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CONTENT

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STUDY OF REGULARITY OF CHANGES IN VOLUMETRIC MASS OF FOAMED GEOPOLYMER MATERIALS ON BASIS OF LIMESTONE WASTE

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The creation of composite construction materials, which have a less harmful impact on the environment both at the stage of their production and in the process of their use, is of great interest in the global construction industry. Recent innovations have led to the creation of foamed geopolymer concrete or geopolymer foam, which includes the operational advantages of thermal and acoustic insulation materials, saves energy by reducing heat loss, and contributes to the reduction of CO_2 *emissions into the environment. For a better understanding of the properties and benefits related to the use of foamed geopolymer materials, this paper presents studies of the volumetric mass of these materials obtained from limestone waste and silicate activator. Samples with a ratio of components (limestone waste: activator) of 70:30, 75:25, and 80:20 were obtained. Studies of the volumetric mass depending on changes in the concentration of alkali in the solution of the gas generation activator showed that the minimum values of the volumetric mass are achieved at 1 mol/L concentration of alkali. In addition, it was found that the best foaming geopolymer material is achieved at a ratio of components of 80:20 and at a content of the gas generation activator solution in the mixture of 18% mass.*

Keywords: *foamed geopolymer, volumetric mass, porosity, thermal insulation material.*

INTRODUCTION

During the last hundred years Portland cement-based concrete materials have become very widespread all over the world due to their reliability, wide availability, relative low cost of raw materials and production technology. It should be noted that since the widespread adoption of "sustainability" as the main criterion for materials evaluation by the engineering community and the public, the building and construction materials industry is facing increasing demands, as Portland cement production is beginning to be regarded as unsustainable. In spite of the fact that the energy input of Portland cement remains lower than that of other building materials [1], the high production volume and the constantly increasing demand leads to a very high consumption of raw materials, resources and energy, which in turn contributes to an increase in greenhouse gas emissions and dust pollution [2]. According to the wording of the World Commission on Environment and Development (WCED) [3], the concept of sustainable development is understood as "the ability to meet our current needs without compromising the ability of future generations to meet theirs". This formulation of sustainability includes an examination of all the characteristics of a particular industry, such as the provision of raw materials, energy consumption, the environmental impact of a material or component in its production and use, and its reusability or recyclability. One important aspect of the cement industry is the future shortage of cheap raw materials due to the high consumption of conventional natural materials. Another important factor for the sustainability of the cement industry is the high energy consumption. Energy is required for the calcination of clinker at 1400-1500°C and the subsequent grinding of clinker and auxiliary materials. The main share of this energy consumption is for the conversion of raw materials into clinker. This very much depends on the type of equipment used in the process. Thus, the inefficient long rotary kilns waste 6 GJ heat per ton of clinker whereas a modern rotary kiln consumes 3,1 GJ heat per ton of clinker. The worldwide average is 3,8 GJ/t clinker [4]. In addition, the energy needed for grinding and crushing cement is 100 kWh/t cement [5]. Total energy consumption from raw material to cement is 3,2 GJ/t cement [5]. High energy consumption is associated with high emissions. For example, each ton of clinker produces 0,9 tons of CO_2. Herewith 0,53 t is for raw material decomposition and 0,37 t for fuel combustion [2]. The problems with regard to CO_2 emissions, the limited availability of raw materials and the high energy consumption will therefore be among the major factors determining the future sustainability of the cement industry.

Therefore, the development of new, environmentally friendly construction materials with a reduced harmful impact on the environment at the stages of their production and operation will be the main direction of development of the global construction industry. In recent decades, materials based on geopolymers have become one of the alternative binders for concrete production [6]. Generally, in terms of energy consumption and CO_2 emissions, geopolymer materials are considered to be much more environmentally friendly in comparison to Portland cement [7,8,9]. Fly ash and metakaolin are the most common raw materials for geopolymers used in construction technology. The fly ash is usually a by-product, in rare cases a waste product, which is produced by the burning of coal and domestic waste. In European countries the ash is fully utilized, but in developing countries the use of fly ash is very low and the consumption of cement is increasing every year. The use of fly ash as a raw material is profitable. It does not require large energy inputs, but a little pretreatment is necessary. The extraction of metakaolin by clay burning requires higher temperatures (750^0C) but it requires much lower temperature in comparison with the production of clinker (1400-1500^0C), that is, this process is less power-consuming. One of the important components of geopolymer materials in terms of environmental impact is an alkaline activator. Alkali production is also a power-consuming process. Thus, the energy required to produce dry sodium hydroxide is 14,9 GJ/t [10], and sodium silicate is 5,4 GJ/t [11]. The most precise values of energy consumption associated with CO_2 emissions may vary depending on the specific method of alkali production. Taking into account that the content of the alkaline activator in the geopolymer mixture is at the lowest possible level, the benefits of geopolymers in terms of environmental impact may be significantly higher. Thus, according to available data, CO_2 emissions during geopolymer production are 60-80% lower than during clinker production [7,8,9].

A relatively novel innovative product is foamed geopolymer concrete. It includes all the advantages of foam concrete and geopolymer technology [12-21]. It makes it possible to reduce the harmful environmental impact of construction materials in terms of used raw materials, CO_2 emissions and operational energy costs. On the other hand, the use of foamed geopolymers allows to create a new type of thermal insulation materials. The advantages of using thermal insulation materials are obvious. This is a significant reduction in heat loss, which reduces energy consumption and, accordingly, CO_2 emissions, as well as the light weight of such materials, which reduces the overall load on the structure [22,23,24]. Another important aspect of geopolymers is the use of wastes from the mining and construction industries, which saves natural raw materials [25,26].

Taking into account the mentioned above, in this study, limestone wastes from the second geological area of Garadagh deposit were used as a raw material for obtaining of foamed geopolymers, and sodium silicate was used as an activator.

EXPERIMENTAL PART

Limestone wastes from the second geological site of Garadagh deposit were used as a raw material for the production of foamed geopolymer materials. The chemical composition of this material is presented in table 1.

Liquid glass $Na_2O(SiO_2)_n$ (sodium silicate) a thick semi-transparent liquid (according to GOST 13079-2021) was used as an activator of the geopolymerization process. Silicate module is 1-3, density is 1300-1360 kg/m^3.

Sodium hexafluorosilicate $Na_2[SiF_6]$, a colorless crystalline powder poorly soluble in water which corresponds to TU 2621-010-69886968-2013 was used as a catalyst for geopolymerization.

As a gas-forming agent used aluminum powder according to GOST 5494-95.

Table 1

Chemical composition of limestone powder, %wt

Calcination losses	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
34,27	15,89	2,51	1,50	42,01	0,82	0,51	0,56	0,43

Crystalline sodium hydroxide (GOST 2263-79) was used as an activator of gas formation process.

Samples of foamed geopolymer materials were prepared by preparing mixtures with the ratio of components limestone wastes: activator of geopolymerization equal to 70:30, 75:25 and 80:20. The content of the alkaline activator solution varied between 14-18%wt. Setting and further hardening of the samples was carried out in specially prepared molds. At the end of 2 days the samples were removed from the molds and subjected to heat treatment at 80^{0}C for 24 hours.

Volumetric mass of samples of foamed geopolymer materials was studied according to GOST 15139-69 by measuring and weighing method. Calculation of the volume of a regular shape sample was carried out according to the formula [22]:

$$V = \frac{1}{3}\pi h \left(\frac{d_1^2}{4} + \frac{d_1 \cdot d_2}{4} + \frac{d_2^2}{4}\right);$$

where h- height of the truncated cone, m; d_1- large diameter of the truncated cone, m; d_2- small diameter of the truncated cone, m.

Volumetric mass of the sample was determined by the formula:

$$\rho_i = \frac{m_i}{V_i};$$

m_i- mass of the i-th sample, kg; V_i- geometric volume of the i-th sample, m^3.

RESULTS AND DISCUSSION

A very important indicator of foam materials is their volumetric mass. Volumetric mass or apparent density is determined from the ratio of the sample mass to its geometric volume. Compared to monolithic (non-foamed) materials, foamed materials have a larger geometric volume within a certain shape and, therefore, a much higher porosity. Thus, volumetric mass is an important indicator of foam materials, characterizing the degree of their porosity and lightness. The higher the porosity of the material, the better its thermal insulation properties. On the other hand, the higher the porosity of the material, the lighter it is and the less pressure it exerts on the structure. Therefore, it was important to characterize our samples of foamed materials in terms of changes in their volumetric mass and the multiplicity of foaming. Our research was carried out by changing two indicators, such as the amount of aqueous alkali solution and the concentration of alkali in the solution. At the same time the amount of aqueous alkali solution varied in the range 14-18% of the mass of the composition, and the normality of the alkali solution varied in the range 0,8-2n. For researches we chose compositions with ratio of filler (waste limestone) to binder (alkali silicate) 70:30, 75:25 and 80:20.

The results of the study of the volumetric mass of the composition 70:30 depending on changes in the concentration of alkali in the gas formation activator solution are shown in fig.1. The amount of alkaline activator introduced into the composition was changed within 14-18%wt. As can be seen from the presented figure, for specimens containing 14%wt. of alkali solution an increase in the concentration of alkali in the gas activator solution leads to a decrease in the volumetric mass of the foamed geo-concrete sample from 1990 kg/m^3 to 253 kg/m^3, that is practically in 7,9 times. What can be caused by such a decrease in the sample volumetric mass? Chemical interaction of aluminum with alkali occurs with the release of hydrogen gas, which

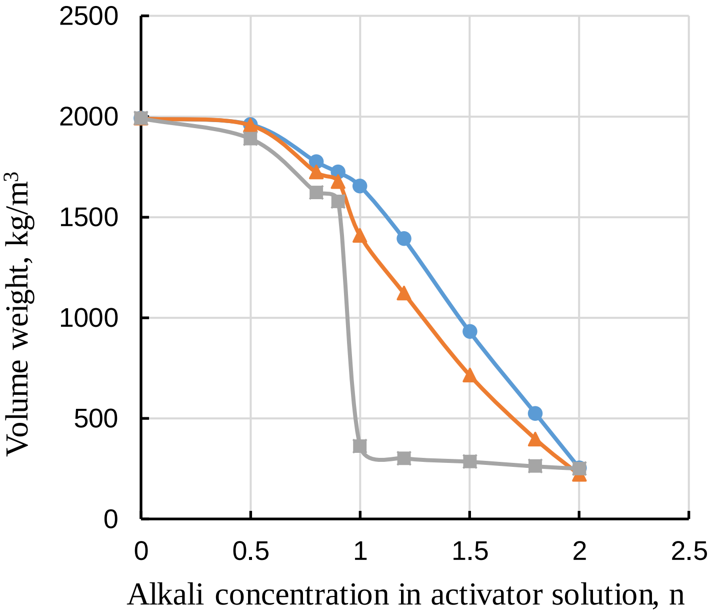

Fig.1. Dependence of the volumetric mass on the concentration of alkali in the solution for geopolymer composition 70:30:

●- activator solution content 14%wt.; ▲- activator solution content 16%wt.; ■- activator solution content 18%wt.

foams the geoconcrete mass. The higher the concentration of the alkaline activator solution, the more active it reacts with aluminum. This, in turn, contributes to the release of more hydrogen gas, which leads to an intensification of the foaming process of the composition. Intensification of the foaming process leads to a decrease in the volumetric mass. The presented dependence shows that by increasing the concentration of alkali in the activator solution from 0 to 1n some decrease in the volumetric mass occurs. In this case, the volumetric mass decreases in 1,2 times. However, when the concentration of the activator solution is increased from 1 to 2n, a sharper decrease in the volumetric mass takes place. The volumetric mass decreases in 6,5 times. Thus, 1n is the threshold concentration above which there is a sharp decrease in volumetric mass. Such a phenomenon has its own explanation. An important condition for the reaction is the complete dissolution of the oxide film on the surface of the aluminum particles introduced into the composition. The rate of dissolution of this film directly depends on the concentration of the alkaline solution. It is clear that the higher the concentration of the alkaline solution, the higher the rate of dissolution of the oxide film and the higher the rate of reaction of aluminum with alkali. The higher the reaction rate, the more hydrogen gas is formed per unit time and the higher the foaming rate. Increasing the multiplicity of foaming leads to a decrease in the volumetric mass. When the concentration of alkali in the activator solution is low and varies between 0-1n, the reaction of alkali with aluminum proceeds at a very low rate, since dissolution of the aluminum oxide film occurs slowly. Because of the sluggish course of the reaction, the volume of hydrogen formed is at a rather low level. For this reason, when the concentration of the activator solution changes from 0 to 1n, a relatively small decrease in the volumetric mass is observed. This indicates a low level of foaming of the composition. In addition, when visually inspecting the sample after curing, a large amount of unreacted aluminum can be observed on its surface. This also indicates that the gas formation reaction is taking place at a very low rate.

A further increase in alkali concentration in the activator solution from 1 to 2n leads to a sharper decrease in the volume weight. The kink in the curve shown in fig.1 testifies to this. Such a sharp decrease in the volume weight can be explained by the fact that, when the concentration of alkali in the activator solution increases, the dissolution rate of the oxide film on the aluminum particles also increases. This circumstance, in its turn, leads to acceleration of aluminum reaction with alkali. In this case, much more hydrogen gas is released per unit time, which contributes to an increase in the foaming multiplicity and a sharper reduction in the volumetric mass. In fig.1 dependence has practically additive character within the limits of alkali concentration in the activator solution of 1-2n. We cannot ignore another factor. This is the amount of heat generated in the reaction of aluminum with alkali. This reaction is exothermic. Studies have shown that the higher the concentration of alkali in the activator solution, the more heat is released in the reaction. In some cases, at high concentrations the composition may be heated up to 75-80^{0}C. Such heating of the foamed geoconcrete composition contributes to more efficient and rapid evaporation of water formed in the parallel reaction of orthophosphoric acid polycondensation. More efficient removal of water from the reaction system accelerates the process of polycondensation and more rapid solidification of the foamed concrete mass, that is, to reduce the life time of the geoconcrete mass. It should be noted that reducing the life time of the foamed concrete mass contributes to a rapid increase in its viscosity, which is important for the retention of hydrogen bubbles in the mass and preventing their degassing. However, in some cases, too rapid increase in viscosity has a negative effect on the foaming process.

The results of research of volumetric mass of specimens containing 16%wt. of activator solution are also presented on fig.1. For these specimens an increase in the concentration of alkali in the activator solution also leads to a decrease in the volumetric mass. Thus, increase of alkali concentration in activator solution from 0 to 2n promotes to decrease of volumetric mass from 1990 kg/m^3 to 220 kg/m^3, that is in 9 times. If we pay attention to the graph, we can see that if the concentration of alkali in the activator solution changes within the range of 0-1n, the volumetric mass decreases slightly by about 1,2 times. The reasons for this insignificant decrease in volumetric mass were discussed above at considering of specimens containing 14%wt. of activator solution. Increase in alkali concentration in the activator solution from 1 to 2 n leads also to sharp decrease in the volumetric mass in 7,6 times which is more than in the case of specimens containing 14%wt. of activator solution. If to compare results of volumetric mass research for specimens containing 14 and 16%wt. of activator solution, we may notice that in the last case after 1n concentration of alkaline activator a steeper curve bend towards decrease of volumetric mass is observed. Although within the concentration range from 0 to 1n in both cases the same regularity of changes in the volumetric mass is observed. Such a steeper of the curve in fig.1 can be explained by the fact that, in comparison with the specimens containing 14%wt. of activator solution, in this case the content of alkaline activator in the geoconcrete composition is higher and is 16 %wt. of the total mass. A higher content of alkaline activator in the composition means a higher content of water in the system, since the activator is presented in the form of aqueous alkali solution. Increasing the water content in the system contributes to some reduction of its viscosity. Reducing the viscosity, in turn, facilitates the foaming process by reducing the resistance of the medium to gas bubbles. Thus, gas bubbles experiencing less resistance of the medium can be more evenly distributed in the system, more foaming the geoconcrete mass. This explains the steeper of the curve for specimens containing 16%wt. of activator and the relatively lower values of the volumetric mass in the 1-2n concentration range of the alkaline activator.

The results of studies of the volumetric mass of foamed geoconcrete compositions with a ratio of components (limestone waste: liquid glass) 70:30 at a constant content of alkaline activator solution 18%wt. are also presented in fig.1.

As it can be seen from the data presented in the figure, increasing the concentration of alkali in the activator solution leads to a gradual decrease in the volumetric mass due to the beginning of the foaming process. In this case, the volumetric mass reduction is 1,3 times. Further slight increase in alkali concentration from 0,9n to 1n leads to collapsing decrease in volumetric mass in 4,4 times. This sharp decrease in volumetric mass, in contrast to previous cases, is observed for the first time on this sample. The reason for this sharp decrease in volumetric mass is the sharp intensification of the foaming process of the sample. This becomes possible due to an increase in the content of the aqueous solution in the foaming mass. Increasing the aqueous solution content helps to liquefy the system and reduce its viscosity. The lower viscosity of the foamed system reduces the resistance of the medium to gas bubbles, which, in turn, are more evenly distributed in the volume of the specimen, resulting in an even greater increase in volume. As in the case of specimens containing 16%wt. of activator, the threshold concentration of alkali in the activator solution after which a sharp decrease in the volumetric mass is observed is at the level of 0,9n. At the same time, increasing the content of the alkaline activator solution up to 18%wt. contributes to increasing the alkali content in the system. At higher content of alkali in the system, all available aluminum in the mixture relatively completely reacts with alkali forming more gas bubbles. This, in turn, leads to more foaming of the sample. A further increase in concentration from 1n to 2n leads to only a slight decrease in the volumetric mass. This is explained by the fact that at higher concentrations of alkali the curing processes of geoconcrete mass increase simultaneously. As a result, the lifetime of the mass decreases and the viscosity of the system increases at a higher rate, which prevents further distribution of gas bubbles in the volume of the mass and a decrease in the volumetric mass.

According to diagram of dependence of volumetric mass on concentration of alkali activator solution for geopolymer composition with the ratio of main components 70:30 shown in fig.1 the alkaline activator content in the mixture varies within 14-18% wt. As can be seen from the figure Increasing the content of the alkaline activator solution from 14 to 18% wt. contributes to improving the foaming of the geopolymer composition. Thus, the minimum values of volumetric mass are observed at samples with the content of activator solution at the level of 18%mass. This is explained by liquefaction of the foamed system and reducing its viscosity, which positively affects the foaming of the material. In addition, the minimum values of volumetric mass are achieved at 1n concentration of alkali in the solution, so the use of more concentrated activator solutions is unreasonable. From the options presented in fig.1 one can choose geopolymer composition with 18% wt. content of activator solution, as the minimum values of volumetric mass are reached in this case.

For further study of samples of foamed geo-concrete were studied geopolymer mixtures with the ratio of components waste limestone: binder = 75:25. Herewith, the concentration of alkali in the activator solution also varied in the range of 0,5-2n, and the content of activator solution was changed within 14-18%wt. The results of the studies are shown in fig.2.

As can be seen from the figure, for specimens containing 14%wt. of activator solution, at increasing of concentration of alkali in the activator solution, there is a natural decrease in the volumetric mass. However, even in this case it has its own features. Thus, when considering the dependence, one may notice that with increasing concentration from 0 to 0,9n there is a relatively monotonic decrease in volumetric mass from 1997 to 1652 kg/m^3 due to foaming. At increase in concentration of alkali within 0,9-1n very sharp decrease of volumetric mass from 1652 to 347 kg/m^3 happens, that is, practically in 4,8 times. The reasons for such decrease in volumetric mass at the content of the activator solution at 14 %wt. is connected with the fact that decrease in quantity of the liquid binder leads to less dilution of the alkaline activator solution. In this case, less diluted alkaline activator solution interacts more actively with aluminum, intensifying the process of gas formation, that is, the process of foaming of the specimen. Further an increase in the alkali concentration from 1n to 2n leads not to a sharp, but relatively monotonic decrease in the volumetric mass from 347 kg/m^3 to 277 kg/m^3. This is explained by the acceleration of the curing process of the geopolymer mass, reducing its lifetime and a rapid increase in the viscosity of the system, which prevents further foaming of the mass. The minimum value of volumetric mass in this case is achieved at 2n concentration of alkali and is 277 kg/m^3.

Further studies were carried out with samples of geo-concrete in which the ratio of the main components is 75:25, and the unchanged content of the alkaline activator solution is 16%wt. The results of the studies are also presented in fig.2.

As can be seen from the figure, an increase in alkali concentration in the activator solution from 0 to 0,5n is practically not accompanied by any change in the volumetric mass. However, at increasing concentration from 0,5n to 1n there is a sharp decrease in the volumetric mass from 1956 kg/m^3 to 264 kg/m^3, that is, practically in 7,4 times. This is explained by a lower dilution of the activator solution due to the reduction of the amount of liquid binder and its relatively higher content in the mixture (16%wt.). All this contributes to a more intensive interaction of the activator with aluminum and a greater foaming of the mixture. Besides, an increase in the amount of the activator solution up to 16% wt. contributes to bigger liquefaction of the mixture and more uniform distribution of gas bubbles in the sample volume. Further increase of alkali concentration in the activator solution does not lead to any significant changes of volumetric mass. The minimum value of volumetric mass is reached at 2n concentration of alkali in the activator solution and is 248 kg/m^3.

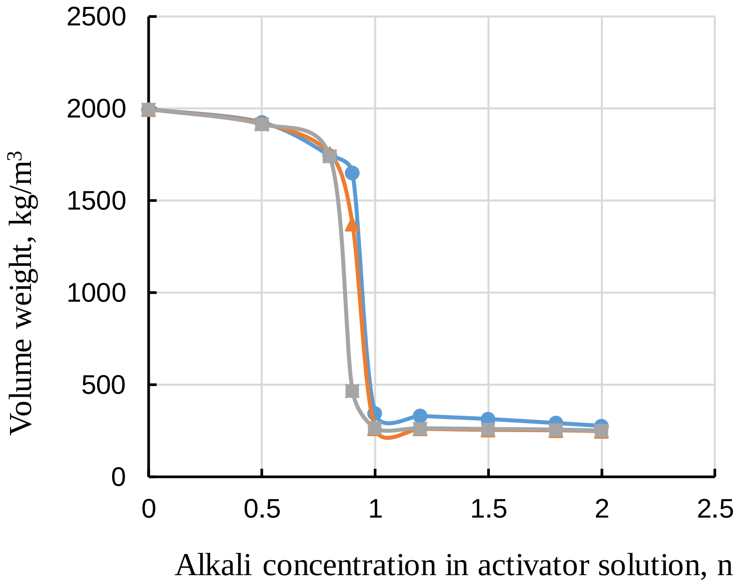

Fig.2. Dependence of the volume weight on the concentration of alkali in the solution for geopolymer composition 75:25:

●- activator solution content 14%wt.;

▲- activator solution content 16%wt.; ■- activator solution content 18%wt.

Further studies were carried out with samples of geo-concrete in which the ratio of the main components is 75:25, and the unchanged content of the alkaline activator solution is 16%wt. The results of the studies are also presented in fig.2.

As can be seen from the figure, an increase in alkali concentration in the activator solution from 0 to 0,5n is practically not accompanied by any change in the volumetric mass. However, at increasing concentration from 0,5n to 1n there is a sharp decrease in the volumetric mass from 1956 kg/m^3 to 264 kg/m^3, that is, practically in 7,4 times. This is explained by a lower dilution of the activator solution due to the reduction of the amount of liquid binder and its relatively higher content in the mixture (16%wt.). All

this contributes to a more intensive interaction of the activator with aluminum and a greater foaming of the mixture. Besides, an increase in the amount of the activator solution up to 16% wt. contributes to bigger liquefaction of the mixture and more uniform distribution of gas bubbles in the sample volume. Further increase of alkali concentration in the activator solution does not lead to any significant changes of volumetric mass. The minimum value of volumetric mass is reached at 2n concentration of alkali in the activator solution and is 248 kg/m^3.

Studies of the volumetric mass of foamed compositions with the ratio of the main components 75:25, however, with the 18%wt. content of the alkaline activator solution in the mixture were carried out. The concentration of alkali in the activator solution also varied in the range of 0,5-2n. The results of the studies are shown in fig.2.

As can be seen from fig.2, increasing the alkali concentration in the activator solution from 0 to 0,8n leads to some decrease in the volume weight. In this case, the volume weight decreases in 1,2 times. In comparison with specimen containing 16%wt. of activator solution, in this case at concentration of 0,9n the volumetric mass value sharply decreases and makes 469 kg/m^3. Such a decrease in volumetric mass at a concentration of 0,9n is explained by the fact that, on the one hand, increasing the content of aqueous alkaline solution in the mixture up to 18%wt. contributes to the liquefaction of the mixture and reduces the viscosity of the system. In this case the formed gas bubbles experience less resistance of the medium, distributing more evenly in the volume of the material and foaming it better. On the other hand, increasing the amount of alkaline solution contributes to its more intense interaction with aluminum and the greater release of foaming gas. In general, increasing the alkali concentration in the solution from 0,8n to 1n leads to a decrease in volumetric mass in 6,6 times. Further increasing of alkali concentration in solution does not lead to any significant decrease of volumetric mass. The minimum value of volumetric mass is achieved at 2n concentration of alkali in the solution and is 251 kg/m^3.

From the summary graph for the composition 75:25 containing activator solution in the range 14-18%wt. and presented in fig.2 it is also clear that the lowest values of volumetric mass are achieved with the content of activator solution at 18%wt. The minimum value of the volumetric mass is achieved at a concentration of 1n. Use of more concentrated activator solutions is unreasonable. On the basis of lower values of volumetric mass, we choose the composition with 18%wt. content of activator solution.

In order to better understand the regularities of the volumetric mass change in the foamed geopolymer materials, the samples with the ratio of the main components 80:20 were investigated.

The content of activator solution in specimen were changed from 14%wt. up to 18%wt. and alkali concentration in the activator solution varied in the range of 0,5-2n. The results of the studies are given in fig.3.

As can be seen from the figure, increasing the concentration of alkali in the activator solution leads to a decrease in volumetric mass, but in comparison with the results shown in fig.1 and 2 this reduction takes place already when using 0,5 n alkali solution. Herewith the volumetric mass equal to 1221 kg/m^3 is reached, that is, the volumetric mass is reduced in 1,4 times. At increasing of concentration from 0,5n to 1n volumetric mass decreases sharply from 1221 kg/m^3 to 302 kg/m^3, that is, in 4 times. At the same time volumetric mass values at alkali concentration in the activator of 0,8n and 0,9n are shifted to the area of lower values. The reasons for that were described above.

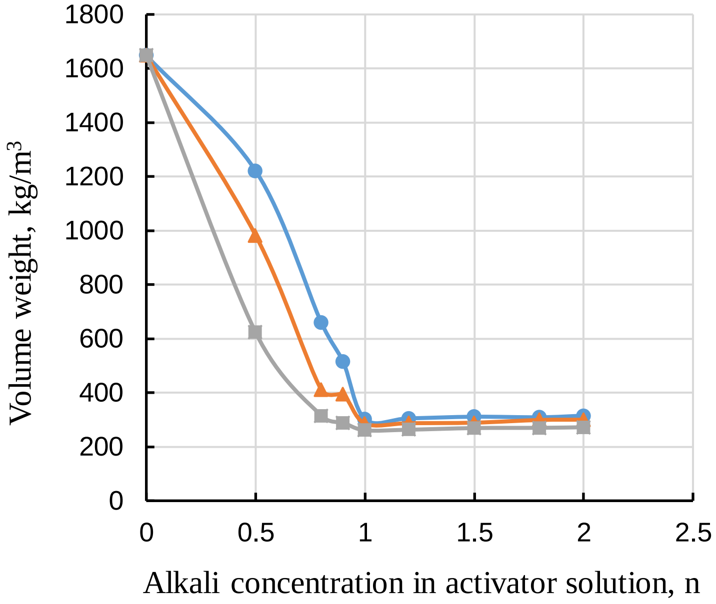

Fig.3. Dependence of the volume weight on the concentration of alkali in the solution for geopolymer composition 80:20:

●- activator solution content 14%wt.;

▲- activator solution content 16%wt.; ■- activator solution content 18%wt.

Thus, the reduction of the liquid binder content in the composition up to 20% wt. contributes to the reduction of the alkaline solution dilution, and it affects the increase of the interaction intensity with aluminum. As a result, gas release and foaming of the material already at low concentrations of alkali in the activator increases. A further increase in alkali concentration from 1n to 2n leads, on the contrary, to a slight increase in the volumetric mass from 302 to 315 kg/m^3. Such a phenomenon is explained by the fact that an increase in alkali concentration activates another parallel process - the curing process of geopolymer mass. The acceleration of this process leads to a rapid growth of the viscosity of the system, which in turn increases the resistance of the medium to the distribution of gas bubbles. This is the reason for some increase in the volumetric mass.

The volumetric mass change of geopolymer compositions with the ratio of the main components 80:20, but with the unchanged content of the activator solution in the mixture at 16%wt. was studied. The concentration of alkali in the activator solution varied in the range of 0,5-2n. The results of the research are shown in fig.3. As can be seen from the figure, the change in the volumetric mass depending on the concentration of alkali in the activator solution occurs according to a similar regularity as in case of specimens containing 14%wt. of activator solution. The difference is that at concentrations of 0,5 n, 0,8 n and 0,9 n values of volumetric mass displaced in the area of lower values. This indicates a more intense foaming process of the samples, which is associated with an increase in the content of the aqueous solution of the alkaline activator in the mixture. As a result of liquefaction of the mixture, the viscosity of the system decreases and the foaming process is more profound. The minimum value of volumetric mass is reached at concentration 1n and is 286 kg/m^3. A further increase in the concentration of alkali in the solution to 2n as in the previous case also leads to some increase in the volumetric mass to 300 kg/m^3.

Research on the study of volumetric mass changes in geopolymer compositions with a component ratio of 80:20 at a constant content of the alkaline activator solution at 18%wt. was also carried out. The concentration of alkali in the activator solution varied in the range of 0,5-2n. The results of the studies are also shown in fig.3.

As can be seen from the figure, an increase in alkali concentration in the activator solution from 0,5n to 1n leads to a decrease in the volumetric mass. In comparison, with specimens containing 16%wt. of activator in this case the values of volumetric mass are displaced to the area of lower values. This is associated with a large liquefaction of the system with a greater amount of aqueous solution of alkaline activator and a greater amount of alkali introduced into the mixture. All this contributes to intensification of foaming of geopolymer composition. Further increasing the concentration of alkali in the solution from 1n to 2n leads to some increase in volumetric mass for the reasons described above. The minimum value of the volumetric mass is also achieved at a concentration of alkali in the solution of 1n and is 261 kg/m^3.

From the summary diagram for the 80:20 geopolymer composition with an activator solution content of 14-18% wt. shown in fig.3, it is clear that the minimum values of volumetric mass are also achieved at 1n concentration of alkali and at 18%wt. content of the alkaline activator solution. Because of the lower values of volumetric mass, the sample with 18% wt.% activator solution content was chosen.

A common diagram of the dependence of the volumetric mass on the concentration of alkali in the solution for geopolymer compositions with a 70:30, 75:25, 80:20 component ratio and with the activator solution content at 18% wt. is given in fig.4.

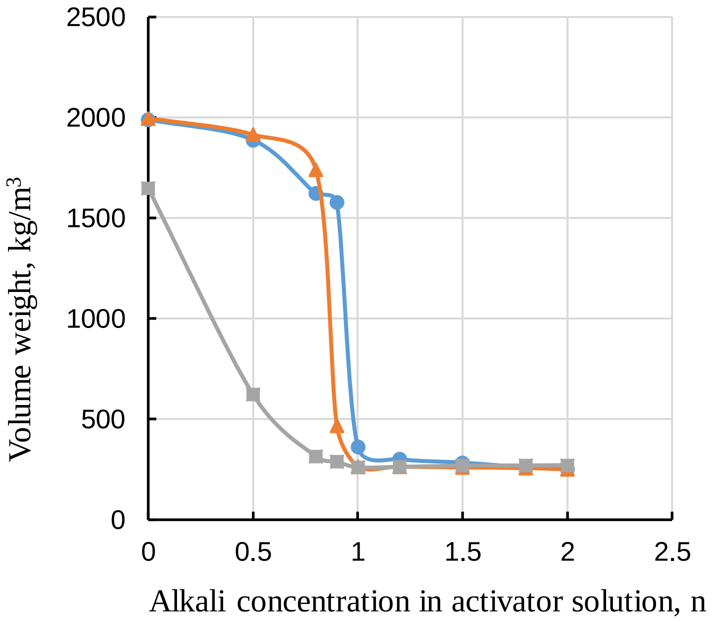

Fig.4. Dependence of volume weight on alkali concentration in solution for geopolymer compositions with 18%wt. activator solution content:

●- 70:30; ▲- 75:25; ■- 80:20.

As can be seen from the figure, the lowest values of the volumetric mass are achieved at a concentration of 1n and the use of more concentrated activator solutions is unreasonable. For further studies the composition with the ratio of components 80:20 was chosen, as only in this case at all concentrations of alkali in the solution lower values of volumetric mass are achieved.

CONCLUSION

1. It was established that increasing the concentration of alkali in the activator solution from 0,5 to 2n contributes to reducing the volumetric mass of foamed geopolymer samples practically at all component ratios.
2. At all component ratios minimum values of volumetric mass are achieved at 1n alkali concentration in the activator solution.
3. At the comparative analysis of results of researches of volumetric mass of samples with a ratio of components 70:30, 75:25 and 80:20 at 18%wt. content of the activator solution the lowest values of volumetric mass are reached for samples with a ratio of components 80:20.

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ИССДЕДОВАНИЕ ЗАКОНОМЕРНОСТЕЙ ИЗМЕНЕНИЯ ОБЪЕМНОЙ МАССЫ, ВСПЕНЕННЫХ ГЕОПОЛИМЕРНЫХ МАТЕРИАЛОВ НА ОСНОВЕ ИЗВЕСТНЯКОВЫХ ОТХОДОВ

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Создание композиционного строительного материала, который обладает меньшим вредным воздействием на окружающую среду как на стадии его производства, так и в процессе его использования представляет большой интерес в мировой строительной индустрии. Недавние инновационные разработки привели к созданию геополимерного пенобетона или вспененного геополимерного материала, который включает в себя эксплуатационные преимущества тепло- и звукоизоляционных материалов, экономит энергию за счет снижения потерь тепла и способствует снижению выбросов CO_2 *в окружающую среду. Для лучшего понимания свойств и преимуществ связанных с применением вспененных геополимерных материалов в данной статье приведены исследования объемной массы этих материалов, полученных на основе известняковых отходов и силикатного активатора. Были получены образцы с соотношением* *компонентов известняковые отходы: активатор 70:30, 75:25 и 80:20. Исследования объемной массы в зависимости от изменения концентрации щелочи в растворе активатора газообразования показали, что минимальные значения объемной массы достигаются при 1н концентрации щелочи. Помимо этого, было установлено, что наилучшая вспениваемость геополимерного материала достигается при соотношении компонентов 80:20 и при содержании раствора активатора газообразования в смеси на уровне 18%масс.*

Ключевые слова: *вспененный геополимер, объемная масса, пористость, теплоизоляционный материал.*

ƏHƏNGDAŞI ƏSASINDA OLAN KÖPÜKLƏNMİŞ GEOPOLİMERLİ MATERİALLARIN HƏCM KÜTLƏSİNİN DƏYİŞMƏSİ QANUNAUYĞUNLUQLARININ TƏDQİQİ

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Həm istehsalı, həm də istifadəsi zamanı ətraf mühitə az mənfi təsiri olan kompozisiya tikinti materialının yaradılması dünya tikinti sənayesi üçün böyük maraq kəsb edir. Son illərdə aparılmış inovasiyalı tədqiqatlar geopolimerli betonun və ya köpüklənmiş geopolimerli materialın yaradılmasına gətirib çıxardı. O, özündə istilik izolyasiya və səs boğucu materialların istismar üstünlüklərini cəmləşdirir, istilik itkilərinin azaldılması hesabına enerjiyə qənaət edir və ətraf mühitə CO_2 *qazının emissiyasının miqdarını azaldır. Köpüklənmiş geopolimerli materialların istifadəsi ilə əlaqəli olan xassə və üstünlükləri daha yaxşı anlamaq üçün bu məqalədə əhəngdaşı tullantıları və silikatlı aktivator əsasında alınmış bu tip materialların həcm kütləsinin tədqiqi nəticələri təqdim olunur. Əhəngdaşı tullantıları:aktivator nisbəti 70:30, 75:25 və 80:20 olan nümunələr alınmışdır. Qələvinin qaz əmələ gətirici aktivator məhlulunda qatılığından asılı olaraq həcm kütləsinin dəyişməsi nəticələrinin tədqiqi göstərdi ki, həcm kütləsinin minimal qiymətləri qələvinin qatılığı 1n olduqda əldə edilir. Bundan başqa, müəyyən edilmişdir ki, geopolimerli materialın ən yüksək köpüklənmə dərəcəsi komponentlərin nisbəti 80:20 və qaz əmələ gətirici aktivatorun məhlulunun qarışıqda miqdarı 18%küt. olduqda əldə edilir.*

Açar sözlər: *köpüklənmiş geopolimer, həcm kütləsi, məsaməlilik, istilik izolyasiya materialı.*

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN THE SOIL OF THE JABRAYIL REGION WITH 2-HYDROXY-5-HALIGENTHIOPHENOLS AND AROMATIC AMINES

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In the interaction of molybdenum and tungsten with 2-hydroxy-5-halogenthiophenols, mixed-ligand complexes (MLC) extractable with chloroform are formed. Aniline, N-methylaniline, and N, N-dimethylaniline were used as the hydrophobic amines. The conditions for the extraction-photometric determination of molybdenum and tungsten are found. The best extractants were chloroform, dichloroethane and carbon tetrachloride. In a single extraction with chloroform, 97.8–98.2% of molybdenum and tungsten are recovered in the form of MLC (in the case of $C_2H_4Cl_2$ *and* CCl_4*, 95–96% of molybdenum and tungsten are recovered). Molybdenum and tungsten MLC extracts obey the basic law of light absorption at concentrations of 0.2–20 and 0.2–19 µg/mL, respectively. It was established by the Nazarenko method that the complexing form of molybdenum and tungsten is* $MeO(OH)^{2+}$*. It was found that MLC are formed at* $pH_{opt.}$ *1.8-5.1. The maximum in the light absorption spectrum is observed at 457–538 nm. The molar light absorption coefficient is* $(3.2\text{-}4.2)\times10^4$*. It has been proven that molybdenum (VI) and tungsten (VI) are reduced to Me(V) by the reagent itself upon formation of a complex with halothiophenols.*

Keywords: *molybdenum, tungsten, 2-hydroxy-5-halogenthiophenol, extraction-photometric method, hydrophobic amines.*

INTRODUCTION

Molybdenum and tungsten (Me (V, VI) = Mo or W) are among those metals that have chromophoric properties, therefore, among the numerous photometric methods for their determination, there are both methods based on the use of colored reagents with chromophore groups, and methods that use colorless reagents. Most methods are highly selective. Numerous methods are known for the photometric determination of molybdenum and tungsten using reagents belonging to various classes of organic compounds [1]. Reagents containing hydroxy and carboxy or two hydroxy groups in the *o*-position to each other interact with molybdenum and tungsten mainly in slightly acidic and neutral media to form colored complex compounds [2, 3]. Molybdenum (VI) in soil and plant samples was determined by spectrophotometric method in the form of Mo(V)-rhodanide complex [4]. Traces of molybdenum (VI) were determined spectrophotometrically using salicylaldehyde hydrazone and acetoacetic acid [5]. Despite the fact that methods based on color reactions of tungsten with various organic reagents are extremely numerous, only a few of them are used in the practice of chemical analysis. The methods with the use of toluene-3,4-dithiol and thiocyanate have become the most widely used [1]. According to the hypothesis of analogies, reactions with reagents of the R-SH type are possible for element ions that form sulfides poorly soluble in water [6]. Methods have been developed for the determination of elements in the form of mixed-ligand complexes (MLC) with 2-hydroxy-5-halothiophenols [7-13] and 2,6-dithiol-4-tert-butylphenol in the presence of hydrophobic amines [14-16].

This work is devoted to the study of the reaction of complex formation of molybdenum (VI) and tungsten (VI) with 2-hydroxy-5-halogenthiophenols (HTP, H_2L, L) and hydrophobic amines (Am). Of the 2-hydroxy-5-halogenthiophenols, 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP) were used. Aniline (An), N-methylaniline (MAn), and N, N-dimethylaniline (DAn) were used as the hydrophobic amine (Am).

EXPERIMENTAL PART

Reagents and solutions. The initial solution (1 mg/mL) of Mo (VI) was prepared by dissolving 1.8402 g of $(NH_4)_6Mo_7O_{24}\times4H_2O$ analytically in hot water. Upon cooling, the solution was diluted with water in a volumetric flask to 1 L. The stock solution (1 mg/mL) of W(VI) was prepared by dissolving an accurate weighed portion of $Na_2WO_4\times2H_2O$ of analytical grade in water. The concentration of the solution of molybdenum and tungsten was determined gravimetrically [11]. Solutions with a concentration of 0.1 mg/mL were obtained by diluting the stock solution. We used a 0.01 M solution of HTP and Am in chloroform. Am was used freshly distilled.

The ionic strength of the solutions was maintained constant ($\mu = 0.1$) by introducing the calculated amount of KCl. A 1M HCI solution was used to create the required acidity of the solutions.

Instruments. Spectrophotometric studies of colored solutions were carried out on KFK-2 and SF-26. The pH of the aqueous phase was measured on an I-120.2. with glass electrode. IR spectra were recorded on a UR-20 spectrophotometer.

Method for the determination of molybdenum and tungsten. Up to 90 µg of molybdenum, 2 ml of 0.01 M HTP solution, and 2.5 ml of 0.01 M Am solution (in the case of tungsten, 80 µg of tungsten, 2.2 ml of 0.01 M HTP solution, and 2.6 ml of 0.01 M Am solution) were introduced into graduated tubes with a capacity of 50 ml. The required pH value was adjusted by adding 1M HCl solution. The volume of the organic phase was adjusted to 5 ml with chloroform, and the volume of the aqueous phase was adjusted to 20 ml with distilled water. The mixture was shaken for 2 min. After 10 min, the organic layer was separated and its optical density was measured at room temperature on KFK-2 at 540 nm (in the case of tungsten, 490 nm).

On the reduction of Me (VI) to Me(V). HTP in an acid medium has reducing properties [10, 11, 13]. It is known that the colored compound with dithiol forms only Me(V), to which Me (VI) is reduced by the reagent itself [1]. To find out whether the valence of molybdenum and tungsten does not change upon interaction with HTP, two series of experiments were carried out. The reaction was carried out with HTP Me(V), obtained by the reduction of $SnCl_2$ and KI, in a hydrochloric acid solution without the use of additional reducing agents. The products of both reactions had light absorption maxima at 540 and 470 nm for molybdenum and tungsten, respectively. Consequently, Me (VI) upon the formation of a complex with HTP is reduced to Me (V) by the reagent itself.

RESULTS AND DISCUSSION

The choice of extractant. The best extractants were chloroform, dichloroethane and carbon tetrachloride. At the same time, the basicity of amines does not have a noticeable effect on the conditions and extraction of complexes. The extractability of the complexes was evaluated by the distribution coefficient and the degree of extraction [17]. The rapid separation of layers and the maximum value of the molar absorption coefficient were obtained by extracting the complexes with chloroform. In a single extraction with chloroform, 97.8–98.2% of molybdenum and tungsten are recovered in the form of MLC. Further studies were carried out with chloroform.

Influence of the pH of the aqueous phase. For the formation and extraction of molibden and tungsten complexes, pH 2.1-5.1 and 1.8-3.1, respectively, is optimal (Fig 1.). The presence of the second ligand led to a shift in the optimal acidity of the complexation to a more acidic region, pHopt is wider than in the case of a two-component compound. At the beginning, with an increase in the acidity of the initial solution, the Me(V) extraction increases, and with a further increase, it gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of H_2L and, most likely, it is in the solution in an undissociated form. With an increase in pH > 7, the formation of MLC is practically not observed, which is apparently associated with a decrease in the degree of protonization of amines.

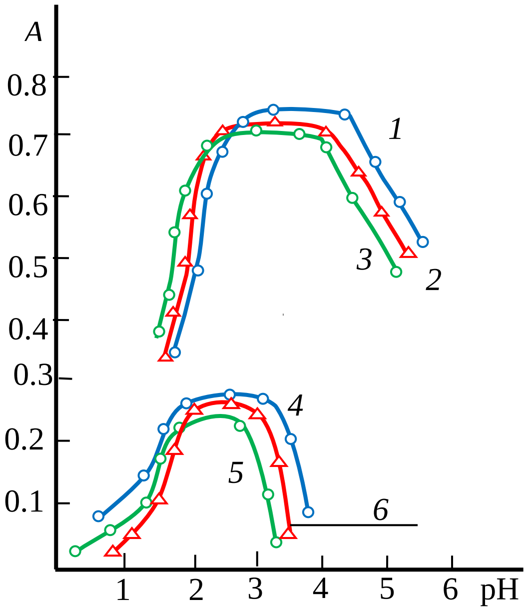

Fig.1. The dependence of the optical density of the MLC of molybdenum and tungsten on the pH of the aqueous phase: *1*-Mo-HCTP-An; *2*-Mo-HBTP-An; *3*-Mo-HITP-An; *4*-W-HBTP-An; *5*-W-HBTP-MAn; *6*- W-HBTP-DAn.
$C_{Mo(V)}=4.16\times10^{-5}$ mol/l; $C_{W(V)}= 1.09\times10^{-5}$ mol/l; $C_L=(1.3\text{-}1.5)\times10^{-3}$ mol/l;$C_{Am}=(1.2\text{-}1.5)\times10^{-3}$ mol/l; KFK - 2; ℓ=0.5cm

From the data given in table 1, it can be seen that, while maintaining the structure and nature of the functional analytical group (FAG), the pH_{50} of the reaction can be shifted to a more acidic region with an increase in the acid dissociation of the complexing groups of the FAG of the reagent forming the analytical form [18] due to the introduction of the L- electrophilic substituents (Cl, Br, I). This phenomenon can be explained by an increase in the negative inductive effect of the substituent.

Table 1

Optimal conditions for the formation and analytical characteristics of molybdenum and tungsten MLC with HTP and Am

Compound	pH$_{formations}$ and extractions	pH$_{optimal}$	λ_{Max}, nm	$\varepsilon \cdot 10^{-4}$ $L \cdot mol^{-1} \cdot cm^{-1}$	lgK_{eq}	lgK_{ex}
$[Mo(HCTP)](AnH)_2$	1.6-5.7	2.8-4.3	535	3.7	2.27	12.4
$[Mo(HCTP)](MAnH)_2$	1.8-6.1	2.8-4.8	537	3.9	2.74	12.6
$[Mo(HCTP)](DAnH)_2$	3.0-7.0	4.2-5.1	538	4.2	2.68	12.8
$[Mo(HBTP)](AnH)_2$	1.5-5.5	2.4-4.1	530	3.4	2.83	12.7
$[Mo(HBTP)](MAnH)_2$	1.6-5.7	2.5-4.8	533	3.6	2.88	12.8
$[Mo(HBTP)](DAnH)_2$	2.9-6.8	4.0-5.1	536	3.8	2.71	12.9
$[Mo(HITP)](AnH)_2$	1.4-5.3	2.1-4.0	527	3.2	2.90	12.9
$[Mo(HITP)](MAnH)_2$	1.5-5.4	2.2-4.7	530	3.3	2.86	13.1
$[Mo(HITP)](DAnH)_2$	2.8-6.7	3.7-5.0	534	3.6	2.81	13.4
$[W(HBTP)](AnH)_2$	0.2-3.2	1.8-2.8	457	4.0	2.91	11.3
$[W(HBTP)](MAnH)_2$	0.3-3.4	1.9-3.0	462	4.1	2.87	11.8
$[W(HBTP)](DAnH)_2$	0.5-3.7	2.0-3.1	468	4.2	2.85	12.4

Absorption spectra. The maximum analytical signal upon complex formation of Mo(V) and W(V) with HTP and Am is observed at 527–538 and 457–468 nm, respectively. The close values of the light absorption maxima allow us to conclude that the resulting complexes are ion associates. The molar absorption coefficients are (3.2-4.2) ×10^4.

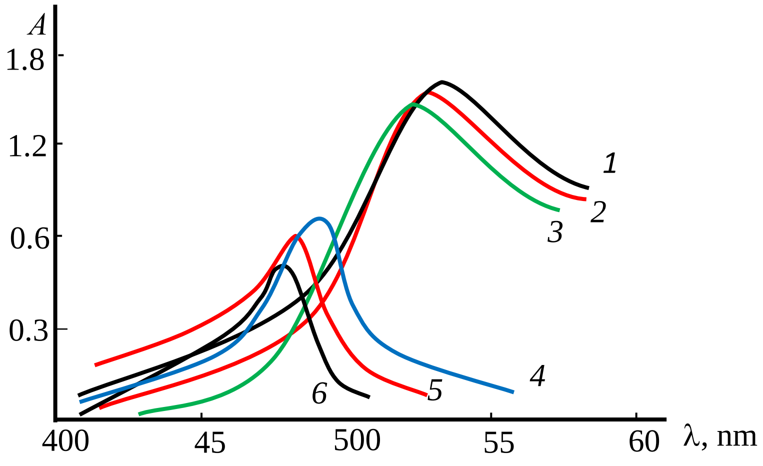

Fig.2. Absorption spectra of molybdenum and tungsten complexes with GTP and Am: *1*-Mo-HCTP-An; *2*-Mo-HBTP-An; *3*-Mo-HITP-An; *4*-W-HBTP-An; *5*-W-HBTP-MAn; *6*- W-HBTP-DAn. $C_{Mo(V)}=4.16\times10^{-5}$ mol/l; $C_{W(V)}= 1.09\times10^{-5}$ mol/l; $C_L=(1.3\text{-}1.5)\times10^{-3}$ mol/l; $C_{Am}=(1.2\text{-}1.5)$)×10^{-3} mol/l; SF-26; ℓ= 1.0 cm

Influence of the concentration of reagents. The optimal condition for the formation and extraction of these compounds is the concentration of (1.3-1.5) ×10^{-3} mol/l HTP and (1.2 1.5) × 10^{-3} mol/l Am. Molybdenum and tungsten MLC extracts obey the basic law of light absorption at concentrations of 0.2–20 and 0.2–19 μg/ml, respectively.

Influence of holding time. MLC Me(V) with HTP and Am are stable in aqueous and organic solvents and do not decompose within three days, and after extraction for more than a month. The maximum optical density of the molybdenum and tungsten complexes is reached within 10 and 15 min, respectively.

Composition and structure of complexes. The stoichiometric reaction coefficients of the interaction of Me(V) with HTP and Am were determined using the methods of relative yield, Asmus straight line, and equilibrium shift [19]. The curves $1/V_n = f(1/m_A)$ plotted for various values of n show that the ratio Me(V): L: Am = 1:2:2. Similar results were obtained by th relative yield and equilibrium shift methods. Using the Nazarenko method, it was established that the complexing form of molybdenum and tungsten is $MeO(OH)^{2+}$ [20].

In the IR spectra of the Me-HTP-An complexes, an intense absorption band appears in the range of 780–810 cm^{-1} due to the stretching vibration of the $MeO(OH)^{2+}$ group. The disappearance of a pronounced band at 2580 cm^{-1} (SH) and in the region of 3200–3600 cm^{-1} with a maximum at 3450 cm^{-1} (OH), observed in the HTP spectrum, indicates that the -SH and -OH groups are involved in complex formation. Absorption bands at 1380 cm^{-1} indicate the presence of protonated aniline [21, 22].

The mechanism of MLC formation can be represented as follows: Molybdenum and tungsten ions, when interacting with two H_2L molecules, form doubly charged anionic complexes, which are extracted with two molecules of protonated Am. The composition of the extractable complexes can be represented by the formula $[MeO(OH)L_2](AmH)_2$.

Let us assume that the following processes occur during complex formation:

$$MeO(OH)^{2+} + 2H_2L \Leftrightarrow [MeO(OH)L_2]^{2-} + 2H^+$$

$$[MeO(OH)L_2]^{2-} + 2AmH^+ \Leftrightarrow [MeO(OH)L_2](AmH)_2$$

The values of the equilibrium constant ($\lg K_{eq}$) and the extraction constant ($\lg K_{ex}$) calculated by the equations

$$\lg K_{eq} = \lg D - 2\lg[\text{AмH}^+]$$

and

$$\lg K_{ex} = \lg D - 2\lg[R^{2-}] - 2\lg[AmH^{+1}]$$

respectively presented in table 1.

The degree of polymerization of the complexes was calculated using the equation given in [23]. The performed calculations showed that the MLC in the organic phase do not polymerize and are in the monomeric form ($\gamma = 1.01–1.05$). Based on the equations of the calibration curves, the limit of photometric detection and the limit of quantitative determination of molybdenum and tungsten were calculated in the form of MLC [24]. In table 1 shows the main spectrophotometric characteristics of the method for determining molybdenum and tungsten. The dependences found by us are consistent with the literature data, indicating that with an increase in pK_1 of the complexing reagents, the strength of the complex compounds formed by them and the pH of the complex formation increase.

Influence of foreign ions. The influence of a number of cations and anions on the accuracy of Me(V) determination was studied. It has been established that large amounts of alkaline, alkaline earth elements, rare earth elements, F^{-}, Cl^{-}, Br–, SO_3^{2-}, SO_4^{2-}, and $C_2O_4^{2-}$ do not interfere with the determination of molybdenum and tungsten. The selectivity of the determination is significantly increased in the presence of masking agents. The interfering effect of Fe (III) and Ti (IV) was eliminated with ascorbic acid, Cu (II) with thiourea, and Nb(V) with oxalate ion. When using a 0.01M EDTA solution, Ti (IV), V(IV), Nb(V), Ta(V), and Fe (III) do not interfere with the determination.

In table 2 shows the data that make it possible to compare the analytical characteristics of methods for the determination of molybdenum [1, 3, 25-31] and tungsten [1,32-37] with some already known methods.

Table 2

Data to compare the analytical characteristics of methods for the determination of molybdenum and tungsten

Me	Reagent(s)	pH	λ, nm	$\varepsilon \cdot 10^{-4}$
Mo	Rezorsan [26]	0.5 M HCl	460	2.34
Mo	Rhodanide [1,25]	0.75M HCl	460	3.86
Mo	8-hydroxyquinoline [1]	3.2-4.2	530	-
Mo	Chlorosulfophenol C [27]	0.5–3. 6		1.3
Mo	Toluene-3,4-dithiol [3,25]	4-12M HCl	680	1.8
Mo	2-amino-4-chlorobenzene-thiol [29,30]	3.9	478	3.6
Mo	HCTP+DAn	4.2-5.1	538	4.2
Mo	HBTP+DAn	4.0-5.1	536	3.8
Mo	HITP+DAn	3.7-5.0	534	3.6
W	Toluene-3,4-dithiol [1]	1.5-2.0	640	1,92
W	8-mercaptoquinoline [32]	0.5-3.0	412	0,367
W	8-hydroxyquinoline [32]	4.4	363	0,64
W	HBTP+An	1.8-2.8	457	4.0
W	HBTP+MAn	1.9-3.0	462	4.1
W	HBTP+DAn	2.0-3.1	468	4.2

The proposed method, under already established optimal conditions, was applied to determine Mo(V) and W(V) in in soils. The proposed methods for the determination of molybdenum and tungsten in soils have been tested 8-hydroxyquinoline and dithiol methods. The results of the analysis are shown in table 3, which indicates a successful applicability of the proposed method to the analysis of real samples.

Determination of molybdenum in soils. The proposed methods for the determination of molybdenum are applied to its determination in light chestnut soil from the Jabrayil region. A mass of 0.5 g was finely ground in an agate mortar and calcined in a muffle furnace for 3 h.Upon cooling, the sample was treated and dissolved in a graphite dish in a mixture of 16 ml of conc. HF, 5 ml of conc.HNO_3, and 15 ml of HCl (conc.) at 50–60^{0}C to remove excess hydrogen fluoride. Another 8 ml portion of conc.HNO_3 was added three times to the solution, which was evaporated each time to 5-6 ml. After that, the solution was transferred into a 100 ml volumetric flask and its volume was brought up to the mark with distilled water. Molybdenum was determined in aliquots of a portion of the solution according to the proposed method.

Determination of tungsten in soils. A mass of 0.5 g was finely ground in an agate mortar and calcined in a muffle furnace for 3 hours. After cooling, the sample was treated and dissolved in a graphite dish in a mixture of 16 ml of conc. HF, 5 ml conc. HNO_3 and 15 ml conc. HCl at 50-60^0 C to remove excess hydrogen fluoride, 8 ml conc. HNO_3 was added three times to the solution, which was evaporated each time to 5-6 ml.

After that, the solution was transferred into a 100 ml volumetric flask and its volume was brought up to the mark with distilled water. Tungsten was determined in aliquots of the solution using the proposed procedures.

Table 3

Correctness and reproducibility of determination of molybdenumand tungsten in soil (n=5, P=0.95)

Method	% , $\bar{X}$(10^{-4})	standard deviation of the average result (10^{-4})	probable relative error, %	direct measurement accuracy
Determination of molybdenum				
Toluene-3,4-dithiol	2.95	0.148	4	(2.95±0.18)
8-Hydroxyquinoline	3.02	0.151	5	(3.02±0.19)
HCTP+DAn	2.85	0.114	4	(2.85±0.14)
HBTP+DAn	2.87	0.087	4	(2.87±0.11)
Determination of tungsten				
Toluene-3,4-dithiol	3.67	0.172	5	(3.67±0.12)
8-Hydroxyquinoline	4.05	0.135	3	(4.05±0.22)
HCTP+DAn	4.00	0.123	4	(4.00±0.14)
HBTP+DAn	3.95	0.111	4	(3.95±0.17)

CONCLUSION

This work is devoted to the study of the reaction of complex formation of molybdenum (VI) and tungsten (VI) with 2-hydroxy-5-halothiophenols and hydrophobic amines.

In a single extraction with chloroform, 97.8–98.2% of molybdenum and tungsten are recovered in the form of mixed-ligand complexes (MLC). For the formation and extraction of molibden and tungsten complexes, pH 2.1-5.1 and 1.8-3.1, respectively, is optimal. The maximum analytical signal upon complex formation of Mo(V) and W(V) with 2-hydroxy-5-halogenthiophenols (HTP) and hydrophobic amines (Am) is observed at 527–538 and 457–468 nm, respectively. The close values of the light absorption maxima allow us to conclude that the resulting complexes are ion associates. The molar absorption coefficients are (3.2-4.2) $\times 10^4$.

The optimal condition for the formation and extraction of these compounds is the concentration of (1.3-1.5) $\times 10^{-3}$ M HTP and (1.2 1.5) $\times$ 10^{-3} M Am. Molybdenum and tungsten MLC extracts obey the basic law of light absorption at concentrations of 0.2–20 and 0.2–19 μg/ml, respectively.

The performed calculations showed that the MLC in the organic phase do not polymerize and are in the monomeric form (γ = 1.01–1.05). The proposed method, under already established optimal conditions, was applied to determine Mo(V) and W(V) in soils.

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СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МОЛИБДЕНА И ВОЛЬФРАМА В ПОЧВАХ ДЖЕБРАИЛЬСКОГО РАЙОНА С 2-ГИДРОКСИ-5-ГАЛОГЕНТИОФЕНОЛАМИ И АРОМАТИЧЕСКИМИ АМИНАМИ

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При взаимодействии молибдена и вольфрама с 2-гидрокси-5-галогентиофенолами образуются разнолигандные комплексы (РЛК), экстрагируемые хлороформом. В качестве гидрофобного амина использовали анилин, N-метиланилин и N,N-диметиланилин. Найдены условия экстракционно-фотометрического определения молибдена и вольфрама. Лучшими экстрагентами оказались хлороформ, дихлорэтан и четыреххлористый углерод. При однократной экстракции хлороформом извлекается 97.8–98.2 % молибдена и вольфрама в виде разнолигандные комплексы (РЛК) (в случае $C_2H_4Cl_2$ *и* CCl_4 *извлекается 95–96 % молибдена и вольфрама). Экстракты РЛК молибдена и вольфрама подчиняются основному закону поглощения света при концентрациях 0.2–20 и 0.2–19 мкг/мл соответственно. Методом Назаренко установлено, что комплексообразующей формой молибдена и вольфрама является* $MeO(OH)^{2+}$. *Было обнаружено, что РЛК образуются при* $pH_{оп}$. *1.8-5.1. Максимум в спектре поглощения света наблюдается при 457–538 нм. Молярный коэффициент светопоглощения составляет* $(3.2\text{-}4.2)\times10^4$. *Доказано, что молибден (VI) и вольфрам (VI) восстанавливаются до Me(V) самим реагентом при образовании комплекса с галогентиофенолами.*

Ключевые слова: *молибден, вольфрам, 2-гидрокси-5-галогентиофенол, экстракционно-фотометрический метод, гидрофобные амины.*

CƏBRAYIL RAYONU TORPAQLARINDA MOLİBDEN VƏ VOLFRAMIN 2-HIDROKSI-5-HALİGENTİOFENOLLAR VƏ AROMATİK AMİNLƏR İLƏ SPEKTROFOTOMETRİK TƏYİNİ

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Molibden və volfram 2-hidroksi-5-halogentiofenollar və hidrofobaminlərlə qarşılıqlı təsirdə olaraq xloroformla ekstraksiya oluna bilən müxtəlif liqandlı komplekslər (MLK) əmələ gətirir. Hidrofob amin kimi anilin, N-metilanilin və N,N-dimetilanilin istifadə edilmişdir. Molibden və volframın ekstraksiya-fotometrik təyini üçün optimal şərait müəyyən edilmişdir. Ən yaxşı ekstragent kimi xloroform, dikloroetan və karbon tetraxlorid müəyyən edilmişdir. Xloroform ilə birdəfəlik ekstraksiya zamanı MLK şəklində 97.8-98.2 % molibden və volfram ($C_2H_4Cl_2$ və CCl_4 halda 95-96% molibden və volfram ekstraksiya olunur) ekstraksiya olunur. Molibden və volframın MLK-lərinin ekstraktları müvafiq olaraq 0.2-20 və 0.2-19 mkq/ml qatılıq intervalında işıq udulmanın əsas qanununa tabe olur. Nazarenko üsulu ilə molibden və volframın kompleks əmələ gətirən ion formasının $MeO(OH)^{2+}$ olduğu müəyyən edilmişdir. MLK pHop. 1.8-5.1-də əmələ gəlir. İşıq udma spektrində maksimum 457-538 nm-də müşahidə olunur. Molar işıq udulma əmsalı (3.2-4.2) $\times 10^4$-dir. Sübut edilmişdir ki, molibden (VI) və volfram (VI) halotiofenollarla kompleks əmələ gətirən reagentin özü tərəfindən Me(V)-ə qədər reduksiya olunur.

Açar sözlər: *molibden, volfram, 2-hidroksi-5-halogentiofenol, ekstraksiya-fotometrik üsul, hidrofob aminlər.*

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SYNTHESIS AND APPLICATION OF EFFECTİVE PLASTICIZERS, ANTIOXIDANTS

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The article presents a one-stage method for the synthesis of effective plasticizers and antioxidants with a heterogeneous catalyst under mild conditions with a high yield. In order to obtain plasticizers and antioxidants, a number of studies were carried out to determine the optimal temperature, amount of catalyst and molar ratio of reacting components based on natural petroleum and aliphatic fatty acids (C_6-C_8) using a heterogeneous catalyst. Based on the studies carried out under optimal conditions (temperature -110-120°C, the amount of catalyst – 1,5 wt.%, acid, the molar ratio of components - acid: alcohol - 2:1,4), mixed diesters were synthesized with a yield of 88-90%. To confirm the structures of the synthesized diesters on the "Alpha" IR Fourier spectrometer, the corresponding IR-spectra were obtained, where the absorption bands characteristic of the carbonyl and ester functional groups appear with greater intensity. The good compatibility of the synthesized plasticizers with the polymer matrix and the effect of these compounds on the reduction of sludge in diesel fuel are shown.

***Keywords**: 1,4-butanediol, natural petroleum acids, mixed diesters, diesel fuel, polyvinyl chloride, plasticizer, antioxidant.*

INTRODUCTION

Mixed diesters of dihydric alcohols and carboxylic acids as plasticizers have a number of specific properties. They almost do not migrate, are practically non-volatile, improve properties and are well compatible with the polymer. These esters are also promising antioxidants for diesel fuels [1–5].

The process of synthesis of ethylene glycol diester of synthetic petroleum acids in the presence of catalytic nano-titanium dioxide has been developed. The optimal conditions for the esterification reaction were found and the advantage of nano-TiO_2 compared to the classical KU-2(H^+) catalyst was shown, and a material balance was drawn up [6].

Obtaining of a mixture of synthetic fatty acids by oxidation of paraffinic hydrocarbons separated from diesel fraction is presented. Based on the synthesized acids in the presence of nano-ZnO, the optimal conditions for synthesizing of monoesters of 1,3-etylene glycol and containing CH_3 and OH functional groups have been defined. Either the physical-chemical indicators used raw material or synthesized esters have been justified via analytical and spectral methods. The material balance of monoesters is presented and the sphere of their application studied [7].

The article [8] presents a one-stage method for the synthesis of mixed diesters based on propylene glycol, synthetic petroleum and aliphatic fatty acids (C_6-C_8) using a ZnO catalyst under optimal conditions - temperature -110 - 120°C, amount of catalyst – 1,3% wt. (acid), molar ratio of components - acid: alcohol - 2:1,3. Diesters have been investigated as plasticizers for polymeric materials and antioxidants for diesel fuel. An analysis of the research results shows that the synthesized mixed diesters can be proposed as effective plasticizers for PVC and new antioxidants for diesel fuels.

In order to increase the range of plasticizers and antioxidants using a ZnO catalyst, a mixed diester of diethylene glycol based on natural petroleum and valeric acids was synthesized, the possibility of complete mixing of the diester with polyvinyl chloride, a decrease in the amount of diesel fuel sediment and its use as an effective plasticizer and antioxidant was established [9].

The article is devoted to the synthesis and application of mixed ethylene glycol diesters based on petroleum and fatty acids by a waste-free method. The properties of mixed diesters of petroleum acids have been studied, physicochemical parameters have been determined by analytical and spectral methods. The degrees of compatibility of ethers with polyvinyl chloride, the ability to extend the service life of diesel fuel have been established [10].

Considering the properties of solvents, plasticizers and antioxidants based on mixed diesters of dihydric alcohols and petroleum acids, we are able to continue our work in this direction.

EXPERIMENTAL PART

To obtain diesters, natural petroleum acids (NPA), aliphatic fatty acids of the C_6-C_8 series ($C_5H_{11}COOH$, $C_6H_{13}COOH$, $C_7H_{15}COOH$), 1,4 - butanediol, and technical-grade ZnO as a catalyst were used as raw materials. At the installation of Meriken Oil Refinery named G. Aliyeva isolated natural petroleum acids from the 90-215°C fraction, having the following physical and chemical parameters: acid number - 235 mg KOH/g, molecular mass – 239 g/mol, n_D^{20}-1,4957, ρ_4^{20}-0,9715 [2,3,9,10].

The IR-spectrum of NPA was recorded on an Alpha IR-Fourier spectrometer manufactured by the German company BRUKER (fig. 1).

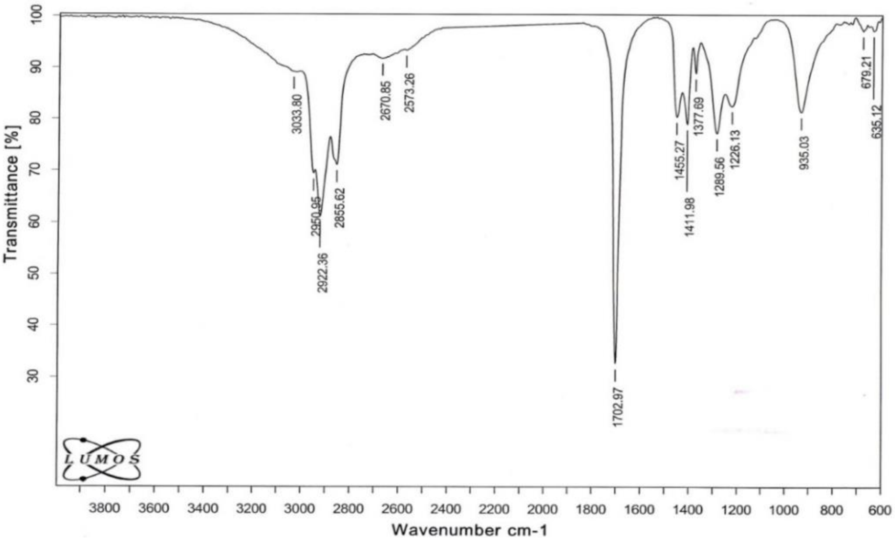


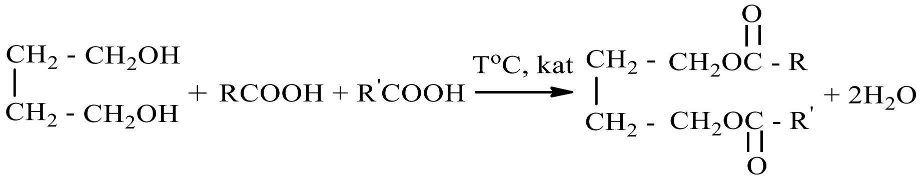
Fig.1. IR - spectrum of NPA

The following absorption bands were observed in the IR- spectrum of NPA:

935 sm^{-1} – deformation vibrations of the O-H bond of the -COOH

	group of the acid;
1226, 1289 sm^{-1}	– C-O bonds of –COOH acid group;
1702 sm^{-1}	– C=O bonds of –COOH acid group;
1377, 1411, 1455, 2855, 2922, 2950 sm^{-1}	– bending and stretching vibrations of C-H bond of CH_3 and CH_2 groups;
2573, 2670 sm^{-1}	– COOH group of acid.

The preparation of mixed diesters of 1,4-butanediol based on NPA and fatty acids with the participation of a ZnO catalyst was carried out by a one-stage method according to the following scheme:



$$\begin{matrix} CH_2-CH_2OH \\ | \\ CH_2-CH_2OH \end{matrix} + RCOOH + R'COOH \xrightarrow{T^oC,\ kat} \begin{matrix} CH_2-CH_2O\overset{O}{\overset{\|}{C}}-R \\ | \\ CH_2-CH_2O\underset{O}{\underset{\|}{C}}-R' \end{matrix} + 2H_2O$$

where: R is the NPA radical, R^1 ÷ C_5H_{11}-, C_6H_{13}- and C_7H_{15}- radicals.

Based on earlier laboratory studies [10], the optimal amount of catalyst, the molar ratio of the reacting components and the temperature regime for mixed diesters of petroleum acids were found:

The optimal mode for 1,4-butanediol diesters based on NPA and fatty acids: the amount of catalyst – 1,5% wt., to the taken acid, the molar ratio of acid:alcohol - 2:1,4, temperature - 110-120°C.

The following is a synthesis based on caproic acid:

- 31,5 g (0,25 mol) 1,4-butanediol, 59,7 g (0,25 mol) NPA, 29 g (0,25 mol) caproic acid ($C_5H_{11}COOH$), 1,33 g (0,016 mol) ZnO catalyst, 85,0 g (0,92 mol) of toluene was loaded into a three-necked flask and the reaction was continued for 4-4,5 hours. Upon completion of the reaction, the reaction product was filtered on a paper filter, the catalyst was removed, after the solvent was distilled off, the raw ether was subjected to vacuum distillation and physicochemical parameters were determined (table 2). The material balance of the process of obtaining a mixed diester of 1,4-butanediol based on NPA and caproic acid is compiled and shown in table.1.

Table 1

Material balance of obtaining a mixed diester of 1,4-butanediol based on NPA and caproic acid

Taken			Received		
Denomination	Amount		Denomination	Amount	
	g	%		g	%
NPA	59,7	28,9	Waters	8,8	4,3
$C_5H_{11}COOH$	29,0	14,0			
1,4-butanediol	31,5	15,2	1,4-butanediol	9,0	4,35
ZnO	1,33	0,64	ZnO	1,28	0,62
Toluene	85,0	41,16	Toluene	82,0	39,7
Total	206,5	100	Mixed diester	102,25	49,5
			Remainder	3,17	1,53
			Total	206,5	100

RESULTS AND DISCUSSION

Other representatives of mixed diesters of 1,4-butanediol based on NPA and fatty acids were synthesized by a similar method, their physicochemical parameters were determined (table 2), and below is the IR- spectrum of the obtained diester based on NPA and caprylic acid (fig.2).

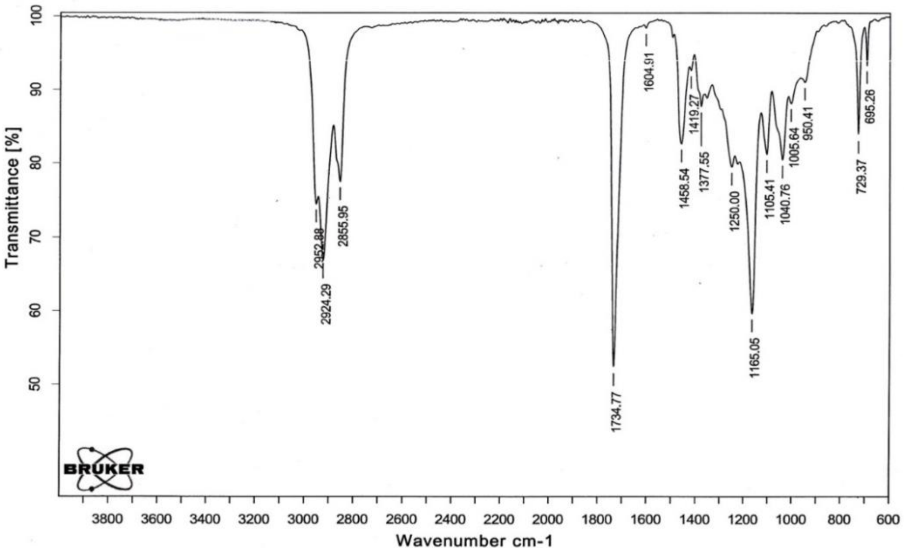


Fig. 2. IR-spectrum of a mixed diester of 1,4-butanediol based on NPA and caprylic acid.

The following absorption bands were observed in the IR-spectrum of the mixed diester:
729 $см^{-1}$ - pendulum vibrations of the C-H bond of the CH_2 group;
1005,1040 $см^{-1}$ - stretching vibrations of the C-O bond of the COH group;
1105,1165,1250 $см^{-1}$ - C-O-C bond of the mixed diester;
1734 sm^{-1} - C=O bond of the mixed diester;
1377, 1419,1458 $см^{-1}$ - deformation vibrations of the C-H bond of CH_3,CH_2 and CH groups;
2855,2924,2952 $см^{-1}$ - stretching vibrations of the C-H bond of the CH_3, CH_2 and CH groups;
1604 $см^{-1}$ - C=C bond of benzen ring.

It is known from scientific sources [12, 13] those heterogeneous catalytic reactions occur on the surface of a solid catalyst and are caused by the activation of reactant molecules upon interaction with the surface.

Since the coordination number of ZnO is 6, such oxides have a high probability of formation of intermediate complexes and decomposition of these complexes. The process of attraction of reacting molecules to the surface of the catalyst weakens the chemical bonds in them, i.e., causes their decomposition and the formation of intermediate unstable activated complexes, which accelerates the formation of the reaction product. Subsequently, a water molecule is split off from this complex and the catalyst is re-reduced (returns to its original state) with the formation of an ester.

In further studies, the compatibility of the synthesized diesters, as well as the industrial plasticizer - dioctyl adipate (DOA) with polyvinyl chloride (PVC) “C-65” was studied [14] and it was found that the compatibility of the synthesized mixed diesters with PVC coincides with the industrial plasticizer DOA.

According to previous studies [15], the properties of these diesters to improve the thermo-oxidative ability of diesel fuels were studied. The work carried out showed that 1,4-butanediol diester based on NPA and caprylic acid reduces the amount of sediment from 4,6 mg/100 cm^3 to 0,4 mg/100 cm^3.

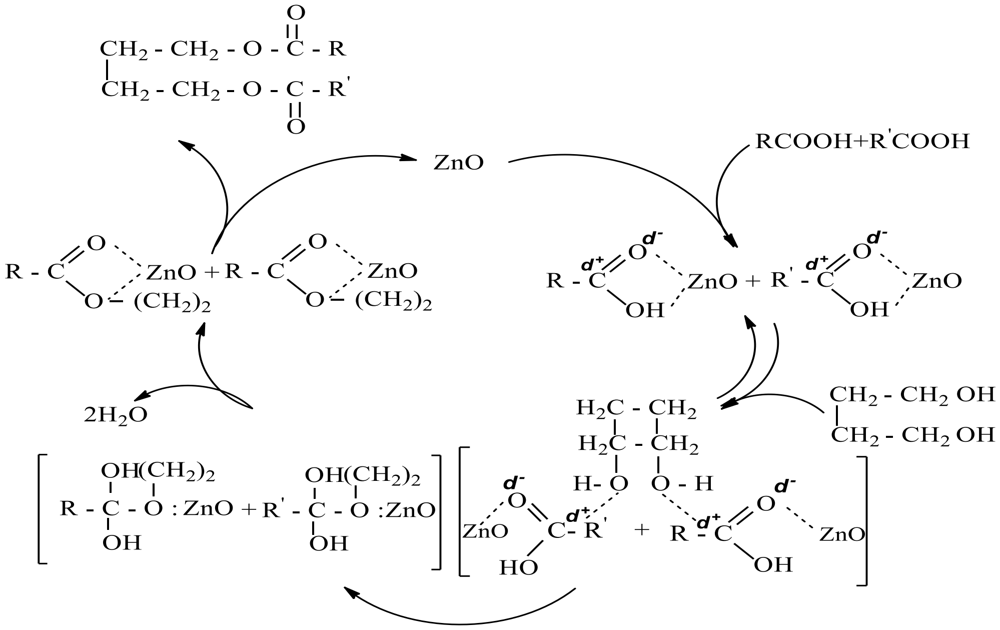
The positive results obtained by us make it possible to increase the range of esters of natural petroleum acids.

Table 2

Some physicochemical parameters of mixed diesters of 1,4-butanediol based on NPA and fatty acids

R	Boiling temperature, °C, $2{,}66\cdot10^{-4}$ MPa	ρ_4^{20}, g/sm^3	n_D^{20}	Acid number, mgKOH/g	Saponification number, mgKOH/g	Kinematic viscosity, mm^2/s	Volatility, %	Yeald, %
C_5H_{11}	195-245	0,9760	1,4608	0,35	281,0	16,20	0,58	90,0
C_6H_{13}	200-250	0,9751	1,4615	0,63	270,2	17,28	0,60	89,1
C_7H_{15}	210-260	0,9700	1,4632	0,44	235,02	19,44	0,63	88,6

Referring to the literature [11] and our studies, the proposed general mechanism for the synthesis of mixed diesters based on natural and aliphatic fatty acids in the presence of technical ZnO as a catalyst can be represented as follows:



here R, R´ are acid radicals.

CONCLUSION

Mixed diesters based on NPA, fatty acids and 1,4-butanediol have been synthesized. The optimal mode was found (amount of catalyst – 1,5% wt., to the taken acid, molar ratio of acid:alcohol - 2:1,4, temperature - 110-120°C) in which the highest yields of the final product are observed. A putative general mechanism for the synthesis of mixed diesters is proposed. The physicochemical parameters of the obtained esters were studied and tested as plasticizers for PVC and antioxidants for diesel fuels.

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СИНТЕЗ И ПРИМЕНЕНИЕ ЭФФЕКТИВНЫХ ПЛАСТИФИКАТОРОВ, АНТИОКСИДАНТОВ

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В статье приведен одностадийный метод синтеза эффективных антиоксидантов и пластификаторов с гетерогенным катализатором в мягких условиях и высоким выходом. С целью получения пластификаторов и антиоксидантов были проведены ряд исследований для определения оптимальных условий: температуры, количества катализатора и мольного соотношения реагирующих компонентов на основе природных нефтяных- и алифатических жирных кислот (C_6-C_8) с использованием гетерогенного катализатора. На основе проведенных исследований, при оптимальных условиях (температура - 110-120°C, количество катализатора - 1,5% мас., по кислоте, мольное соотношение компонентов - кислота: спирт - 2:1,4) были синтезированы смешанные диэфиры с выходом 88-90%. Для подтверждения структур синтезированных диэфиров на «Alpha» ИК-Фурье-спектрометре были получены соответствующие ИК-спектры, где с большей интенсивностью проявляются полосы поглощения характерные для карбонильной и сложноэфирной функциональных групп. Показана хорошая совместимость синтезированных пластификаторов с полимерной матрицей и влияние этих соединений на уменьшение осадка в дизельном топливе.

Ключевые слова: *1,4-бутандиол, природные нефтяные кислоты, смешанные диэфиры, дизельное топливо, поливинилхлорид, пластификатор антиоксидант.*

SƏMƏRƏLİ PLASTİFİKATORLARLARIN, ANTİOKSİDANTLARIN SİNTEZİ VƏ TƏTBİQİ

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Məqalədə heterogen katalizator ilə yumşaq şəraitdə yüksək çıxımla səmərəli plastifikatorların və antioksidantların sintezi verilmişdir. Plastifikatorların və antioksidantların alınmasının optimal şəraitinin: temperaturun, katalizatorun miqdarının və reaksiyaya daxil olan komponentlərin (1,4-butandiol, təbii neft- və C_6-C_8 *sıra alifatik yağ turşuları): təyini üçün heterogen katalizatorun istifadəsi ilə bir sıra tədqiqatlar aparılmışdır. Aparılmış tədqiqatlar əsasında (temperatur- 110-120℃, katalizatorun miqdarı – 1,5% kütlə, turşuya görə, komponentlərin molyar nisbəti – turşu:spirt – 2:1,4) seçilmiş optimal şəraitdə 88-90 % çıxımla qarışıq diefirlər sintez olunmuşdur. Sintez olunmuş diefirlərin quruluşunun təsdiqlənməsi üçün "Alpha" İQ-Furye spektrometrində İQ-spektrlər çəkilmiş və yüksək intensivliklə karbonil və mürəkkəb efir funksional qruplarını xarakterizə edən udma zolaqları müşahidə olunmuşdur. Sintez olunmuş plastifikatorların polimer matrisa ilə yaxşı qarışması və bu birləşmələrin dizel yanacağında çöküntünün miqdarının azalmasına təsiri göstərmişdir.*

Açar sözlər: *1,4-butandiol, təbii neft turşuları, qarışıq diefirləri, dizel yanacağı, polivinilxlorid, plastifikator, antioksidant.*

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RESEARCH OF PHYSICAL-CHEMICAL PROPERTIES OF ESSENTIAL OIL FROM CHAMOMILE

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The article presents the results of the research of substances obtained from the hydrodistillation and solvent extraction of the chamomile plant growing in the Western region of Azerbaijan. The average amount of essential oil from the hydrodistillation of chamomile flower according to the wet raw material was 11.1±1.24%, and the average amount of the essential oil from the extraction in ethyl alcohol was determined to be 1.54 ±0.04%. The composition of the essential oil obtained from common chamomile flowers, rich in biologically active substances and important for treatment, was studied by physico-chemical methods (chromatographic, Ultraviolet (UV) and Infrared (IR) spectroscopic). It was determined that the main components (up to 50%) of the oil obtained from common chamomile flowers are sesquiterpenes, including. consists of cadinene, farnesene, α-bisabolol, ß-bisabolol, as well as their oxides, khamazulene. The assessment of the dynamics of obtaining essential oil from chamomile flowers in different periods of the year showed that it is 2.5-3.5% of the collection of dry raw materials, depending on its yield.

***Keywords**: chamomile, essential oil, hydrodistillation, extraction, bisabolol, chromatography.*

INTRODUCTION

The use of plants is as old as human history. Plants that were used only as food in the past have come to be valued differently by people over time. People have benefited from "useful plants" in various ways with knowledge and experience gained from nature, information passed from generation to generation. Food, beverage, flavoring, preservative, feed, paint, cosmetic, fuel and insulation material, etc. like, in addition to these, plants called "medicinal plants" were also used as medicinal substances and are used today [1].

According to the World Health Organization (WHO), about 20000 plants are currently used as medicine in medicine. These plants are widespread in the flora of the country, especially as a result of the geographical location, climate and plant diversity, agricultural potential and large surface area in the Republic of Azerbaijan [2].

"Medicinal plants" are generally used in the treatment of certain diseases and in the preparation of cosmetics, while "aromatic plants" are used as spices and additives in food or beverages for their smell and taste properties. Every year, interest in the use of medicinal plants among the population and doctors increases, and this is natural. In modern medicine, herbal preparations take the first place among other medicines. Every third medical preparation is made on the basis of plant materials. The main elements that determine the therapeutic properties of medicinal and aromatic plants are the active substances in its composition. The proportion of essential oil in essential oil plants varies depending on many factors such as the genetic structure of the plant, plant organs (morphogenetic variation), the period of plant development (ontogenetic variation), temperature changes during the day (daily variation) and climate and environmental factors [3].

In recent years, in addition to intensively conducted studies on the composition of biologically active organic compounds that make up medicinal plants, the identification of a number of chemical components in their composition is one of the actual problems. This is due not only to the role of many important trace elements, but also to environmental factors. When preparing infusions for the treatment of a number of diseases, a certain part of mineral substances can pass into the aqueous solution. In addition, it is interesting to study the qualitative and quantitative composition of the mineral substances contained in plants growing in the Western region, which is one of the main researches and developed zones of the flora of Azerbaijan, both from the point of view of use and from the point of view of ecological and chemical safety. It is known that the growth conditions of plants can have special physico-chemical and biological characteristics [4].

Many essential oils are used in various diseases in addition to their antiseptic properties. Of these, eucalyptus essential oil is for the respiratory tract, juniper essential oil is antiseptic for the urinary tract, thyme oil is fungicidal (fungal killer), chenopod essential oil is anthelmintic (cleanses intestinal worms). It is known that peppermint oil increases gastric juice, essential oils such as fennel and anise have carminative (gas re-moving) effects, and chamomile has anti-inflammatory (anti-inflammatory) effects [5].

Common chamomile, an annual herb in the Compositea family with anti-inflammatory properties, is a medicinal and aromatic plant that blooms with white flowers between May and August. The difference between it and wild chamomile is that the yellow flower base is hollow and the fragrance is more effective and pleasant. Among the chamomile species with the highest economic value, it can be said that common chamomile grows naturally in every region of Azerbaijan, and some are cultivated is cultivated. Common chamomile is native to Eastern Europe and Asia Minor. Today it has spread to many parts of the world. It is widely distributed in the Western region and Kura-Araz plain in our country [6].

In world pharmaceutical practice, more than 40% of drugs are obtained from plant raw materials. The main reason for this is that herbal remedies are close to the natural metabolites of the body due to their structural characteristics, they are not harmful and can be used for a long time without causing adverse effects. Chamomile is one of the plants that can be used as a raw material in the purchase of medicinal and cosmetic products. Common chamomile (Chamomile Recutita L.), which is the most commonly used type of chamomile, was used in the study. Extraction of essential oil rich in biologically active substances from its flowers and its physico-chemical properties have been studied by various methods. This plant is used in folk medicine as an anti-inflammatory, antiseptic and pain reliever. Most of the mentioned beneficial properties of chamomile are due to the presence of biologically active substances such as α-bisabolol, bisabolal oxides and chamazulene [7].

EXPERIMENTAL PART

There are 50 species of chamomile in the world flora. Chamomile belongs to the Asteraceae or daisy family. Although there are a number of species known only as chamomile, only three of them are used as useful plants for humans. The most famous is Chamomilla recutita or Matricaria (Medical Chamomile), also known as Apothecary

Chamomile, German Chamomile, Hungarian Chamomile, False or Wild Chamomile. These are the same chamomiles that are familiar to everyone with their white and yellow flowers. In the wild, it is distributed almost throughout Europe and is cultivated in most European countries and the United States. Another popular species of chamomile, Anthemis nobilis is commonly known as the Roman and English chamomile. It is cultivated as a medicinal plant in England, Belgium, France and the United States [8].

Common chamomile and aromatic chamomile (Chamomilla suaveolens) are found in 3 species in the Caucasus, including 2 species in Azerbaijan. Common chamomile species are widespread in the Ganja-Gazakh region of Azerbaijan. Based on the analysis of landscape and geological factors, we selected the common chamomile plant growing in the plain area of the Western region (geographical coordinates 41°05′ 36" N. L. 45°21′ 58" N.L.) in the study.

The primary raw material (Common chamomile) was collected from the natural bisenos of Dashkasan district of Western region in the first week of every month from April to October. The selection of chamomile flowers and the average calculation of the samples were carried out in accordance with ISO 21769-84. Before the experiments, the raw materials were crushed to 2-3 mm in a laboratory grinder. Biologically active components from Common chamomile flowers were obtained by 2 standard methods:

1. The hydrodistillation method is the distillation of a mixture of raw materials and water in the process of obtaining essential oil from chamomile flowers. After the essential oil extraction process was carried out for 2 hours, the experiment was stopped. 500 ml isolab jacketed heater, 500 ml isolab glass flask and clevenger were used in the experiments of essential oil determination by hydrodistillation method. The quantitative content of the essential oil obtained by hydrodistillation in the Ginzburg unit was determined.

2. Extraction is a method of separating essential oils with mild organic solvents. Due to their nature and properties, essential oils are well soluble in various light and volatile organic substances. The process of extracting essential oil from chamomile flowers was carried out in two stages: extraction with ethyl alcohol in a Soxhlet device, that is, the actual separation of the components from the flowers, and then the separation of the solvent by distillation. The resulting vapor carries with it the volatile components of the essential oil. The steam is then cooled with running water, and the liquid mixture of water and essential oil is stratified in the receiver. Since the obtained essential oil is lighter than water, it accumulates in the upper layer of water [9].

The component composition of essential oil of chamomile flowers was determined by the gas-liquid chromatography method in AutoSystem XL (PerkinElmer) flame ionization detector chromatograph.

The UV/Vis 6850 spectrophotometer manufactured by JENWAY was used to study the essential oil obtained from the chamomile flowers by UV (Ultraviolet) – pectroscopic method. The optical transmittance of the device is 0.1 nm. The spectra were recorded in the 200–500 nm wavelength range in steps of 1.0 nm.

The IR (Infrared) spectrum of the essential oil obtained from the chamomile flowers was recorded on the "ALPHA" IR-Fourier spectrometer of the German "Bruker" company. The IR spectra of the substances were recorded in the wave number range of 600-4000 cm^{-1} at a temperature of 25°C.

RESULTS AND DISCUSSION

The yield of essential oils obtained from chamomile by extraction and hydrodistillation methods was calculated according to the wet weight ratio of the plant using the following formula [10]:

$$\text{Yield of essential oil, \%} = \frac{\text{Amount of essential oil, g}}{\text{Amount of raw materials, g}} * 100\%$$

The results of the essential oil obtained by hydrodistillation and extraction processes from chamomile flowers taken in different weight amounts are given in table 1.

As can be seen from table 1, the maximum amount of essential oil obtained by hydrodistillation method is 1.24 %, and the maximum amount of essential oil obtained by extraction method is 1.77 %. It was determined that the amount of essential oil obtained by the extraction method is higher than the amount of essential oil obtained by the hydrodistillation method. This is based on the fact that the extraction method involves the evaporation and subsequent condensation of the solvent and the ability of the solvent vapor to absorb the essential oils. The average amount of essential oil was 1.1 ± 1.24 % and 1.54 ± 0.04 % according to the wet raw material in the determined optimal options.

Table 1

Material balance of the hydrodistillation and extraction processes

The name of the raw material	Amount of raw materials, (g)	Amount of essential oil, (g)	Yield of essential oil, (%)	Average amount, (%)
Results of the hydrodistillation process				
Common chamomile (Chamomilla Recutita L.)	200.48	2.12	1.05	1.1±1.24
Common chamomile (Chamomilla Recutita L.)	200.74	2.49	1.24	
Results of the extraction process				
Common chamomile (Chamomilla Recutita L.)	100.12	1.32	1.31	1.54 ±0.04
Common chamomile (Chamomilla Recutita L.)	100.35	1.78	1.77	

The simplest methods of determining the authenticity of essential oils are to determine their organoleptic properties (color, transparency, smell, taste) and physicochemical properties (density, refractive index, kinematic viscosity, pH). Physico-chemical properties of the obtained essential oil were studied by different methods and the obtained results are presented in table 2.

As can be seen from the table, the density of essential oils (ISO 279-2014) is usually less than one. The refractive index (ISO 280-2014) is almost constant for all oils (table 2). According to the value of the refractive index, it can be judged that certain components are predominant in the oil. The highest breakdown is characteristic of oils with a high content of aliphatic terpenes with three double bonds, and the lowest for tricyclic terpenes. Identification of the components included in Common chamomile oils was carried out by various methods: introducing known pure substances, measuring the physical constants of substances isolated by preparative chromatography, IR and UV spectroscopy methods [11]. Chromatographic, Ultraviolet (UV) and Infrared (IR) spectroscopic methods are used to check the purity of essential oil and to analyze its composition.

Table 2

Physicochemical characteristics of essential oil

Color	Smell and taste	Density at 20°C, g/sm^3	N_D, 20°C	Kin. visco. 20°C, mm^2/s	pH	Brix 25° °Bx	Absorbans
yellow	specific	0.9478	1.3457	1.725	4.21	0.5	0.995
yellow	specific	0.8475	1.2471	1.347	5.14	0.1	0.973
yellow	specific	0.8347	1.2531	1.612	6.12	1.5	0.951
yelow	specific	0.8741	1.2458	1.456	5.0	1.5	0.893

Gas-liquid chromatography is used to obtain characteristic chromatographic profiles of components present in high amounts in medicinal plants. The advantage of this method for obtaining repeatable chromatographic spectra is the high sensitivity of the method when using universal detectors such as flame ionization and mass spectrometry. In addition, the high separation power of the quartz capillary columns used allows the analysis to be performed in a short time.

To determine the naturalness and composition of essential oils, enantioselective gas-liquid chromatography is used, which allows determining the ratio of diastereomers of oil components that can serve as chemomarkers of their origin. Chromatograms allow to determine the composition of essential oils or a detailed "map" of the distribution of all its components, the authenticity and naturalness of the essential oil. A common method for the analysis of complex mixtures of terpene compounds (mono-, sesqui-, diterpenes) is gas-liquid chromatography.

To carry out chromatography, a small sample (0.001 µl) of essential oil is evaporated (at a temperature of 250°C) into a narrow quartz capillary tube (inner diameter 0.25 mm) with a length of 30 meters using a microsyringe. Under the influence of a carrier gas (usually helium, hydrogen or nitrogen) constantly flowing through this tube, the essential oil in the form of vapor moves through the tube. Simultaneously, the column temperature rises from 50°C to 220°C at a rate of 3-4 degrees/min. The inner surface of the tube (which is called a column) is covered with a thin layer (0.25 microns) of a neutral liquid of a polymeric nature [12].

15 components (83.05% of the whole oil) were determined in chamomile essential oil by gas-liquid chromatography analysis. The main components of the oil (up to 50%) are sesquiterpenes, incl. consists of cadinene, farnesene, bisabolole, oxides of bisabolole, khamazulene. The main components of chamomile oil: α-bisabolol (2.39%), β-farnesene (3.09%), azulene (4.68%), hamazulene (8.22%), spatulenol (8.24%), α - farnesene 0.1%, germacrene D 1.0%, peral 0.80%, longycyclene 1.12%, spiroether 0.82%, dicycloether 0.20%, bornyl acetate 3.48%, caryophyllene 1.41%, longifolene 0.95%, terpineol, 3.80% murolene 0.12%, α-cadinene 2.20%, γ-cadinene 2.00%, α-curcumene 0.10%, and triacetin (46.69%), which accounts for 73.31% of the total

volatile substances. Substances such as xamazulene, in-ene-dicycloether, α-bisabolol oxide A, α-bisabolol oxide B, t-β-farnesene and spathulenol are permanent components of chamomile essential oil. Khamazulene is not a native component of chamomile flowers, but is formed from its matrix by the effect of heating temperature applied to plant materials to obtain the essential oil.

The analysis and percentage of the individual components in the essential oil were calculated according to ISO4724:2004 and ISO 18393365-004-2010 document. In the chromatogram of the essential oil, the capture of the peak of sesquiterpenes with a tricyclic structure coincides with the gas-liquid chromatographic profile (reference) for the essential oil presented in the document ISO 4724:2004 and ISO 18393365-004-2010 [13].

UV spectroscopy with the use of mathematical processing of the spectra confirmed the presence of sesquiterpenes with different chemical structures in the studied extracts. Essential oils were characterized by UV spectroscopy at 40°C. UF spectroscopy analyzes of chamomile extracts are reported in the literature [14]. UV spectra of the extract obtained at 40°C are shown in fig 1. The spectrum of the essential oil has two peaks at approximately 230 nm and approximately 340 nm. It is reported that matricine and dicycloethers absorb at 244 nm. We cautiously attribute the broad band at 200-350 nm to α-bisabolol and its oxides. Additionally, an unidentified fluorescent peak appears at ca. 220 nm.

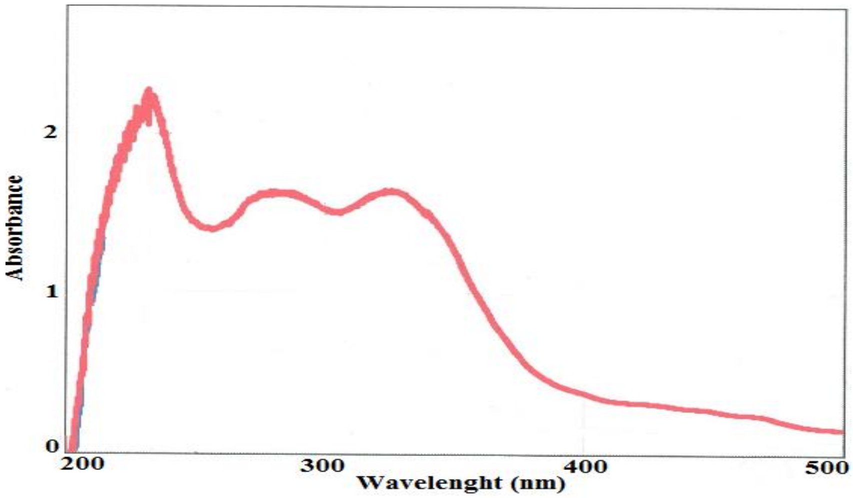

Fig. 1. UV absorption spectrum of essential oil from Common chamomile.

Infrared spectroscopy substantially complements UV spectroscopy. For the chemistry of terpenes, two parts of the spectrum are most important [15]. Absorption bands in the region of approximately 3650-2650 cm^{-1} (excluding C-H vibrations) in the case of terpenoids are almost always characteristic of O-H bond vibrations. When properly interpreted, absorption bands in this region can serve as evidence for the presence of hydroxy or related groups. Absorption in the second and more important part of the spectrum (approximately 1820-1640 cm^{-1}), if it is sufficiently intense, it usually corresponds to C=O vibrations. By the position of the absorption maximum in this region, it can be determined whether the compound is a saturated or conjugated ester, aldehyde, ketone, acid, lactone, or anhydride. Important, but less general, are data on absorption in other parts of the spectrum. Thus, a weak absorption band in the region of 3050 cm^{-1} indicates the presence of a methylene group in the cyclopropane ring [16]. Functional groups and components related to the following absorption bands were observed in the IR spectrum of the essential oil obtained from the chamomile plant (fig. 2.):

1743, 1238, 1021 sm^{-1}	-C=O, -C-C-O, -O-C-C (ester group) Matricine
1743 sm^{-1}	-C=O (ketone group) Apigenin-7-glucoside
1050, 919, 1452 and 1374 sm^{-1}	-C-O, -C-C-C (vibration, isopropyl group) α-Bisabolol
1080 and 1167 sm^{-1}	-C-O-C Dicycloether

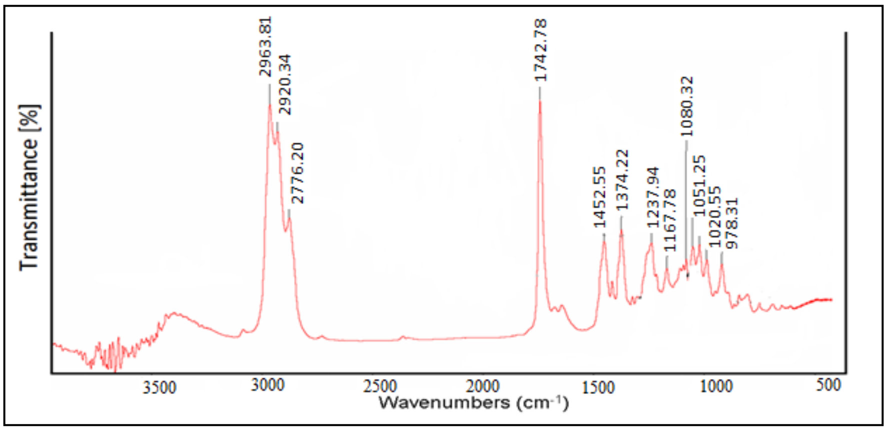

Fig. 2. IR spectrum of essential oil from Common chamomile.

During our research, depending on the season, the rate of yield of essential oil obtained from the flowers of the common chamomile plant growing in the Western region of Azerbaijan was also studied.

The amount of essential oil of common evening primrose varies throughout the year and has 2 maximum percentages: in spring - in April (3.4%) and in autumn - in September (3.5%) based on the mass of dry raw materials. In the months of May-June, a decrease in the amount of essential oil was observed, which confirms that essential oils participate in the growth of the plant. When exposed to high solar heat in the summer months, a decrease in the amount of essential oil is observed in the composition of the plant.

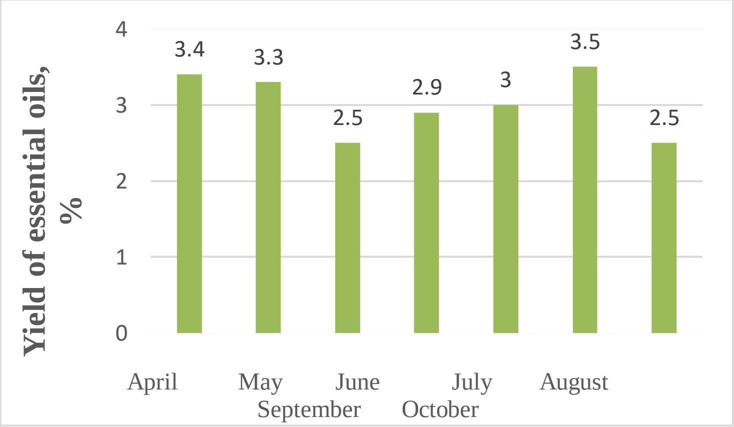

Fig. 3. Seasonal dynamics of essential oil release from Common chamomile.

Oil accumulation was noted from July to September, which is explained by the intensification of physiological processes and activation of metabolism in the flowers of the plant. In September, the increase in the amount of essential oil is due to the end of the formation of flowers. A decrease is observed in October, which is due to the slowing down of metabolism or metabolic processes in plants. In addition, plants that are in a state of forced dormancy (metabolism does not take place in the dark) also react to the reduction of daylight hours (fig. 3.).

CONCLUSION

The results of the study of substances obtained from the flowers of the chamomile plant growing in the western region revealed that the average amount of essential oil based on wet raw material from hydrodistillation was 11.1±1.24%, and the average amount of essential oil based on wet raw material from ethyl alcohol extraction was determined to be 1.54 ±0.04%.

The assessment of the dynamics of obtaining essential oil from chamomile flowers in different periods of the year showed that, depending on its productivity, it makes up 2.5-3.5 percent of the collection of dry raw materials.

Biologically active components (vitamins, di- and triterpenes) are kept in the essential oil obtained after extraction. They are sterile and have antioxidant properties. The obtained extracts contain a high number of oils in addition to the essential oil, which has a positive value. Because the oil part together with the aromatic component is a biologically active complex suitable for use in cosmetic products. Various ointments and lotions are prepared from these extracts for cosmetology preparations.

The essential oil obtained from the chamomile plant has been used as a disinfectant and anti-inflammatory in skin diseases in the form of a solution and ointment prepared in alcohol.

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ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ ЭФИРНОГО МАСЛА РОМАШКИ

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В статье представлены результаты исследования веществ, полученных гидродистилляцией и экстракцией с растворителем растения ромашки аптечной, растущей в Западном регионе Азербайджана. Среднее количество эфирного масла методом гидродистилляции цветков ромашки аптечной влажного сырья составило 11.1±1.24%, а среднее количество эфирного масла методом экстракции в этиловом спирте определено как 1.54±0.04%. Физико-химическими методами (хроматографическим, ультрафиолетовым (УФ) и инфракрасным (ИК) спектроскопическим) изучен состав эфирного масла, полученного из цветков ромашки обыкновенной, богатого биологически активными веществами и важного для лечения. Установлено, что основными компонентами (до 50%) масла, полученного из цветков ромашки обыкновенной, являются сесквитерпены, в том числе. состоит из кадинена, фарнезена, *α-бисаболона, β-бисабола, а также их оксидов, хамазулена. Оценка динамики получения эфирного масла из цветков ромашки в разные периоды года показала, что в зависимости от ее продуктивности она составляет 2.5-3.5% сбора сухого сырья.*

Ключевые слова: *ромашка, эфирное масло, гидродистилляция, экстракция, бисаболол, хроматография.*

ÇOBANYASTIĞINDAN ALINAN EFİR YAĞININ FİZİKİ-KİMYƏVİ XASSƏLƏRİNİN TƏDQİQİ

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Məqalədə Azərbaycanın Qərb bölgəsində bitən çobanyastığı bitkisinin hidrodistilləsindən və həlledici ilə ekstraksiyasından alınan maddələrin tədqiqinin nəticələri təqdim olunmuşdur. Çobanyastığı çiçəyinin hidrodistilləsindən yaş xammala görə efir yağının orta miqdarı 11.1±1.24%, etil spirtində ekstraksiyasından yaş xammala görə efir yağının orta miqdarı 1.54 ±0.04 % müəyyən edilmişdir. Bioloji-aktiv maddələrlə zəngin, müalicə əhəmiyyətli adi çobanyastığı çiçəklərindən alınan efir yağı fiziki-kimyəvi metodlar ilə (xromatoqrafik, Ultrabənövşəyi (UB) və İnfraqırmızı (İQ) spektroskopik) tədqiq edilərək tərkibi öyrənilmişdir. Müəyyən edilmişdir ki, adi çobanyastığı çiçəklərindən alınan yağın əsas komponentləri (50% -ə qədər) sesquiterpenlər, o cümlədən. kadinen, farnesen, α-bisabolon, ß-bisabolol, həmçinin onların oksidləri, xamazulendən ibarətdir. Çobanyastığı çiçəklərindən ilin müxtəlif dövrlərində efir yağının alınma dinamikasının qiymətləndirilməsi göstərmişdir ki, onun məhsuldarlığından asılı olaraq quru xammalın kolleksiyasının 2.5-3.5% -ni təşkil edir.

Açar sözlər: *çobanyastığı, efir yağı, hidrodistillə, ekstraksiya, bisabolol, xromatoqrafiya*

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CONVERSION OF PROPYLENE AND ISOBUTYLENE ON A HIGH SILICA ZEOLITE CATALYST

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As you know, over the past decade, due to the intensive increase in oil production, the number of gaseous hydrocarbons released at oil refineries and petrochemical plants has sharply increased. In this regard, the targeted conversion of gaseous hydrocarbons into valuable intermediates on zeolite catalysts is a topical issue. In the process of conversion of gaseous hydrocarbons, depending on the nature of the reagent and temperature, seal products of various structures can be formed on the catalyst surface. There are different opinions on the influence of the seal products on the catalyst activity. In some cases, the accumulation of SP on the catalyst surface adversely affects its activity, and in other cases, vice versa. In works devoted to the study of oligomerization and aromatization of C_2-C_4 olefins on zeolite catalysts, the question of the formation of SP was practically not considered.

Keywords: *isobutene, zeolite, seal products.*

INTRODUCTION

In the presented work, the activity of the H-HSZC catalyst in the conversion of propylene and isobutylene, as well as coke deposition, regeneration of coked catalyst samples, and the effect of compaction products on the general acidic properties of the catalyst were studied [1-8]. The reaction products were analyzed on an LKhM-8MD chromatograph and a UR-20 spectrometer. Differential thermal analysis of catalyst samples carbonized at different temperatures was carried out on an E. Paulik, H. Erdei derivatograph (MOM) in the temperature range 20-1000°C. The results obtained show that the compaction products, being a by-product of the conversion of olefins, reduce the number of acid sites [9-15]. In this case, the formation of liquid products during the conversion of propylene and isobutylene is observed only after the accumulation of 5.5-7.6% of the SP on the catalyst surface. As is known, the mechanism of conversion of olefins has been sufficiently studied, but it is appropriate to note that with the advent of new experimental and theoretical data, there is a need to revise the mechanism and kinetics of conversion of olefins on zeolite catalysts [16-20].

In the presented work, the activity of the H-HSZC catalyst in the conversion of propylene and isobutylene, as well as coke deposition, regeneration of coked catalyst samples, and the effect of compaction products on the general acidic properties of the catalyst were studied.

EXPERIMENTAL PART

The research object was the H-HSZC. Before carrying out the experiments, the high-silica zeolite catalyst was regenerated at 500-550°C in an air flow, then purged with nitrogen. To remove residual oxygen, nitrogen was passed through a reactor with a copper catalyst at 450°C.

Propylene and isobutylene were obtained by dehydration of isopropyl alcohol and trimethylcarbinol on α-Al_2O_3; at the temperature of ~50^{o}C. The activity of the catalyst was determined in a laboratory flow setup with a reactor with a catalyst volume of 1 cm^3. The acidic properties and the amount of SP accumulated at various temperatures of 180° - 450°C) during the conversion of propylene and isobutylene were determined on a McBen gravimetric apparatus [10]. The acidic properties of the initial and coked at different temperatures catalyst samples were studied by adsorption of ammonia molecules. The change in the catalyst mass was determined using a KM-6 cathetometer. The nature of sealing product (SP) was also investigated by taking derivatograms and X-ray diffraction patterns of samples coked at different temperatures. The reaction products were analyzed on an LXM-8MD chromatograph and a UR-20 spectrometer.

Differential thermal analysis of catalyst samples carbonized at different temperatures was carried out on an E. Paulik, H. Erdei derivatograph (MOM) in the temperature range 20-1000°C.

X-ray phase analysis was performed on a DRON-2 device (Cu, Kα-radiation, Ni-filter). For these analyzes, a sample of the catalyst worked out at various temperatures was examined.

RESULTS AND DISCUSSION

Fig.1 shows the accumulation of SP and the yield of liquid products as a function of time during the conversion of propylene (a), isobutylene (b) and the regeneration of the coked catalyst from temperature. Under these conditions, one can observe the accumulation of the maximum amount of SP – 7.8% within 20-25 minutes from the beginning of the process. In this case, the formation of liquid products is not observed, and the evolution of hydrogen and unreacted propylene is observed in the gas phase. A parallel study of the activity of the H-HSZC catalyst on a flow-through unit and the accumulation of SP on the gravimetric unit showed that the formation of liquid products is observed only after the accumulation of 7.8% of seal products on the catalyst surface (fig.1; curve 1). As can be seen, the regeneration curve of the coked catalyst has a stepped shape. The first loose part of SP is removed by supplying nitrogen, and the second graphite-like part is removed by combustion with the supply of oxygen (fig.1, curve 3). We obtained such a character of catalyst regeneration while studying the processes of conversion of ethylene and butylenes [11, 12]. During the conversion of propylene, the yield of liquid products is observed at 225°C. As the temperature rises, the yield of liquid products increases. The maximum yield of liquid products is observed at 320°C and is 79% (W = 300^{-1} hours^{1}). In this case, the propylene conversion is 98%. At relatively low temperatures (220°-280°C), the liquid product consists mainly of aliphatic hydrocarbons. With an increase in the temperature of the process, the formation of aromatic hydrocarbons is observed in the liquid product. In the temperature range 400° -450°C, the bulk of liquid products consists of aromatic hydrocarbons. The results of the analysis of liquid products during the conversion of propylene are presented in table 1. Analysis of liquid products was carried out in the factory laboratory of the "Azneftyanajag" Production Association by group analyzes according to MRTU 38-1-259-67. The results of the analysis showed that the liquid products formed at 300°C actually represent a gasoline fraction (boiling point below 180°C, with an octane number of 89-90). As can be seen from the table, the catalyzate obtained at 300°C contains mainly olefins, naphthenes, paraffins, and along with them, minor amounts of aromatic hydrocarbons have been identified.

IR spectral studies of propylene compaction products on a high-silica zeolite catalyst showed that at a temperature of 200-250°C, hydrocarbons of a linear structure are mainly formed, and at higher temperatures (300% C), hydrocarbons of a nonlinear structure.

The study of the propylene conversion process showed that the conversion rate and catalyst selectivity significantly depend on the temperature and contact time. The analysis of these results showed that at a contact time 8 sec. the maximum yield of liquid products is reached at a reaction temperature of 320°C and is 79%. Based on chromatographic analysis, it was shown that the gaseous products consist of unreacted propylene, C_2, C_3H_8, C_3H_6, n-C_4H_{10}, i-C_4H_{10}, i-C_4H_8, butene-1, cis-butene 2 and trans-butene-2.

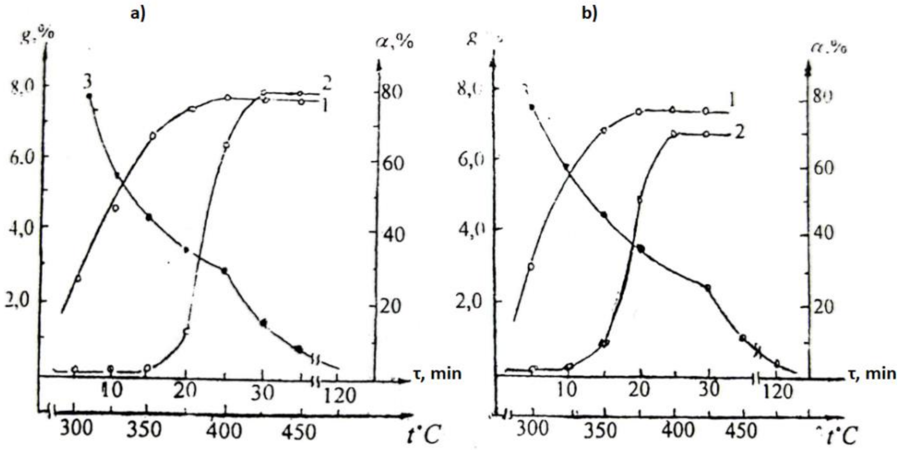

Fig.1. Dependence of the accumulation of seal products (1), the yield of liquid products on time (2) in catalyst regeneration on temperature (3) during the conversion of propylene at 320°C (a) and isobutylene at 300°C (b).

On the thermogram of the catalyst carbonized at 320°C during the conversion of propylene (fig.2, b), a stepwise decrease in mass is observed on the TG line, accompanied by an extensive exothermic effect with two maxima at 460 and 550%. The presence of two maxima indicates that there are two different components in the seal products, differing in properties and chemical composition. In addition, this may indicate that in the course of regeneration at temperatures above the temperatures of their formation, SPs undergo changes, leading to an increase in the ratio of S/H in their composition.

X-ray phase analysis of the initial and coked at 400°C catalyst was carried out in order to determine the violation of the crystallinity of the zeolite framework during the process and the possibility of the formation of new crystal structures during the deposition of SP.

It should be noted that the isobutylene conversion process is similar in some characteristics to the propylene conversion process. The process of isobutylene conversion on H-HSZC was carried out at a temperature range of 150-450°C and various space velocities (300, 500, 1000 h^{-1}). At 200°C, the degree of conversion of isobutylene was 40.0; 38.4; 36.5% at volumetric velocities of 300, 500, 1000h^{-1}, respectively. With increasing temperature, the conversion of isobutylene increases and at 400° - 450°C reaches 98%.

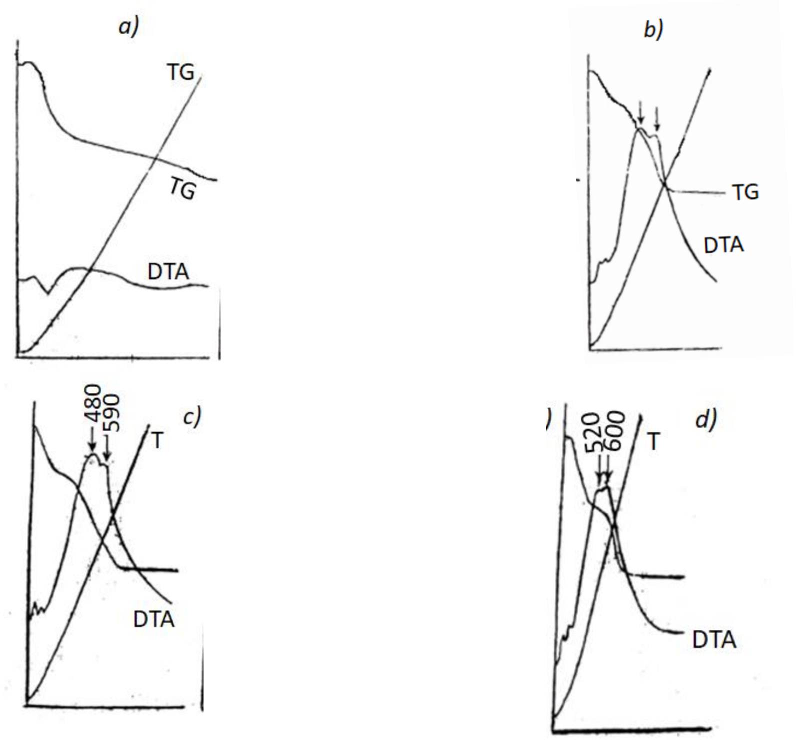

Fig.2. Differential thermal analysis of the initial (a) and carbonized H-HSZC catalyst during the conversion of propylene (6) at 320°C and isobutylene at 350 and 400°C (c and d).

The products of isobutylene conversion at H-HSZC consist of gaseous, liquid and SP. Based on chromatographic and IR spectroscopic analyzes, it was found that gaseous products consist of unreacted isobutylene, C_2, C_3H_8, C_3H_6, C_4H_{10}, i-C_4H_{10}, butene-1, cis-butene-2, trans-butene-2, C_5. Liquid products are composed of aliphatic and aromatic hydrocarbons – benzene, toluene and meta-xylene. Based on this, it can be assumed that, in addition to oligomerization of isobutylene and intermediate products of its conversion, they undergo dehydrogenation, isomerization, cracking, dehydrocyclization, etc.

The formation of gaseous products begins at a temperature of 250°C, while the gas phase consists of hydrocarbons C_2, C_3H_8 and C_3H_6.

With increase in temperature the yield of gaseous hydrocarbons increases and in the temperature range of 400-450°C it is 53-55%. At the same time, iso- and n-butane, butene-1, cis- and trans-butene-2 were found in gaseous products. At temperatures of 400° - 450°C, in addition to the aforementioned gaseous products, C_5 hydrocarbons are also formed.

The effect of temperature on the yield of liquid products in the process of isobutylene conversion is shown in fig.3. The formation of liquid hydrocarbons begins at a temperature of 180°C, up to the temperature of the amount of C_5. With increase in temperature, the yield of gaseous products increases

To study the nature of seal products in the process of propylene conversion on H-HSZC, thermogravimetric and X-ray phase analysis of the coked catalyst was carried out. Figure 2 shows a differential thermal analysis of a coked catalyst during the conversion of propylene at 320°C for 10 hours. As can be seen, on the TG curve of the initial sample (fig.2, a), a gradual decrease in its mass is observed, and on the DTA line, a small endothermic effect is observed with a maximum at 130°C. The appearance of an endothermic effect on the DTA line can be associated with the removal of molecularly adsorbed water. A weak endothermic effect is observed on the DTA line in the temperature range 600-800°C, which is associated with the gradual dehydroxylation of the catalyst surface.

Table 1

Characterization of liquid propylene conversion products at 300°C

№	Indicators	Oligomerization products
1	Density at 20°C	0,7508
2	Fractional composition, % of boil off at oC	
3	Start of boiling	47
4	10%	62
5	20%	74
6	30%	85
7	40%	100
8	50%	110
9	60%	130
10	70%	140
11	80%	160
12	90%	200
13	End of boiling	238
14	Iodine number	120
15	Sulfur content	
16	Acidity, mg KOH/100 ml	0,1
17	Chemical composition of carbohydrates, mass %	
18	Unsaturated	56,5
19	Aromatic	5,7
20	Naphthenes	20,2
21	Paraphines	17,6

On the thermogram of the catalyst carbonized at 320°C during the conversion of propylene (fig.3), a stepwise decrease in mass is observed on the TG line, accompanied by an extensive exothermic effect with two maxima at 460 and 550°C. The presence of two maxima indicates that there are two different components in the compaction products differing in properties and chemical composition. In addition, this may indicate that during regeneration at temperatures above the temperatures of their formation, C/H undergo changes, leading to an increase in the C/H ratio in their composition.

X-ray phase analysis of the initial and coked at 400°C catalyst was carried out in order to determine the violation of the crystallinity of the zeolite framework during the process and the possibility of the formation of new crystal structures during the deposition of SP.

Comparison of the obtained diffraction patterns of the initial and coked catalyst showed that with the accumulation of compaction products on the catalyst surface, new crystal structures are not formed. Small changes in the intensity and insignificant displacement of some peaks may indicate an insignificant violation of crystallinity as a result of the accumulation of SP in the channels and cavities of the zeolite matrix.

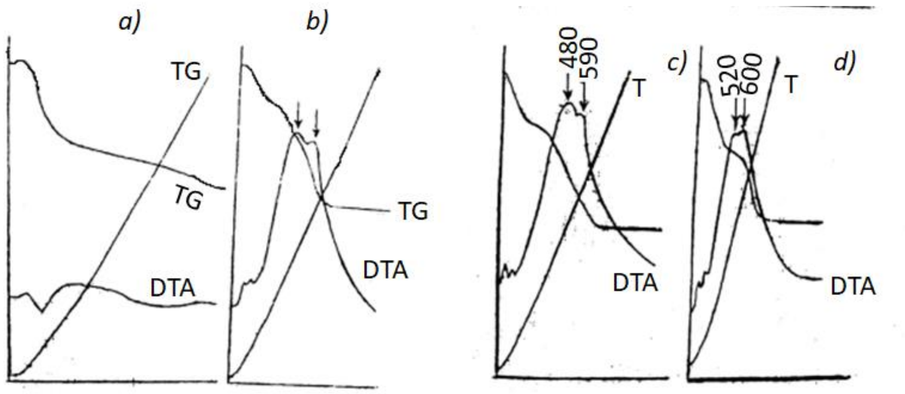

Fig.3. Differential thermal analysis of the initial (a) and carbonized H-HSZC catalyst in the process of the conversion of propylene (b) at 320°C and isobutylene at 350 and 400°C (c and d).

The data obtained show that during the conversion of propylene on a high-silica zeolite catalyst at temperatures of 250-450°C at the beginning of the process for 20-30 minutes, compaction products are deposited on the catalyst surface, and only after that the catalyst acquires high activity.

It should be noted that the isobutylene conversion process is similar in some characteristics to the propylene conversion process. The process of isobutylene conversion on H-HSZC was carried out at a temperature range of 150-450°C and various space velocities (300, 500, 1000 h^{-1}). At 200°C, the degree of conversion of isobutylene was 40.0; 38.4; 36.5% at volumetric velocities of 300, 500, 1000h^{-1}, respectively. With increasing temperature, the conversion of isobutylene increases and at 400° - 450°C reaches 98%. The products of isobutylene conversion at H-HSZC consist of gaseous, liquid and SP. Based on chromatographic and IR spectroscopic analyzes, it was found that gaseous products consist of unreacted isobutylene, C_2, C_3H_8, C_3H_6, C_4H_{10}, i-C_4H_{10}, butene-1, cis-butene-2, trans-butene-2, C_5. Liquid products are composed of aliphatic and aromatic hydrocarbons – benzene, toluene and meta-xylene. Based on this, it can be assumed that, in addition to oligomerization of isobutylene and intermediate products of its conversion, they undergo dehydrogenation, isomerization, cracking, dehydrocyclization, etc.

The formation of gaseous products begins at a temperature of 250°C, while the gas phase consists of hydrocarbons C_2, C_3H_8 and C_3H_6.With increase in temperature the yield of gaseous hydrocarbons increases and in the temperature range of 400-450°C it is 53-55%. At the same time, iso- and n-butane, butene-1, cis- and trans-butene-2 were found in gaseous products. At temperatures of 400 – 450°C, in addition to the aforementioned gaseous products, C_5 hydrocarbons are also formed.

The effect of temperature on the yield of liquid products in the process of isobutylene conversion is shown in fig.4. The formation of liquid hydrocarbons begins at a temperature of 180°C, up to 250°C, liquid products consist of isobutene dimers and trimers, the yield of which at 180-200°C is 33, 40%, respectively. An increase in the reaction temperature to 400°C leads to a decrease in the yield of oligomers, and aromatic hydrocarbons appear in the reaction products: benzene, toluene, and metaxylene. As can be seen, of the yield of liquid products on temperature is extreme.

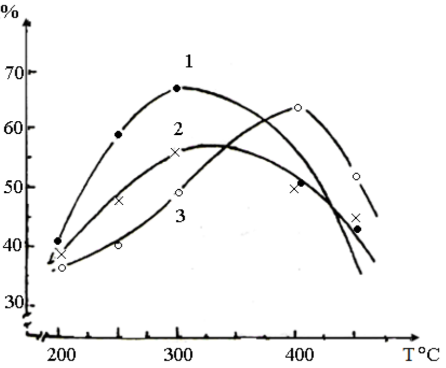

Fig.4. Dependence of the yield of liquid products on temperature at various volumetric velocities (1-300, 2-500, 3-1000 h^{-1})

Depending on the values of the volumetric velocity, the maximum yield of liquid products occurs at different temperatures. An increase in the space velocity leads to a shift in the maximum towards higher temperatures. An increase in temperature to 450°C leads to a decrease in the yield of liquid products, which is accompanied by an increase in the yield of gaseous products. A characteristic feature of this process is the fact that in the initial period the catalyst exhibits non-stationary activity. In the process of isobutylene conversion on H-HSZC, a high degree of isobutene conversion (90%) takes place during the first 10-30 minutes, however, there are no liquid hydrocarbons among the products of the process, hydrogen and a small amount of methane are contained in the gas phase. It was also found that in the initial period, coke-like compaction products are deposited on the catalyst surface. Figure (1; b) shows the dependence of the accumulation of compaction products on the catalyst surface, the yield of liquid products on time (curves 1, 2), and catalyst regeneration depending on the temperature (curve 3). As can be seen, within 20-30 minutes from the beginning of the process, SP accumulate on the catalyst surface, reach the maximum amount (7.6%) and do not change further, and only after that the formation of liquid products is observed.

The nature of the accumulated SP in the process of isobutylene conversion at H-HSZC was also studied by differential thermal analysis of coked at 350 and 400°C for 10 hours (fig.5). On the thermogram of the catalyst carbonized at 350°C, the mass loss on the TG curve has a stepwise character. The DTA curve shows an extensive exothermic effect with two maxima at 520° and 600°C. The presence of two maxima indicates that the SP contain at least two different components, differing in properties and chemical composition. This may indicate that, at relatively high temperatures, an increase in the C/H ratio in the composition of SP occurs. A similar picture is observed for samples coked at 350° and 400°C. In these cases, there is also an exothermic effect due to the combustion of SP with two maxima. With an increase in the temperature of SP deposition, the maximum on the DTA curves shifts towards higher temperatures. These results show that the temperature of SP formation affects not only their maximum amount, but also the physicochemical characteristics of SP.

As it is known, the conversion of hydrocarbons on zeolite catalysts occurs at acid sites [2, 4, 7]. Coke deposition is also associated with the presence of acid sites in the catalyst. Naturally, the accumulation of SP on acid sites can change both the number of acid sites and their strength. The effect of the degree of coke formation on the acidic properties of H-HSZC in the process of isobutylene conversion was studied by adsorption of ammonia at 20°C. It was found that the initial sample of H-HSZC adsorbs 8.5% of ammonia.

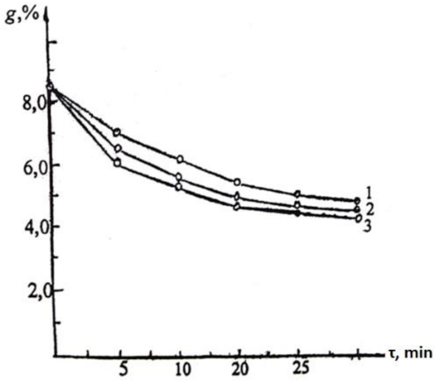

Fig.5. Dependence of the amount of adsorbed ammonia on the degree of coking of the H-HSZC in the process of isobutylene conversion at 300°C (1), 400 °C (2) and 450°C (3).

Figure 4 shows the dependences of the amount of adsorbed ammonia on the coking time of the catalyst at temperatures of 300°, 400°, and 450°C. As can be seen, with an increase in the coking time, the total catalyst of the samples decreases. This decrease is most noticeable during the first 10 minutes when the amount of NH_3 adsorption decreases from 8.5 to 6.3; 5.7; 5.2 respectively.

CONCLUSION

The results obtained show that the compaction products, being a by-product of the conversion of olefins, reduce the number of acid sites. In this case, the formation of liquid products during the conversion of propylene and isobutylene is observed only after the accumulation of 5.5-7.6% of the SP on the catalyst surface. As is known, the mechanism of conversion of olefins has been sufficiently studied, but it is appropriate to note that with the advent of new experimental and theoretical data, there is a need to revise the mechanism and kinetics of conversion of olefins on zeolite catalysts.

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ПРЕВРАЩЕНИЕ ПРОПИЛЕНА И ИЗОБУТИЛЕНА НА ВЫСОКОКРЕМНИСТНОМ ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ

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Как известно, за последнее десятилетие в связи с интенсивным ростом добычи нефти резко увеличилос количество газообразных углеводородов, выбрасываемых на нефтеперерабатывающих и нефтехимических заводах. В связи с этим актуальным вопросом является целенаправленная конверсия газообразных углеводородов в ценные интермедиаты на цеолитных катализаторах. В процессе конверсии газообразных углеводородов в зависимости от природы реагента и температуры на поверхности катализатора могут образовываться продукты уплотнения различного строения. Существуют разные мнения о влиянии продуктов уплотнения на активность катализатора. В одних случаях накопление ПУ на поверхности катализатора *отрицательно сказывается на его активности, а в других - наоборот. В работах, посвященных изучению олигомеризации и ароматизации олефинов C_2-C_4 на цеолитных катализаторах, вопрос образования ПУ практически не рассматривался.*

Ключевые слова: *изобутен, цеолит, продукты уплотнения,*

YÜKSƏK SİLİSİUMLU SEOLİT KATALİZATORU ÜZƏRİNDƏ PROPİLEN VƏ İZOBUTENİN ÇEVRİLMƏSİ

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Məlum olduğu kimi, son on ildə neft hasilatının intensiv artımı ilə əlaqədar neft emalı və neft-kimya zavodlarından atmosferə atılan qaz halında karbohidrogenlərin miqdarı da kəskin artmışdır. Ümumiyyətlə qaz halında olan karbohidrogenlərin seolit katalizatoru üzərində qiymətli sıxlaşma məhsullarının məqsədyönlü çevrilməsi actual məsələlərdən biridir. Qaz halında olan karbohidrogenlərin çevrilməsi zamanı reagentin xarakterindən və temperaturdan asılı olaraq katalizatorun səthində müxtəlif strukturların sıxlaşma məhsulları əmələ gələ bilər. Sıxlaşma məhsullarının katalizatorun aktivliyinə təsiri haqqında müxtəlif fikirlər mövcuddur. Bəzi hallarda İB-nin katalizator səthində toplanması onun aktivliyinə mənfi təsir göstərirsə, digərlərində isə əksinədir. Seolit katalizatorlarında C_2-C_4 olefinlərinin oliqomerləşməsi və aromatizasiyasının öyrənilməsinə həsr olunmuş tədqiqatlarda İB əmələ gəlməsi məsələsi praktiki olaraq nəzərdən keçirilməmişdir.

Açar sözlər: *izobuten, seolit, sıxlaşma məhsulları*

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STEAM CONVERSION OF ETHANOL TO HYDROGEN OVER CO-CE-O CATALYSTS

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In the offered article, the reaction of steam conversion of ethanol to hydrogen over binary cobalt-chromium oxide catalysts was explored. It had been found that at temperatures up to 400°C, ethanol is mainly converted into ethyl acetate. It is shown that with increasing reaction temperature, the yield of ethyl acetate passes through a maximum. At the high temperatures of the ethanol steam reforming reaction, the main reaction product is hydrogen. The peak yield of hydrogen is detected over the catalyst Co: Ce=1:9 at 650°C and is equal to 89.9%. It has been demonstrated that carbon monoxide and methane are by-products of the reaction of the steam conversion of ethanol into hydrogen.

Keywords: *Ethanol conversion, binary catalysts, cerium oxide, hydrogen, ethyl acetate.*

INTRODUCTION

As it is identified, hydrogen will be the leading type of fuel in the adjoining forthcoming. There are countless methods for producing hydrogen, namely coal gasification, steam reforming of various organic compounds, water electrolysis, etc. [1–3]. One of the promising methods for producing hydrogen is the reaction of steam reforming of ethanol on various catalytic systems [4, 5]. The steam reforming reaction of ethanol to hydrogen is interesting from both a sustainable development and an environmental point of view, as a result of the use of bioethanol as a feedstock, greenhouse gas emissions into the atmosphere are reduced.

It is determined from the periodic literature that various catalytic systems are used to carry out the reaction of steam reforming of ethanol into hydrogen [6–8]. According to our previous studies, binary catalysts based on cerium oxide with nickel oxide additives are highly active in the ethanol steam reforming reaction [9, 10]. In this regard, this work is devoted to the study of the effect of cobalt oxide on the activity of cerium oxide in the reaction of steam conversion of ethanol into hydrogen.

EXPERIMENTAL PART

Our researches were carried out on the “Chrom-5” Czech chromatograph. Selected gas chromatograph is a device for analyzing complex gaseous substances by differentiating them into mono-components. The components of the mixture are analyzed for qualitative and quantitative characteristics. Researches can be carried out using any physical and chemical methods. If the chromatograph failed to separate the sample into elements, then the substance is considered to be homogeneous. Gas chromatographs are an integral part of chromatography and are widely used in research activities of various profiles, from pharmaceuticals to the mining industry.

Binary cobalt–cerium oxide catalysts of various compositions were prepared by co-precipitation from aqueous solutions of cobalt nitrate and cerium nitrate. The resulting mixture was evaporated and dried at 100-120°C, decomposed to complete release of nitrogen oxides at 250°C, and then calcined at 700°C for 10 hours. Thus, 9 catalysts were synthesized with an atomic ratio of elements from Co: Ce=1:9 to Co: Ce=9:1.

The activity of the synthesized catalysts in the reaction of ethanol oxidation was researched on a flow unit at a space feed rate of 1800 h^{-1} in the temperature range of 200–700°C. 5 ml of the investigated catalyst with a grain size of 1.0–2.0 mm was loaded into a quartz reactor, and its activity in the ethanol steam reforming reaction was considered. The yields of ethanol conversion products, as well as the conversion of ethanol, were determined on a chromatograph with a flame ionization detector and a 3 m column filled with a specially treated sorbent Polysorb-1 s.

The yields of hydrogen, methane and carbon monoxide were determined on a chromatograph with a column 2 meters long filled with activated carbon. The amount of carbon dioxide formed was determined on a chromatograph with a 6-meter column filled with a brand sorbent «Celite» coated with Vaseline oil.

RESULTS AND DISCUSSIONS

Based on our laboratory studies of the steam conversion of ethanol to hydrogen, it was determined that the main products of the reaction are hydrogen and carbon monoxide. Methane, ethylene, acetaldehyde, carbon dioxide and ethyl acetate are also formed as by-products. Raising the reaction temperature above 400°C points to a change in the direction of the reaction towards the formation of hydrogen.

Figure 1 shows the results of studying the activity of the Co-Ce=1-9 sample in the reaction of steam conversion of ethanol into hydrogen. It can be seen that the conversion of ethanol in this sample begins at a temperature of 300°C. At this temperature, 10.7% hydrogen, 0.8% methane and 6.1% ethyl acetate are produced. With a further increase in the reaction temperature, the yield of hydrogen increases and its maximum value is 89.9% at a temperature of 650°C. With increasing temperature, the yield of ethyl acetate also increases, and at 400°C, the maximum yield of ethyl acetate is 38.1%. The output of carbon monoxide is observed starting from a temperature of 500°C, and its maximum yield is observed at a temperature equal to 700°C and is 22.8%.

Figure 1 also displays that the maximum yield of carbon dioxide is equal to 48.2%. The highest yield of methane on this sample is observed at a temperature of 550°C and is 12.3%. Figure 1 also demonstrates that the maximum conversion of ethanol already at a temperature of 550°C reaches 100%. Similar dependences are also observed for other binary cobalt–cerium oxide catalysts.

The conducted experiments also showed that the activity of the researched catalysts depends rather strongly on the component composition of the binary cobalt–cerium oxide catalysts.

In the table 1 is demonstrated the dependence of the activity of binary cobalt-cerium oxide catalysts of various compositions in the reaction of steam reforming of ethanol at 350°C on the atomic ratio of cobalt to cerium. We can see from table1 that, at low temperatures, ethyl acetate and hydrogen are the main products of the ethanol conversion reaction, and carbon oxides and methane are also formed as by-products. With an increase of the atomic ratio of cobalt to cerium, the yield of ethyl acetate passes through a maximum on the sample Co: Ce=4:6 (45.1%) and with a further increase in the content of cobalt in the catalyst composition drops to 24.9% on the sample Co: Ce=9:1.

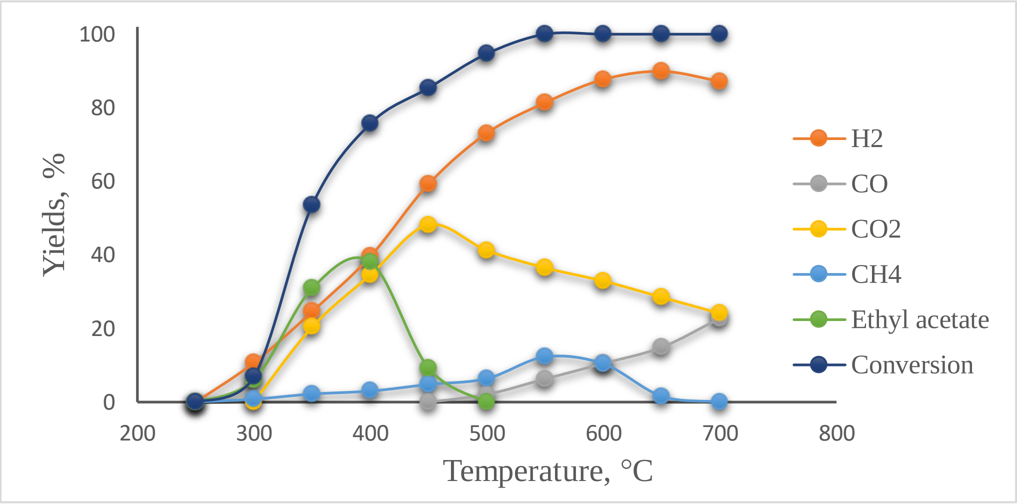

Fig.1. Effect of reaction temperature on the activity of the catalyst Co: Ce=1:9 in the reaction of steam reforming of ethanol.

The yield of hydrogen, with an increase in the content of cobalt in the composition of the catalyst, first decreases and then, starting from the sample Co: Ce=8:2, increases again. At 350°C, the yield of hydrogen does not exceed 24.6%.

Table 1

Reliance of the yields of ethanol steam reforming products over the atomic ratio Co/Ce. T = 350°C

Atomic ratio Co/Ce	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Reaction products	Yields of reaction products, %								
H_2	24,6	13,6	12,6	11,6	12,3	12,3	4,3	21,7	22,6
CO	0	0	1,9	2,1	1,7	1,5	1,2	2,4	2
CO_2	20,4	10,6	18,3	10,1	12,1	24,1	8,3	22,8	25,9
CH_4	2,2	0,6	1,1	1,1	0,5	0,7	0	0	0
Ethyl acetate	30,9	29,8	41,5	45,1	44,3	42,8	33,4	27,3	24,9
Conversion	53,5	41	62,3	58,4	58,6	69,1	42,9	58,6	52,8

Table 1 also demonstrates that the yield of methane at does not exceed more than 2.2% and decreases with an increase in the content of cobalt in the composition of the catalyst, while the yield of carbon monoxide slightly increases and also does not exceed more than 2.4%.

Other dependences of the yields of reaction products over the atomic ratio of cerium to cobalt are observed at temperatures above 500°C, when the direction of the ethanol conversion reaction changes towards the formation of hydrogen.

The upshots of revising the dependence over the binary cobalt–cerium oxide catalysts activity of various compositions during the reaction of steam reforming of ethanol at 650°C on the atomic ratio of cobalt to cerium are displayed in the table 2. It can be comprehended that with an increase in the cobalt content in the catalyst composition, the hydrogen yield diminutions from Co: Ce=1:9 to 44.9% on a Co: Ce=6:4 trial and then intensificated slightly.

In contradistinction to low temperatures at 650°C, the maximum yields of methane and carbon monoxide at do not exceed respectively 11.8 and 28.6%. It should also be distinguished that methane formation on catalysts with a high cobalt content is not observed over the entire temperature range studied. Table 2 is also illustrated that ethyl acetate is not formed on all the considered models at high temperatures. The conversion of ethanol at high temperatures on all the premeditated samples practically reaches 100%.

Table 2

Yields dependence of the ethanol steam reforming products over
the atomic ratio Co/Ce. T = 650°C

The atomic ratio of Co/Ce	1-9	2-8	3-7	4-6	5:5	6-4	7-3	8-2	9-1
Products of reaction	Yields of reaction products, %								
H_2	89,9	75,7	64,9	63,4	57	44,9	48,8	83,7	59,3
CO	14,9	28,6	1,9	2,4	1,6	1,8	6,6	2,4	4,7
CO_2	28,5	44,8	43,2	38,2	27,3	28,3	42,4	40,9	35,7
CH_4	1,6	5,8	4,3	3,1	10,9	11,8	0	0	0
Ethyl acetate	0	0	0	0	0	0	0	0	0
Conversion	100	100	100	100	100	100	100	91,2	90,3

CONCLUSION

1. At temperatures up to 400°C, ethanol is mainly converted to ethyl acetate, while at high temperatures of the ethanol steam reforming reaction, the main reaction product is hydrogen.
2. The highest yield of hydrogen is observed over the catalyst Co: Ce=1:9 at 650°C and it is equal to 89.9%.

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ПАРОВАЯ КОНВЕРСИЯ ЭТАНОЛА В ВОДОРОД НА CO-CE-O КАТАЛИЗАТОРАХ

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В представленной статье изучена реакция паровой конверсии этанола в водород на бинарных кобальт-церий оксидных катализаторах. Установлено, что при температурах до 400°C этанол в основном превращается в этилацетат. Показано, что с ростом температуры реакции выход этилацетата проходит через максимум. При высоких температурах реакции паровой конверсии этанола основным продуктом реакции является водород. Наибольший выход водорода на наблюдается на катализаторе. Co: сё=1:9 при 650°C и равен 89.9%. Показано, что побочными продуктами реакции паровой конверсии этанола в водород являются моноксид углерода и метан.

Ключевые слова*: Конверсия этанола, бинарные катализаторы, оксид церия, водород, этилацетат.*

CO-CE-O KATALIZATORLARININ ÜZƏRINDƏ ETANOLUN HIDROGENƏ BUXAR FAZALI KONVERSIYASI

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Təqdim olunan məqalədə etanolun binar kobalt-serium oksid katalizatorlarının üzərində buxar fazasının iştirakı ilə hidrogenə çevrilməsinin reaksiyası tədqiq edilmişdir. Müəyyən edilmişdir ki, 400°C-ə qədər olan temperaturda etanol əsasən etil asetata çevrilir. Göstərilmişdir ki, reaksiya temperaturunun artması ilə etil asetatın məhsulu maksimumdan keçir. Yüksək temperaturda etanolun buxar fazalı konversiya reaksiyasının əsas reaksiya məhsulu hidrogendir. Ən yüksək çıxım 650°C-də Co: Ce=1:9 katalizatorunda müşahidə edilir və 89,9%-ə bərabərdir. Etanolun hidrogenə buxar fazasına reaksiyasının yan məhsulu karbon monooksid və metan olduğu göstərilir.

Açar sözlər: *Etanolun çevrilməsi, binar katalizatorlar, serium oksidi, hidrogen, etil asetat.*

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BIOCOATING ON OIL AND GAS PLATFORMS – THE ROLE OF PERIPHYTON AND THE SOOLIGOMER – BASED COMPOSITE USED AGAINST CORROSION

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Periphyton, which forms a biological cover by accumulating a large number of organisms, develops in large quantities in the underwater parts of ships and hydraulic structures, causing serious damage to facilities, especially maritime. Thus, periphyton organisms, which choose the submarine part of the ship as a substrate, cause the surface of the ship to be eroded and the speed of the ship to decrease by up to 50%. Therefore, the article investigates the use of varnish-based coatings based on urea-modified resorcinol formaldehyde soligomers to protect marine equipment and facilities from corrosion. For comparison, parallel studies were performed for both modified and unmodified resorcinol-formaldehyde oligomers. One of the main reasons for using the modified resorcinol-formaldehyde oligomer as a mask is the increased resistance to oil and gasoline at high temperatures. The optimum temperature for the synthesis of urea-resorcinol-formaldehyde soligomer was determined as 70ºC. Below this temperature, the amount of target product decreases, and at higher temperatures, the amount of soluble fraction decreases as the production process progresses. Changing the amount of modifier affects the speed and output of the process. When the amount of final product at 70°C ranges from 0.01 to 0.05 moles of urea, the yield ranges from 65,18 to 80,27%. In this case, the productivity of the soluble fraction decreases, the amount of the insoluble fraction increases. A comparative analysis of the main parameters of the urea-resorcinol-formaldehyde soligomer with that of the resorcinol-formaldehyde oligomer shows that the molecular weight, hardness, viscosity, density and softening temperature of the soligomer increase when the optimal amount of urea is 0.03 mol.

Keywords: *periphyton, biological coating, modification, synthesis, oligomers, resorcinol-formaldehyde oligomer, urea, sooligomers.*

INTRODUCTION

The intensification of technological processes in the oil and gas extraction industry, the transportation of hydrocarbons over long distances, the increase in the volume of production equipment and facilities, etc. Considering the adverse effects of the factors, corrosion protection issues are even more important.

The crucial attention of researchers around the world, including in Azerbaijan, is focused on solving the problems of corrosion protection of equipment and devices made of metal. However, taking into account the known theoretical and practical principles of the corrosion process, it would be appropriate to change the working conditions of metal-made equipment and devices, to apply new methods to prevent corrosion, to synthesize corrosion protective compounds for known working conditions, and to examine corrosion resistance under these conditions. The protective properties of anti-corrosion coating compositions have been studied in marine and coastal areas where humidity is high. From the results of the research it was established that ordinary water is not considered a destructive medium, corrosion is observed only when the water contains a small amount of such salts. It is known from the literature that the corrosion rate in distilled water does not exceed 1.0 g/m^2 in 24 hours, and in a sample of this water in contact with air, the corrosion rate increases approximately 2.0-2.5 times.

Seawater, which contains various salts, occupies a special place in the corrosion of equipment and devices made of metal.

Seawater erodes equipment and installations made of X18H10T carbon steel faster and loses approximately 8 g/m^2 of mass in 24 hours. Corrosion in seawater is electrochemical in nature. Therefore, additional chemical processes can be observed during corrosion. Basically, a hydroxide layer forms on the corroded surface.

The general minerality and chemical composition of seawater has a direct destructive effect. At the same time, it is known that the corrosion rate increases approximately 2.5 times when the temperature rises from 8-10 ℃ to 27-28℃.

Considering the assembly, organization of production processes, transportation of oil and gas, maintenance and operation of equipment and facilities in the Caspian Sea production sites, the corrosion process in this region has always been in the focus of attention as the main problem.

Interest in this area is due to high humidity, temperature changes, the presence of a wet layer that remains on equipment and devices for a long time due to condensation, etc. are factors. Air humidity increases the corrosion rate, when the temperature of the atmosphere changes, the total humidity increases, evaporates and the contact time at the metal-water phase boundary is shortened. Significant amounts of Cl and SO_4 ions are also formed in this region, and these ions cause the formation of a mineralized water layer on the surface [6-8].

In order to protect equipment and installations from corrosion in specified environments, the aim of research work is mainly to improve functionality by modifying existing oligomers and to prepare anti-corrosion coating compositions by using them as binders.

Many factors (where the equipment or installation is operated, its size, structure, material, environmental cleanliness, indoor or outdoor operation, etc.) must be considered in preparing a protective coating composition [9-10]

EXPERIMENTAL PART

The main reagent in the synthesis of resorcinol - formaldehyde oligomer is resorcinol (m-dioxyphenol) and a 37% solution of formaldehyde in water (formalin). Urea was used as a modifier.

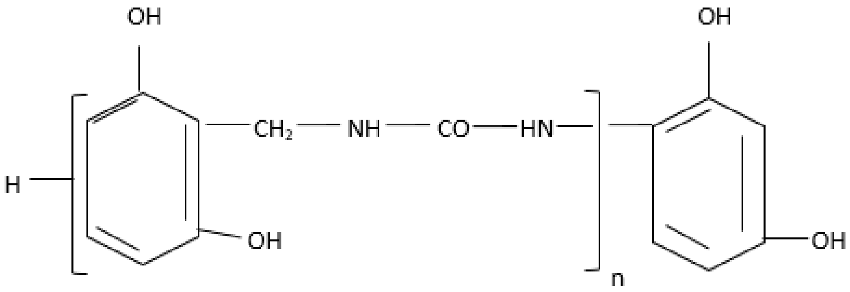
The synthesis of resorcinol-formaldehyde oligomer and resorcinol-formaldehyde sooligomer was carried out in a laboratory reactor. The first step is completed by obtaining a solid-liquid mixture at 70 ℃ for approximately one hour with continuous stirring of the reaction mass. In the second step, the reaction mass is poured from a three-necked flask into a porcelain vessel, paraformaldehyde and glycerine are added to solidify.

The main parametrs of the modified resorcinol-formaldehyde oligomer and the unmodified resorcinol-formaldehyde oligomer were examined (table 1). The solubility of the co-oligomer was tested in different solvents and it was determined that the best solvent for the co-oligomer was acetone [11-12]. The IR spectrum of the resorcinol-formaldehyde oligomer and the urea-modified resorcinol-formaldehyde sooligomer was investigated. The 1400-1740 cm^{-1} absorption band observed in the IR spectrum confirms the existence of CH_2-NH linkage. Observation of 3000-3400 cm^{-1} and 1240 cm^{-1} absorption bands in the IR spectrum of the sooligomer and functional groups such as -OH, -NH, respectively confirms its positive effect [13].

RESULTS AND DİSCUSSION

According to the results of physical-chemical and spectral analysis, it can be said that chemical modification occurs during the modification of resorcinol-formaldehyde oligomer with urea.

Based on the studies, the possible structure of the urea-modified sooligomer can be shown as follows:



where n = 3 – 5

The effective use of urea-modified resorcin-formaldehyde sooligomer, as well as its thermooxidative degradation under dynamic thermogravimetry conditions, were also studied for use as a binder in the preparation of an anti-corrosion coating composition. Thermogravimetric research was carried out in the Paulnik – Paulnik – Erdeil derivatograph system. Thermophysical parameters of modified resorcinol - formaldehyde sooligomer at 100 - 900 ℃ were also investigated [14].

The effective use of urea-modified resorcin-formaldehyde sooligomer, as well as its thermooxidative degradation under dynamic thermogravimetry conditions, were also studied for use as a binder in the preparation of an anti-corrosion coating composition.

Table 1

Main parameters of resorcinol-formaldehyde oligomer and urea-modified sooligomer

	Parameters	RFO	RFSO
1	Density, kq/m^3	1200	1260
2	Softening temperature ℃	80	95
3	Degree of solidification, %	96,8	98,7
4	Molecular mass	580	920
5	Adhesive strength, MPa	16	22
6	The amount of hydroxyl groups, %	18	15,8

Mass loss due to temperature (at 100°C) started at 3.272, 576.6 ^{0}C - 15% and 90°C - 75.651 %. The remaining mass was about 25%. The presence of amide and hydroxyl groups in modified resorcinol-formaldehyde solegomer based composites improves the main performance parameters. Thus, when the functionalized oligomer is used as a binder, a sharp difference is observed in the curing process of the composite (compared to the composite made on the basis of the unmodified oligomer). The presence of an additional amide group in the solegomer participates in the structuring process during the solidification process. The formation process of the network structure is explained by the degree of solidification, and the criterion of the degree of solidification is explained by the amount of the gel fraction. The amount of gel fraction in the modified resorcinol-formaldehyde solegomer was measured by the extraction method and calculated by the following formula:

$$F = \frac{G_{0-}\,G}{G_0} \times 100\%$$

where, F – gel – fraction amount in %, G0 – sample mass before extraction in q, G – sample mass after extraction.

Acetone was used as solvent in the extraction process. The optimal regime of the curing process, that is, the effect of temperature and curing time on the degree of curing was studied (fig.1).

To prepare the implicit compound against corrosya, the fully dried sooliqomer is dissolved in acetone at the temperature of the herb, then the calculated amount of filler is added, it is taken as a mass of 50 - 60 minutes.

From bauxite slurry as filler (Fe_2O_3 -48.75%, Al_2O_3 -75.56%, MgO - 5%, SiO_2 - 4.98%, CaO -1.32%, SO_3 - 1.166%, Na_2O + K_2O - 1%) ,26 and volatile substances – 11.72% content)) were used. Bauxite slurry is a waste of the alunite processing process, it is a red powder dispersed compound with a density of 3700 kg\m^3. The composition consists of a specified amount of oxides, which, if the amount of these oxides is sufficient and forms an adsorption relationship with the solegomer, leads to an increase in its resistance to corrosion and at the same time a decrease in cost.

The main parameters of the anti-corrosion coating composition based on urea-modified resorcinol-formaldehyde sooligomer were studied (tab.2).

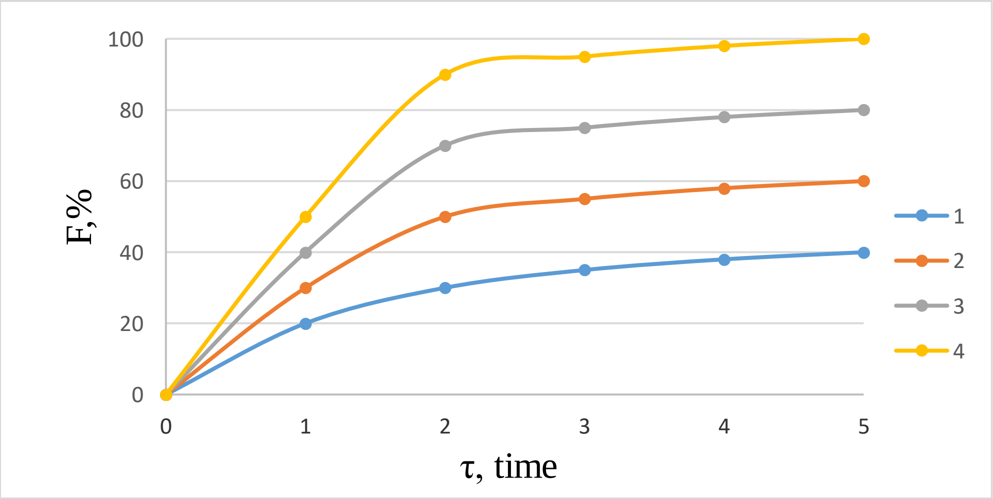


Fig.1. Time dependence of the amount of gel fraction at different temperatures

(1 - 120 °C; 2 - 130 °C; 3 -140 °C; 4 - 150 °C).

The coating composition is applied to the cleaned surface in two layers (50-55 µm each). Then the samples are hardened by thermal or chemical method.

Table 2

The main parameters of the coating composition based on urea-modified resorcinol-formaldehyde sooligomer

№	Indicators	RFO – i	RFSO - i
1	VZ – viscosity with device, C	58	68
2	Solidity, ş.v.	0,8	0,95
3	Adhesive strength, MPa	2,2	2,8
4	Resistance to alcohol, petrol and oil	Not variation	
5	Heat resistance, °C	180	210

The protective coating composition based on resorcinol-formaldehyde-urea sooligomer was tested in sea water for 12 months and positive results were obtained. The mass loss during the test was in the range of 0.012-0.028%.

For corrosion protection of equipment and devices operating in various environments, it is recommended to use a urea-modified resorcinol-formaldehyde sooligomer-based anti-corrosion coating composition.

CONCLUSİON

The protective coating composition based on resorcinol-formaldehyde-urea sooligomer was tested in sea water for 12 months and positive results were obtained. The mass loss during the test was in the range of 0.012-0.028%.

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БИОПОКРЫТИЕ НА НЕФТЕГАЗОВЫХ ПЛАТФОРМАХ - РОЛЬ ПЕРИФИТОНА И КОМПОЗИТА НА ОСНОВЕ СООЛИГОМЕРА, ПРИМЕНЯЕМОГО ПРОТИВ КОРРОЗИИ

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Перифитон, образующий биологический покров за счет скопления большого количества организмов в больших количествах развивается в подводных частях кораблей и гидротехнических сооружений, нанося серьезный ущерб сооружениям, особенно морским. Так, перифитонные организмы, избравшие в качестве субстрата подводную часть корабля, вызывают эрозию поверхности корабля и снижение скорости корабля до 50 %. Поэтому в статье исследуется применение лакокрасочных покрытий на основе мочевино-модифицированных солигомеров резорцинoформальдегида для защиты судового оборудования и сооружений от коррозии. Для сравнения были проведены параллельные исследования как для модифицированных, так и для немодифицированных резорцинoформальдегидных олигомеров. По результатам исследования установлено, что соолигомер, полученный в качестве связующего из модификации резорцинoформальдегидного олигомера, синтезированного по реакции поликонденсации, более пригоден для использования для получения экологически чистого композиционного материала. Сравнительный анализ основных параметров карбамидо-резорцинoформальдегидного солигомера с олигомером резорцинoформальдегида показывает, что молекулярная масса, твердость, вязкость, плотность и температура размягчения солигомера увеличиваются при оптимальном количестве мочевины 0,03 моль.

Ключевые слова: *перифитон, биопокрытие, модификация, синтез, олигомеры, резорцинoформальдегидный олигомер, мочевина, соолигомеры.*

NEFT – QAZ PLATFORMALARINDA BİOLOJİ ÖRTÜK – PERİFİTONUN VƏ ONUN ƏMƏLƏ GƏTİRDİYİ KORROZİYAYA QARŞI İSTİFADƏ OLUNAN SOOLİQOMER ƏSASLI KOMPOZİT

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Tərkibində çoxlu sayda canlılar toplamaqla bioloji örtük əmələ gətirən perifiton gəmilərin sualtı hissələrində, hidrotexniki qurğuların üzərində küllü miqdarda inkişaf etməklə qurğulara, xüsusilə gəmiçiliyə çox ciddi ziyan vurur. Belə ki, gəminin sualtı hissəsini özünə substrat seçən perifiton orqanizmləri gəmi səthinin korroziyaya uğramasına və gəminin hərəkət sürətinin 50%-ə qədər aşağı düşməsinə səbəb olur. Bu səbəbdən dəniz şəraitində istismar olunan avadanlıq və qurğuların korroziyadan qorunması məqsədi ilə karbamidlə modifikasiya olunmuş rezorsin-formaldehid sooliqomeri əsasında hazırlanan lak-boya örtüklərindən istifadə olunması istiqamətində tədqiqat işləri aparılmışdır. Müqayisə məqsədilə həm modifikasiya olunmuş sooliqomer, həm də modifikasiya olunmamış rezorsin-formaldehid oliqomeri ilə paralel olaraq tədqiqatlar aparılmışdır. Modifikasiya edilmiş rezorsin-formaldehid oliqomeri əsaslı kompozitdən qoruyucu örtük kimi istifadə edilməsinin əsas səbəblərindən biri yüksək temperaturda neft və benzinə qarşı müqavimətin artmasıdır. Karbamid-rezorsin-formaldehid sooliqomerinin sintezi üçün optimal temperatur 70 ℃ olduğu müəyyən edilmişdir. Bu temperaturdan aşağı temperaturarda məqsədli məhsulun məhsuldarlığı aşağı olur, daha yüksək temperaturlarda isə həll olunan fraksiyanın miqdarı azalır. Modifikatorun miqdarının dəyişdirilməsi prosesin sürətinə və çıxışına təsir edir. 70 ℃ - də hazır məhsulun çıxımı karbamidin mol miqdarı 0,01 ilə 0,05 mol arasında dəyişdikdə çıxım 65,18 - 80,27 % aralığında dəyişir. Bu zaman həll olunan fraksiyanın məhsuldarlığı azalır, həll olunmayan fraksiyanın miqdarı artır.

Karbamid-rezorsin-formaldehid sooliqomeri ilə rezorsin-formaldehid oliqomerinin əsas parametrlərinin müqayisəli təhlili göstərir ki, karbamidin optimal miqdarı 0,03 mol olduqda sooliqomerin molekul kütləsi, sərtliyi, özlülüyü, sıxlığı və yumşalma temperaturu artır.

Açar sözlər: *perifiton, bioloji örtük, modifikasiya, sintez, oliqomer, rezorsin,formaldehid, karbamid, sooliqomer, korroziya.*

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SYNTHESIS OF N_4, N_5-DI (N_1', N_1'-DIDODESOXYMETHYLAZON-N'-MONODODESOXYMETHYLAZONE) DIPHENYLCARBAZONE COMPOUND AND RESEARCH AS A CORROSION INHIBITOR

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On the basis of α- chlordecoxymethyl ether and chlorazone, the compound N_4*,* N_5*-di (*N_1*',* N_1*'-didodesoxymethylazon-N'-monododesoxymethylazone) diphenylcarbazone (comp. KB-4) containing 6 groups* $C_{12}H_{25}OCH_2$*, 16 nitrogen atoms, 6 groups* C_6H_5*, 4 azonyl groups. During the study, it was found that these new compounds have both economic and environmental high-performance inhibitory properties. Under laboratory conditions, the anti-corrosion inhibitory effectiveness of the KB-4 compound was determined. In the study of 0.20; 0.25; 0.5 mg/l concentrations of compound KB-4, its inhibitory efficiency was 99.96-100%. From an environmental and economic point of view, this compound is several times more effective than the inhibitors currently used in the oil and gas and petrochemical industries to protect steel process equipment in the most aggressive environments. Thus, the use of a new guanidine derivative compound KB-4 for corrosion protection of steel process equipment in the oil and gas and petrochemical industries can be considered scientifically substantiated.*

Keywords: *diphenylcarbazone, α- chlordecoxymethyl, ether, chlorazone, synthesis, research, inhibitor, corrosion.*

INTRODUCTION

As can be seen from the technical literature [3] and the results of our long-term studies [1,2,5-11], organic compounds containing nitrogen atoms, as well as a large number of functional groups, have highly effective inhibitory properties.

Previously, we synthesized diphenylcarbazone derivatives containing 9.12 nitrogen atoms, several $–CH_2OR$ ether and C_6H_5 – groups, as well as other functional groups. Even with an increase in the number of $–CH_2$ groups in these compounds, the inhibitory efficiency increased at the lowest concentrations.

From this point of view, we have synthesized a new derivative of diphenylcarbazone, unknown in the literature, based on α-chlorodecoxymethyl ether and chlorazone (compound KB-4), containing 16 nitrogen atoms, 6 $-CH_2OC_{12}H_{25}$ groups, 6 $-C_6H_5$ groups.

Synthesis of a new derivative of diphenylcarbazone (Comp. KB-4) was carried out in several stages. At the beginning, $C_{12}H_{25}OCH_2Cl$ and N1', N1'-didecoxymethylazone-N'-monodecoxychloroazone esters were synthesized. The composition and structure of the synthesized ethers were determined by known methods. At the last stage, by carrying out the reaction between the synthesized N_1', N_1'-didodecoxymethylazon-N'-monododecoxymethylchlorazone ether and diphenylcarbazone, its new derivative, unknown in the literature, N_4, N_5-di (N_1', N_1'-didodesoxymethylazon-N'-monododesoxymethylazone) diphenylcarbazone (Comp.KB-4) was obtained.

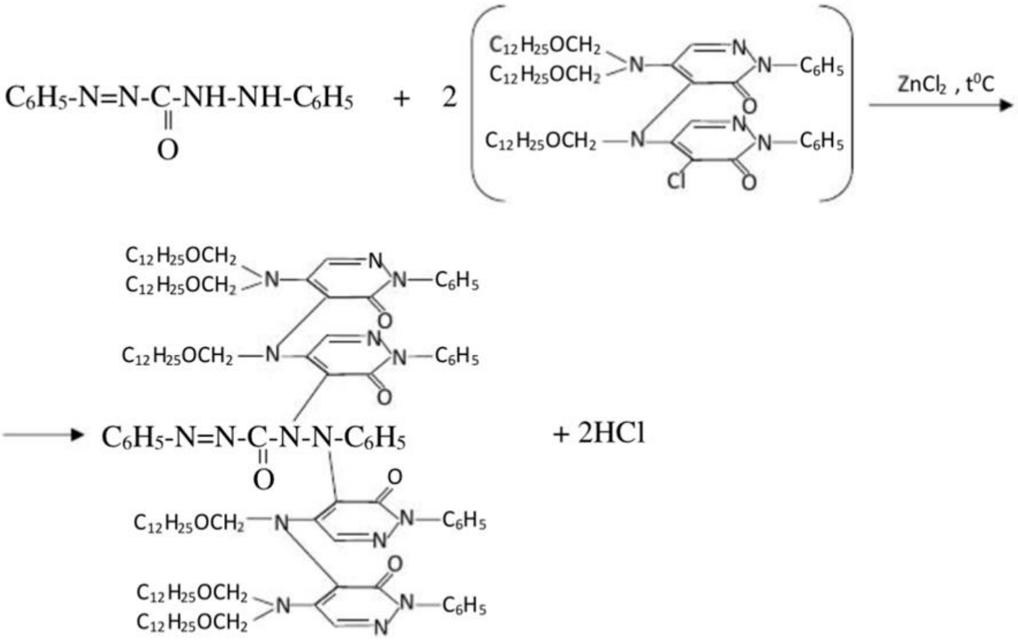

Fig. 1. Comp. KB-4.

EXPERIMENTAL PART

Synthesis of N_4, N_5-di N'-monododesoxymethylazone) diphenylcarbazone (Comp. KB-4). 2 g of $ZnCl_2$, (0.001 g-mol) of diphenylcarbazone are placed in a flask for synthesis and 50 ml of ethyl alcohol are added, heated to 70^0C with stirring until the diphenylcarbazone is completely dissolved. Then, (0.002 g-mol) N'_1, N'_1-didodecoxymethylazone-N'-monododecoxymethylchlorazone ester (0.002 g-mol) was added to the mixture gradually. Stirring is continued for 6 hours at the temperature of the condensation of the alcohol. After that, 100 ml of 10% NaOH solution is added to the reaction flask at room temperature, stirred for 0.5 h, 200 ml of distilled water are added. The organic layer is taken up in diethyl ether, dried over $CaCl_2$ after distillation of the ether. The residue is distilled in a vacuum plant to isolate N_4, N_5-di (N_1', N_1'-didodesoxymethylazon-N'-monododesoxymethylazone) diphenylcarbazone (comp. KB-4), which is a weak yellow viscous liquid with a sharp specific odor.

The compositions and structures of the synthesized compound KB-4 were established on the basis of elemental analysis, IR, mass and NMR spectra.

In the mass spectra of compound KB-4, it was determined that its molecular mass corresponds to molecular ions of 2000 m/e.

In the IR spectrum of this compound, they appear as an intense band of a simple ether group C-O-C 1050, 1080 cm^{-1}; bond C-N 1310-1350 cm^{-1}; CH_2 group 2950 cm^{-1}; CH_3 group 1380, 1400, 1460, 2990.3030 cm^{-1}; NH group 2910, 3113, 3340, 3360, 3400, 3450 cm^{-1}; belonging to the azone group C=C bond 1680 cm^{-1}; in the benzene ring C=C bond 1440-1465, 1500-1510, 1590-1600 cm^{-1}; C_6H_5 group 700-780 cm^{-1}.

In the NMR spectra of compound KB-4, singlets at 3.94-4.40 ppm and 4.75-5.55 ppm correspond to the protons of the methylene groups of the fragments > N-CH_2 - and > N -CH_2 - O, there are signals of the methylene groups of the ring (wide intense multiplet in the region of 1.41-1.82 ppm), the methyl group (triplet 0, 8-1.21 ppm), groups - CH_2O - (doublet 2.05 ppm). In the range of 6-8 ppm two doublets correspond to the signals of two nonequivalent m-protons of the benzene ring in the azonyl group, which confirms the structure of the synthesized compound KB-4.

Data on the yield, physicochemical constants, elemental analysis of the synthesized N_4,N_5-di(N_1',N_1'-didodesoxymethylazon-N'-monododesoxymethylazone)-diphenylcarbazone (compound KB-4) are presented in table 1.

Table 1

Elemental analysis, physicochemical properties, yield of synthesized new diphenylcarbazone derivative N_4,N_5-di(N_1',N_1'-didodesoxymethylazon-N'-monododesoxymethylazone)diphenylcarbazone (comp. KB-4)

Conditional connection number	Yield, %	T_{bor}°C (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found/ Calculated	Brutto Formula, Mol. Weight	Elemental analysis, % Calculated/ Found		
							C	H	N
Comp. KB-4	98,91	285-286 (2)	1,5097	1,8780	654,71 654,62	$C_{131}H_{196}N_{16}O_{11}$ 2168	72,51 72,34	9,04 8,86	8.12 7,91

The inhibitory efficacy of the synthesized new derivative of diphenylcarbazone, compound KB-4, was studied in highly [3% NaCl + oil (10:1) + H_2S 500 mg/l; 0.3 N HCl + gasoline (1:7) + H_2S 1000mg/l] aggressive media prepared under laboratory conditions by the “gravimetric” method, according to the methods indicated in the literature [1,2,4-11]. Studies have shown that the inhibitory effectiveness of compound KB-4, even at its lowest concentrations of 0.20; 0.25; 0.5 mg/l was 99.96-100%.

According to the studies, the KB-4 compound in its economic and environmental significance is 10 times higher than the results for inhibitors that have received patents and inventor's certificates over the past 10 years, as well as inhibitors used against corrosion in the oil and gas and petrochemical industries.

Based on the explanations of the results of our previous studies [5–11], as well as scientific and theoretical data obtained from the literature [12–24], the inhibitory efficacy of the new diphenylcarbazone derivative compound KB-4 can be substantiated as follows. The presence in the Comp. KB-4 32 double bonds, 16 nitrogen atoms, 6 -$CH_2OC_{12}H_{25}$ groups, 6 C_6H_5 groups, an increase in internal Van der Waals forces, as well as an increase in electron density in the composition of the compound, contributes to the formation of coordination bonds on the steel surface with this compound, which leads to to passivate the metal surface.

The results of our studies on the study of the inhibitory effectiveness of Comp. KB-4 are presented in table 2.

As can be seen from table 2, the synthesized new derivative of diphenylcarbazone Comp. KB-4 at a concentration of 0.25; 0.5; 1.0 mg/l has 99.96-100% inhibitory activity and exceeds in its qualities the [8] compound known in the literature, which received an author's certificate and conditionally called by us compound A, even at its high concentration.

As a result of the study, we can assume that the synthesis of a new derivative of diphenylcarbazone (comp. group KB-4) includes an inhibitor of formation in the oil and gas production, oil refining and petrochemical industries to protect steel process equipment from the release and release of significant, both economic and environmental efficiency.

As can be seen from the composition and structure of the new derivative of diphenylcarbazone (Comp. KB-4) can find their application as additives, biologically active substances, insecticides, flotation reagents, as well as in other areas.

Table 2

The results of the study of the inhibitory efficacy of a new derivative of diphenylcarbazone (comp. KB-4)

Reference number of the compound	Inhibitor concentration, mg/l	3% NACl + oil (10:1) + + H_2S 500 MG/L		0.1 N HCl + gasoline (1:7) + + H_2S 1000 MG/L	
		Corrosion rate, g/cm^2•h	Inhibitory efficiency, %	Corrosion rate, g/cm^2•h	Inhibitor efficiency, %
Without inhibitor		2,56		3,65	
Comp. KB-4	0,20 0,25 0,5	0,0006 0,0002 0,0001	99,97 99,99 100	0,0007 0,0001	99,96 100
A [10]	200		98,5		96

From the above, it follows that the synthesis of compounds of this type and their study in the synthesis of organic and petrochemicals can be assessed as very relevant.

RESULTS AND DISCUSSION

As can be seen from the information and explanations given in the above-mentioned literature, the effectiveness of corrosion inhibitors currently used in the oil-gas and petrochemical industry is not 100%.

The synthesis and research of new corrosion inhibitors of economic and environmental importance is one of the most urgent topics in preventing the corrosion of steel technological equipment, which is one of the main environmental problems in the oil-gas and petrochemical industries. For this purpose, a new derivative of diphenylcarbazone, N_4,N_5-di(N_1',N_1'-didodesoxymethylazon-N'-monododesoxymethyl-azone)diphenylcarbazone compound KB-4, which is high-quality, inexpensive and meets all the requirements of modern environmental safety, was synthesized by us for the first time and researched as a corrosion inhibitor.

This compound is several times superior to the inhibitors shown in the literature and used in the industry due to its hardness of use and 100% inhibitory property in a strong corrosion environment at high temperature (i.e. up to 200^{0}C).

CONCLUSION

Taking into account the environmental and economic effectiveness of the above-mentioned and synthesized the new derivative of diphenylcarbazone conditionally marked KB-4, to guarantee can use of this substance for corrosion protection of steel technological equipment under the high temperature and aggressive environments in the oil-gas and petrochemical industries.

Based on the scientific explanations given above about the inhibitory efficiency of the KB-4 compound, we consider it appropriate to use that compound for corrosion protection of the large-diameter pipe surface used in the transportation of gas and crude oil containing free H_2S gas.

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СИНТЕЗ СОЕДИНЕНИЯ N_4, N_5-ДИ (N_1’, N_1'-ДИДОДЕЦОКСИМЕТИЛАЗОН-N'-МОНОДОДЕЦОКСИМЕТИЛАЗОН) ДИФЕНИЛКАРБАЗОНА И ИССЛЕДОВАНИЕ В КАЧЕСТВЕ ИНГИБИТОРА КОРРОЗИИ

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На основе α-хлордецоксиметилового эфира и хлоразона получено соединения N_4,N_5-*ди*(N_1',N_1'-*дидодецоксиметилазон-N'-монододецоксиметилазон)дифенилкарбазон (соед.КБ-4), содержащее 6 групп* $C_{12}H_{25}OCH_2$, *16 атомов азота, 6 группы* C_6H_5, *4 азонильные группы. В ходе исследования было установлено, что эти новые соединения обладают как экономическими, так и экологическими высокоэффективными ингибирующими свойствами. В лабораторных условиях определяли антикоррозионную ингибирующую эффективность состава КБ-4. При исследовании 0,20; 0,25; 0,5 мг/л при концентрации соединения КБ-4 его ингибирующая эффективность составила 99,96-100%. С экологической и экономической точки зрения этот состав в несколько раз эффективнее ингибиторов, применяемых в настоящее время в нефтегазовой и нефтехимической промышленности для защиты сталеплавильного технологического оборудования в самых агрессивных средах. Таким образом, применение нового соединения производного гуанидина КБ-4 для защиты от коррозии стального технологического оборудования нефтегазовой и нефтехимической промышленности можно считать научно обоснованным.*

Ключевые слова: *дифенилкарбазон, α-хлордецоксиметил, эфир, хлоразон, синтез, исследование, ингибитор, коррозия.*

N_4, N_5-Dİ (N_1’, N_1'-DIDODESOKSİMETİLAZON-N'-MONODODESOKSİMETİLAZON) DİFENİLKARBAZON BİRLƏŞMƏSİNİN SİNTEZİ VƏ KORROZİYA İNHİBİTORU KİMİ TƏDQİQİ

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α- xlordesoksimetil efiri və xlorazon əsasında tərkibində 6 qrup $C_{12}H_{25}OCH_2$, *16 azot atomu, 6 qrup* C_6H_5, *4 azonil qrupu olan* N_4, N_5-*di* (N_1’, N_1'-*didodesoksimetilazon-N'-monododesoksimetilazon) difenilkarbazon (komp. KB-4) birləşməsi sintez olunmuşdur. Tədqiqat zamanı məlum olub ki, bu yeni birləşmələr həm iqtisadi, həm də ekoloji cəhətdən yüksək effektiv inhibitor xüsusiyyətlərinə malikdir. Laboratoriya şəraitində KB-4 birləşməsinin korroziyaya qarşı inhibitor effektivliyi müəyyən edilmişdir. Araşdırma nəticəsində müəyyən edilmişdir ki, KB-4 birləşməsinin 0,20; 0,25; 0,5 mq/l konsentrasiyalarında belə onun inhibitor effektivliyi 99,96-100% təşkil etmişdir. Ekoloji və iqtisadi nöqteyi-nəzərdən bu birləşmə ən aqressiv mühitlərdə polad texnoloji avadanlıqların qorunması üçün hazırda neft-qaz və neft-kimya sənayesində istifadə olunan inhibitorlardan bir neçə dəfə daha effektivdir. Beləliklə, neft-qaz və neft-kimya sənayesində polad texnoloji avadanlıqların korroziyadan mühafizəsi üçün quanidinin yeni törəməsi KB-4 birləşməsindən istifadə olunmasını elmi əsaslandırılmış hesab etmək olar.*

Açar sözlər: *difenilkarbazon, α-xlordesoksimetil, efir, xlorazon, sintez, tədqiqat, inhibitor, korroziya*

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ELIMINATION OF ENVIRONMENTAL POLLUTION CAUSED BY DIESEL TRUCKS IN KARABAKH REGION

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The demand for diesel fuel produced in the Republic of Azerbaijan is high, and reducing its impact on the environment is one of the topical issues. The purification of diesel fraction and its positive and negative aspects have been studied. Research has been conducted on low-energy external agents used to conduct processes in milder conditions. In order to obtain diesel fuel that meets the Euro standard indicators, polycyclic aromatic hydrocarbons were removed from the diesel fraction obtained from the primary processing of oil by using the extraction method. The extraction process was performed under the influence of a magnetic field. N-methylpyrrolidone and its mixture with various acids were used as an extractant in the research work. The amount of polycyclic aromatic hydrocarbons in the diesel fuel purified under the influence of the magnetic field was 6%, which meets Euro-5 diesel standards.

Keywords: *diesel fraction, polycyclic aromatic hydrocarbons, extraction method, magnetic field, N-methyl-pyrrolidone.*

INTRODUCTION

The quality indicators of diesel fuel produced in the Republic of Azerbaijan do not meet the latest EURO standards and therefore have harmful effect on the environment. Since various machinery, trucks, and vehicles used in the liberated areas run on diesel fuel, the cleaning of diesel fuel is one of the urgent issues for environmental protection.

Diesel fuel produced in the Republic of Azerbaijan is obtained from the primary processing of crude oil and by the hydrogenation method. If we look at the main products processed at the oil refinery in 2021, we will see that the main production focus is fuel for internal combustion engines. In 2021, from raw materials 1265.5 thousand tons of motor gasoline, 491.8 thousand tons of jet engine fuel, 2395.8 thousand tons of diesel fuel, and 269.9 thousand tons of liquefied gases were produced. As can be seen from here, the main direction of oil refining is the production of diesel fuel for users [1].

Smoke gases produced by the combustion of diesel fuel in cars have a harmful effect on the environment as well as on the human body. [2-3] found that polycyclic aromatic hydrocarbons (PAHs) contained in smoke gases due to incomplete combustion of fuels have a high carcinogenic effect on living organisms, and the easy collection of PAHs in different places results in their easy entry into the food chain. More than 100 PAHs exist in nature, and 16 of them are listed as major pollutants in Europe and the United States.

The amount of PAHs in soil samples at large truck stop located on the side of a major use highway was investigated in [4]. Soil samples taken from 0-15 cm and 15-30 cm depth were analyzed by gas chromatography/mass spectrometric analysis and PAH content was between 16.4-32.0 mg/kg and 18.6-26.6 mg/kg, respectively. The concentration of PAHs obtained here exceeded the limit of permissible concentrations determined for soils in most developed countries of the world.

In order to comply with environmental requirements, it is required to control the amount of sulfur and aromatic hydrocarbons in the produced fuels. Therefore, fuel purification is one of the topical issues. The purification of aromatic hydrocarbons from the diesel fraction is one of the serious problems. In [5], a crude sample containing 20.1% aromatic hydrocarbons and 166 ppm sulfur was purified by extraction process using acetonitrile as a solvent. The process was carried out at low temperature and atmospheric pressure. After purification, the amount of aromatic hydrocarbons was 7.2%, and the amount of sulfur was 73.2 ppm.

In order to obtain high-quality low-viscosity diesel fuel, a hydrocracking process was carried out in the presence of a zeolite catalyst based on nickel oxides and molybdenum oxides. The process was carried out at a temperature of 340–380°C, a pressure of 15–18 MPa, and hydrogen recirculation [6].

Purification of motor fuels with selective solvents was carried out by the extraction method. Distillates of motor fuels were purified from aromatic and sulfur compounds and resins with organic solvents and ionic liquids. The advantage of the extraction method over the hydrogenation method was shown [7].

In [8], the purification of PAH was carried out by a one-step extraction method from petroleum residues purified from asphalt with a mixture of N-methylpyrrolidone with 10, 15 and 20% wt. ethylene glycol. A total of eight types of carcinogenic PAHs were purified from a feedstock consisting of a heavy vacuum gasoil mixture with a asphalt-refined petroleum residue, using a four-stage countercurrent extraction method using a mixture of N-methylpyrrolidone and 10% mass ethylene glycol. The extraction process was performed at a ratio of 2:1 and a temperature of 45°C. After extraction, the amount of PAH in the raffinate was reduced from 37.9 mg/kg to 0.4 mg/kg.

Purification of aromatic hydrocarbons and sulfur from diesel fuel obtained primary processing of crude oil was studied [9]. Extraction method was used for this purpose and dimethylformamide chosen as an extractant Studies were conducted on different ratios of extractant and raw materials, and the best result was obtained at a ratio of 3:1. At this time, when carrying out a 2-stage extraction process, a decrease in the amount of aromatic hydrocarbons by 5 times and a decrease in the amount of sulfur from 2% to 0.33% were observed.

EXPERIMENTAL PART

As a result of studies [10,11], it was determined that technological processes are carried out in lighter conditions by using external influences that require less energy (electric field, electromagnetic field, magnetic field, ultrasonic field, acoustic field, vibration field). One of the effective, economically profitable and easy-to-use means of external influence is the energy of the magnetic field [12]. Currently, the energy of the magnetic field is widely used in scientific research and normal life. Special equipment (magnetron, magnet activator) is used to create the magnetic field [13].

The catalytic cracking process of vacuum gas oil and its mixture with cottonseed oil under the influence of a magnetic field was studied [14]. It was determined that when using a magnetic field, the productivity of diesel fractions increases by 19.7-25% mass in the process of catalytic cracking of vacuum gas oil and its mixture with 5%

cottonseed oil at a temperature of 500 °C.

As mentioned above, one of the non-traditional methods for cleaning raw materials from unwanted impurities is the use of a magnetic field. In our studies before investigating the effect of the magnetic field, studies were conducted in the direction of determining the optimal parameters of the purification process of diesel fuel from polycyclic aromatic hydrocarbons by using N-methylpyrrolidone as an extractant [15-17]. For this purpose, the scheme of the device on which we conducted the research is shown in fig.1.

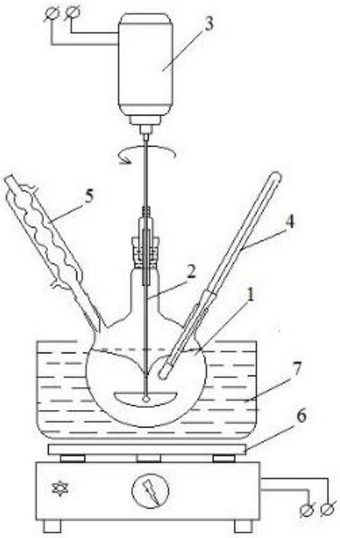

Fig.1. Extraction device.

1-three-necked round-bottom flask, 2- glass stirrer, 3- electric motor, 4- thermometer, 5- countercooler, 6- heater, 7- water bath.

Table 1

The characteristics of the diesel fraction

№	Indicators	Values
1	Density, at 20°C, kg/m^3	0.8450
2	Total amount of sulfur, % (wt.)	0.0895
3	Kinematic viscosity, mm^2/s	6.2
4	Freezing temperature, °C	-36
5	Turbidity temperature, °C	-25
6	Flash point, °C	72
7	Iodine number	1.83
8	Acidity	57.7
9	Aromatic hydrocarbons, % (wt.)	18.08
10	Actual resin, % (wt.)	3.4
11	Fractional composition, % (wt.)	
	Begining of boiling, °C	222
	50% boils , °C	296
	96% boils , °C	357
	End of boiling, °C	367
12	Residue	3.8

Researches were carried out under the influence of magnetic field by using N-methylpyrrolidone as an extractant to remove polycyclic aromatic hydrocarbons from the diesel fraction obtained from primary oil processing.

The characteristics of the diesel fraction used in the experiment is given in table 1.

IR spectra of the diesel fraction were determined on the "BRUKER Research Spectrometers" device, and the number of aromatic hydrocarbons was determined by sulfation and iodine number method.

RESULTS AND DISCUSSION

The results of studies conducted to determine the optimal values of the parameters that affect the process (raw material-extractant ratio, temperature, number of mixer cycles) are shown in the following figures 2,3,4.

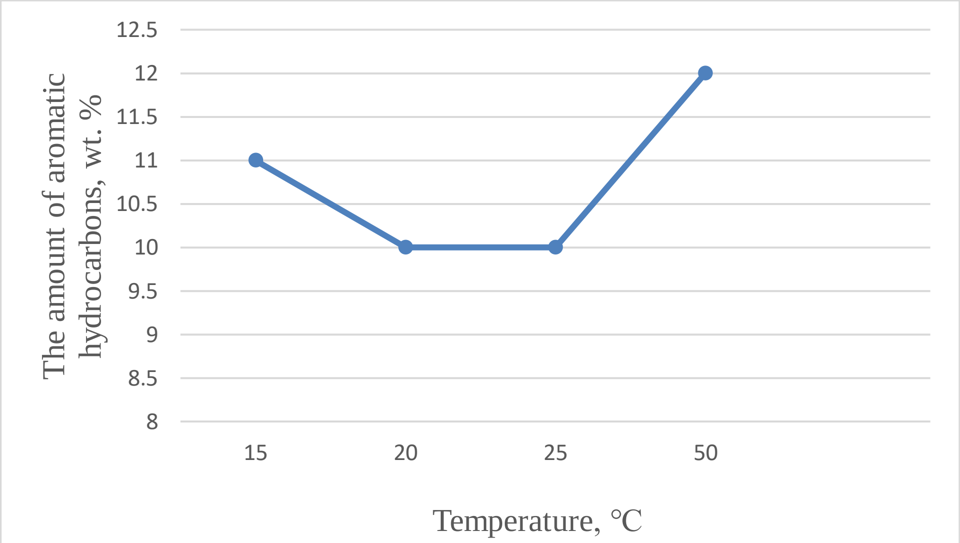

Fig. 2. Effect of temperature on the extraction process.

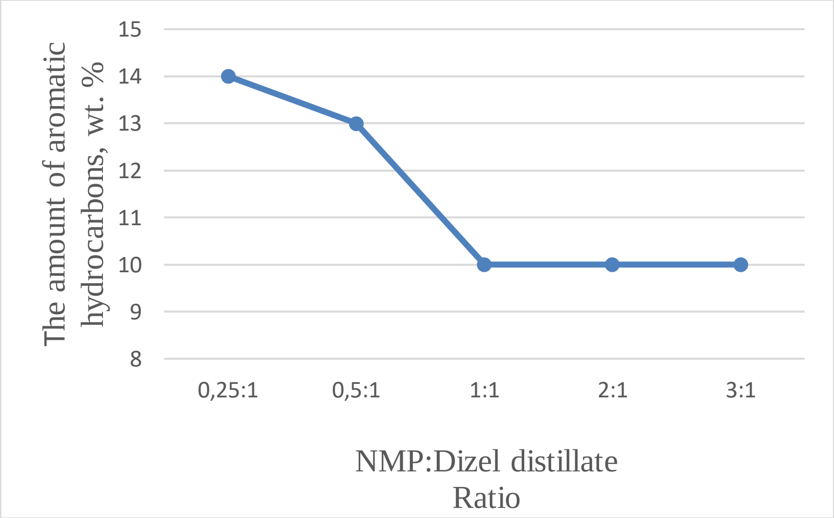

Fig.3. Influence of the raw material-extractant ratio on the extraction process.

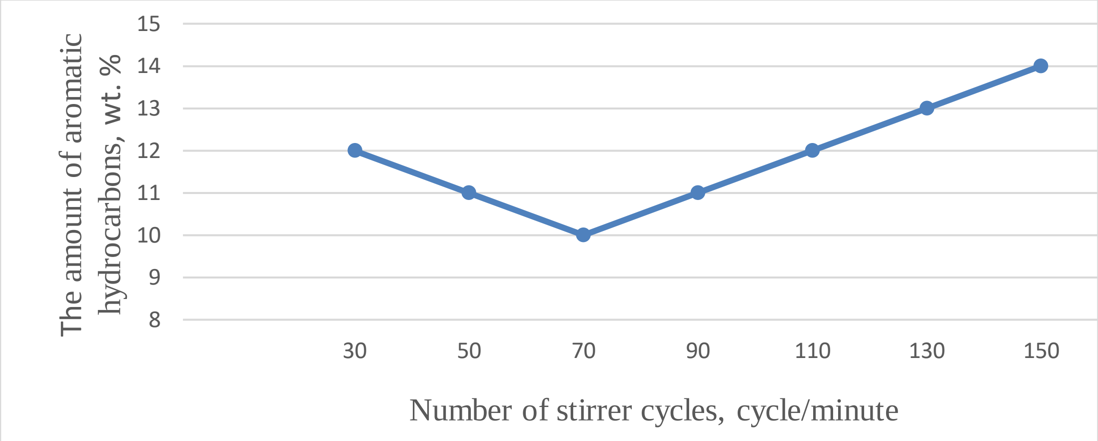

Fig.4. Influence of the number of stirrer cycles on the extraction process.

As can be seen from the graphs, the optimal parameters of the extraction process are as follows:

- Diesel fraction: N-methylpyrrolidone - 1:1
- Temperature - 25^{0}C
- The number of cycles of the mixer - 70 rpm.

Then experiments were carried out at different values of the intensity of the magnetic field affecting the process. The results of the research are given in table 2.

As can be seen from the table, a high degree of purification corresponds to a magnetic field strength of 20 mT. At the optimum value, the amount of polycyclic aromatic hydrocarbons is 6% (mass.), which corresponds to the Euro-5 standard.

When a magnetic field is introduced into the system, a new layer is formed, which is different from the layer formed by the components of the diesel fraction, which ensures the penetration of the solvent into all layers. These changes ensure the selective distribution of the components between the phases and their dissolution by N-methylpyrrolidone.

Table 2

Effect of magnetic field on the extraction process

Magnetic field intensity, mT	Amount of aromatic hydrocarbons, % (wt.)	Sulfur content, % (wt.)
0	10	0,075
5	10	0,075
10	9	0,051
15	7	0,037
20	6	0,032
25	7	0,032
30	7	0,032
35	8	0,034
40	7	0,035
45	7	0,035
50	7	0,035

CONCLUSION

Under the influence of a magnetic field, the amount of aromatic hydrocarbons in diesel fuel decreases from 18.08% to 6%.

The optimal process parameters are determined as follows:

- Diesel fraction: N-methylpyrrolidone - 1:1
- Temperature - 25^0C
- The number of cycles of the mixer - 70 rpm.

As a result of the influence of the magnetic field on the process, a new structure is formed, which is characterized by high homogeneity, regularity, and low viscosity. As a result, molecular, convective diffusion is reduced, which means that interfacial distribution of components occurs, and the necessary hydrocarbons are separated through solvents.

As a result of the research, it was identified that the amount of aromatic hydrocarbons in the diesel fraction obtained during the primary processing of oil after extraction under the influence of a magnetic field complies with the EURO-5 standard.

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УСТРАНЕНИЕ ВРЕДА ОКРУЖАЮЩЕЙ СРЕДЕ ОТ ДИЗЕЛЬНЫХ АВТОМОБИЛЕЙ В КАРАБАХСКОЙ ОБЛАСТИ

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Спрос на дизельное топливо, производимое в Азербайджанской Республике, высок, и снижение его воздействия на окружающую среду является одним из актуальных вопросов. Изучены процессы очистки дизельной фракции, их положительные и отрицательные стороны. Проведены исследования низкоэнергетических внешних агентов, используемых для ведения процессов в более мягких условиях. Для получения дизельного топлива, соответствующего показателям Евростандарта, из дизельной фракции, полученной при первичной переработке нефти, методом экстракции были удалены полициклические ароматические углеводороды. Процесс экстракции *осуществлялся под воздействием магнитного поля. В качестве экстрагента в работе использовали N-метилпирролидон и его смесь с различными кислотами. Количество полициклических ароматических углеводородов в дизельном топливе, очищенном под действием магнитного поля, составило 6 %, что соответствует нормам дизельного топлива Евро-5.*

Ключевые слова: *дизельная фракция, полициклические ароматические углеводороды, метод экстракции, магнитное поле, N-метилпирролидон.*

QARABAĞ BÖLGƏSİNDƏ DİZEL YANACAĞI İLƏ İŞLƏYƏN YÜK MAŞINLARININ ƏTRAF MÜHİTƏ VURDUĞU ZİYANIN ARADAN QALDIRILMASI

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Azərbaycan Respublikasında istehsal olunan dizel yanacaqlarına olan tələbat yüksəkdir və onun ətraf mühitə olan təsirinin azaldılması aktual məsələlərdən biridir. Dizel fraksiyasının təmizlənməsi və onların müsbət və mənfi cəhətləri tədqiq olunmuşdur. Prosesləri daha yüngül şəraitdə aparmaq üçün istifadə olunan az enerji tələb edən xarici təsir vasitələri haqqında tədqiqatlar aparılmışdır. Avro standartı göstəricilərinə cavab verən dizel yanacağını alınması üçün neftin ilkin emalından alınan dizel fraksiyasının ekstraksiya üsulu ilə politsiklik aromatik karbohidrogenlərdən təmizlənməsi prosesi aparılmışdır. Ekstraksiya prosesi maqnit sahəsinin təsiri altında yerinə yetirilmişdir. Tədqiqat işində ekstragent kimi N-metilpirrolidondan və onun müxtəlif turşularla qarışığından istifadə edilmişdir. Maqnit sahəsinin təsiri altında təmizlənmiş dizel yanacağında politsiklik aromatik karbohidrogenlərin miqdarı 8% olmuşdur ki, bu da Avro-5 dizel standartlarına cavab verir.

Açar sözlər: *Dizel fraksiyası, aromatik karbohidrogenlər, ekstraksiya üsulu, maqnit sahəsi, N-metilpirrolidon.*

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STUDY OF THE INTENSIFICATION OF THE DEAPHALTIZATION AND CATALYTIC CRACKING PROCESSES IN A MAGNETIC FIELD

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The deasphalting process of the vacuum residue has been studied in the magnetic field in order to odtain the suitable DAO for mixing with the vacuum gas oil for the subsequent catalytic cracking process conducted in a constant magnetic field.

The probable mechanism of action of a magnetic field on the de-asphalting process has been studied. The study examined the catalytic cracking of a mixture of vacuum gas oil and tar deasphalted oil products in the presence of a magnetic field, and found that the findings could serve as a foundation for producing high-quality gasolines with high octane ratings. The quality of the deasphalted oil obtained was found to be impacted by a range of factors, including the process temperature, settling time, and solvent-to-raw material ratio. Taking these variables into account, the study evaluated the effect of magnetic treatment on the raw materials during the deasphalting process, and identified the optimal conditions for achieving the desired results. The researchers also explored the impact of magnetic treatment on the settling time and discovered that it accelerated the settling process. In addition, the explanation of the mechanism of action of a costant magnetic field on the process of catalytic cracking in terms of singlet-triplet state of ions and radicals has been given.

Keywords: *deasphaltization, catalytic cracking, deasphaltization temperature, magnetic treatment of raw materials, asphalt-resin substances.*

INTRODUCTION

At present, extensive research is being carried out to develop a technology for increasing the yield of motor fuels by involving heavy oil residues in the process. It has long been known that a magnetic field affects the yield and ratio of products of some chemical reactions and processes. The results of the study of catalytic cracking of a mixture of vacuum gas oil with tar deasphalted oil products in a magnetic field can be used as the basis for obtaining high-octane gasolines. From this point of view, of great interest is the use of preliminary magnetic treatment of tar in the deasphaltization process [1].

In the composition of the tar after the vacuum distillation of fuel oil, in addition to a certain number of oils, there are also compounds that exhibit high surface activity, which, as is known, activate the catalytic cracking process. Therefore, if the tar is subjected to deasphaltization and the main part of the asphalt-resin substances with high coking capacity, as well as containing the main part of organometallic compounds, which are strong poisons for the catalyst, is removed from its composition, then it is possible to investigate the cracking of a mixture of this deasphalted oil with vacuum gas oil.

The quality of the resulting deasphalted oil depends on various factors such as process temperature, settling time, solvent: raw material ratio, etc. considering all these factors, the effect of magnetic treatment of raw materials on the deasphaltization process was studied and the optimal conditions for this process were identified. It should be noted that pentane, hexane and gasoline were used as a solvent, which began to boil at 80°C and did not contain aromatic hydrocarbons. For deasphalted products obtained at various solvent: raw material ratios: 2:1, 3:1, 4:1, 5:1, the physical and chemical properties were studied and the patterns of changes in their properties with changing ratios of the tar solvent were established. Temperature is one of the most important factors influencing the deasphaltization process.

The solvents we have chosen are non-polar solvents, and therefore, at ordinary temperatures, they are mixed with the liquid components of the raw material in almost all proportions, and the solubility of solid components in them obeys the general theory of the solubility of solids in liquids. With increasing temperature, the solubility of substances in such solvents decreases. The deasphaltization process is based on this.

Figure 1 shows the change curves dependence of the deasphalted oil yield on temperature. As can be seen from these curves, with magnetic treatment of tar, as well as without it, the optimum temperature is 160°C at which the yield of pentane deasphalted oil is 59%mass, hexane 68% mass, and gasoline 72%mass. A further increase does not have a significant effect on the deasphaltization process and only leads to an increase in energy consumption.

EXPERIMENTAL PART

The influence of magnetic treatment of raw materials on the settling time was also investigated. The results showed that magnetic pre-treatment accelerates the settling process.

Based on the foregoing, the effect of magnetic treatment of raw materials on the deasphaltization process can be explained as follows. As you know, all substances according to their magnetic properties can be divided into several groups, such as diamagnets, paramagnets and ferromagnets.

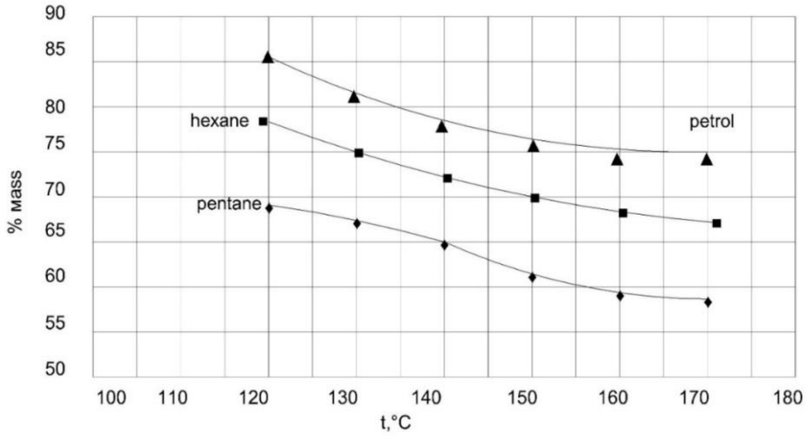

Fig.1. Dependence of the amount of deasphalted oil yield on the deasphaltization temperature with magnetic treatment and at ratio of solvent: raw material 4:1.

Oil belongs to diamagnets, that is, when such substances are placed in a magnetic field, the electron shells of atoms and molecules begin to process in it as a whole, while the system acquires magnetization for some time opposite to the vector of the external magnetic field [2]. The heavier the oil, the greater its magnetic susceptibility. Asphalt-resin substances are one of the heaviest components of oil and, in addition, contain almost all organometallic compounds, which are the most magnetically susceptible during magnetic treatment. When dissolved in solvents, these magnetized particles are the centers of coagulation and, as a result, the formed undissolved coagulates are rapidly precipitated. This can explain the improvement in the quality of the deasphalted oil during the magnetic treatment of tar.

The experiments were carried out under normal conditions and with preliminary treatment of the tar with a magnetic field. The results of studies of the properties of the obtained tar deasphalted oil products are presented in tables 1 and 2.

As can be seen from table 1, regardless of which solvent was used, the optimal ratio can be considered 4:1. In addition, an increase in the solvent: raw material ratio leads to an increase in the cost of its regeneration from extract and raffinate solutions. Thus, the conducted studies show that the most optimal in terms of the quality of the obtained deasphalted oil, as well as from an economic point of view, is the ratio of solvent:tar 4:1.

Table 1

Physical and chemical characteristics of deasphalted oil products obtained at different ratios of solvent: raw material at 160°C without magnetic treatment of tar

Indicators	Deasphaltizat											
	pentane				hexane				petrol			
	2:1	3:1	4:1	5:1	2:1	3:1	4:1	5:1	2:1	3:1	4:1	5:1
Yield, %mass	69	62	59	58	78	72	68	67	84	77	72	70
Density, g/cm^3	0.8899	0.886	0.8835	0.883	0.8965	0.893	0.8095	0.8898	0.908	0.9015	0.8925	0.8905
Sulfur content, %mass	1.18	1.09	1.06	1.05	1.19	1.15	1.09	1.08	2	1.5	1.19	1.08
Viscosity at 100°C, mm^2/s	112	108	105	103	112	110	108	107	120	114	111	110
Coking, %mass	7.5	7	6.4	7.9	7.3	6.8	6.5	8.4	7.9	6.9	6.9	6.6
Resin content 96, mass	5.5	4.2	3.2	2.95	5.9	4.55	3.4	3.2	9.5	7.9	4.6	3.9
Asphaltenes, % mass	1	0.7	0.3	0.28	1.3	0.9	0.35	0.33	1.6	1	0.4	0.38

The process of magnetic treatment of tar deasphalted oil products and their physical and mechanical properties were studied, and the optimal conditions for the deasphaltization process were determined.

It is shown that the deasphalted oil products obtained after preliminary magnetic treatment can be used as an additive to the catalytic cracking raw material – vacuum gas oil. To study the effect of a magnetic field on the deasphaltization process, experiments were carried out at various solvent: raw material ratios, at 160°C, and at a magnetic induction flux of 1.4.

As can be seen from table 2, the deasphaltization process indicators improve with the preliminary treatment of tar with a magnetic field. So, the content of resins at a ratio of solvent:raw material: 4:1, in the case of pentane deasphalted oil, decreases from

3.2%mass to 3.0%mass, the content of asphaltenes is from 0.3 to 0.26%mass, coking from 6.4 to 6.0%mass, the change in viscosity is insignificant from 105 to 104 mm^2/sec., the sulfur content decreases from 1.06 to 1.04%mass.

Table 2

Physical and chemical characteristics of deasphalted oil products obtained at different solvent: raw material ratios at 160°C with magnetic treatment of tar

Indicators	Deasphaltizat											
	pentane				hexane				petrol			
	2:1	3:1	4:1	5:1	2:1	3:1	4:1	5:1	2:1	3:1	4:1	5:1
Yield, %mass	64	60	55	53	70	67	59	55	77	70	63	60
Density, g/cm^3	0.8899	0.885	0.8825	0.8825	0.896	0.893	0.89	0.8995	0.91	0.903	0.8915	0.89
Sulfur content, %mass	1.19	1.09	1.04	1.02	1.18	1.1	1.07	1.06	2	1.4	1.12	1.05
Viscosity at 100°C, mm^2/s		107	104	102	112	110	107	106	118	112	120	108
Coking, %mass	6.3	6.1	6	5.9	6.6	6.4	6.3	6.2	7.3	6.7	6.4	63
Resin content 96, mass	4.3	3.8	3	2.8	4.6	4.1	3.2	3.1	8.3	6.5	4	3.7
Asphaltenes, % mass	0.8	0.6	0.26	0.25	1.2	0.7	0.3	0.28	1.5	0.8	0.32	0.31

Tar deasphalted oil products contain in their composition mainly compounds exhibiting high surface activity. Many researchers have proven that additives with surface-active properties activate the process of catalytic cracking [3, 4, 5].

This can be explained from the point of view of controlled phase transitions by prof. Sunyaev Z.I. The essence of this theory lies in the control of physical transformations with the help of activating additives. According to this theory, with the help of such additives, it is possible to influence the physical transformations of the components of petroleum raw materials during catalytic processes (fig.2). These transformations include:

the formation and coexistence of oil dispersed systems such as liquid emulsion and foam at temperatures of the catalytic process;

the influence of the obtained oil dispersed systems properties on the final results of the process;

establishment of adsorption-desorption equilibrium between initial and final reaction products in adsorption layers on the surface of solid catalysts in heterogeneous catalysis.

Schematically, the adsorption-desorption of complex structural units (as in the terminology of the theory-controlled phase transitions are called gas bubbles with hydrocarbons adsorbed on it) can be depicted as shown in fig.2.

Based on this scheme, the probable mechanism of action of the deasphalted oil can be explained as follows: During the cracking of pure gas oil, gas bubbles form on the surface of the liquid phase, which then pass into the interfacial layer and rise. At the same time, they increase in size, collapse, form again, and collapse again, exchanging their contents with the liquid phase. As a result of this, the formed heavy molecules of the compaction reaction are deposited on the surface of the solid wall, the pores are coked. If there are surfactants in the composition of the raw material, which are in large quantities included in the composition of the deasphalted oil, they are adsorbed on the interfacial surface bubble-continuous phase, as a result of which the lifetime of the gas-liquid emulsion and foam increases.

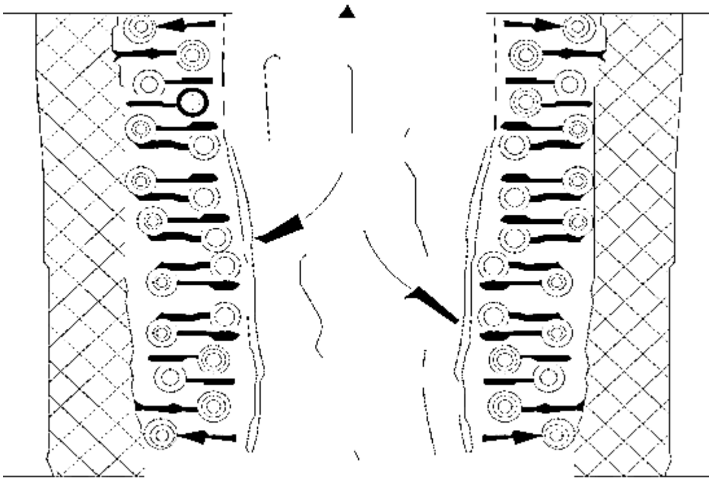

Fig.2. Schematic representation of adsorption-desorption of complex structural units: 1 – pair solid wall surface; 2 – liquid phase (absorption layer); 3 – interfacial layer (black dots – adsorption of associates, white dots – desorption of gas bubbles); 4 – vapour phase.

RESULTS AND DISCUSSION

As bubbles with surface-active properties rise, they become more and more saturated with compaction products, sulfur-, nitrogen-, oxygen- and organometallic compounds, and at the same time, without being destroyed, they pass through the entire interfacial layer, removing all of the above compounds from the reaction zone, poisonous catalyst. This apparently explains the increase in the yield of heavy gas oil when tar deasphalted oil is added to vacuum gas oil.

Another evidence of such a mechanism of action of the deasphalted oil is a decrease in the yield of coke and the content of isobutane and dry gas in the gas composition.

According to Wojciechowski and Korma, coke, methane, ethane, ethylene, propane, and isobutane are secondary products of the cracking reaction [6].

Previously, experiments were carried out with a mixture of vacuum gas oil with pentane deasphalted oil in the optimal ratio of 87:13%vol. The purpose of these experiments was to test the effect of the magnetic field on the catalytic cracking process. As a result of the studies, it was found that the magnetic field affects the process of catalytic cracking, and the optimal value of the magnetic induction flux is 0.4 T.

Table 3 shows the dependence of the yield of catalytic cracking products on the percentage of gasoline deasphalted oil obtained without preliminary magnetic treatment of tar in vacuum gas oil in a magnetic field of 0.4 T.

As can be seen from this table, in contrast to previous experiments, where the gasoline yield during cracking of pure vacuum gas oil was 46.0% mass, in a magnetic field this figure is already 46.9% mass, when mixed raw materials are cracked, the gasoline yield initially slightly drops to 46.5%mass, at 5% deasphalted oil content, and then with an increase in the content of the latter in the mixture, it grows to 47.5% mass, with the optimal content of deasphalted oil in the raw material. Thus, in comparison with cracking under normal conditions, in a magnetic field the yield of gasoline increases by 1.8% mass. As can be seen from table 3, the coke yield in a magnetic field decreases by 0.1% and is 3.4% mass.

Table 3

Catalytic cracking of vacuum gas oil mixture with gasoline deasphalted oil (deasphalted oil obtained without magnetic treatment of tar)

Products	The content of deasphalted oil in raw materials, %vol.						
	0	5	10	13	15	20	25
Hydrogen	0.3	0.3	0.3	0.25	0.3	0.35	0.35
Dry Gas	2.3	2.3	2.2	2	2.3	2.55	2.75
Isobutane	1.7	1.9	1.7	1.3	1.6	1.9	2.2
Butylenes	13.7	14	13.8	13.9	13.7	13.8	13.6
Total gas	18	18.5	18	17.5	17.9	18.6	18.9
Gasoline n.cn 195°C	46.9	46.5	47	47.5	46.9	45.5	43.8
Fraction 195-350°C	20.2	20.2	18.9	18.6	19.1	20	21.5
Fraction above 350°C	11.4	11.4	12.6	13	12.4	12	11.1
Coke	3.5	3.6	3.5	3.4	3.7	3.9	4.7

The results of catalytic cracking of the pentane deasphalted oil mixture were expected to be superior to the results of the cracking of the gasoline deasphalted oil mixture, which are presented in table 4.

Thus, the yield of gasoline increases to 48.0% mass, and the yield of coke decreases to 3.1% mass (table 4). Much less gas formation as well. With a 13% content of pentane deasphalted oil in the raw material, the gas yield is 16.7%mass, against 17.5% mass in the case of gasoline deasphalted oil.

Table 4

Catalytic cracking of vacuum gas oil mixture with pentane deasphalted oil in a magnetic field (deasphalted oil obtained without magnetic treatment of tar)

Products	The content of deasphalted oil in raw materials, %vol.						
	0	5	10	13	15	20	25
Hydrogen	0.3	0.3	0.25	0.2	0.25	0.3	0.35
Dry Gas	2.3	2.3	2.05	1.8	1.95	2.2	2.45
Isobutane	1.6	1.6	1.2	1	1.1	1.4	1.9
Butylenes	13.7	13.7	14	13.7	13.7	13.6	13.6
Total gas	18	17.9	17.5	16.7	17	17.5	18.3
Gasoline n.cn 195°C	46.9	47	47.5	48	47.8	46.5	45
Fraction 195-350°C	20.2	19.6	19.5	17.9	18.5	19.4	20.2
Fraction above 350°C	11.4	12	13.2	14.3	13.5	13.1	12.2
Coke	3.5	3.5	3.3	3.1	3.2	3.5	4.3

Changes in the composition of the gas in both cases are of the same nature, that is, the content of hydrogen, dry gas and isobutane decreases. Also, the influence of the magnetic field on the cracking of vacuum gas oil mixtures with deasphalted oils obtained by magnetic treatment of tar was studied (fig.3). Experiments were carried out with mixtures of deasphalted oil, obtained by magnetic processing of tar, with vacuum gas oil.

As can be seen from fig.3, the gasoline yield during catalytic cracking of this mixture passes through an extremum, as in previous experiments at 13% deasphalted oil content in the mixture. When comparing the results of this experiment with the results of cracking, where pentane deasphalted oil obtained without magnetic treatment of tar was used as a raw material component, we see that the results of the first one is slightly better. Thus, in the case of gasoline deasphalted oil obtained by magnetic treatment of tar, at the optimal ratio of vacuum gas oil: deasphalted oil, the gasoline yield is 48.2%mass, the coke yield decreases to 2.8%mass, i.e., 10% less than in the case of pentane deasphalted oil obtained without magnetic treatment of tar. The gas yield is reduced to 14.3%mass.

Even better results are shown in the cracking of vacuum gas oil mixture with pentane deasphalted oil obtained by magnetic treatment of tar, which is shown in figure 4.

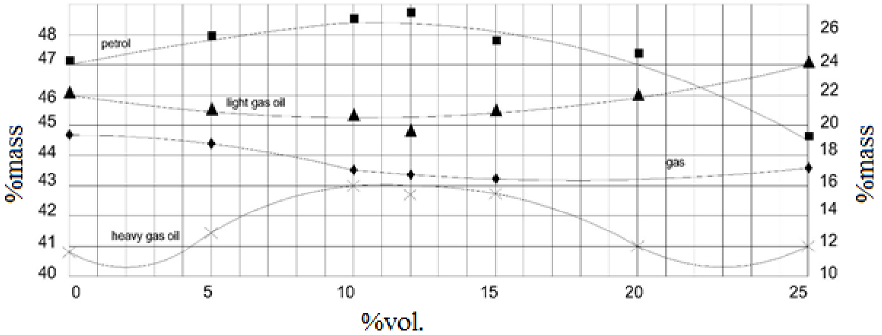

Fig.3. Dependence of the yield of cracking products on the content of gasoline deasphalted oil in the raw material in a magnetic field (deasphalted oil obtained by magnetic processing of tar):

a – gas; b – petrol; c – light gas oil; d – heavy gas oil.

CONCLUSION

As can be seen from figure 4, the yield of gasoline in this case reaches its maximum value, compared with all previous experiments, it is 48.9%mass, and the yield of coke decreases to 2.6%mass, the yield of the fraction 195-350°C slightly decreases, but the yield of heavy cracking gas oil increases from 11.4 to 14.9%mass. As can be seen from the analysis of the data in table 3, the content of the deasphalted oil in the mixture, the volumetric ratio of CO_2:CO in the regeneration gases, the content of hydrogen, dry gas and isobutane in the composition of the cracking gases is minimal.

When analyzing the regeneration gases, one more property of the added deasphalted oil was revealed. As it turned out, the addition of deasphalted oil to the cracking raw material leads to an increase in the CO_2:CO ratio in the regeneration gases. The data from these analyzes are shown below. An increase in the ratio in regeneration gases means a decrease in emissions of such a dangerous toxic substance as carbon monoxide into the atmosphere.

To explain the effect of a magnetic field on the yield of catalytic cracking products, let us use the cell effect. It was first considered by Frank and Rabinovich. It is known that in the gas phase the fragments of a decaying molecule fly apart. The essence of the “cellular effect” is that fragments of a molecule in a condensed medium do not necessarily diverge, daughter ions can recombine and again give the parent molecule, the precursor of this pair of radicals, or enter into a disproportionation reaction and give molecular products of a different structure, in our case, compaction products. Such a reaction is called geminal or cellular recombination, and the recombination product is called cellular [7].

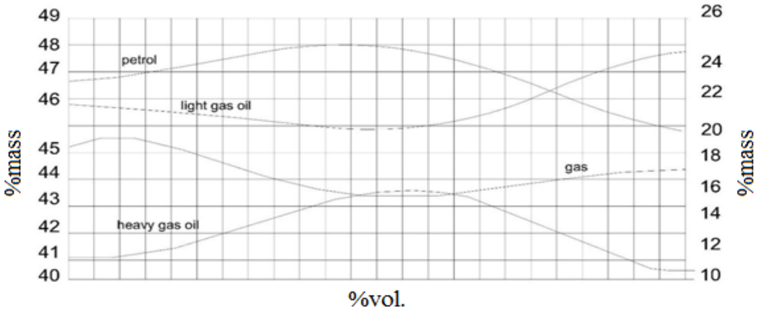

Fig.4. Dependence of the yield of cracking products on the content of pentane deasphalted oil in the raw material in a magnetic field (deasphalted oil obtained by magnetic processing of tar):

a – gas; b – petrol; c – light gas oil; d – heavy gas oil.

Ions and radicals in a cell can be in two electronic spin states: singlet or triplet. The probability of recombination in these states is not the same. Indeed, for the vast majority of molecules, the electronic ground state is a singlet, and the triplet is an excited state. A stable product must arise from ions and radicals in the singlet state.

The main ways of their transformation, including changes in their multiplicity, can be depicted as follows (figure 5): Of these processes, only the S-T intercombination transition depends on the interaction of unpaired electrons with external magnetic fields. This is the physical nature of magnetic effects in the recombination of ions and radicals.

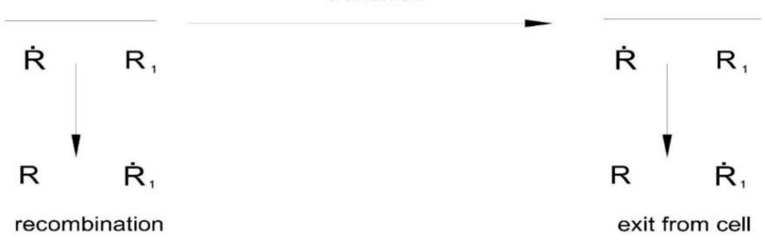

Fig.5. Pathways for the transformation of ions and radicals.

For the first time, physically based ideas about the role of S-T transitions in the process of recombination of ions and radicals and the possible mechanism of the influence of a magnetic field on the reaction were proposed by Brocklehaust [8]. He formulated two propositions:

for chemical reactions, singlet-triplet transitions in ions and radicals can affect the ratio of reaction products;

these intercombination transitions themselves are induced by the paramagnetic relaxation of the electron spins of the partners.

So, summing up the above, we can explain the influence of a magnetic field on cracking as follows: during catalytic cracking of vacuum gas oil, as well as its mixture with tar deasphalted oil, decomposing molecules form correlated ions in the singlet state. Under the influence of a magnetic field, the transition of ions from the singlet state to one of the triplet ones occurs. According to the literature data, the probability of recombination of diffusion ions and radicals increases with increasing magnetic field induction.

The foregoing suggests that in the initial section of the increase in the magnetic field, the probability of the formation of compaction products as a result of ion recombination decreases due to the prevalence of the effect of reducing the probability of recombination of correlated ions over the effect of increasing the probability of recombination of diffusion ions.

With a further increase in the magnetic flux, the rate of decrease in the probability of recombination of correlated ions decreases, while that of diffusion ions continues to increase, as a result of which there is a tendency to increase the probability of densification reactions, which in turn leads to an increase in the yield of coke. When analyzing the quality of cracked light gas oil, it can be seen that its density slightly increases, which can be explained by an increase in the proportion of heavy hydrocarbons in its composition, which in turn is caused by a decrease in coke yield.

Table 5

The quality of cracking products of vacuum gas oil and its mixtures with tar deasphalted oil products in a ratio of 87:13 under optimal conditions

Options	Clean vacuum smart oil	Vacuum gas oil pentane deasphalter		Vacuum gas oil gasoline deasphalter	
	Cracking in a magnetic field	Cracking in a magnetic field	Without magnetic treatment	Cracking in a magnetic field	Without magnetic treatment
Petrol					
Density at 20°C, kg/m^3	746.9	739.6	743.2	741.5	745.8
Sulfur content, %mass	0.14	0.12	0.13	0.14	0.15
Octane number	79	82	80	81	80
Group at/in the composition %mass					
Unlimited	18.9	19.3	19.2	19.1	19
Aromatic	23.9	25.5	24.8	25.4	24.6
Naphthenic	10.2	10.9	10.8	10.8	10.7
Paraffin	47	44.3	45.2	44.7	45.7
Light gas oil					
Density at 20°C	921.1	922.5	923.2	922.7	924.1
Sulfur content, wt.	0.71	0.73	0.74	0.75	0.77

This apparently explains some increase in the sulfur content in the composition of light gas oil. Thus, the analysis of the experimental data showed that the best is deasphalted oil obtained after preliminary magnetic treatment of tar, and they can be used as an additive to the catalytic cracking raw material – vacuum gas oil to produce high-quality fuels.

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МАГНИТНОСТЬ ПРОЦЕССОВ ДЕАСФАЛЬТИЗАЦИИ И КАТАЛИТИЧЕСКОГО КРЕКИНГА ИССЛЕДОВАНИЕ ИНТЕНСИФИКАЦИИ В ПОЛЕ

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С целью получения ДАО, пригодного для смешивания с вакуумным газойлем для последующего процесса каталитического крекинга, проводимого в постоянном магнитном поле, был исследован процесс деасфальтизации гудрона в магнитном поле.
Исследован вероятный механизм влияния магнитного поля на процесс асфальтирования. В ходе исследований изучался каталитический крекинг смеси вакуумного газойля и нефтепродуктов рафинирования асфальта в присутствии магнитного поля, и было

определено, что полученные выводы могут быть положены в основу получения С высокими октановыми показателями. Было обнаружено, что на качество получаемой битуминозной нефти влияет ряд факторов, включая температуру процесса, время отстаивания и соотношение растворителя и исходного сырья. С учетом этих переменных в ходе исследований было оценено влияние магнитной обработки на сырье в процессе асфальтирования и определены оптимальные условия для получения желаемых результатов. Исследователи также исследовали влияние магнитной обработки на время осаждения и обнаружили, что она ускоряет процесс осаждения. Кроме того, дано объяснение механизма воздействия постоянного магнитного поля на процесс каталитического крекинга с точки зрения синглетно-триплетного состояния ионов и радикалов.

Ключевые слова: *деасфальтизация, каталитический крекинг, температура деасфальтизации, магнитная обработка сырья, асфальтосмолистые вещества.*

ASFALTSIZLAŞMA VƏ KATALİTİK KREKİNG PROSESLƏRİNİN MAQNİT SAHƏSİNDƏ İNTENSİVLƏŞDİRİLMƏSİNİN TƏDQİQATI

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Sabit maqnit sahəsində aparılan sonrakı katalitik krekinq prosesi üçün vakuum qazoylu ilə qarışdırmaq üçün uyğun DAO-nun əldə edilməsi məqsədilə maqnit sahəsində vakuum qalığının asfaltdan təmizlənməsi prosesi tədqiq edilmişdir.

Asfaltlanma prosesində maqnit sahəsinin ehtimal olunan təsir mexanizmi tədqiq edilmişdir. Tədqiqat zamanı maqnit sahəsinin mövcudluğunda vakuum qazoylu və qatranla asfaltdan təmizlənmiş neft məhsulları qarışığının katalitik krekinqi tədqiq edilmiş və tapıntıların yüksək oktan göstəricilərinə malik yüksək keyfiyyətli benzinlərin istehsalı üçün zəmin ola biləcəyi müəyyən edilmişdir. Alınan asfaltdan təmizlənmiş neftin keyfiyyətinə proses temperaturu, çökmə vaxtı və həlledicinin xammala nisbəti də daxil olmaqla bir sıra amillərin təsir etdiyi aşkar edilmişdir. Tədqiqat zamanı bu dəyişənlər nəzərə alınmaqla, asfaltlama prosesi zamanı maqnitlə müalicənin xammala təsiri qiymətləndirilmiş, arzu olunan nəticələrin əldə edilməsi üçün optimal şərait müəyyən edilmişdir. Tədqiqatçılar həmçinin maqnit müalicəsinin çökmə müddətinə təsirini araşdırmışlar və bunun çökmə prosesini sürətləndirdiyini aşkar etmişlər. Bundan əlavə, ionların və radikalların təkli-üçlü vəziyyəti baxımından katalitik krekinq prosesinə kostant maqnit sahəsinin təsir mexanizminin izahı verilmişdir.

Açar sözlər: *deasfaltizasiya, katalitik krekinq, deasfaltizasiya temperaturu, xammalın maqnitlə təmizlənməsi, asfalt-qatran maddələri*

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RESEARCH OF CONSERVATİON LİQUİDS MADE ON THE BASİS OF RESİDUAL FATTY ACİDS, NITRO COMPOUNDS AND ADDİTİVES BASED ON DERİVATİVES OF NATURAL PETROLEUM ACİDS

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Within this research project, we have analyzed petroleum acids as a basis of corrosion inhibitors. We conducted several laboratory experiments to define the best conditions to get maximum efficiency. First, we take combinations of fatty acids and polyethylene polyamine (PEPA) in a range of different molar ratios under different circumstances. We applied specific thermo humidity chamber, sea water and sulfuric acid solutions to create conditions which enhance corrosion rate. Then we went further to get higher efficiency, we added nitro compounds with different molar ratios. After presence of nitro-components, final experiment results were obtained. After completions of several experiments, we get best possible results when we applied reaction between imidazoline and residual fatty acids with nitro compound in a 1:2 mole ratio. It becomes clear that we need to keep specific molar ratio to enhance corrosion protection period.

***Keywords**: conservation liquids, corrosion, inhibitors, corrosion inhibitors, imidazoline, fatty acids.*

INTRODUCTİON

Since the storage, transportation and operation of metal equipment are mainly in atmospheric conditions, their protection from atmospheric corrosion is of great importance.

It should be noted that atmospheric corrosion is a continuous process, and the dissolution of metals in this process, in most cases, depends on the characteristics of climatic conditions, the degree of air pollution with various chemical compounds and additives.

The fact that some chemical substances have inhibitory properties has been known since the time when mankind was familiar with chemical compounds. The research work on studying the mechanism of this process started after the second half of the 20th century, because until this period, mineral oils were mainly used to protect metal devices, mechanisms and equipment from corrosion. However, they could not prevent water vapors from penetrating the metal surface, which could cause intensification of rust on the metal surface, so the protective ability of oils used without inhibitors was very low [1].

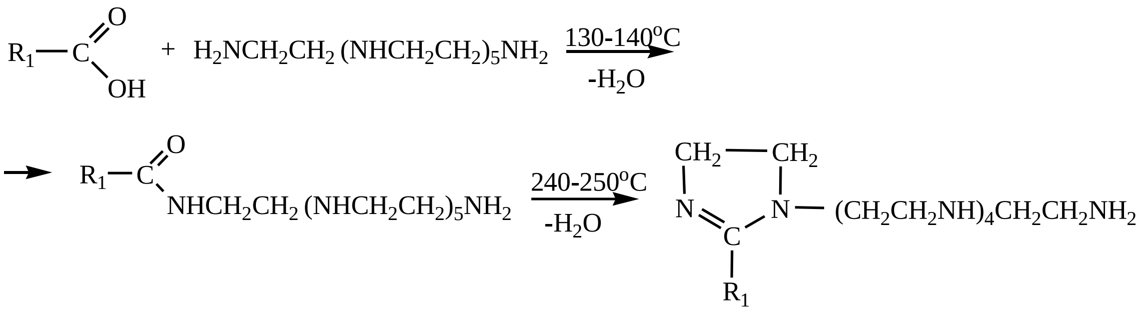
The use of conservation liquids and lubricants to prevent atmospheric corrosion is technically more convenient and cheaper [2]. Currently, along with the intensive development of technology, the demand for conservation fluids and lubricants is increasing year by year, and at the same time, the requirements imposed on them are becoming stricter.

EXPERIMENTAL PART

Inadequate protection of various metal equipment from corrosion and the shortening of their service life causes great damage to the oil-gas-chemical industry. Corrosion protection remains one of the area which needs to be improve. One of the most effective and reliable methods of corrosion protection in the oil and gas industry is the application of corrosion inhibitors.

Taking into account that corrosion is such a large-scale problem, various methods are currently applied to define most eeffective ways wagainst corrosion issue. One of the key methods is systenthesize of imidazolines [3]. To do that, initially, a reaction of technical petroleum acid with PEPA in a 1:1 mol ratio was carried out.

Scheme of the reaction of technical petroleum acid with polyethylene polyamine (PEPA).



RESULT AND DISCUSSION

The physicochemical parameters of the synthesized imidazoline compound were determined. The obtained imidazoline derivative is a reddish brown, alkaline liquid insoluble in water, but well soluble in organic solvents [4]. Some indicators of the imidazoline derivative are listed in table 1.

Table 1

Physico-chemical parameters of imidazoline derivatives

Synthesized imidazoline compounds	Relative density at 20°C, ρ, kg/m^3	Light absorption coefficient, n_D20	Freezing temperature ,°C	Average molecular weight, M_r	Yield of imidazoli ne %
Imidazoline synthesized on the basis of PEPA and TNT	1193	1,5109	-16 (minus)	428	91

It needs to be point out that imidazoline derivatives synthesized on the basis of TNT and PEPA [5].

In order to conduct research, complex mixture of imidazoline which synthesized on the basis of technical petroleum and corn fatty acid acid and polyethylene polyamine (PEPA) as a component of conservation liquids in different molar ratios (1:1, 1:2, 1:3, 1:4 and 1:5) prepared.

Research works were carried out with conservation liquids by adding 6% of the prepared compositions to turbine oil. In this case, we used T-30 type as a turbine oil.

Tests of the corrosion protection effect of the prepared conservation fluids on "Steel-3" brand steel samples in three environments (in sea water, in a 0.001% solution of sulfuric acid in water and in the "Q-4" thermo-humidity chamber) were conducted [6]. As a result of the tests, it was found that the addition of 6% additive to T-30 turbine oil leads to a further increase in the corrosion protection effect of metal plates.

For example: T-30 turbine oil in the "Q-4" thermohumidity chamber had a corrosion protection effect of metal plates for 35 days, while the 6% addition of imidazoline and corn acid in a 1:3 mol ratio to turbine oil showed a higher result of 229 days.

As a result of the tests, it was found that the metal plates of conservation fluids prepared on the basis of the composition of imidazoline with corn acid in a 1:3 mol ratio have a corrosion protection effect, while those prepared on the basis of the compositions of other ratios (1:1, 1:2, 1:4 and 1:5 mol ratios) Metal plates of conservation fluids have a higher corrosion protection effect.

Since the synthesized nitro compounds are highly effective as preservation liquids, tests were conducted in various environments using the preparation of compositions from these compounds [7].

As a raw material for the nitration reaction, α-olefin (tetradecene-1) synthesized on the basis of ethylene oligomerization at the Nizhnekamsk oil and organic synthesis production unit of the Russian Federation was taken. Their nitration takes place under milder conditions (at 70-90ºC, normal pressure) and the reaction product mixture of nitro compounds is produced with a high yield. is taken. NO_2, N_2O_4 and nitric acid in various concentrations are used as nitrifiers [5].

Preservative liquids were prepared and tested by mixing the synthesized nitro compound and the mixture of imidazoline with residual fatty acids (1:1, 1:2, 1:3, 1:4 and 1:5 mol ratio) in different molar ratios by adding 12% to T-30 oil.

Table 2

Test results of preservative fluids based on synthesized imidazoline and corn fatty acid

№	Composition of preservation liquids, %	Amount of inhibitors (%)	Corrosion protection period (DAYS)		
			«Q-4» thermohumidity chamber	Sea water	In a 0.001% solution of H_2SO_4
1	T-30 oil		35	16	10
2	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:1 mole ratio	6	22	6	7
3	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:2 mole ratio	6	107	37	38
4	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:3 mole ratio	6	229	117	117
5	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:4 mole ratio	6	125	46	48
6	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:5 mole ratio	6	136	59	59

Table 3

Test results of preservation liquids prepared on the basis of a mixture of synthesized nitro compound and imidazoline with residual fatty acids

№	Composition of preservation liquids, %	Amount of inhibitors (%)	Corrosion protection period (DAYS)		
			«Q-4» thermo-humidity chamber	Sea water	In a 0.001% solution of H_2SO_4
1	T-30 oil + nitrocompound	12	110	79	48
2	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:1 mole ratio + nitrocompound	12	113	78	80
3	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:2 mole ratio + nitrocompound	12	283	154	155
4	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:3 mole ratio + nitrocompound	12	247	118	120
5	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:4 mole ratio + nitrocompound	12	275	119	119
6	T-30 oil + reaction of imidazoline and residual fatty acids in a 1:5 mole ratio + nitrocompound	12	109	33	37

As a result of the tests, it was found that the composition of the synthesized nitro compound and imidazoline with residual fatty acids showed a high result as a preservative liquid.

As can be seen from the results of the tests, the effect of corrosion protection of metal plates of the "Steel-3" brand in different environments (G-4 hydrochamber, sea water and 0.001% H_2SO_4 environment) with the addition of 12% of nitriding to T-30 oil without inhibitor and 12% addition of nitriding to T-30 oil) 35, 16, 10 and 110, 79, 48 days, respectively. 283, 154 and 155 days were shown in addition of imidazoline with residual fatty acids (1:2 mol ratio) and 12% amount of nitro compound to T-30 oil.

CONCLUSION

To sum up, it can be highlighted that application of synthesized imidazoline and residual fatty acids is enhance carrosion protection periods. However, to get better results, it can be concluded that it is more appropriate to use the composition of synthesized imidazoline with residual fatty acids and nitro compound as an inhibitor to create more effective preservation liquids. In this way, we would manage to enhance operability period and realibity of equipment and steel pipelines.

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ИССЛЕДОВАНИЕ КОНСЕРВАЦИОННЫХ ЖИДКОСТЕЙ НА ОСНОВЕ ОСТАТОЧНЫХ ЖИРНЫХ КИСЛОТ, НИТРОСОЕДИНЕНИЙ И ПРИСАДОК НА ОСНОВЕ ПРОИЗВОДНЫХ ПРИРОДНЫХ НЕФТЯНЫХ КИСЛОТ

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В рамках этого исследовательского проекта мы проанализировали нефтяные кислоты как основу ингибиторов коррозии. Мы провели несколько лабораторных экспериментов, чтобы определить наилучшие условия для получения максимальной эффективности. Во-первых, мы берем комбинации жирных кислот и полиэтиленполиамина (PEPA) в различных молярных соотношениях при различных обстоятельствах. Мы применили специальную камеру термовлажности, морскую воду и растворы серной кислоты, которые увеличивают скорость коррозии. Затем, чтобы получить более высокую эффективность, мы добавили нитросоединения с различным молярным соотношением. После добавления нитрокомпонентов получены окончательные результаты эксперимента. После завершения нескольких экспериментов мы получили наилучшие результаты, после проведения реакции между имидазолином и остаточными жирными кислотами с нитросоединениями, взятых в молярном соотношении 1:2. Исследования показали, что для увеличения периода защиты от коррозии необходимо соблюдать определенное молярное соотношение.

Ключевые слова: *консервационные жидкости, коррозия, ингибиторы, ингибиторы коррозии, имидазолины, жирные кислоты.*

TƏBİİ NEFT TURŞULARININ TÖRƏMƏLƏRİNİN QATQILARIN ƏLAVƏ EDİLMƏSİ, QALIQ YAĞ TURŞULARI VƏ NİTROBİRLƏŞMƏ ƏSASINDA HAZIRLANMIŞ KONSERVASİYA MAYELƏRİNİN TƏDQİQİ

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Bu tədqiqat layihəsi çərçivəsində neft turşularının korroziyası inhibitorlarının əsası kimi təhlil edilmişdir. Maksimum səmərəliliyi əldə etmək və əlavə olaraq, uzun müddətli korroziyaya davamlı inhibitor əldə etmək üçün bir neçə laboratoriya sınaqları keçirilmişdir. İlkin olaraq, müxtəlif şəraitlərdə müxtəlif molyar nisbətlərdə yağ turşuları və polietilenpoliamin (PEPA) birləşmələri götürülmüşdür. Korroziya sürətini artırmaq məqsədilə xüsusi rütubət kamerası, dəniz suyu və sulfat turşusu məhlulları tətbiq edilmişdir. Sonra daha yüksək effektivlik əldə etmək üçün müxtəlif molyar nisbətlərə malik nitro birləşmələri əlavə edilmişdir. Nitrobirləşmələrin ən optimal mol nisbəti müəyyən edildikdən sonra son sınaq nəticələri qeyd edilmişdir. Aparılmış təcrübələrin yekunu olaraq imidazolin və qalıq yağ turşularının nitrobirləşmələri ilə 1:2 mol nisbətində reaksiyasını tətbiq etdikdə mümkün olan ən yaxşı nəticələri əldə etdik. Qeyd etmək lazımdır ki, korroziyadan qorunma müddətini artırmaq üçün xüsusi molyar nisbətləri tətbiq etmək lazımdır.

Açar sözlər: *konservasiya mayeləri, korroziya, inhibotrlar, korroziya əleyhinə inhibotrlar, imidazoline, yüksək molekullu neft turşuları.*

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INVESTIGATION OF ARYLALKYLATION REACTIONS OF LIQUID PRODUCTS OF PYROLYSIS WITH 130-190°C FRACTION IN THE PRESENCE OF HYDROCHLORIC ACID IMPREGNATED KH-30 CATALYST OF PHENOL

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Alkylation reactions of 130-190°C fraction of liquid products of pyrolysis with the presence of KH-30 catalyst impregnated with hydrochloric acid of phenol were studied. As a result, the effect of various parameters - reaction temperature, duration, molar ratios of initial components and the amount of catalyst - on the yield and selectivity of the target product was investigated. It was determined that the yield of para-arylalkylphenol is 78.6%, and the selectivity is 94.3%. Although more than 100 years have passed since the study of alkylation reactions of phenol, the preparation of alkylphenols and their various derivatives has not lost its relevance even today. Alkylphenol-based chemical compounds are finding new effective areas of use: they are insecticides, pesticides, etc. against agricultural pests. they are used as a ligand for catalytic precursors used in the production, oligo- and polymerization of olefins, and as an extractant in the purification of oil fractions from aromatic hydrocarbons.

Keywords: *phenol, fraction 130-190°C, catalyst, arylalkylation, para-arylalkylphenol.*

INTRODUCTION

The 130-190°C fraction of liquid products of phenol and pyrolysis was taken as raw material for research. Newly expelled and purified phenol was used for experiments: T_{boil} - 182°C, $T_{melting}$ - 41°C, molar mass – 94 [1].

Fraction of liquid products of pyrolysis Fraction of liquid products of pyrolysis is obtained from the rectification of liquid products obtained as a result of pyrolysis of low-octane gasoline and has the following physicochemical parameters: T_{boil} - 130-190°C, n_D^{20}- 1.5160, ρ_4^{20} - 0.8578, molar mass - 120.

KH-30 impregnated with 10% hydrochloric acid was also used as a catalyst for alkylation reactions. The catalyst is prepared according to the following procedure. The KH-30 catalyst is first kept in distilled water for 1 day, separated from the water, then 10% hydrochloric acid is soaked in the catalyst and evaporated, it is dried in an oven at 100°C, and the temperature is continuously raised from 200°C to 600°C. Then the catalyst is cooled and used [2].

Arylalkylation reactions of phenol with fraction of liquid products of pyrolysis were carried out in a flask under laboratory conditions. The mixture of components is mixed in the reaction zone for 2-8 hours with the presence of KH-30M catalyst, cooled to 40°C, filtered and separated from the catalyst while hot, and rectified. First, fraction of pyrolysis liquid products and phenol, which do not react up to 200°C, are rectified, and then the target products are rectified in vacuum (10 mm Hg) [3-5]. The composition, physic-chemical parameters and structures of alkylphenols removed from alkylate are determined by spectral methods.

EXPERIMENTAL PART

Chromatographic analysis of reaction and rectification products was carried out on LXM-72 chromatograph. Column length - 2m, solid carrier - chromaton - N-AW DMC acid-washed and silanized with dimethylchlorosilane 0.2 ± 0.25mm fraction, 5% SE-30 methylsiloxane elastomer was taken as stationary phase. Initial column temperature 50°C, final temperature 280°C, programming speed - 10 °C/min, carrier helium gas rate - 50 ml/min, evaporator temperature - 300°C, chart tape speed - 60 mm/h. 100% of the sum of the areas of the total peaks was taken as the basis for calculating the number of components in %.

Separation of pyrolysis liquid products was done in order to increase the concentration of unsaturated hydrocarbons (especially styrene and α-methylstyrene) in the fraction.

In order to find the effective conditions of the arylalkylation reaction of phenol with PMMF, the effect of various parameters - reaction temperature, duration, mole ratios of primary components and the amount of catalyst - on the yield and selectivity of the reaction products was investigated. The temperature of alkylation reactions of phenol is 80-140°C, the duration of the experiment is 2-8 hours, the molar ratio of phenol to Fraction of liquid products of pyrolysis is from 1:1 to 1:4, and the amount of catalyst is 5-15% (table 1).

The pyrolysis liquid product brought from the Sumgayit "Sintez Kauchuk" plant and expelled from it is provided in a high-level table of more than 130 - 190°C.

Table 1

Fractional composition of pyrocondensate and FLPP

Hydrocarbons	Pyrocondensate	FLPP
$\sum C_4$	0.25	-
$\sum C_5$	7.17	-
$\sum C_6$	8.32	1.67
$\sum C_7$	3.58	1.04
Benzene	22.75	6.21
$\sum C_8$	4.76	2.05
Toluene	17.81	5.33
$\sum C_9$	2.58	3.61
Ethylbenzene	2.60	3.17
m- xylene	3.25	7.73
p- xylene	1.63	5.20
o- xylene	3.56	6.53
isopropylbenzene	2.21	5.26
styrene	10.83	32.18
α- methylstyrene	1.87	5.96
Vinyltoluene	4.60	7.37
inden	0.59	4.28
indan	1.14	-

One of the important factors in the study of alkylation reactions of phenol with FLLP is the amount of catalyst used to carry out the reaction.

RESULT OF EXPERIMENT

Table 2 shows the results of the chromatographic analysis of FLLP before and after the reaction.

It can be seen from table 2 that styrene, α-methylstyrene, vinyltoluene and indene are included in the alkylation reaction with phenol. After the reaction, the density of styrene in FLLP decreased from 32.18 to 34.2%, the density of α-methylstyrene decreased from 5.96 to 0.95%, the density of vinyltoluene decreased from 7.37 to 1.78%, and the density of indene decreased from 4.28% to 4.28% [6-8].

Table 2

Results of chromatographic analysis of FLLP before and after reaction

Hydrocarbons	Before the reaction	After the reaction
$\sum C_6$	1.67	3.52
$\sum C_7$	1.04	2.86
Benzene	6.21	11.77
$\sum C_8$	2.05	5.13
Toluene	5.33	9.07
$\sum C_9$	3.61	5.82
Ethylbenzene	3.17	6.27
m- xylene	7.73	10.75
p- xylene	5.20	8.54
o- xylene	6.53	11.30
isopropylbenzene	5.26	12.43
styrene	32.18	3.42
α- methylstyrene	5.96	0.95
Vinyltoluene	7.37	1.78
Phenol	-	2.52
inden	4.28	0.56

The table shows the results of alkylation reactions of phenol with FLLP in the presence of KH-30 catalyst impregnated with hydrochloric acid.

The effect of the molar ratio of the initial components in the reaction mixture is also important. The direction of the reaction can be regulated by increasing or decreasing the concentrations of the primary components [9-12].

Since the unsaturation of FLLP is 32-35%, a 1:3 mole ratio of phenol to fraction can be considered acceptable. At these molar ratios of primary components, the yield of para-arylalkylphenol is 78.5%, and the selectivity is 94.3% with respect to the target product.

As we know, in the alkylation of phenol with FLLP, when the reaction temperature increases from 80 to 110°C, the product yield increases from 36.7 to 78.5% (at this time, the selectivity changes from 86.1 to 94.3%). Alkylphenyl ethers are obtained at low reaction temperatures. With increasing temperature, the alkyl group migrates to the ortho-position closer to the hydroxyl group of phenol. The presence of ortho-alkylphenol up to 5-8% in alkylate is explained by this factor. By increasing the reaction temperature to 140°C, the yield of the target product decreases to 67.0%, and the selectivity decreases to 76.2%. The decrease in selectivity is explained by the formation of di- and tri-substituted alkylphenols at high temperatures.

One of the main factors affecting the yield and selectivity of the target product is the reaction time. By increasing the mixing time of the primary components taken for the reaction in the flask from 2 to 5 hours, the yield of the target product increases from 28.3 to 78.5% according to the phenol taken. By increasing the meeting time of the components up to 8 hours, the yield of the target product is 69.6%, and the selectivity is 89.4%. The relatively low selectivity is explained by the acquisition of side products.

The effect of the molar ratio of the initial components in the reaction mixture is also important. The direction of the reaction can be regulated by increasing or decreasing the concentrations of the primary components.

As it is known, by taking the molar ratio of phenol to FLLP of 1:3, a high value of yield and selectivity of the target product can be achieved.

Para-arylalkylphenol is removed from the alkylate by rectification and its physicochemical parameters are determined. The results are given in table 3.

Table 3

Para-arylalkylphenol is separated from alkylate by rectification and its physicochemical parameters

Example	$T_{boil.}$,^{0}C 10 mm c.st.	n_D^{20}	ρ_4^{40}	Mol. Mass	Element analysis, %				Functional composition, %	
					Calculated		Found		OH	
					C	H	C	H	Calculated	Found
p-alkyl-phenol	160-180	1.5675	0.973	200	84.3	7.1	84.2	6.8	8.6	8.3

CONCLUSION

The reactions of p- alkylphenol components of the 130–190°C fraction of pyrolysis products in the presence of a zeolite-containing KN-30 catalyst were studied. It has been established that under the optimal mode, the yield of the target p- alkylphenol is 81.2% of the amount predicted theoretically for the given amount of phenol, and the selectivity is 94.7% for the target product.

Thus, as a result of the conducted research, it was determined that the arylalkylation reactions of phenol with hydrochloric acid-impregnated KH-30 catalyst and pyrolysis fluid fraction at 130-190□C are carried out under milder conditions, different from other known alkylation reactions, and the yield and selectivity of the target product are high.

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ИССЛЕДОВАНИЕ РЕАКЦИЙ АРИЛАЛКИЛИРОВАНИЯ ЖИДКИХ ПРОДУКТОВ ПИРОЛИЗА ФРАКЦИИ 130-190°С В ПРИСУТСТВИИ ПРОПИТАННОГО СОЛЯНОЙ КИСЛОТОЙ КАТАЛИЗАТОРА КН-30 ФЕНОЛА

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Исследованы реакции алкилирования 130-190°С фракции жидких продуктов пиролиза в присутствии катализатора КН-30, пропитанного соляной кислотой фенола. В результате было исследовано влияние различных параметров - температуры реакции, продолжительности, мольных соотношений исходных компонентов и количества катализатора - на выход и селективность целевого продукта. Было определено, что

выход пара-арилалкилфенола составляет 78,6%, а селективность - 94,3%.
Хотя с момента изучения реакций алкилирования фенола прошло более 100 лет, получение алкилфенолов и их различных производных не утратило своей актуальности и в настоящее время. Химические соединения на основе алкилфенолов находят новые эффективные области применения: это инсектициды, пестициды и др. против сельскохозяйственных вредителей. их используют в качестве лиганда для каталитических прекурсоров, используемых в производстве, олиго- и полимеризации олефинов, а также в качестве экстрагента при очистке масляных фракций от ароматических углеводородов

Ключевые слова: *фенол, фракция 130-190°С, катализатор, арилалкилирование, пара-арилалкилфенол.*

FENOLUN XLORID TURŞUSU HOPDURULMUŞ KH-30 KATALİZATORUNUN İŞTİRAKI İLƏ PİROLİZİN MAYE MƏHSULLARININ 130-190°C FRAKSİYASI İLƏ ARİLALKİLLƏŞMƏ REAKSİYALARININ TƏDQİQİ

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Fenolun xlorid turşusu hopdurulmuş KH-30 katalizatorunun iştirakı ilə pirolizin maye məhsullarının 130-190°C fraksiyası ilə alkilləşmə reaksiyaları tədqiq olunmuşdur. Nəticədə müxtəlif parametrlərin-reaksiyanın temperaturunun, müddətinin, ilkin komponentlərin mol nisbətlərinin və katalizatorun miqdarının-məqsədli məhsulun çıxımına və seçiciliyinə təsiri araşdırılmışdır. Müəyyən edilmişdir ki, reaksiyanın tapılmış optimal şəraitində para-arilalkilfenolun çıxımı götürülən fenola görə 78.6%, seçiciliyi 94.3% olur.Fenolun alkilləşmə reaksiyalarının tədqiqindən 100 ildən artıq müddət keçməsinə baxmayaraq, alkilfenollar və onların müxtəlif törəmələrinin alınması bu gün də öz aktuallığını itirməmişdir. Alkilfenol əsaslı kimyəvi birləşmələrin yeni səmərəli istifadə sahələri aşkarlanmaqdadır: onlar kənd təsərrüfatı zərərvericilərinə qarşı insektisidlərin, pestisidlərin və s. alınmasında, olefinlərin oliqo- və polimerləşməsində istifadə olunan katalitik prekursorlara liqand kimi, neft fraksiyalarının aromatik karbohidrogenlərdən təmizlənməsində ekstragent kimi istifadə olunurlar

Açar sözlər: *fenol, fraksiya 130-190°C, katalizator, arilalkilləşmə, para-arilalkilfenol.*

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EFFECT OF LOW OXIDATION TEMPERATURE ON PROPERTIES AND SERVICE LIFE OF PETROLEUM ROAD BITUMEN

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Studies were researched based on the quality and operating properties of oxidized road bitumen at different temperature conditions. The improvement of the quality of road oil bitumen, including the thermooxidative resistance to aging, at the production stage with the reduction of the oxidation temperature has been theoretically and empirically justified. BND 60/90 bitumen samples were taken during the research. The samples taken were analyzed according to the temperatures of 200, 220, 250 and 280 °C. Here, in order to increase the resistance of bitumen samples taken at 160 °C to aging due to thermooxidative effect, softening temperature, fragility temperature, penetration at 25 °C, mass loss, limiting shear stress, softening temperature in Petri cups and the relationships between them were studied in different regimes. It was determined that the preparation of asphalt-concrete mixtures and road surfaces from bitumen obtained as a result of oxidation of raw materials at a temperature of 220 °C is considered more favorable. It has been studied that bitumen oxidized at a temperature of 220 °C allows to extend the service life by 1.3-1.5 times due to its aging resistance.

Keywords: *bitumen, oxidation temperature, softening temperature, fragility, mass loss, road surfaces, aging resistance, limited shear stress, thermooxidative effect.*

INTRODUCTION

Oil bitumens are widely used in many fields of national economy. In economically developed countries, their production volume is 10-15% of all processed oil. More than 90% of the total amount of bitumen consumed in many industries is artificial bitumen obtained from oil; their world production is tens of millions of tons. About 10 million tons of bitumen are produced annually, and about 70% of it is road bitumen. Due to the daily needs, worldwide economic growth, road-destroying motor vehicles increase production activities. In addition, given the gradual disappearance of conventional oil, oil industries are looking for new, easier bitumen production to solve road infrastructure problems. however, they face the major challenge of developing less expensive techniques. The service life and crack resistance of the asphalt-concrete coating depends on the quality and properties of the bitumen.

Bitumen consists of a mixture of high-molecular hydrocarbons of the methane and naphthenic series and their oxygenated, sulfurous and nitrogenous derivatives. Element composition of bitumen, %: C – 70-80; H – 10-15; S – 2-9; O – 1-5; N – 0-2. These elements are found in bitumen in the form of hydrocarbons and their compounds with sulfur, oxygen and nitrogen. The chemical composition of bitumen is quite complex. Thus, they can contain saturated hydrocarbons from C_9H_{20} to $C_{30}H_{62}$. Bitumen is defined as a virtually non-volatile, adhesive, and waterproofing material derived from crude oil or present in natural asphalt, completely or nearly soluble in toluene, and highly viscous or nearly solid at ambient temperatures.

Road bitumen is mainly used for the construction and repair of road and airfield surfaces. Oil road bitumens are divided into viscous and liquid types: BND (oil road bitumen) and BN (oil bitumen). Viscous oil road bitumens are produced in five varieties: BND 40/60, BND 60/90, BND 90/130, BND 130/200, BND 200/300; oil (BN) - four types: BN 60/90, BN 90/130, BN 130/200, BN 200/300. The letters BND stand for "oil bitumen", the numbers 40/60, 60/90, etc. indicate the permissible limits for the degree of penetration depth of a standard needle at 25℃, which indirectly characterizes the viscosity of bitumen. BND brand bitumens adhere well to stone materials and have high enough plasticity at low temperatures and are resistant to climatic effects. Technical characteristics of viscous petroleum bitumen are standardized by GOST 22245-90. Viscous petroleum road bitumen is used for liquefaction in the preparation of hot, hot and cold asphalt mixes, surface cleaning, impregnation, as well as preparation of cold asphalt-concrete, surface cleaning and road mixing [1-8].

EXPERIMENTAL PART

Road bitumens have good operational properties only in a very specific proportion of their constituents. Their components are consisted of asphaltenes, resins and oils. The hardness and high softening temperature of bitumen are determined by asphaltenes, the flexibility and cementing properties by resins, and the frost resistance by oils. The dependence of the operating properties of bitumens on their chemical composition is characterized by the ratio of the asphaltene content to the total content of asphalt-resin substances A/(A+C) and their ratio to the sum of hydrocarbons and resins A/(C+M). At the same time, the specific weight of asphaltenes in the total amount of asphalt-resin substances is 0.39-0.44, and the ratio of hydrocarbons and resins is 0.25-0.30.

What we got about the composition of bitumen of data (table 1) allows to determine the main regularities between the oxidation temperature and the properties of raw materials.

Table 1

Group chemical composition of bitumens obtained at different oxidation temperatures

№	Content (by mass, %)			$\frac{A}{(A+C)}$	$\frac{A}{(C+M)}$	Bitumen brand	Oxidation temperature
	Asphaltenes (A)	Resins (C)	Oils (M)				
1	21.13	35.82	43.05	0.37	0.27	BND 60/90	200℃
2	22.10	35.18	42.72	0.39	0.28	BND 60/90	220℃
3	23.28	35.84	40.88	0.39	0.30	BND 60/90	250℃
4	27.36	36.28	36.36	0.43	0.38	BND 60/90	280℃

As expected, the oxidation of raw materials to bitumen at 250 and 280°C leads to an increase in the amount of asphaltenes, which leads to an increase in fragility temperature and a decrease in penetration. The decrease in oil content explains both the low frost resistance of these bitumens and, as a result, the low plasticity interval. However, the increased content of resins leads to their high elasticity at 25°C. Reducing the oxidation temperature to 200 and 220℃ helps to reduce the content of asphaltenes in bitumen by increasing the number of oils and keeping the same number of resins. This leads to an increase in penetration, a decrease in the fragility temperature and an increase in the plasticity interval, which allows the bitumen to show good adhesive properties. This can be explained as bitumens with a wider plastic range contain significant amounts of aromatic hydrocarbons and resinous substances, which increase the polarity of the binder and consequently improve its adhesion to stone materials. In addition, bitumens obtained from the oxidation of raw materials with a decrease in temperature to 200-220 ℃ should contain more polar and high molecular weight asphaltenes.

RESULTS AND DISCUSSION

As we mentioned above, the main technology of bitumen production in our country is the process of blowing oil residues and oil tars with air which is called oxidation. The quality of oxidized bitumen normalized by the current standard - AZS 050-2001 constitutes the requirements that meet this technology. However, the increasing demands on the materials used in road construction today require the need to improve the quality.

Bitumens obtained by the oxidation method, regardless of the origin of the raw materials, are not sufficiently resistant to aging processes as a result of thermal oxidation. To eliminate this deficiency, it can be achieved by reducing the oxidation temperature of raw materials to 200-220℃ and observing all the main parameters of oxidation at the bitumen production stage. Therefore, a decrease in the oxidation temperature should lead to an increase in the thermal oxidation resistance of bitumen.

Evaluation of thermal oxidation resistance of bitumens obtained as a result of oxidation of raw materials at temperatures of 200, 220, 250, 280 ℃ in laboratory conditions was carried out according to the method indicated below. To increase aging resistance, change in softening temperature, fragility, penetration at 25 ℃ and weight loss were determined [9].

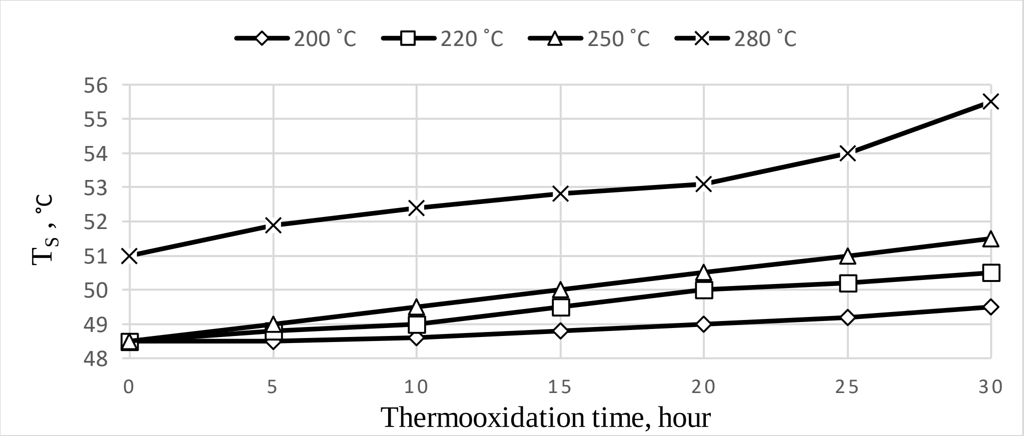

Fig.1. Change of softening temperature (T_S) of bitumen samples under thermooxidative effect at 160 ℃.

As can be seen from fig.1, the change in the softening temperature of bitumen obtained at the oxidation temperature of 200 °C is 2, 3, and 4.5 times less than the bitumen obtained at the temperatures of 220, 250, and 280 °C, respectively. In figure 2, the change in penetration is 1.4 times less in the bitumen obtained at a temperature of 280 °C. In figure 3, the change in fragility temperature of bitumen obtained at temperatures of 250 and 280 °C is 1.5 and 2 times lower.

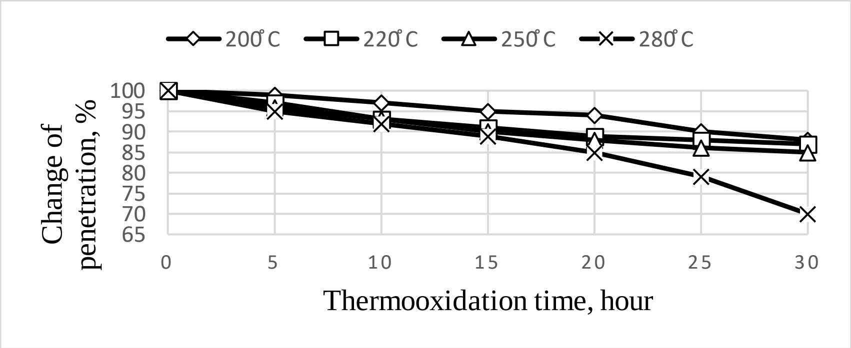

Fig.2. Change of penetration of bitumen samples at 160°C due to thermooxidative effect.

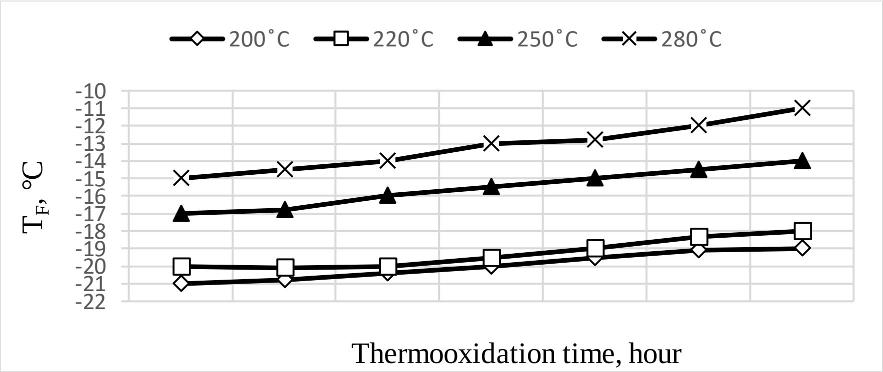

Fig.3. Change of Fraass fragility temperature (T_F) of bitumen samples under thermooxidative effect at 160°C.

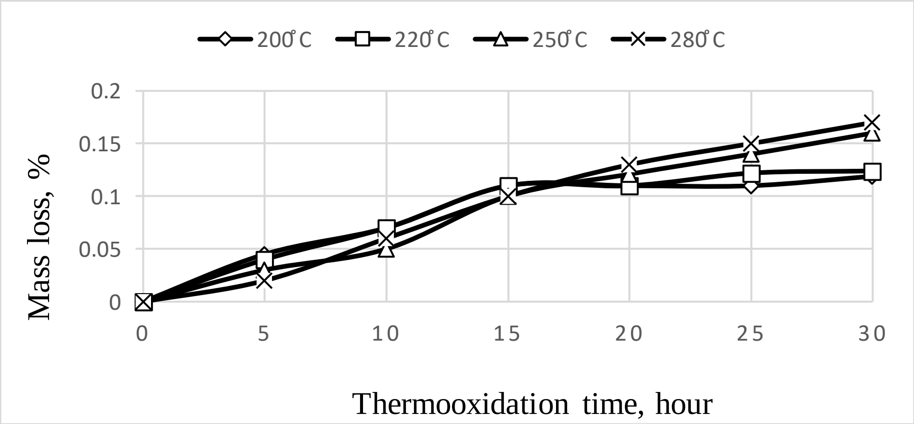

Fig.4. Mass loss (%) of bitumen samples during thermooxidative action at 160°C.

In the initial period, mass loss in bitumen obtained by oxidation occurred more intensively during temperature reduction and stabilized after 15 hours of heating (fig.4). This is believed to be related to their transition to equilibrium after oxidation.It is believed that the test stage for the aging of bitumen in a thin layer at 160℃ for 5 hours was carried out and the obtained results corresponded to the use of bitumen on pavement for one year.

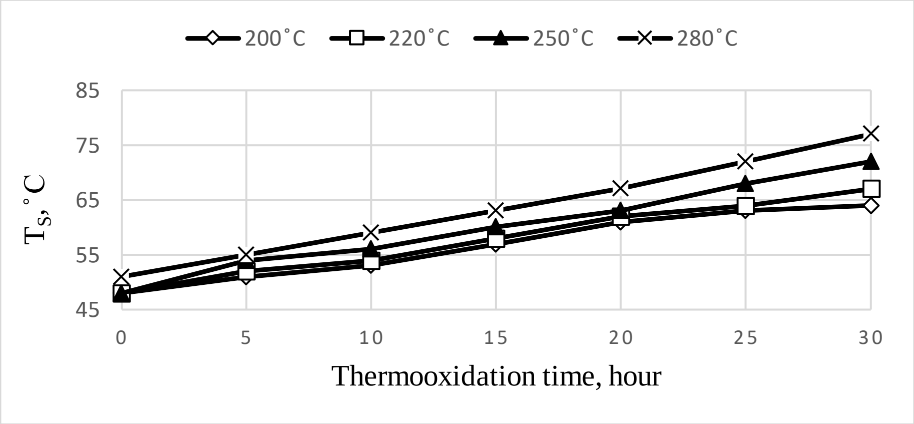

Fig.5. Variation of softening temperature (T_S) of bitumen samples placed in Petri cups at 160 ℃ under thermooxidative effect.

We determined the changes in softening temperature according to GOST 18180-78. The total time of bitumen heating reached 30 hours, and the softening temperature during heating was periodically determined every 5 hours (fig.5). In parallel, the change in the limiting motion stress in the 30 µm bitumen layer was determined.

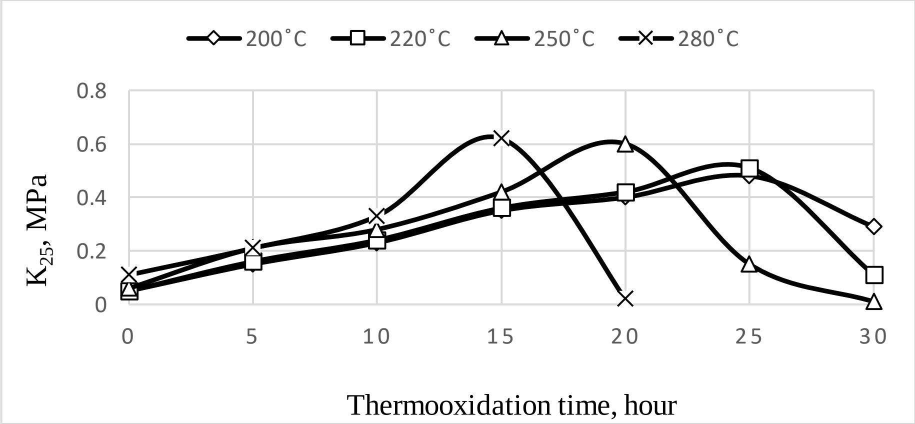

Fig.6. Change in limiting shear stress (K_{25}) of bitumen samples under thermooxidative effect at 160 ℃ temperature.

For bitumen obtained as a result of oxidation at temperatures of 200 and 220 ℃, the change in softening temperature during thermal aging of bitumen in a thin layer is less intense (fig.5).

Thus, after 30 hours of heating, the softening temperature of bitumen oxidized at high temperature increases more sharply.

According to the date in fig. 6, increasing the cohesion (adhesion) strength of the samples analyzed at the initial stage occurs due to structuring processes, which as a result, allowsimproving asphalt-concrete properties.

Later, the dispersed system is destroyed due to destruction processes. For bitumens obtained by oxidation at temperatures of 200 and 220 ℃.

This period is 1.3 times less than bitumen oxidized at 250 °C and 1.7 times less than bitumen oxidized at 280 °C.

This level corresponds to an annealing temperature in the range of 60 - 65 °C (fig. 7). At this time, asphalt-concrete coatings usually destroy bitumen observed with aging.

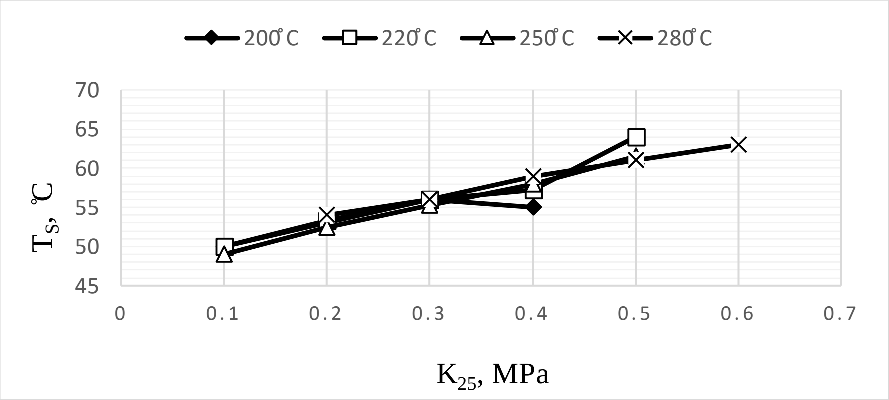

Fig.7. Relationship between softening temperature (T_S) and limiting shear stress (K_{25}) for given bitumen samples.

Similar studies aimed at studying the thermooxidative resistance to aging of bitumen samples at temperatures of 220 and 250 °C were carried out.

For each 1 kg of bitumen, the oxidation process was carried out by continuously blowing the oxidized mass of bituminous raw materials with an air supply of 0.84 – 1.40 m^3/min.

After reaching the commercial quality of the bitumen, the air supply was stopped, the bitumen was cooled by circulation through a cooler and injected into the fuel filling station.

The liquid and gaseous products formed during the oxidation process in the reactor enter the condenser-cooler, and from there the separator, where it is separated into mixed distillate (also called "black diesel fuel") and gases.

Gases are burned in the furnace. Distillate is added to boiler fuel.

The results of studying the thermooxidation resistance of bitumen obtained by industrial oxidation are the same as the data obtained for bitumen oxidized in laboratory conditions (fig.8-14).

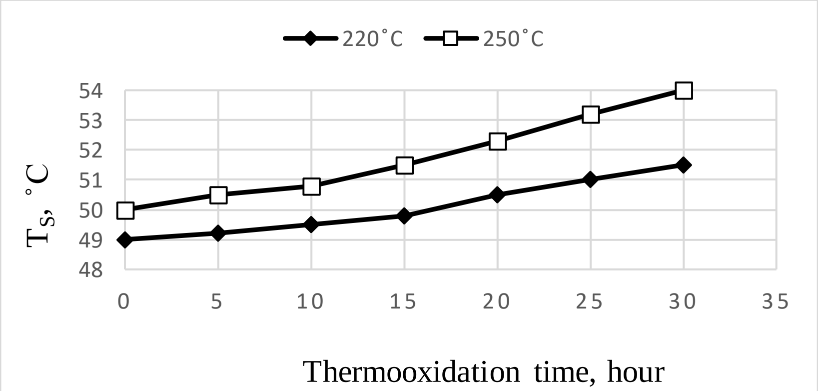

Fig.8. Change of softening temperature (T_S) of bitumen samples under thermooxidative effect at 160°C.

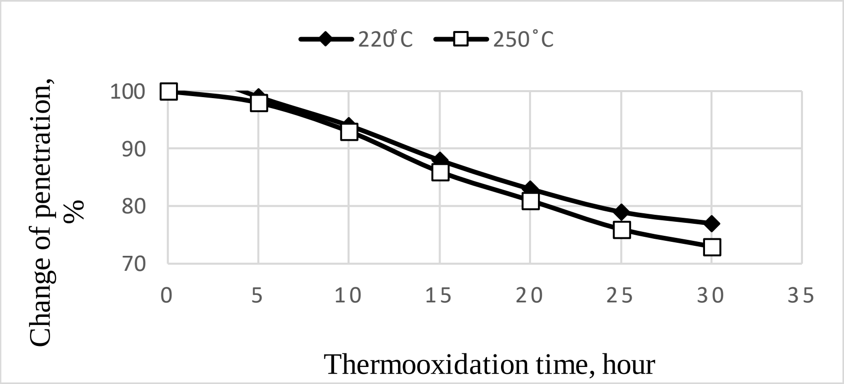

Fig.9. Change of penetration of bitumen samples at 160°C due to thermooxidative effect.

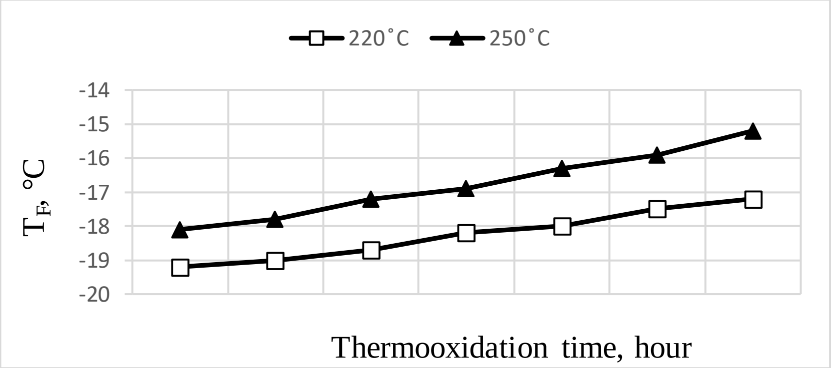

Fig.10. Change of Fraass fragility temperature (T_F) of bitumen samples under thermooxidative effect at 160°C.

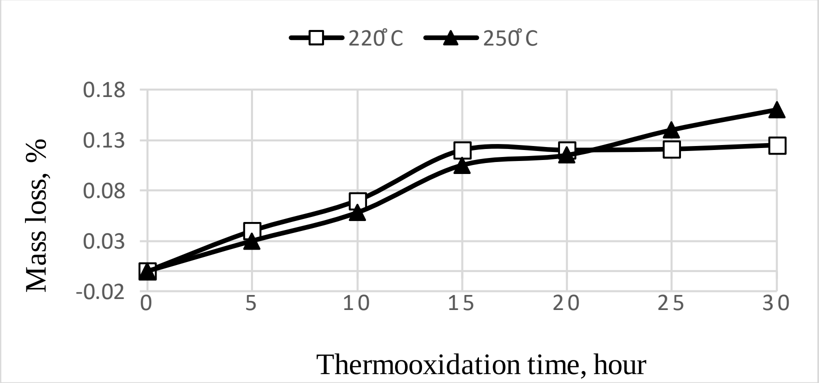

Fig.11. Mass loss (%) of bitumen samples during thermooxidative action at 160 °C.

The following conclusion can be reached based on the experiments conducted to study the thermal oxidation stability of bitumen obtained as a result of oxidation of raw materials under different temperature conditions. Reducing the oxidation temperature in the bitumen production process to 200-220°C allows obtaining a binder with increased thermooxidative resistance to aging. Despite the significant reduction in the productivity of the oxidizer, during the production of bitumen at low temperatures, road builders will build better quality and more durable asphalt concrete pavements.

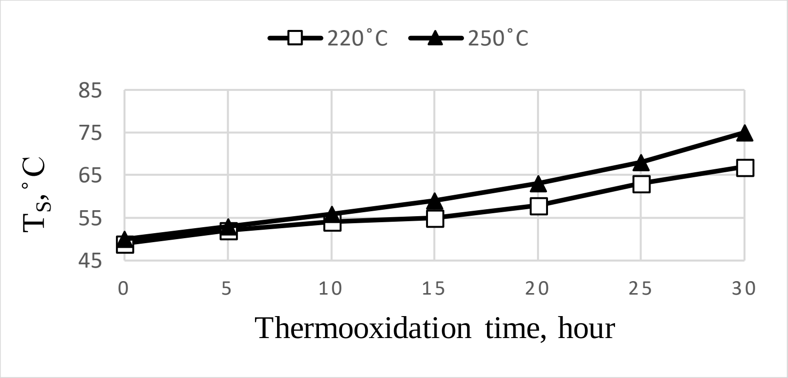

Fig.12. Variation of softening temperature (T_S) of bitumen samples placed in Petri cups at 160 °C under thermooxidative effect.

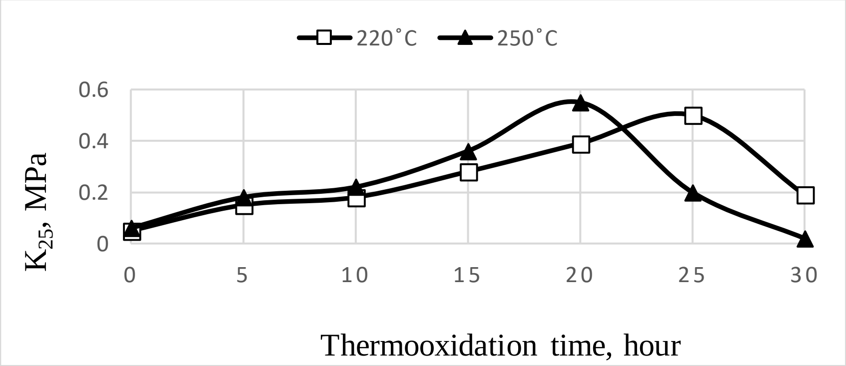

Fig.13. Change in limiting shear stress (K_{25}) of bitumen samples under thermooxidative effect at 160 °C temperature.

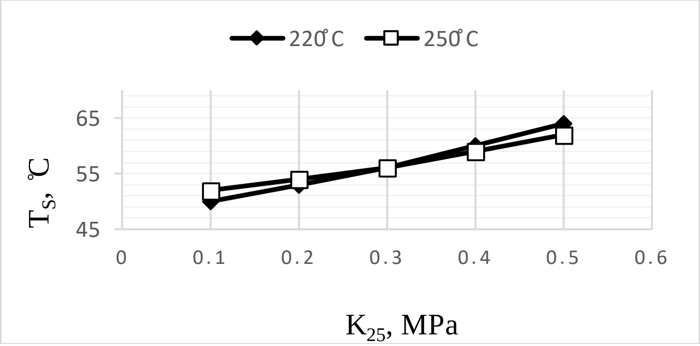

Fig. 14. Relationship between softening temperature (T_S) and limiting shear stress (K_{25}) for given bitumen samp

CONCLUSION

1. Experimental studies conducted in laboratory conditions confirmed the correctness of theoretical assumptions about the effectiveness of reducing the oxidation temperature of raw materials in bitumen production.

2. As a result of the experiments conducted on the thermooxidation stability of bitumen obtained as a result of the oxidation of raw materials at different temperature conditions, it was found that reducing the oxidation temperature to 200-220°C during bitumen production allows saving energy.
3. The conducted regression analysis proved the regularity of the influence of the oxidation temperature of raw materials on their thermooxidative resistance to aging in bitumen production. The higher the bitumen production temperature, the faster it ages out.
4. Bitumen obtained as a result of oxidation of raw materials at a temperature of 220 °C is considered more favorable for preparing asphalt-concrete mixtures.
5. Aging resistance of bitumen allows to extend the service life by 1.3-1.5 times.

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ВЛИЯНИЕ НИЗКОЙ ТЕМПЕРАТУРЫ ОКИСЛЕНИЯ НА СВОЙСТВА И СРОК СЛУЖБЫ НЕФТЯНЫХ ДОРОЖНЫХ БИТУМОВ

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Исследования проводились на основе качества и эксплуатационных свойств окисленных дорожных битумов в различных температурных условиях. Теоретически и эмпирически обосновано повышение качества дорожных нефтяных битумов, в том числе *термоокислительной стойкости к старению, на стадии производства при снижении температуры окисления. При проведении исследований были отобраны образцы битума БНД 60/90. Взятые пробы анализировали при температурах 200, 220, 250 и 280℃. Здесь для повышения стойкости образцов битума, отобранных при 160℃, к старению за счет термоокислительного эффекта, температуры размягчения, температуры хрупкости, пенетрации при 25℃, потери массы, предельного напряжения сдвига, температуры размягчения в чашках Петри и соотношений между ними изучались в разных режимах. Определено, что более выгодным считается приготовление асфальтобетонных смесей и дорожных покрытий из битума, полученного в результате окисления сырья при температуре 220°С. Изучено, что окисление битума при температуре 220℃ позволяет продлить срок службы в 1,3-1,5 раза за счет его стойкости к старению.*

Ключевые слова: *битум, температура окисления, температура размягчения, хрупкость, потеря массы, дорожные покрытия, устойчивость к старению, ограниченное напряжение сдвига, термоокислительный эффект.*

AŞAĞI OKSİDLƏNMƏ TEMPERATURUNUN NEFT YOL BİTUMLARININ XASSƏLƏRİNƏ VƏ İSTİSMAR MÜDDƏTİNƏ TƏSİRİ

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Oksidləşmiş yol bitumlarının müxtəlif temperatur şəraitlərində keyfiyyəti və istismar xassələri əsasında tədqiqatlar aparılmışdır. Oksidləşmə temperaturunun azalması ilə istehsal mərhələsində yol neft bitumunun keyfiyyətinin, o cümlədən köhnəlməyə qarşı termooksidləşdirici dayanıqlılığının yaxşılaşdırılmasını nəzəri və təcrübi cəhətdən əsaslandırılmışdır. Tədqiqat zamanı BND 60/90 markalı bitum nümunələri götürülmüşdür. Götürülən nümunələr 200, 220, 250 və 280℃ temperaturlara uyğun olaraq analiz edilmişdir. Burada 160℃ temperaturda götürülən bitum nümunələrinin termooksidləşdirici təsir nəticəsində köhnəlməyə qarşı dayanıqlılığını artırmaq məqsədi ilə müxtəlif rejimlərdə yumşalma temperaturu, kövrəklik temperaturu, 25℃ olan penetrasiyası, kütlə itkisi, məhdudlaşdırıcı sürüşmə gərginliyi, Petri boşqablarında olan yumşalma temperaturu və onlar arasındakı əlaqələr üzrə tədqiqatlar aparılmışdır. Müəyyən edilmişdir ki, xammalın 220°C temperaturda oksidləşməsi nəticəsində alınan bitumlardan asfalt-beton qarışıqlarının, eləcə də yol səthlərinin hazırlanması daha əlverişli hesab olunur. Tədqiq edilmişdir ki, 22℃ temperaturda oksidləşmiş bitum köhnəlməyə qarşı davamlılığına görə istismar müddətini 1,3-1,5 dəfə uzatmağa imkan verir.

Açar sözlər: *bitum, oksidləşmə temperaturu, yumşalma temperaturu, kövrəklik, kütlə itkisi, yol səthləri, köhnəlməyə qarşı dayanıqlılıq, məhdud kəsilmə gərginliyi, termooksidləşdirici təsir.*

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TAKING CONCRETE SAMPLES BASED ON WASTE ALUMINUM

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The presented article is about obtaining concrete samples using aluminum generated as waste or by-product from household, industry. Shikhlar sand, M400 cement produced by the Norm plant, and various aluminum wastes were used as starting raw materials for the purchase of concrete samples. Concrete samples based on waste aluminum were prepared according to the mixing ratios of M500 concrete, known from the industry. Various aluminum wastes (aluminum wire, aluminum foil and aluminum sawdust) 5%, 10% gravel, which is a natural raw material in concrete samples. 15%, 25%, 30%. The indicators of the received concrete samples were compared with the indicators of classical concrete.

Keywords: *solid industrial waste, waste aluminum, recycling, obtaining concrete samples.*

INTRODUCTION

In today's world, the increase in the volume of consumption and related production has also increased the demand for natural resources. In this case, there is a shortage of raw materials needed for production, which causes a delay in the process. As a result, the possibility of meeting the ever-increasing consumer needs decreases. In recent years, as a way out of this situation, recycling has been directed [1].

By means of recycling, the waste considered unsuitable for use gains the ability to be produced and consumed again. Recycling meets the raw material needs of production and at the same time creates economic efficiency because it provides raw materials that cost less in terms of energy and budget [1].

Based on research studies, 3778.2 thousand tons of waste were generated in Azerbaijan in 2021. This amount is 9.4% more than the previous year. 68.3% of the collected waste was solid household waste. 31.7% was waste generated during the production activity of various enterprises. 12.3% of production waste generated in different areas of industry was used as raw material in enterprises. The remaining 34.2% was sold within the country, and 1.8% was exported. 6.9% of production waste was placed in landfills for disposal, 44.8% remained in enterprises [2].

Waste is classified into different categories. For example, production (industry) and consumption (municipal-household) waste.Recyclable waste includes bio-waste, polyethylene, metal, glass, paper, cardboard, etc. includes. Aluminum is the most widely used metal material in the world after steel, and its annual consumption is 88 million tons [3]. According to the North American Aluminum Industry Sustainability Report published by the Aluminum Association, worldwide aluminum recycling is increasing up to 90% in transportation and construction, and up to 70% in the production of beverage cans [4-11].

The properties of aluminum make it suitable for its use as an important material in construction and other fields. Thus, aluminum is a light and active metal: Aluminum's inherent strength makes it particularly useful as a structural material, weighing up to 65% less than steel. Aluminum is naturally corrosion resistantcreates a protective oxide coating. Various types of surface treatments can further enhance this feature. Aluminum material integrity and processingit can be made in any shape and size without compromising its ability. Aluminum is a good reflector of visible light and heat. This makes it an ideal material for reflecting sunlight and saving energy. Recyclable aluminum can be recycled without losing its quality [5,6]. Aluminum remelting saves up to 92% of the energy required for primary aluminum production. Aluminum construction products and their surface treatments do not pose a threat to the environment during use [12].

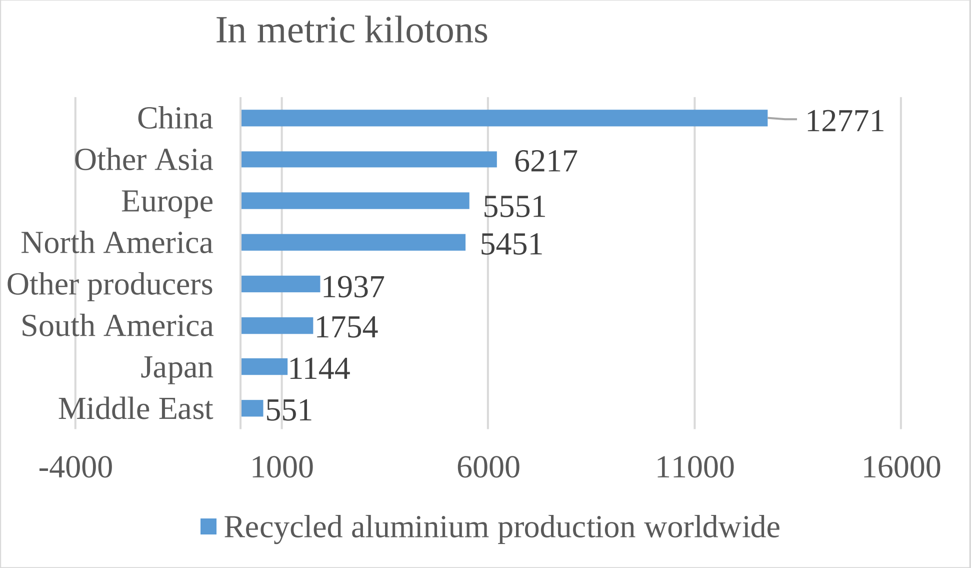

Fig. 1. Global production of recycled aluminum in 2021.

In 2021, China was at the forefront of recycled aluminum production, recycling about 12,771 metric tons of the metal that year. Despite being third in the standingsWith Europe recycling half the volume of the Chinese market, it left all other countries behind (fig.1.).

The main purpose of the research work was to obtain concrete samples from the point of view of environmental and economic efficiency using aluminum, which is household and industrial waste. It is to create raw material for recycling business by using aluminum waste. It is to buy new concrete samples using waste aluminum as raw material and compare the results obtained with the purchase of classic concrete.

EXPERIMENTAL PART

In the preparation of concrete samples, waste aluminum was used as a substitute and reusable raw material for natural gravel.

During the research, concrete samples were taken in laboratory conditions based on aluminum waste. Concrete samples were prepared based on aluminum foil obtained from household waste, aluminum sawdust and wire from industrial waste, M400 cement produced by Norm plant, Shikhlar sand, gravel and water.The natural gravel used in the concrete samples was crushed, sieved with a size of 3-7 mm, washed and dried in an oven. Gravel, which is a natural raw material, was replaced with aluminum waste containing 5%, 10%, 15%, 25%, 30%. The ratio of water and cement was taken the same in all samples.

RESULTS AND DISCUSSION

The purchase of concrete samples on the basis of waste aluminum was carried out in accordance with the procedure for the preparation of M500 brand concrete known from classical literature. Accordingly, the initial raw materials of the concrete materials purchased on the basis of aluminum sawdust, foil and wire are given in tables 1-3.

Table 1

Mass composition of concrete samples based on aluminum sawdust

Concrete samples	Percentages of recycled aggregates %	Water/Cement	Starting raw materials g/cm^3				
			Cement	Water	Rude aggregate		Fine aggregate
					Natural raw materials	Recycled raw materials	Natural raw materials
Y5	5%	0.401	132.72	53	327.8	17.2	225.62
Y10	10%	0.401	132.72	53	310.5	34.5	225.62

Y5- 5% used aluminum sawdust
Y10- 10% used aluminum sawdust

As can be seen from table 1, crushed waste aluminum sawdust was taken with different percentage contents (5%, 10%) and replaced gravel, which is a natural raw material. The used gravel is pre-fractionated and washed and dried.

Table 2

Mass composition of concrete samples based on aluminum foil

Concrete samples	Percentages of recycled aggregates %	Water/Cement	Starting raw materials g/cm3				
			Cement	Water	Coarse aggregate		Fine aggregate
					Naturally raw material	Recycled raw materials	Natural raw materials
F5	5%	0.401	132.72	53	327.8	17.2	225.62
F10	10%	0.401	132.72	53	310.5	34.5	225.62

F5- 5% used aluminum foil
F10- 10% used aluminum foil

Table 2 shows the mixing composition of concrete sample materials made on the basis of household waste aluminum foil. Aluminum foil has replaced gravel, which is a natural raw material, with 5% and 10% contents.

In Table 3, aluminum-based wire scraps replaced gravel, which is a natural raw material, in contents of 5%, 10%, 15%, 25%, 30%. The concrete samples were prepared in a rectangular mold of size 4x4x16 cm and a cube mold of size 4x4x4 cm. The samples were dried in the open air for 28 days without sunlight

Table 3

Mass composition of concrete samples based on aluminum wire

Concrete samples	Percentages of recycled aggregates %	Water/Cement	Starting raw materials g/cm3				
			Cement	Water	Coarse Aggregate		Fine aggregate
					Natural raw materials	Recycled raw materials	Natural raw materials
M5	5%	0.401	132.72	53	327.8	17.2	225.62
M10	10%	0.401	132.72	53	310.5	34.5	225.62
M15	15%	0.401	132.72	53	293.3	51.7	225.62
M25	25%	0.401	132.72	53	258.8	86.2	225.62
M30	30%	0.401	132.72	53	241.5	103.5	225.62

M5 - 5% used aluminum foil
M10- 10% used aluminum foil
M15- 15% used aluminum foil
M25- 25% used aluminum foil
M30- 30% used aluminum foil

Hardening, workability and swelling of concrete were also observed and recorded. The drying of the received concrete samples does not lag behind the drying of classic concrete. The study aims to study some properties of concrete samples (density, water resistance, resistance to temperature, shock and bending) obtained from aluminum waste by saving local and natural raw materials.

CONCLUSION

The formation of aluminum-based waste, sources of generation, environmental effects, possibilities of reuse were studied. In the research work, concrete samples were obtained using aluminum waste in the content of 5%, 10%, 15%, 25%, 30%. The drying time of these samples is not far behind the drying time of classic concrete composites. Thus, the reuse of waste aluminum can play a positive role in solving environmental problems, reducing the amount of waste, and saving raw materials.

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ОТБОР ОБРАЗЦОВ БЕТОНА НА ОСНОВЕ ОТХОДОВ АЛЮМИНИЯ

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Представленная статья посвящена получению образцов бетона с использованием алюминия, образующегося в виде отходов или побочного продукта в быту, *промышленности. В качестве исходного сырья для получения образцов бетона использовали Шихларский песок, цемент марки М400 производства завода «Норм», различные отходы алюминия. Образцы бетона, на основе алюминиевых отходов, готовили в соответствии с известными в промышленности соотношениями смешивания бетона марки М500. Различные отходы алюминия (алюминиевая проволока, алюминиевая фольга и алюминиевые опилки) заменили, 5%, 10%, 15%, 25%, 30% гравия, являющийся природным сырьем в образцах бетона. Показатели полученных образцов бетона сравнивались с показателями классического бетона.*

Ключевые слова: *твердые промышленные отходы, отходы алюминия, переработка, получение образцов бетона.*

TULLANTI ALÜMİNİUM ƏSASINDA BETON NÜMUNƏLƏRİNALINMASI

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Təqdim olunan məqalə məişətdən, sənayedən tullantı kimi və ya yan məhsul kimi yaranan alüminiumdan istifadə etməklə beton nümunələrinin alınmasıdır. Beton nümunələrinin alınmasında başlanğıc xammal olaraq Şıxlar qumu, Norm zavodunun istehsalı olan M400 markalı sement, müxtəlif alüminium tullantıları istifadə olunmuşdur. Tullantı alüminium əsasında beton nümunələri sənayedən məlum olan M500 markalı betonun qarışma nisbətlərinə uyğun olaraq hazırlanmışdır. Müxtəlif alüminium tullantıları (alüminium məftil, alüminium folqa və alüminium yonqar) beton nümunələrində təbii xammal olan çınqılı 5%, 10%. 15 %, 25%, 30% nisbətlərində əvəz etmişdir. Alınan beton nümunələrin göstıriciləri klassik betonun göstəriciləri ilə müqayisə olunmuşdur.

Açar sözlər: *bərk sənaye tullantıları, alüminium tullantıları, təkrar emal, beton nümunələrinin alınması.*

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RESULTS OBTAINED IN THE DIRECTION OF PRODUCING AVIATION OILS FROM THE MIXTURE OF BAKU “NEFT DASHLARI” OILS

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The purpose of the currently presented article is to obtain some results in the direction of producing aviation oils from a mixture of Baku "Neft Dashlari" oils. Deasphaltizates (I and II stages) obtained as a result of the tar deasphalting of "Neft Dashlari" oil were used as raw materials. In order to increase the chemical resistance of the oil, processing of the oil with various reagents was carried out with different methodologies, including using ordinary 98% sulfuric acid and bleaching earth, neutralization with activated sulfuric acid and bleaching earth, some adsorbents, including silica gel, and selective solvents.

Based on the obtained results, it can be noted that the deasphaltizate of ready "Neft Dashlari" oil can be used as a raw material for the production of high-grade aviation oils. The most effective and, at the same time, the most cost-effective way of cleaning is the cleaning of the deasphaltizate of "Neft Dashlari" oil with NM-Pyrollidone. Here, the versatility of the method and the fact that not only the stability of the oil but also the viscosity curve improve, however, at the same time as a result of processing with significant losses of oil and reagent, attract special attention.

All the other methods described in this article have some effect, that is, firstly, either the chemical stability is increased or the viscosity curve is improved, and therefore their combination is required; secondly, they are still less effective and also require large losses.

***Keywords**: aviation oils, NM-Pyrrolidone, selective solvent, sulfuric acid, viscosity, viscosity index, silica gel, sulfuric acid.*

INTRODUCTION

Over the past few decades, many advancements have taken place in the field of aviation, which has led to an increase in the demand for modern oils. Improvements in engine performance through more modern maintenance practices and increased fuel efficiency, resulting in higher operating temperatures and pressures, have been the basis for the development of modern aviation oils [8-10].

The primary functions of oils within an engine include services such as reducing friction, cooling, sealing, cleaning, and protecting moving parts. Aviation oils form a fluid barrier between moving parts to prevent friction and wear. As for cooling, oil provides up to 40 percent of the cooling of an aircraft's air-cooled engine. The oil creates a seal between the piston rings and the cylinder walls. This helps reduce wear, provide better compression and keep contaminants out of the system while improving fuel efficiency [11-13].

Oils become contaminated when they are used in engines. Contaminated oils are cleaned of dirt, metallic materials and unburned carbon by means of an effective dispersant. Oils must be renewed at certain intervals. A typical oil change interval varies between 25-50 hours depending on the type of engine. In addition to the hourly interval, oils should be changed quarterly or seasonally. This process helps prevent corrosion by removing moisture from the engine and oil. Oil types were developed by the military in the 1940s and later standardized by the Society of Automotive Engineers (SAE). The system classifies engine oils according to their viscosity. Oils are classified according to their viscosity measured at high temperature for single-grade oils and at low and high temperatures for multi-grade oils.

A different viscosity classification is used for aircraft engines than automotive and SAE. 65W-30, 80W-40, 100W-50 and 120W-60 standards are applicable for aircraft engines. Later, the SAE automotive classification system was adopted for aviation multigrade oils, and ranges such as 15W-50, 20W-50, 25W-60 can be found [3].

SAE standards for lubricants include J1966 and J1899. SAE standard J1966 specifies requirements for non-dispersible (single grade) mineral lubricants used in four-stroke piston aircraft engines. It covers the same requirements as the former MIL-L-6082 military specification. J1899 specifies requirements for lubricating oils containing ashless dispersant additives, identical to MIL-L-22851 [1].

Below are some technical terms, specifications, and descriptions of the various types of lubricants used in the aviation piston engine industry.

Viscosity is a measure of an oil's resistance to shear or flow. High viscosity indicates high resistance to flow and low viscosity indicates low resistance. It varies depending on the temperature and also depends on the pressure. An increase in temperature causes a decrease in viscosity, while a decrease in temperature causes an increase in viscosity. High pressure causes an increase in viscosity, which increases the film thickness of the oil. Viscosity is measured by shear and time. When measured by shear, it is expressed in centipoise and is known as dynamic viscosity. Kinematic viscosity is expressed in centistokes and is usually given at two temperatures, 40 ^{o}C and 100 ^{o}C. Kinematic viscosity is measured as the time taken for a sample of oil to flow through a viscosity tube at standard temperature. This value is converted into centistokes [4].

While viscosity is an oil's intrinsic resistance to flow, its viscosity index is simply its resistance to changing flow characteristics as a result of temperature changes. If the oil's viscosity changes very little despite significant temperature changes, the oil has a high viscosity index. The viscosity index is an arbitrary numbering system. Higher numbers mean the oil's viscosity changes less with temperature, while lower numbers mean it changes more. Single-grade oils typically have a viscosity index of 90 to 110. Multigrade oils with a viscosity index of 150 or higher can withstand extreme temperature changes and maintain their viscosity characteristics better. Some automatic transmission fluids are so multigrade that they can have a viscosity index of 200. Multigrade oils are common in applications such as aviation oil, automatic transmission fluid, power steering fluid, gear oil, and hydraulic fluid.

Viscosity index can be increased by adding viscosity modifiers or viscosity index improvers to base oils. Several types of polymers are used to modify the viscosity index of aviation oils. Viscosity modifiers are available in a variety of molecular weights, so they can be selected based on the most desirable performance and cost characteristics.

Along with the viscosity, the pour point of oils is also determined, which is considered the lowest temperature at which the oil will flow. Oils are usually selected if the pour point is ensured to be significantly lower at the expected ambient temperatures.

The flash or flash point of oils is the lowest temperature to which a lubricant must be heated before it vaporizes, ignites when mixed with air and exposed to a flame source, but does not continue to burn. It is used to determine transport and storage temperature requirements along with potential product contamination [7].

Paraffin-naphthenic oils are available in Azerbaijan, and a number of them, including aviation oils, are being studied. The purpose of the currently presented article is devoted to obtaining some results in the direction of producing aviation oils from the mixture of Baku "Neft Dashlari" oils.

EXPERIMENTAL PART

Deasphaltizates [6] (stage Ⅰ and Ⅱ) obtained as a result of tar deasphalting of Neft Dashlari oil were used as raw materials (table 1).

The data given in Table 1 were obtained as a result of the study of the properties of the Neft Dashlari oil reserve.

Table 1

Standard properties of "Neft Dashlari" oil

Standard Properties	"Neft Dashlari" oil	
	Ⅰ stage	Ⅱ stage
Density 15 ºC	0.905	0.905
Viscosity 100 ºC E_{100}	3.65	4.12
Viscosity 50 ºC E_{50}	32	38.7
Viscosity index	93	90
Flash point ºC (Brenken)	258	258
Flash point ºC (MP)	270	271
Freezing temperature ºC	-10	-10
Coking rate according to Conradson	0.8	0.8
Ash content in weight percent	0.003	0.002
Acidity in mg KOH	0.00	0.00
Resins according to Marcousson	2.6	2.6

Simultaneously with the study of standard properties, the stability and chemical stability of "Neft Dashlari" oil was determined.

Its stability is determined by oxidizing the oil with oxygen in a special flask at a temperature of 200ºC under slight pressure for 2.6 hours.

RESULTS AND DISCUSSION

In terms of stability, the deasphaltizate obtained from "Neft Dashlari" cannot be directly used as aviation oil, so we intend to conduct research by presenting a number of purification methods.

In order to increase the chemical resistance of the oil, the treatment of the oil with various reagents was carried out with the following methodology [5]:

a) Neutralization with conventional 98% sulfuric acid and bleaching earth.
b) Neutralization with activated sulfuric acid and bleaching earth.

c) Some adsorbents, including silica gel.
d) Selective solvents.

a) Cleaning oil with conventional 98% sulfuric acid and bleaching earth**.**Acids are taken in the amount of 1 and 3% of the total oil. 10 and 30% bleaching earth is taken. Acid is added to oil at a temperature of 30-40 ºC and mixed with oil for 1 hour. Precipitation lasts for 20 hours: after precipitation, the acid resin falls down and the bleaching soil of Zikeyevo is added to the oil. Mixing the oil with the soil lasts about 1 hour. Separation of soil from oil is carried out with a manual filter press.

It should be noted that the viscosity does not undergo a noticeable change, although there is a certain general decrease and some improvement in it.

Table 2

Dependence of the coking number on the amount of sulfuric acid

Sulfuric acid content %	Coking number
0	16
0.2	13.6
0.4	12.2
0.6	11
0.8	10.3
1	9.8
1.5	9.1
2	8.8
3	8.6

b) Cleaning oil with activated sulfuric acid**.** The activation of the acid was obtained by adding different concentrations of potassium dichromate ($K_2Cr_2O_7$). Cleaning conditions: acid cleaning temperature 30-40 ºC, soil cleaning temperature 150 ºC.

Treatment of oil with activated acid significantly improves chemical resistance and in some cases (5% activated acid and 40% soil) significantly reduces the overall viscosity of the oil, and also slightly improves the viscosity index; but at the same time, if we compare these results with those obtained during cleaning with ordinary sulfuric acid, it can be concluded that the activated acid does not have a greater effect.

Table 3

% dependence of the coking number on the amount of Sulfuric acid ($K_2Cr_2O_7$)

Sulfuric acid content (%) %$K_2Cr_2O_7$	Coking number
0	15
0.2	13.9
0.4	13.1
0.6	11.9
0.8	11
1	10
1.5	8.9
2	8
3	7.8

c) Cleaning of oil deasphaltizate from “Neft Dashlari” oil with adsorbents**.** Bleaching Zikey soil. The first experiments were conducted with Zikey soil. As a result, oil samples with the following qualities were obtained (graph 1). It is also clear from the graph that it is possible to obtain high-quality samples with high chemical stability by treating the oil with Zikey soil. It should be noted that although the improvement of oil stability is directly proportional to the increase in the amount of adsorbent added to the oil, this dependence occurs only to a certain extent.

Here, the turning point and at the same time the optimal soil area should be considered in the amount of 40%; Oil treated with this amount has the best quality in terms of resistance, but oil treated with 60% is considered the worst. It can be seen that the results obtained here and the conclusions drawn regarding the improvement of chemical resistance coincide with the opinions repeatedly expressed by researchers working in this field.

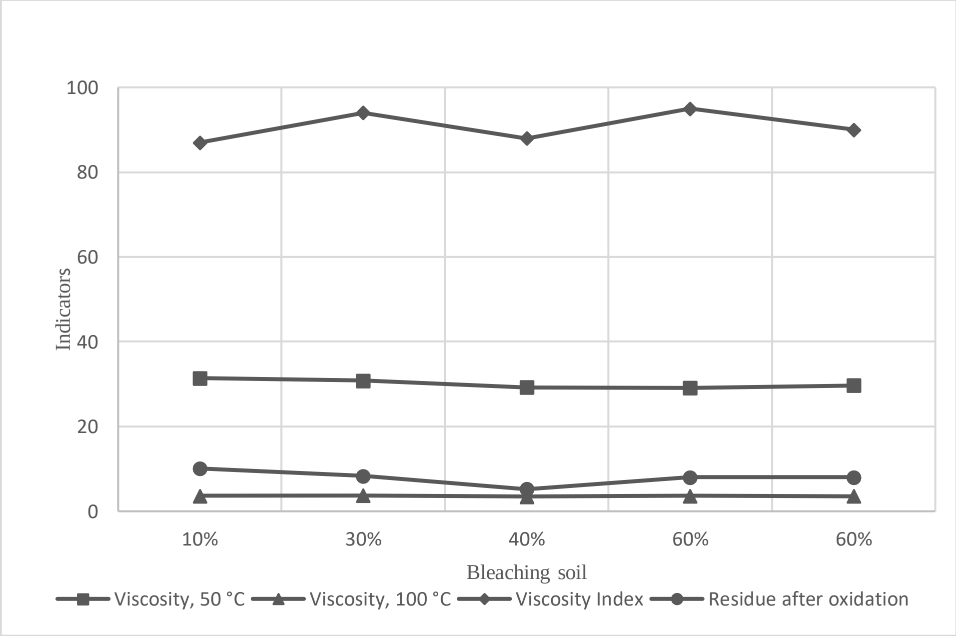

Fig.1. Dependence of certain indicators on the amount of bleaching earth

It should also be noted that a certain general decrease in the viscosity of oil is observed during purification with Zikeyevo soil, but it is obvious that this decrease is practically insignificant and cannot be of any importance.

Silica gel. The results of the experiments on the purification of "Neft Dashlari" oil asphalt with silica gel are given in the graph below.

It is very important to note that when oil is cleaned with silica gel, the improvement of the chemical resistance of the obtained samples occurs more sharply than when cleaned with Zikeyevo soil. Already 10% silica gel is enough to reach almost optimal values for stability. Further increase in the amount of silica gel no longer has a noticeable effect. In its lower part, the curve follows a straight line to increase the chemical resistance of the oil.

d) Treatment of oil with selective solvents is carried out either in separating funnels or in metal reactors with mixing.

The reaction mixture is heated in an oil bath or over an open flame. Precipitation of NM-Pyrrollidone and furfurol occurs at about 15-20ºC.

After precipitation, the oil was distilled with superheated steam at a temperature of 200-220ºC for NM-Pyrrollidone and 120-130ºC for furfurol, as the oil still contained some of the solvent In order to find the optimal conditions for cleaning with NM-Pyrrollidone, for example: processing temperature, precipitation temperature, exposure time and amount of reagent, many experiments were conducted, as a result of which it can be concluded that with NM-Pyrrollidone cleaning, the oil is processed in several stages.

The most optimal temperature during processing is 35 and 85 ºC. A number of experiments have shown that at low temperatures (about 25-40 ºC) a better and more complete removal of the high-viscosity part of the oil and a relatively small amount of asphalt-resin substances; was clearly noticeable with a slight improvement in color and coke content (not less than 0.40).

Precipitation of NM-Pyrrollidon with extracted substances was carried out at a temperature not exceeding 20 ºC.

The table below shows the results of deasphaltization of "Neft Dashlari" oil using NM-Pyrrolidone. Purification with NM-Pyrrollidone takes place in two steps: one at 85 ºC and another at 35 ºC.

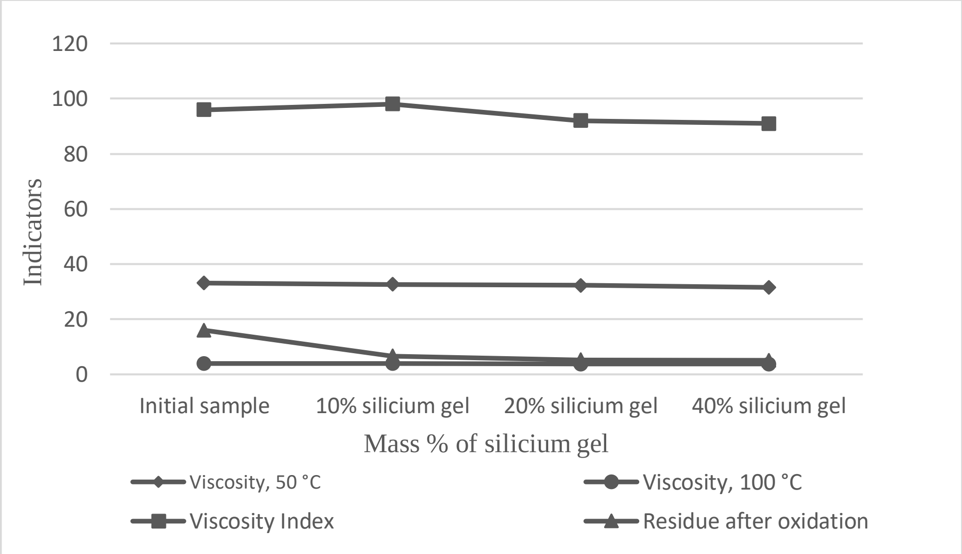

Fig.2. Oil purification with silica gel.

Table 4

The effect of the amount of silica gel on the coking number.

Amount of silica gel, mass %	Coking number
0	16
1	14
2	12
5	8.4
7	7.5
8	7
9	6.5
10	6.1
15	5.2
20	5.1
30	5.1

The data in table 5 shows that approximately 150% NM-Pyrrollidone by volume of oil is sufficient to obtain high-quality samples.

Table 5

Refinement of "Neft Dashlari" oil deasphaltizate with NM-Pyrrollidone

Indicators	Original oil	100% NM-Pyrrolidone	150% NM-Pyrrolidone	300% NM-Pyrrolidone
Viscosity, 50ºC	36	28.5	27.36	26.68
Viscosity, 100ºC	4.1	3.83	3.94	3.83
Viscosity index	95	106	112	112
Resin, mg	3	0.76	0.6	-
Amount of coke, mg	0.87	0.58	0.2	0.21
Sediment, mg	16	0	0	0
Iodine number	1.57	0.56	0.65	0.57
Flash Temperature ºC	270	280	285	-

Under favorable processing conditions, the yield of refined oil is always equal to 85-90% of the weight of the initial product.

Under favorable processing conditions, the yield of refined oil is always equal to 85-90% of the weight of the initial product.

As for the remaining 10-15% extracted with NM-Pyrrollidone, this extract turns into a highly viscous dark green oil after the NM-Pyrrollidone is distilled. Its indicators are as follows:

Table 6

Performance of NM-Pyrrollidone after distillation

Density 15ºC	0.942	Iodine number	5.5
Viscosity 100ºC	5.6	Coke	3.0
Heavy asphalt	0.0	Tar	6
Flash point ºC	255		

Thus, by treatment with NM-Pyrrollidone, the deasphaltizate of "Neft Dashlari" oil is split into two fractions, each of which becomes a fully usable benign oil. Based on the changes in the properties of refined oils (reduced viscosity at low temperatures, reduced iodine, tar, and coke content), it can be assumed that NM-Pyrrollidone extracts from "Neft Dashlari" oil deasphaltate, mainly high molecular weight, polycyclic naphthenic and aromatic hydrocarbons are the main carriers of viscosity, as well as is a significant part of unsaturated compounds and asphalt-resin substances.

CONCLUSION

Summarizing the results of the work done in terms of finding ways to improve the deasphaltization of "Neft Dashlari" oil, the following general conclusions can be drawn.

1. The deasphaltizate of finished "Neft Dashlari" oil can serve as a raw material for the production of high-grade aviation oils.
2. The most effective and at the same time the most cost-effective way of cleaning is the cleaning of the deasphaltizate of "Neft Dashlari" oil with NM-Pyrollidone.

Here, the versatility of the method, the fact that not only the stability of the oil but also the viscosity curve is improved at the same time as a result of processing with significant losses of oil and reagent, is particularly fascinating.

All the other methods described in this article have some effect, that is, firstly, either the chemical stability is increased or the viscosity curve is improved, and therefore their combination is required, and secondly, they are still less effective, and also require large losses.

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РЕЗУЛЬТАТЫ, ПОЛУЧЕННЫЕ В НАПРАВЛЕНИИ ПРОИЗВОДСТВА АВИАЦИОННЫХ МАСЕЛ ИЗ СМЕСИ МАСЕЛ БАКУ "НЕФТ ДАШЛАРЫ"

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Цель представленной статьи посвящена получению некоторых результатов в направлении получения авиационных масел из смеси бакинских масел «Нефть Дашлары». В качестве сырья использовали деасфальтизаты (I и II стадии), полученные в результате деасфальтизации нефти «Нефть Дашлары». С целью повышения химической стойкости масла проводилась обработка масла различными реагентами по разным методикам с использованием обычной 98%-ной серной кислоты и белильной земли, нейтрализации активированной серной кислотой и белильной землей, некоторых адсорбентов, в том числе силикагеля, и селективные растворители.

На основании полученных результатов можно отметить, что деасфальтизат готовой нефти «Нефть Дашлары» может быть использован в качестве сырья для производства высокосортных авиационных масел. Наиболее эффективным и в то же время наиболее экономичным способом очистки является очистка деасфальтизата нефти «Нефть Дашлары» НМ-Пиролидоном. Здесь особое внимание обращают на себя универсальность метода, то, что улучшается не только стабильность масла, но и кривая вязкости, но при этом в результате обработки со значительными потерями масла и реагента.

Все остальные методы, описанные в этой статье, имеют некоторый эффект, то есть, во-первых, либо повышается химическая стабильность, либо улучшается кривая вязкости, и поэтому требуется их комбинация, а во-вторых, они все же менее эффективны, а также требуют больших потери.

***Ключевые слова**: Авиационные масла, NM-пирролидон, селективный растворитель, серная кислота, вязкость, индекс вязкости, силикагель, серная кислота.*

BAKININ “NEFT DAŞILARI” NEFTLƏRİNİN QARIŞIĞINDAN AVİASİYA YAĞLARININ ALINMASI İSTİQAMƏTİNDƏ ƏLDƏ OLUNAN BƏZİ NƏTİCƏLƏR

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Hal-hazırda təqdim olunan məqalənin məqsədi Bakının “Neft daşları” neftlərinin qarışığından aviasiya yağlarının alınması istiqamətində əldə olunan bəzi nəticələrin alınmasına həsr olunur. Xammal kimi Neft daşları neftinin qudronun asfaltsızlaşdırılması nəticəsində alınan deasfaltizatlar (I və II pilləli) istifadə olunmuşdur. Yağın kimyəvi müqavimətinin yüksəldilməsi baxımından yağın müxtəlif reagentlərlə işlənməsi adi 98% sulfat turşusu və ağardıcı torpaqlarla neytrallaşdırma, aktivləşdirilmiş sulfat turşusu və ağardıcı torpaqlarla neytrallaşdırma, bəzi adsorbentlər, o cümlədən, silikagel, seçici həlledicilərdən istifadə edərək müxtəlif metodologiyalar ilə həyata keçirilib.

Əldə olunan nəticələrə əsasən qeyd etmək olar ki, hazır “Neft daşları” neftinin deasfaltizatı yüksək dərəcəli aviasiya yağlarının alınması üçün xammal kimi istifadə edilə bilər.

Təmizləmənin ən effektiv və eyni zamanda ən sərfəli yolu "Neft daşları" neftinin deasfaltizatının NM-Pirollidon ilə təmizlənməsidir. Burada üsulun çoxşaxəliliyi, yağın və reagentin əhəmiyyətli itkiləri ilə emal nəticəsində təkcə yağın dayanıqlığı deyil, həm də özlülük əyrisinin eyni zamanda yaxşılaşması faktı xüsusilə diqqəti cəlb edir.

Bu məqalədə təsvir olunan bütün digər metodlar müəyyən təsir göstərir, yəni birincisi, ya kimyəvi dayanıqlıq artır ya da özlülük əyrisində yaxşılaşma olur və buna görə də onların birləşməsi tələb olunur, ikincisi isə onlar hələ də daha az təsir göstərirlər, həm də böyük itkilər tələb olunur.

Açar sözlər: *Avaiasiya yağları, NM-Pirollidon, seçici həlledici, Sulfat turşusu, özlülük, özlülük indeksi, silikagel.*

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