation, which would supply gas from Azerbaijan's Shah Deniz gas field to Turkey and Europe. The ongoing development of Azerbaijan-Turkey-Georgia partnership in the region led to the strengthening of its integration into the European Union and Euro-Atlantic structures [14]. All projects were the results of successful economic policies.

SOCAR, which has been pursuing the oil strategy that has guided the economic policy of the Azerbaijani state for many years, is distinguished by its successful activities in this area. SOCAR has continued its economic development for many years as the national oil company of the Republic of Azerbaijan and has strengthened its position as a competitive company in the world’s financial markets. Today, the company successfully continues its work with foreign oil companies in the fields of exploration, drilling, production, and construction. SOCAR has signed numerous contracts, with its closest brother, Turkey. Turkish companies TPAO, BOTAS, and others are important partners of SOCAR.

SOCAR's strategic development trend also includes expanding the company's activities in foreign markets, investing and acquiring assets abroad, establishing representative offices in leading countries, and economic ties with neighboring countries [15].

SOCAR has signed and successfully implemented the climate change mitigation strategy for 2010-2020 and joint projects with the Global Gas Flaring Reduction Partnership (GGFR). As part of its oil strategy, SOCAR has integrated the oil industry's production facilities and research institutes into its structure.

4.Conclusion

The successful implementation of national leader Heydar Aliyev's national oil strategy has enabled Azerbaijan to become a strong and independent partner in the field of energy security. The oil strategy of the Republic of Azerbaijan continues to serve the protection of national interests.

5.References

1. Nagiyev, A., (Novruzov V., Allahverdiyev H., Alirzayev A.) Heydar Aliyev and the economy of Azerbaijan. Baku: 1998, p. 137.
2. History of Azerbaijan. 7 volumes. I volume. Baku: 2008, 608 pages, p. 322.
3. Khalilov, J.R. Azerbaijan-USA: some aspects of political and economic schools (in the 90s of the XX century) Scientific works of the Institute of History of the Azerbaijan National Academy of Sciences. Volume 21 134-152, p. 135. Baku: 2007.
4. Report on sustainable development, p. 3. Baku: 2014.
5. Heydar Aliyev's new oil strategy p. 12.
6. Heydar Aliyev’s oil strategy for the independence and welfare of Azerbaijan, part I., p. 16. Baku: 2001.
7. Report on sustainable development., p. 3., Baku: 2014.
8. Heydar Aliyev's oil strategy for the independence and prosperity of Azerbaijan, part II, p. 4. Baku: 2001.
9. Heydar Aliyev's new oil strategy p. 15.
10. Heydar Aliyev's new oil strategy p. 22.
11. Khalilov, G. Problems of international law and domestic legislation on ecological safety of the Baku-Tbilisi-Ceyhan oil pipeline named after Heydar Aliyev., 392 pages., p. 28. Baku: 2009.
12. Mehdiyev, R. New policy: towards development. Volume, p. 76. Baku.
13. Sustainable Development Report, p. 14. Baku: 2014.
14. Kazimli, X. Continuation of the great policy. Volume II, 712 pages, p. 407. Baku: 2007.
15. Sustainable Development Report, p. 24. Baku: 2014.

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HISTORY OF CONSTRUCTION OF THE CASPIAN-ORSK OIL PIPELINE

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Abstract. The article is dedicated to the construction of the Caspian-Orsk oil pipeline, which has played an important role in the development of the oil industry in Kazakhstan. The oil pipeline was built in 1932-1935. Thousands of people from all over the country took part in the construction. The courses for the indigenous people were organized. As a result, hundreds of Kazakhs became builders. By order of the people's commissar for heavy industry G.K.Ordzhonikidze, the First All-Union Competition for the Best Construction Project was organized. The builders of the Caspian-Orsk oil pipeline took part in it. In connection with the construction of the Caspian-Orsk oil pipeline, the production of oil in the Emba oil-bearing area tripled. The 720 km long Caspian-Orsk oil pipeline ranked second after the Baku-Batumi oil pipeline. During the Great Patriotic War, the Caspian-Orsk oil pipeline played a significant role in the transportation of Baku oil products to the central part of the country. The oil pipeline existed until the beginning of the XXI century.

Key words: Council of Labor and Defense, transport, oil pipeline, trenches, water pipeline, Orsk, Emba, Guryev, Iskene, Koschagyl, socialist competition, shock work.

1.Introduction

The history of Kazakhstan's pipeline system has its origins in the first decade of the twentieth century. But the most powerful Caspian-Orsk oil pipeline, which was built in the thirties of the twentieth century, is truly the beginning of the history of the oil pipeline system in Kazakhstan.

2.Method

Empirical, theoretical, qualitative, quantitative, multi-method, longitudinal, cross-sectional study, case study methods were used in the study.

3.Results and Discussion

The Caspian-Orsk pipeline gave a powerful impetus to the development of the oil-bearing region of Kazakhstan. As a result, the oil industry of Kazakhstan reached a new stage of its development.

The success of the first five-year plan marked the beginning of technical reconstruction in the oil industry. Such measures as the transition to the rotary drilling, the expansion of auxiliary enterprises, the creation of facilities and resources in Guryev, and others had a crucial role in increasing the drilling rate and the scope of deep-hole prospecting, as well as in the discovery of the rich oil fields. But these measures were not enough for the commercial development of the new oil fields.

The task of developing the newly discovered oil fields required a new approach to solving the problem of technical reconstruction. Academician I.M. Gubkin believed the solving of the problem of transport and water supply to be the most important condition for the development of the Ural-Emba oil industry. He emphasized that the successful development of Emba is impossible without the fundamental solving of these problems [1].

The transportation problem included the issues of transportation of oil and delivery of the petroleum equipment, construction materials, and food for the developing industry of Emba. To successfully resolve all these issues, it was necessary to build an oil pipeline and a railway connecting the Ural-Emba oil region with the main railway line of the country. But at that time, when the construction scale throughout the Soviet Union was huge, the state could not build the railway and the oil pipeline, requiring considerable expenses, at the same time. In this regard, the priority was given to the oil pipeline construction.

The priority of the oil pipeline construction was caused by the tasks of commercial development of the new oil fields. The organization of oil production at the newly discovered oil fields was hindered by the oil transportation problem. This problem could be solved by building a 65 km long oil pipeline towards the Caspian Sea. But it would be only a half-measure and not a fundamental solution to the problem of oil transportation from the Emba oil fields.

The transportation of oil to Astrakhan by sea, firstly, would increase the load on the Volga river and railway routes, which were already busy with the transportation of Caucasian oil, and secondly, the need for oil and oil products grew at the extremely quick rate due to the creation of industrial bases and increased mechanization of agriculture in the Urals, Siberia, and Kazakhstan. The transportation of the Emba oil should be organized to first satisfy the needs of these areas. The transportation of oil across the Caspian Sea and Volga significantly lengthened the route and increased the cost of transportation.

Besides, the Caspian and Volga route was closed for 4 - 5 months a year, which required the construction of huge tanks for the storage of oil in winter. For this reason, the construction of an oil pipeline, ensuring the direct delivery of oil to the consumption areas, was more profitable in economic and technical terms. Finally, the transportation of the Emba oil through the main Volga river and railway route was strategically unprofitable. In case of an attack on our country, this main route with the technologies applicable at that time would turn into one of the most vulnerable places. All these circumstances resulted in the need for an oil pipeline from the Emba oil fields to the inland.

On March 8, 1932, the Council of Labor and Defense adopted the resolution on the construction of the Caspian-Orsk oil pipeline with a total length of 702 km and oil refineries in the city of Orsk. Although this construction required large amounts of capital, it has positively resolved the mentioned problems related to the transportation of the Emba oil. The construction of the oil pipeline was very complicated. The pipeline route crossed 13 rivers, rocks, gullies, numerous sors (salt lakes), and railways. The works at the route were to be carried out under the conditions of the waterless steppe and lack of roads, far from supply bases and settlements. The equipment and materials had to be transported for a distance of hundreds of kilometers along the route. There was a lack of cars, tractors, excavators, and other mechanisms at that time. The republic had no staff for the pipeline construction. Most of the builders were the Kazakhs, who had no experience of work in industrial construction. (From the thesis by K. Temirgaliyev).

But labor enthusiasm and firm determination of the building team to provide the industrial entrprises, collective and state farms of the Urals, Siberia, and Kazakhstan with the Emba oil ensured successful overcoming of all difficulties.

Starting from May 1932, a lot of work on the organizational arrangement of all elements of construction and staffing with engineers, technicians, and workers was started.

At the beginning of May, the supply department with two sectors of technical and food supply was organized [2].

The supply department had to carry out the transportation of a part of equipment and materials during the navigation of 1932 in order to ensure the front of construction works at the line, as well as the transportation of the necessary reserve of food. In June, the first, the second and the third construction sites were created. On August 1, the fourth site was created [3].

In June 1932, a transport office was established in Dossor, which ensured the transportation of all construction equipment along the pipeline route. For the delivery of pipes to the sections, the truck convoys of 10-15 cars and cart convoys of 30 - 50 carts were organized. As the works were started in the second half of August, the water train was organized directly on the line for the uninterrupted supply of workers with drinking water. The water from Guryev was delivered to the 1st and 2nd sites by train, and to the 3rd and 4th sites by cart transport and cars. Behind Dossor, water tanks were placed every 15 km. In Guryev, Dossor and Makat, and behind Makat every 60 km, the gasoline storage tanks were built for car fueling [2, case 23, case 38, p. 36, 38].

All measures for the organization of the supply department, construction sites, transport office, and other construction elements were taken under the supervision of the Guryev and Ural-Emba district party committees.

The party cells carried out the big mass organization work among the workers. At the sites, in the transport office, and among the loader teams, the socialist competition was started, the people were awarded following the competition results, and the red and black boards were arranged to record the results of five-day, decade, and monthly tasks.

The works on the creation of the construction sites, truck convoys, train teams, and loader teams for the fulfillment of the production tasks gave the first results. So, the telegram addressed to the Council of People's Commissars of the USSR, the People’s Commissariat for Heavy Industry and the oil pipeline construction trust management said that as of July, 15 1932, 140 km of pipes was delivered to Guryev, 30 km of pipes was on the way, 71 km was delivered to the line, and the works on pipe welding were started [2, p.11, list 2, case 38, p. 7].

By the end of the year, 150 km of pipes was delivered to the route, 57 km of trenches was dug, and 52 km of pipes was cleaned. 120 km of 150 km of pipes, delivered to the route, was welded, and their use for the transportation of water to the Dossor and Makat oil fields was started [2, case 196, p. 11].

In the practical activities of the party committee and party cells, much attention was paid to the training and education of workers, especially from the local indigenous population. The schools, circles, and courses were organized at the construction enterprises to improve the general education literacy and the qualification of the workers. For example, the transport office alone provided the courses for training of excavator drivers and drivers, as well as one school for illiterates [4].

However, the training of staff from among the Kazakh workers in such specialties as tractor drivers, locksmiths, turners, excavator drivers, and carpenters was insufficient. That's why the party committee at its meeting held on September 17, 1933, obliged the construction management to take the following control figures into account when preparing a plan of staff training in these professions for the winter of 1933-34: at least 15 percent of the students at the courses of drivers and tractor drivers must be Kazakh workers, at the courses of locksmiths and turners – at least 10 percent, and at the welding courses – at least 15 percent, etc. [5].

The party cells paid great attention to the international education of the workers. At party meetings, the questions were raised related to the strengthening of friendship and mutual help among the workers of the construction. In their speeches, the activists, mentioning some facts of unfriendly attitude towards the Kazakh workers, emphasized the necessity need to strengthen educational work among the workers and the need to explain their duty towards the Kazakh workers to liquidate illiteracy among them and improve their qualification. The party meeting resolved to train and actively nominate Kazakhs to administrative and economic positions, create circles for the study of Russian and Kazakh languages, include the national issue in the program of the current policy circles, and provide the red corner with the sufficient number of literature in the Kazakh language. The meeting called on the communists and the cell bureau to prevent any manifestations of both the great-power chauvinism and local nationalism immediately [4, p. 129].

The party committee of the oil pipeline went deep and took an active part in the construction. In 1934, the gap between the delivered pipes and their welding, tarring and filling at the 6th site of the oil pipeline (Kinzhaly - Orenburg-Tashkent road crossing) began to widen. The party committee has sent the best tarring team of the 3rd site to close the gap. Before the arrival of this team, the tarrers of the 6th site tarred 400 meters per day. Due to the correct allocation of duties and the preliminary preparation of the tar, the tarring team of the 3rd site has reached the rate of 2 000-2 500 meters of tarred pipes per day. Following its example, the tarrers of the 6th site achieved the same results. The shock work of the tarrers increased the labor activity among the welders and workers engaged in lowering into trenches and their backfilling with earth [4, p. 130].

The gap between the delivered pipes and subsequent works was liquidated. Here is another example of the active influence of the party committee on the construction of the oil pipeline. The construction of the pipeline in 1934 was extended over great distances. In order to improve the management of the construction site and provide prompt assistance, the party committee has assigned its members and construction managers to some of the most important objects. For example, Baybakov and Roschchin were assigned to the 2nd site, Altynbekov and Peshtich – to the 4th site and the cart fleet, Ivzhenko, Baranov and Shostakov – to the 5th site, Serov and Vulgin – to the 6th site, Rusakov and Larin – to the south base of the transport office, Bleyalkin and Pavlovich – to the Dzhurun fleet depot, Vyrostkov – to the 1st welding team [4, p. 129].

As a result of the labor efforts of the construction team, 334 km of the oil pipeline was built during 1933 and 1934, and together with 1932 - 450 km, two oil pumping stations and tanks for 12 000 tons were built, and 550 km of communication lines were laid.

In 1935, the party and government have set a big and challenging task to the builders: complete the construction of the Caspian-Orsk main pipeline and construct the oil pipelines Koschagyl – main line and Iskine – main line. To understand the level of importance of this task, we can just mention that the construction team was to build 434 km of the oil pipeline and four oil pumping stations of six. Thus, the builders had to perform the work of the previous two and a half years in just one year.

But the workers, engineers and technicians had a great experience in construction by this time. Besides, by the beginning of 1935, the construction management had a lot of machines and mechanisms, including 303 cars, 60 tractors, 17 excavators, 60 electric welding units and 50 gas welding units [6].

All this created favorable conditions for the fulfillment of the task set by the party and the government.

Although the construction department had powerful equipment and the sufficient number of workers, engineers and technicians, it was not enough to fulfill the state task. The successful completion of construction depended largely on the proper labor management and well-coordinated work of all elements of the construction, as well as enthusiasm and labor heroism of the construction team.

The party and trade union organizations of the construction site have started the intense organizational work to mobilize workers to fulfill the tasks of the party and government. The big mass explanatory work was carried out regarding the order of the people's commissar for heavy industry G.K.Ordzhonikidze of March 23, 1935, on the organization of the First All-Union Competition for the Best Construction Project from April 1, 1935 to January 1, 1936 [4, p. 130].

As a result of the mass political work, the team of workers, engineers and technicians decided to complete the construction of the oil pipeline by the fifteenth anniversary of the founding of the Kazakh Republic and to begin pumping oil to Orsk. The builders assumed the certain obligations to lay out 390 km of pipes, dig 417 кkm of trenches, weld 434 km of pipes and lower 440 km of pipes into the trench, complete the construction of four oil pumping stations, and reduce the construction cost by 15 percent compared to

1934 [4, p. 30].

From the first days of April, a wide wave of socialist competition and shock work started at the construction. The builders were stepping up the pace of the oil pipeline construction month by month. By June 10, 130 km of pipes were transported along the route, 191 km of trenches was dug, and 65 km of pipes was welded [4, p. 130].

It means that the work of the whole year 1933 was done in just two months and 10 days. The transport team of the Dossor fleet depot has reached significant success in the socialist competition. In July, according to the results of the competition, it was awarded the transferable Red banner of construction. In August, the transport workers gained new labor victories. The fleet depot exceeded the pipe delivery target by 122 percent. From April 1 to September 1, 1935, the fleet depot made 2 mln 18 thousand tonne-kilometers instead of the planned I mln 971 thousand tonne-kilometers [4, p. 129-130].

The oil pipeline from the Koschagyl oil field to the main pipeline, construction of which began in the middle of March 1935, was being built at an accelerated pace. Here the socialist competition was headed by the best diggers Zamada Shembayev, Oran Akzhigitov, and Jumabay Toguzbayev. During one shift, they threw out 20-20-25 km of land from the trench, exceeding the standards by 2,5-3 times [6, September 16]. The party organization of the Zhilokosinsky district have provided great assistance in the construction of the oil pipeline, having sent 200 workers to dig the trench.

Thanks to the labor heroism of the workers, engineers, and technicians headed by the communists, construction of the oil pipeline came nearer to the end. As of August 20, 1935, 704 km of pipes was transported along the oil pipeline route, and 654 km of the trench was dug. [6, September 3]. Now the builders had to transport 5 km of pipes and dig 58 km of the trench. But 3 of 58 km crossed the rocks. It delayed the works and threatened the fulfillment of the assumed obligations. 120 best shock workers of the southern sites were sent by the party committee and the construction management to help the workers of the northern site [4, p. 130]. These comrades who have been working at the construction from the very beginning shared their production experience to the workers of the northern site who were not engaged in the construction in late 1934 and early 1935 and did not have enough experience. The joy and understanding of the upcoming completion of construction caused a new energy surge among the workers, engineers, and technicians. As a result of truly heroic labor, the last 58 km of the oil pipeline was successfully overcome.

On October 11, at 9:30 am, the pumping of the Koschagyl oil into the Koschagyl – main line oil pipeline was started. On December 7, at 8 pm, oil entered Orsk and began to fill the tanks of the Orsk oil refinery [7].

Thus, overcoming extreme difficulties, the building team has fulfilled its obligation with flying colors. The country has got the second largest main oil pipeline after the Baku-Batum oil pipeline.The builders have performed a large volume of construction works. To imagine the scope of the works performed, we can just mention some figures. So, the weight of the pipes laid constituted 80 thousand tons, the earthwork scope – 1 900 thousand cubic meters, the weight of the cargos transported - 12,5 mln tonne-kilometers [1, p. 129]. Besides, 6 powerful oil pumping stations were built, a communication line was laid, the oil storage tanks with a capacity of tens of thousands of tons and houses for the service staff were built.

During the construction, hundreds of skilled construction workers have grown. It should be noted that from among the Kazakh workers who had no previous skills of industrial labor, many highly qualified electric and gas welders, turners and locksmiths, drivers and signalers, carpenters and plasterers were trained, and some of them were nominated to administrative and technical positions.

In 1933, Kozhar Kadraliyev was engaged in the oil pipeline construction. In the beginning, he was an ordinary digger. Kadraliyev fulfilled his daily tasks with great difficulty. But by the end of the year, he was removing 15 cubic meters of soil from the trench, significantly exceeding the output standard. In 1934, the construction management appointed him as the foreman of diggers. Kadraliyev’s team became the best shock team of the construction. He achieved it through his example and due to the proper labor organization. He personally threw out 20-25 cubic meters of soil from trenches. In August 1935, Kadraliyev was appointed the deputy head of the camp. The building team nominated him as a member of the anniversary delegation of the Kazakh SSR for a report to the party’s Central Committee and the Soviet government on the success of socialist construction in the republic for 15 years [6, October 3].

Plasterer Namazbayev was highly esteemed among the builders. In 1932, he was a digger, and in the evenings, he attended the courses for training of the plasterers. Having passed the exams, he received the qualification of a plasterer. Almost all production facilities and residential buildings at the 4th pumping station were plastered by Namazbayev at high quality standards.

Yedigayev worked his way from an ordinary train worker to a qualified tractor driver. He fulfilled the task of transportation of pipes and equipment for the fourth oil pumping station for 250 percent using the “Stalinets” tractor. Yedigayev readily shared his knowledge with others. He has trained Buramabayev and Nugmanov for independent tractor operation [5, November 14].

Jekumbayev and Kadyrov became highly qualified electric welders [1, p. 17].

On October 17, 1985, the Presidium of the Central Executive Committee of the KASSR awarded 12 best builders with an anniversary badge «15 years of Kazakhstan» for shock and dedicated work in the course of the construction of the Caspian-Orsk main oil pipeline [4, p. 130].

The construction of the Caspian-Orsk main oil pipeline with branch lines to Koschagyl and Iskine was of great importance for the further development of the Ural-Emba oil region. Thus far, oil transportation was one of the main and most difficult problems in the commercial development of the newly discovered oil fields. Now, with the completion of the pipeline, the problem of oil transportation has been resolved.

The Emba oil producers have got great opportunities for extensive works on including the new oil fields into the number of oil-producing fields. The coming of the Emba oil to Orsk, where the oil refineries have been built by this time, made it possible to improve the supply of oil products to the national economy of the Urals, Siberia, and Kazakhstan, which contributed to the economic growth of these regions.

February 1, 1934, marks the beginning of the operation of the Iskine field. It was the second field to come into operation after the nationalization of the oil industry. The Iskine fields that were included in the number of oil-producing fields had a crucial importance in overcoming the lag of the oil industry. Since 1934, the oil industry of Kazakhstan has been steadily increasing oil production.

In 1934, the large-scale capital construction was launched at the Iskine field. In May, the construction of a water pipeline and a narrow-gauge branch of the Guryev-Dossor railway began.

In June, the construction of an electric power plant and the tanks for storage of oil and water began. Along with the production facility, the utility and housing construction was started.

The field management focused on the construction of the railway and the water pipeline. The supply of the field with drinking and process water, the transportation of materials and equipment, and all works on the field development and construction, in general, depended on the construction of these facilities. The bureau of the Guryev district committee of the AUCP(b) has also emphasized the need for acceleration of the pace of construction of the railway and the water pipeline at its meeting on May 21, 1934. The short deadline was set for the completion of the railway and the water pipeline. The bureau obliged the district committee of the union of oil producers to send the responsible workers to the field to assist the field committee in improving the cultural-mass work among the builders for a term of one month.

In July, the works on pipe welding were completed, and the supply of the field with freshwater started. At the end of 1934, the temporary traffic was launched along the rail line from the 58th kilometer of the Guryev-Dossor railway to Iskine. In the summer of 1935, the water pipeline and the narrow-gauge branch were introduced into full-time service. At the end of August, the electric power plant produced commercial currents [4, p. 129-130].

In the second half of 1933, the construction of the Koschagyl field was started. Unlike the Iskine field, it was built in a remote steppe region, far from railways and comfortable earth roads, as well as at a considerable distance from the facilities and resources in Guryev and Dossor. The field construction was started under the conditions of a severe shortage of construction materials, mechanisms, vehicles, and houses for workers. The builders lived in the hastily built dugouts - temporary barracks. In the annual report of the trust manager for 1934, it is stated that the field construction "...had to be started literary in the bare steppe, where there were no auxiliary enterprises producing construction materials, except for some residential houses" [4, p. 130].

Putting of the new wells in Koschagyl into operation was delayed due to the lack of an oil pipeline. In this regard, on October 16, 1934, the bureau of the Guryev district committee of the CPK(b) has decided to ask the People's Commissariat for Heavy industry and the government of Kazakhstan to build an oil pipeline connecting the Koschagyl field with the 3rd oil pumping station of the Caspian-Orsk main oil pipeline [4, p. 129-130].

This decision of the district committee of the party was supported. The oil pipeline construction was started in March 1935.

The decision of the commissariat for heavy industry on the construction of the Koschagyl-main line oil pipeline and the work on its building caused a new surge of energy among the drillers, operators, engineers, and technicians of the field.

For three months of 1935, the Koschagyl field produced 53 188 tons of oil, and in 1936 – 234 368 tons of oil. It resulted in a significant increase in oil production at Emba. Compared to 1934, the oil production in 1935 increased by 9,8 percent, and in 1936 – by 94,3 percent. The sharp increase in oil production was caused mainly by putting the Koschagyl field into operation. But the importance of the Koschagyl field is not limited to this. Its national economic significance lies primarily in the fact that it has become the main base for the commercial development of the richest oil fields of the entire South Emba region (Karaton, Kulsary, etc.).

In the course of preparatory works on putting the Iskine and Koschagyl fields into operation, as well as the construction of the Caspian-Orsk oil pipeline, one of the most important problems in the development of the Emba's oil resources was solved: the water problem. Since the end of 1936, water has been supplied to Dossor and Makat through the completed section of the oil pipeline from Ural. In 1934, a 4-inch water pipeline with a length of 20 km was laid from the oil pipeline to the Iskine field. The Koschagyl was also provided with water for domestic needs. It was supplied with water from the Emba River through an 18 km long water pipeline built in 1934. The problem of water supply was finally solved in 1938 after the construction of a 640 km long water pipeline Guryev-Koschagyl with branches to all Emba fields [4, p. 130].

4.Conclusion

The Caspian-Orsk pipeline gave a powerful impetus to the development of the oil-bearing region of Kazakhstan. As a result, the oil industry of Kazakhstan reached a new stage of its development.

5.References

1. «Big Emba», Volume 1, publishing house of the Academy of Sciences of the USSR, M-L, 1937, p. 27.
2. State Archives of the Atyrau region (SAAR), p. 146, list 5, case 237, p. 41, p. 44.
3. The 1st site had a construction scope from Guryev to the 61st km, the 2nd site – from the 61st km to the 121st km, the 3rd site – from the 121st km to the 185th km, and the 4th site - from the 185th km to the 225th km.
4. Mukhitov K. «History of construction of the Caspian-Orsk oil pipeline», National history, №3, 2019. pp. 124-133, p. 126.
5. «Oil pipeline shock worker» newspaper of general circulation, 1933, № 9, August 22.
6. Newspaper «Prikaspiyskaya kommuna», 1935, № 246, October 24.
7. Balgymbayev N.B., Oil Emba. Chronicle of the centuries-old history. A., 2001, 456 p. p. 77.

OR-VII-5

UNOPENED PAGES OF THE HISTORY OF AZERBAIJAN’S CASPIAN OIL

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Abstract. The article is devoted to the study of the unopened pages of the history of Azerbaijan's Caspian oil. The author wrote the article on the basis of new documents he has found in the state archives as a result of his many years of research, and the facts reflected in the new scientific literature published in recent years. The article says that after World War II, a large amount of energy resources were needed to restore the war-torn territories of the former USSR. The discovery and commissioning of the Caspian oil fields were deliberately obstructing by high-ranking central government officials. As a result of the measures taken by the leaders of Azerbaijan their prevention in response, the facts of the damage caused by Armenian criminals in this area were scientifically analyzed. The author talks about the work done by national leader Heydar Aliyev in the 70s and 80s of the XX century for the development of Azerbaijan's Caspian oil industry. After the restoration of the state independence of the Republic of Azerbaijan, as a result of the national oil strategy developed by it, the "Contract of the Century" was signed on September 20, 1994 and implemented. The aggressors of the Russian Federation used the Armenian army as a deadly tool to prevent this. The author provides a scientific analysis of the facts of violation of all these aggressive plans by the Great Leader.

Keywords: Azerbaijan, Caspian oil, industry, Contract of the Century, Russian Federation, Armenia

1.Introduction

Azerbaijan is considered the home of both onshore and offshore oil production. For the first time in world practice, as a result of many years of scientific and practical research of Azerbaijani scientists and engineers, oil-well No.1, daily yielding 100 tones gushed in oil-bearing “Neft dashlary” (“Oil Rocks”) area of the Caspian sea in November 7, 1949. After such a promising achievement, on December 11, 1949, the Council of Ministers of the USSR adopted a resolution “On strengthening measures for the exploration and exploitation of offshore oil fields in the Azerbaijan SSR”, according to which, by the decision of the Council of Ministers of the USSR on December 11, 1949, the Central Management for the development of offshore fields, the Azmorneft Association of the Azerbaijan SSR, was created under the Ministry of Oil Industry of the USSR, which was responsible for the preparation of the Caspian oil fields for exploitation. This turned out to be by no means an easy matter, because the leadership of the Soviet empire – its administrative command system and its servitors – the Armenian-Dashnak leaders were not interested in the economic strengthening of the Muslim republics and, first of all, Azerbaijan.

2.Results

As is known, in the post-war period, significant difficulties began to appear in supply of petrochemical products to the entire economy and the military-industrial complex of the USSR. After the victory in the war of 1941-1945, gained in the first place, due to Baku oil, it was necessary to open additional energy resources to restore the destroyed by the war and to create new sectors of the economy in a number of regions, including in Azerbaijan. As military historians write, the war was fought in the territory of 40 countries with a population of 1.700 million people, where the armies of 61 states fought. The total death toll in World War II is about 60 million people. In this terrible war, the USSR lost 29 million people, out of which 626 thousand were people from the Azerbaijan SSR. As a result of military operations, 73 thousand settlements and villages, 1700 cities and towns were ruined, 32 thousand industrial enterprises, 65 thousand km railways were destroyed, and 35 million people were left homeless [1.5.9]. Although until the mid-50s Azerbaijan remained the main center of oil production in the USSR, it also coped with the significantly increased needs for oil products. It should be taken into consideration that during the war, Azerbaijan SSR provided up to 85-90% of the needs of the front in all types of oil products and therefore bore the heaviest burden of the war [2.95-108]. During the war, exploration and drilling works as a matter of fact, were interrupted, some of the qualified personnel went to the front, as a result of which no significant deposits were discovered on land. The exploration of oil deposits in the Caspian Sea, on the one hand, was aimed at covering the energy deficit that had worsened in the post-war years in the country, and, on the other hand, at overcoming the firm trends to drop in production observed in onshore fields. Thus, the exploration of the Caspian oil and the emergence of a new sub-branch of the republic’s oil industry were an objective necessity, but this process ran against fierce resistance from the enemies of the Azerbaijani people in the person of Armenian chauvinists disguised as a communist and their patrons in the central leadership of the country. Ignoring the scientifically grounded forecasts of the Azerbaijani oil industry workers about the great economic prospects of the Caspian offshore fields, these forces launched wide activity at all levels in order to prevent the implementation of these plans.

On July 29, 1954, a meeting of oil industry activists of the republic was held in Baku, with the participation of the former oil industry minister of the USSR N.Baybakov. The meeting was devoted to the discussion of the resolution of the Council of Ministers of the USSR from July 9, 1954 "On measures for the further development of the oil industry". In his report on the problems of the development of the Azerbaijani oil industry, the chief geologist of "Azmorneftrazvedka association B.Babazadeh focused on deliberate interference in putting into operation of the offshore oil fields. He noted that still in 1948, on the eve of putting the Caspian fields into operation, the adviser to the Minister of Oil Industry of the USSR A.G.Helkvist – then the chief geologist of Azneft – during the conversation with B. Babazadeh in his office proposed him to renounce the idea of developing offshore fields, saying: "There is nothing on the sea, and I have been saying this for a long time. Let's write a letter to the Minister Comrade Baibakov stating that "work at sea should be suspended, because there is nothing there". Babazadeh, who was well aware of the presence of the richest deposits in the Caspian Sea, resolutely rejected this proposal and noted that oil deposits in the Caspian Sea not only well as those of Absheron, but also excel them. B.Babazadeh stated that Helkvist in every possible way tried to convince the first secretary of the Central Committee of the Communist Party of the Azerbaijan SSR M.Bagirov that the main oil fields are located in Ganja and Shamakhy regions, but did not achieve success. (3.145) However, later, working as an adviser to the USSR Ministry of Oil Industry, he had managed to convince Minister N.Baibakov in the rightness of his "theory". Helkvist and the Armenian lobby supporting him, as arguments for their view point, cited a steady decline in onshore oil production after 1951 and the discovery of new deposits in the west of the republic. They insisted that the drop in production is costly for the republic and as a result, the oil industry is turning into an ineffective sector of the economy.

N.Baibakov, who spoke at the meeting, began to prove that the allocation of 10.2 billion rubles, allocated in 1948-1953 for the capital construction in the oil industry of Azerbaijan, were an unjustified waste resulting from the friendship between M.Bagirov and I.Stalin. Allegedly, M.Bagirov, in his own careerist goals, repeatedly "wrung out" large sums from Stalin under the pretext of increasing the rate of oil production, which, according to N.Baybakov, testifies to the anti-state activities of M.Bagirov, who by his actions caused significant economic damage to the state [4.249].

It is known that M.Bagirov headed Azerbaijan in the 30-50s of the last century. His governing in our history is characterized as a tragic and contradictory period. However, it is hardly logical to imagine the desire of the leader to obtain funds from the central government for the development of the oil industry as an anti-state act. The groundlessness of such opinions is obvious. Archival documents of the time indicate that the creation and development of new promising sectors of the economy in post-war Azerbaijan seriously worried the Armenian-Dashnak elements, who found shelter in the central government under the wing of A.Mikoyan.

Not succeeded to prevent the start of the development of large oil fields in the Caspian Sea in 1948-1949, this Armenian lobby began in every possible way to convince the USSR government members of the economic inefficiency and absence of any prospect in the oil industry of Azerbaijan and, in particular, the development of fields in the Caspian Sea. Moreover, they especially "emphasized" first of all, on the allegedly excessive high prime cost of Caspian oil in comparison with cheap oil from fields put into service in the first half of the 50s in the eastern regions of the USSR.

However, all these "arguments" did not stand up to any scientific criticism. It is known that oil produced in Azerbaijan, including from the bottom of the Caspian sector related to it, differs significantly from the Tatar, Bashkir, Volga, etc. oils in terms of its chemical characteristics and productivity. So, if the sulfur content in Azerbaijani oil does not exceed 0, 3%, then in the composition of oil from the listed regions it is 2-5% [5.96]. Right up to the end of the 50s, high-quality fuel and oils made only from Azerbaijani oil were used in all branches of metallurgy in the USSR. In 1956 alone, 2.177 thousand tons of low-sulfur fuel oil was sent from Azerbaijan to metallurgical enterprises in other regions of the USSR. Another conspicuous evidence of the high quality and economic efficiency of Azerbaijani oil can be the extremely low prime cost of petrol produced from it. So, in the 50s, the cost of 95/130 petrol in Baku was 820 rubles, in Novoufimsk – 1158 rubles, aviation benzine 91/115 in Baku – 520 rubles, in Grozny – 890 rubles [6.97]. Despite all these obvious facts, our ill-wishers did not abandon their attempts to undermine the economy of Azerbaijan and to inflict damage on our people. At the above-mentioned meeting in Baku, despite the convincing arguments of the Azerbaijani oil workers, it was announced that, in accordance with the resolution "On measures for the further development of the oil industry", the main investments in the Azerbaijani oil industry in 1955 were reduced by 2.2 times and amounted to 700 million rubles, and Azerbaijan was included in the list of economically unpromising oil regions.

The decision-making of this decree led to a 2.2- times reduction in oil production in the republic compared with the previous year, and a 4.4- times reduction in exploratory drilling. However, despite such a sharp decline in capital investments, the oil production plan for 1955 was maintained at the same level [7.18]. It was a heavy blow to the oil industry and, on the whole, to the economy of Azerbaijan; in this way, the governing bodies of the empire, for which our country was just an outlying colony, fulfilled part of the aspirations of its Armenian servitors. The latter, inspired by this success, trebled their efforts in order to prove to their masters the complete economic insolvency of the oil industry of Azerbaijan and achieve its definitive liquidation. To this end, at the end of 1956, Deputy Chairman of the Gosplan (State Planning Committee) of the USSR Mkrtychyan addressed to the chairman of the party control committee N.Shvernik with a letter in which he proved the economic ineffectiveness and unprofitability for the country of the oil industry of Azerbaijan, first of all, allegedly offshore oil production in Caspian Sea. However, N.Shvernik, having contacted the then leader of Azerbaijan I.Mustafayev, comprehended the real core of the issue. In February 1957, I.Mustafayev wrote and personally took to N.Shvernik a 13-page letter, which convincingly proved the economic efficiency of the oil industry of Azerbaijan and the Caspian oil fields. A copy of the letter is kept today in the Archive of Political Documents of the Administrative Department of the President of the Republic of Azerbaijan [8, 95-108]. Later, Academician I.Mustafayev recalled that he visited N.Khrushchev with this letter and told him that the State Planning Committee had developed a plan for economic sabotage against the USSR, about which he had already applied to the Party Control Committee under the Central Committee of the CPSU. After that, the supreme bodies of the country took drastic measures, as a result of which the sabotage was promptly stopped.

Thus, due to the timely intervention of the republic's leadership, the oil industry and, on the whole, the economy of Azerbaijan was partially helped out from the next blow. Nevertheless, the Armenian subversives had managed to achieve their goal – in 1957, the domestic oil industry was deprived of annual allocations for drilling, exploratory drilling and for oil produced (at the rate of 10 rubles per ton).

Despite all the underhand plotting and destructive activities of the Armenian lobby and its patrons – the imperial leaders, for the first time in world practice, Azerbaijani oil industry workers were able to start industrial exploitation of the richest deposits at the bottom of the Caspian Sea. During the meeting with the members of the consortium on the "Contract of the Century" on January 25, 1995, President of the Republic of Azerbaijan Heydar Aliyev said: "As a result of intensive work and great efforts of Azerbaijani scientists, engineers, geologists, oil industry workers, oil masters, oil has been producing on the Caspian Sea for over 45 years" [9].

Due to intensive and comprehensive preparatory work, the Ghurgan-deniz, Gum adasi, Glinyaniy and Garadag-deniz oil deposits were identified and put into operation. And 422 million tons over the past 48 years from 1949 to 1960, 45 million tons of oil was produced at the world-famous offshore oil field "Neft Dashlary" ("Oil Rocks") located at110 km distance from Baku [10, 11-13]. Why did they so insistently interfered with the discovery and development of these deposits, the exploitation of which was originally planned for a 25-year period, but which served the huge empire for almost 42 years? What was the purpose? Of course, now it is much easier to answer this question than in previous years, because Azerbaijan is now an independent state. As President Heydar Aliyev noted at the same meeting: "The Azerbaijani people, the Azerbaijani state have become full masters of their wealth. All this created an opportunity for an independent Azerbaijani state to independently use oil fields at its own discretion... The negotiations, conducted for more than three years with the largest oil companies in the world for the exploitation of oil deposits, have constantly been in the focus of attention of Azerbaijan and, one can say, the whole world ... In some circles of the international community there were forces that were extremely hostile to this matter. In some circles of the international community there were forces that were extremely ill-disposed about this case. There were powerful forces that at various levels and directions obstructed the preparation and signing of this contract. But the constructive activity of the independent state of the Republic of Azerbaijan, our cooperation with the oil companies of foreign countries, based on sound principles, made it possible to eliminate all these obstacles"... [11,166]. If you carefully read these lines, the answer to the above-mentioned question will be much easier. Hence it appears that the forces that prevented the Azerbaijani state from the use of its wealth and raising the economy have not remained in the past, they still exist. Their main goal, both then and now, is to deprive Azerbaijan of the opportunity for economic development and state independence. However, all their efforts by the far-sighted policy of the President of the Republic of Azerbaijan Heydar Aliyev were nullified.

On September 20, 1994, a contract was signed between SOCAR and the largest oil companies of the USA, Russia, Turkey, Saudi Arabia, Great Britain and Norway [11, 168]. This document, which went down in history as the “Contract of the Century”, confirmed the fact that independent Azerbaijan has become the sole master of its wealth. Others followed the “first swallow”: over the past period: SOCAR signed more than 20 contracts with the largest companies of the USA, Russia, Turkey, Great Britain, France, Italy, Iran, Saudi Arabia and Japan for the development of fields in the Azerbaijani sector of the Caspian Sea. All these contracts are being fulfilled.

It is regretful that there are certain forces in the Russian Federation that are evidently not satisfied with that as things now stand. They are doing their best to prevent the continued progress of fruitful cooperation between the Republic of Azerbaijan and foreign countries in the development of its oil resources. To all appearances, the imperial forces cannot accept the situation in terms with the loss of lands and resources, which over the past centuries they have become accustomed to consider their property. So, immediately after the conclusion of the “Contract of the Century” in September 1994, the Russian Foreign Ministry made a special statement on its non-recognition. The authorities of this country, which cited the unresolved issue of the status of the Caspian as a pretext, now speaking through some of its representatives, declare the possibility of using force if the “Contract of the Century” is implemented. In this regard, a document prepared at the Institute for Defense Research under the General Staff of the Ministry of Defense of the Russian Federation entitled “Conceptual rules for the strategy of countering the main external threats to the national security of the Russian Federation” is characteristic. The authors of this document enunciate that an important task is to prevent the implementation of the Caspian oil contract in its current form, for which a set of measures is also proposed, namely: 1)blocking the Azerbaijani sector of the Caspian Sea, and even its entire post-Soviet part, until the final determination of the status of the sea; 2)in order to prevent the activities of foreign oil companies; 3)obstacles to direct access from the main territory of Azerbaijan to Turkey; 4) pressure on Baku through the threat of an Armenian attack on Ganja and Yevlakh, etc. [12, 17].

4.Conclusion

As we can see, the traditionally anti-Azerbaijani orientation of the ruling circles of Russia, dating back to the times of Peter I, exists today as well. Militaristic circles of a neighboring power to implement their aggressive plans. This is evidenced by the speeches of representatives of the supreme authorities of the Russian Federation, starting from President Boris Yeltsin, Vice-President A.Rutsky, Foreign Minister A.Kozyrev, Head of the RF Ministry of Defense P.Grachov, leader of the Liberal Democratic Party V.Zhrinovsky and their protégé, President of Armenia R.Kocharian... [13, 210-211]. However, the consistent and purposeful policy of consolidation our country in the international arena, pursued by President Heydar Aliyev, will inevitably lead these aggressive attempts to a natural collapse. This is evidenced by the results of the successful foreign policy pursued by the head of the Azerbaijani state over the past ten years.

5.References

1. Sultanov Chapay. Istoriya ne lyubit soslagatelnogo nakloneniya, i vsyo je… (History does not like the subjunctive mood, and yet). Baku: Chashyoglu, 2011, 685 p. (in Russian).
2. Archive of Political Documents of the Administrative Department of the President of the Republic of Azerbaijan (hereinafter APDADPRA), f.1, inv.282, doc.21, sh.95-108.
3. APDADPRA, f.1, inv.282, doc.11, sh.145.
4. APDADPRA, f.1, inv.282, doc.11, sh.249.
5. APDADPRA, f.1, inv.282, doc.21, sh.96.
6. APDADPRA, f.1, inv.282, doc.21, sh.97.
7. APDADPRA, f.1, inv.282, doc.11, sh.18.
8. APDADPRA, f.1, inv.282, doc. 21, sh.95-108.
9. «Azerbayjan» (the “Azerbaijan” newspaper), 26 January 1995 (in Azerbaijani).
10. Amirov A. Morskiye neftyaniki – laureatı Leninskoy premii (Marine Oil Workers – Lenin Prize Laureates). Baku: 1961, 89 p. (in Russian).
11. Aliev Ilham. Kaspiyskaya neft Azerbaydjana. Moskva: İzestiya, 2003, p.166, 168 (in Russian).
12. Zhurnal «Kapital». Baku: 1997, №3, 712 p.
13. Pashayev Arif, Sultanov Chapay. Azerbaydjan v tsifrax, grafikakh, kartakh i foto. Baku: 2012, p. 210-211 (in Russian).

PP-VII-12

COOPERATION BETWEEN THE REPUBLIC OF AZERBAIJAN AND THE EUROPEAN UNION (EU) COUNTRIES IN THE FIELD OF ENERGY SECURITY

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Abstract. The relations of the European Union with the USSR are based on the Trade and Cooperation Agreement signed in 1989. On January 31, 1992, a new stage in relations began with the EU's recognition of the independence of the Republics of Azerbaijan, Armenia and Georgia. Relations between the EU and the South Caucasus can be divided into four periods; 1991-1996; 1996-2001; 2001-2003; 2003. Under the TACIS Program, the EU has two more dynamic and important programs in favor of the strategic interests of the countries of the South Caucasus. These are TRACECA (Transport Corridor Europe-Caucasusus-Asia) and INOGATE (Interstate Oil and Gas Transport to Europe).

Keywords: European Union, Traseca, OSCE, Neighborhood Policy, INOGATE, TACIS

1.İntroduction

The XXI st century has entered the world as a competition for geopolitical dominance between the United States and Western Europe. This competition is more pronounced in the economic, cultural and political spheres. The European Union (EU), which was founded in 1951 and formally established in 1993, increased its membership from 15 to 25 in 2004. The single "eurozone", which has been in place since 1999, and its 450 million citizens, has had a say in the international division of labor and in international trade, as well as in its expansionist policies.

2.Method

Empirical, theoretical, qualitative, quantitative, multi-method, longitudinal, cross-sectional study, case study methods were used in the study.

3.Results and discussion

Using the methods, the relations of the European Union with the Caucasus republics, including Azerbaijan, were determined.

The European Union's relations with the Caucasus countries are based on the Trade and Cooperation Agreement signed with the USSR in 1989. After the collapse of the Soviet empire in 1991, the European Union developed a special TACIS program to carry out democratic reforms, create market economy infrastructure, and develop trade, transport, and customs between the newly independent states through technical assistance and expert assistance. On January 31, 1992, a new stage in relations began with the EU's recognition of the independence of the Republics of Azerbaijan, Armenia and Georgia. Relations between the EU and the South Caucasus can be divided into four periods; 1991-1996; 1996-2001; The period after 2001-2003 and 2003. [9, p. 231] Although the EU recognized the independence of the new states established in the South Caucasus on 31 January 1992, the EU was not interested in establishing closer ties with these states. It should be noted that the ethnic upheavals and coups that took place in the newly independent states after the collapse of the Soviet Union characterized the South Caucasus as an unstable region. Despite the policy of non-interference in the processes taking place in the region, the preservation of the independence of the newly formed South Caucasus states was also of great importance for the EU. To this end, within the framework of the EU's concept of a "transition country" for the South Caucasus, technical and financial assistance was provided to countries in the region to make the transition from a socialist system to a democratic and market economy. Special programs have been developed to provide this assistance, including the TACIS (Technical Assistance to the Commonwealth of Independent States) program, which was established at the Rome Summit in 1990 due to the scope of its work and budget. The TACIS Program has 3 main objectives.1. To assist in the transition and formation of a market economy and a democratic society. 2. Facilitate the adaptation of the world economy and, in particular, to the economies of the EU member states. 3. Development of partnership and bilateral relations between the AB and the countries of the South Caucasus. In addition, under the TACIS Program, the EU has two more dynamic and important programs in favor of the strategic interests of the South Caucasus countries. These are TRACECA (Transport Corridor Europe -Caucasus-Asia) and INOGATE. (Interstate Oil and Gas Transport to Europe) The TRACECA program is a very important program for the countries of the South Caucasus, Central Asia and the European Union. The idea of this program, which is considered to be the revival of the ancient Silk Road, was born in 1993 in Brussels at the suggestion of the European Commission. especially in Europe. This corridor is also of great importance for Europe. Because the EU is dependent on the consumption of Russian natural gas. Through this corridor, Central Asia (Kazakhstan oil and Turkmen gas) facilitates the transfer of Caspian oil and gas to Europe and significantly reduces Europe's dependence on Russia. Another important program funded under the TACIS program, the INOGATE program, is in a more specific direction, focusing on the development and modernization of oil and gas transportation, as well as the identification of alternative sources of oil and gas, and so on. works in the direction. The INOGATE program attaches great importance to the Caucasus region, especially to energy resources in the Caspian Basin. Baku-Supsa (1997-1998), Baku-Tbilisi-Ceyhan (BTC) (2002-2006) oil pipelines and Baku-Tbilisi-Erzurum (BTE) (2006-2007) aimed at delivering Azerbaijani oil to Europe The company also transports Kazakh oil and Turkmen gas through the pipeline. [2]

The legal basis for comprehensive relations between the Republic of Azerbaijan and the EU is the "Agreement on Partnership and Cooperation between the European Union and its Member States on the one hand, and the Republic of Azerbaijan on the other hand" signed in Luxembourg on 22 April 1996 and entered into force on 22 June 1999. (In fact, the history of this cooperation dates back to 1993. On April 7, the EU issued a statement on the Nagorno-Karabakh conflict.) This agreement covers all possible areas of cooperation between Azerbaijan and the EU, in particular political and economic. The agreement provides a framework for all forms of non-military cooperation between Azerbaijan and the European Union. TES was signed for a period of 10 years, and since the implementation of the Agreement expired in 2009, its implementation is extended for 1 year each year. [4] [10] Following the fifth wave of EU enlargement, a new strategy called "Wider Europe - New Neighborhood Policy" was created to work more closely with the countries of the region. The EU was not interested in extending the strategy, which was approved by the European Parliament in 2004, to the South Caucasus. However, the "Rose Revolution" in Georgia in 2003 led to a radical change in the EU's views on the South Caucasus. The Action Plan submitted to the South Caucasus states in 2005 was adopted by all three states in 2006. It includes a number of framework agreements and memoranda. [8, p.203]

Although the Action Plan provides for a just solution to the Abkhazian problem in the Republic of Georgia, it does not say a word about Nagorno-Karabakh. The EU intends to use the South Caucasus as a tool to gain access to the East and not depend on Russia. The South Caucasus states, in particular the Republics of Georgia and Azerbaijan, intend to break free from Russian influence, rapidly integrate into the European Union indirectly to the West and become equal EU members. (1) On May 14, 2009, the German Bundestag adopted a resolution on strengthening security, stability and democracy in the South Caucasus. "All states must recognize the right of Azerbaijan, Georgia and Armenia to freely choose their partners and allies as defined by the OSCE Charter in Paris. The principles of the OSCE Charter guarantee the right to territorial integrity and sovereignty. Borders can be changed only by agreement between the parties. It forms the basis of all efforts to resolve conflicts in the South Caucasus, as well as in other regions of Europe. " The document states that the three countries of the South Caucasus, as a region connecting Europe with Central and South-West Asia, play an important role in ensuring the energy supply of Germany and Europe as producers of oil and gas and transit, and after their accession to the Council of Europe. It is reflected that they found their permanent place in the family. [7, pp.240-242] The resolution notes that this close cooperation is based on the historical connection of the region with the European cultural space. The resolution called for further strengthening the EU's relations with the region under the Eastern Partnership program, supporting the Czech Republic's intention to implement the Nabucco project during its EU presidency, as well as promoting infrastructure development in the region. [3]

In 1999, the European External Action Service was established and headed by the High Representative of the European Union for Foreign Affairs and Security Policy. According to the Center, one of the most unsuccessful areas of the EU's policy in 2011 was the settlement of the Nagorno-Karabakh conflict, but the most successful policy areas were trade and energy relations with its Eastern neighbors. One of the key achievements in this direction was the mandate given to the European Commission in September 2011 to negotiate with the Republics of Azerbaijan and Turkmenistan on the construction of the Trans-Caspian gas pipeline. Azerbaijan has a special place in European energy security plans as both a producer and a transit country. [6, p.315]

Since May 2004, the European Union has been working with the countries of the South Caucasus, allocating 255 million euros for the implementation of the Neighborhood Policy. The main goal of the EU's New Neighborhood Policy project in the region is to accelerate the political and economic rapprochement of the South Caucasus countries with European values. [5, pp. 85-87] Of course, the South Caucasus countries are also interested in this issue and with the European Union. Efforts to expand bilateral relations On January 1, 2007, the TACIS program was replaced by the European Neighborhood and Partnership Instrument (EPA). Under this tool, € 61 million has been allocated under the Annual Action Programs for Azerbaijan for 2007-2009. AQTA has three main strategic objectives: to promote democracy and human rights, to facilitate the transition to a market economy and to promote sustainable development, as well as to develop cooperation in areas of mutual interest. In addition, during the meeting of EU Foreign Ministers in Brussels on May 26, 2008, Poland and Sweden launched the "European Neighborhood Partnership" initiative. The initiative, which aims to establish a single format for the Eastern European Neighborhood Policy countries, covers Azerbaijan, Georgia, Armenia, Ukraine, Moldova and Belarus (Eastern Partner countries). The Eastern Partnership Summit was held on May 7, 2009 in Prague. The summit adopted a Joint Declaration defining the main goals and principles of this initiative, as well as the process of future cooperation, and thus officially launched the Eastern Partnership. Within the framework of this format, it is planned to hold a biennial meeting of heads of state and government of the Eastern Partnership countries, and an annual meeting of Foreign Ministers of the European Union and Eastern Partner countries.

4.Conclusion

Each Eastern Partnership country is at a different stage in the process of implementing Integrated Border Management - a process that involves the development of a national strategy and action plan for Integrated Border Management. The EU's draft Eastern Partnership document states: "The exchange of values on democracy, the rule of law and respect for human rights, as well as the principles of a market economy, sustainable development and good governance, will form the core of this Partnership."

5.References

1 .http://www.qafsam.org/page/143/az
2. Relations of the Republic of Azerbaijan with the European Union http://www.mfa.gov.az/content/566
3. Azerbaijan newspaper, May 16, 2009.
4. https://www.economy.gov.az/article/eu-ve-azerbaidjan/22009
5. Rashad Gasimzade. European Union and Azerbaijan: "New Neighborhood Policy" "Adiloglu" Publishing House, Baku 2011. 152 p.
6. The main directions of the foreign policy of the Republic of Azerbaijan (1991-2016) / collection of articles /. Baku: “Poliart” MMC, 2017, 904 p
7. Hasanov AM Caspian-Black Sea Basin and Geoeconomics of the South Caucasus: Azerbaijan's Energy Policy. Baku, “Zardabi LTD” LLC, 2016, 296 p.
8. Hasanov AM Geopolitics of Azerbaijan. Textbook. - Baku, “Zardabi LTD” LLC, 2015.1056 p.
9. Hikmet Babaoglu “World politics and international relations” Baku-2010 587 pages.
10. http://eu.meclis.gov.az/?/az/content/317

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THE ROLE OF MIDDLE EAST OIL RESERVES IN US ENERGY SECURITY

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Abstract. The article discusses policies of the USA in relation to OPEC and its Arab member countries. Import of energy resources from countries in the Middle East meets almost one-third of American demand. The Foreign policy of the US is aimed at strengthening its position in the market of hydrocarbon resources in the Middle East in order to sustain the growth of American economy and satisfy needs of its citizens. In addition, recent shifts in American energy sector affected its relations with OPEC as well.

Keywords: oil reserves, oil consumption, distribution policy, energy security policy, doctrine, import, stable supply of energy resources, shale oil production

1.Introduction

While maintaining its leadership in the international arena, the United States strives to ensure the security of the country, its economic independence, the "welfare of its people, its internal stability and the high patriotism of its people. In this regard, Barack Obama, US President, stated by referring to "Washington's world leadership" almost in his every appeal. We, Americans must be an example to others and always go ahead. It is what makes us special. We believed that we would reduce our dependence on oil imports and protect our planet. Today America is the number one in the gas and oil sector, and America is number one in the wind power industry, too. Every three weeks, we run more solar energy than we did in 2008. This year, a nuclear family was able to save about $ 750 at the expense of lower gas prices and higher gasoline standards." (Obama, 2019). Achieving economic growth and prosperity through cheaper, more sufficient, more sustainable and more reliable power resources is the primary goal of US energy policy. In this regard, the United States, which has a great deal of power and authority, prefers the policy of keeping the world's energy needs under control in order to achieve its goal.

2.Results

However, events in the oil and natural gas markets and increasing integration because of deep globalization can have a negative impact on the energy security of the United States, as it affects in each country. In this regard, the international policy pursued by the US, as a major producer and consumer of energy resources in the world to regulate global energy challenges, incorporates several key elements, such as diversification of energy and energy resources around the world, as well as their transportation line, cooperation with other countries - negotiation with oil exporting countries in particular regarding disruptions in transportation and the use of strategic oil reserves, dialogue with leading oil producing countries on oil production and market prices, and increasing energy efficiency to reduce global oil dependence, along with expanding access to alternative energy sources.

Arab OPEC member countries have more than half of the world's oil reserves, and in addition to the high oil quality, low production costs have always attracted the attention of western countries whose industry is heavily dependent on oil. Despite being an undeveloped industrial base, the region has significant strategic advantages because of its rich oil reserves and the location of important intersections. In addition, the oil factor is based on the policy that the United States has set regarding OPEC and its Arab-member countries. Generally, USA is one of the competent players of energy regulation policy, in addition, consumes 70% of the world's mineral and mining resources (Amanov 2007, p.149).

The energy policy of the United States is, above all, global. The main element of this policy is the versatility of the growing demand and resources around the world. Currently, the United States has established close relationships with the world's most important oil and gas countries to ensure their own energy security and the continuation of the global economic system. This factor should be considered as the main reason for the US to take action and pursue its policy towards OPEC countries, which have significant oil reserves in their lands.

In the 1990s, US governors worked to ensure the country's long-term energy security. The increasing dependence of the US economy on oil imports has raised concerns in this regard. In the 2000s, the United States, in particular, faced with the fact that oil imports from the Gulf countries have increased. Therefore, the US has set a strategic goal to provide all sorts of energy that can meet both itself and the world's energy demand (Kısajik 2019). The US does not want to depend on a single energy source in oil imports.

An increase in the number of oil exporters will reduce the risk of oil exports to the US, Western Europe and Japan, in the event of any political turmoil that may arise in the Middle East. This situation will also affect the Gulf countries and OPEC to set the world oil prices. Overall, 54% dependence on oil imports of the US in 2006 is expected to increase to 70% by 2025, with 25% of world oil consumption. The United States still has 70 million barrels a day of oil consumption, and is assumed to rise to 115 million barrels by 2020. The Gulf countries, which own 65% of the world's oil reserves, have a 20% role in meeting the United States' oil demand (Bayraç 2010, p.1). Although America and the United States were allies during World War II, the struggle between them for the aforementioned reasons regarding access to oil resources by OPEC Arab-member states were not slowing down. In the course of this struggle, the United States declared Saudi Arabia's protection vital for them on February 18, 1943 because of the fear of Saudi Arabia being influenced by the United Kingdom, and embedded it into the scope of the Lend-Lease Act [9] and provided American aid to the country. However, the UK still had the advantage over Middle East oil. Thus, in 1943, the UK controlled 81% of Middle East oil production and the United States only 14%. All this prompted the US government to have direct contact with the British government, which resulted in the signing of the Anglo-American Petroleum Agreement in 1944. The United States hoped to abolish restrictions imposed by the British on American oil companies operating in the Middle East through this agreement. The agreement also envisages the establishment of an International Petroleum Commission to control world oil production, supply and demand.

The focus of US foreign policy towards the Middle East after the Second World War was to provide a constant flow of oil. In addition, Great Britain, weakened after World War II, failed to fulfill its commitments to Turkey and Greece. In 1947, the United States provided $ 400 million in aid to Turkey and Greece through a program called the Truman Doctrine (Encyclopedia Britannica 2019) and undertook this commitment. With the fall of Turkey and Greece under the influence of the Soviet regime, the oil-rich Middle East would face the Soviet threat and the solution would be in favor of the Soviet Union. Thus, the United States' need for foreign oil and its focus on areas where American oil companies can produce more and cheaper oil in the face of growing global demand have increased the importance of Middle East oil to the United States.

The emergence of the Suez crisis in 1956 has started a new phase in US policy towards the Middle East. Due to the growing Soviet influence in the region, plans to establish a Middle East defense organization have been made with the support of Great Britain and the United States. In addition, US President Dwight Eisenhower made a statement that the US would support Middle Eastern states in any way, including the use of military force and military assistance to countries in the region, in the event that these countries were attacked by a communist-dominated state. Beginning in 1969, the United States began to build regional policy under the Nixon doctrine, which intended preventing the United States from directly interfering in the region's conflicts and instead, it will be satisfied with military and economic assistance.

The establishment of OPEC, the decline in oil production during the Arab-Israeli war, and the embargoes were the first objections to the US political hegemony of the Arab world thanks to the oil factor. The Arab states have announced o impose an oil boycott against states backing Israel, and prices have jumped sharply due to oil shortages. Because, thanks to the support of the United States, Israel returned the lost territories and signed an agreement to end the war with Syria and Egypt in November. On October 17, OPEC opposed US policy, imposed an embargo on oil exports, and raised oil prices exporting by up to 70% to US allies in Western Europe. Overnight, the price of a barrel rose from $ 3 to $ 5.11 per barrel (in January 1974 OPEC raised the price to $ 11.65 per barrel). Although President Richard Nixon has made strict restrictive measures on the use of energy resources, but it has not helped to find a way out of the situation and the economic downturn in Western countries has begun. During the peak of the oil crisis in the 1970s, the price of a gallon of gas in the United States rose from 30 cents to $ 1.2.

Although an embargo imposed against the United States in March 1974 was abolished, its impact has not been eliminated. The rise in oil prices has made a boomerang effect and has led to a rise in prices of all services and goods. That is why President Ford had to adopt a program to fight inflation. Against this background, revenues from the sale of oil by the major oil producing countries in the Arab world rose at an invisible pace during 1973-1978.

The Islamic Revolution of Iran in 1979 and the occupation of Afghanistan by the Soviet Union in that year made the interference of US into the region crucial, as the two events changed the balance of power in the region for the benefit of the Soviet Union. In the 1980, the US changed its policy regarding the region and adopted the Carter Doctrine. Jimmy Carter, the president of the United States, disclosed new policy in detail to the US Congress on January 23, 1980. In his speech, Carter said that any foreign effort to gain dominance in the Middle East would be considered a threat to US strategic interests, and if such a situation arose, any military action would be taken. This was the reaction of the US to the occupation of Afghanistan by the USSR during the Cold War (Encyclopedia Britannica, 2019).

Thus, the region, which owns 60% of the world's oil reserves, is playing a key role in maintaining US global leadership. The United States believes that it has the right to control the region's energy resources and to fight against countries that are out of policy to provide sustainable energy flows. The United States does not conduct any operations against countries that they have good relationship in principle. For example, the US will not enter into conflict situations with Saudi Arabia - OPEC member as long as they understand each other. With the end of the Cold War, the US government has developed a new strategy towards the Middle East, based on three basic principles: Arab-Israeli reconciliation, dual containment, political and economic reforms. When these strategies failed one by one, George W. Bush, who came to power in 2001 with a claim to change Clinton's unsuccessful Middle East policy, began to pursue a policy that could regain weakening authority of US in the region. Under the influence of the new conservatives during his presidency, the doctrine of radical and preventive war was realized mora than the strategy of containment. Thus, the doctrine emphasized the importance of using military intervention when it was necessary to maintain and strengthen American leadership in the region. At that time, according to data prepared by the National Energy Policy Development Group during Bush’s presidency, the US oil demand will increase and the Gulf region's energy resources will play a key role in meeting these needs (Altunişık 2009, p.70-75).

The fight against radical Islamist terrorists, believed to have originated in the Middle East along with the September 11 attacks, and keeping weapons of mass destruction out of some regimes in the region were also key factors determining US policy in the Middle East. Afghanistan was the first stop for America seeking to gain global power after the terrorist attacks of September 11, 2001, and began air strikes on October 8, 2001. However, the world community did not tend to welcome it unambiguously and wondered why the US first chose Afghanistan as its target. This has led to the idea that Afghanistan is at an important junction between Central Asia and the Middle East, has geopolitical importance in terms of oil and natural gas resources, and has important political and economic goals behind the operation.

After the attack on Afghanistan, the US further expanded its understanding of global terrorism and stated that it would intervene in countries around the world, supporting terrorism, producing weapons of mass destruction or possessing them, and asked all countries to support it in this regard. To this end, the new American leadership has taken a bigger step by planning to attack Iraq because of having the weapons of mass destruction, and increased its presence in the region by attacking Iraq on March 20, 2003 with the help of Allied forces. As it obviously seems, the actual purpose of the Greater Middle East project, implemented by the United States to promote democracy and greater freedom, is to control the region's oil and other energy resources, and to ensure the sustainable and safe transportation of energy resources.

Changes in US energy policy since the beginning of the 21st century have also affected relations with the Near East and the Middle East. Rising production costs of importing energy resources require the United States to implement measures such as energy efficiency and energy saving, boost domestic production, and expand the use of alternative energy sources. In addition, because of increased shale oil production, oil refineries in US began to receive light crude oil, in turn, it contributed reducing dependence on imported oil from unsustainable regions of Africa and the Middle East.

During the period 2008-2013, the United States reduced daily crude oil imports from 9.7 million barrels to 7.7 million barrels. In 2015, for the first time in the last 45 years in the United States, there has been a decline in imports of oil and oil products thanks to an increase in domestic production. One of the possible geopolitical implications of this energy revitalization in North America is that these factors have also led to a drop in global prices. The Ministry of Energy reports that oil produced in Canada is well suited to US refineries, and most of the plants have been provided with all the technology required to process Canadian heavy and high-quality oil. In 2015, Canada increased its shipments by up to 10% and exported to the United States at a record volume - 3.2 million barrels per day. In 2015, the United States imported 7.4 million barrels of oil per day, and Canada imports one of every four barrels of "black gold" imported into the United States. In addition, Canada purchases almost all oil exported by United States exports (422,000 barrels per day) (Regnum.ru, 2019). Thus, increased domestic oil production and increased energy supplies from outside the Middle East, especially from Canada to the United States, could pose a threat to OPEC countries in the medium term, while lower oil prices could lead to lower revenues of OPEC member oil exporting countries.

4.Conclusion

Finally, it is difficult to imagine about US policy in the Middle East that they would abandon the Carter Doctrine and allow the Persian Gulf region to be controlled by Russian, Indian or Chinese (Гаранина, 2014, p.203). US interests in the Middle East are linked not only to economic factors but also to military factors in terms of ensuring regional security and fighting against global terrorism. In this regard, the increase in shale oil production and changes in the import structure give more opportunities to the United States to implement its foreign policy. The imposition of sanctions against countries that are major producers of energy resources (mainly in relation to Iran) can be a good example. Along with it, as trade in the Persian Gulf, which plays a key role in the formation of oil prices, is carried out in dollars, the decline of US dependence on foreign imports still does not mean that the US's strategic interest in the Persian Gulf is diminishing.

5.References

1.Obama, B., 2011. Remarks by the President in State of the Union Address // White House transcript. January, 25.
2.Encyclopedia Britannica. (2019). Carter Doctrine | United States foreign policy initiative. [online] Available at: https://www.britannica.com/topic/Carter-Doctrine [Accessed 17 Sep. 2019].
3.Encyclopedia Britannica. (2019). Lend-lease | United States [1941]. [online] Available at: https://www.britannica.com/topic/lend-lease [Accessed 17 Sep. 2019].
4.Encyclopedia Britannica. (2019). Truman Doctrine | Definition & Facts. [online] Available at: https://www.britannica.com/event/Truman-Doctrine [Accessed 17 Sep. 2019].
5.Amanov, Ş., 2007. ABD'nin Orta Asya Politikaları. Gökkubbe Yayınları, İstanbul: (s. 149).
6.Altunişık, M.B. and Altunışık, M.B., 2009. Ortadoğu ve ABD: yeni bir döneme girilirken. Ortadoğu Etütleri, 1(1), pp.70-75.
7.Bayraç, H.N., 2010. Küresel Enerji Politikalari ve Türkiye (p.1-3)
8.Kısajik, S. (2019). Uluslararası Politika Akademisi – (UPA) – Rusya, Abd Ve Türkiye'nin Enerji Politikalari Çerçevesinde Doğalgaz Boru Hatti Projelerinin İncelenmesi. [online] Politikaakademisi.org. Available at: http://politikaakademisi.org/2012/08/02/rusya-abd-ve-turkiyenin-enerji-politikalari-cercevesinde-dogalgaz-boru-hatti-projelerinin-incelenmesi/ [Accessed 19 Sep. 2019].
9.Гаранина, О.Л., 2014. Перспективы добычи сланцевой нефти в США и последствия для мирового рынка нефти. Проблемы национальной стратегии, (4), p.185.
10.Regnum.ru. (2019). Канада завоевывает нефтяной рынок США: экспорт достиг рекорда. [online] Available at: https://regnum.ru/news/economy/2117518.html [Accessed 27 Aug. 2019].

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ON THE HISTORY OF ABSHERON'S OIL PRODUCTION

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Abstract: The given article overviews some historical works of the 19th century on production and processing of oil in oil-rich region of Azerbaijan – in the Absheron Peninsula. It provides brief information on works of Gulishambarov, Ragozin, Lisenko, Mendeleyev, Sokolovsky and other authors.

The tsarist government did not know how to manage oil affairs, did not think about the development of the oil industry, but only about the treasury revenues, only collected taxes on the sale of oil, this just implies an indirect collection from wells.

After the cancellation of the ransom system at the Absheron fields, a rapid growth in oil production and its processing began. At the suggestion of D.I.Mendeleyev Baku oil had to be processed in the central regions of Russia for the development of the Russian industry. D.I.Mendeleyev stubbornly insisted on the transfer of oil refineries to Nizhny Novgorod. This means that artificial barriers were being prepared for the industrial development of Baku.

Keywords: Azerbaijan, Absheron, Baku, oil, kerosene

1.Introduction

The oil industry of Azerbaijan has passed a long historical way of development and today has become the leading sector of the economy of the Republic. Currently, industrial production and processing of oil are important, and in general, they are the main stimulus for the country's socio-economic development. Thanks to the increase in oil production and its sale, there is a rise in the culture and economy of all regions of the Republic, which in their development have left far behind all neighboring states.

2.Results

Even in antiquity and the Middle Ages, some Muslim authors, travelers, geographers and historians, such as Istakhri Iskhak (VIII century), Ahmed Baladzori (IX century), Masudi (X century), Abu Dulaf (X century), Hamdullah Kazvini (1339), ar-Razi (1601); Venetian Marco Polo (XIV century); German traveler Adam Olearius (1636); Turkish author Evliya Chelebi (1647); Swedish traveler Kempfer (1683) and many others in their writings wrote about the Absheron's oil and its production.

Johann Lerch, who traveled in the Caspian Sea in 1735, writes the following: "Oil does not start burning soon; it is dark brown in color and when it is distilled it turns light yellow. Former oil is somewhat turbid, but after distillation, it becomes so light as alcohol and this ignites very quickly, but retains, as simple, its smell and black smoke "[6, 85]. This means that in some way, even the most primitive, they knew how to process and refine oil.

The Baku khans used oil at all times and took the income from its sale for themselves, as can be seen from the journey of Gmelin, who writes the following: "One black oil is used for burning, and for this a great bargaining is being set up. For a fifteen pound batman, it is paid 5 kopecks, and the income from it, as well as from salt, which is sold for 7 kopecks and a half, goes to Khan. Both white and black oil are stored and transported in leather bags, called tuluk ... "[1, 73].

Industrial oil production in Azerbaijan begins in the second half of the 19th century. Also in research books, for the first time, comprehensive coverage of oil production appeared at the end of the 19th century, written mainly by Russian authors. One of the first such editions is the book "Oil and Oil Industry!" (With the attachment of the study of the Caucasian oil of Mr. Markovnikov and Ogloblin)" by the famous oil industrialist V.I.Ragozin [15]. In this book, the author describes the development of the world oil industry, but also pays special attention to the history of the Absheron – Baku oil. His book consists of 18 chapters, where 2, 7-10, as well as the 15th chapters are devoted to the refining, transportation, sale and proceeds from the sale of Baku oil.

V.I.Ragozin, as an interested industrialist, closely followed how researchers study the quality of oil, compare Baku oil with American oil, and what kind of oil they prefer, although the plant technology of oil business in those years in Russia was ahead of scientific research conducted in laboratory conditions. Especially important were laboratory studies and analyses conducted back in 1878 by the researcher Lisenko, who "was the first to draw attention to the fact that when distilling Caucasian (Absheron – R.T., R.A.) kerosene, distillates were obtained, the specific weight of which was significantly higher than the corresponding American kerosene grades, which was later confirmed by comparative distillations of Russian and American kerosene made by Biel and Wilm. This sharp difference between our kerosene led Lisenko to the conviction of its viscous quality, which was soon refuted by practice, and Biel and Wilm showed that under the same combustion conditions Russian (Absheron – R.T., R.A.) kerosene gives more light than American kerosene "[15, 155]. At the same time, the advantage was given to Balakhani oil [15, 159].

Ragozin writes that during the seizure of Baku it turned out that all the oil wells, except two, belonged to Huseyn Khan, "and therefore they entered the group of Russian state property" [15, 227]. He adds after "However, the treasury did not use them until 1820, and the oil industry during this time was completely free from any taxes "[15, 227], with which it is difficult to agree. Since the tsarist government collected taxes from the sale of oil, that exactly implies the indirect collection from the wells.

We must agree with the author that the state did not really know how to manage oil affairs, did not think about the development of the oil industry, it only thought about treasury revenues. The "Expedition of the Supreme Georgian Government" in charge of oil affairs here sometimes gave the oil wells at the mercy, then returned them to the hands of the state, moreover, this was repeated almost every 2-3 years [15, 228]. But it became known for sure that under the ransom system, oil brought in more income than when it was in the hands of the state.

Ragozin in his book gives a table of the purchase of the oil system from 1821 to 1873, where the periods of the most successful development of the oil business are more than clearly observed. For clarity, we present this table here with small abbreviations, leaving the numbers untouched [15, 229-230].

From what year to what year	**In whose hands**	**Income amount in rubles**
1821 - 1825	For ransom, per year	181 000
1825	In government administration	76 000
1826 - 1830	For ransom, per year	97 000
1830 - 1834	For ransom, per year	91 000
1834 - 1838	In government administration, per year	85 000
1838	In government administration, per year	97 000
1839	In government administration, per year	81 000
1840	In government administration, per year	105 000
1841	In government administration, per year	117 000
1842	In government administration, per year	124 000
1843	In government administration, per year	119 000
1844	In government administration, per year	125 000
1845	In government administration, per year	100 000
1846	In government administration, per year	93 000
1847	In government administration, per year	94 000
1848	In government administration, per year	108 000
1849	In government administration, per year	100 178 r. 60 k.
Since January 1 to April 1, 1850	In government administration, per year	98 933 r. 31 k.
Since April 15, 1850 to April 15, 1954	At the mercy of Kunudzhalov, Babalasov and Ter-Gukasov per year	111 000
Since April 15, 1854 to April 15, 1862	At the mercy of Ter-Gukasov per year	117 000
Since April 15, 1862 to January 15, 1863	At the mercy of Ter-Gukasov per year	117 000
Since January 1, 1863 to 1867	At the mercy of Mirzoev per year	162 000
Since January 1, 1867 to 1873	At the mercy of Mirzoev per year	136 000
At the same time, net income from oil, mainly from the Absheron oil		4 422 187 r.

The author notes that the Prussian-subjects Siemens brothers, who took out 2 wells in Kakheti, paid 4,800 rubles annually, which was considered insignificant in comparison with the income from the Absheron wells [15, 231].

V.Ragozin describes in detail both the volume of oil production, as well as its cost by region, including abroad, mainly through Anzali. The author pays attention to new entrepreneurs – Kokorev-Gubonin, who at that time were building a large plant at the Firm of the Trans-Caspian Trade Partnership [15, 242-243].

The book also pays special attention to the development of the oil industry in the Balakhany, Surakhany, Bibi-Heybat and other fields [15, 261-263, 286-307, etc.]. Much attention is paid to the application of innovations in production, especially photogenic production [15, 286], transportation of oil to refineries and after processing to consumers, cost, and so on.

Some of the first studies of the history of Baku oil are the scientific works of S.I.Gulishambarov [4; 3; 2] – article in the "Mining Journal" "Materials for the history of photogenic production", "A brief outline of the development of the oil industry in the Caucasus", "The activities of L.E.Nobel in the Caucasus" and others. In his research papers on the oil industry, the stages of development of the industry are considered. On the basis of archival materials from the Caucasian governorship, the author also established the names of the first oil producers in Absheron.

Referring to the issue of industrial production and oil refining in Baku, S.I.Gulishambarov writes that the first "photogenic plant on the Absheron Peninsula was built in 1859 in Surakhani, near the monastery of fire worshipers. ... The initiative of this great cause belongs to the Transcaspian Trade Partnership represented by its founder V.A.Kokorev, who, long before the discovery of oil in America, conceived the device of a photogenic plant and was able to realize his idea only in 1859, with the assistance of the famous chemist Yu.Liebig. Thus, V.A.Kokorev is the first pioneer of the photogenic business not only in the Caucasus, but throughout Russia "[4, 327-328].

In the work "Materials for the history of photogenic production" S.I.Gulishambarov first named the names of mining engineer Nikolai Voskoboinikov [3, 331], who built his plant in 1837 on the Absheron Peninsula and self-taught inventor Javad Melikov [3, 342-343], who created a distillation unit. This work by S.I.Gulishambarov was the first historical study devoted to the oil business.

The article "Oil as fuel" by S.Gulishambarov, published in the "Gorny Zhurnal" in 1880, is devoted to oil and its derivatives - waste, linking the future with oil heating [5, 251-276].

Chemist-technologist, doctor of chemistry, professor K.I.Lisenko, who for eleven years was the editor of the "Gorny Zhurnal" (1877-1888) also published a book about the activities of L.E.Nobel "In memory of Ludwig Emmanuilovich Nobel" [7].

Attention is drawn to the works of the Russian scientist-chemist D.I.Mendeleyev [11; 8, etc.]. In particular, he is the main initiator of the refining of Baku oil far from Baku.

One of the important works of D.I. Mendeleyev is his article "Oil Industry in the North American State of Pennsylvania and the Caucasus", where he compares the process of extraction, industrial processing and transportation of oil. Compared to free oil production in America, there were many artificial barriers in the development of oil production in Russia – large taxes, ransom, excise taxes, etc. Mendeleyev, referring to this issue, writes in his work: "At first, our Baku oil fields were bought off, and the tax ransom cannot engage in rational production of oil production. He had no time to dig wells – after all, it will take a year and a half or at least a year, and his ransom will end in two or three years, where can he spend the money on this! ...

But in 1872 the ransom was destroyed, the oil areas were sold to private ownership. The business began to develop, and quickly. In 1872, 1,500 thousand poods of oil were produced, and in 1874 - more than 5 million poods, and more than 100 distillation plants appeared. But the prices of American kerosene began to fall rapidly, and that is why the prices of Russian kerosene fell" [12, 509].

D.I.Mendeleyev on behalf of the Minister of State Property, M.N.Ostrovsky, in the summer of 1886, visited the Absheron Peninsula – oil fields and in the same year published a book with his proposals. In particular, he considered oil refining in Baku inexpedient and suggested transporting it to the central industrial regions of Russia. In his opinion, the transportation of oil by rail was expensive for the state and proposed to build a pipeline along the Baku-Batum route. Mendeleyev is the main initiator of the refining of Baku oil far from Baku, which can be assessed as a desire to hinder the industrial development of both the main city and the whole of Azerbaijan. He wrote about his thoughts on pumping Baku oil to Batum, and from there and to other places as follows: "The oil pipeline trade should be carried out not as a satisfaction of the Baku demand, but as a stimulus for our entire oil industry. I stand for it precisely for this reason" [10, 509].

Mendeleyev wrote about Baku oil in several of his works. But, the most important of them is the "Baku Oil Business in 1886" [8]. In more than two hundred pages book, he advocates from beginning to end the idea of building a pipeline along the Baku-Batum route. He also returned to this question in subsequent articles. In this sense, his report to the Oil Excise Tax Commission is interesting, where he compares American and Baku oil. He writes, “The oil produced in America today gives during processing ... lighting oil [which] has a flash usually below 25° C., and the one with a flash above 30° is valued much higher and only a small amount is obtained” [13, 725].

Referring to his research, the author writes “a mixture (I note that every commercial oil product is a mixture) of Baku kerosene with an intermediate oil, which makes up 40 to 50% of our oil, burns in the best ordinary kerosene lamps and represents, if it does not contain gasoline, a flash above 40° (from 50° to 70°), and therefore contains many conditions for rapid and widespread distribution. If such lighting oil enters the markets, it will expand the consumption of oil lighting, since its quality can successfully compete with American kerosene, and will be bought even at prices higher than American kerosene” [13, 725-726].

After the abolition of the ransom system at the Absheron fields, a rapid growth in oil production and its processing began. Now on the agenda was the issue of transporting this oil, and at the suggestion of D.I.Mendeleyev and in its raw form, that is, processing was provided for in other places. This means that artificial barriers were being prepared for the industrial development of Baku, also at the suggestion of the chauvinist D.I.Mendeleyev. In the article “Where to build oil plants” [9, 249-341], he also insists on the transfer of oil refineries to Nizhny Novgorod, in addition to economic considerations, as he notes in this article, also because of the start of a new war with the Ottoman Empire in 1877 [9, 258-259].

One of the important works on the history of oil in the Caucasus is the article by the mining engineer N.A.Sokolovsky “Outline of the development of the Caucasian oil industry over a period of 10 years from 1873 to 1883” [16]. Here the author describes the process of an industrial revolution and the development of oil production after the abolition of the ransom system on the Absheron Peninsula in a 10-year period. He also pays attention to the role of the technical intelligentsia in the industrial revolution.

4.Conclusion

Thus, we briefly considered the issue of the fact that the history of the formation and development of Baku oil, albeit inconsistently, but initially, was paid attention by historians, including by the oil owners themselves, such as V.I.Ragozin, K.I.Lisenko, D.I.Mendeleyev, N.A.Sokolovsky and others, who left behind valuable information on this topic.

5.References

1. Gmelin S.G. Puteshestvie po Rossii dlya izsledovaniya vsekh tryokh tsarstv v prirode (Travel across Russia to explore all three kingdoms in nature), 1785, V, III, 336 p. (in Russian).
2. Gulishambarov S.I. Deyatelnost L.G. Nobelya na Kavkaze (L.E.Nobel's activities in the Caucasus). Tiflis: 1889. 36 p. (in Russian).
3. Gulishambarov S.I. Kratkiy ocherk razvitiya kerosinovogo proizvodstva na Kavkaze. Kratkiy ocherk razvitiya neftyanoy promyshlennosti na Kavkaze (A brief outline of the development of kerosene production in the Caucasus. A brief outline of the development of the oil industry in the Caucasus). Sankt-Peterburg: 1887. 48 p. (in Russian).
4. Gulishambarov S.I. Materialı dlya istorii fotogenovogo proizvodstva (Materials for the history of photogenic production) // Gorny zhurnal. 1880, V. 4. №11-12, p. 327–344 (in Russian).
5. Gulishambarov S.I. Neft, kak toplivo (Oil as fuel) // Gorny zhurnal. 1880, V. 2. №6, p. 251-276. (in Russian).
6. Lerkh I. Puteshestvie s 1733 po 1735 g. iz Moskvy v Astrakhan, a ottuda po stranam, lezhashshim na zapadnom beregu Kaspiyskogo morya (Travel from 1733 to 1735 from Moscow to Astrakhan, and from there to the countries lying on the western coast of the Caspian Sea) // Novıye ezhemesyachnıye sochineniya, k polze i uveseleniyu sluzhashshikh Akademii nauk. Sankt-Peterburg: 1790, fevral, XLIV, p.69-97. (in Russian).
7. Lisenko K.I. Pamyati Ludviga Emmanuilovicha Nobelya (In memory of Ludwig Emmanuilovich Nobel). Sankt-Peterburq: 1889. (in Russian).
8. Mendeleyev D.I. Bakinskoye neftyanoye delo v 1886 g. (Baku oil business in 1886) // Sochineniya v 25 tt. t. 10 (835 p.). Leningrad-Moskva: 1949, p. 595-713 (in Russian).
9. Mendeleyev D.I. Gde stroit neftyanye zavody? (Where to build oil factories?) // Sochineniya v 25 tt. t. 10 (835 p.) Leningrad-Moskva: 1949, p. 249-341. (in Russian).
10. Mendeleyev D.I. Mnenie o Baku-Batumskom nefteprovode (Opinion on the Baku-Batum oil pipeline) // Sochineniya v 25 tt. t. 10. Leningrad-Moskva: 1949, p. 507-511(in Russian).
11. Mendeleyev D.I. Neftyanaya promyshlennost v Severo-Amerikanskom shtate Pensilvaniya i na

Kavkaze (Petroleum industry in the North American state of Pennsylvania and the Caucasus) // T. 10, p. 17-244 (in Russian).

12. Mendeleyev D.I. O neftyanom promysle v Amerike i ob otnoshenii ego k russkomu neftyanomu promyslu na Kavkaze (On the oil field in America and its attitude to the Russian oil field in the Caucasus) // Sochineniya. T. 25. Leningrad-Moskva: Izd-vo Akademii nauk SSSR, 1952, p. 495-513. (805 p.) (in Russian).
13. Mendeleyev D.I. Osvetitelnoye maslo russkoy i amerikanskoy nefti (Dolozheno v Komissii po aktsizu na neft) (Lighting kerosene of Russian and American oil (Reported to the Oil Excise Duty Commission)) // Sochineniya v 25 tt., t. 10 (835 p.). Leningrad-Moskva: 1949, p. 725-729 (725-726). (in Russian).
14. Mendeleyev D.I. Sochineniya (Essays), v. 10, p. 725. (in Russian).
15. Ragozin V.I. Neft i neftyanaya promishlennost. (S prilozheniem izsledovaniya kavkazskoy nefti gg. Markovnikova i Ogloblina). S 7-yu litograficheskimi kartami (Oil and oil industry (With the attachment of the study of Caucasian oil by Mr. Markovnikov and Ogloblin) With 7 lithographic maps). Sankt-Peterburg: 1884, 580 p. (in Russian).
16. Sokolovskiy N.A. Ocherk razvitiya kavkazskoy neftyanoy promıshlennosti za period 10 let s 1873 po 1883 g. (An outline of the development of the Caucasian oil industry over a period of 10 years from 1873 to 1883.) // Vestnik promyshlennosti, 1884, avqust, s. 111-122; sentyabr, p. 90-107 (in Russian).

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EARLY ON SOME FEATURES OF THE OIL BUSINESS EVOLUTION IN AZERBAIJAN IN THE XIX-EARLY XX CENTURIES

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Abstract. It is known that in the XIX-early XX centuries the evolution of oil business in Northern Azerbaijan has come a long way. Until the early XIX century, the oil industry here was purely artisanal, but the Absheron oil fields played a significant role in the income of the khan's treasury. Immediately after the Russian occupation in 1806, the oil fields that came under the control of the new colonial regime were handed over for ransom, the main reason for this was the backward, feudal economic system of the Russian Empire, as well as the complete ignorance of the oil matter by the new owners. However, the reforms carried out after the shameful defeat in the Crimean War (1853-1856) significantly accelerated the socio-economic development of the empire, and the demand for oil increased significantly. As a result, tsarism abolished the ransom system in February 1872, and in December the oil lands were put up for auction in what looked like de facto private property. In a short time, oil Baku became the main link in the imperial fuel complex, the world's "Oil Academy". The rapid development of the oil industry played an important role in many areas of the socio-economic, socio-political and cultural restoration of Northern Azerbaijan.

Keywords: Baku, oil, Romanovs Russia, occupation, evolution, oil boom, "oil academy", fountain, auction.

1.Introduction

In the XIX – early XX centuries, much work was done to study the history of Azerbaijan's oil industry. Although very valuable information about the state of the Baku oil fields and the evolution of the oil business was collected in Russian-language sources and literature of the XIX century, significant scientific research on the history of this field was carried out during the XX century. B.Akhundov, A.Sumbatzade, M.Ismayilov, S.Aliyarli, M.Jafarov, M.Mammadov, Sh.Salimov and many others did a lot in this regard. However, a number of features of the oil business evolution during this period, including the role of the rapid development of the oil industry in socio-economic, socio-political, cultural and ideological evolution, have not yet been sufficiently studied.

2. Experimental part

The rapid economic development brought about by the reforms after the severe defeat in the Crimean War required radical changes in the oil matter, as a result of which in 1872 the oil industry was transferred to a market economy. The oil boom became a serious locomotive of the local economy, gave a powerful impetus to the formation of the national bourgeoisie, and this last social force played an important role in the development of the national intelligentsia and public figures. All of this played an important role in the rapid development of national self-consciousness and the restoration of national statehood in the late XIX – early XX centuries.

3. Results and discussion

As is known, the Azerbaijani oil and oil business have a rich thousand-year history. Even in ancient times, our oil and oil products, known as "Midia oil", were used not only for various domestic and veterinary purposes on the Absheron Peninsula and in other regions of Azerbaijan, but also in various ways it was delivered to neighboring countries, was widely used in everyday life, medicine and veterinary medicine, fuel, building materials and as ointments. The very rich oil fields of Absheron, oil "springs" coming out of these fields, gas "fountains" erupting into the sea and on land, "volcano", "shades" of oil carved in the sands of Shuvelan and others, seem wonderful for their time. His blessings amazed travelers and others who visited our country from time to time. About these wonders of nature, these blessings of God were written and told more than once by those who came to our Motherland from many parts of the world for different purposes, and some even built a temple here - the Surakhan temple. [1, p.547]; [2, p.417; 14].

Despite all this, until the middle of the XIX century, production in the rich Absheron oil fields was purely artisanal and developed very slowly. At the end of the XVIII century and the beginning of the XIX century, the entire South Caucasus, as well as the territory of Azerbaijan, became a battleground between the three empires fighting for dominance here - the Romanovs Russia, the Ottoman Empire and the Gajar Iran. Despite all the efforts of the United Kingdom and France, which understood that the Russian Empire was seeking control over the transit trade routes between Asia and Europe, in the first third of the XIX century, the Romanov Empire defeated the declining Ottoman Empire in four wars, then the emerging Gajar Empire and conquered the Southern Caucasus. As a result of these wars, all the lands of Northern Azerbaijan, from the borders of Georgia and Derbent to Surmali, from Borchaly and Signagh to Lankaran and Astara, from Jar and Balakan to Erivan, Nakhchivan and Karabakh, became a colony of the Romanov Empire.

Even during the first Russian-Gajar war (1804-1813), one of the regions that the Russian invaders really wanted to seize were the Absheron Peninsula and Baku, the capital of the eponymous khanate, surrounded by rich oil fields, with a convenient seaport and a bay. The colonialists even lost the commander-in-chief of the Russian troops in the Caucasus, General of Infantry Pavel Sisianov: in February 1806, Sisianov was killed at the gates of Baku. However, in early October of the same year, the Baku fortress was occupied by the Romanovs and the oil fields fell into the hands of the Russian occupiers [8, p.49].

The invaders, who seized military and political dominance here, were well aware that oil fields and salt lakes were one of the main sources of income for the Baku khan’s treasury. The advantages of oil and many oil products also attracted them strongly. Back in 1723, during the next invasion of the Russian invaders into Azerbaijan, in the summer of the same year, the commander of the Russian army that occupied Baku, General Matyushkin, sent white oil to his Tsar Peter I (1682-1725). “Peter the Mad”, delighted by the bright light of white oil, wrote to Matyushkin: “Send a thousand pounds, not, ten thousand pounds, no, as much as possible”. From the beginning of autumn 1806, the homeland of this miracle was already in the clutches of St. Petersburg. Rich oil wells, salt lakes, multi-colored oil – "nöyüt" and even pure white oil spontaneously flowed to the surface of the earth (we are not mistaken: our fields were so rich that pure white oil was extracted from wells drilled like ordinary water wells). Voskoboinikov, who studied the natural resources of these new colonies under the auspices and consent of the tsarist authorities after the Russian occupation, compiled a detailed description of the natural resources of Absheron, as well as the famous Ilisu baths and the rock salt mines of Nakhchivan. He gave a detailed description of the Absheron oil fields, salt lakes, etc. in an extensive article published in the 1930s in the Journal of the Ministry of Public Education, which enjoyed great prestige in Russian scientific circles at that time. In addition, he spoke about 15 of the operating in Surakhany kerosene wells and devoted much space to a detailed description of these wells [2, p.69]; [10, pp.50-73]. By the way, according to various sources, even in modern offshore oil fields, a certain amount of kerosene was extracted from newly drilled wells.

But the trouble was that in 1806 the invaders who conquered these riches knew nothing about the oil matter, they had no idea how to profit from oil. Therefore, the Russian authorities decided to ensure a stable income for the imperial treasury by immediately renting out Baku oil fields and salt lakes (according to some sources as early as 1806, and according to some as 1808), and leasing these sources of income for a short period (4-5 years). This situation lasted until 1872. During this period, the tsarist colonists, considering the extremely low income, terminated the treaty several times (1826, 1834, 1850). But then took the oil fields under the economic control of the imperial treasury, and each time returned to the ransom system of obligations with remorse [2, p.69].

The medieval ransom system did not only justify the hopes of the Russian authorities for large profits, but also seriously hampered the development of the oil industry as a whole. The fact is that the redeemers, most of whom were Armenian businessmen, were not sure that they could again “win” the use of oil fields at the next limited “auctions”, so they tried to get their investments in obligations to the Treasury and earn as much money as possible ... They did not care about the expansion of oil fields, the introduction of new equipment and technologies that require significant costs to increase production, they did not think about cleaning wells, rebuilding mines, finding new oil fields, or improving working conditions.

Naturally, although oil refining was weak, it gradually expanded, and production gradually increased. Individual businessmen and officials engaged in production, transportation, oil refining, etc. tried to introduce certain innovations in the field, albeit on a very limited scale. For example, according to some sources, technical equipment was brought to Baku from Tiflis in 1847 in order to apply the drilling method. Information about the drilling of such a well by the world’s first drilling method in Baku as early as 1848, 11 years before the United States, found its place in our historiography [2, p.69; 6, p.41].

But on the whole, the economy of the Russian Empire, which was quite backward for its time, based on feudal rules, and the very poor state of the market economy did not create such a large demand for liquid fuel, which could play a major role in sufficiently stimulating the extraction and production of this fuel.

However, the reforms carried out after the infamous defeat in the Crimean War (1853-1856), which shook the empire, accelerated economic development, the growth of industry and railways, as well as the growth of steam maritime transport, increasing the demand for oil and petroleum products almost exponentially. Oil and oil products were becoming one of the main factors of economic development. Since 1859, the oil refineries of Melikov, Kokorev, Gubonin and others began to operate in the mining regions around Baku, and the Witte's paraffin-candle factory in Pirallahi, in the early 1860s, a new well was drilled (but the master driller ordered the well to be buried immediately, believing that the noise from the well was the sound of hell), production growth is gradually accelerating, after the Shemakhi earthquake of 1859, the first features of the future industrial giant began to appear around Baku (in 1859, the population of this city was less than 9000), a small provincial city that became the center of the province [2, p.96].

In 1871, an oil well drilled in the Baku fields was put into operation, and this perfect technical innovation gave a strong impetus to the rapid expansion of drilling and exploration, the commissioning of deeper oil projects, and the rapid growth of production. It should also be noted that the colonial regime, on the other hand, gradually realizing that oil would become the most profitable commodity in international markets, finally, in early 1872, agreed to abandon the ransom system and move to a system in the oil industry that would operate on the basis of free enterprise, an independent private economy, and the rules of a market economy.

However, the Romanovs government, which was primarily concerned with the revenues of the tsarist treasury, first introduced a special excise tax on refineries, or rather "oil reservoirs" on February 1, 1872, and two weeks later canceled this system, and promulgated a law on the sale by auction of the oil-producing lands of Absheron at very low prices (10 rubles per year for tithes) and on a long-term (for thirty or more years) lease (in fact, in private ownership). The oil lands of Absheron were divided into 47 plots of 10 dessiatines each (1 dess. = 1,036 ha) and put up for the first auction in December 1872 [2, pp.218-233; 3, p. 8].

These events, which led to the dominance of the rules of the free market economy in the oil business, in a short period of time paved the way for the oil industry to become the locomotive of the economy of Northern Azerbaijan, the leading industry. It was the oil industry that began to play the role of the nucleus of the formation of the industrial giant of Greater Baku. The rapid development of oil production and refining, the emergence of fabulous oil revenues was accompanied by a number of serious socio-economic characteristics and led to significant results.

First, the expansion of oil production and refining led to the emergence of a number of new industries for the Azerbaijani economy, and the more rapid development of a number of traditional industries. The first narrow gauge railway (as well as pipelines) in Azerbaijan was built between oil fields, mechanical production, production and use of electricity, the newest shipyards and ship repair yards for their time, cooper, production of chemicals used in oil production and refining, the emergence and expansion of banking enterprises (banks, trading houses, credit institutions, mutual funds, etc.), rapid population growth (tens of thousands of unskilled laborers, skilled workers and businessmen from different regions of the Caucasus, the Volga region, South Azerbaijan and others who arrived to earn money rushed to Baku, as a result of which the population in 1897 exceeded 110 thousand people; on the eve of the First World War, there were already more than 240 thousand people in Baku, and about 400 thousand in the Big Baku Industrial Region) and so on, all this was associated with the development of the oil industry.

With the commissioning of the Tiflis-Baku railway in 1883, the Baku oil industry and the economy of Azerbaijan as a whole received a shorter and more accessible route to international markets via the Baku-Tiflis-Batum-Poti-Black Sea line.

Oil transportation led to the expansion of not only railways, but also maritime transport and highways (Millions of dollars in oil revenues prompted the Romanovs government, following the Poti-Tiflis-Baku megaproject, to build a pipeline that would invest in a major transportation project such as the Baku-Batum oil pipeline (1897-1907)). At the same time, with the commissioning of the Port-Petrovsk-Baku railway at the beginning of the XX century, the oil industry has significantly expanded its access to the markets of the North Caucasus and Russia. The production of the tanker "Zoroastr" and other modern ships was directly related to the development of the oil industry.

The emergence and expansion of various food and light industry enterprises in Baku, Ganja, Shemakha, Derbent, Lankaran was also directly and indirectly related to the needs of the oil industry.

Following the metallurgical industry, both foreign and Russian and local capital began to be invested in the oil industry. The fabulous revenues of Baku oil began to attract Nobels, Rothschilds, Vishaus and Benckendorffs from all over the world. The rapid formation and rapid growth of industrial, banking, financial capital, organization of production and trade led to the emergence of new forms of monopolies, monopoly associations, companies, firms, trading houses, monopoly associations such as the Baku White Oil Industrialists, founded in 1893. Production, processing, transportation, sale, etc. - the most advanced forms of economic organization in the late XIX - early XX centuries dominated both the oil and other industries [see: 2, p.15, etc.].

The rapid development of the oil industry also contributed to the formation and development of the national capital of Azerbaijan and its transformation into equal competitors with the most serious representatives of Russian and foreign capital in various sectors. Until the 1970s, national investors, mainly concentrated in trade, light and food industries, joined the oil business from the first oil auctions and soon became representatives of the national capital, such as H.Z.Tagiyev, who organized a multi-million production. It is true that Tagiyev sold his oil company to the British in 1896. However, he and his wife managed to retain their membership on the board of directors, owning a 200,000-ruble stake in the British company Oleum, based at his mines. The proceeds from the sale of 5 million rubles allowed him to create the largest giant of the entire Caucasian textile industry – the Caucasian Cloth Factory. He was able to provide decent wages for a significant part of the population of Baku, employing about 3,000 women, the vast majority of whom were Muslim. The incomes received at the beginning of the XX century by Tagiyev, A.Nagiyev, Sh.Asadullayev, M.Mukhtarov, and others, who were included in the top twenty oil magnates, in turn, played a great role not only in the development of our national economy, but also in the development of the national culture, education of the national intelligentsia and the emergence of Baku architecture. In the second half of the XIX - early XX centuries, the Baku oil industry played an important role in the development of science and culture of Northern Azerbaijan, in the preparation of the national intelligentsia and prominent national political figures.

4.Conclusion

Unfortunately, most of the income from this natural resource, which God gave to our people, went to the treasury of the colonial Russian Empire, to the pockets of foreign businessmen, and the real owners of this wealth did not get a very large share. According to the calculations of some authors, if the revenues from Baku oil remained in Baku, “it would be possible to cover its streets with gold several centimeters thick ...”.

The oil policy developed and implemented by the Great Leader H.A.Aliyev less than thirty years ago and successfully continued by his worthy successor, President I.H.Aliyev, the large-scale achievements of our young republic in all spheres, even in wartime, at the expense of the income received once again shows that the above conclusion is not in vain.

5.References

1.Azerbayjan tarikhi. XIII-XVIII esrler. 7 jildde, III c. (History of Azerbaijan. XIII-XVIII centuries. In 7 volumes. Volume III) – Baku: Elm, 2007 (in Azerbaijani).
2.Azerbayjan tarikhi. XIX esr. 7 jildde. IV cild (History of Azerbaijan. XIX century. In seven volumes. Volume IV) – Baku: 2007 (in Russian).
3.Akty, sobrannye Kavkazskoy Arkheograficheskoy Komissiey (Acts collected by the Caucasian Archaeographic Commission), v.I, dok. 653; v. II, dok.589-590 (in Russian).
4.Akhundov B.Yu. Monopolisticheskiy kapital v dorevolyutsionnoy bakinskoy neftyanoy promıshlennosti (Monopoly capital in the pre-revolutionary Baku oil industry) – Moskva: 1959 (in Russian).
5.Bakinskie izvestiya (Baku news), 1878, №2 (in Russian).
6.Gagemeyster Yu.A. Zakavkazskie ocherki, ch.3 (Transcaucasian essays, part 3) – Sankt-Peterburg: 1845 (in Russian).
7.Dubrovin N. Zakavkaze ot 1803 po 1806 gg. (Transcaucasia from 1803 to 1806) – Sankt-Peterburg: 1866 (in Russian).
8.Ibragimbeyli X.M. Rossiya i Azerbaydzhan v pervoy treti XIX veka (Russia and Azerbaijan in the first third of the XIX century) – Moskva: 1969 (in Russian).
9.Igamberdyev M.A. İran v mezhdunarodnyx otnosheniyakh v pervoy treti XIX v. (Iran in international relations in the first third of the XIX century.) – Samarkand: 1961 (in Russian).
10.Jurnal Ministerstva Narodnogo Prosveheniya (Journal of the Ministry of National Education) 1833, kn.49.
11.Kader S.A. Neft i eyo derzhava (Oil and its power) – Mogilev: 1907 (in Russian).
12. State Historical Archive of the Republic of Georgia, f.12/5, doc 2634.
13.Sadıkhzade S.M. Proniknovenie angliyskogo kapitala v neftyanuyu promıshlennosti Azerbaydzhana (Penetration of British capital into the oil industry of Azerbaijan) – Baku: 1967 (in Russian).
14. unesco.preslib.az/az/page/TNkhIGCDU

PP-VII-16

TRANSPORTATION OF BAKU OIL

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Abstarct. An important factor in the process of turning Baku into a world center of the oil industry was the solution of the issues of transportation of oil cargo.

Among the pressing problems caused by the rapid development of the oil industry and the need to export oil on a large scale to the domestic markets of Russia was the transportation of oil products.

In the interests of reducing the transport costs of its enterprise, the Nobel bro. In 1878 built the first pipeline in Baku with a pumping station for pumping oil. Transportation of oil by rail in tank cars has significantly reduced transportation costs. For this it was necessary to establish business with the long-distance transportation of oil. For oil trading within the country and abroad, the Transcaucasian Railway was built in 1883.

Only with the opening of the Baku-Tiflis railway, which connected the two seas - the Caspian and the Black, it became possible to massively enter the markets of central Russia, as well as the world of products of the Baku oil industry.

Thus, the railway, having provided a cheap route for the export of oil and oil products to the Black Sea ports, and from there to the European markets, encouraged capitalists to expand production.

Consequently, the Baku oil-industrial region had two exits to the oil products sales markets - sea and rail.

Ludwig Nobel was the first in the world to order a vessel made of Bessemer steel.

Sven Almqvist and Ludwig came up with the design of a loading steam passage, divided into compartments to prevent the formation of will in kerosene and oil. The steamer was named “Zoroaster” – in honor of the prophet of the fire-worshipers Zarathustra (Za-Ratushtra).

The merchant fleet of the Caspian Sea, the main item of cargo turnover of which was Baku oil, was an important factor in the economic life of Russia. The bulk of Baku oil was delivered to Russia through the Caspian Sea; she also traveled by sea to the Trans-Caspian region and Iran. By the beginning of the XX century, on average, 80% of oil products were exported from Baku by sea. Speaking about improving the transportation of oil, it is necessary to emphasize the role and importance of the oil tanker fleet for the transportation of oil products along the Caspian Sea and the Volga Mainline. On the Caspian Sea large tankers “Zaroaster”, “Buddha”, “Nordenskjold” built in Sweden by order of the Nobel Brothers Company in 1880.

Keywords: Baku, transportation, oil, br. Nobel, sea, route (navigable), railway

1.Introdaction

An important factor in the process of turning Baku into a world center of the oil industry was the solution of the issues of transportation of oil cargo. Even at the First Congress of Oil Industrialists, it was noted that only through penetration into Europe, the Baku industry, which prevails in the region, becomes not only national, but also transnational. Without export to Europe, it will never be able to become a significant industry.

2. Experimental part

Among the pressing problems caused by the rapid development of the oil industry and the need to export oil on a large scale to the domestic markets of Russia was the transportation of oil products. The possession of vehicles gave enterprises enormous advantages in the trade of oil products. At the beginning of the XX century, there were several large companies in the Baku region that were engaged in oil production, processing and marketing of products in the markets, consumption. The form of organization of production for these companies was the most perfect, since they produced their own product and communicated directly with their consumers.

The struggle for mastering the transportation of oil acquired a particularly acute character. Each large firm tried to concentrate in its hands the greatest possible number of vehicles [12, 26].

In connection with the general development of the oil industry, major successes were also achieved in the transportation of oil and its products. In the interests of reducing the transport costs of its enterprise, the Nobel bro. In 1978 built the first pipeline in Baku with a pumping station for pumping oil. Transportation of oil by rail in tank cars has significantly reduced transportation costs. For this it was necessary to establish business with the long-distance transportation of oil. For oil trading within the country and abroad, the Transcaucasian Railway was built in 1883. In July 1907, a kerosene pipeline was put into operation along this road, which connected Baku with the shores of this road of the Black Sea and its port city of Batumi.

The project of the Caspian Black Sea oil pipeline not only did not receive the support of the oil owners, but from the majority of them provoked resistance.

In general, the Caspian fleet by the beginning of the XX century. accounted for 26% of the total number and 36.4% of the net tonnage of merchant ships in Russia [2, 12].

The Absheron Peninsula is the main place of oil production; in its eastern part it adjoins the Caspian Sea. From here, through the Caspian-Volga route, it was connected by waterways, both with most of European Russia, and with the Transcaucasian region and Iran. On the western side, the peninsula could be connected with the entire central southern Caucasus and the Black Sea, and through the Black Sea with central Russia and abroad. Consequently, the Baku oil-industrial region had two exits to the oil products sales markets - sea and rail. Oil tankers across the Caspian transported oil and oil products to Astrakhan for sales in Russia and abroad only during the six-month navigation. Therefore, during the steel time, refineries in Russia and abroad, which did not have crude oil in reserve, stood idle. At the same time in Baku in 1880-1881. Accumulated such a large amount of crude oil that production was temporarily suspended and oil was even released into the sea. The first crisis of overproduction of oil arose in 1882 and then repeated after 4 years.

Due to the impossibility of export and the lack of a sufficient number of storage tanks, 25,747,520 poods were burnt and released into the sea. oil residues. In the Baku region itself, in the 1980s, the demand for kerosene, the main oil product, was less than 5% of its production. Therefore, the problem of exporting oil products from Baku was of paramount economic importance as a necessary condition for the existence and further development of the oil industry and it was no coincidence that it was in the center of attention of Baku oil industrialists and various government agencies. It was necessary to connect Baku, which made it a major industrial center, which was considered in the world market, by rail with the Black Sea [6, 37].

Back in the 90s of the XIX century G.Z. Tagiyev first proposed a project for the construction of the Shusha-Yevlakh railway. In 1898, he applied to the Administration of the Transcaucasian Railway with a petition to issue him the relevant documents drawn up in 1891. For the construction of the railway lines, the permission of the Senate was necessary. But G.Z. Tagiyev, together with Hasai-khan Usmiyev, provided plots of land belonging to them for construction, for which the permission of the Senate was no longer required. G.Z. Tagiyev's proposal found a positive response in the Ministry of Ways of Communication, but for some unknown reason the project was not implemented at that time.

Thus, the construction of the Transcaucasian railway was primarily due to the needs of the Baku oil industry. Despite the proximity of oil sources to Baku, where refineries were concentrated, the delivery of oil by carts almost doubled the cost of oil itself, reaching 8 and even 9 kopecks per pood at a crude oil price of no more than 4 kopecks. The construction of the “oil section” had its purpose to reduce the cost of delivery of crude oil, to free the breeders from transporting it in expensive wooden dishes and to ensure the non-stop delivery of the raw product to the photogenic factories, the overcrowding of which on a small area occupied by a black city deprived them of any the possibility of arranging extensive tanks for storing large oil reserves [2, 47].

Ludwig Nobel was the first in the world to order a vessel made of Bessemer steel. In November 1877, he approached a contractor who would later supply the Nobel Brothers with many ships built at the Lindholmen shipyard in Norrkoping. This shipyard belonged to the Mutalskiy machine-building plant, headed by Sven Almqvist. Sven Almqvist and Ludwig came up with the design of a loading steam passage, divided into compartments to prevent the formation of will in kerosene and oil. The steamer was named “Zoroaster” – in honor of the prophet of the fire-worshipers Zarathustra (Za-Ratushtra). Eight separate cisterns were installed on Zoroaster, which were removed if it was necessary to reduce the draft in shallow water. In May 1878, Hjalmar Crusell sailed the steamer across the Baltic Sea, then along the Russian river system and delivered it to Baku. Since the Nobel brothers were Swedish subjects, their ship-owning company was formally headed by the Finnish Russian Bilderling.

During 1881-1882 another branch of the Mutal shipyard - Lindholmen shipyard in Gothenburg – supplied the partnership with a total of six vessels, which were named "Moses", “Magomed”, “Brahma”, “Socrates”, “Spinoza” and “Darwin”. The first ocean-going tanker was built in 1886, “Petroleum” – after the death of Ludwig Nobel, the ship was named after him.

Zorastr has attracted the attention of ship owners and competitors. The Mutalsky plant and the Lindholmen shipyard began to receive orders for ships and machines from the Russian government, from the port authorities, from private entrepreneurs in Baku and Odessa. The Nobel Oil Company has placed orders for a tanker with 53 tanks and various equipment for it at the Mutal Machine Building Plant and at the shipyards of Lindholmen, Bergsund and Kokum. Subsequently, the ships for the partnership were built in Obu (the Swedish city of Turku-SG) and at the plant in Kolomna [5, document No. 220, p.704].

Storage in tanks made it possible to have oil reserves, and the demand for it would be constantly satisfied. Reservoirs were filled in the summer months. Warehouses were built along the entire length of the waterways. From the cargo berths of Baku, tankers went to Astrakhan, where the oil was loaded onto barges, and then, with the help of small tugs, the barges were delivered to Tsaritsyn, where large cylindrical tanks stood ready for long-term storage. The tanks were equipped with a double bottom and lightning conductors [5, p.726].

However, let's get back to the transportation of oil cargo. Only with the opening of the Baku-Tiflis railway, which connected the two seas - the Caspian and the Black, it became possible to massively enter the markets of central Russia, as well as the world of products of the Baku oil industry. The outstanding educator-democrat Hasanbay Zardhabi, keenly noticing new trends in the economic life of Azerbaijan, considered the construction of the Baku-Tiflis railway the second most important factor after the oil industry that had a strong impact on the economy of Azerbaijan. By the end of the 90s of the XIX century, the share of the Baku-Tiflis line in the freight traffic of the entire Transcaucasian railway. was 98%. the most intensive work on the line was at the Baku station. Only in 1890 55.2 million poods of cargo were exported from here in the western direction, while from the rest of the stations of the Baku-Tiflis line – 20.86 million poods. [4, p. 351].

Thus, the railway, having provided a cheap route for the export of oil and oil products to the Black Sea ports, and from there to the European markets, encouraged capitalists to expand production. For the period from 1877 to 1882. oil production increased from 1.6 million poods. up to 50 million poods, or 4 times the export of oil and oil products – from 6 million poods. up to 31 million bud., or 5 times. And from 1883 to 1900, there was a colossal increase in both production and export. production increased from 60.4 million poods. up to 603.8 million poods, or 10 times; export of oil and oil products from 34.2 mln. poods. up to 443.1 million poods, or 13 times. By the end of the XIX century. in the total export of oil and oil products, the railroad accounted for 20% of the export. At the same time, this indicates the predominance of the export of oil products by sea. Therefore, the industrial boom in the Baku oil industry has sharply increased the number of shipments through the Baku port. So, the cargo turnover in the Caspian Sea from 1893 to 1901. more than doubled. With the expansion of shipping, the development of commercial ports – Petrovsk, Krasnovodsk, Astrakhan and Baku - proceeded. Bakinsky commercial port in terms of cargo turnover among all commercial ports of Russia at the beginning of the XX century. ranked first. Freight transportation was dominated by the largest oil companies – Partnership “br. Nobel", the Caspian-Black Sea society, G.Z.Tagiyev of his own bulk fleet [11, p.23].

The role of transport in stimulating the oil industry was determined not only by the fact that it accelerated the transportation and sale of oil products, but, starting in 1883, the railway itself became a consumer of oil fuel. Fuel oil, which was previously taken out at oil refineries as waste, is now used as fuel. In the same years, the Caspian sea and Volga river fleets, as well as most of the factory enterprises of the central industrial and middle Volga regions of Russia, entered the ranks of consumers of oil fuel. In such conditions, the profitability of converting crude oil not so much into kerosene as into residues from the distillation of oil into kerosene became obvious to large oil producers. in fuel oil, which, moreover, was not imposed by the tsarist government with an excise tax. Particularly active in the supply of fuel oil to the railways under long-term contracts was the Nobel bro. In 1892, out of the total amount of 110 million poods of oil fuel consumed within the Russian Empire, the share of sea and river shipping accounted for 50% of the factory industry – 28%, railway transport – 22%. The noted, being an incentive in the development of the oil refining industry, has significantly changed the structure of distillation at oil refineries [1, p.42].

The merchant fleet of the Caspian Sea, the main item of cargo turnover of which was Baku oil, was an important factor in the economic life of Russia. The bulk of Baku oil was delivered to Russia through the Caspian Sea; she also traveled by sea to the Trans-Caspian region and Iran. By the beginning of the XX century, on average, 80% of oil products were exported from Baku by sea. Speaking about improving the transportation of oil, it is necessary to emphasize the role and importance of the oil tanker fleet for the transportation of oil products along the Caspian Sea and the Volga Mainline. On the Caspian Sea large tankers “Zaroaster”, “Buddha”, “Nordenskjold” built in Sweden by order of the Nobel Brothers Company in 1880. If in 1881 there were only 11, then in 1884 only the Nobel Brotherhood had a whole flotilla of 69 ships, 12 large sea steamers, 10 smaller ones for the Volga, 8 iron barges.

By the end of the XIX century, the Caspian merchant fleet included 261 steam ships, 527 sailing ships.

Between the Russian Society of Shipping and Trade and Partnership “bro. Nobel” contractual relations existed since 1881, when the first contract was signed, according to which the Partnership “bro. Nobel” rented for 3 years (1892 -1894) ROPIT has all of its oil-loading facilities and, first of all, bulk steamers for the export of oil products of the Black Sea abroad. After the expiration of this contract, it was renewed several times with minor changes. The last time the agreement was extended in 1903 for 3 years, until April 1, 1906 inclusive [9, p.117].

The attempt of the Volga shipowners – oil carriers to organize their union was unsuccessful: "...it was thwarted by less patient steamers, who took at their own risk the delivery of goods to the Nobel Brothers Company at their proposed price, bypassing the union and on terms of more difficult delivery account, etc. .P.". Subsequently, all attempts of small and medium-sized Volga shipowners to unite their oil transportation facilities also encountered strong opposition from the Nobel bro., Which together with Mazut Island held a monopoly position in the domestic trade of oil products in Russia, and ultimately failed completely. Carrying out a significant part of the oil-loading sea and river transportation with the help of its vast fleet, the Nobel Brothers company transferred part of the freights along the Volga mainly to the largest shipowning companies and societies, entering into long-term agreements with them and often participating in them with their own capital. So, in November 1910, the transportation in the navigations of 1911-1912 was handed over to the Eastern Island of Warehouses. 12 million poods of fuel oil [11, p.56].

After cleaning, the oil products were transported to the next link in the "system" – for export by sea. Kerosene was poured into large oak barrels, which were then loaded onto the ship. In the sea, barrels were often broken and their contents spilled into prisons. Can't you pour oil or kerosene directly into the ship's hull? The brothers came up with this idea at the same time. Russian shipowners ridiculed the Nobel proposal "transports oil like grain": if the Americans still don't do this, then the idea is crazy! However, since the 1960s, the Americans have been transporting oil through the Atlantic Ocean and have tried more than one ship design, so the idea of a tanker was a trend of the times. Ludwig once designed ship steam engines, this experience has come in handy now.

Ludwig remained very pleased with the new storehouse in Tsaritsyn.

Arriving in the Caucasus in 1890, Marcus Samuel Jr. immediately realized what benefits the sea transportation of oil to the Far East promises. The scope for activity was incredible! Markus decided to secretly organize the marketing of Rothschild oil at the same time in many eastern ports so that Standard Oil simply did not have time to lower prices and knock out a new competitor. With the help of paternal connections, Marcus Samuel Jr. and his brother launched a large-scale oil trade in the Far East. In August 1892, the first bulk steamer, named after the shell, "Barnyanga", sailed through the Suez Canal. This circumstance greatly annoyed the leaders of Standard Oil, who were denied permission to sail tankers through Suez. Almost all the oil that subsequently went to the East this way belonged to the company of Marcus Samuel Jr., who, together with the Rothschild house, built a whole flock of oil tankers.

The Nobels take over the sale of 800 thousand tons of oil produced by the syndicate, but, as Alfred put it, "lawyers and other squabbers are trying to split the union". The cooperation of the seven firms is going wrong, and the Nobel Brothers Partnership is looking for an agreement with the Rothschild BNITO and the Armenian Mantashev, whose Baku company has noticeably expanded during the crisis years.

The Nobel Partnership came out of the crisis with a profit of three million rubles. The Rothschilds lost 1.2 million. The Americans sensed a weak link in the Rothschild clan – Marcus Samuel's transport flotilla. Standard Oil offered Marcus Samuel to buy the fleet from him on favorable terms, but after long hesitation he declined the offer ... for sentimental reasons. By this time, Marcus Samuel had been elected mayor of London, and he fulfilled his duties with great joy. His company must continue to be British! He decided.

The Russian government stood up for the national oil industry and, among other things, lowered tariffs for the transportation of goods by rail.

"Brothers Nobel partnership" really "stays afloat". 1894 is a record year for earnings, and with Alfred's blessing, shareholders are paid 10%. When the company does not have enough accumulated funds and additional funds are required, Al-Fred helps with this. The partnership, having requested the approval of the treasury, increases the share capital to 20 million rubles. They begin to speculate with Nobel shares, and Alfred, having thrown some of his own into the market, receives a double price for them [11, p. 236].

At first, large firms also entered into the "Agreement of shipowners", although they led an independent line in it. Some works erroneously asserted that such large firms as Nobel Brothers, Mazut Island and others entered into separate agreements with shipowners, which essentially turned X into an appendage of the largest firms. D.M. Efendizade is absolutely right, stating that "the primary task of the" Agreement of shipowners ... "was the release from the burdensome guardianship of the largest monopolistic enterprises ...". This is confirmed by the decision of the constituent assembly of the syndicate that the purpose of the union is to free one from the dependence of "exporters" [4, 16].

The Nobel Brothers Company waged a decisive struggle against the unification of the Caspian ship owners, which threatened to undermine their monopoly position. By the beginning of 1910, "Nob-Mazut" managed to concentrate in its hands 280 ships with a total capacity of 8559 thousand cubic meters. foot. The connection of the Volga Island to the Nobmazut was significantly strengthened. A number of agreements were concluded with individual shipowners prohibiting them from independently transporting oil products.

The Nobels, however, were recognized as the owners of enterprises and assets in Europe and Iran, and in order to be able to dispose of these funds, they established several new firms, including – in 1922 – the Iranian commercial and industrial partnership. His property included three vessels for river transportation of oil, which at that time were under construction in Sweden (the vessels were sold to the company at a price below their cost). The assets of the partnership also include warehouses for products and oil pipelines in Northern Persia.

The ship-owning company founded by the Nobels got the Zoroaster diesel tanker, which was under construction when the revolution broke out at the Swedish shipyard Jotaver-ken. The tanker brought them good profits for several years, but the crisis of the late 1920s led to a decrease in freight prices and losses, so the ship was sold and the company was liquidated [4, p.12].

In the second half of the 80s, large tankers began to be built on the Caspian Sea, for the draft of which the 9-foot roads were no longer deep enough. Then he was transferred to a depth of 12 feet, where the sea is rough, the waves are higher and the constant rolling is more noticeable. The partnership set up a landing stage there, more suitable for both office work and housing. From early spring to late autumn, life boils there, as the sea itself often boils, especially during autumn storms.

This was the tremendous contribution of the Partnership to Russian industry and the state. American competitors, whose goods, despite the toll, continue to penetrate into Russia, since the organization of bulk transportation were not able to fight, step by step gave up their positions and in 1882 brought 532,000 poods of kerosene to Russia for the last time. And it must be said at the same time that as far as the Americans were at first, in relation to oil production and the production of kerosene, teachers of the Russians, they were also the students of these latter in the matter of bulk transportation of kerosene by water. Their first ocean-going tankers were built according to the drawings and calculations of the Nobel Brothers Company, which provided them with the opportunity to get acquainted with the rich material obtained. Needless to say, Russian oil industrialists and shipowners understood their initial delusion and, having a vivid and vivid example before them, one after another acquired bulk steamers on the seas, and iron barges on the Volga for the transportation of kerosene. This was the first broad reform in the court business, the creator of which was Ludwig Emmanuilovich Nobel.

The share of the Nobel Brotherhood remained significant in the Caspian merchant fleet. The Partnership after the Dadashevs took the second place in the ownership of bulk vessels. However, the company still had a monopoly position in the sea transportation of oil, the bulk of which it transported on its own ships. In 1900-1907. sea export of the was expressed in 920165 thousand poods of oil products.

The share of the Nobel Brothers in the total export of oil products by sea from Baku to the Volga ranged from 30 to 45% of the annual export. In February 1907, the company exported 26 million poods of oil residues to Nizhny Novgorod, which was 85% of the total amount of oil delivered for transportation in this area [7, p.41].

At the beginning of XX century, Partnership belonged to the priority in technical improvement in the fleet. In 1903, for the first time in the world "Partnership Nobel Brothers, the Diesel engine was used as a driving force on the Volga ships, which laid the foundation for the transition in the future and in the Caspian from steam to heat.

4.Conclusion

The First World War put an end to the international cartel "Europeishe Petroleum Union" with Russian, German and French capital and an extensive distribution network, including in England. Since Germany and England were at war, and the trust was registered in Germany, in England it was considered an enemy.

5.References

1. Britta Osbrink «Imperiya Nobeley» (Nobels Empire). Moskva: 2005.
2. Veliyev T.T. Iz istorii stroitelstva zheleznıx dorog v Azerbaydzhane v kontse XIX – nachale XX veka (From the history of the construction of railways in Azerbaijan in the late 19th - early 20th centuries) // Izv. AN AzSSR. Seriya ist., filos. i prava, 1984, №2.
3. Gasanbek Zardabi. Izbrannıe stati i pisma (Selected articles and letters). Baku: 1962.

4. Quseynova D.S. Rabochie-moryaki Kaspiya (90-e gody XIX veka – 1907 g.) (Workers-sailors of the Caspian Sea (90s of the 19th century – 1907)). Baku: Izd-vo Elm, 1981.
5. Монополистисhеский капитал нефтуаной промыshленности России, дос.№225 (monopoly capital of the Russian oil industry).
6. Muradalieva E.B. Goroda Severnogo Azerbaydzhana vo II polovine XIX v. (The cities of Northern Azerbaijan in the II half of the 19th century). Baku: 1991.
7. Muradalieva E.B. Krov zemnaya – neft Azerbaydzhana i istoriya (Earthly blood – oil of Azerbaijan and history). Baku: 2005.
8. Obzor bakinskoy neftyanoy promyshlennosti za 1900 g. Ch.I (Overview of the Baku Oil Industry for 1900. Part I). Baku: 1901.
9. Russkiy torgoviy flot. Spisok sudov k 1 yanvarya 1901 g. (Russian merchant fleet. List of ships by January 1, 1901)
10. 30-letie deyatelnosti Tovarishshestva neftyanogo proizvodstva br.Nobel. 1879-1909 (30th anniversary of the Nobel Brothers Oil Production Partnership. 1879-1909). Sankt-Peterburg: 1909.
11. Trudy I syezda neftepromıshlennikov v gorode Baku (Proceedings of the I Congress of Oil Workers in Baku). Baku: 1885.
12. Efendi-zade D.M. Formirovanie monopolisticheskogo kapitala v torgovom sudoxodstve na Kaspiyskom more (Formation of monopoly capital in merchant shipping in the Caspian Sea). Moscow, 1967, p. 203.

PP-VII-17

ON THE HISTORY OF THE COUNCIL OF THE CONGRESS OF BAKU OIL INDUSTRIALISTS

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Abstract: The paper describes the socio-economic conditions that led to the formation of the Council of the Congress of Baku Oil Industrislists in the last quarter of the 19th century, and reflects the specific features of its activities in the first years of the organization of the Congress. With the establishment of this organization, the management of the administrative and economic sphere of the mining and plant region was transferred to the Congress of Baku Oil Industrialists. It is clear from the general content of the article that in the first years of its activity, all small, medium and large companies had the same rights and privileges, as the census system was not yet applied at the congresses.

Key words: oil industry, ransom system, excise tax, congress

1.Introduction

The historical period of Northern Azerbaijan, covering the second half of the 19th century, was characterized by the introduction of a new administrative-territorial system based on provincial and district governance, the implementation of a number of bourgeois and peasant reforms, the emergence of capitalist relations in the economy – a difficult and confusing period, characterized by the introduction of the oil industry at a high stage of capitalist development. It was during this period that the penetration of foreign capital into the Baku oil region led to the establishment of a number of oil industry companies. At that time, the military backwardness of tsarist Russia from a number of European countries allowed oil entrepreneurs working in the Russian Empire to freely build their business. In this context, the main task of the Congress of Baku Oil Industrialists, founded in 1884, was to submit petitions of oil entrepreneurs to state bodies to reach appropriate decisions on issues related to the oil industry. During this period, large companies operating in the oil industry, which were more productive in the production and sale of oil than small and medium-sized companies represented at the Baku Congress of Oil Industrialists, concentrated almost all the benefits in their hands.

2. Experimental part

With the establishment of the Baku Congress of Oil Industrialists, the relations of the oil industrialists represented in this organization with the government bodies were established, the essence of which included the features of the tsarist government's oil policy in Northern Azerbaijan. The emergence of a sectoral business organization that regulated the relationship between the oil industrialists and government agencies played a major role in raising petitions to government agencies on various issues in the oil industry. In the first years of the Congress, all small, medium and large companies had equal rights, as the census system had not yet been introduced.

3. Results and discussion

In the second half of the 19th century, the existence of a ransom system in the Greater Baku industrial district, and the persistence of primitive equipment in the extraction and transportation of oil, slowed down the development of the oil industry. Since new oil fields were not sufficiently discovered, there was no increase in oil production. Due to the non-abolition of the ransom system, new oil lands were not explored, and oil production was limited to the territory of oil fields leased by the redeemers [1, p. 14]. In 1864, the abandonment of the forced labor of serfs in the oil industry of Northern Azerbaijan and the implementation in 1872 of measures to abolish the ransom system eliminated the factors that hindered the development of the Baku oil industry. If the first of these measures created conditions for the use of cheap labor in the oil industry, the second led to the unhindered flow of large capitalist flows into the oil industry [1, p. 14]. The introduction of hired workers in the oil fields stimulated the capitalist development of the oil industry [2, p. 163]. The growing demand for kerosene in the inner provinces of Russia was also one of the main factors behind the increase in oil production. Due to the lack of long transport routes from Baku to the inner provinces of Russia, it was impossible to transport all the oil produced there. Russian industrialists met their fuel needs mainly from American oil. This situation hampered the rapid development of the oil industry [2, p. 163].

Already in the early 70s of the 19th century, primitive oil wells were liquidated in the Baku oil industry, manual oil extraction was stopped and wells appeared. However, the method of transporting oil from the place of production to the territory of the refinery was still carried out using carts in barrels or leather bags. The delivery of oil by such an ordinary method cost from 6 kopecks to 9 kopecks per pood. Such a high cost of oil production led to its use in an imperfect way. Very low quality kerosene produced as a result of oil refining does not exceed 30% of production, and the remaining product was burned as unnecessary waste. Kerosene obtained by this method was exported to Astrakhan in barrels on sailing ships [3, p. 345]

Thanks to the initiative of L.E.Nobel, a representative of foreign capital operating in Baku, the carts were replaced with steam lines made of metal pipes in the method of oil transportation. In return, the price of oil transported from the oil fields to the refinery fell from 6-9 kopecks to 1 kopeck per pood. Later, sailing ships with barrels were replaced by water steamers. At that time, even America did not have such equipment. Qualitative changes in the oil industry led to the production of lubricants in Baku. Although the Russian engineer-technologist V.I.Ragozin produced lubricating oil long ago, his sphere of activity covered the territories outside the Baku oil region [3, p. 346]. With the production of lubricating oil, oil residues began to be used as fuel. Tanks were built to improve methods of extraction, processing and transportation of oil, and the Nobel brothers introduced tanker wagons on the Gryaze-Tsaritsyn railway [3, p. 346].

The laws of February 1 and 17, 1872, which represented the interests of the tsarist government, were among the factors that led to the abolition of the ransom system. The entry into force of these laws has led to the sale of oil lands and oil fields to private individuals, which led to a significant increase in revenues to the state treasury. Although the excise on kerosene slowed down the development of the oil industry, it opened wide opportunities for the rapid development of various sectors of the oil industry [4, p. 88].

The entry of national capital into the sphere of production was particularly characteristic in the socio-economic development of Northern Azerbaijan in the second half of the 19th century. There were four main groups of capital in the oil industry - industrial capital, commercial capital, foreign capital, as well as capital groups organized by the military and representatives of the tsarist government. The trade capital included entrepreneurs of national enterprises H.Z.Tagiyev, Sh.Asadullayev, M.Nagiyev and others. Initially, they preferred to open enterprises as trading houses, but after the adoption of certain laws, they began to establish joint-stock companies with representatives of industrial capital and foreign capital groups [5, p. 92].

The availability of rich fields, cheap land and labor made it possible to work without large investments in production. Such conditions led to the creation of a large number of small companies, which was one of the main features of the early development of the oil industry. These companies were created by local business owners. In the early 70s of the XIX century, small entrepreneurs held 88% of boreholes and paid 94,5% of the total cost of oil fields [1, p. 18].

The initial stage of development of capitalist production in Baku was based, one might say, on Russian capital as a whole. Russian entrepreneurs accounted for 50% of the total amount paid for the oil fields at auctions held after the abolition of the ransom system. As a result of these auctions, 40% of all oil wells fell into the hands of Russian capitalists. The participation of the local bourgeoisie of Azerbaijan in the development of the Baku oil industry was very limited. With the exception of large oil entrepreneurs such as Sh.Asadullayev, M.Nagiyev, H.Z.Tagiyev, M.Mukhtarov most of the local wealthy spent less money and invested in highly profitable industries [6, p. 27].

The company “Nobel brothers” played an important role in the transportation of oil and oil products necessary for the development of the Baku oil industry. In order to reduce transportation costs, in 1878, for the first time in Baku, was built a pipeline with a pumping station for pumping oil. This pipeline connected the Balakhani oil field to the Nobel Brothers’ refinery in Black City at a distance of 9 versts. The implementation of this measure was very important and gave impetus to the construction of oil pipelines in Sabunchu, Ramana and other regions. Already in 1882, 6 oil pipelines operated in the Baku oil region [1, p. 21]. In 1879, the Nobel Brothers became a joint-stock company and established the Nobel Brothers’ Oil Production Association [1, p. 21].

Representing the French capital, the Rothschild company managed to launch 135 small and medium enterprises in a short period of time. Rothschild carried out all his business activities through the “Caspian-Black Sea Oil Industry and Trade Society”. The largest oil transportation and oil trading company of this company was “Mazut” society [7, p. 83]. Although the activities of French capital consisted mainly of trade and credit operations, many oil sources in Balakhani, Sabunchu, Ramana, Surakhani, Bibi-Heybat, as well as most of the oil and refineries in Keshla, belonged to the Rothschild. In addition, he had oil depots in the main points of Russia, merchant ships for the transportation of oil products in the port of Batumi [7, p. 83].

After the abolition of the ransom system, the oil industry, which fell into the hands of large capitalists, opened up a wide path of development, and oil production began to increase from year to year. If in 1872 1,4 million poods of oil was produced in the Baku oil region, in 1875 this figure rose to 5,4 million poods and in 1885 to 115 million poods [1, p. 22]. From 1870 to 1880, oil production increased 10 times, and the production of white oil, the main product of the processing industry, increased more than 8 times. The complete ousting of American white oil from the Russian market was the result of the success of the Baku oil industry. If in 1877, American oil consumption in Russia was 26,5%, in 1880 this figure dropped to 12%, and in 1885 its supply was stopped once and for all [1, p. 22]. If in 1873 there were 680 workers engaged in oil extraction in Baku oil filds, in 1883 their number increased to 1254 [1, p. 22].

Almost simultaneously with the construction of the first oil pipeline in Baku, the construction of the Baku-Balakhani railway was launched to connect oil sources with plants, and in 1879 this railway line was put into operation. Already in 1880, the Surakhani plants were connected to the Balakhani-Sabunchu oil sources by a railway line at a distance of 19 km. One of the important measures ahead was the regulation of long-distance transportation of oil and oil products in the Baku industrial region. Completion of the South Caucasus railway construction in 1883 opened wide opportunities for the sale of oil inside and outside the country [1, pp. 22-23].

According to the law of February 1, 1872, the excise tax on kerosene production slowed down the development of the oil industry. This rule applied the tax collected from white oil production to the benefit of the state. After the introduction of the tax, the construction of oil refineries depended entirely on the consent of the excise office. In essence, the excise tax, although was a small amount for the owners of kerosene plants, significantly slowed down the technical development of the oil industry [2, p. 205]. After the abolition of the ransom system in 1872, a tax of about 25 kopecks was levied on each pood of kerosene. The introduction of the excise tax began to negatively affect the production of petroleum products. The plant owners tried to produce more kerosene during the day, which had a negative impact on the quality of the product and meeting the needs of consumers. In the Russian markets, buyers increasingly preferred American kerosene. The sharp decline in the price of kerosene in Baku led to the bankruptcy of many enterprises, especially small ones [1, p. 23].

In order to eliminate the above-mentioned shortcomings occurring in the oil industry, at the suggestion of the Baku Governor Staroselsky, a commission was established under the chairmanship of the oil industry entrepreneur Benkendorf, which proposed to abolish the excise tax and impose a duty on imported petroleum products from abroad in the amount of 20 kopecks for each pood [8, appendix, p. 103]. This tax system, introduced by the Minister of Finance to increase state treasury revenues without taking into account the interests of oil industry entrepreneurs and consumers, slowed down the development of the oil industry. From the collection of taxes, the state received only 1.145.952 rubles of income, which could not guarantee the rapid development of the oil industry. According to this, on September 1, 1877, the tsarist government was forced to completely abolish the excise tax [1, pp. 23-24].

Implementation of this measure led to a softening of the conditions of bureaucratic administrative regulation. During the 80s of XIX century, the amount of white oil, gasoline and oil products produced by the plants of Baku industrial district rose from 8 million poods to 68 million poods, the fuel balance of the country changed dramatically. In the 80s, the Caspian and Volga shipping, part of the railway transport began to use fuel oil as fuel [2, p. 206]. The abolition of the excise tax also led to an increase in the production of kerosene. If in 1873 white oil export to Russia amounted to 823.800 poods, in 1876 this figure rose to 4.594.766 poods, and a year after the abolition of excise taxes, i.e in 1878 to 6.255.911 poods [8, appendix, p. 104]. In the early 80s, the operation of the oil-producing fleet for the transportation of oil products across the Caspian Sea and the Volga River played an important role in improving oil transportation. “Zoroaster”, “Buddha”, “Nordenshild” and other large-capacity vessels, built in Sweden at the request of the Nobel Brothers and first launched in the Caspian Sea in 1880, accelerated the oil transportation. The number of ships continued to grow in the following years. If in 1881 their number was 11, already in 1884 only the Nobel Brothers had a whole fleet of 69 ships [6, p. 21].

Despite the development observed in the Baku oil industry, the existing difficulties in the transportation of oil remained. The lack of vehicles to transport oil across the Black Sea made it difficult to transport Baku kerosene, which was used in many cities in Europe and Asia. However, oil and petroleum products were transported to Russian cities, as well as to Astrakhan on oil tankers across the Caspian Sea for sale abroad. However, this process did not fully meet the existing demand, as it took place only during the 6-month navigation season (the period when the ships were on voyage - P.Kh.). As a result, oil refineries operating in Russia and abroad did not work whole winter season, starting from the end of autumn due to the lack of sufficient crude oil reserves [1, pp. 24-25]. Irregular supply of oil to oil refineries led to the fact that these enterprises were out of work. There were also serious losses in oil production. Due to the lack of conditions for the export of oil and oil products, oil producers, as well as owners of oil refineries, were forced to dump oil residues into the sea and burn them, which was one of the reasons for the crisis in the early 80s of the XIX century [5, p. 39].

As mentioned above, the completion of the South Caucasus Railway in 1883, which connected Baku-Tiflis and then the Batum-Black Sea port via Poti, was the starting point in the process of selling oil scraps in Baku for 5-7 years. In 1884 alone, more than 5 and a half million poods of various petroleum products were exported from Baku along the South Caucasian railway in tanks and barrels [5, p. 40]. Due to the high demand for oil, oil production in Baku began to grow rapidly. If in 1876 Baku produced 8 million poods of oil, in 1885 this figure rose to 93 million poods [9, p. 71].

Thus, the introduction of new equipment in the production, processing and transportation of oil led to the rapid development of the oil industry. Baku oil was the main export source of oil and oil products transported outside Russia. The launch of foreign capital in Baku, along with local oil industry entrepreneurs, signaled an increase in competition for oil production in the near future. This factor would lead to the formation of groupings among oil industry entrepreneurs in terms of oil production, refining and transportation. [1, p. 25].

Due to the entry of the oil industry into the stage of capitalist development, small, medium and large companies began to appear one after another in the Baku oil region. There was a need to establish an organization headed by entrepreneurs to submit petitions to the relevant administrative bodies on various issues related to the oil industry. The activity of this organization was to serve the interests of the upper circles of the oil industry bourgeoisie. [1, p. 26].

Back in 1883, when the Minister of State Property MN Ostrovsky visited Baku to get acquainted with the oil business, he approved the proposal to convene periodic congresses of oil workers. The main task of the convened congresses was to regulate the principles of mediation between oil industry entrepreneurs and government agencies. The congresses gave oil industry entrepreneurs the opportunity to petition government agencies on any issue related to the oil industry. At the same time, government agencies could communicate with entrepreneurs in the oil industry through congresses and had the authority to submit for initial discussion various projects related to the oil industry [10, p. 59-60].

In accordance with a letter of the Minister of State Property dated January 7, 1884, the Committee of Ministers ordered the convening of congresses of oil industry workers with the participation of local mining entrepreneurs, representatives of the Railway Administration and shipping companies involved in oil transportation. The Council of Congress of Baku Oil Industrialists had to reach an agreement with the chief of the Caucasian civilian unit before the next congress was convened and submit a petition to the Minister of State Property. Accordingly, the Minister of State Property determined the time and place of the congress. At the same time, the chairman of the congress was appointed by the Minister of State Property. “Regulations” of the Committee of Ministers on the convocation of congresses of oil industrialists was approved by the tsar on February 3, 1884 [1, p. 26].

Thus, in accordance with the approval of the “Regulations” by the tsar, in 1884, a branch business organization – the Congress of Baku Oil Industrialists was established, and in the same year the first congress of this organization was held. The processes taking place at this congress showed that the oil industrialists were mainly trying to discuss issues related to the oil business. This was due, on the one hand, to the fact that the entrepreneurs of the oil industry pursued their own material interests, and, on the other hand, to the fact that the congress organization did not pay much attention to the administrative and economic sphere due to lack of funds [1, p. 27].

The representatives of the oil industry at the first Congress of Baku Oil Industrialists held in October-November 1884 were 25 mining entrepreneurs, 46 factory owners and 28 owners of both mines and factories. At this congress, a general fund of oil industrialists was established and a congress council consisting of 4 people was created under the name of “permanent executive commission” [11, p. 1]. At the second Congress of Baku Oil Industrialists held in March-April 1885, the project “Congress Council, rules of rights and responsibilities of its officials” was adopted. According to these rules, the composition of the Council of the Congress was elected at each subsequent congress of oil industrialists. The number of officials on this council was determined by the decision of each subsequent congress. The responsibilities of the Congress Council included reviewing the budget expenditure and revenue reports received by its Bureau, drawing up a special protocol, overseeing the proper spending of budget expenditures, drafting an action plan for the forthcoming Congress, and other similar powers [12, p. 62].

The “Regulations of the Congresses of Oil Industrialists", developed at the III Congress of Baku Oil Industrialists in March-April 1886 and approved by the Minister of State Property M.N.Ostrovsky on March 18, 1887, remained in force throughout the entire existence of the congress organization. The “Regulations” included the purpose of the Congress, the rules of its activity, the rights and responsibilities of persons operating within the organization, meeting time, place of holding and so on. According to the “Regulations”, the main purpose of the Congress was to periodically publish statistics on the oil industry, monitor administrative and economic activities, and submit petitions to government agencies on all issues necessary for the development of the oil industry and etc. The congresses were held regularly – almost every year. If there was a need to discuss urgent issues, then emergency congresses were convened. All issues discussed at the congresses were resolved by voting, and if an equal number of votes were collected, the decision made by the chairman of the congress was decisive [1, p. 28]. In accordance with the “Regulations” of the Council of the Congress of Baku Oil Industrialists, oil industry entrepreneurs who needed to discuss any issue at the congresses together with a statement submitted an explanatory note to the Council of the Congress. If the explanatory note was signed by at least 5 oil industrialists, then this issue was included by the Council of the Congress in the action program of the next congress [1, p. 28].

The Congress of Baku Oil Industrialists reflected in its activities the interests of a wide range of oil industrialists during the first 4-5 years after its foundation. Since the first and second congresses of 1884-1885 did not yet impose a censorship restriction, small and medium-sized oil industrialists, along with large oil industrialists, had equal rights in the process of discussing and resolving all issues. Also, the majority of the members of the Railway Commission and the Council of the Congress elected at the II Congress were the representatives of these companies [1, p. 47].

4.Conclusion

Thus, it becomes known that with the entry of the oil industry in Northern Azerbaijan into the stage of capitalist development, the flow of foreign companies to the Baku oil industry, the transfer of oil land to private entrepreneurs, the introduction of technical improvements in the transportation of oil, factors such as the widespread use of labor in various branches of the oil industry led to the fact that many oil industry companies functioned in Baku and it became necessary to establish the Congress of Baku Oil Industrialists organization to regulate their relations with government circles. After the establishment of this organization, it voluntarily took over the management of the administrative and economic sphere of the mining and processing region and carried out many socio-economic activities on its own, without the support of the government.

5.References

1.Khalilov P.R. Baku Neft sanayechileri Gurultayinyn faaliyyeti tarikhinden (XIX esrin sonu – XX esrin evvelleri) (From the history of the Baku Congress of Oil Workers (late 19th – early 20th centuries)). Baku: “Turkhan” NPB, 2018, 212 p. (in Azerbaijani)
2.Azerbayjan tarikhi. Yeddi jildde. IV jild (XIX esr) (History of Azerbaijan. In seven volumes. Volume IV (19th century)). Baku: Elm, 2000, 508 p. (in Azerbaijani)
3.Inostrannye kapitalı v neftyanom dele (Foreign capital in the oil business) // «Neftyanoe delo», 1899, 15 aprelya, №7, p. 344-349. (in Russian)
4.Ismayilov M.A., Ibrahimov M.J. Azerbayjan neft sanayesinin ingilabagederki tarikhi (Pre-revolutionary history of Azerbaijan's oil industry). Baku: Elm, 1991, 284 s. (in Azerbaijani)
5.Muradverdiev A.Sh. Azerbaydjanskaya neft i kapital (Azerbaijan oil and capital). Moskva: İzvestiya, 2001, 567 p. (in Russian)
6.Akhundov B.Yu. Monopolisticheskiy kapital v dorevolyutsionnoy Bakinskoy neftyanoy promıshlennosti (Monopoly capital in the pre-revolutionary Baku oil industry). Moskva: İzdatelstvo Sotsialno-Ekonomicheskoy Literatury, 1959, 296 p. (in Russian)
7.Akhundov B.Yu. K voprosu ob inostrannom kapitale v dorevolyutsionnoy Bakinskoy neftyanoy promıshlennosti (On the issue of foreign capital in the pre-revolutionary Baku oil industry) // Azerbayjan SSR Elmler Akademiyasynyn Khaberleri. № 4, aprel, 1953. Baku: Azerbayjan SSR EA Neshriyyaty, p. 77-99. (in Russian)
8.Trudy dvenadtsatogo ocherednogo syezda neftepromyshlennikov v g. Baku (s 21 aprelya po 5 maya 1898 g.) (Proceedings of the 12th Ordinary Congress of Oil Industrialists in Baku (from April 21 to May 5, 1898)). Baku: Tipografiya «Aror», 1898, 178 p. (in Russian)
9.Monopolisticheskiy kapital v neftyanoy promıshlennosti Rossii (1883-1914). Dokumenty i materialy (Monopoly capital in the oil industry in Russia (1883-1914). Documents and materials). Moskva-Leningrad: İzdatelstvo Akademii Nauk SSSR, 1961, 796 p. (in Russian)
10.Gulishambarov S.I. Obzor fabrik i zavodov Bakinskoy gubernii (Overview of factories and plants in Baku province). Tiflis: Tipografiya kantselyarii Glavnonachalstvuyushego grazhdanskoyu chastyu na Kavkaze, 1890, 278 p. (in Russian)
11.«Neftyanoe delo» (Journal "Oil business"), 1909, 31 oktyabrya, № 20. (in Russian)
12.Trudy vtorogo syezda neftepromyshlennikov v gor. Baku (s 15-go marta po 9-e aprelya 1885 goda) (Materials of the II Congress of Oil Workers in Baku (from March 15 to April 9, 1885)). Otdel I i II. Tiflis: Tipografiya Ya.I. Libermana, 1887, 180 p. (in Russian)

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THE INFLUENCE OF THE BAKU OIL INDUSTRY REGION ON THE DEVELOPMENT OF THE TRANSPORT SYSTEM IN THE CASPIAN REGION IN THE LAST THIRD OF THE XIX - FIRST DECADE OF THE XX CENTURIES.

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Abstract. The article analyses the process of development of the Baku oil industry, which had a significant impact on the development of sea and railway transport in the Caspian region. Owing to the growth and development of these modes of transport, Baku oil is transported both to the domestic markets of Russia and to foreign markets.

Keywords: the Caspian region, the Transcaucasian region, the Caspian Sea, North Azebaijan, kerosene, partnership "br. Nobel," petroleum products, capitalist relations, oil companies, joint-stock companies, trade and transport fleet, railway.

1.Introduction

The great economic, financial and military importance of oil determines its role in the world politics and explains interest in various problems related to the history of the oil industry. Russia's oil industry was one of the most monopolized sectors of the Russian economy. The oil industry was developed mainly in one of the provinces of the Transcaucasian region - in the Baku province.

The economic ties of the Baku province with Russia were carried out: along the Transcaucasian railway, along the Vladikavkaz railway, along the Caspian Sea, through Astrakhan and Baku, along the Black Sea, through Batum and Poti. Oil balanced import and export, in that period of time the oil industry was a large consumer of Russian semi-finished products.

The main part

In the 90s of the XIX century two companies were engaged in the export of oil products from Russia to Europe: Br. Nobel and the Caspian-Black Sea Society of the Rothschilds [1, p.121]. The oil business required a powerful fleet in the Caspian Sea. The latter was equally exterritorial, albeit to a lesser extent. Thus, in the South Caucasus an industrial oasis was created, firmly soldered with Russia by common economic interests. All this makes Baku stand out in the form of a special "field of exterritorial industry in the Transcaucasian Territory." Such a methodological technique allows a more meaningful approach to the study of the national economic life of the region. Highlighting the Baku region, taking into consideration its industrial life completely separately, you can more correctly understand the essence of the economy of the South Caucasus as an agrarian country in advantage. In connection with the development of the oil industry, Baku is becoming the centre of large sea transport.

In 1877 up to 4 1/2 million poods of photogen were exported from the Baku oil industry region. By the end of the XIX century the export of petroleum products from Baku to foreign markets amounted to 31.3 million poods, and the export to Russia amounted to 85.9 million poods. The growth of oil fuel consumption in Russia is also visible from the export of oil residues to Astrakhan - this is the most important distribution point through which all national economic consumers of liquid fuel were supplied. On average, annually in 1889-1893 94.2 million poods were exported here, in 1894-1898 - 180,2 million poods. Wherein, oil consumption by factories and plants by this time ranged from 200 to 500 thousand poods in 7 provinces of Russia; from 500 thousand up to 1 million poods - in 8 provinces; from 1 to 5 million. poods - in 11 provinces; from 5 to 10 million poods - in 3 provinces; in the Vladimir province - 13,2 million poods; in the Moscow province - 30.3 million poods [2, p. 90]. The transportation of kerosene in 1890 was occupied by 20 steam ships with a total capacity of 764,891 poods, and 3 sailing vessels with a total capacity of 82,224 poods, and the total number is 23 vessels with a capacity of 847,115 poods of kerosene.

In 1899 through the efforts of the partnership "Br. Nobel" an association of Baku shipowners, engaged in the transportation of oil through the Caspian Sea, was created. This agreement was based on a single freight rate for all owners of bulk ships. However, the Partnership failed to achieve a limit on the number of transportation, which was the main task in creating this union. Therefore, the partnership "Br. Nobel "did not take any steps to extend this association to the next navigation. In 1900 672.4 tons of solar oils, that were not subject to excise, were exported, 567.4 tons of which were exported inside the Empire (through Astrakhan - 547,4 tons, by the Caspian Sea through Petrovsk - 1,8 tons, and along the Baku - Petrovsk Railway - 19,2 tons) for adding to vegetable oils and further processing into vaseline, perfume and other oils; the rest part (55,5 tons) was sent to the Trans-Caspian region (3 tons) and spent within the Transcaucasian Territory mainly on fuel; 49,0 tons were exported to Batum. [3, p.56].

According to the markets, the export of lubricating oils itself was distributed as follows: to Batum - 9.295,8 tons, to Persia - 43 tons and to the Empire - 3.617,1 tons, and namely: through Astrakhan - 2.594,0 tons (engine oil - 2.093,1 tons, spindle 377 tons and cylinder - 123,0 tons). Although the number of steam vessels is significantly less than the number of sailing vessels and the total capacity of the first vessels exceeds the capacity of the latter by 37.8%, nevertheless, the bulk of petroleum products was exported by steam vessels and the value of the sailing fleet decreases from year to year. In 1900 out of 351.694,3 tons of liquid oil cargo, 332.095,3 tons are sent by bulk, or 94,4% falls on steam ships and only 19,599 tons, or 5,3% - on sailing ships.

The number of transportation made by the fastest schooners to the 12-foot raid reached 60. Freight for transportation by sea throughout 1900 year was very low, due to increased competition between shipowners and excess of supply.

Almost 80% of all petroleum products were exported from Baku through the Caspian Sea, which led to the dependence of oil producers on shipowners. This predetermined the creation of their own filling fleet by the largest oil companies. The pioneer in this area was the partnership of oil production "Br. Nobel "and the Caspian-Black Sea Society of the Rothschilds. On the ships of these two companies 37.1% of all oil cargo with fluctuations 33.4 - 42.1% per year with an upward trend were exported from Baku in 1900-1909 years [4, p. 24].

Other oil producers were also engaged in the transportation of their own oil. Shipowners, who exported their own oil, were called "exporters" in their circle. Possessing one fourth of the total tonnage of the entire Caspian steam merchant fleet, "exporters" transported more than 60% of all oil products from the Baku oil region on their ships [5, p.105]. Speaking about oil transportation, we cannot help noting the peculiar relations that developed between the "exporters" and the so-called "clean" shipowners. The "exporters" were interested in the presence of medium and small bulk shipping enterprises, the vessels of which could be used in case of increased demand for oil products. The "exporters" had to resort to the services of "clean" shipowners quite often. So, in the first decade of the 1900s. the partnership "Br. Nobel" exported 60,3% of all its petroleum products on foreign ships (with fluctuations: 47,5% - 70,1% per year downward) [6, p. 516]. Trying to subjugate the Caspian bulk fleet, the Partnership tried to create an organization of small and medium shipowners, whose services it used.

In 1904 "the Union of Bulk Ships" appeared. It included almost all owners of bulk vessels of the Caspian Sea, except "Mazut", ESTS and some "exporters." For members of the association the partnership "Br. Nobel" raised freight rates somewhat. But an indispensable condition for joining "the Union of Bulk Ships" was the deprivation of counterparties of independent freight transactions. Thus, the partnership "Br. Nobel" took on the functions of the distribution body of a monopolistic association. In 1904 79.1 million poods were exported through the Batumi port, accounting for 70,6% of the total export. In the same year 21,2% with an absolute figure of 21,2 million poods were exported through the port of Novorossiysk. In the following years the participation of the Novorossiysk port in the export of petroleum products decreased until 1911, when it was again restored to almost the same size, in which it remains in 1913.

The Astrakhan market received all petroleum products 246.739.9 poods from Baku along the Caspian Sea in 1906, in 1907 - 284.478 poods [7, p. 87]. Export of goods from the Baku port (in poods): 1910 - 13.918.211; 1911 - 16.498.625; 1912 - 16.736.664. Import of goods into the Baku port: 1910 - 36.716.236; 1911 - 41.582.424; 1912 - 43.007.103. [8, p.76].

The export of goods from the Baku port is increasing every year. Accordingly, with trade activities, the revenues brought by the Batumi port were also significant, in which the growth of customs revenues, which increased from 1.165 thousand rubles in 1908 to 1.336 million rubles in 1911, is noteworthy [9, p. 6].

Export of petroleum products abroad through the Batumi port with 3 million poods in 1883, having risen within 20 years up to 79 million poods in 1904, in the next 1905 year found a sharp drop, having fallen to 37 million poods. In the 1900s (the period of maximum export of petroleum products) Russia's participation in world oil production was expressed in 51 - 52% of the whole production, while the main competitor - the North American States occupied only 39 - 48%. The Astrakhan market received all oil products 2.467.399 poods from Baku in 1906, including oil and its residues 205,3 million poods; in 1907 - 2.844.788 poods, including oil and its residues 232,5 million poods.

In 1912 a cargo of 7.500 arrived at the Baku port [11, p. 71]. The composition of petroleum products exported from Baku to the internal provinces of Russia also changed: along with kerosene, which occupied the main place among them, gasoline, lubricating oils and etc were exported. At this latter level with minor fluctuations, the export of oil and its products lasted until 1913. In 1913 export-import transportation on the Caspian Sea amounted to 224 thousand tons in general. Cabotage transportation accounted for 5349 thousand tons (51.9%) [12, p. 28].

The organizers of the trust immediately faced the acute problem of providing a new association with transport. The enterprises, included in the RMPC, were mainly oil-based and did not have the necessary vehicles and storage facilities. Therefore, it was decided to include in the ESTS trust, which was not bound by any obligations with the main rivals of the RMPC - the partnership "Br. Nobel" and the "Shell" group [13, p. 546]. The Navy of the Russian Empire after the outbreak of World War I began to use oil and oil products much more.

So, if in 1913 the Caspian flotilla received 250 thousand poods, in 1916 the fleet received 18 million poods of fuel oil and about 0,8 million poods of various petroleum products. From May 1916 to May 1917, the Russian Navy received more than 20 million poods of various oil fuel. It should be noted that almost all deliveries of gasoline, kerosene, solar oils, motor fuel and fuel oil to the Russian Navy were carried out under contracts with Partnership "Br.Nobel". These digital data once again prove that at the beginning of the XX century Baku oil occupied a leading place in the supply of the Russian Navy. The importance of the Baku oilfield was also in the development of railway transport. In 1900 672,4 tons of solar oils that were not subject to excise were exported, 567,4 tons of which were exported inside the Empire (through Astrakhan - 547,4 tons, by sea, through Petrovsk - 0.8 tons and along Baku - Petrovsk Railway - 19,2 tons) for adding to vegetable oils and further processing into vaseline, perfumery and other oils; the rest part (55,5 tons) was sent to the Trans-Caspian region (3 tons) and spent within the Transcaucasian region mainly on fuel; 49,0 tons were exported to Batum. Out of the total amount of lubricating oils - 12.917,5 tons, the share of refined machine oil, the main product of production and export, falls 9.936 tons, refined spindle oil - 1,616 tons, refined cylinder oil - 262,0 tons. The remaining 1,101,4 tons make up unrefined oils, i.e. distillates of cylinder, machine and spindle oil. The export of lubricating oils itself was distributed in markets as follows: in Batum - 9.295,8 tons, in the Empire 3.617,1 tons, namely: through Astrakhan 2.594,0 tons (machine oil - 2.093,1 tons, spindle oil - 377 tons and cylinder oil - 123,0 tons), in Petrovsk - 570,4 tons, along the Baku-Petrovsk line of the Vladikavkaz railway - 163,2 tons, in the Trans-Caspian region - 19,5 tons, in Transcaucasia by rail - 95,8 tons, by sea - 5,1 tons, and by tug - 168,5 tons. In the Empire 99,86% (3,612,8 tons) was exported in the refined form and only 5,0 tons (i.e. 8,14%) as distillate; in Batum 11,10% (1.096,5 tons) goes in unrefined form for further processing at foreign conversion plants and 88,21% (8.203,3 tons) - in refined form [14, p. 57]. As of January 1, 1901, the bulk fleet of the Caspian Sea included 126 steam ships, with a capacity of 4.690 tons of cubic feet and 156 sailing vessels with a capacity of 2.915,0 tons of cubic feet, and the total amount is 282 vessels with a capacity of 7.606,2 tons of cubic feet [15, p. 58].

In terms of the export of petroleum products from Baku by rail in 1900 significant changes, on which high hopes were pinned in terms of increasing its throughput, took place. However, these changes fell far short of expectations and, if the general movement along the Transcaucasian Railway intensified, this only slightly affected the export of oil products in general, and in particular the export of kerosene, a large share of which, as in 1899, was sent to the Black Sea by district route, reducing the profitability of state roads and increasing the overhead costs of exporters. In order to increase the transportability of the Transcaucasian Railways, which did not meet the modern state of the Baku oil industry: 1) it was considered necessary to build a kerosene pipeline from the station Mikhailovo to the station Batum; 2) to arrange a double path from Baku to the station Balajara; 3) to lay the fourth filling branch in the Black town, between the northern and southern branches, parallel to them; 4) to adapt filling stations in the Black Town for the production of filling at night and 5) in the more distant future to lay a kerosene pipeline to the station Wolf Gate, where to transfer the filling of tank cars. During 1900 only the first two assumptions out of five were fulfilled, i.e. a double path was laid to the station Balajara and there was an open action from the kerosene pipeline from the station Mikhailovo to the station Batum. Of the remaining assumptions, so far only rails have been laid on a new branch in the Black Town, but tank cars are not filled on it; some work on setting the electric lighting was started, which, however, was soon suspended; the question of the organization of filling tank cars at the Wolf Gate station has not gone out of the field of assumptions yet [16, p. 62]. In 1882, according to the Baku Customs and Transcaucasian Railway, 500.000 poods of kerosene were exported, unrefined oil - 1.199.722 poods [17, p. 33].

The normal need for photogen in the domestic Russian markets was determined as 12 million poods by the oil producers, and the productive strength of all plants exceeded 20 million poods of annual production. The total number of photogenic plants is 230, and 198 of them are in Baku; but only 135 are in action. The oil industry of Azerbaijan had a great influence on the development of Russian industry. On average, more than 100 million rubles annually went to the state treasury from Azerbaijani oil [18, p.22].

4.Conclusion

The development of the Baku oil industry region had a huge impact not only on shipping on the Caspian Sea, but also on the development of railways, expressed both in the quantitative growth of freight transportation and in their composition. At the same time, the possibility of fast and cheap transportation of petroleum products to the central regions of Russia, in its turn, stimulated the rapid development of the oil industry on Absheron. Oil and its refined products quickly turned Baku into a major industrial, trade and geopolitical centre, which has an influence on a vast territory. Russian capitalism drew North Azerbaijan in world merchandise circulation.

The cargo-intensive sea and railway transport arteries of the Baku oil industry region led to a significant integration of socioeconomic and sociocultural processes, to a significant expansion of the spatial contours of the Caspian region in the last third of the XIX - the first decade of the XX centuries.

5.References

1. Izmetyeva T. F. Russia in the European market system. M., 1991.
2. Perschke L. L. Report of the head of excise taxes of the Transcaucasian Territory on the progress of excise in 1900 St. Petersburg, 1902.
3. Perschke L. L. Report of the head of excise taxes of the Transcaucasian Territory on the progress of excise in 1900 St. Petersburg, 1902.
4. Report of the Head of Baku Commercial Port for 1900-1909 Baku, 1901 - 1910.
5. CSHA OF THE RUSSIAN FEDERATION. F. 95, op. 4, d. 1089.
6. CSHA OF THE RUSSIAN FEDERATION. F. 1458, on. 1, d. 48.
7. A short essay on the state of the Baku oil industry in 1908, Baku, 1908.
8. SHA. F.387. Op.1. Unit. 127.
9. Economic note on the importance of the Batumi port and development prospects. Tiflis. 1925.
10. A short essay on the state of Baku industry in 1907 - Baku, 1908.
11. Shapsovich M.S. The whole Caucasus. Industry, trade, agriculture of the North Caucasus and Transcaucasia. Baku, 1914.
12. RSHA OF THE RUSSIAN FEDERATION. F. 206. Оп. 1. 1015. L. 27.
13. Monopolistic capital in the oil industry of Russia (1883 - 1914). M., 1973.
14. Perschke L. L. Report of the head of excise taxes of the Transcaucasian Territory on the progress of excise in 1900 St. Petersburg, 1902.
15. Perschke L. L. Report of the head of excise taxes of the Transcaucasian Territory on the progress of excise in 1900 St. Petersburg, 1902.
16. Perschke L. L. Report of the head of excise taxes of the Transcaucasian Territory on the progress of excise in 1900 St. Petersburg, 1902.
17. SHA. F. 509.Op.1. 51.
18. Azizov T. Azerbaijan XX Esrin Evvelerinde. - Baku, 1997.

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ORGANIZATION OF THE OIL INDUSTRY IN AZERBAIJAN AND INTERESTS OF THE WORLD-LEADING STATES IN AZERBAIJANI OIL (late 19th - early 20th century)

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Abstract. The article examines the history of the formation of the oil industry in the late 19th - early 20th centuries during the tsarist colonization of Azerbaijan. Although the problem has been investigated by many researchers, the article is the first to use the tables of the German consulate in Baku, which reflect the state of the oil industry. The article analyzes the expansion of activities of foreign oil companies and changes in international relations after the abolition of the existing system of ramson for oil-bearing lands by the tsarist government.

Keywords: oil, Balakhany, Sabunchu, Ramani, Zabrat, Bibi-Heybat, Surakhani

1.Introduction

The history of written information about the existence of oil fields in Baku and Absheron, which are considered the "Pennsylvania" of Azerbaijan (emphasized by us – N.H.), dates back to the early Middle Ages. In the works of historians there is evidence that oil from Azerbaijan was exported to Iran in the 3rd-4th centuries.

In the 13th century, Marco Polo wrote about Baku oil, which was repeatedly shipped to Baghdad as a means of lightening. Science knows that in the 15th century, the Azerbaijani geographer Abdurrashid Bakuvi reported about 200 halvars of oil per day being produced in Baku, and in the 16th century, the Turkish traveler Katib Chalabi reported about 500 wells near Baku. Kempfer, Gmelin and Lerch reported about oil wells in Baku in the 18th century. Lerch wrote that in 1735, out of 52 oil wells in Balakhani, 26 survived, and the oil produced was transported to Baku by leather tulugs. Interestingly, the German traveler Lerch, who worked as a doctor in Russia, did not report the use of oil.

2. Experimental part

During the period of the khanate, the use of kerosene as a petroleum product was widespread [5, 1-3; 4, 8].

In Eichwald's book, dated 1825, "Reise auf dem Caspishhen Meere und Caucasus", he described 16 oil wells near Surakhani and the oil produced from them. According to Eichwald, the depth of the wells was 3-4 fathoms (1 fathom – 2.13 meters), and they contained no more than 2-3 poods of oil in summer and 1 pood in winter. Oil was packed in small tulugs and delivered to Baku, where it was stored in warehouses [3, 32; 6, 6].

Oil of Baku and Absheron has attracted the attention of Europeans since the 17th century. German scientist Adam Oleari and secretary of the Swedish embassy in Iran E.Kempfer wrote about the presence of "***special oil***" on the Caspian coast (emphasized by us – N.H.). Every European traveler who visited the Caucasus considered it his duty to visit Ateshgah in Surakhany [6, 6].

During the tsarist colonization, scientific knowledge about the quality of oil was sufficient. The healing properties of the oil have been known in the treatment of rheumatism, scurvy and skin diseases.

According to Gmelin, the Baku khan earned 40 thousand rubles a year from oil sales. After the Gulistan Treaty, oil wells and oil-bearing lands came under the control of the tsarist government. Until 1873, the oil fields were under the jurisdiction of either the tsarist treasury or redeemers. [5, 1-3]. After the cancellation of the ransom system, along with investments in the oil industry in Baku, the application of scientific and technical potential was accelerating [2, 28].

The formation of the oil industry in Baku began in 1860 [5, 3]. Thanks to the rapid penetration of oil into all spheres of society, new industries were being created.

According to G.E.Starchev, the creation of the oil industry in Baku began in 1860 with the opening of the plant by Kokorev and Gubonin. Eichler, Master of Chemistry at Moscow University, was invited to work in the field of oil distillation and refining. Balakhani oil was purchased from the redeemer Mirzoyev at 45 kopecks per pood, and at the initial stage the refinery produced very low quality kerosene. And this product was bought for 4 rubles 50 kopecks and sold in Moscow for 6 rubles. Despite the country's colonization, the Baku oil industry began to operate in this way. As seen, it was very difficult to extract and refine oil, nevertheless, it was sold at a very low price – 45 kopecks per pood. At the same time, the owners of the factories were highly dependent on the oil producers. Since the existing system of obligations impeded the general activities of oil owners, the state of the oil industry and the commission created in 1867 believed that crude oil should be exempted from any taxes at any cost, at least in the American example kerosene should not be taxed. As a result, in 1872 the system of obligations was abolished [5, 3].

After the abolition of the ramson, the tsarist government put forward for discussion a bill on the transfer of oil-bearing lands to foreigners. The project was intended to limit the transfer of oil-bearing lands to foreigners. Although the tsarist government did not intend to completely open the Baku oil industry to foreigners, it was forced to do so, since international relations were not in favor of the tsarist government. In such conditions, the positions of foreign companies in the Baku oil industry were strengthening, including the house of the Rothschild banker, who bought the Caspian-Black Sea Society in 1886. Until 1883, American kerosene retained its positions in the Russian market and exceeded Baku kerosene in quality. However, since this year, the import of American kerosene into Russia has been suspended, because, on the one hand, Baku kerosene has already surpassed American's in quality, and on the other hand, this was due to a qualitative change in international relations. The construction of the Transcaucasian railway in 1883 also influenced the state of the oil industry in Azerbaijan.

During this period, the American company “Standard Oil” was ousted from the domestic markets of Russia and became the main competitor of the Caucasian oil industry in the world market [2, 50-51]. In the midst of the Russian-German conflict, the Rothschilds began to finance tsarism. After Otto von Bismarck ordered the expulsion of Russian deposits from German banks at the end of 1887, the tsarist government began to move closer to French banks [2, 51]. The unification of Germany into a single state and bringing to a high level of its military and economic power in a short period of time led to a radical change in the system of international relations. [5, 20].

3. Results and discussion

At a time when international relations were escalating to the limit, it is a good idea to keep track of the number of wells in the oil fields around Baku. In 1878, there were 47 wells in Balakhany, 204 wells in Sabunchi, Ramani and Zabrat, 19 wells in Bibi-Heybat, 22 wells in Surakhani, 4 wells in Binagadi, 2 wells in Masazir, 1 well in Bulbula and 2 wells in Khirdalan. There were a total of 301 oil wells in Baku and its suburbs [5, 15].

German sources consider 1902 to be a turning point in the history of the oil industry of Absheron. Referring to these sources, we can present a table of oil production rates from 1895 to 1902 [7, 18]:

Years	Product / pood	Percentage difference
1894	297,5	
1895	377,4	26,8
1896	386,2	2,3
1897	421,7	9,2
1898	486,0	15,3
1899	525,3	8,5
1900	600,7	14,4
1901	671,2	11,8
1902	636,4	5,2

The table below shows the volume of oil produced in the Balakhani, Sabunchu, Ramani and Bibibeybat fields in 1900-1902 [7, 19]:

Area	1900	1901	1902
Balakhani	124,7	117,8	101,8
Sabunchu	251,6	295,2	267,1
Ramani	114,8	124,1	140,0
Bibibeybat	109,2	133,6	127,4

By analyzing the figures, one can trace the impact of the economic crisis of 1900-1903 on the oil industry of Azerbaijan.

As in different periods of history, during the tsarist colonization, Azerbaijani oil was in the center of attention of the states of the world. With the opening of a kerosene plant in 1863 as a result of Mendeleev's research, Russia was able to attract more European attention [3, 33]. Oil, which was originally used as a lighting medium, has become a commercial commodity over time and Mendeleev first spoke about Caucasian oil, which became a commercial product in 1823. [1, 215-216].

In the second half of the 19th – early 20th century, European countries, especially Germany, had enough to monitor the state and dynamics of the oil industry in Azerbaijan to monitor the power of Russia. This is evidenced by the information provided by the German consulate in Baku on the current economic situation in Azerbaijan. Germany tried to get rid of its dependence on the United States for importing kerosene. Back in 1897, because of such economic interests, the German government approached Russia with a proposal to sign an oil deal. The proposal reflected a tax cut on exported kerosene. However, the Nobels, as soon as they learnt of this, opposed the proposal of the German government [6, 22]. The German consulate in Baku was instructed not only to monitor the entire economic situation in Russia, but also to monitor the general state of the oil industry so that the Russian government did not put forward any claims against any agreement that might be signed. On the basis of documents from the Political Archives of the Germany Ministry of Foreign Affairs in Berlin a study was carried out and a comparative analysis of the general decline of the oil industry in Russia, drilling in the oil industry over ten years (1893-1902) is given in the following table [7, 19-20].

	1893	1894	1895	1896	1897	1898	1899	1900	1901	1902
Number of productive wells	458	532	604	736	917	1107	1357	1710	1924	
Number of newly drilled wells	60	102	157	209	300	456	592	468	282	180
Number of unproductive wells	401	345	317	344	419	468	594	842	1273	
Average productivity of wells (in thousands of poods)	709	559	625	526	461	439	387	351	349	

As can be seen from the table below, although the number of productive wells was higher than in the previous years, the number of new wells, depending on the management, decreased sharply compared to previous years, and the number of unproductive wells increased rapidly. The economic crisis affected the oil industry, and compared to 1893, the annual productivity and productivity of wells decreased.

The export of all oil products from Baku amounted to 513,2 million poods for 10 years (1893-1902) and the table below shows an increase of 25 million poods compared to the previous year [7, 20]:

Years	1893	1894	1895	1896	1897	1898	1899	1900	1901	1902
Oil products (in million poods)	248.2	288.4	284.3	306.8	346.4	392.4	385.4	441.5	488.2	513.2

As of 1902, 101.1 million poods of oil products were transported by rail from Azerbaijan, and 409.4 million poods across the Caspian [7, 21]. In 1901, 83 companies were engaged in the transportation of oil from Baku [2, 73].

4. Conclusions

It is known that the formation and development of the oil industry has led to an increase in demand for all goods [7, 7]. Thanks to oil, which quickly penetrated into all spheres of society, large-scale industries were created. We are probably right when we say that the Volga and Caspian shipping companies are in debt to oil. The demand for electricity from oil drilling has led to an increase in the number of electrical machines. In the late 19th – early 20th centuries, with the development of the oil industry, an increase in the number of industries, the number of sources of income and changes in the activities of the world banking system directly led to changes in international relations.

5.References

1. Sadıgov H. Azerbayjan Avropa dovletlerinin diplomatiyasinda (1747-1829) (Azerbaijan in the diplomacy of European countries). Baku: Tefekkur, 2004. (in Azerbayjani).
2. Salimov Sh. Beynelkhalg munasibetlerde Azerbayjan nefti (Azerbaijani oil in international relations). Baku: 2004. (in Azerbayjani).

3. Huseynova N. XIX esrin II yarisi – XX esrin evvellerinde Azerbayjan neft senayesinin veziyyeti ve khariji neft shirketlerinin fealiyyeti (The oil industry of Azerbaijan and the activities of foreign oil companies in the second half of the 19th century – at the beginning of the 20th century) // Tarikh ve onun problemleri. Baki: 2018. №3. (in Azerbayjani).
4. Muradverdieva L. Bakinskaya neft (Baku oil). Baku: 2006. (in Russian).
5.Startsev Q.E. Bakinskaya neftyanaya promishlennost. Istoriko-statisticheskiy ocherk (Baku oil industry. Historical and statistical sketch). Baku: 1901. (in Russian).
6. Sultanov Ch.A. Neft (Oil). Baku: tom I. (in Russian).
7. Auswärtiges Amt-Politisches Archiv (Foreign Office-Political Archive). R.901, II 9707. (in Germany).

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"ECONOMİC EFFİCİENCY OF ASSESSMENT OF DAMAGE TO THE ENVİRONMENT DURİNG THE USE OF OİL RESOURCES İN AZERBAİJAN”

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Abstract In the conditions of new economic relations, efficient use of Natural Resources and Environmental Protection are of global nature in meeting the needs of the population and industry. Sustainable socio-economic development depends on the correct use of the environment and natural resources by responding to the needs of the society, maintaining the quality of the Natural Resources Potential of the environment, giving the productive forces to use the next generation corresponding to the level of development. Therefore, the interaction of nature and society, the impact of these relations and the search for solutions are important conditions. This is an actual problem of studying the economic aspects of efficient use and protection of the environment and Natural Resources, studying general law. From the experience of ubyektiv indicators of environmental management activities and the state of the environment, it is known that the current methods of managing environmental safety are not sufficiently effective. For this reason, it is extremely important to reorganize, improve ecological management.

The main purpose of the article is to determine the directions of solving these problems and to make relevant proposals. The multifaceted nature of the problem and its effective solution are very important.

Key words: Ecology, eco-economic resources, eco-Economic Policy, Environmental Protection, energy security, environmental safety, ecological management

1.Introduction

The interaction of the environment and society occurs on the basis of the implementation of effective use of nature. One of the important issues in this direction is the replacement of production facilities with low-cost and waste-free industrial facilities.

In the XX century, scientific and technical development led to the strengthening and pollution of the impact on the environment. At present, the study of the characteristics of anthropogenic impact on the environment and ensuring ecological safety is one of the main global problems.

A large number of laws have been adopted on efficient use of Natural Resources and protection of natural environment. These can be attributed to a number of other laws” on Earth” on Environmental Protection“, “ on ecological safety“, “ on water supply and wastewater treatment " [1].

Analysis of the composition of the economic impact of Environmental Protection in the present period can be considered positive and negative motivation. These mexanizm interrelated speed of action kastararak manifests itself as a single system.

According to the official data of the state committee of the Republic of Azerbaijan, the impact on the environment continues in 2016-2017 [2,3].

As a result of the analysis, hazardous production waste management, disposal and generation decreased in 2017 compared to 2016. The establishment of such wastes amounted to 632.6 thousand tons in 2016 and 266 thousand tons in 2017.

At the same time, the ironing of such waste was 25.9 thousand tons in 2016 and 35.8 thousand tons in 2017. The effective use of waste and recycling khammal both improves the environmental well-being and saves the initial natural heat creates an optimal condition for the reuse of khammal. Currently, the level of re-use of khammal in our country consists of enterprises operating in Baku and varies between 12-18 per cent. At the same time, recycling is 7-10 times less than that of developed countries, approximately 5-6 per cent of the waste used as a whole [4].

At a time when our country became independent and switched to the market economy, it needs to benefit from the experience of developed countries in order to use natural resources and the basic oil, chemical and petrochemical resources to fully waste-free technology. The organization of relations between fields and enterprises is part of very important ecological measures. All this shows the urgency of the need to further improve the socio-economic impact of ecological regulation of the impact of waste and recycling on the natural environment.

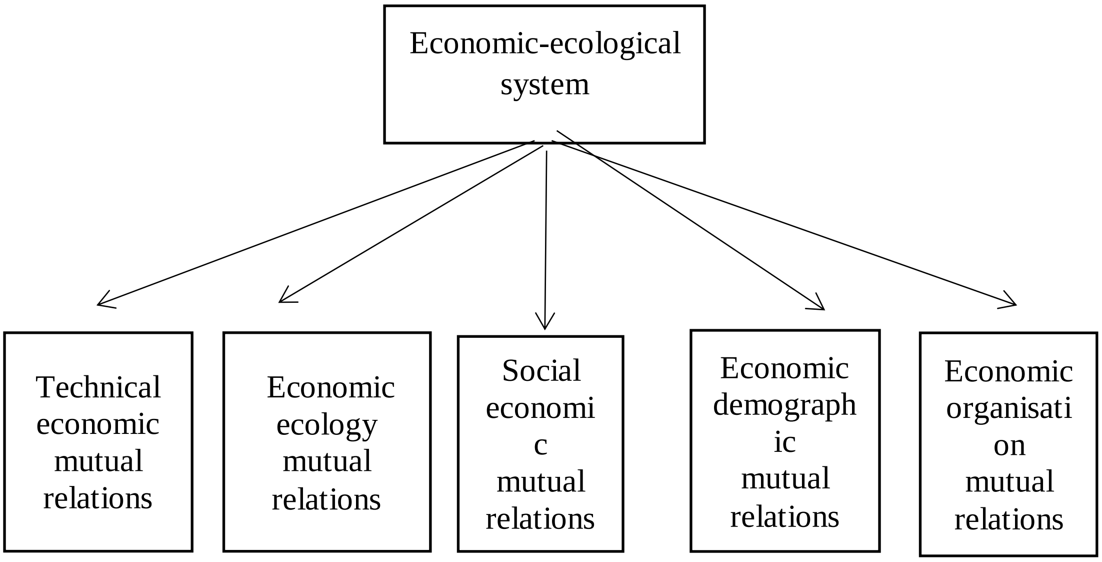

Figure 1. Methodical basis of nature-preserving and resource-preserving activity.

As is known, the energy industry is one of the main factors affecting economic and social development. Ecological-efficient oil and gas production means ecological balancing of adaptation of economic growth and sustainable development of the sphere in the long term.Such an ecological balancing is possible in the conditions of ecological and economic competition [5].

In this regard, the state regulation of oil and gas production primarily envisages the implementation of a regional policy, which, in turn, should be aimed at sustainable development of society with the interest of producers in the state policy and eco-friendly conditions of natural use.

For the implementation of an effective ecological policy, the following are necessary :

- expressing the complexity of the damage to the environment when oil and gas fields are being operated;
-to identify and classify the location and role of damages arising at all stages of the production process;
- to measure the importance of economic losses during the operation of the fields for economic purposes;
- to regulate production activities in the direction of ensuring logical compromise between production goals and their economic results.

For more than 200 years, energy and petrochemical resources have been used in the production of electricity in the world. About 87% of the electricity produced in the modern period falls to organic fuels [6].

Since the protection of the environment and the solution of ecological problems are a common problem of mankind, the conference, which was held in Denmark in 2018, demonstrates the seriousness of the issue. The concept organized on the basis of these principles has already been approved and included in the “National Environmental implementation plan”. With the decision of the Cabinet of Ministers of the Republic of Azerbaijan to take and finance measures related to environmental protection, the regulations on “state fund for Environmental Protection”was prepared in accordance with the law of the Republic of Azerbaijan “on Environmental Protection” in 2014. At present, payments for the use of natural resources are cleared by laws “on Environmental Protection”, “on underground and their use”.In addition, the state program on the use of alternative and renewable energy resources in Azerbaijan was approved by the order of the president of the country on October 21, 2004 in order to develop the use of renewable energy sources taking into account the concrete implementations for the development of National Energy. The order dated September 28, 2006 contained the” comprehensive action plan for 2006-2010 on improvement of Ecology in the Republic of Azerbaijan " [7].

The area of acute ecological problems in the Republic is the sphere of oil and gas production. The ecological situation here, especially in the exploitation zone covering the old deposits, is of acute nature. For this purpose, implementation of ecological activities, complex measures in accordance with international norms and Standards, Assessment of environmental impact of enterprises ' activities, ensuring ecological safety during oil and gas production and processing, etc. in order to solve such problems, the Department of Ecology was established in accordance with the decree of the president of the Republic of Azerbaijan “on improvement of the structure of the State Oil Company of the Republic of Azerbaijan” dated September 14, 2006. Organization of environmental protection work in organizations and enterprises, determination and formalization of integrated ecological policy on SOCAR, preparation and implementation of ecological programs, treatment of wastewater, maximum efficient use of financial resources allocated in this direction, etc. such issues are one of the important tasks facing the Department of Ecology. At the same time, the effective activity of SOCAR Ecology Department is also important in terms of ensuring sustainable development of the national oil and gas sector. Thus, the effective activity here brings additional stimuli to SOCAR's reputation, which plays an important role in maintaining the company's internal production stability and perspektiv Development [8].

The rapid development of all sectors of the economy in the last century resulted in an increase in the negative impact of human activity on the environment and excessive exploitation of Natural Resources. In recent years, Azerbaijan has made significant achievements in the fields of social and economic development, and the sustainability of these achievements has been recognized as the main priority.

In 2003, Azerbaijan adopted a national program on eco-sustainable socio-economic development. According to the action plan to ensure the sustainability of the environment, which is one of the Millennium Development Goals, the principles of sustainable development are included in state policies and programs.

In modern conditions, the state regulation of Environmental Protection and the use of nature requires the compilation of certain forecast documents. Effective use of natural resources makes it necessary to implement the following measures. Methods of calculating damage to the environment are reflected in the literature. Currently, 2 methods for determining the damage have been developed: direct method of calculation and empirical method of calculation.

There is a need for economic efficiency to be taken to assess environmental damage and reduce environmental pollution. It addresses the issues of determining the damage caused by various components associated with the violation of ecology of the general economic damage used to determine economic efficiency. From a theoretical point of view, the annual value of the total economic damage to the environment as a result of pollution can be determined by the following formula. The modern system of payments for environmental pollution by enterprises is based on the calculation of economic damage using the method of generalized indirect estimates. According to a simplified interpretation of this method, the total (total) economic damage (D_e), the damage caused to the environment by man-made pollution is defined as the amount of damage caused by atmospheric pollution (D_p), waters (D_w), soils (D_s), that is

$$D_e = D_p + D_w + D_s \qquad (1)$$

The calculation of economic damage for individual components of the environment-the atmosphere, water and soil - can be made using the formula

$$D_e = \sum \mathrm{P_i}\,\mathrm{M_i} K_e \qquad (2)$$

where D_e — economic damage from environmental pollution, thousand \$ / year; $\mathrm{P_i}$ — standard of payment for environmental pollution, \$/т; $\mathrm{M_i}$ — mass of the pollutant released into the environment by its individual components, т; K_e — coefficient of the ecological situation and ecological significance of the region. We will determine the possible economic damage caused to the atmospheric air from the emissions of pollutants for the average OGD enterprise in Azerbaijan.

From the expression (2)

$$D_e = (\mathrm{P}_s \mathrm{M}_s + \mathrm{P}_{l.g.} \mathrm{M}_{l.g.}) \times \mathrm{K}_e \qquad (3),$$

where $\mathrm{P_s}$ and $\mathrm{P_{l.}}$ – accordingly, the standard of the company's payment for the release of solid and liquid and gaseous particles;

$\mathrm{M_s}$ and $\mathrm{M_{l.g.}}$ – accordingly, the mass of solid, liquid and gaseous particles ejected;

$\mathrm{K_e} = 2$ - coefficient of ecological situation and significance of the Apsheron Peninsula.

Using expression (3) and data from table 2, for a single, medium-sized enterprise, we get:

$$D_{\mathrm{a}} = (10 \times 30 + 5{,}8 \times 16000\ ) \times 2 = (300 + 92800) \times 2 = \ 186200\,\$/year$$

Table 1.Emissions of pollutants into the atmosphere according to the average OGPD for 2018

Pollutants	Emission mass, t / year	Standard fee, \$ / t
Solid particles	30	10
Liquid and gaseous particles (nitrogen oxide, non-methane hydrocarbons, etc.)	16000	5,8

Given that there are eight OGPD subordinated to “Azneft”, this figure increases about 8 times, and the annual economic damage from air pollution alone, in General for the Association, will amount to about 1.5 million US dollars.

Thus, despite all the positive developments in the field of pollution reduction in SOCAR, there is still a need to improve the effectiveness of measures to manage environmental and economic risks [10,11].

. A number of extremely important, environmentally-oriented initiatives do not sufficiently cover land-based enterprises and focus mainly on sea-based enterprises.

It should be noted that in the conditions of a market economy, which is the main engine for the development of economic relations in the Republic, there is an administrative form of management for all OGPD. These enterprises are characterized by the absence of economic freedoms, and they are completely dependent on the Association. Enterprises do not have the freedom to sell their products or any other type of economic activity. Undoubtedly, this affects the interest of OGPD employees in the final product of production, and also slows down the implementation of incentive measures when evaluating the work of employees by the management of enterprises. This also affects the effectiveness of risk management measures.

According to article 27 of the law [9] “production control in the field of nature protection and nature management is carried out by the environmental service of the enterprise, organization and institution”. In this regard, the Department of environmental protection plays an important role in assessing the environmental and economic risks of OGPD and finding methods for their management. Relatively new in comparison with other divisions of the enterprise, this Department was created in all OGPD of the Association as part of the “plan of comprehensive measures to improve the environmental situation in the Republic of Azerbaijan for 2006-2010”. The work of the Department is closely linked to the SOCAR environmental Department and is sufficiently effective in implementing measures aimed at improving the environmental situation in the fields recommended by the Department.

4.Conclusions

The analysis of the current state of environmental and economic risk management for SOCAR showed that, despite all the positive developments in reducing environmental pollution, the company still needs to improve the effectiveness of measures to manage these risks.

In particular, despite the successful implementation of a number of measures to reduce air pollution, the amount of air emissions from stationary sources at the company's enterprises remains significant. It is shown that the annual economic damage from air pollution alone, in general for Azneft, is about 1.5 million US dollars.

A number of extremely important, environmentally-oriented initiatives are not enough the project covers OGPD land and focuses mainly on enterprises that develop sea deposits both independently and jointly with foreign companies.

At the same time, even for these enterprises, the implemented measures still require further improvement of their efficiency.

In order to improve the effectiveness of risk management, it is proposed to move away from the centralized form of management at the company level and form a risk management system (RMS) directly at the enterprises themselves. To implement this approach, we recommend some changes in the organizational structure of enterprises, including the creation of a Department for managing all risks that may be exposed to the enterprise. The creation of such a Department directly in the OGPD will allow for more effective use of the potential and real capabilities of the enterprise in conditions of uncertainty and associated risks, and the necessary optimization of risk management directions and methods, which are reflected in the risk minimization program developed to ensure the sustainable development of the enterprise.

5.Reference

1. Azərbaycanın Statistik göstəricilərinın materialları, Bakı 2018
2. A. Sadıqov, İ. Xəlilov Ekologiya və ətraf mühitin mühafizəsi, 2009, 345 s
3. Azərbaycanda Ətraf mühit. Azərbaycan Respublikası Dövlət Statistika komitəsi, Bakı, 2018, 139 s.
4. Raibə Cəfərova “Təbiətdən İstifadənin İqtisadiyyatı” (dərs vəsaiti). Bakı – 2014
5. Abdullayev K.,Məmmədov R.,Lətifov Y. Enerji ehtiyatları, elektrik enerjisi istehsalı və ətraf mühit, II cilddə, Bakı: “Zaman-3”, 2005, 408 s
6. Azərbaycan Respublikasında ekoloji vəziyyətin yaxşılaşdırılmasına dair 2006-2010 –cu illər üçün kompleks tədbirlər planı, Bakı, Xalq qəzeti, 29.09.2006.
7. Агаева З.Р. Утилизация отходов производства ряда присадок, загрязняющих окружающую среду// Азербайджанское нефтяное хозяйство//.№6 2005, 52-56
8. Тихомиров Н.П. Методы анализа и управления эколого – экономическими рисками. Учебное пособие. – М.: Юнити – Дана, . – 350 с. 2003
9. Законодательство об Азербайджанских ресурсах «об охране и природные материалы"» Baku, 1992. URL: http://files.preslib.az/projects/azereco/ru/eco_m4_2.pdfCommon, M. and Stagl,

10. S. 2005. Ecological Economics: An Introduction. New York: Cambridge University Press.
11. Eduardo Olaguer, Atmospheric Impacts of the Oil and Gas Industry, 2016
12. Fisher, B., R.K. Turner and P. Morling, 2009. Defining and Classifying Ecosystem Services for Decision Making. Ecological Economics 68: 643–653.
13. Harris J. (2006). Environmental and Natural Resource Economics: A Contemporary Approach. Houghton Mifflin Company.
14. Martinez-Alier, J., Ropke, I. eds. (2008). Recent Developments in Ecological Economics, 2 vols., E. Elgar, Cheltenham, UK.

OR-I-4

STUDY OF EFFICIENT PROCESSING TECHNOLOGIES OF PRODUCTS OBTAINED IN OIL REFINING AND PETROCHEMICAL PROCESSES

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Abstract. The paper deals with the study of ecologically safe processing processes of by products obtained during the secondary refining processes of oil. Oil refining and pertochemical products put new demands at the modern stage. Creation of directed processing technologies, approach to the ecological probems of the processes from new context to establish more efficient deep processing technologies of hydrocarbon resources, to reduce the amount of by products formed during the processes, to involve them in the main processes are the part of these requirements. The requirements dictated by XXl century can initially be reviewed at two planes; economical and ecological. In fact, ecological requirements do not essentially deny economical bases. On the contrary, by considering the factors which highlight the aim of ensuring the environmental protection, meeting the global cataclysms gives an impulse to it. Extension of studies on the creation of new technological rocesses ensuring the modern requirements, acceleration of applications of obtained positive results in industry for the development of two directions are the important tasks of the modern life. One of these directions is to create new, processing technologies that are conform to modern processes directed to the increase in target product production of by-products formed during production processes. Our researches are mainly directed to the scientific studies of these problems and appplication of the results.

Key words: hydration process, dry gas, butane-butylene fraction, butylene-butadiene fraction, coking, catalytical cracking, mixed fractions, catalyst, pyrolysis process.

1.Introduction

The efficient use of by products formed with target products during integration process of oil refining and petrochemical productions opens wide possibilities for scientific studies on the enhancement of economical efficiency of productions, raw material resources, processing depth [1]. It is known that by products with different compositions, including gas fractions comprising mainly C1-C4 are formed during secondary refining processes of oil. Gas fractions are mainly used as a fuel component in these plants. It is known that gas fractions formed during the process contain sulphuric compounds. Sulphuric compounds in gas fraction are exposed to certain transformations during roasting and thrown into atmosphere and pollute environment. Against the background of ecological crisis formed in modern life this cannot be acceptable. From the other side the composition of gas fractions comprising by-products formed during processing process are rich with the components suitable for pyrolysis. We may show dry gas along with coke in coke production in the unit [2], C_1-C_2 fraction (dry gas) and C_3–C_4 (propane-propylene + butane –butylene) fractions as a by-product along with gasoline fraction in catalytic cracking unit [3], butylene-divinyl fraction in which non-saturated hydrocarbons dominate during pyrolysis as an example. Whether more or less in quantity the variety of compositions limits the direct application possibilities of these gases in any process and from this point there is a need for scientific studies for each individual case. In this direction more efficient processing technology possibilities of gas components formed during these processes were investigated in our researches [4,5].

During the production of coke in various raw materials – Tar oil +> 420 °C fraction separately, tar oil +> 420 °C fraction + heavy resin (heavy resin fraction obtained in "EP-300" unit) 27-29% of chromatographic composition of dry gas obtained during processing is ethane-ethylene fraction, and 19-21% is propane-propylene fraction.

Basing to the technological researches we may state that from the point of efficient use of raw materials by using potential opportunities of gas-separating joint of EP-300 unit the separation of the components in dry gas which are more valuable than the value of fuel gas is of great importance from the point of effiicient use of hydrocarbon resources and enhancement of processing depth. If we consider that dry gas contains up to 0,98-1,02% of hydrogen sulfide and this causes ecological crisis in environment during roasting, these researches are essentially relevant in terms of ecological protection along with economic efficiency. In order to use butane-butylene fraction in catalytic cracking unit, butylene-divinyl fraction obtained during pyrolysis separately or as a raw material in the form of a composite mixed at various ratios should pass through special processing stages. Thus, butane-butylene and butylene-divinyl fractions contain large amount of non-saturated hydrocarbons and the target product yield decreases during their pyrolysis and the amount of wastes thrown into atmosphere increases.

The paper is presented as a part of the results of scientific researches on the efficient processing technologies of abovementioned gas fractions obtained separately or as a composite in the form of by-products. In the secondary refining processes of oil C_1-C_2 (dry gas) and C_3–C_4 (propane-propylene + butane –butylene) are also formed along with target products in the secondary refining of oil. One of the efficient use of these fractions is to involve directly to the processes by appointment separating to the target components and using potential opportunities of gas-separating network (section) of pyrolysis units. It is known that raw materials comprising saturated hydrocarbons are mainly used as a pyrolysis raw material [6].

When raw material comprising non-saturated hydrocarbon is fed directly to pyrolysis furnaces by-products are formed much more than the target products along with ethylene and propylene by the decomposition of existing non-saturated hydrocarbon components and as the amount of non-saturated hydrocarbons increases in raw material the amount of by-products increases, coke formation in furnaces is accelerated [7, 8]. As a result, operating life of furnaces shortens and they are put on premature maintenance to clear round coke layer formed along diameter in pipes which limits the heat transfer and flow of reaction product inside the pipe.

This causes additional expenses, increase in cost price of used products and pollutes atmosphere due to the release of a large amount of carbon monoxides into atmosphere during treatment process. In our researches the main object is to investigate the technological parameters which enables to use by-products formed during oil refining and petrochemical processes as a direct raw material by considering abovementioned defects.

2.Experimental part

The description of experimental installation of pyrolysis. Figure 1 shows the principal diagram of the laboratory installation for studying the kinetic laws of pyrolysis process developed by the central scientific-research laboratory “Ethylene-Polyethylene”.

To determine the composition of gas components we used interstate standard ethylene-propylene chromatographic analysis methods in accordance to GOST 24975.1-2015. Raw material – mixture of gases comprising saturated hydrocarbons is fed to mixer from container 1, where water steam enters from tank 2. The mixture of hydrocarbons and water steam enter into convection section of furnace 6 at an ambient temperature.

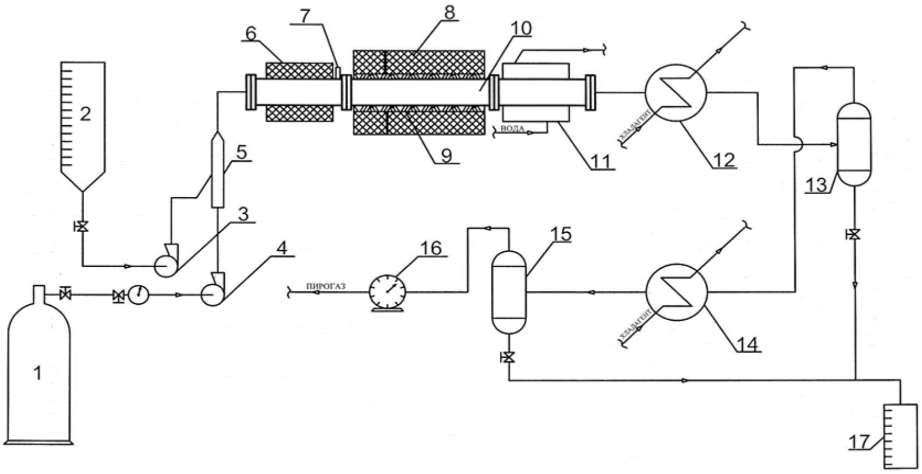

Fig. 1. Principal laboratory diagram of pyrolysis process: 1 – container for raw material; 2 – water tank; 3, 4 – pumps; 5 – mixer; 6, 8 – heating furnace; 7 – thermowell; 9 – lead jacket for even reactor heating; 10 – reactor for pyrolysis; 11, 12, 14 – coolers; 13, 15 – separators; 16 – gas meter; 17 – condenser tank.

Length and internal diameter of convection section are l=60 cm, di = 10 mm. From convection section water and raw material steams enter to radiant section coil of furnace 8 at 500^{0}C which is divided into two zones: heating zone (its length is 30 cm) and reaction zone (120 cm); internal diameter of coil is di = 10 mm. In coil 10 isothermal mode is used; temperature in the reaction zone equals to the maximum temperature, given by the pyrolysis conditions (775-850^{0}C). At this temperature thermal decomposition of hydrocarbons occurs resulting in the formation of olefines. At slow cooling of pyrolysis gases in pipeline at the output the secondary reactions begin to occur from the furnace, as a result of which the compositions of ethylene and propylene reduce. Therefore, at the output of pyrogas from the furnace coolers 11 and 12 are installed, in which cooling agent (for example, water, dry ice) is used for fast cooling. Cooled pyrogas is directed to separator 13. From separator liquid products of pyrolysis are accumulated in the tank 17, where their amount is defined, then they are sent to chromatograph for analysis. Gaseous products from separator 13 are cooled by cooling agent in additional cooler 14, after which sent to separator 15, where further separation of gaseous products and residual liquid products of pyrolysis happens; liquid products are sent to meter 17, gaseous products are sent through meter 16 to chromatograph for analysis.

3.Results and discussion

Chromatographic composition of tar oil in coke production taken as a research object – low sulphur containing oil of Azerbaijan and dry gas components (other components are not shown, since they are not related to the subject of the paper) separated in catalytic cracking process and obtained during using heavy pyrolysis resin as an additional raw material along with fractions given from catalytic cracking unit at 420°C are shown in table 1, the composition of fractions rich in non-saturated hydrocarbons formed in catalytic cracking and pyrolysis processes are are shown in table 2.

When reviewing the composition of gas components given in table 2 we see that ethylene+ethane is 27.4% of gas components, but propylene+propane is 36.4% of gas components and it would be more efficient to give them directly to gas-separating section of pyrolysis unit after treating them from sulphuric compounds to separate them to individual components. Decomposition of ethane and propane and pyrolysis of the fraction will cause loss of target raw material and loading of excess energy. As table 2 shows butane-butylene and butylene-divinyl fractions contain large amount of non-saturated hydrocarbons and this is not efficient during the process.

Table 1. Chromatographic composition of dry gas with coking installation and catalytic cracking, % mass.

Components	Compositions, % mass		
	Tar oil+>420°C fraction	Tar oil +>420°C fraction +heavy resin	Separated from average CC unit
Hydrogen	1,20	1,1	1,31
CO_2	0,48	0,30	3,20
CO	1,12	0,85	13112
CH_4	45,96	44,12	12,34
Nitrogen	0,18	0,10	7,38
Ethylene	3,7	4,68	10,68 6,5
Ethane	23,8	24,8	14,11 20.9
Propane	12,7	13,6	7,645 14,2
Propylene	6,3	6,8	27,42 22,2
n-C_4H_{10}	1,1	0,9	1,45
n-C_4H_{10}	0,66	0,58	2,31
Trans butene-2	0,45	0,41	1,18
n-C_5H_{12}	0,7	0,67	7,53
cis- butene-2	0,13	0,11	2,07
H_2S	1,02	0,98	>20000
Total:	100	100	

Table 2. Qualitative composition of butane-butylene fraction obtained from cracking unit, as well as butylene-divinely fraction obtained from pyrolysis.

Components	Butane-butylene fraction	Butylene-butadiene fraction	Mixed fraction
C_3H_8	-	0,3	1,4
C_2H_6	0,01	-	0,07
C_3H_6	1,3	0,02	1,93
n-C_4H_{10}	35,61	16,48	16,78
n-C_4H_{10}	9,25	9,08	15,89
Propadiene	-	-	0,73
Acetylene	-	-	0,02
Trans 2-butene	11,72	10,92	2,73
Butene-1	8,65	13,06	6,38
Isobutylene	12,54	12,24	22,25
n-pentane	-	-	0,03
cis-butene-2	9,80	4,74	1,8
n-pentane	-		0,01
1,2-butadiene	-	0,08	0,07
Butadiene-1,3	1,27	31,45	28,1
methylacetylene		0.01	0,01
Isoprene			1,01
Trans 2-pentene			0,01
n-hexane			0,01
Vinylacetylene		1,55	0,77
Ethylacetylene		0,10	0,01
CH_4	0,16		
H_2			
C_5+C_6 olefins	9,68		
CO_2	0,01		
Total	100,0		100,0

It is known that during divinyl pyrolysis aromatic compounds and resins are mainly produced. Pyrogas produced from the decomposition of butylenes does not contain much propylene, it contains considerably less ethylene. From other side the presence of divinyl in pyrolysis raw material causes hard-to-treat deposits in coils in the convection section of pyrolysis furnace [7,8] and carbon monoxides formed during their treatment process leads to much more environmental pollution than the norms provided in normative - technical documents. One of the efficient processing methods of raw materials comprising non-saturated hydrocarbons is the complete hydrogenation of divinyl and butylene till butanes [9,10]. As a result we obtain a good pyrolysis raw material which provides high yields of ethylene and propylene. Hydration of mixed butane-butylene and butylene-divinyl fractions is perfomed in the presence of palladium catalyst «OleMax-450» and «OleMax-453» produced by «Clariant» in a liquid phase at 60-80^{0}C.

Hydration of divinyl occurs primarily on the first layer of the reactor filled with the catalyst «OleMax-450»:

$$C_4H_6 + H_2 \rightarrow \text{1- } C_4H_8 + 28\ \text{kcal/g}\cdot\text{mol}$$

Apparently, butylene is formed first and is transformed to n-butane on the next stage (in the second layer in the reactor filled with catalyst «OleMax-453»):

$$\text{1-}\quad C_4H_8 + H_2 \rightarrow \text{n-}C_4H_{10} + 30\ \text{kcal/g}\cdot\text{mol}$$

Hydration of butylenes in fractions takes place simultaneously. Cis-butene-2 and trans-butene-2 are transformed to n-butane:

$$\text{2-}\quad C_4H_8 + H_2 \rightarrow \text{n- } C_4H_{10} + 28\ \text{kcal/g}\cdot\text{mol}$$

Isobutylene is transformed to isobutane:

$$\text{iso-}C_4H_8 + H_2 \rightarrow \text{iso- } C_4H_{10} + 28\ \text{kcal/g}\cdot\text{mol}$$

Propylene contained in hydrocarbon C_4 fractions is hydrated from catalytic cracking to propane:

$$C_3H_6 + H_2 \rightarrow C_3H_8 + 30 \text{ kcal/g} \cdot \text{mol}$$

Hydration of propylene proceeds more slowly than butylenes.

Hydrogen with the drier C-2_{1-2} of gas-separating installation «EP-300» is used for hydration process. The composition of hydrogen fraction conforms to the standard TR 38.30302-88 and is given in table 3.

Table 3. Composition of hydrogen fraction obtained from «EP-300».

№	Components	Required norm, %
1	Hydrogen, volume ratio %, not less than	90
2	Methane, volume ratio %, not less than	8,9
3	Carbon monoxide, volume ratio %, not less than	0,001
4	Carbon dioxide, volume ratio %, not less than	0,003
5	Oxygen, volume ratio %, not less than	0,05
6	Mass concentration of water steam at 20^0C, pressure 101,3 Kpa (760 mmHg), g/m^3, not more than	0,86
7	Sulfide, amount %, not more than	Not acceptable

As a result of complete hydration of non-saturated and diene hydrocarbons (divinyl and butylene), we obtained pyrolysis raw material with high yield of ethylene and propylene in the composition of butylene-butadiene fraction C_4 till n- and iso-butane. In the composition of mixed fraction after hydrogenation process mass ratio of propylene reduces from 1,93% to 0,0 %; propadiene - from 0,73% to 0,0 %; trans-butene-1 - from 2,73% to 0,0 %; butene-1 - from 6,38% to 0,0 %; isobutylene - from 22,25% to 0,60%; cis-butene-2 - from 1,80% to 0,89%; butadiene-1,3 - from 28,1% to 0,02 %.

In laboratory experiments when oily gas fraction obtained in catalytic cracking unit as a raw material for pyrolysis is undegone pyrolysis by mixing it with ethane fraction obtained in pyrolysis at different ratios, in the range of 825-855°C ethylene yield is found to be 20-22%, propylene yield is 20-23% (mass ratio), under the same conditions when hydrogenated fraction is used ethylene yield is found to be 32,4%, propylene yield is 17,5%. As per the experimental results considering economical and ecological relevance of by-products produced during oil refining and petrochemical processes more efficient processing diagram is suggested.

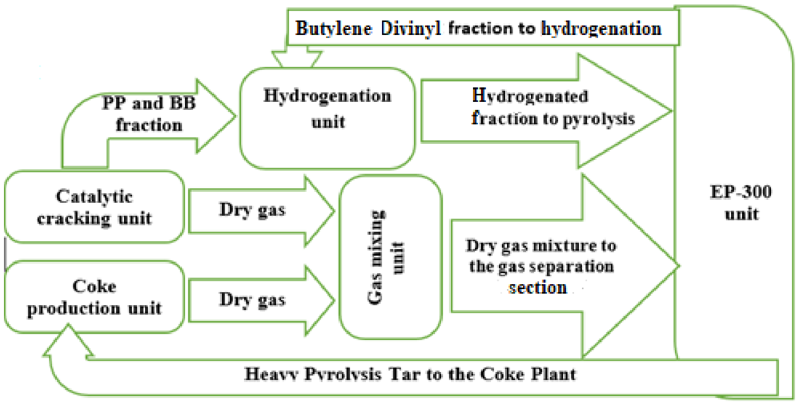

Fig. 2. Rational processing block of by-products.

4. Conclusions

The proposed processing method allows increasing efficiency coefficient of a primary product in the production of target product, and reducing the amount of wastes thrown into atmosphere.

5.References

1.A.Mammadov, I.P.Semyonov, A.I.Absattarov // «Experience in processing of fractions C_2-C_3 in catalytic cracking units on ethylene and propylene production plant» Chemical technology, №11, 2017, p.32-39.

2. Delayed coking process and production of petroleum cokes specialized in application/ G.G.Valyavin, V.P.Zaporin, R.G.Gabbasov, T.I.Kalimullin .// Oil and Gas Territory, 2011. – №8 – p. 44-48.

3. V.S.Aliyev, M.I.Rustamov, E.I.Pryanikov. Modern state and ways of intensifying catalytic cracking process. Baku, Azarnashr. 1966, p.242
4.Aliyev A.M., Babayev A.I., Tahirov A.Z., Huseynova A.M., Ismayilov N.R. Mathematical modeling and optimization of industrial process of pyrolysis of ethane with butane-butylene fraction in view of feedback // Azerbaijan Chemistry Journal, 2010, № 2, p.16-24.
5. Babayev A.I., A.M.Aliyev, A.Z.Tahirov, A.M.Huseynova. Modeling and optimization of industrial processes of pyrolysis of paraffine hydrocarbons and their mixtures with feedback // II International conference of D.I.Mendeleyev Russian chemical society «Innovative technologies and biotechnology of materials and products», Theses, Moscow, 2010, p. 11-13.
6.T.I.Mukhina, N.L.Barabanov, S.E.Babash, V.A.Menshikov, G.L.Avrekh. Pyrolysis of hydrocarbon raw material. Moscow, Publishing house «Chemistry» 1987, pp. 239.
7. F.A.Samadov, A.Yu.Morozov, N.A.Samoylov, T.R.Prosochkina. Mathematical modeling of non-stationary process of pyrolysis of hydrocarbons // Petrochemistry. – Moscow, 2019. – № 2. – p. 143 – 151.
8. R.R.Salimgareev, S.B.Rachkovsky. Modeling of work mode of pyrolysis pipe still // Bulletin of Kazan Technological University – 2016. – №12. – p.79 – 81.
9. Patent №2658417 Russian Federation B 01 J 8/22, B 01 J 19/00. Method of increasing efficiency of selective hydrogenation / O.K.Shurupov, V.P.Zakharov, F.B.Shevlyakov and others; applicant and patentee FSBEI of Higher Education 120 "Bashkir State University". – №2017119294; applied 01.06.2017; published. 21.06.2018, Bulletin. 18. – 9 p.
10. Enhancement of the Efficiency of Selective Hydrogenation of Acetylene Hydrocarbons in the Butylene–Butadiene Fraction during Butadiene-1,3 Production / O. K. Shurupov, I. S. Nasyrov, V. P. Zakharov et al. // Petroleum Chemistry. – 2018. – Vol. 58. – №10. – pp. 905–909.

PL-9

COMPLEXES OF OIL PORPHYRINS WİTH D-METALS, THEİR STABİLİTY AND USE İN CATALYSİS

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Abstract: The study of the properties and use of natural metalloporphyrins in the development of new highly selective methods for the oxygenation of hydrocarbons at moderate temperatures is an urgent problem. The present work is devoted to the extraction of metalloporphyrins from oil residues and the creation on their basis of effective catalytic systems for the oxidation of alkenes. The separation of metalloporphyrins from oil residues was carried out using new bifunctional organic extractants having the nature of keto-alcohols and providing a greater degree of extraction of porphyrins in comparison with the known traditionally used extractants. The results of a study of a number of new bifunctional organic reagents as extractants for the selective extraction of oil porphyrins from asphaltenes are presented, their spectral characteristics are studied, the dependence of the degree of extraction on the mass ratio of the extractant and the crude oil is revealed. The best results were obtained with a mass ratio of 1:30. The isolated mixture of metalloporphyrins is first subjected to demetallization with hydrochloric acid (pH = 1-2), turning into a mixture of porphyrins, then, to obtain individual metal porphyrin complexes, the required transition metal ions are introduced into the porphyrin ring by treating the mixture with these metal salts. It was shown that the yield of synthesized oil porphyrins is 42-85%, depending on the nature of the metal. The composition and structure of the synthesized oil metalloporphyrins containing iron, cobalt, nickel, manganese are established by modern methods of physico-chemical analysis. The catalytic properties of synthesized metalloporphyrins in the epoxidation of unsaturated alkenes have been investigated. Their dioxide adducts were obtained, and a mechanism was proposed for the oxidation of alkenes with the formation of oxinoid structures as a result of the decomposition of the oxygen complexes of metal porphyrins.

Key words: oil metalloporphyrins, bifunctional extractants, asphaltenes, dioxide adducts, alkenes epoxidation.

1.Introduction

Interest in the porphyrin complexes of transition metals is growing due to the possibilities of their use as catalysts. In the literature [1–8] there are a sufficient number of works in which porphyrin complexes of transition metals are used as highly selective catalysts for the oxidation of hydrocarbons at moderate temperatures. Unlike metal complexes of organic compounds, porphyrin transition metal complexes can be considered as reconstructed natural enzymes. However, synthetic metalloporphyrins are practically insoluble in hydrocarbons and require the use of complex and expensive additional chemicals to homogenize the system. In this regard, natural metalloporphyrins are of particular interest, which, due to the presence of ether, ester fragments and alkyl radicals in the side branches, dissolve well in hydrocarbons.

Among natural metalloporphyrins, oil metalloporphyrin complexes are particularly interesting, which are distinguished by their simplicity of preparation and potential applications in petrochemical processes. Literature sources [9–15] provide information on their use for producing high-octane gasolines as antiknock agents to gasolines in the catalytic purification of natural gas from hydrogen sulfide and to create a membrane material for purifying natural gas from radon.

Oil metalloporphyrins are extremely interesting objects for creating supramolecular formations of various structures that exhibit unique photophysical and chemical properties [1, 16]. This work is devoted to the current research topic of oil porphyrins, the interest in which has been steadily growing in the last two decades. The main task and merit of the presented work is its practical orientation, which is lacking in the vast majority of other works in this area carried out by well-known foreign and domestic teams.

It is no secret that the study of the applied properties of oil porphyrins is inhibited by the complexity of their isolation in pure form. The study is aimed at solving the problem of extracting oil porphyrins and studying their catalytic properties by the example of the epoxidation of olefins, well studied for synthetic metalloporphyrin catalysts.

In this paper, let's present the results of studies on the synthesis and selection of effective extractants for the separation of metalloporphyrins from oil residues, the development of a method for the synthesis of catalytic systems based on extracted porphyrins, and their study as catalysts for the alkene oxidation reaction.

2. Experimental part

The primary task to accomplish the purpose of this study was to extract natural metalloporphyrins from oil residues.

The heavy oil residues (asphaltenes) of the Azerbaijan oil of the Oil Rocks deposit, the characteristics of which are given in **Table 1**, were used as feedstock for the production of individual metal porphyrin complexes. 1 [17].

Table 1. Characteristics of oil used in the Oil Rocks field

Field	Depth, m	Density, kg/m^3	Viscosity at 20 °C, mm/s^2	Pour temperature, °C	Content, %				Fraction yield, %	
					Sulfur	Resin	Asphaltenes	Paraffin wax	To 200° C	To 300 °C
Oil Rocks	2600	884-887	20,8-29,8	-20	0,16-0,21	10,0-12,0	0,10-0,58	0,30-1,0	10-20	42-52

Extraction chromatographic isolation of metalloporphyrins from asphaltenes.

To isolate the porphyrin concentrate from asphaltenes, gasoline was added to the oil sample in the flask (i.e. boiling fractions of 35-85 °C) to lower the viscosity. Then the extractant was poured into the flask and the mixture was carefully mixed. In this case, the oil sample in the solvent disintegrated into small droplets, thereby achieving good extraction. The mixture was heated with stirring at a temperature of 50-120 °C for 2 hours. After this period, the mixture settled at room temperature for 5 hours. Then the extract was filtered, the filtrate in the presence of porphyrins had a pink color. It was noted that if porphyrin was absent or there were very few, the color was slightly green.

The solvent was completely removed in vacuum using a water-jet pump. The remainder in the flask in the form of a colored oil film was transferred with benzene into a measuring vessel (35-40 ml) and diluted to a certain color depending on the content of porphyrin complexes, making sure that the initial optical density was not more than 0.6- 0.8. The measurements were carried out on a SPICORD UV-VİS and SF-26 spectrophotometer.

The contents of vanadyl- and nickel- porphyrins were determined spectrophotometrically.

$$C_{VP}=(4,76\cdot V\cdot A_{568})/m\cdot l, \qquad (1)$$

$$C_{NiP}=(3,15\cdot V\cdot A_{528})/m\cdot l, \qquad (2)$$

where C_{VP}, C_{NP} – respectively, the concentration of vanadyl and nickel porphyrins, mg/100 g of oil; V – volume of solvent, cm^3; A_{568} and A_{528} are optical densities at the maxima of the analytical absorption bands; m – a sample of oil asphaltene, g, l – cell thickness.

Reference A was taken from the baseline, for which the background absorption curve of resinous components was used. The concentration of vanadyl porphyrins in asphaltenes, determined according to UV spectroscopy, was 180-195 mg/100 g. The degree of extraction of vanadyl porphyrins was calculated from their content in asphaltenes and in extracts.

The method of obtaining oxygen adduct

2.28 g of cobalt (II) oil porphyrin complex and 40 ml of carbon tetrachloride were placed in a 100 ml metal ampoule, the ampoule was connected to an oxygen cylinder under a pressure of 5.0 MPa and the rocker was turned on. The reaction was carried out at room temperature for 3 hours. The end of the reaction was established by stopping the absorption of oxygen. At the end of the reaction, the contents in a metal ampoule were cooled at normal pressure, and the precipitate formed was filtered through a glass filter. The obtained brown solid precipitate 1.52 g (62.3%) after washing with oil ether and drying at room temperature was analyzed using cobalt spectrophotometric method [9, 14]. The cobalt content in the sample of the oxygen adduct determined by atomic absorption spectrometry [19] was 6.25%.

The method of epoxidation of alkenes with a dioxid adduct

0.45 g of oxygen adduct and 35 g (0.5 mol) of 1-pentene were placed in a metal ampoule and heated at 60 °C for 3 hours, then the reaction mixture was filtered using a glass filter, the filtrate was determined by GLC yield 1,2-oxidopentane, amounted to 65% (according to the olefin taken in the reaction).

Physico-chemical methods for the study of synthesized metalloporphyrin complexes

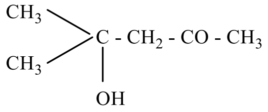
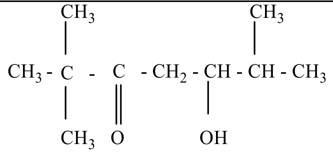
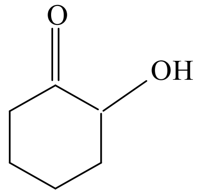
IR spectra were recorded on a SPECORD-M80 spectrometer in the region of 4000-400 cm-1 in KBr tablets. Electronic spectra were recorded using UV/Vis SPICORD and SF 16 spectrophotometers. To determine the content of metals (Mn, Fe, Co, Ni) in the isolated metalloporphyrins, the AAS-300 atomic absorption spectrometer, Perkin-Elmer, was used. Gas-liquid chromatographic analyzes were carried out on an LKhM-8MD chromatograph, column sizes 5*2.5 m, carrier helium gas, absorbent PEG-1000. The obtained epoxy compounds were identified by GLC and specific chemical transformations characterizing the oxirane ring.

3. Results and discussion

To isolate a mixture of metalloporphyrins from oil residues, the selective extraction method is usually used in petrochemistry using an ethanol-acetone mixture as an extractant with a degree of isolation of porphyrins in the amount of 50-60%, as well as a method using dimethylformamide (DMF) with a significantly higher degree of isolation [18 -20], although, along with metalloporphyrins, various classes of organic substances are extracted, which is a drawback of this method.

In order to increase the selectivity and efficiency of the extraction of metal porphyrins from oil for extraction chromatographic isolation, new bifunctional organic extractants were synthesized and proposed for use: 2-methyl-pentanon-4-ol-2 (I), 2,2,5-trimethylheptanone-3- ol-5 (II), 2-hydroxycyclohexanone (III). **Table 2** shows some characteristics of extractants I-III.

Table 2. Some characteristics of synthesized by extractants I-III used for the selective extraction of oil metalloporphyrins

№	The structure and name of ketone alcohols	Molecular mass	Characteristic absorption bands in the IR spectrum, ν cm^{-1}
I	 $(CH_3)_2C(OH)-CH_2-CO-CH_3$ 2-methylpentanon-4-ol-2	116	3520 (-OH), 1708 (C=O)
II	 $CH_3-C(CH_3)_2-C(=O)-CH_2-CH(OH)-CH(CH_3)-CH_3$ 2,2,6-trimethylheptanon-3-ol-5	172	3595 (-OH), 1711 (C=O)
III	 2- hydroxycyclohexanone	114	3340 (-OH), 1715 (C=O)

Synthesis of bifunctional extractants (I-III)

Samples of bifunctional ketone alcohols are synthesized as follows:- obtaining 2-methylpentanon-4-ol-2 (I).

1 mol of acetone was placed in a 250 ml round bottom flask with a Soxhlet stirrer and reflux condenser. The sleeve was filled to half with barium oxide, covering it with a lid on top. The flask was heated in a water bath. The end of the reaction was established by stopping the boiling of the liquid in a boiling water bath (30 hours), after which the contents of the flask after filtration were distilled in vacuum, boiling temperature 83 ºC; n_D^{20}1.4235. The product yield was 70%;

- obtaining 2,2,5-trimethylheptanon-3-ol-5 (II).

To magnesium shavings (0.6 mol) coated with 40 ml of ether was added dropwise 0.5 mol of bromine pinacoline [(CH3) 2-C-CO-CH2Br] and 0.6 mol of methyl ethyl ketone in 160 ml of ether. The reaction was initiated by the addition of a small amount of magnesium activated with methyl iodide. After the start of the reaction, 200 ml of benzene was rapidly added with vigorous stirring. The mixture was boiled for another 1 hour, and then upon cooling, it was hydrolyzed with a calculated amount of hydrochloric acid in 200 ml of water. The organic layer was washed with 100 ml of water, then 200 ml of 1 N sodium hydroxide was added with stirring over 1 hour to destroy the bromketone residues. After distillation, ketol was obtained with a yield of 66%, boiling temperature 87–88 ºC; n_D^{20} 1.4339;

- obtaining 2-hydroxycyclohexanone (III).

A solution of 10 g (0.102 mol) of cyclohexene oxide and 0.12 ml of boron trifluoride etherate in 40 ml of dimethyl sulfoxyl (dimethyl sulfoxide prepared by azeotropic distillation with benzene) was heated in a steam bath for 22 hours. The catalyst was introduced into the reaction mass twice at 15 and 20 hours in the amount of 0.06 ml and 0.04 ml, respectively. The reaction mixture was poured into ice water and extracted with chloroform. The extract was dried, the solvent (chloroform) was distilled off, 2-hydroxycyclohexanone was obtained from the residue, yield 76%, boiling temperature 83–88 ºC.

Asphaltenes extracted from heavy oil do not dissolve in extractants (I-III) at temperatures below 100ºC, however, at higher temperatures, the dissolution of oil in these extractants becomes noticeable. Unlike bifunctional extractants, monofunctional compounds, such as acetone, ethyl alcohol, DMF [18] dissolve oil quite noticeably. This makes it difficult to isolate pure metalloporphyrin concentrates. Due to the fact that bifunctional extractants do not dissolve oil and selectively extract metalloporphyrins from oil, it becomes possible to obtain oil metalloporphyrin concentrates in high yields. The results of these studies are given in Table 3.

Table 3. Solubility of asphaltenes extracted from heavy oil with extractants (I-III).

Extractants	Solubility, mg/g			
	50 °C	100 °C	120 °C	140 °C
2-methylpentanon-4-ol-2	-	-	6,5	12
2,2,6-trimethylheptanon-3-ol-5 (II)	-	-	5,8	9,6
2-hydroxycyclohexanone (III)	-	-	3,7	6,4
Acetone	25	58	102	117
Ethanol	18	22	87	103
DMF	-	38	54	73

Table 4 contains results of the extraction of metalloporphyrins from asphaltenes with the introduction of extractants I-III.

Table 4. The results of extraction chromatographic isolation of vanadyl and nickel porphyrins from asphaltenes with a mass ratio of extractant/asphaltene equal to 1:30

Extractants	MP extraction degree, %							
	50 °C		100 °C		120 °C		140 °C	
	VP	NP	VP	NP	VP	NP	VP	NP
2-methylpentanon-4-ol-2 (I)	28,7	-	56,6	-	73,8	6,4	87,4	11,2
2,2,6-trimethylheptanon-3-ol-5 (II)	19,2	-	32,6	-	53,1	-	62,4	-
2-hydroxycyclohexanone (III)	42,5	-	69,6	1,8	92,4	2,8	98,7	6,1
Acetone	23,5	6,4	-	-	-	-	-	-
Ethanol	11,4	5,8	-	-	-	-	-	-
DMF	29.3	1.3	33.4	2.1	58.1	3.5	63.2	5.8

Fig.1 shows the dependence of the degree of extraction of asphaltenes on the mass ratio of extractant/asphaltene.

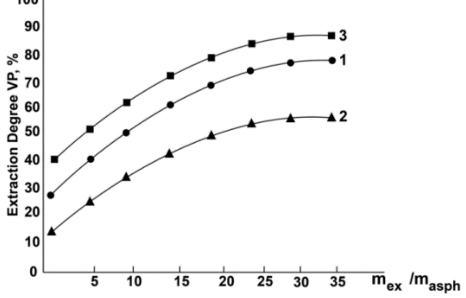


Fig. 1. The dependence of MP extraction degree from the mass ratio of extractant/asphaltene. at $T_{ex.}$=120 °C: • – diacetone alcohol; ▲ – 2,2,5-trimethylheptanon-3-ol-5▲ – 2-hydroxycyclohexanone

A study of the influence of the ratio of the mass of extractant to the mass of asphaltene taken on the efficiency of extraction of natural metalloporphyrins showed that the degree of extraction of metalloporphyrins (MP) increases with an increase in this indicator. The most optimal results are obtained with a mass ratio of extractant to asphaltene equal to 1:30. A further increase in the ratio of extractant/asphaltene does not lead to a change in the extraction degree.

Synthesis of metalloporphyrin catalysts

The porphyrin mixture isolated from oil residues can't be used as a catalyst for the oxygenation of hydrocarbons, since different metals direct the reaction by a different mechanism. In this regard, the mixture of metalloporphyrin complexes of oil was further subjected to the following transformations for the synthesis of target catalysts containing individual transition metals.

The following is a description of the synthesis of metal-individual metalloporphyrin complexes from porphyrin concentrate:

1. The oil porphyrin concentrate is demetallized by mixing it with a dilute hydrochloric acid solution (7-9%). As a result of this treatment, oil metalloporphyrin complexes decompose into the corresponding porphyrin and metal ion, which passed into the aqueous layer. The first stage can be represented as follows:

$$MP+4NaX\rightarrow[Na_2P]\cdot 2X+MX_2,$$

where $[Na_2P]$ is a doubly charged porphyrin cation, MP-metalloporphyrin complex, X-ion of chlorine (Cl^-).

Treatment with a hydrochloric acid solution was carried out until the characteristic absorption bands at 515 nm, 563 nm and 528 nm in ultraviolet radiation/species disappeared spectra, which indicates the complete decay of the oil metalloporphyrin complex.

2. The complex $[N_2P]\bullet 2X$ was neutralized with alkali to pH = 6-8 in order to obtain oil porphyrin:

$$[Na_2P]\cdot 2X+2NaOH\rightarrow P+2NaX+2H_2O.$$

After neutralization, the reaction mass was washed with water until a neutral reaction was dried by azeotropic distillation with benzene. After removal of benzene, the oil porphyrin is distilled in a deep vacuum.

3. The isolated oil porphyrin was dissolved in benzene, and pre-prepared sodium phenyl in excess was added to the resulting solution. As a result of this reaction, the hydrogen atoms of two nitrogen of the porphyrin ring were replaced by sodium atoms according to the scheme:

$$P+2PhNa\rightarrow Na_2P+2C_6H_6,$$

where P – a doubly charged porphyrin anion

Next, the disodium derivative is treated in absolute alcohol with the acetate of the desired transition metal (Fe, Mn, Co, Ni). Moreover, almost with a quantitative yield, the corresponding individual metal complex is formed:

$$Na_2P+M(OCOCH_3)_2\rightarrow PM+2CH_3COONa.$$

After distillation of ethyl alcohol to 1/3 of the volume, colored crystals of MP-metalloporphyrin complexes are separated from the solution upon standing. Isolated metalloporphyrins are characterized by IR spectra. **Table 5** shows the values of the melting temperature, yields and results of elemental analysis of the synthesized metalloporphyrins.

Table 5. Physico-chemical properties of synthesized metalloporphyrin catalysts

Metalloporphyrins	Melting point, °C	Yield, %	Found, %		
			C	H	N
CoP	257	85	72.04	6.68	10.39
FeP	261	87	71.63	6.71	10.57
NiP	283	90	71.65	6.71	10.39
MnP	271	42	71.6	8.10	12.30

4. Discussion of results

The research results (Table 4) indicate that the extractants I-III synthesized in this work are superior to the widely used extractants, such as acetone, ethyl alcohol, and DMF, in the extraction efficiency of metalloporphyrins.

When passing from 2-methyl-pentanon-4-ol-2 to 2-hydroxycyclohexanone, the degree of extraction increases sharply and the latter almost quantitatively extracts porphyrins at temperatures of 120-140 °C.

The metal porphyrins extracted from oil residues served as the basis for the synthesis of metal porphyrin complexes of iron (FeP), cobalt (CoP), nickel (NiP) and manganese (MnP). The formation of metalloporphyrin complexes (MP) as a result of these transformations was established using spectral data. In the IR spectra of metal porphyrins based on the oil porphyrin complex (OPC), characteristic bands were found that confirm the presence of the hemin ring. Thus, pyrrole fragments are characterized by absorption bands at vibrational frequencies of 1507, 1522, and 1608 cm^{-1}. Absorption band at 856 cm^{-1} corresponds to non-planar deformation vibrations of the methine bridges of the porphyrin ring. The absorption band at 636 cm^{-1} corresponds to signals of non-planar deformation vibrations of the = NH, -CN and C = N groups of the group are characterized by absorption bands at 1376 cm^{-1} and 1441 cm^{-1}, respectively. Table 6 contains spectral characteristics of synthesized metalloporphyrins.

Table 6. Spectral characteristics of synthesized oil metalloporphyrin complexes

Metalloporphyrins	Absorption bands in the electronic spectrum maximum, nm	Absorption bands in the IR spectrum maximum, ν cm^{-1}
CoP	417, 533, 551	1507, 1522,1608 (p.r.), 856(CH_2),636 (=NH)
FeP	411, 534, 570	1512, 1520, 1599 (p.r.), 850 (CH_2),634 (=NH)
NiP	405, 520, 556	1503, 1517, 1602 (p.r.) 847(CH_2),641 (=NH)
MnP	415, 528, 557	1506, 1512, 1600 (p.r.) 845(CH_2),639(=NH)

Electronic absorption spectra in the ultraviolet and visible spectral ranges, oil porphyrin concentrate and metalloporphyrins are shown in **Fig. 2**. Let's note that the UV/species spectra of all oil metalloporphyrins are usually characterized by an intense Soret band (λ_{Max} ~400 nm). In addition to this band, four so-called Q low-intensity bands are observed in the electronic absorption spectra.

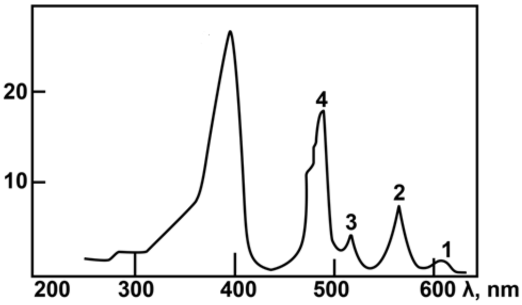


Fig. 2. Electronic absorption spectra of oil porphyrin in paraffin at a temperature of 25 °C

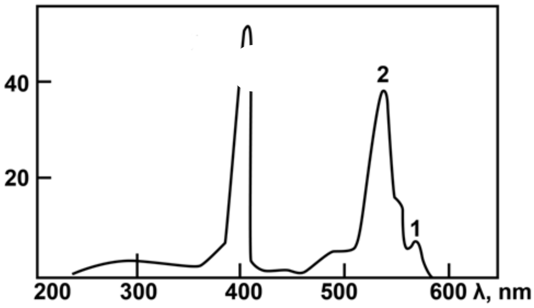


Fig. 3. Electronic absorption spectra of metalloporphyrin in paraffin at a temperature of 25 °C

The spectrum of a solution of oil porphyrin in the visible region (Fig. 2) consists of four main absorption bands. A comparison with the spectrum of metal porphyrins by the example of metalloporphyrin (Fig. 3) shows that bands 1 and 3 are much more intense, and the intensity of band 2 is approximately the same as that of oil porphyrin. The introduction of an iron atom into the porphyrin ring leads to a narrowing of the Soret band. In addition, instead of four bands, two (1 and 2) bands are observed, with noticeably different intensities. It should be noted that the form of the electronic absorption spectra of porphyrins noticeably differs for different porphyrins and in different media [19-21].

In order to study the catalytic properties of the synthesized metalloporphyrin catalysts in the oxidation reaction of unsaturated hydrocarbons, their oxygen species were synthesized.

The scheme of oxygenation and the formation of the oxygen adduct is shown by the example of a cobalt porphyrin sample:

$$2PCo^{II}+O_2\rightarrow PCo^{III}\ldots O\text{–}O\ldots Co^{III}P \qquad (1)$$

The infrared spectral data of the cobalt porphyrin complex and its dioxide adduct are shown in Fig. 4

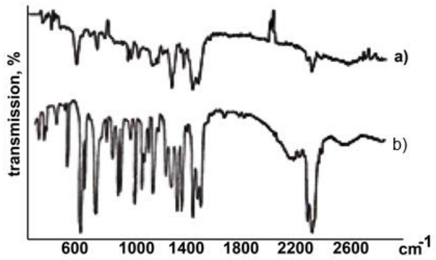


Fig. 4. IR spectra of metalloporphyrin complexes: a – cobalt porphyrin complex, b – adduct of cobalt porphyrin complex

The IR spectrum of the oxygen complex (2) **Fig. 4** shows a characteristic absorption band at 1127 cm^{-1}, confirming the presence of a oxygen fragment in complex (2). The IR spectra of both porphyrin complexes and their dioxide adducts are fairly well described in the literature [22, 23]. They indicate that the frequencies ν (O-O), characteristic of complexes of transition ions with molecular oxygen, are found in the region of 1104-1226 cm^{-1}. In this regard, it can be argued that the absorption band at 1127 cm^{-1} is formed during the interaction of molecular oxygen with metalloporphyrins and may be an indicator of the formation of dioxide adducts of metalloporphyrins with molecular oxygen.

When comparing the cobalt content in the complex compound (1) and the oxygen adduct (2), it was found that the molar ratio of the complex to molecular oxygen is 2:1.

An important feature of the dioxide adduct of the cobalt (II) oil porphyrin complex (2) is that such dioxide adducts epoxidize olefins [22, 23]. Thus, the previously prepared adduct (2) epoxidizes 1-pentene, forming 1,2-oxidopentane.

The totality of the obtained results allows to state that although the electron transfer from Co (II) to oxygen is completed completely, the obtained oxygen-oxygen adduct (2) can’t be represented as a complex in which cobalt (P) ion combines with singlet oxygen.

It should be noted that the oxygen dioxide anion (O_2^{2-}) in the complex compound (2) can’t directly epoxidize the olefin, because O_2^{2-} anion is not electrophilic. An alternative mechanism for the epoxidation of alkenes with a dioxide adduct (2) allows the occurrence of oxinoid resonance structures A and B resulting from the decomposition of the cobalt (II) dioxide porphyrin complex (2):

$$PCo^{III}\ldots O\text{—}O\ldots Co^{III}P\rightarrow PCo{=}O\leftrightarrow PCo^{+}O^{-} \qquad (2)$$

The formation of 1,2-oxidopentane is quite possible in the interaction of 1-pentene with an oxinoid resonance structure A having electrophilic oxygen according to the scheme (fig. 5):

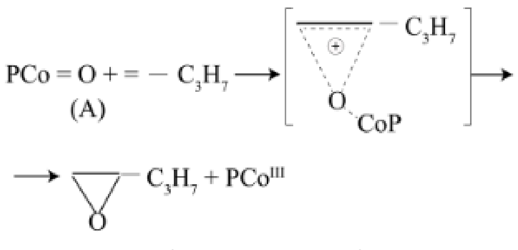


Fig. 5. Mechanism of 1,2-oxidopentane formation

The resulting 1,2-oxidopentane was identified by gas-liquid chromatography.

It turned out that during the oxidation of pentene-1 in the presence of catalytic amounts of the considered oil metalloporphyrin complexes at room temperature, pentane oxide is formed in yields of 27-47%. By a similar method, the epoxidation of trimethylene, cyclopentene, 1-methylcyclohexene and styrene was also carried out. The results of experiment[illegible]a on the epoxidation of olefins by molecular oxygen in the presence of oil metalloporphyrins indicate the possibility of their use as eloxidizing catalysts.

5. Conclusions

1. A highly effective method for the separation of metalloporphyrin concentrate from heavy oils and oil products using highly selective bifunctional organic compounds (ketone alcohols) with respect to metal porphyrins has been developed. The synthesized bifunctional compounds are superior in the efficiency of extraction of metalloporphyrins in comparison with known extractants. The best results were shown by estrogen-2-hydroxycyclohexanone.

2. Based on the porphyrin concentrate isolated from heavy oil residues, individual oil porphyrin complexes Mn, Fe, Co, and Ni were synthesized by a specially developed technique. The structure of the synthesized oil metalloporphyrin complexes and their oxygen species adducts were characterized by IR and electron spectroscopy.

3. The catalytic properties of the synthesized oil metalloporphyrin complexes were studied in the alkenes oxygenation reaction. An alternative mechanism for the epoxidation of alkenes by a dioxide adduct is considered, which allows the formation of oxinoid resonance structures.

References

1. Len, Zh. M. (1998). Supramolekulyarnaya himiya: Kontseptsii i perspektivy. Novosibirsk: Nauka, 334.
2. Groves, K., Lee, J. (2000). The porphyrin handbook. Vol. 4. Academic Press, 17–39.
3. Suslick, K. S. (2000). The porphyrin handbook. Vol. 4. Academic Press, 41–63.
4. Marchon, J.-C., Ramasseul, R. (2003). Chiral Metalloporphyrins and Their Use in Enantiocontrol. The Porphyrin Handbook, 75–132. doi: https://doi.org/10.1016/b978-0-08-092385-7.50009-4
5. Sheldon, R. A. (Ed.) (1994). Metalloporphyrins in catalytic oxidation. Marcel Dekker Inc, 390.
6. Barona-Castaño, J., Carmona-Vargas, C., Brocksom, T., de Oliveira, K. (2016). Porphyrins as Catalysts in Scalable Organic Reactions. Molecules, 21 (3), 310. doi: https://doi.org/10.3390/molecules21030310
7. Lesage, S., Xu, H., Durham, L. (1993). The occurrence and roles of porphyrins in the environment: possible implications for bioremediation. Hydrological Sciences Journal, 38 (4), 343–354. doi:https://doi.org/10.1080/02626669309492679
8. Imran, M., Ramzan, M., Qureshi, A., Khan, M., Tariq, M. (2018). Emerging Applications of Porphyrins and Metalloporphyrins in Biomedicine and Diagnostic Magnetic Resonance Imaging. Biosensors, 8 (4), 95. doi: https://doi.org/10.3390/bios8040095
9. Meunier, B. (1992). Metalloporphyrins as versatile catalysts for oxidation reactions and oxidative DNA cleavage. Chemical Reviews, 92 (6), 1411–1456. doi: https://doi.org/10.1021/cr00014a008
10. Achugasim, O., Ojinnaka, C., Osuji, L. (2013). Management of petroporphyrins in a crude oil polluted environment. European Chemical Bulletin, 2 (10), 794–796. doi:http://dx.doi.org/10.17628/ecb.2013.2.794-796
11. García-Arellano, H., Buenrostro-Gonzalez, E., Vazquez-Duhalt, R. (2004). Biocatalytic transformation of petroporphyrins by chemical modified cytochrome C. Biotechnology and Bioengineering, 85 (7), 790 798. doi: https://doi.org/10.1002/bit.20023
12. Maravin, G. B., Avdeev, M. V., Bagriy, E. I. (2000). Okislitel'naya funktsionalizatsiya nasyshchennyh uglevodorodov na metallokompleksnyh katalizatorah porfirinogo ryada. Neftehimiya, 40 (1).

REGULARITIES OF RHENIUM AND RUTHENIUM COORDINATION WITH ORGANIC NITROGEN-CONTAINING LIGANDS

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Abstract: The paper presents the results of research on the development of effective methods for the synthesis of complex rhenium and ruthenium compounds with a number of organic nitrogen-containing ligands. The composition, structure, and physical and chemical properties of new complexes of these transition-valence metals are studied, and patterns of changes in physical and chemical properties depending on the nature of the ligand are revealed. The composition and structure of the synthesized compounds are established on the basis of a set of data from elemental analysis, IR spectroscopy, ESP, and thermogravimetry. Based on the data set type of coordination of ligands: bidentate coordination of o-phenanthroline, monodentate-amide of nicotinic acid through the nitrogen atom of heterocycle and monodentate benzimidazole coordination through the pyridine nitrogen atom. A method for the synthesis of rhenium and ruthenium phthalocyanins is proposed.

Key words: complexes of rhenium and ruthenium, nitrogen-containing organic ligands, o-phenanthrolin, benzimidazol, a phthalocyanine.

1.Introduction

Currently, a huge amount of experimental and theoretical material has been accumulated in the field of coordination compound chemistry, which allows us to predict the activity of complexes in relation to living organisms, polymer-composite materials, and other objects [1-7, 10]. Today it is possible to perform complex syntheses of complexes with previously defined properties. Moreover, these complexes may have different structures and levels of complexity. It is well established that a number of complex compounds of rhenium and ruthenium exhibit antitumor properties. The coordination chemistry of these metals has developed significantly in recent years, driven largely by interest in the development of radiopharmaceuticals. It was found that their complex compounds can be successfully used for the diagnosis and treatment of cancers of various human organs. In this case, the radiotherapy drug can be delivered directly to the patient's diseased organ using specific molecular carriers, i.e. in the form of coordination compounds with a certain type of ligands and a certain structure [11-14].

However, much remains unexplored in the chemistry of these metals, and no regularities have yet been established in changing the physical and chemical properties of their compounds depending on the nature of the ligands.

Against the background of research in the field of complex compounds of rhenium and ruthenium with S - and P-containing ligands, there is a certain gap in the study of compounds with N-containing ligands [13]. This fact played a significant role in the formulation of this study.

All this makes it necessary to find new, convenient and purposeful ways to synthesize rhenium (V) and ruthenium (IV) complexes with nitrogen-containing ligands and to study the resulting compounds in more depth.

The aim of this work is to develop effective methods and optimal conditions for synthesis, to study the composition, structure and physical and chemical properties of new rhenium and ruthenium complexes with a number of organic ligands containing N-donor atoms. Determining the features of their structure, finding out the regularities of changes in physical and chemical properties depending on the nature of the ligand and various factors in order to identify the most promising substances with directed physiological activity.

2. Experimental part

The choice of ligands is not accidental, but is justified on the one hand by their wide use in medical chemistry, on the other hand by the fact that they contain donor nitrogen atoms in their composition.

It is known that coordination compounds of PM usually enhance the physiological activity of their constituent organic molecules. However, some metal ions have toxic effects and other harmful side effects on the body.

In this respect, the selected metals are an exception, since they are non-toxic elements. According to the literature data, some complex compounds of these enzymes show a protective effect in ulcerative diseases, have anti-carcinogenic activity, and are growth-regulating drugs of a number of agricultural crops. In this regard, it is of great interest to obtain and study Re and Ru complexes with the above ligands.

$H_2[ReOCl_5]$, where (x = Cl, Br), was used as the starting substances, which we obtained using the methods given in. Rhenium was determined as perrenate of Nitron [20], carbon, hydrogen and nitrogen-on an automatic analyzer of the company "Karlo Erba". The IR spectra of the obtained complexes were taken using the Specord M-80 and Specord 75-IR spectrometers, and the electronic absorption spectra were taken using the Specord UV VIS device. Thermal analysis was performed on the q-1500 d derivatograph of the "Paulik-Paulik-Erdei" system. Molar electrical conductivity of solutions of complexes was determined by the conductometric method. EPR spectra were taken using Radiopan SE/x2542 radio spectrometers. The mass spectra were obtained on the “Kratos” MS 890 mass spectrometer.

Synthesis of $[PhenH_2][ReOCl_5]$ (I). a Solution of 1.10- phenanthroline in hydrochloric acid was added to a solution of $H_2[ReOCl_5]$ in HCl. The reaction takes place at room temperature and stirring for 1.0 h. the fine-crystalline precipitate of light brown color Was filtered out after a day, treated with a weak HCl solution, washed with ether and dried at 105°C to constant mass.

Found,%: Re-25.01; C-19.10; H-1.72; N-4.03
For $[PhenH_2][ReOCl_5]$
Calculated,%: Re-24.44; C-18.90; H-1.58; N-3.68

Synthesis of $[PhenH_2][ReOBr_5]$ (II). An equivalent amount of 1.10-phenanthroline solution in HBr was added to the oxobromorenic acid solution in concentrated HBr. When stirring for 1.5 hours, the precipitation is completed in the form of small reddish crystals. The precipitate was filtered out a day later, washed with 5 mol / l HBr, benzene, ether, and dried in a thermostat at 105°C to constant mass.

Found,%: Re-23.68; C-17.64; H-1.81; N-3.22
For $[PhenH_2][ReOBr_5]$
Calculated,%: Re-23.22; C-17.96; H-1.50; N-3.49

Synthesis of $[ReOCl_3Phen]$ (III). 0.5 g of $PhenH_2[ReOCl_5]$ was placed in a test tube with two taps. For 1.5 hours, dry argon was passed through the test tube and heated in the argon current at a temperature of 195°C. Then the test tube was cooled, without stopping the argon supply, to room temperature. After thermal decomposition (I), the color of the substance changes to yellow-green.

Found,%: Re-38.24; Cl-21.40; N-5.74
For $[ReOCl_3Phen]$
Calculated,%: Re-38.10; C-21.76; N-5.73

Synthesis of [ReOBr3Phen] (IV). In the argon current, the $PhenH_2[ReOBr_5]$ suspension (0.5 g) in a test tube with two tubes was maintained at 190°C for 3 hours, then cooled in an inert atmosphere. After dehydrohalogenation and rearrangement (II), substance IV has a light green color.

Found,%: Re-29.36; C-22.85; H-1.07; N-5.10
For $[ReOBr_3Phen]$
Calculated,%: Re-29.94; C-23.15; H-1.29; N-4.50

Synthesis of $[HL]_2[ReOCl_5]$ (V). 0.46 mmol of benzimidazole was added to 40 ml of a solution of 0.15 mol $H_2[ReOCl_5]$ in HCl (8 mol/l) with strong stirring. The mixing was continued for 24 hours, the yellow precipitate was filtered out, successively washed with HCl (30 ml) and hexane (150 ml), and dried to a constant mass over KOH in a vacuum desiccator.

Found,%: Re-29.97; Cl-28.31; N-9.24; C-27.35; H-2.38
For $[HL]_2[ReOCl_5]$
Calculated,%: Re-30.14; Cl-28.73; N-9.07; C-27.20; H-2.27

Synthesis of $[HL]_2[ReOBr_5]$ (VI). 0.91 mmol of benzimidazole was added to 40 ml of a solution of 0.29 mol $H_2[ReOBr_5]$ in HBr (7 mol/l) with intensive stirring. After 16 hours of mixing, a reddish-yellow precipitate fell out. The precipitate was filtered out and washed with HBr (60 ml) hexane (120 ml). Dried over dry AIR in a vacuum desiccator to a constant mass.

Found,%: Re-22.02; Br-46.89; N-6.56; C-20.13; H-1.47
For $[HL]_2[ReOBr_5]$
Calculated,%: Re-22.16; Br-47.61; N-6.67; C-19.99; H-1.67

Synthesis of $[ReOL_2Cl_3] \cdot 2H_2O$ (VII). 0.45 mmol of benzimidazole was added to 40 ml of a solution of 0.15 mol $H_2[ReOCl_5]$ in HCl (6 mol/l) while stirring. After 24 hours of mixing, the light marsh-colored precipitate was separated by filtration. After cleaning, 40 ml of HCl and 30 ml of hexane were dried over solid KOH in a vacuum desiccator to a constant mass.

Found,%: Re-31.80; Cl-18.24; N-9.47; C-29.09; H-2.81
For $[ReOL_2Cl_3] \cdot 2H_2O$

Calculated,%: Re-32.06; Cl-18.34; N-9.64; C-28.93; H-2.75

Synthesis of [ReOL$_2$Br$_3$] · 2H$_2$O (VIII). 0.80 mmol of benzimidazole was added to 40 ml of the mixture of 0.30 mmol $H_2[ReOBr_5]$ in HBr (5 mol/l) with strong stirring. After 24 hours of mixing, the green precipitate was separated from the reaction mixture by filtration. Washed with 5 mol / l HBr (70 ml) and hexane (120 ml), dried over dry KOH in a vacuum desiccator to a constant mass.

Found,%: Re-25.89; Br-33.65; N-7.76; C-23.60; H-2.20

For $[ReOL_2Br_3] \cdot 2H_2O$

Calculated,%: Re-26.07; Br-33.60; N-7.84; C-23.52; H-2.24

PcRe Synthesis. A mixture of 0.3350 g (1.8 mmol) 4-tert-butylphthalodinitrile and 0.2412 g (0.9 mmol) ammonium perrenate was heated in a sealed ampoule for 1 h at 2000C. The product was crushed, washed on a filter with hot water and hexane, and chromatographed on a column with aluminum oxide. The yield was 49.6 % of the theoretical one.

PcRu Synthesis. A mixture of 1.50 g (8.2 mmol) of 4-tert-butylphthalodinitrile and 0.15 g (0.57 mmol) of ruthenium chloride was heated in a sealed ampoule for 2 hours at 2500C. The product was ground, washed, and chromatographed in a similar manner. The yield was 75 % of the theoretical one.

Table 1. Characteristics of synthesized complex compounds Re (V) with phenanthroline.

The formula of complex compounds	Color	The results of elemental analysis				
			Re	C	H	N
$[PhenH_2][ReOCl_5]$	Fine crystalline precipitate light brown	Found: Calculated:	25,01 24,44	19,10 18,90	1,72 1,58	4,03 3,68
$[PhenH_2][ReOBr_5]$	Fine crystalline red precipitate	Found: Calculated:	23,68 23,22	17,64 17,96	1,81 1,50	
$[ReOCl_3Phen]$	Yellow-green crystalline precipitate	Found: Calculated:	38,24 38,10	21,40 21,76	5,74 5,73	5,74 5,73
$[ReOBr_3Phen]$	Light green crystalline precipitate	Found: Calculated:	29,36 29,94	22,85 23,15	1,07 1,09	5,10 4,50
$[PhenH_2][ReOCl_5]\cdot H_2O$	orange crystalline precipitate	Found: Calculated:	25,03 24,44	19,06 18,90	2,02 1,58	4,13 3,68
$[PhenH_2][ReOBr_5]\cdot H_2O$	Fine crystalline red precipitate	Found: Calculated:	23,79 23,22	17,55 17,96	1,47 1,50	3,25 3,49

3. Results and discussion

The interaction of oxochloroenicic acid solution in hydrochloric acid with an equivalent amount of hydrochloric acid solution of o-phenanthroline isolated the compound $[PhenH_2][ReOCl_5]$ - (I). the Complex $[PhenH_2][ReOBr_5]$ - (II) was obtained by adding a solution of o-phenanthroline in HBr to a solution of oxobromorenicic acid in Hydrobromic acid. Oxochloro - and oxobromorenates of o-phenanthroline were deposited as small crystals with light brown (I) and reddish (II) color:

$$Phen + H_2[ReOX_5] \rightarrow [PhenH_2][ReOX_5]$$

These formulas were written on the basis of data from elemental analysis and IR spectroscopy. Thus, the IR spectra of sodinenii I and II have wide absorption bands in the region of 3300-3340 cm^{-1}, which are typical for protonated nitrogen atoms in a heterocycle and confirm the formation of an outer-sphere cation $[PhenH_2]^{2+}$.

On the heating curves of compounds I and II, decomposition is accompanied by two endothermic effects at 84 and 186°C for $[PhenH_2][ReOCl_5]$ and 87, 188°C for $[PhenH_2][ReOBr_5]$. The first endothermic effect corresponds to the removal of crystallization water, the second is associated with dehydrohalogenation. In order to obtain substances formed after removal of HX (X = Cl, Br), compounds I and II were subjected to thermal action in an inert atmosphere. By heating at slightly higher temperatures (190-195°C) the second endothermic effects were obtained by compounds of the composition [$ReOCl_3Phen$] - (III) and [$ReOBr_3Phen$] - (IV). When heated, dehydrohalogenation occurs and the ligand passes from the outer sphere to the inner sphere of the complex, and the color of the substances changes to yellow-green (III) and light green (IV). The reaction proceeds according to the scheme:

$$[PhenH_2][ReOX_5] \rightarrow [ReOX_3Phen] + 2HX \quad (X=Cl, Br).$$

In support of this scheme of thermal decomposition with the release of two hydrogen halide molecules and the entry of the o-phenanthroline molecule into the inner sphere of the complexing atom, data from elemental analysis and a comparative study of the IR spectra of the initial and obtained compounds speak. In the IR spectra of compounds III and IV, absorption bands in the region of 3300-3340 cm^{-1} disappear due to the presence of protonated nitrogen atoms of the heterocycle in the outer-sphere cation $[PhenH_2]^{2+}$ of compounds I and II. The intense band in the region of 848 cm^{-1} caused by fluctuations of free o-phenanthroline in the IR spectra of compounds III and IV splits into two bands: less intense at 848 cm^{-1} and low-intensity at 843 cm^{-1} (III) and 840 cm^{-1} (IV), which confirms the entry of the phenanthroline molecule into the internal coordination sphere of the rhenium atom (V). Changes in intensities and shifts in absorption bands on the electronic spectra of compounds III-IV relative to I-II in the visible and near UV regions that characterize the phenanthroline chromophore system indicate the transition of the phenanthroline molecule from the outer sphere (I-II) to the inner sphere of the complexing atom (III and IV). The band at 19050 cm^{-1} splits into two bands with a significant hyperchromic shift at 23500 and 22500 cm^{-1}, and for the long-wave absorption band in the region of 12020 cm^{-1}, a hyperchromic shift is observed (Δ550 cm^{-1}). Based on the above and taking into account the fact that the complex anions $[MeOX_5]^{2-}$ (x= Cl, Br) have the configuration of a flattened octahedron, the structure of compounds (III and IV) is established.

Interaction of initial rhenium compounds with benzimidazole [9] in the corresponding solutions of HX (x= Cl, Br), the type of complexes obtained depends on the concentration of HX. Thus, when adding benzimidazole to solutions of $H_2[ReOX_5]$ in 8 mol/l HCl and 7 mol/l HBr, respectively, compounds of the composition $[HL]_2[ReOCl_5]$ - (V) and $[HL]_2[ReOBr_5]$ - (VI) (L-benzimidazole) were obtained. These are fine-crystalline substances of yellow (V) and reddish-yellow (VI) colors, slightly soluble in polar and insoluble in non-polar organic solvents.

Using the rhenium compounds trans [$ReOCl_3(Ph_3P_2)$] and $H_2[ReOBr_5]$, benzimidazole complexes ($C_7H_6N_2L$) were synthesized. The structure and composition of the obtained coordination compounds were established on the basis of IR and UV spectroscopic data and the results of elemental analysis. In the synthesized complexes, on the basis of a set of physicochemical studies, the monodentate coordination of benzimidazole was determined.

Table 2. Element analysis results of rhenium complex compounds with benzimidazole

Compounds	Brutto-formula	Amount (find/calculated), %			
		Re	C	N	H
I	$ReC_{21}H_{18}N_6Cl_3O$	27,97/28,1	39,0/38,0	12,7/12,7	2,96/2,72
II	$ReC_{14}H_{14}N_4Br_5O$	22,2/22,0	19,8/20,0	6,3/6,7	1,44/1,67

The IR spectrum of complex (V) contains characteristic absorption bands of individual functional groups and bonds in the regions indicated below.

IR spectrum (ν, см$^{-1}$) 3412, 3104, 2924, 1624, 1500

1480, 1424, 1248, 930, 748, 620, 420, 320, 306.

The localization of the places of coordination in the complex was determined based on the results of the analysis of IR spectroscopy data.

The absence of the absorption bands of stretching vibrations, characteristic of the conjugated C = C and C = N bonds in the region of 1700–1800 см$^{-1}$, indicates the delocalization of the electron density inside the imidazole ring as a result of the coordination of the imidazole ligand and the formation of complex V. The shift to the high-frequency region (30–44 см$^{-1}$) and an increase in the intensity of the absorption bands corresponding to the stretching vibrations of the imidazole ring (1480–1580 см$^{-1}$) indicate the coordination of rhenium with benzimidazole due to the nitrogen atom of pyridine benzimidazole. This fact is confirmed by the appearance in the spectrum of the complex compound of intense absorption bands in the regions of 748, 620, 420 см$^{-1}$. These lines can be attributed to vibrations of the Re – N bond. The absorption bands of stretching vibrations of the NH group (3400–3100 см$^{-1}$) remain unchanged. The absorption bands located in the range 320–306 см$^{-1}$are related to the vibrations of the Re – Cl bond. The absorption bands at 930 см$^{-1}$ indicate the retention of the Re = O bond. The absence of νP–C-aril absorption bands (510–530 см$^{-1}$) in the complex compound (V) indicates that all triphenylphosphine ligands are replaced by benzimidazole.

Based on the data of infrared spectroscopy, it can be argued that the coordination of the rhenium atom occurs with the help of the nitrogen atom of pyridinebenzimidazole, and the ligand is monodentate.

Analysis of the electronic absorption spectra of solutions of benzimidazole and complex (V) in water and methanol showed that the absorption bands in the regions 35760, 36600, 37100, 38700 (α-band) and 39800, 40700 см$^{-1}$ (p-band) change intensity, and are also characterized by a hypsochromic shift (1000-1500 см$^{-1}$) (Fig. 1, 2).

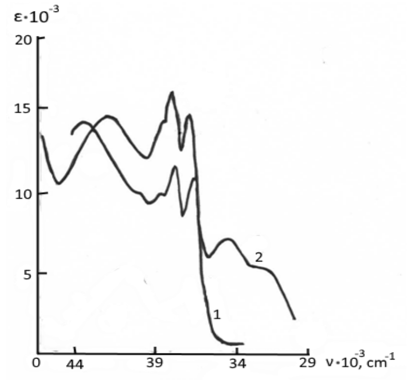

Fig.1. Electronic absorption spectra of solutions [$ReOCl_2L_3$]Cl (1) and [$LH]_2[ReOBr_5$] (2) in the UV region

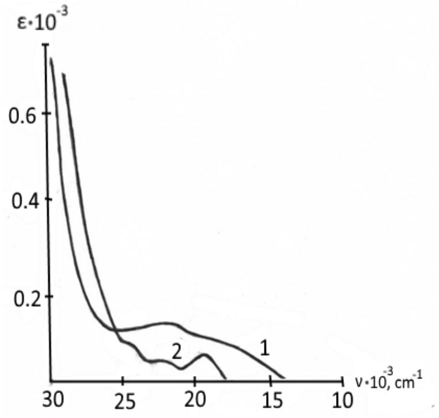

Fig.2. Electronic absorption spectra of solutions [$ReOCl_2L_3$]Cl (1) and [$LH]_2[ReOBr_5$] (2) in the visible area

The shift of the π-band, in comparison with the-band, is much larger. This is the result of the coordination of benzimidazole at the expense of the tertiary nitrogen atom.

Based on the data of IR spectra, electronic absorption spectra and elemental analysis, the structural structure of the[$ReOL_3Cl_2$]Cl complex was established.

Another complex VI of rhenium with benzimidazole was obtained using rhenium oxohalide $H_2[ReOBr_5]$ as a starting reagent. As a result, an orange-colored complex (VI) $[LH]_2[ReOBr_5]$ was obtained, here LH$^+$ is a benzimidazolium ion. The IR spectrum of the obtained compound (VI) contains the following absorption bands, ν, см$^{-1}$: 3380, 1573, 1240, 1113, 980, 953, 920, 880, 726, 713, 580.

The composition of the complex was established using elemental analysis (Table 1). The electronic absorption spectra are shown in Fig. 1 and 2

The presence of a broad absorption band in the region of 3380 см$^{-1}$ in the IR spectrum of complex II indicates protonization of nitrogen atoms of the heterocycle and the presence of the $[LH]^+$ cation in the outer sphere.

A clear peak at 953 см$^{-1}$ indicates retention of the Re = O bond.

The totality of the results obtained makes it possible to establish the structure and composition of the synthesized complexes of rhenium with benzimidazole and determine the monodentant coordination of the latter.Data from elemental analysis and measurements of molar electrical conductivity of compounds V and VI indicate the formation of onium complexes. Along with the characteristic bands of benzimidazole, bands appear in the IR spectra of these compounds at 1000-1010 cm^{-1} due to valence fluctuations of the onium complex V (Re=O). The bands characteristic of protonated benzimidazole $\delta(NH^{+)}$ appear in the region of 1600-1610 cm^{-1}. The expanded singlet in the PMR spectra of compounds V and VI at 7.2 m. d. corresponds to two NH groups. When using $H_2[ReOX_5]$ solutions in acids with concentrations of 6 mol/l HCl and 5 mol/l HBr, respectively, compounds of the composition $[ReOL_2Cl_3]\cdot 2H_2O$ - (VII) and $[ReOL_2Br_3]\cdot 2H_2O$ - (VIII) were obtained. The formation of these complexes is confirmed by measurements of molar electrical conductivity. The absorption bands characteristic of the protonated nitrogen atom of the heterocycle disappear in the outer-sphere cation in the IR spectra of compounds VII and VIII. The 441 cm^{-1} band corresponds to fluctuations in the V (Re-N) bond, and the absorption band at 951-953 cm^{-1} is caused by fluctuations in the Re=O bond in complexes in which benzimidazole molecules are coordinated to the oxygen of the renil group in the TRANS position.

Interest in the phthalocyanin (Pc) class of compounds is due to the fact that they are synthetic analogues of porphyrins widely distributed in nature and exhibit unique physical, chemical and catalytic properties, being promising catalysts for hydrocarbon oxidation reactions [8].

Based on them, it is possible to create new materials, models of natural biological systems and effective catalysts.

One of the most interesting is manganese phthalocyanine – PcMn), an active catalyst for the mild oxidation of organic compounds. However, this complex forms a large number of coordination forms that easily pass into one another, which complicates its use.

In this regard, phthalocyanins of the closest analogues of manganese – rhenium (PcRe), and ruthenium (PcRu) may be of great interest. The General tendency to decrease activity during the transition to heavier elements in one subgroup of the periodic table allows us to expect a decrease in the ability of these complexes to form coordination derivatives and their mutual transition, which, in turn, may be a favorable factor for catalysis.

To isolate pure products, solutions in benzene were subjected to chromatography on a column with Al_2O_3. Upon elution with benzene, there were two main fractions: metal-free phthalocyanine in small quantities and the corresponding phthalocyanines of rhenium and ruthenium.

Figure 3 shows ESP solutions, the ratio of the peak heights of the main bands 368-370 and 651-697 nm is 45%; sattelites 625-630 and 668 nm are well resolved, this is typical for Monomeric forms of phthalocyanines. Judging by the spectrum, the synthesis results in only one form of rhenium phthalocyanine and ruthenium phthalocyanine.

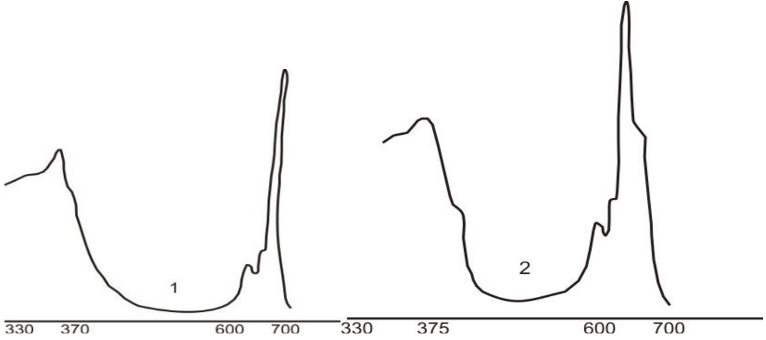

Fig. 3. Electronic absorption spectra of rhenium phthalocyanins (1) and ruthenium (2) in benzene.

The IR spectrum of the complexes has a band of 945 cm^{-1}, which corresponds to the Re=O, Ru=O bond. The absence of any bands in the range of 3100-3700 cm^{-1} indicates that the molecules do not contain OH groups either in the ligand or in the metal atom.

The mass spectra contain a peak of a molecular ion with a mass of 939, which corresponds to the formula $4\text{-}(t\text{-}Bu)_4PcReO$ and the peak of the molecular ion with a mass of 829, which corresponds to the formula $4\text{-}(t\text{-}Bu)_4PcRuO$. Thus, the mass spectrometry data confirm the assumption that the resulting compounds have PcReO and PcRuO structures.

A more detailed study of the complex formation process at various temperatures and concentrations of HCl was studied using the example of phenanthroline complexes of rhenium with the aim of modeling this process.

The dependence of the values of the thermodynamic functions of the process of complexation of rhenium(V) with phenanthroline on the concentration of HC1 are shown in figures 4-6. From the data in fig. 4 it can be seen that the value of ΔG for the monosubstituted complex increases with increasing concentration of HC1. However, this increase on going from 5 mol/l to 6 mol/l HC1 becomes more noticeable. The dependences $\Delta G_i=f(C_{HCl})$ for two, three, four, and five-substituted complex forms are extreme. However, to the least extent, this character is manifested for the disubstituted complex. For the dependences $\Delta H_i=f(C_{HCl})$ (Fig.5) for the first complex forms formed in the solution, an increase in the value of ΔH is observed with an increase in the concentration of HC1. This experimental fact can presumably be associated with the fact that with an increase in the HC1 concentration, the competition between chloride ions and phenanthroline molecules for a place in the internal coordination sphere increases, as a result of which the heat generation process in the system intensifies. For three, four and five-substituted phenanthroline complexes of rhenium (V), the dependence $\Delta H_i=f(C_{HCl})$ has an extreme character and the maxima on these curves appear at an HCl concentration of 5 mol/l. This means that at this concentration the reaction proceeds with the greatest heat release. Similar dependences are observed for the value of ΔS_i (Fig.6).

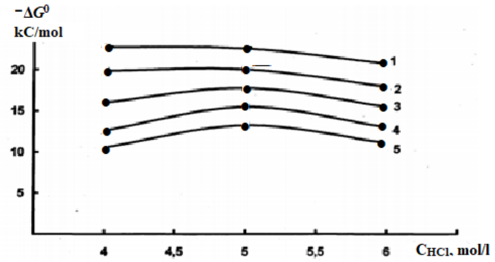

Fig. 4. Dependence of ΔG^0 on the HCl concentration for oxochloro-phenanthroline complexes of rhenium (V) 1-pK_1 2-pK_2; 3-pK_3; 4-pK_4;5-pK_5

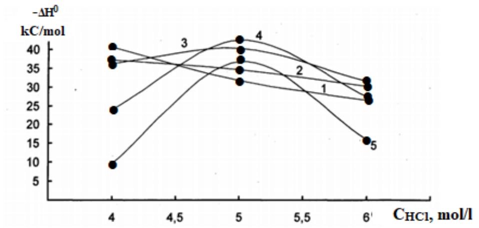

Fig. 5. Dependence of ΔH^0 on HCI concentration for oxochloro-phenanthroline complexes of rhenium (V) 1-pK_1 2-pK_2; 3-pK_3; 4-pK_4;5-pK_5

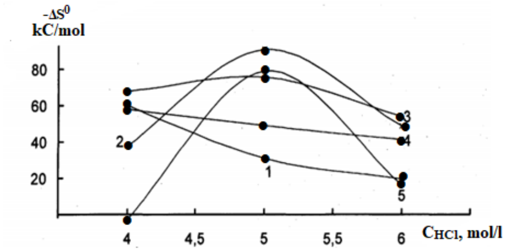

Fig. 6. Dependence of ΔS^0 on the HCI concentration for oxochloro-phenanthroline complexes of rhenium (V) 1-pK_1 2-pK_2; 3-pK_3; 4-pK_4;5-pK_5

Figure 7-9 shows the dependence of the thermodynamic functions on the number of attached phenanthroline molecules. Figure 7 shows that the dependence $\Delta G_i = f(n_{Etthio})$ in media with an HCl concentration of 6 mol/l and 5 mol/l has a straight-line character, that is, with an increase in the number of coordinated phenanthroline molecules, the value of ΔG increases. In a medium of 4 mol/l HCl, the value of ΔG increases with increasing n, but not according to a linear law, which is associated with the influence of hydrolytic processes. The fact that the value of ΔG increases with increasing n is associated with a decrease in the probability of the entry of subsequent phenanthroline molecules into the inner sphere of the complexes. In a medium of 4 mol/l HCl, the value of ΔH increases with increasing n (Fig. 8), and in a medium of 5 mol/l HCl, it decreases upon going from monosubstituted to four-substituted, and then increases again on going from four to five-substituted. In a medium of 6 mol/l HCl, the value of ΔH decreases when going from mono- to two- and three-substituted complexes, then increases again when going to four and five-substituted complexes. A similar dependence is observed for the change in the value of ΔS (Fig.9).

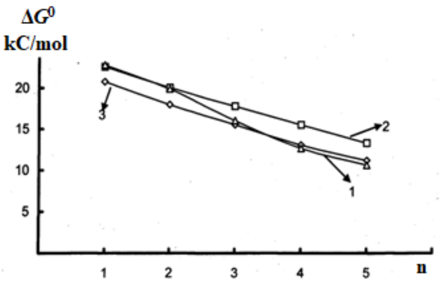

Fig. 7. Dependence of ΔG^0 on the number of attached ligand molecules in media of 4 mol/l (1), 5 mol/l (2), 6 mol/l (3) HCl for phenanthroline complexes of rhenium

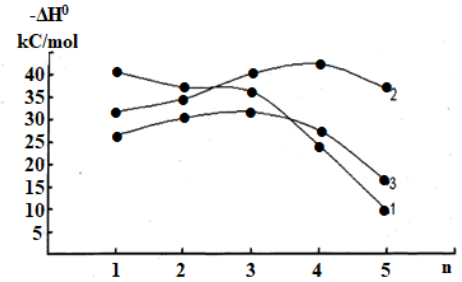

Fig. 8. Dependence of ΔH^0 on the number of attached ligand molecules in media of 4 mol/l (1), 5 mol/l (2), 6 mol/l (3) HCl for phenanthroline rhenium complexes

In order to study the dependence of the speed of complex forms on temperature, to identify its optimal value and to approximate the results obtained, a model was compiled in the form of a linear function. Data processing began with clarification of the correctness, therefore, it was checked for uniformity of variances. Cochran's criterion is calculated; G = 0.468. This value is less than the critical one, so the hypothesis of homogeneity takes place here. The coefficients of the equations were calculated for all five complex forms.

$Y=3,4-0,021X$; $Y=2,9-0,113X$; $Y=2,5-0,09X$; $Y=2,133-0,1037X$; $Y=1,866-0,081X$

As can be seen from the equations, for all complex forms the "-" sign at the temperature factor shows that it has a negative effect on the constant, and therefore on the rate of the process, although this effect is not very significant. This result indicates the exothermicity of the complexation of rhenium (V) with phenanthroline. From a comparison of the equations, we can conclude that the rate of formation of the second complex is most sensitive to a change in the temperature factor, while the formation of the first can be considered the limiting stage of the process.

4. Conclusions

1. Methods of Synthesis have developed and Re(V), Ru(IV) complex compounds with three types of N-donor containing ligands (phenanthroline, benzimidazole, and phthalocyanine) have been obtained.
2. Based on the cumulative results of the conducted studies it was established: -during the synthesis of phenanthroline complexes, a rearrangement occurs due to dehydrohalogenation and the transition of the outer-sphere ligand into the inner sphere of the complex.
3. The composition of benzimidazole complexes depends on the concentration of HX (x = Cl, Br) in the medium. At high concentrations, onium - type complexes are formed; at low concentrations, complexes with monodentate-coordinated ligands are formed through an atom of unsubstituted nitrogen of the imidazole ring
4. New methods of synthesis of rhenium and ruthenium phthalocyanins are Proposed. These methods are characterized by availability and high yields. It was found that only one form of PcRe and PcRu phthalocyanins is formed as a result of synthesis. Various physical and chemical methods have allowed us to attribute the structure of PcReO and PcRuO to these forms.
5. In order to simulate the process of formation of new rhenium complex compounds the dependence of the rate of complexformation and the influence of the concentration of HCl and the number of coordinated ligand molecules on the thermodynamic characteristics of the process was situated, which made it possible to calculate the coefficients of the equations of linear functions, enthalpy, entropy and Gibbs energy of this process.

References

1. Espenson I.H. // Inorg.chem. 2001. V 40 p. 67/7.
2. Henderson N., Mc.Coffrey L.I., Nicholson B.K. // I. Chem. Soc. Dalton Trole 2000 p. 2753.
3. Dublin M., Villamil SH. F., Stopani AO. M.// Agent. Medicina 2002. V 61. P.345.
4. Banerjee s., Bhattacharyya S., Dirghandi B.K., Menon M., Chakiavorty A. //Inorg. chem. 2000. v. 39 p. 6.
5. Paula A., Domingos A., Gargia R., Santos Z., // Inorg. chem. 2000 v. 39. P.5669. https://doi.org/10.1021/ic000481n
6. Alessia E., Zangrando E., Iengo E., Macchi M., Marzi P.A., Marzilli L.G. //Inorg. chem. 2000 v. 39. P. 294.
7. Agaguseynova *M.M., Jabbarova N.E. Coordination compounds* of transition metals in catalysis. Baku: Elm Publishing House. 2006. 244 p.

8. Agaguseynova *M.M.*, Gudratova F.D. “Synthesis of rhenium phthalocyanine complexes by the reaction of tert-butylphthalodinitrile with ammonium perranate and peculiarities of their structure”. Processes of Petrochemistry and Oil Refining. Vol.19, №4, 2018 p.450-454.
9. Agaguseynova *M.M.*, Gudratova F.D. “Synthesis and study of Re(v) complex compounds with benzimidazole”. Azerbaijan Chemical Journal №3. 2017 p.39-42
10. Аминджанов А.А., Вербицкая Н.А., Кадлинова О.А., Сливинский В.И. «Регулирование структура и свойств материалов комплексных соединений рения (V). Композитные материалы» 2011. Т 5. № 1. С.57-61.
11. Yoshimira T., Sno C., Tsuge K., İshiroka S., Nozaki K., Kitamera N., Shinohara A., Excited-state properties of octahedral hexarhelium complexes with redox-active heteroaromatic ligands // J. Inorg. chem. 2010 v.49 p.531-540.
12. Elizabeth B. Baker, Allison A. Haase, Robert M. Reich, Debbil C.Crans, Fritz E. Kühn «Orgametallic and coordinatium rhenium compaunds and their Polential is cancer therapy» Coordination Chemistrry Reviews 2019 v 393 p. 79-11.
13. Richard D.Adams, Burjor Captain, Mark D. Smith, Chad Beddie, Michael B. Hall. Unssaturated Platinum- Rhenium cluster complexes. DOI: 10.1021/ja070773o
14. Justin J, Wilson and Stephan J, Lippard. Synthetic Methods for the Preparation of Platinum Anticancer Complexes. Chemical Reviews. 2014. 114(8). P. 4470-4495. DOI: 10.1021/cr4004314

USING DATA MINING TECHNOLOGY FOR ANALYSIS OF HYDROGEN-PEROXIDE DECOMPOSITION REACTION

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Abstract. Nowadays new information technologies have a great impact on the development of Chemistry science. Scientific researches related to this field reveal inevitability of new approaches to investigation of chemical reactions. New approach to decomposition rate of hydrogen-peroxide was reviewed in this work. Production rule is extracted from data by using clustering method and the results based Larsen fuzzy inference method is analyzed. The problem is based on the application of Data Mining Technologies.

Key words: Data Mining technology, Larsen implication, reaction rate, fuzzy reasoning

1.Introduction

The hydrogen peroxide decomposition reaction which is one of the major reactions in the hydrogen peroxide chemistry is its decomposition into water and oxygen.

There are two features of this reaction. First, it is one of the rare decomposition reactions associated with exothermic processes. Second, the reaction proceeds with the release of a large amount of energy, which creates a greater thermal effect than the well-known exothermic reactions.

The influence of catalysts on the decomposition of hydrogen peroxide has been repeatedly studied. The decomposition of hydrogen peroxide can be very intensive. When a thicker solution is used an explosion is able to occur. Sometimes the noticeable decomposition of H2O2 can be caused by additives that cannot even be determined by chemical analysis.

Hydrogen peroxide is a strong environmentally friendly oxidizer and is actively used in the chemical industry. When applied properly, hydrogen peroxide is a durable and safe reagent, soluble not only in water but also in many organic solvents.

Hydrogen peroxide is used in the synthesis of propylene oxide, organic peroxides (for example, benzene peroxide), epoxidized plasticizers, in the production of refractory additives and initiators for radical polymerization, in the synthesis of pharmaceuticals, surfactants, herbicides.

The hydrogen peroxide’s unique properties determine its use in various environmental technologies, especially in the treatment of wastewater.

Hydrogen peroxide is used in paper factories, at waste processing plants, in pharmaceuticals, chemical and petrochemical industries to reduce toxicity and smell.

One of the significant applications of hydrogen peroxide is the treatment of drinking water. Hydrogen peroxide is used to neutralize excess ozone in the final stage of water treatment, in order to meet the highest quality requirements for the water. The research of the decomposition reaction of hydrogen peroxide is a topical issue.

The sharp increase in chemistry science is related to its union with other sciences. Information processing methods and modes are used for behaviour analysis of chemical processes. Nature of information is one of the obligatory factors in controlling chemical processes. In addition, it is too complicated to control the behaviour of chemical processes without enough information. The reason for that is the impossibility of determining distinctive parameters of the process accurately.

Such problems are controlled by human operators based on linguistic measure. Controlling processes characterized by huge amounts of data requires new practical skills from researchers and it relates to applied chemistry and information technology. In these cases obtaining useful knowledge from the given data is a actual issue[1-5].On the other hand, there is millions of information in the collected database related to long term experiments, scientific literature about chemical reactions. Instead of doing experiments, obtaining knowledge and rate of chemical reactions by using methods based on innovative technologies is actual problem.

Chemical reactions can have various rates[6-8]. In [6], determining the rate of chemical reaction by using fuzzy logic and approximate reasoning. Moreover, scientific researches related to chemical reaction modeling based on indefinite parameters and variable data are not common. For solving such kinds of problems methods based on new approaches are used. These methods allow describing by words. The data that is described by words is easy to understand, however it is impossible to process by using classic math methods. The main aim in this work is to define the decomposition rate of hydrogen-peroxide. For this reason data obtained from internet sources is used.

2.Preliminaries

Fuzzy Set[1]. Firstly, let X be the universe set of the objects, then let x be the elements of the universe set of X. Secondly, let A be the subset of X which is used for membership function μ_A from X to {0,1} can be specified as follows:

$$\mu_A(x) = [1 \text{ if and only if } x \in A \text{ and } 0 \text{ if and only if } x \notin A]$$

[0,1] is the value set, where 1 specifies the membership and 0 shows non-membership. If the value set is in the range of [0,1], then we can say A is fuzzy set. $\mu_A(x)$ is the extent of the membership of elements x in the fuzzy set A, $\mu_A : X \to [0,1]$. If the value of the $\mu_A(x)$ is close to 1, it means x is attributing to the fuzzy set A[1].

$$A = [(x, \mu_A(x)), x \in X]$$

Fuzzy number, Triangular Fuzzy Number[1].

Firstly, let y be the fuzzy number and let X be the universe set. If y is both normal and convex, then we can say that y is a fuzzy subset of the universe set X. There are 2 significant characteristics of Fuzzy numbers:

1) Membership function of them, that is $\mu_y(\mathbf{x})$ is continuous from R to {0,1}.
2) Their membership function ($\mu_y(x)$) is convex and normal that is there exists a number such as y_0 that enables $\mu_y(x) = 1$.

If a triangular fuzzy number y is expressed as (y_1, y_2, y_3), then the membership function of the triangular fuzzy number $\mu_y(x)$ can be indicated with the followings:

$$\mu_y(x) = \begin{cases} \dfrac{x - y_1}{y_2 - y_1}, & \text{If } y_1 \le x \le y_2 \\ \dfrac{y_3 - x}{y_3 - y_2}, & \text{If } y_2 \le x \le y_3 \\ 0, & \text{otherwise} \end{cases}$$

Fuzzy C-means algoritm[4].

The algorithm for fuzzy c-means clustering consist of an iterative clustering method whose output is optimal "c" partition, extracted by minimizing the goal function FCM.

Basic steps of the algorithm are:

1.Define the membership values using the below given mathematical expression.

$$\sum_{j=1}^{c} \mu_j(x_i) = 1, i = 1,2,\ldots,k$$

2. Determine the centroids using given math equation.

$$C_j = (\textstyle\sum_i [\mu_j(x_j)]^m x_i) / (\sum_i [\mu_j(x_j)]^m)$$

3. Determine dissimilarly between the data points and centroid using the distance measure.

$$D_i = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}$$

4.Replace the new membership matrix:

$$\mu_j(x_j) = \frac{\left[\dfrac{1}{d_{ji}}\right]^{\frac{1}{m-1}}}{\sum_{k=1}^{c}\left[\dfrac{1}{d_{ki}}\right]^{\frac{1}{m-1}}}$$

5. Repeat step 2,unless the centroids are not changing.

Larsen fuzzy inference algorithm[9].

1) Fuzzification: the membership function is being determined for each term:

$$A_1(x_0), A_2(x_0), B_1(x_0), B_2(x_0)$$

2) Fuzzy inference: Firing level of the rule is being obtained:

$$\alpha_1 = A_1(x_0) \Lambda B_1(y_0),$$
$$\alpha_2 = A_2(x_0) \Lambda B_2(y_0),$$

where, $\wedge$ - min operation. On the next step fuzzy sets are formulated:

$$\alpha_1 C_1(z), \quad \alpha_1 C_2(z)$$

3) Result of the composition as membership function is being defined the following form:

$$\mu_\Sigma(z) = C(z) = (\alpha_1 C_1(z)) \vee (\alpha_2 C_2(z))$$

In general case the result for n rule can be written as below:

$$\mu_\Sigma(z) C(z) = \bigcup_{i=1}^{n} (\alpha_i C_i(z))$$

4) At last, if it is necessary centroid method is being used for defuzzification.

3. Statement of the problem

Goal is to define the rate coefficient for hydrogene-peroxide decomposition reaction. For this reason hydrogene-peroxide decomposition reaction is modelled during 550 sec. Initial data for solution of this problem is:

$$K = [6.1, 6.9] \cdot 10^{-5} \cdot s^{-1}$$
$$\Delta = \frac{[H_2O_2]_{t=550s}}{[H_2O_2]_0} = e^{-kt}$$

$\delta = (100 - \Delta)\%$ is the expression of the hydrogene-peroxide decomposition during 550 sec. Relations between this indicator and rate coefficient is obtained by using computer simulation(Table 1).

Table 1. Values of delta and K

Iterations	delta	K
1	3,299344	6,1
2	3,315298	6,13
3	3,33125	6,16
4	3,347199	6,19
5	3,363145	6,22
6	3,379089	6,25
…	…	…
8	3,410969	6,31
9	3,426905	6,34
10	3,442838	6,37
…	…	…
22	3,633832	6,73
23	3,649731	6,76
…	…	…
29	3,745071	6,94
30	3,760951	6,97

Table 1. Values of delta and K(continue)

4.Solution of the problem

By using given data in Table 1 clusters is obtained and created the fuzzy model. Before using the FCM algorithm, the following parameters must be specified: the number of clusters, c=4, the fuzziness exponent, m=2, the termination tolerance, *ε=0.000.*

From the given clustering algorithm below shown clusters are obtained.

Centers of obtained clusters are: C1=(3.5272; 6.5289)
C2= (3.3336; 6.1645)
C3=(3.6265; 6.7161)
C4=(3.7251; 6.9022)

The reason for chosing Fuzzy C-means is its advantages:

1)Obtaining the best result from the data compare to k-means algorithm.

2) Variety from k-means algorithm here each point doesn’t belong to one cluster and considered in several clusters.

Values of membership functions is obtained as follows on every cluster by using computer simulation:

μ_{C_1}	μ_{C_2}	μ_{C_3}	μ_{C_4}
0.0628	0.0204	0.9012	0.0099
0.0250	0.0072	0.9626	0.0033
0.0006	0.0001	0.9992	0.0001
0.0264	0.0055	0.9646	0.0023
0.1596	0.0258	0.7993	0.0100
0.4184	0.0478	0.5080	0.0171
0.7101	0.0473	0.2196	0.0154
0.9172	0.0224	0.0508	0.0065
…	….	….	….
0.9525	0.0250	0.0150	0.0053
0.7771	0.1455	0.0436	0.0242
0.5052	0.3801	0.0527	0.0454
0.0633	0.8897	0.0127	0.0263
0.0025	0.9943	0.0006	0.0020
0.0102	0.9678	0.0029	0.0156
…	….	….	…..
0.0020	0.0087	0.0009	0.9822
0.0013	0.0047	0.0006	0.9870
0.0097	0.0314	0.0047	0.8711
0.0177	0.0515	0.0090	0.6429
0.0170	0.0455	0.0090	0.3575
…	….	….	….
0.0017	0.0039	0.0009	0.0179
0.0002	0.0004	0.0001	0.0016
0.0039	0.0081	0.0023	0.0273
0.0105	0.0212	0.0064	0.0640

Production rules extracted from data is formulated as follows:

If the percentage of hydrogen peroxide decomposition is about 3.53 THEN the coefficient rate is about 6.53

If the percentage of hydrogen peroxide decomposition is about 3.33 THEN the coefficient rate is about 6.16

If the percentage of hydrogen peroxide decomposition is about 3.63 THEN the coefficient rate is about 6.72

If the percentage of hydrogen peroxide decomposition is about 3.72 THEN the coefficient rate is about 6.9

Larsen fuzzy inference method is applied on the obtained model. Larsen implication is the following form:

$$x \rightarrow y = xy$$

Fuzzy relations based on Larsen implication on the obtained rules are (Table 2-5):

Table 2. Fuzzy relation matrix for first rule

	0,1	0,4	0,92	1	0,37	0,26	0,2
0	0	0	0	0	0	0	0
0,73	0,073	0,4	0,6716	0,73	0,2701	0,1898	0,146
0,91	0,091	0,4	0,8372	0,91	0,3367	0,2366	0,182
1	0,1	0,4	0,92	1	0,37	0,26	0,2
0,87	0,087	0,4	0,8004	0,87	0,3219	0,2262	0,174
0,08	0,008	0,08	0,0736	0,08	0,0296	0,0208	0,016
0,01	0,001	0,01	0,0092	0,01	0,0037	0,0026	0,002

Table 3. Fuzzy relation matrix for second rule

	0,02	0,61	0,86	1	0,5	0,34	0,21
0,03	0,0006	0,0183	0,0258	0,03	0,015	0,0102	0,0063
0,6	0,012	0,6	0,516	0,6	0,3	0,204	0,126
0,71	0,0142	0,61	0,6106	0,71	0,355	0,2414	0,1491
1	0,02	0,61	0,86	1	0,5	0,34	0,21
0,8	0,016	0,61	0,688	0,8	0,4	0,272	0,168
0,54	0,0108	0,54	0,4644	0,54	0,27	0,1836	0,1134
0,01	0,0002	0,01	0,0086	0,01	0,005	0,0034	0,0021

Table 4. Fuzzy relation matrix for third rule

	0,03	0,63	0,7	1	0,74	0,5	0,04
0,34	0,0102	0,2142	0,238	0,34	0,2516	0,17	0,0136
0,61	0,0183	0,61	0,427	0,61	0,4514	0,305	0,0244
1	0,03	0,63	0,7	1	0,74	0,5	0,04
0,73	0,0219	0,63	0,511	0,73	0,5402	0,365	0,0292
0,41	0,0123	0,41	0,287	0,41	0,3034	0,205	0,0164
0,2	0,006	0,2	0,14	0,2	0,148	0,1	0,008
0,13	0,0039	0,13	0,091	0,13	0,0962	0,065	0,0052

Table 5. Fuzzy relation matrix for fourth rule

	0,05	0,67	0,9	1	0,92	0,67	0,3
0,2	0,01	0,134	0,18	0,2	0,184	0,134	0,06
0,31	0,0155	0,31	0,279	0,31	0,2852	0,2077	0,093
0,73	0,0365	0,67	0,657	0,73	0,6716	0,4891	0,219
1	0,05	0,67	0,9	1	0,92	0,67	0,3
0,73	0,0365	0,67	0,657	0,73	0,6716	0,4891	0,219
0,21	0,0105	0,21	0,189	0,21	0,1932	0,1407	0,063
0,01	0,0005	0,01	0,009	0,01	0,0092	0,0067	0,003

Result on the third step Larsen fuzzy inference algorithm is given in Table 6. Disjunction ($\vee$) operation is used in this stage. At last the following operations are performed and obtained the following relation matrix.

$$\mu_\Sigma(z)=C(z)=C_1'(z)\vee C_2'(z)=(\alpha_1\wedge C_1((z))\vee(\alpha_2\wedge C_2(z)).$$

Table 6. General relation matrix based on four relation matrix

$$R=\begin{array}{|ccccccc|}\hline 0{,}0102 & 0{,}2142 & 0{,}238 & 0{,}34 & 0{,}2516 & 0{,}17 & 0{,}06 \\ 0{,}073 & 0{,}61 & 0{,}6716 & 0{,}73 & 0{,}4514 & 0{,}305 & 0{,}146 \\ 0{,}091 & 0{,}67 & 0{,}8372 & 1 & 0{,}74 & 0{,}5 & 0{,}219 \\ 0{,}1 & 0{,}67 & 0{,}92 & 1 & 0{,}92 & 0{,}67 & 0{,}3 \\ 0{,}087 & 0{,}67 & 0{,}8004 & 0{,}87 & 0{,}6716 & 0{,}4891 & 0{,}219 \\ 0{,}0108 & 0{,}54 & 0{,}4644 & 0{,}54 & 0{,}27 & 0{,}1836 & 0{,}1134 \\ 0{,}0039 & 0{,}13 & 0{,}091 & 0{,}13 & 0{,}0962 & 0{,}065 & 0{,}0052 \\ \hline\end{array}$$

Result of the fuzzy inference algorithm on the new input based on the general relation matrix

0,1	0,0102	0,1	0,1	0,1	0,1	0,1	0,06
0,2	0,073	0,2	0,2	0,2	0,2	0,2	0,146
0,34	0,091	0,34	0,34	0,34	0,34	0,34	0,219
1	0,1	0,67	0,92	1	0,92	0,67	0,3
0,43	0,087	0,43	0,43	0,43	0,43	0,43	0,219
0,08	0,0108	0,08	0,08	0,08	0,08	0,08	0,08
0,02	0,0039	0,02	0,02	0,02	0,02	0,02	0,0052
Y1	0,1	0,67	0,92	1	0,92	0,67	0,3

It is obtained that if decomposition percentage is 3.45 then rate is approximately 6.412..The result demonstrated in the figure.

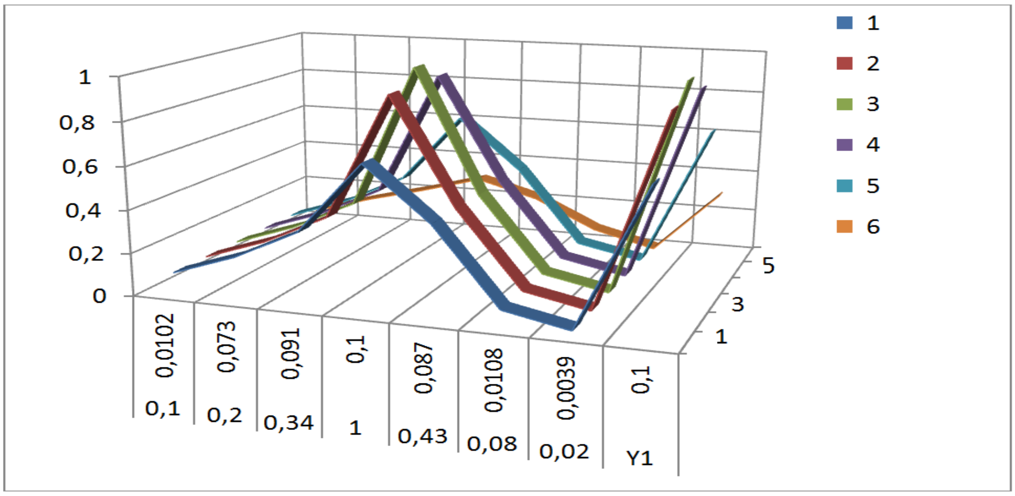

Figure 1. Relation between decomposition percentage and rate of hydrogene-peroxyde.

5.Conclusion

The new approach for defining decomposition rate of hydrogen-peroxide is applied in this work. Method of obtaining clusters from statistic variables are proved ,4 clusters have already been acquired and production rules are established related to clusters. During composition of clusters various values of m is examined and qualitative fuzzy model related on proposed parameters have been generated. Terms are represented by triangular fuzzy numbers in a model. By using this terms is created fuzzy relation on the rules and is fulfilled Larsen fuzzy inference algorithm. By using the proposed approach researchers can define rate of reaction accurately.

References

1. Aliev R.A., Aliev R.R., Soft Computing and its Application. World Scientific, New Jersey, London, Singapore, Hong Kong,2001, -444 p
2. Latafat Gardashova, Yunis Gahramanli, Mehseti Babanli. Fuzzy Neural Network Based analysis of the Process of Oil Product Sorption with Foam Polystyrene . Int. Journal of Engineering Research and Application. Vol. 7, Issue 9, (Part -7) September 2017, pp.85-90
3. Arpita Nagpal , Aman Jatain , Deepti Gaur. Review based on data clustering algorithms. Proceedings of 2013 IEEE International Conference on Information and Communication Technologies (ICT 2013),pp.171-176.
4. Dongkuan Xu, Yingjie Tian. A Comprehensive Survey of Clustering Algorithms. Ann. Data. Sci. (2015) 2(2):165–193
5. Kamalpreet Bindra , Anuranjan Mishra. A Detailed Study of Clustering Algorithms.6th International Conference on Reliability, Infocom Technologies and Optimization (ICRITO) (Trends and Future Directions), Sep. 20-22, 2017,pp.370-377
6. Babanli M.M. Evaluation of desirable isothermal reactions rate in uncertain environment.Advances In Intelligent Systems And Computing Series, Springer,2019, pp 366-372
7. Nowicki, L., Siuta D., Godala, M.: Determination of the chemical reaction kinsetics using isothermal reaction calorimetry supported by measurements of the gas production rate. A case study on the decomposition of formic acid in the heterogeneous Fenton reaction. Thermochimica Acta **653**, 62–70 (2017)
8. Jafarli M. (2020) Evaluation of Desirable Isothermal Reactions Rate in Uncertain Environment. Advances in Intelligent Systems and Computing, vol 1095. Springer,pp.376-372
9. https://studbooks.net/2042716/informatika/algoritm_larsena_larsen

PP-VII-1

RECONSTRUCTION OF SUMGAYIT CHEMICAL AND PETROCHEMICAL INDUSTRY AND FOREIGN RELATIONS (2003-2008).

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Abstract. The article describes the implementation of a comprehensive action plan to strengthen production at Sumgayit chemical and petrochemical enterprises in 2003-2008, the export of a part of the company's products, the establishment of business relations with major companies in many countries, ensuring foreign investors, investment and credit resources to be directed to promising projects in the chemical and petrochemical complex, to achieve better results in product sales, to export products to the markets of Russia, Turkey, Poland, the Islamic Republic of Iran, Ukraine, Belarus, Uzbekistan and a number of Western countries, reconstruction and development of Sumgayit petrochemical industry on the basis of modern technology to withstand competition in the world market to help Sumgayit petrochemical industry compete in the world market, restoration and development of modern petrochemical companies, the establishment of joint ventures and representative offices of the petrochemical company in many countries - Ukraine, China, Germany, Russia and Azerbaijan, implementation of large-scale technical measures for the production of much-needed products.

The study focused on increasing the range and quality of products in the Sumgayit chemical industry, increasing profitability, organizing the production of products in high demand in the country and other regions, as well as the creation of flexible production complexes, implementation of the State Program, accelerating measures to further improve socio-economic indicators of the chemical industry, the increase in production in the chemical and petrochemical industries over the years.

Consequently, it was concluded that as a result of the application of new technology, the range and total volume of production of Sumgayit chemical and petrochemical products has increased several times, wide opportunities for the production of chemical products meeting modern world standards have been created, foreign economic relations have been established, foreign exchange inflows to Azerbaijan as a result of exports have been provided.

Keywords: Chemical industry, petrochemical industry, **"Azerikimya" State-Owned Company**, foreign economic relations, “Synthetic rubber”, “Surfactants”, “Organic synthesis”, “Ethylene-polyethylene”

1.Introduction

The chemical and petrochemical industries, which are one of the main sectors of the Azerbaijani economy, are mainly concentrated in Sumgayit city. Revenues from the Sumgayit chemical industry were mainly included in the USSR budget during the Soviet era. However, after gaining independence, Sumgayit chemical industry began to serve the interests of the Republic of Azerbaijan by restructuring and became one of the most important sectors of our economy. From this point of view, the study of the history of Sumgayit chemical and petrochemical industry is scientifically relevant.

In accordance with the program of the President of the Republic of Azerbaijan on accelerating the socio-economic development of the republic, a comprehensive action plan has been developed at “Azerikimya” State Company to strengthen the stable financial discipline of its enterprises. “Azerikimya” State Company produced products worth 323,178.6 million manat in the first 8 months of 2004, an increase of 28.4 percent compared to the same period of 2003. The eight-month production forecast was fulfilled by 114 percent. Most of the products produced at the company's enterprises were exported. Business relations have been established with large companies in many countries, including the United States, Turkey, Russia, Switzerland, Germany, Ukraine and other countries. The strategic goal of the foreign economic relations mechanism was to ensure that foreign investors, investments and credit resources were directed to perspective projects in the chemical and petrochemical complex. [19]

The remaining months of 2004 were more successful for the chemists of the Organic Synthesis Plant. During six months, 25.8 billion manat products were produced instead of 20.5 billion manat, the forecast task was fulfilled by 126.1 percent. Compared to last year, the volume of production increased by 44.1%. Higher results were achieved in product sales. In addition to those intended for consumer markets, chemical products worth 14 billion manat were sent under various names. The produced propylene oxide and polyester resins are mainly exported to the Russian market, as well as to Turkey and Poland. Relations have also been established with the Islamic Republic of Iran. Iranian companies are showing great interest in polyester resins. Many products were sent to the neighboring country. [18]

The capacity of the chemical and petrochemical complex in Sumgayit allowed the industry to operate with high productivity and profitability, and the several-fold increase in the price of petrochemical products on world markets in recent years was one of the main factors characterizing the development of this industry. [8 p 126]

In order to withstand competition in the world market, in connection with the restoration and development of Sumgayit petrochemical industry on the basis of modern technology, the introduction of new technologies in enterprises owned by Azerikimya State Company, as well as building production of polypropylene at the Ethylene-Polyethylene Plant, ammonia and carbamide at the Organic Synthesis Plant, new ion-exchange membrane caustic soda and chlorine at SAM plant are planned. In the field of technical support in the butadiene department at the “Synthesis Rubber” plant, in latex and pyrcondensate department, bitumen production and polyethylene pipe section at the ethylene-polyethylene plant, creation of new facilities and expansion works in the epoxy resin department at the “Organic Synthesis” plant and restoration works were carried out in 4 areas. The work of the sulfuric acid department in “Super-phosphate” OJSC has been partially restored. Output in the chemical and petrochemical industries amounted to 377.3 billion manat. Compared to last year (2003), the volume of production increased by 50.8 percent or 127.1 billion manat. The share of chemical industry products in the total output of the processing industry was 65.8%. [25]

Titan, a leading petrochemical company, has joint ventures and representative offices in many countries - Ukraine, China, Germany, Russia and Azerbaijan. In accordance with Titan's investment program, extensive reconstruction and restoration work began at the enterprise producing additives in Sumgayit in 2001. Device for preparation of paints and varnishes was put into operation. Extensive technical measures have been taken to consume solvents in high demand in consumer markets, and the reconstruction of old facilities has been completed. In the next stage poductivity of the plant was increased 3 times taking into account the demand. [15]

In recent years, the work of chemical plants in a number of CIS countries has been restored, and the production of chemical products has accelerated. In this regard, given the competition in the CIS, the sale of chemical products should be a very important, vital issue for our chemical industry. According to the agreement, joint ventures will be established in Latvia in the near future, which will primarily regulate the sale of products produced by enterprises of our republic. The first Azbalt enterprise has already started operating. In the near future, polyethylene coatings, bags and other consumer goods are planned to produce at the workshops of the Azerbaijani-Latvian joint venture "Azbalt" on the basis of chemical raw materials and semi-finished products purchased in the country. [19]

In 2004, product release of Sumgayit chemical and petrochemical industry amounted to 593.7 billion manat. Compared to 2003, the volume of production increased by 63.7 percent or 231.4 billion manat. The special share of chemical industry products in the total product release of the processing industry was 64.3%, and the volume of loaded products was 578.4 billion manat. [21]

Work to increase the range and quality of products in the Sumgayit chemical industry, rase profitability, restore the production of previously existing products with the introduction of new technologies, organize the production of products in high demand in the country and other regions, as well as achieve flexible end products is one of the main tasks ahead. In connection with the implementation of the State Program, the development of appropriate technical conditions for the reconstruction and development of the petrochemical industry on the basis of modern technology for the construction of new caustic soda and chlorine productions by polypropylene at the Ethylene-Polyethylene plant and ion-exchange membrane method at the Surfactants Plant, work on determining the cost of facilities to be built has intensified. Work has begun to restore the production of epoxy resins at the “Organic Synthesis” Plant. [22]

In the first quarter of 2005, product release of Sumgayit chemical and petrochemical industry amounted to 141.5 billion manat, and compared to the same period in 2004, production increased by 16.0 percent and 19.5 billion manat. The special share of chemical industry products in the total product release of the processing industry was 57.5%. [24]

According to 2005 data, the products produced by the "Azerikimya" State Company account for 60-65% of the total industrial production in Sumgayit. The company's products were exported to more than 20 countries around the world. Since the beginning of the year, up to 400 billion manat worth of chemical products have been sent to Western Europe, CIS countries, Turkey and the Islamic Republic of Iran. [16]

In july 2005, output of Sumgayit chemical and petrochemical industry amounted to 308.2 billion manat, and the volume of production compared to the same period in 2004 was 23.6 percent or 58.9 billion manat. The share of chemical industry products in the total output of the processing industry was 67.9%. The volume of loaded products amounted to 291.2 billion manat, and the share of chemical products in the volume of chemical production was 94.7 percent, the share of chemical products in the total volume of loaded products was 68.0 percent, and the volume of product balance was 27.6 billion manat. The remainder of chemical products was 54.8% of the total balance. [23]

Taking into account the growing demand in the world market for chemicals and petrochemical products, the management of Azerkimya State Company has developed promising investment projects for the country's main hydrocarbon resources and natural resources. [16]

In September 2005, the head of the Sumgayit City Executive Power decided to hold the next scientific-practical conference on "Directions of development of the chemical industry" in order to further improve the socio-economic indicators of the chemical industry and accelerate the measures taken. [26]

In order to stabilize the work of the chemical sector, the country's leadership and the Cabinet of Ministers have increased the supply of naphtha, the main raw material for this sector, to the main forecast level - 250,000 tons. This has created a solid basis for the harmonious operation of chemical enterprises, especially the EP plant. In general, 37,160 tons of high-pressure polyethylene and 2008,000 tons of propylene have been produced since the beginning of the year. The volume of consumer goods increased 3.3 times. 70% of the products are exported to foreign markets. The main buyers of high-pressure polyethylene are Turkish companies. In addition, product is exported to CIS countries, China and the Islamic Republic of Iran. [16]

On october 12, 2005 a scientific-practical conference on "Development directions of the chemical industry" was held in Sumgayit. First of all, the conference participants got acquainted with the exhibition, which reflects the activities of chemical and petrochemical enterprises, Sumgayit research centers, newly established industries, businesses, and exchanged business views on the products and technical innovations. An extensive resolution was adopted on the issue discussed at the conference. [11]

Strong development of the chemical industry is one of the most important issues for the country's economy. The increase in oil production in our country has opened wide opportunities for the fundamental renewal of the chemical and petrochemical complex due to the efficient use of hydrocarbon resources. According to our chemists, a number of measures should be taken to mobilize the chemical industry as a whole, to process products to the final stage, to carry out technical and organizational work, to master the technology of new products using local raw materials. For this, the production of benzene, ethylbenzene, styrene, synthetic rubber and detergents must be achieved. High octane component production technology should be implemented by hydrogenation of polypropylene, low-pressure polyethylene, dichloritane, polyvinyl chloride, epoxy resin, polyisobutylene, propylene, olegolieri and heavy proliferation fraction. [16]

Gaining independence of the Republic of Azerbaijan and the application of new technologies in close cooperation with the developed countries of the world in a short period of time, their connection to existing networks requires the development of project documents that meet world standards. The State Design Institute has taken important steps in this area. The project estimates developed by the institute fully meet modern world standards and are welcomed by leading companies. The institute is constantly expanding its international relations. It also collects information on newly created technological equipment and facilities in cooperation with the Russian Federation, Ukraine, Kazakhstan and European countries, and allocates a large space for them in project work. [3]

Since 1993, Azerbaijani economy, including the chemical and petrochemical industries, has entered a new stage of development and has undergone a great development. Progress has been made in this area over the past 10-12 years as a result of mobilizing potential at the Synthesis Rubber Plant, technical and technological renewal and modernization of production facilities. Competitive products are exported to Austria, Germany, the Netherlands, Switzerland, Italy, France, China, Turkey, Iran and other developed countries. The EP-300, which is the main processing unit of the chemical and petrochemical complex, releases several chemical components during the technological process. Pyrocondensate is the main source of raw materials for benzene, toluene, ethylbenzene, styrene. Latexes and rubbers are made on the basis of them in the next stages. For this purpose, an action plan has been developed at the enterprise and its implementation has been started in stages. [4]

It should be noted that in 2001-2006, the production of marketable products increased by almost 3 times, while the cost of this product increased only 2.1 times, and this factor indicates that there is enough potential to raise the level of profitability in the petrochemical sector. [7 p 46-47]

During the first 9 months of 2005, the output of the chemical and petrochemical industry amounted to 480.4 billion, and compared to the same period of the last year, production increased by 27.0 percent or 102.3 billion manat. The share of chemical industry products in the total output of the processing industry was 70.0%. The volume of loaded products was 467.0 billion manat. [5]

The report of the commission established by the order of the head of the city executive power on the implementation of the “ Program on Socio-Economic Development of Regions of the Republic of Azerbaijan (2004-2008)” in Sumgayit city notes that constructions of the productions of a new caustic soda and chlorine with ion exchange membrane method at the "Surfactants" plant, processing of polypropylene, pyrocondensate and heavy resin at the Ethylene-Polyethylene Plant, ammonia and urea at the Organic Synthesis plant as were planned for 2004-2008, necessary work has been done for development of appropriate technical conditions and in the field of determining the cost of facilities to be built. Negotiations were held at the "Surfactants" plant to purchase raw materials and resume production of chlorinated paraffin products of various brands. Contracts have been signed for the purchase of raw materials for the resumption of carboxide-methylcellulose production. [2]

The Ethylene-Polyethylene Plant of “Azerikimya” State Company is one of the enterprises occupying a special place in Sumgayit's industry. According to the results of 2005, commodity products worth 375.1 billion were produced. 70% of products produced in accordance with world standards are exported to foreign countries - Russia, CIS and Baltic countries, Turkey, China and Iran. As a result, the republic receives a large amount of currency. [10]

The potential of the chemical and petrochemical complex, which is important in the existing potential of the Sumgayit industrial complex, should be seriously assessed with scientific and technical substantiation, based on this potential, the issues of effective use of existing opportunities and creation of a complex based on new technologies should be considered. [9 p 44]

In 2005, the volume of marketable products at the Organic Synthesis Plant reached 963.3 billion manat, which is an increase of 46.4 percent compared to the previous year. Higher attainments were achieved on individual products. During the year, 11,518 tons of propylene oxide, 6,414 tons of polyester resin were released, and additional costs are reduced to a minimum. [13]

Upon completion of the second stage of the reconstruction, the main petrochemical products to be produced by “Azerikimya” SC in a year will be: Ethylene-120,000 tons, propylene 101,000 tons, polyethylene-118,000 tons, polypropylene 100,000 tons, styrene-butadiene rubber and latex-21,000 tons, pyrocondensate – 159,000 tons. [19]

The pace of development of the Sumgayit petrochemical industry has been in the focus of attention of the state, chemical scientists and specialists as an important area in the development of the economy of the independent Republic of Azerbaijan. They expressed their scientifically based and comprehensive considerations in the press and scientific journals about the future development and prospects of this field. The development of Sumgayit's chemical plants is in line with the growth of Azerbaijan's rich hydrocarbon reserves. Sumgayit's chemical industry is experiencing a new period of progress. It should be noted that after signing of the "Contract of the Century", wide opportunities have emerged for the development of joint programs to provide the chemical industry with modern technology and close cooperation with foreign companies for Sumgayit chemical industry. These opportunities have been used effectively and are being done.

At the Cabinet of Ministers the issue of applying preferential prices for energy carriers in order to restore the activities of large industrial enterprises of the country was considered and necessary measures were taken. Due to the introduction of preferential prices for energy carriers, there has been a revival in the activities of enterprises subordinated to the "Azerikimya" State Company. [12]

During the problems related to energy prices, the main focus was on technical innovation. The vast majority of existing problems have been resolved. In the propylene oxide department, which produces commodity products, a program has been developed to set up technical processes in accordance with the requirements of the day. This has allowed to increase the efficiency of production processes and raise productivity to the design capacity, prevent the loss of raw materials, as well as improve management, and ensure high level of work of auxiliary fields. [17]

Holding a tender for signing the Feasibility Study (FS) of projects related to the establishment of a chemical and petrochemical complex in Azerbaijan as a result of technical and creative cooperation between “Azerikimya” State Company and a number of leading companies of the and the fact that its winner is the British company “Nexant”, which has a very prestigious and rich scientific and practical experience, indicates the successful beginning of great prospects for the chemical industry of our country. The company conducted analyzes on the issues of technology, equipment, study of marketing and sales markets, economic efficiency indicators and others. A feasibility study that meets international standards has been prepared and submitted to the Azerbaijani side for the opening of financing and the start of construction work. An important requirement in this regard is that each chemical technology and equipment to be imported to our country must reflect the latest achievements of modern automation and computerization, as well as must be superior to both the quality and efficiency of the product and its environmental compliance. [1]

The only chlorine and caustic soda production operating at the Surfactants Plant, one of the oldest enterprises in Azerbaijan's chemical industry, also needs to be modernized. Taking into account the development of other industries in the country - oil, energy and non-ferrous metallurgy, there is a need to create a new, more modern and highly productive production. Another production line of great economic and commercial interest to the enterprise is the production of alkylbenzene, which can be reconstructed using more contemporary technology. The creation of a new chemical and petrochemical complex will create conditions for the creation of additional jobs. [6]

Since 2003, the strengthening of the processing industry in our country and therefore the organization of processing of semi-finished chemical products was also relevant, and the restoration of many chemical and petrochemical industries was included in the "Regional Development Program in the Republic of Azerbaijan for 2004-2008" with a feasibility study . [20]

If the existing potential of large chemical enterprises in Sumgayit is used effectively, the city's industrial capacity could be increased several times, and Sumgayit could increase its status as an industrial center and use its labor resources efficiently for at least the next 10-15 years. As one of the main non-oil sectors in Azerbaijan, the chemical and petrochemical complex is particularly distinguished by its potential. With the increase in oil production in the Caspian Sea, the role of the oil refining and petrochemical industry in further strengthening the economy of the Republic is growing. [8 p 125]

Sumgayit chemistry is experiencing a new period of development. The market for isopropyl alcohol has expanded in recent years, and purchasing power has increased. Turkey, Iran, Russia, Ukraine, Belarus, Uzbekistan and a number of Western countries are the main buyers. Such a valuable product is used as a solvent both in industry and in various fields. Demand for isopropyl alcohol ether has also increased in the markets. Products are exported to Russia, Georgia and other republics. Butadiene is also used to make a wide range of products. [14]

As a result of the research, the following conclusions were reached:

-As a result of the application of new technology, the range and total volume of production of Sumgayit chemical and petrochemical products has been increased several times, new facilities have been put into operation, ample opportunities have been created for the production of chemical products meeting modern world standards;

-Application of new technologies in Sumgayit chemical and petrochemical industry has laid the foundation for the organization of production of chemical and petrochemical products that can compete in a market economy, increase production volume, reduce production costs, minimize the consumption of raw materials and supplies, eliminate dependence of the chemical industry on other countries

-As a result of establishing foreign economic relations, sending chemical and petrochemical products to the world market, provided the inflow of currency to Azerbaijan.

5.References

1. Akhundov F. Chemical and petrochemical complex will be built on the basis of new technologies. Sumgayit newspaper. August 25, (2007).
2. Report of the commission established by the order of the head of the city executive power on the implementation of the State Program of socio-economic development of the regions of the Republic of Azerbaijan (2004-2008) in Sumgayit. Sumgayit newspaper. January 18, (2006).
3. Babayev N. Reconstruction and design in the chemical industry. Sumgayit newspaper. September 24, (2005).
4. Balakishiyev I. New projects are being implemented, production facilities are being put into operation (Synthesis Rubber Plant). Sumgayit newspaper. October 5, (2005).
5. How we finished nine months. Information of Sumgayit city statistics department. Sumgayit newspaper. November 2, (2005).
6. Ahmadov A. The beginning of a new stage of development (SAM plant). Sumgayit newspaper. September 22, (2007).
7. Aliyev Sh. Chemical and petrochemical complex of Azerbaijan: potential assessment and reconstruction directions. Science and education, 46-47(2012).
8. Aliyev Sh. Salahov M. Prospects for effective use of the potential of the industrial complex in Sumgayit. “Reports”, №5, ANAS, Baku, 125 (2008).
9. Aliyev Sh. Sumgayit industrial center: use of existing potential, modernization and modernization priorities. Science and education, Baku, 44 (2012).
10. Huseynov D. Chemists are determined to contribute to the implementation of the adopted forecasting tasks. Sumgayit newspaper. February 25, (2006).
11. Scientific-practical conference "Development directions of the chemical industry". Sumgayit newspaper. October 15, (2005).
12. Gafaroglu S. The harmony of work was restored in chemical enterprises. Sumgayit newspaper. April 7, (2007).
13. Gafaroglu S. The chemists started the new year with an optimistic mood. Sumgayit newspaper. January 18, (2006).

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ORGANİC SYNTHESİS PRODUCTS BASED ON PETROCHEMİCAL İNDUSTRY WASTES

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Abstract. Cyclopentadiene and the dimeric form are taken to produce cycloolefins that do not occur naturally.Great interest in the production of dicyclopentadiene begins in 2008, when the possibility of the process of polymerization of the dimeric form was studied. Dicyclopentadiene is highly reactive and undergoes a polymerization reaction. One of the rational method of using dicyclopentadiene is its polymerization, on the basis of which polydicyclopentadiene is obtained. Polydicyclopentadiene is a thermosetting polymer compound and has the following features: high resistance to the action of various chemical reagents; reduced density; increased resistance to various temperatures. These materials have no natural analogues. They can be used freely and as a modification. For this purpose, a dimeric monomer with a purity of about 95-97% is used. Dicyclopentadiene with the required purity is not produced, therefore, the creation of new technologies for the production of a dimeric form of increased purity is a topical issue.The separation of the dimeric form from pyrocondensate has its own problems: the formation of resinous compounds; difficulty in separating the target component. These problems prevent the isolation of the dimeric form of increased purity, and also leads to a decrease in the yield of the dimeric form.Isolation of the dimeric form of increased purity (no impurity) and productivity by means of improved industrial technology.

Keywords. Cyclopentadiene, dicyclopentadiene, dimer, dimerization conditions, target product, monomer, raw material parameters, high purity dimer, graphical dependencies.

1.Introduction

The level of development of the petrochemical industry increases annually. This is due to the increased demand for lower olefins such as ethylene and propylene. An increase in the production of lower olefins leads to an increase in the yield of cyclopentadiene and its dimeric form, dicyclopentadiene. These hydrocarbons are obtained as by-products during the pyrolysis of petrochemical feedstocks. They can be used to produce a number of valuable products such as petroleum resins, adamantane, polyester oligomers, diene rubbers, as well as pesticides and insecticides. Based on the latter, the following are envisaged for this: determination of the unique conditions for the dimerization of cyclopentadiene contained in the raw material; lower gum formation based on monomerization of the dimeric form; study of the conditions for the formation of dimer concentrate; which was obtained by dimerization; achieving the maximum removal of low-boiling hydrocarbons from the feed, and also leads to a decrease in the productivity of the dimer and the selectivity of the process.

Pyrocondensate, which consists of the following fractions, is taken as a raw material from petrochemical products: C_5 fraction (with a boiling point of 20-25^{0}C) containing the following valuable hydrocarbons: n-pentane, isopentane, isoprene, cyclopentane, cyclopentadiene; C_6-C_7 fraction (boiling point 60-120^{0}C), containing mainly aromatic hydrocarbons and a small amount of dienes; and C_8-C_9 fraction (boiling point 100-210^{0}C), containing mainly hydrocarbon alkyl substituted arenes and monomeric forms, and dicyclopentadiene about 15-25%[1].

This work is devoted to the isolation and use of dicyclopentadiene, which is formed as a by-product based on the pyrolysis process, which has the main goal of obtaining lower olefins (propylene and ethylene). The paper considers modern technologies for the isolation of dicyclopentadiene.The dimer yield depends on the type of raw material used. It has a high reactivity and participates in the polymerization reaction, on the basis of which various polymers are obtained. As a raw material for the production of the dimeric form, C_5-C_9 fractions are taken, which are obtained during the pyrolysis of low-octane gasoline. Based on experimental data, it was determined that the unique temperature regime of the dimerization stage raw material is 980C and dicyclopentadiene is obtained with a yield of 70-75% and a purity of 96-98% when using as a raw material C_5-C_9 pyrocondensate fractions containing about 20-25% of cyclopentadiene and its dimer.

2.Methods of obtaining

There are two ways to obtain dicyclopentadiene: the first is to obtain the dimeric form together with other hydrocarbons (mainly isoprene); the second way is to obtain pure dicyclopentadiene.

The first way. Carried out in conjunction with the process of extractive rectification. This makes it possible to jointly obtain the dimeric form and isoprene

The production of isoprene together with dicyclopentadiene is possible using extractive rectification. The latter makes it possible to obtain dimer and isoprene together, which can be carried out in two versions: at the end, in the middle, and also at the beginning of the process. For separation, choose different separators (extractants), which are organic compounds of different classes. Examples include various ketones (acetone and methyl ethyl ketone); furfural; alkylacetamide [2].

The first option - carry out extractive rectification at the beginning of the process, while the C_5 fraction is fed for separation and the following fractions are obtained: isoprene; cyclopentadiene and pentane-pentene. The rectification is carried out in several columns

Based on the concentration of cyclopentadiene present in the feed, the dimerization step is carried out at a constant temperature and in the liquid phase. Dicyclopentadiene is separated from a mixture of hydrocarbons having a reduced boiling point by rectification.

In order to produce a dimeric form of increased purity, dicyclopentadiene is monomerized, and then secondary dimerization is carried out. Thus, dicyclopentadiene is produced with a purity increased to 85-95%.Unlike the stage of monomer dimerization, its dimeric form (dicyclopentadiene) decomposes both catalytically (in the presence of catalysts) and thermally (at high temperatures).

Extractive rectification is also carried out in intermediate stages, with the initial stage being the process of dimerization of the C5 fraction. Dicyclopentadiene, which is contained in the feedstock, is separated together with the separating agent from the bottom of the separating column. Regeneration of the separating agent is carried out to obtain the dimeric form. This dicyclopentadiene is combined with dicyclopentadiene, which is obtained by processing the cyclopentadiene-piperylene fraction used by BESF. The need for extractive rectification has increased with an increase in demand for isoprene used in the production of synthetic rubber [3].

At present, the demand for lower olefins is increasing every year and this leads to a significant increase in the yield of cyclopentadiene, as well as its dimeric form, dicyclopentadiene.

Consideration of the dimer production technology; study of the unique conditions for the formation of dicyclopentadiene of high purity and yield. For this, the following are considered: unique conditions of dimerization; the conditions for the concentration of dicyclopentadiene and the reduction of the formation of resin at the stage of monomerization.

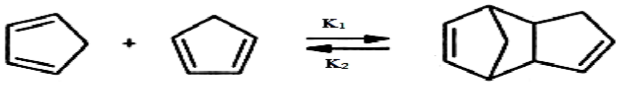
Scientific novelty. For the first time, a dimeric form of increased purity and yield from the pyrolysis condensate fraction was obtained during the pyrolysis of petrochemical raw materials. It has been determined that when intrinating, which is an inhibitor, is added to the monomerization system, gum formation decreases.

3.Experimental technique

Isolation of the dimeric form (dicyclopentadiene) is a difficult process carried out in the following stages:

- Stage of cyclopentane dimerization in C_5 fraction of low-octane gasoline pyrolysis;
- Rectification of the obtained dicyclopeniadiene followed by obtaining a technical product;
- Stage of monomerization of dicycopentadiene concentrate;
- Stage of selective dimerization of cyclopentadiene;
- Stage of obtaining dicyclopentadiene rectification.

Dimerization of the monomer contained in the feedstock.The formation of dicyclopentadiene is carried out on the basis of a reversible reaction, which is shown below:



(1)

In the course of the dimer formation process, various reactions take place, on the basis of which various foreign products are obtained. These include the formation of the trimeric form, as well as the reaction of joint polymerization of the monomer (cyclopentadiene) with other dienes. Many of these reactions are carried out under room conditions and their rate increases with temperature, therefore it is necessary to carry out dimerization under such unique conditions that it would be possible to eliminate the implementation of the above reactions [4]. These by-products decrease the yield of the target product, since the monomer is not completely converted into the component under study (see Fiq.1.)

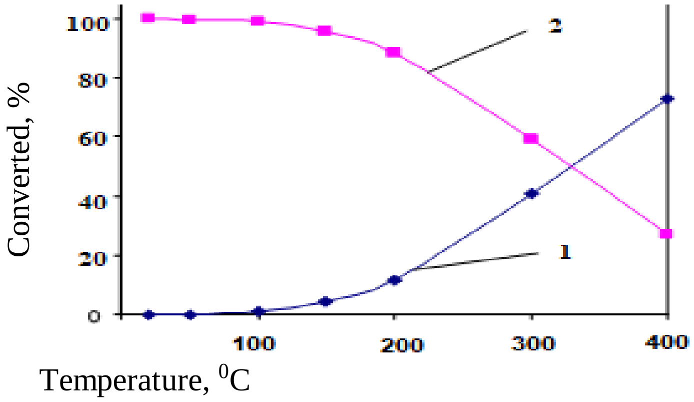


Fig.1. Temperature influence on equilibrium position. 1-dicyclopentadiene; 2-cyclopentadiene

The process was carried out for about 3.5 hours, taking into account the temperature 90^0-120^{0}C, and each time, after an hour, samples are taken from the reaction zone in a certain amount and the results are presented for chromatographic analysis, which are indicated in table.1.

Table 1.Results of chromatographic analysis of the dimerization stage

Components	The original Content	Content aft stabilizati	Process duration, ho			Content after cooling
			1.5	2.5	3.5	
1	2	3	4	5	6	7
Process temperature 95^{0}C						
Soprene	10,5	10,1	10,7	9,2	9,8	9,30
Sodimers	-	0,22	0,25	0,41	0,45	0,75
Light hydrocarbons	76,5	76,8	76,2	76,1	76,42	76,05
Heavy residue	0,5	0,25	0,38	0,58	0,74	0,79
Cyclopentadiene	14,98	9,58	8,47	7,56	5,69	4,31
Dicyclopentadiene	0,80	5,25	5,68	10,23	10,95	11,51
Conversion rate		34%	40,2	52,3%	61,5%	64,8%
Process temperature 135^{0}C						
Light hydrocarbons	78,5	78,41	77,52	76,85	76,45	75,21
Sodimers	0,35	1,12	1,25	1,58	1,65	1,98
Soprene	10,65	10,48	9,85	9,81	8,98	8,52
Heavy residue	0,02	0,95	1,25	1,45	1,53	1,86
Cyclopentadiene	6,75	8,47	3,58	2,74	2,61	2,1534
Dicyclopentadiene	0,52	9,36	13,47	14,01	14,25	14,087

As can be seen, on the basis of experimental data, upon reaching a certain temperature (135^{0}C), the degree of conversion (conversion) changes little. On the basis of the above table, it can be seen that with increasing temperature, the monomer content decreases, and heavy residues gradually increases. Below is a graph that describes the effect of temperature on formation occurs starting at a temperature of 135^{0}C [5]. Also, the effect of temperature on the degree of conversion, as well as on the selectivity of this process, was studied, which are shown in the form of a graphical dependence of temperature and the corresponding parameters (see Fig.2. and Fig.3).

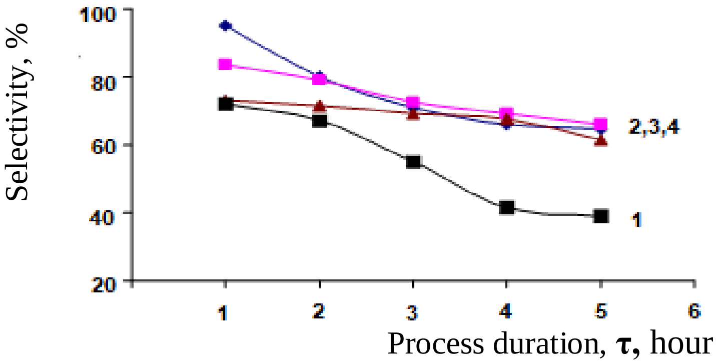


Fig.2. Graphical dependence of selectivity on temperature**.**
1-at T = 125^{0}C; 2-at T = 115^{0}C; 3-at T = 105^{0}C; 4-at T= 95^{0}C

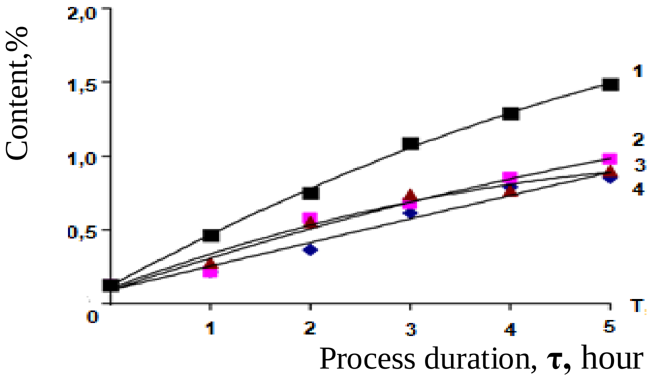


Fig.3. Dependence of the content of heavy hydrocarbons on temperature
1-at T = 125^{0}C; 2-at T = 115^{0}C; 3-at T = 105^{0}C; 4-at T = 95^{0}C

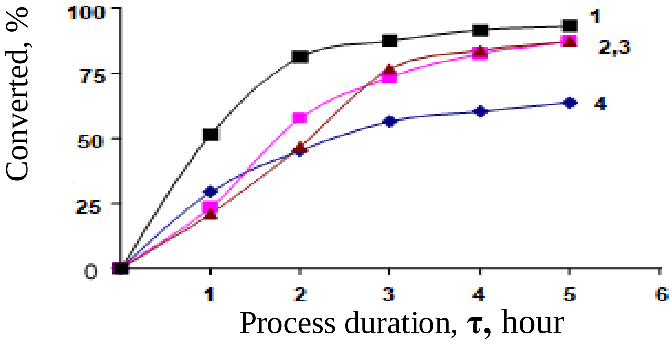


Fig.4.Graph of the dependence of the degree of conversion on temperature
1-at T = 125^{0}C; 2-at T = 115^{0}C; 3-at T = 105^{0}C; 4-at T = 95^{0}C

The content of monomer and dimer in the streams are shown in table.2.

Table 2. Content of components in streams containing monomer.

The name of the components and their percentage	Distillates		
	K$_1$-50	K$_2$-30	K$_3$-550
Cyclopentadiene	11,4-16,6	13,7-19,81	18,2-27,4
Dicyclopentadiene	-	-	0,3-3,1

Light hydrocarbons	65,3-74,5	5,4-11,7	55,3-78,9
Benzene	1,4-5,4	59,1-6,8	0,05-1,5
Carbon disulfide	0,25-1,25	2,1-,2	-
Thiophene	-	0,05-0,32	-
Heavy hydrocarbons	-	-	0,2-0,3

Table 3. Indicators of raw materials used to obtain a dimer of high purity

Indicators	Results
Density, g /cm^3 (at 20^{0}C)	0,675-0,695
Appearance	Colorless liquid
Light hydrocarbon content, %	62,5-75,3
Cyclopentadiene content, %	14,9-22,5
Dicyclopentadiene content, %	0,05-1,25
Heavy hydrocarbons content, %	0,02-0,4
Content of C_5 hydrocarbons, %	20,7-32,4
Content of carbon disulfide, in %	0,15-1,35

4.Conclusions

For the first time, the technology of production of high-purity dicyclopentadiene from C_5-C_9 pyrolysis condensate fraction obtained by pyrolysis of low-octane gasoline was studied. Dicyclopentadiene was obtained with a yield of 96-98%.

A technological scheme was proposed for obtaining high purity of dicyclopentadiene from petrochemical raw materials. The material balance of the process was calculated, and the consumption ratios for auxiliary materials and raw materials were determined. The unique conditions for the implementation of dimerization of the cyclopentadiene monomer, which is contained in the feedstock, have been studied: the time is 3.5 hours; under a pressure of 0.6-0.8 MPa; the temperature regime of the stage is 80-120^{0}C. Under these conditions, the conversion is increased to 87% and the selectivity is 95%.It was determined that on the basis of rectification in two stages for concentrating dicyclopentadiene, it includes the following: separation of lower hydrocarbons with a boiling point of 25-40^{0}C and azeotropic rectification for the separation of carbon disulfide and dienes together with methanol, as an agent, in a ratio of 0, 5: 1. This makes it possible to isolate dicyclopentadiene with a major component of 95%.

The isolated dicyclopentadiene was found to have a high purity of 96% and is suitable for the polymerization reaction.

5.References

1.Гоготов, А.Ф.Инновации в ингибировании.Терпенофенолы - новое поколение высокоэффективных ингибиторов полимеризации для процессов переработки жидких продуктов пиролиза /А.Ф. Гоготов, И.И.Батура, И.Ю. Чукичева и др.// Журнал Нефтепереработка и нефтехимия. №1. Стр.27-31. Москва (2016).

2. Т.И.Айралова, Тагиев Е.И.Синтез производных на основе карбамида и побочных продуктов производства бутиловых спиртов и разработка ингибиторов коррозии на их основе. Журнал "Наука и Просвещение", №1, Стр.39-42. Пенза (2019).

3. T.İ.Ayralova, Abdullayeva L.K. Inteqrated processing of pyrolysis by-products – allen and methylacetylene. Журнал "Наука Просвещение", №1, Стр.36-39. Пенза (2019).

4. T.İ.Ayralova, Hasanzade A.S.High purity dicyclopentadiene from petrochemical feeds. Журнал "Наука и Просвещение", №1, Стр.20-23, Пенза (2019).

5. Т.И.Айралова, Сеидов Е.И. Использование жидких продуктов пиролиза углеводородного сырья в синтезе нефтеполимерных смол. Журнал "Наука и Просвещение", №1, Стр.39-42. Пенза, (2019).

PP-IV-1

THE IMPACTOF MUNICIPAL SOLID WASTE INCINERATION ASH ON BETONAND CEMENT

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Abstract. In this article studied the impact of solid remnants (ash residues) on cement and concrete. It also should be noted that the increase in the amount of added ash residues from 10 to 20%, 60 mPa continuously increases and at the end of the observation period, it increases evenly. There are have been studied the influence of various factors on the strength of concrete (strength of the binder-alkaline solution, temperature and length of curing, etc.).It was observed that amidst increasing in the concentration of the binder - sodium hydroxide and silicate - the strength of concrete increases as well. The mixture containing an ash residue with a mass ratio of sodium silicate solution to the alkali solution of 2.0. was chosen as the optimal one. Temperature and length of curing of ash cement also showed positive dynamics of concrete compressive strength.

Keywords: municipal solid waste, ash residues, cement, concrete, strength, bonding, time and temperature of curing.

1. Introduction

Today, for the time being, the disposal of household and industrial waste is a valid environmental issue.

In the reason for the exponential growth of urbanization and industrialization, the amount of municipal solid waste (MSW) is increasing rapidly. In addition, disposal of municipal solid waste (MSW) is becoming a frequently serious obstacle for many urban municipalities because of the increasing volume of generated municipal solid waste, increasing costs of landfill operations or due to a lack of landfills. Every year, land plots are allocated for the storage of household and industrial waste, which can be used for agricultural land, as well as for the constructions. With increasing awareness of the environment andits potentially hazardous consequences, the use of these materials has become an attractive option of recycling alternative. The use of various wastes for these purposes is a practical implementation of the concept of industrial metabolism, which consists in the use of waste from one industry as a raw material for another.

The main guiding principle of SWM is the rule of 3R's (waste reduction, reuse and recycling), which gradually began to be carried out starting from the 20th century in EU countries [1]. The waste management system was first developed in the EU countries, due to the early and rapid development of the economy, the lack of resources and irrational usage of an area in numerous European countries [2,3]. The way to manage above-mentioned types of waste includes landfilling, composting, incineration, etc.

Fig. 1 reveals that landfill was the dominant SWM method in 1995 in these countries, but this figure has been steadily declining since then, while incineration and waste packaging in the waste management process increases dramatically with significant increases in waste recycling. [3].

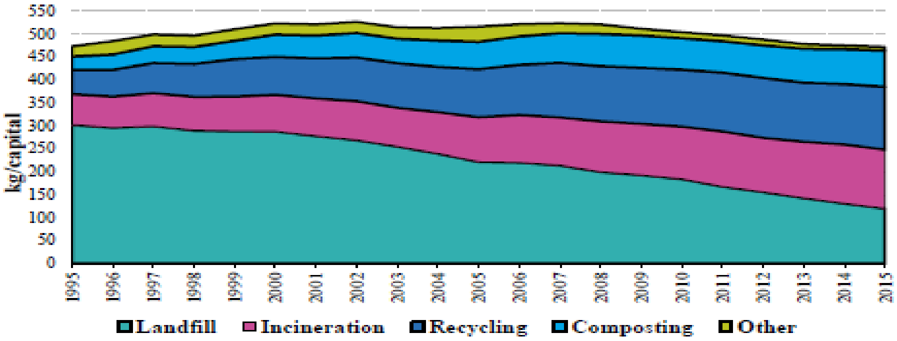

Figure 1. Household waste treatment in the period of years 1995-2015 (Eurotat 2017)

The global production of cement is growing annually (in 2018 it reached about 5 million tons per year and is growing annually by 5-10%). Concrete mixes with ash have greater cohesion, less water separation and delamination. Concrete has high strength, density, water resistance, resistance to sulfate corrosion, and lower thermal conductivity [3-7].

In connection with the increase in the amount of household waste in Azerbaijan on the territory of the former Balakhani landfill for waste disposal, by the order of the President of Azerbaijan Ilham Aliyev dated December 28, 2011, the “Balakhani industrial zone” with a total area of 7 hectares began its activity. The Balakhani industrial zone concentrates on the production in the field of waste processing. The management company of the industrial park is "Tamiz Shahar" JSC

Balakhani Industrial Park includes two plants on sorting and incineration. This is the largest waste processing station in Eastern Europe and the CIS. The plant is built adopting 4G technology and fully complies with local and European environmental protection standards.The enterprise's capacities allow to process up to 200 thousand t. of municipal solid waste (MSW)from which up to 40% of secondary raw materials are extracted: metals, glass, cardboard, plastic and other materials [13].

The ash of incineration plants contains oxides of CaO, SiO_2, Fe_2O_3 and Al_2O_3, similar to the composition of raw materials for cement production, this may become a possible substitute for raw materials in the production of cement [3-5, 8-12]. The incineration of waste generates a large amount of fly ash and bottom ash, which can be used as a filler additive in building materials for road construction and other fields.

2.Metod

Compression tests were performed on a YAW-300D computerized bending-compression machine with a maximum bending and compressive force of 300 and 10 kN, respectively. Samples for compression tests were prepared in special molds with dimensions 40:40:40 mm. After holding in the mold and special heat treatment, the samples were brought to a state corresponding to the standards for a day at room temperature. After holding in the mold and special heat treatment, the samples were brought to a state corresponding to the standards for a day at room temperature. The compressive strength of concrete samples is calculated by the formula:

$\sigma = F / S$; where, σ - compressive strength, MPa; S- cross-sectional area of concrete sample, mm2, F- maximum compressive force, N.

The arithmetic mean of the three experiments was taken as the desired test result

2. Results and discussions

In this article presents the results of studying the effect of various factors, such as the amount of ash, an activator-binder alkaline solution, temperature and time of curing, etc. on the strength of ash concrete.

The ash concentration varied from 10-30%, and the activators from 5-10%. The kinetics of changes in the strength of concrete with different ash content was determined experimentally. The results of the observation are given in Figure 2.

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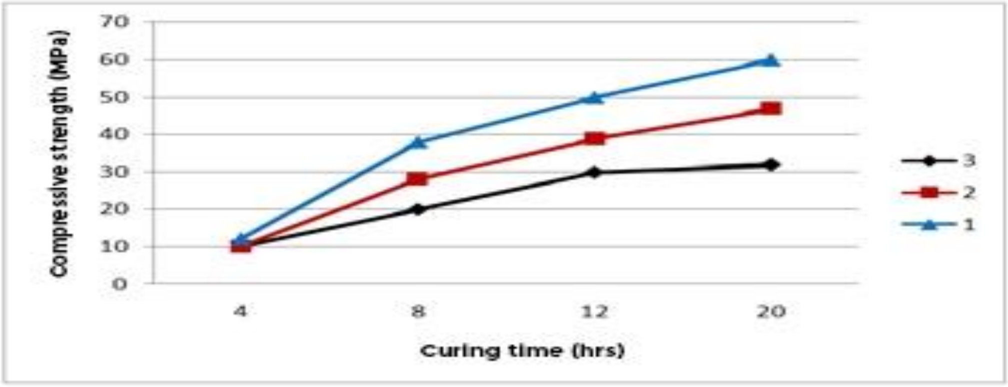

Figure 2. Kinetics of changes in concrete strength.Curves: 1 - 10%, 2 - 20% and 3 - 30% ash.

The results showed that the highest strength, about 60 MPa, is possessed by concretes with an ash content of 10-20%. which strngth increases uniformly on the 20th day and later. An increase in the amount of ash from 25% and more with the same amount of activator tends to decrease the compressive strength of concrete.

The concentration of sodium hydroxide (NaOH) solution.

Mixtures produced to analyse the effect of sodium hydroxide solution on the compressive strength of concrete. The test cylinders were left at ambient conditions for approximately 30 minutes prior to the initiation of dry cure in the oven. The curing time was 24 hours at various temperatures.

Resulted measurements on day 7 of the compressive strength of the test cylinders are shown in Table 1.

In Table 1, the difference between mixture 1 and mixture 3 is the concentration of the NaOH solution in terms of molar (second column). Blend 3 with a higher concentration of NaOH solution gives higher compressive strength than blend 1. A similar trend is observed for blenders 2 and 4.

The ratio of dissolved sodium silicate to dissolved sodium hydroxide. The effect of the ratio of dissolved sodium silicate to NaOH solution in bulk on strength in concrete can be seen by comparing the results of mixtures 1 and 2, as well as mixtures 3 and 4 in the table. For mixtures 1 and 2, although the concentration of NaOH solution (in terms of molarity) is the same, in mixture 2 the ratio of sodium silicate to the solution of NaOH is higher than in mixtures 1. This change increases the compressive strength of mixture 2. A similar trend is also observed in the results of mixture 3 and 4. The results are shown in the table. Mixtures 2 and 4 with a mass separation of sodium silicate solution with NaOH dissolution 2.0.

Table 1. Change in the strength of concrete depending on the amount of activator - alkali and sodium silicate

Mixture	Concentration of NaOH liquid (in Molars)	Ratio of sodium silicate to NaOH solution (by mass)	Comressive strength at 7th day (MPa)
			Cured for 24 hours at 60 ° C
1	5 M	0,5	15
2	5 M	2,0	47
3	10 M	0,5	40
4	10 M	2,0	58

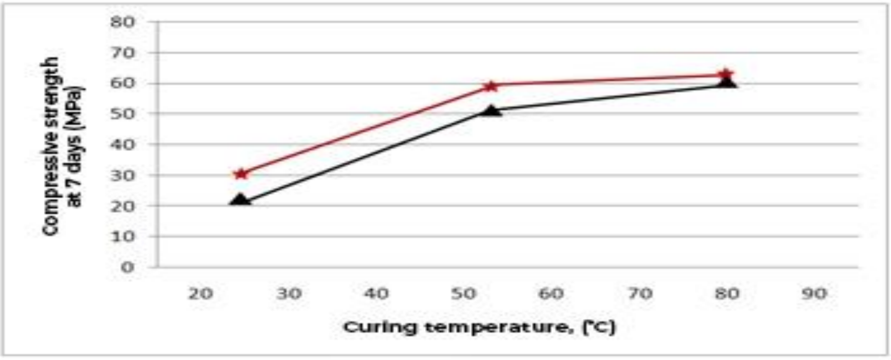

Figure 3. Impact of temperature on compressive strength
Curves: ★ - mixture 4; ▲ - mixture 2

Curing temperature. Figure 3 shows the effect of cure temperature on compressive strength for mix 2 and 4 after dry curing of test cylinders in an oven for 24 hours. All other test variables were constant. A higher cure temperature resulted in greater compressive strength, although raising the cure temperature above 60 ° C did not significantly increase the compressive strength.

Figure 4 demonstrates the effect of curing temperature for different oven holding times. Five different curing temperatures were used, i.e. 30 ° C, 45 ° C, 60 ° C, 75 ° C and 90 ° C.

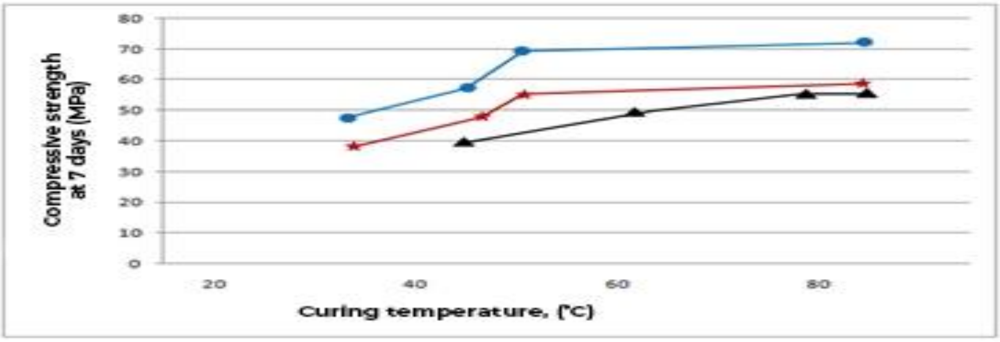

Figure 4. Effect of curing temperature on compressive strength
Curves: ● - mixture 4 – 24 h., ★ - mixture 2 – 24 h.,
▲ - mixture 2 – 6 h.

The cure was carried out in an oven for 24 hours for mix 2 and 4 and 6 hours for mix 2 only. The results revealed in Figure 4 confirm that higher cure temperatures resulted in higher compressive strengths for both 6 hours and within 24 hours of curing.

Curing time. Geopolymer concrete can be obtained by adopting the generally accepted technologies used in the manufacture of Portland cement concrete. In the laboratory, fly ash and aggregates were first dry mixed together in a container for about three minutes. An alkaline NaOH liquid was mixed with water. The liquid component of the mixture was then added to the dry materials and mixing was continued for another four minutes. Fresh concrete can be processed for up to 120 minutes without any signs of setting and without any decrease in compressive strength. Fresh concrete was cast into special moulds and compacted using conventional methods. The compressive strength and workability of geopolymer concrete also depend on the wet mixing time. As the wet mixing time increased, the compressive strength of the hardened geopolymer concrete increased with a slight loss of workability in the fresh concrete.

Although low calcium ash-based geopolymer concrete can be cured under ambient conditions, thermal curing is generally recommended. Heat curing contributes significantly to the chemical reaction that takes place in the geopolymer paste. Both the curing time and the curing temperature affect the compressive strength of geopolymer concrete.

To investigate the effect of cure time, tests were prepared using Mix 2. Test cylinders were cured for various cure periods from 4 hours to 96 hours (4 days).

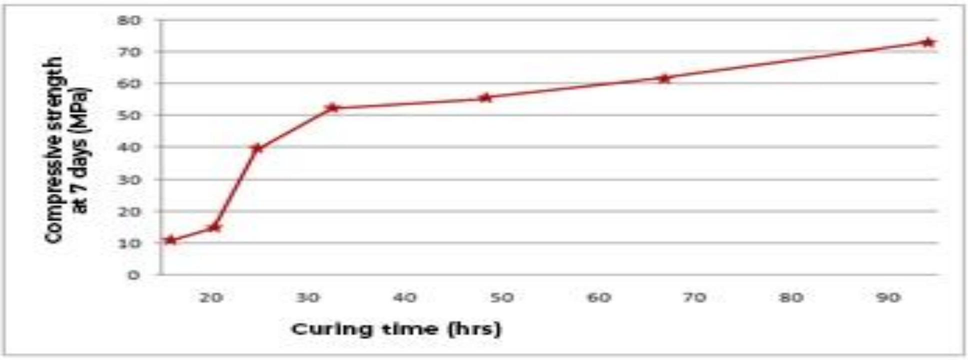

Figure 5. Influence of curing time on compressive strength for
★ - mixture 2

Figure 5 presents the results of these tests at the temperature of 60 °C. Longer cure times improved the polymerization process, resulting in higher compressive strength. The rate of increase in strength was rapid up to 24 hours of cure.

Impact of the mass ratio of water to geopolymer mass and sodium oxide on the strength of concrete.

The test specimens were cylinders with a size of 100–200 mm, thermoset in an oven at various temperatures for 24 hours. The results of these tests, presented inFig. 5, show that the compressive strength of geopolymer concrete decreases with an increase in the ratio of water mass to geopolymer by mass.

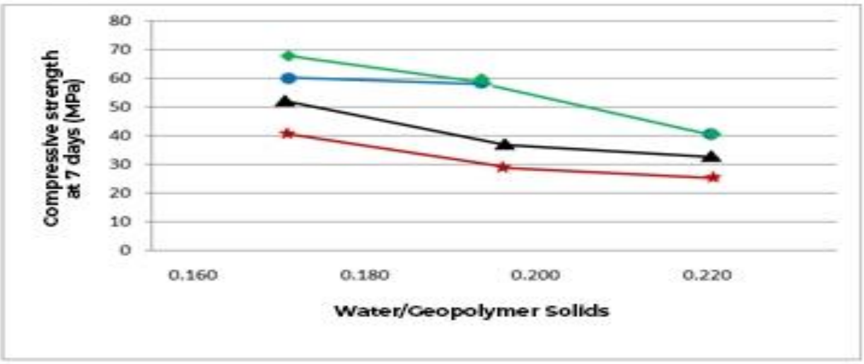

Figure 6. Effect of water-to-geopolymer solids ratio by mass on compressive strength of geopolymer concrete

Curves: ◆ - 90 °C; ● - 75 °C; ▲ - 45 °C; ★ - 30°C

As can be discerned from the above, the interaction of various parameters in terms of compressive strength and workability of geopolymer concrete is complicated. To support in the development of low calcium ash-based geopolymer concrete

mixes, a single parameter has been developed called the “water to geopolymer ratio” by weight. For this parameter, the total mass of water is the sum of the mass of water contained in the sodium silicate solution, the mass of water in the sodium hydroxide solution, and the mass of additional water, if any, added to the mixture. The mass of the geopolymer solids is the sum of the mass of ash, the mass of sodium hydroxide solids and the mass of solids in a sodium silicate solution (i.e., the mass of Na_2O and SiO_2).

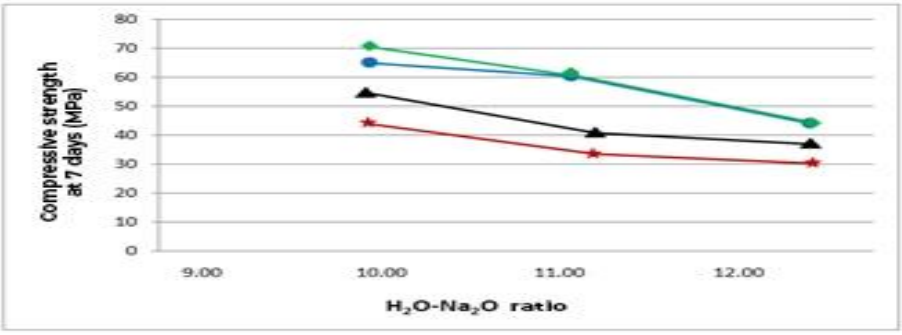

Figure 7. Effect ofH_2O-to-Na_2Omolar ratio on comressive strength

Curves: ◆ - 90 °C; ● ★ - 75 °C; - 45 °C;
▼ - 30 °C

The test cylinders were cured for 24 hours at various temperatures. Figure 7 shows the effect of the H_2O-Na_2O molar ratio on the compressive strength of geopolymer concrete at different curing temperatures. An increase in this ratio provides the decreasing of the compressive strength of the concrete.

3. Conclusions

As a result of the study of the effect of ash residues of solid waste on the properties of cement and concrete based on it:

A method has been developed for obtaining concrete samples with the addition of bottom ash from MSW processing, activated with an alkaline solution. The results showed that the highest strength, of the order of 60-70 MPa, is possessed by concretes with an ash content of 10-20%, and on the 20th day and at a later date, the strength gradually increases. An increase in the amount of ash from 25% and more with the same amount of activator, there is a tendency for the compressive strength of concrete to decline.

The optimal concentration of the alkaline solution was chosen - 5M. A higher concentration (in terms of molar) of sodium hydroxide solution leads to a higher compressive strength of geopolymer concrete based on bottom ash.

It has been established that the higher the ratio of the mass of sodium silicate solution to sodium hydroxide solution by weight, the higher the compressive strength of concrete. The optimal mixture was chosen containing an ash residue with a mass ratio of sodium silicate solution to the alkali solution of 2.0 and was used as the main mixture to study the influence of other parameters.

It was revealed that the curing temperature affects the strength of ash concrete. A higher curing temperature leads to a higher compressive strength of concrete, although an increase in temperature above 60 ° C does not significantly increase the compressive strength.

The molar ratio of H_2O-Na_2O and Na_2O-SiO_2 showed that only the range from 10.0 to 14.0 is possible. When the molar ratio H_2O-Na_2O is less than 10.0, concrete mixtures are difficult to process; on the other hand, when the value is exceeded 14.0, there is a significant separation of the ingredients of the mixture due to the presence of excess water. With an increase in the ratio of the mass of H_2O to the mass of concrete, its compressive strength also decreases.

5.References

1. EPA (2017). United States Environmental Protection Agency-Environmental Topics.
2. EEA (2013). European Environment Agency-Managing municipal solid waste - a review of achievements in 32 European counties.
3. Eurostat, (2017). Statistical office of the European Union Situated in Luxembourg (statistic on Municipal waste statistics in Europe checked in 2017).
4. Banar, M.; Zkan, A. Characterization of the municipal solid waste in Eskisehir City, Turkey. *Environ. Eng. Sci.* 2008, *25*, 1213-1219.
5. Belevi, H.; Moench, H. Factors determining the element behavior in municipal solid waste incinerators. 1. Fieldstudies. Environ. Sci. Technol. 2000, 34, 2501–2506. [Cross Ref].
6. Born, J.G.P., & Veelenturf, R.A.L. (1997). MSWI residues in the Netherlands putting policy into practice. Studiesin Environment Science 71, 841-850.
7. Bilodeau A., Malhotra V.M. Concrete incorporation high volume of ASTM Class F fly ashes, mechanical properties and resistance of deicing salt scaling andchloride-ion penetration // Proceedings Fourth International Conference. Istanbul, Turkey, 3–8, May 1992. P. 319– 349.
8. Karanjekar, R.V., Bhatt, A., Altouqui, S., Jangikhatoonabad, N., Durai, V., Sattler, M.L., Hossain, M.D.S., & Chen, V. (2015). Estimatingmethaneemissionsfrom landfills based on rainfall, ambient temperature, and waste composition: The CLEEN model. Waste Manag. 46, 389–398.
9. Klein, R., Baumann, T., Kahapka, E., &Niessner, R. (2001). Temperaturedevelopmentin a modern municipal solid waste incineration (MSWI) bottom ash landfill with regard to sustainable waste management. J. Hazard. Mater. 83, 265–280.
10. Kowalski, P.R., Kasina, M., &Michalik, M. (2016). Metallic Elements Fractionation in Municipal Solid Waste Incineration Residues. Energy Procedia 97, 31–36.
11. Lee, V.K.C.; Kwok, K.C.M.; Cheung, W.H.; McKay, G. Operation of a municipal solid waste co-combustion pilot plant. *Asia-Pac. J. Chem. Eng.* **2007**, *2*, 631-639.
12. Liu, A., Ren, F., Lin, W.Y., & Wang, J.-Y. (2015). A review of municipal solid waste environmental standards with a focus on incinerator residues. Int. J. Sustain. BuiltEnviron. 4, 165–188.
13. ttps://tamizshahar.az

USE OF THERMAL POWER PLANTS İN THE PRODUCTİON OF PHOSPHOROUS FERTİLİZERS FROM ASH RUST

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Abstract: The composition of ash rust from thermal power plants was studied in this article. The same time was shown the methods of its use were studied, the possibility of developing phosphorus mineral fertilizers at different stages of production technology.

Keywords: straw, ash rust, fertilizer, microelements, superphosphate "chorus", kWh of electricity.

1.Introduction

The most important indicator of a country's development is the amount of electricity per capita. In developed countries, the amount of energy per capita is 14 times higher than in developing countries. This figure also differs between developed countries. For example, in Norway, a person consumes 25,000 kWh of electricity per year, while in Sweden it is 16,000 kWh, in France 6,000 kWh, and in Italy 3,000 kWh. In Bangladesh, this figure is only 46 kWh [1].

Although many technologies are currently being developed to generate electricity, 75% of the world's electricity is produced by thermal power plants, and 90% in Azerbaijan. These power plants account for 27% of all industrial emissions. Depending on the type and composition of the fuel, the amount and composition of waste released into the environment also varies. When using both fuel oil and coal as fuel, a large amount of pulverized waste (ash) is obtained, in which various metal oxides are of special importance.

It is known that the capture and use of industrial waste is important both from an environmental and economic point of view. Among the large-tonnage industrial wastes, the amount of straw collected at Thermal Power Plants (TPPs) is in the millions in the world and in our country in hundreds of tons, and this amount is increasing every year. Approximately 10-30% of such waste is ash and 70-90% is rust [2]. It is known to obtain superphosphate and ammonium phosphate enriched with phosphorites on the basis of sulfuric acid (P_2O_5e.f.t .: H2SO4: P2O5 m.k.). The study was performed at a mass ratio of 1: 0.11: 0.08 to 1: 0.56: 0.08 for 45 minutes at a temperature of 70^0C [3].

Literature studies show that there are many opportunities to use kulpasa. It is used as a fertilizer in the neutralization (calcification) of acidic soils, as a micronutrient additive (Cu, Mo, Ni, Zn, Mn, etc.) in the preparation of mixed compound fertilizers, as a neutralizer in the granulation of fertilizers (superphosphate), in the absorption of fluorinated gases. as a means of eliminating decay, in the adsorption of heavy metals in water, in the construction industry, in the process of obtaining fertilizers based on potassium silicate, etc. is considered useful [4]. Although the area of application is sufficient, thermal power plant ash rust is almost never used. Studies show that the use of wastes containing complex micronutrients is more important than the use of water-soluble salts of micronutrients [5]. This idea is based on the fact that water-soluble trace elements are quickly washed away. The analysis shows that the microelements are unevenly distributed in the composition of the pulp, and most of them are in particles smaller than 1 mm. Therefore, the first stage of using kulpas requires its fractionation, crushing and grinding. One of the simplest methods is to treat the mulch with macro-fertilizers or limestone. The use of such a hut can be arranged near the area where this waste is collected. This is due to the fact that long-distance transportation of waste is not economically feasible.

2.The experimental part

Due to the large number of compounds and elements in the composition of the ashtray, their amount varies widely.

The amount of compounds and elements in the pass of the thermal power plant, in%: CaO - 2,0-65,0; SiO_2-10.0-68.0; MnO 54-8.66; MgO -2.12-12.0; Al_2O_3 -0.4-16.8; Fe_2O_3-10,3-14,2; TiO_2-0.68-0.93; Na_2O-1.00-2.56; K_2O-3.70-4.54; P_2O_5-0.0-0.14; SO_3- 0.14-1.45, Cu, Mo, Zn. Ni, S and other compounds are 6.56-11.60 [6]. The use of this waste as a complex additional source of raw materials, as well as to increase the production of mineral fertilizers is a topical issue.

The study looked at the use of thermal power plant huts as fertilizer and fertilizer additives. The chemical composition of the ash used as fertilizer contains 64% of CaO and MgO compounds and 5.1% of silicon oxide (SiO_2). Depending on the needs of the land used in agriculture, 1-2 tons of boiler ash is used every 2 or three years for 1 hectare.

The ashes are poured into the acidic area and mixed with the soil, creating favorable conditions for agriculture. Due to their small size, the grains perform a useful function by protecting the soil moisture [7].

Physico-chemical properties of fertilizers obtained in the neutralization of phosphate acid contained in superphosphate from the thermal power plant, as a powder in the process of granulation from the ash part and by mixing superphosphate "chorus" obtained in high proportions of mineral acids (sulfate, nitrate, phosphate, etc.) in different proportions. The experiments were performed using known methods [8-11].

In order to obtain fertilizer from the mulch by technological method, superphosphate chorus is first prepared from apatite with 60-66% sulfuric acid in accordance with (0.75-0.90): 1 mass at a temperature of 45-600 C and intensive mixing for 10-25 minutes. Then it is granulated and dried from the superphosphate chorus with a straw in the ratio of 1: (0.45-0.65) by mass. The obtained granular fertilizer contains many trace elements (Mn, Cu. Mo, Zn, Ni, etc.) despite the fact that the amount of phosphorus is less than the norm. On the basis of the experiments, the dependence of the grain yield, grain yield, hygroscopic point and degree of adhesion of the obtained granular fertilizer on the composition and temperature of the charge was studied. This dependence is given in Table 1.

As can be seen from the table, the analytical indicators of fertilizers obtained using TPP ash rust fully comply with the requirements of existing normative documents (TS 5956-92)

Physico-chemical parameters of granular superphosphate obtained as a result of experiments are given in Table (Table 2).

Table 1. Dependence of yield of 1-4 mm grains, hygroscopic point and degree of decay on the composition and temperature of the charge

№	The composition of the charge, the mass fraction	Frost temperature, ^0S	Granules 1-4 mm in size., %	Hygroscopic point, %	Sticky rate, point
	Thermal Power Plant Passage: Superphosphate chorus				
1	1 : 0,1	35	46	50	V
2	1 : 0,15	38	51	50	V
3	1 : 0,20	39	63	55	IV
4	1: 0,25	43	68	60	IV
5	1 : 0,30	47	71	65	III
6	1 : 0,35	49	76	80	II
7	1 : 0,40	50	78	82	II
8	1 : 0,45	52	80	85	I
9	1 : 0,50	53	81	86	I
10	1 : 0,55	56	83	90	II
11	1 : 0,60	58	84	75	II
12	1 : 0,65	61	79	70	III
13	1 : 0,70	62	73	77	IV
14	1 : 0,75	63	71	68	IV
15	1 : 0,80	65	69	65	III
16	1 : 0,85	66	65	60	IV
17	1 : 0,90	67	64	50	IV
18	1 : 0,95	68	63	50	V

Table 2. Physicochemical parameters of granular superphosphate

№	P_2O_5 , %				Granules. mm.%				Mec. strengthening., kg/cm^2	F, %
	free	soluble in water	appropriation	common	<1	1-4	4-6	>6		
1	1,7	16	19	20	2	84	14	0	19	1,20
2	1,9	16	19	20	1	90	9	0	20	1,11
3	2,0	16	19	20	0	91	8	1	21	1,00
mid	1,86	16	19	20	1	88	11	0	20	1,12

3.Analysis.

The analysis of experiments shows that the straw is suitable for use in the process of neutralization of phosphoric acid in superphosphate, and in addition the mechanical strength of the obtained fertilizer grains (1.6-2.4 MPa), the amount of grains 1-4 mm (2-5%) and, accordingly, technological equipment productivity is also increasing. Experiments show that the use of thermal power plants is environmentally and economically important. However, in order to choose a more efficient direction, large-scale agrochemical experiments require technical, economic and environmental evaluation of the results.

4.Results.

The use of straw in the powdering of grains eliminates the decomposition of the fertilizer and allows it to be partially enriched with trace elements. It is clear from the results of experiments that when using straw, the yield of 1-4 mm grains of fertilizer based on superphosphate chorus increases, hygroscopicity decreases and, accordingly, the leaves disappear.

5.References

1. N.I.Ivanov and I.M. Fadin. Engineering ecology and environmental management. M. "Logos", 2004, 518 pg.
2. M.A. Panchenko, Assessment of the negative impact on the ecological state of the environment of emissions of pollutants into the atmosphere from heat power enterprises, Chita 2016 pg. 29-35.
3.Alimov U.K., Ortikova S.S., Namazov Sh.S., Reimov A.M., Kaimakova D.A. A rational way to solve the problem of processing off-balance ore of phosphorites of the Central Kyzylkum for ammophosphate fertilizer // Uzbek chemical journal (Tashkent). - 2015. - No. 5. - pg. 56-60.
4. Pozin M.E. and other Workshop on the technology of inorganic substances. L. Khimiya, 2005, 376 p.5.Mohammed Ashraf, Manish Mokal and J. Bhattacharya Fly Ash India New Delhi Use of Fly ash in high Performance Concrete & Self Compacting Concrete. 2005, pg.29-33.
6.Patent AZ, i2009 0069 14.04. 2009 (Humbatov M.O., Shirinova D.B., Mustafayev I.A., Mehraliyev Ch.A.).
7. Noskov A.S., Savinkina M.A., Anischenko L.Ya. The impact of thermal power plants on the environment and ways to reduce the damage. Novosibirsk. Ed. State Public Library for Science and Technology, 2005. pg. 25-28.
8.Abdulhalim KaraGin1. Murat DoLruyol. An Experimental Study on Strength and Durability for Utilization of Fly Ash in Concrete Mix.2014. pg. 75-79
9. Gritsina V.G., Kotlyarova E.G. Productivity, seed quality and profitability of soybean varieties depending on the level of fertilization.//Innovations in the agro-industrial complex: problems and prospects № 4 (16) .2017 .pg.51-62
9. Shafran S.A. The dynamics of the use of fertilizers and soil fertility//Agrochemistry. - 2004. - No. 1. - pg. 9-17.
10. Nilovskaya N.T., Karmanenko N.M. Techniques for managing the production process of winter wheat with agrochemical agents at low temperature effects and various weather conditions of growing. - M .: VNIIA, 2009 .-- 120 pg.
11. Shamshidinov I. T., Mirzakulov Kh. Ch., Mamazhanov Z. N. Research of the process of obtaining fertilizer such as double superphosphate from karatau phosphorites.//Chemistry and Chemical Technology. Tashkent Institute of Chemical Technology. No. 1 (55), 2017, pg.12-15

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