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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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HETEROGENEO-CATALYTIC SYNTHESIS OF VINYL CHLORIDE AND CHLOROPRENE FROM ACETYLENE

Abstract. For the catalytic hydro chlorination of acetylene in the vapor phase based on local raw materials for the Zola-gel technology, we selected an active and high-performance catalyst $(ZnCl_2)_x*(FeCl_3)y*(CuCl_2)_z$ and also under the influence of various factors (partial pressure, temperature, ratio of reagent properties, contact time, catalyst concentration) the yield and reaction rate were studied with the participation of the selected catalyst. Based on the results obtained, a kinetic equation was proposed that satisfies the reaction, its adequacy is estimated, and a scheme of the reaction mechanism and the basis on the kinetic model are proposed. Because of studying the influence of the mass transfer coefficient on the process productivity and the influence of other factors, the technological parameters of the catalytic flocculants of vinyl chloride and the chloroprene extraction reactor of acetylene were calculated and the main indicators of the compatibility of technological capabilities of environmental and economic factors were substantiated. The successful development of the production of VC from ethylene was associated with the search for a cheaper hydrocarbon feed than acetylene. Analysis of the structure of the cost price of VC obtained by various methods shows that the acetylene method gives the highest cost, with acetylene accounting for about 90%. However, the world hydrocarbon price environment is constantly changing. In the future, it is possible to increase prices for oil and gas raw materials, the convergence of prices for acetylene and ethylene, and the latter may lose its main advantage in this regard.

Keywords: vinyl chloride, synthesis, acetylene, polyvinyl chloride, catalyst.

Introduction. It is shown for example; that the cost of VC is approximately the same if the cost of acetylene is higher than ethylene, even by 40%. A known method of producing VC by gas-phase hydro chlorination of acetylene at 80–200 ^{0}C in the presence of a fluidized catalyst bed - mercuric chloride on activated carbon and isolation of the target product by distillation. This method is characterized by insufficiently high productivity of the used catalyst. Vinyl chloride (VC) and chloroprene are a valuable monomer for the production of polyvinyl chloride - artificial rubber and others. Polyvinyl chloride (PVC) is one of the most versatile thermoplastics with a wider range of applications than all other plastics. Not surprisingly, it is used everywhere and has a positive attitude towards it. Indeed, PVC is a universal, stable, hygienic, safe and cost-effective material that has significant advantages over other materials. Over 90% of vinyl chloride is consumed in the production of polyvinyl chloride. PVC is used for molding and molding of hard products - window and doorframes, water pipes, technical and construction products. From plasticized PVC (flexible PVC) linoleum is made, insulation for wires. Apply PVC for the manufacture of artificial leather, shoes, chemical dishes [1]. Vinyl chloride is currently mainly produced in several ways [2].

Methods for producing vinyl chloride. Synthesis of VC by alkaline dehydrochlorination of one, 2-dichloroethane. In industry, two methods for dehydrochlorination with alkali are used to obtain VC from DCE: in the liquid phase: $CH_2Cl - CH_2Cl + NaOH \rightarrow CH_2 = CHCl + NaCl + H_2O$; in the gas phase: $CH_2Cl - CH_2Cl \rightarrow CH_2 = CHCl + HCl$.

Liquid phase dehydrochlorination is carried out in vertical batch or continuous cylindrical reactors equipped with a jacket and a propeller stirrer. Methyl or ethyl alcohol and 42% alkali are charged to the reactor, and then DCE is gradually added.

Due to the presence of alcohol, which dissolves both DCE and alkali, the process takes place in a homogeneous liquid medium. Temperature 85–90 ^{0}C at a pressure of 2 atmospheres. The duration of the process is 5–6 hours. The disadvantage of this method is the frequency. The consumption of alkali and alcohol is also great. For 1 kg of VC, 0.82 tons of solid alkali and 0.12 kg of alcohol (100%) are needed. Therefore, a continuous process of alkaline dehydrogenation of DCE has been developed - by mixing DCE with 6% sodium hydroxide solution, at T = 140 ^{0}C and a pressure of 10–12 atmospheres. Contact duration 2-3 minutes. The yield of BX is 90–92%.

Getting VC through the stage of formation of DCE. The synthesis of chemical compounds of their ethylene and chlorine is carried out in two stages: chlorination of ethylene; the removal of hydrogen chloride.

Ethylene chlorination is usually carried out in the liquid phase. As a feedstock, both concentrated ethylene and ethylene diluted with inert gases are used. The reaction proceeds according to the scheme:

$$CH_2 = CH_2 + Cl_2 \rightarrow CH_2Cl - CH_2Cl.$$

The reaction is carried out in a DCE solution at a temperature of 25–50 ^{0}C and a pressure of 1 to 20 atmospheres in the presence of chlorides. The yield of DCE reaches 95% with an ethylene conversion of 98%.

The removal of hydrogen chloride can be carried out in various ways. In one method, dichloroethane is treated with alcohol alkali or an aqueous alkali solution:

$$CH_2Cl - CH_2Cl \rightarrow CH_2 = CH_2Cl + HCl$$

However, due to the consumption of large quantities of auxiliary substances, this method is very disadvantageous and is currently almost never used in industry. Thermal decomposition of dichloromethane is widely used in industry:

$$CH_2Cl - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

Pyrolysis is carried out at a temperature of about 500 ^{0}C above pumice or kaolin. The reactor consists of two pipes inserted into each other (with a diameter of 100 and 70 mm). The VC yield is up to 95%, and the degree of DCE conversion is maintained at a level not exceeding 50%. Specific capital costs for the production of VC by this method are relatively small. The advantage of the method is the availability and low cost of raw materials. The main disadvantage of this method is the need for the disposal of large quantities of hydrogen chloride [3].

The combined process of obtaining VC from a concentrated mixture of acetylene and ethylene. The process consists in obtaining one, 2-dichloroethane from ethylene, followed by its thermal dehydrochlorination at 400–450 ^{0}C in VC; Hydrogen chloride released in this process is sent to acetylene hydrochlorination. The process is described in the following diagram:

$$CH \equiv CH + HCl \rightarrow CH_2 = CHCl$$
$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$$
$$ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

The combined method for producing VC turned out to be 30 and 14% more economical than alkaline dehydrochlorination of 1, 2-dichloroethane and acetylene hydrochlorination, respectively, since 50% of acetylene is replaced with less expensive ethylene; At the same time, hydrogen chloride is skillfully used.

The mixture is sent for hydro chlorination, which is carried out at 180 ^{0}C; the degree of acetylene conversion is close to 100%. After extraction of the BX from the gas, the gas enters into the chlorination of the ethylene contained in it. The ratio between chlorine and ethylene provides a 2–3% excess of ethylene versus stoichiometric; the one, 2-dichloroethane formed after cooling and purification is transferred to dehydrochlorination, the degree of conversion of 1, 2-dichloroethane per passage is about 70%.

This method is economically disadvantageous, as half of the ethylene is replaced by acetylene that is more expensive.

Obtaining VC by catalytic chlorination of ethane. The Lummus Co announced the technology it developed for producing VC in a single reactor, which simultaneously carries out the stages of chlorination, oxidative chlorination and dehydrochlorination (the so-called “transcat process”).

The yield of vinyl chloride is 98% for chlorine and 80% for ethane. Thanks to the use of cheaper ethane, the cost of VC is reduced by 25%. The method is applicable to other combined processes.

In addition to the above, there are two more ways of synthesizing VC: oxidative chlorination of ethylene with ammonium chloride and oxidation of ethyl over chromium oxide precipitated on alumina.

Chlorine-balanced process for producing VC from ethylene. This process is a combination of three reactions: direct additive chlorination of ethylene in one, 2-dichloroethane, thermal dehydrochlorination of one, 2-dichloroethane in VC and oxidative chlorination of ethylene in VC using hydrogen chloride formed during dehydrochlorination:

$$2H_2C = CH_2 \rightarrow 2\ ClCH_2 - CH_2Cl$$
$$ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$
$$CH_2 = CH_2 + 2HCl + 0{,}5O_2 \rightarrow CH_2 = CHCl + H_2O$$
$$3CH_2 = CH_2 + 2Cl_2 + 0{,}5O_2 \rightarrow 3CH_2 = CHCl + H_2O$$

As a result, VC is obtained from ethylene, chlorine, and oxygen, chlorine is completely consumed, and hydrogen chloride is not formed.

The ox chlorination step is carried out in a fluidized bed reactor at a pressure of 0.3-0.5 MPa at 210-250 ^{0}C. Ethylene, recycle gas and hydrogen chloride are mixed in a mixer, to which technical oxygen is added.

The pyrolysis of DCE in VC and HCl is carried out in a tube furnace under a pressure of 1.5-2.0 MPa and 500 ^{0}C. The resulting vinyl chloride contains 99.9% of the basic substance and is quite suitable for subsequent polymerization. Currently, this method is one of the most economical to obtain VC [4].

Getting VC from acetylene. The liquid-phase method for producing VC from acetylene and hydrogen chloride consists in passing the latter through a catalyst. The process is carried out at a temperature of 50-95 ^{0}C in the bubble-type reactors. The concentration of HCI in water should be at least 5%. Acetylene conversion per passage is 40-50% on copper catalysts and 75-90% on mercury.

Of great interest is conducting studies on the hydro chlorination of acetylene in the liquid phase in the presence of a homogeneous or suspension sublimate catalyst. The main difficulty in the implementation of the process is the choice of structural materials for a strapped reactor; for pumps, valves, etc.

The main advantage of the liquid-phase process [5] is the relative ease of solving the problem of heat removal, and, consequently, the enlargement of the reaction apparatus. The disadvantages of the process include the lower conversion of acetylene and the selectivity of the process, as well as the greater complexity of the hardware design of the reaction unit and the technological scheme [6, 7].

In order to eliminate this drawback, it is proposed that the catalyst used in the process be further promoted with lanthanum chloride. The performance of the catalyst is increased by 15-20%. The content of active substance (mixture of mercuric chloride and lanthanum chloride or their compounds) in the catalyst is 12.9 wt. percentage. The temperature of the process is 220 ^{0}C. Thus, the obtained data can be the basis for the development of a fundamentally new technological scheme for the production of VC from acetylene [8].

Hydrochlorination of acetylene in the gas phase. The successful development and implementation of this process in the industry was facilitated by the simplicity of technological design and high rates. The process is carried out in a stationary catalyst bed. The reactor is a shell-and-tube apparatus, in which the refrigerant circulates in the annular space, the catalyst is loaded into the tube space [9-14]. The temperature of the process is 120-220 ^{0}C. The catalyst is mercury dichloride (mercuric chloride) deposited on activated carbon. The sublimate catalyst (average mercuric chloride content 10-12%) is characterized by high activity and selectivity, the degree of acetylene conversion is about 99%, and the selectivity according to VC is 98-99%. As a rule, hydrochlorination is carried out in a mode with 5-10% excess hydrogen chloride. The unit capacity of the reactor is 2-10 thousand tons per year. Due to the rapid development of the production of VC based on ethylene according to a balanced scheme, the process of hydrochlorination of acetylene has now lost the position of the leading industrial method and exists only as a chemical stage of combined schemes.

First subjected to hydrochlorination without separation, and then ethylene is chlorinated to dichloroethane, after dehydrochlorination of which the resulting VC is returned to hydrochlorination.

The successful development of the production of VC from ethylene was associated with the search for a cheaper hydrocarbon feed than acetylene. Analysis of the structure of the cost price of VC obtained by various methods shows that the acetylene method gives the highest cost, with acetylene accounting for about 90%. However, the world prices for hydrocarbons are constantly changing. In the future, it is possible to increase prices for oil and gas raw materials, the convergence of prices for acetylene and ethylene, and the latter may lose its main advantage in this regard. It is shown for example; that the cost of VC is approximately the same if the cost of acetylene is higher than ethylene, even by 40%.

All of the above convincingly shows that the problem of creating new production of VC from acetylene at the modern technical and economic level, as well as the improvement and intensification of existing ones, is relevant [15]. The production of VC from acetylene in our country has a low technological level. One of the most mastered methods is the combined method described above. The Japanese company «Kureha» developed this technology [16-17].

VC at the stage of hydrochlorination of acetylene is formed by the interaction of acetylene contained in the cracking gas of naphtha and hydrogen chloride, obtained at the cracking stage of DCE in the presence of a catalyst - mercuric chloride supported on activated carbon, by the reaction:

$$CH \equiv CH + HCl \rightarrow CH2 = CHCl + 25.5 \text{ kcal / g·mol}$$

Further development of the industrial method of producing VC from acetylene can go along the path of creating aggregates of large unit capacity (60-120 thousand tons per year). However, the increase in the productivity of acetylene hydrochlorination reactors in a stationary catalyst bed is limited primarily by the heat removal rate. A study of the kinetics of this reaction showed that under industrial conditions, the specific activity of the catalyst is 10-15% of the kinetically possible. An increase in the load on the catalyst without effective heat removal leads to overheating of the catalyst, sublimation of mercury chloride and its entrainment and, ultimately, a significant reduction in the life of the catalyst. Therefore, the implementation of the acetylene hydrochlorination reaction in a stationary unit of high unit power will require significant complication of the hardware design of the reactor unit. Therefore, further improvement of the catalyst is necessary [18].

For effective heat removal, dilution of the catalyst with inert materials is also used, and dilution is carried out only in the first catalyst layer. This reduces local overheating and prevents rapid degassing of the catalyst [19].

A.L. Macho and B.K. Turin dealt with the issue of increasing catalyst productivity. The process of obtaining VC from acetylene is carried out on a catalyst, which is a mechanical mixture of activated carbon without any impregnation and coal impregnated with a 10% mercuric chloride solution, in a ratio of 1: 3. It is proposed to conduct the process first on a mixture of activated carbon without impregnation and coal, impregnated with a 10% solution of mercuric chloride, and then on the catalyst, consisting of coal, impregnated with a 10% solution of mercuric chloride and 8% solution of ammonium vanadium. The reaction gas mixture is fed from the bottom up. A moving layer of heat carrier (water) of isothermal cooling removes heat from the reaction zones. The performance of the method increases by 1.5 times [20].

The traditional method of manufacturing the catalyst is to impregnate the carrier with an aqueous solution of mercuric chloride followed by drying.

The method of manufacturing such a catalyst developed at TU NPO Sintez (Moscow) consists in the fact that mercuric chloride is applied to the carrier by sublimation of dry salt, followed by absorption on the surface of activated carbon. This method is called STO - dry heat treatment. According to the developers, the SRT method makes it possible to obtain a better catalyst, since the mercuric chloride is deposited in fact with a monomolecular layer, that is, the probability of cluster formation is reduced. Such a catalyst is characterized by a longer service life and, possibly, increased activity. According to the staff of NPO Sintez, the application of the STO method can extend the life of the catalyst by 1.5–2 times. In addition, the stage of preparation of an aqueous solution of mercuric chloride and, as a consequence, the removal of mercury containing wastewater is excluded. [Nineteen].

Thus, all of the above makes this method quite promising in technical and economic terms, which explains the continuation of work to improve it.

Currently, the annual global productivity of vinyl chloride is 42 million tons of which 98% is spent on polyvinyl chloride. The largest vinyl chloride companies are Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult, which produce vinyl chloride by catalytic hydrochlorination of acetylene. The disadvantages of their methods are: they use a toxic substance ($HgCl_2$), unstable catalysts, a low degree of catalyst activity (0.5-1 year), and also due to the volatility of mercuric chloride, the low-temperature process (150-180 ^{0}C) is another disadvantage of this method lies in the fact that the catalyst carrier is activated carbon, which corresponds to its low mechanical strength [21-23].

The most convenient way to obtain vinyl chloride in the Republic of Uzbekistan is the preparation of a cheap, active, selective and high-performance catalyst based on domestic raw materials for the catalytic hydrochlorination of acetylene.

In general, the reaction of catalytic hydro chlorination of acetylene is as follows:

$$HC{=}CH + HCl \rightarrow CH2 = CHCl,\ \Delta H = -112.4\ kJ / mol.$$

The process of acetylene hydrochlorination is in addition to reversible. At low temperatures, the equilibrium mixes to the right, at 200 ^{0}C Kp = $8{\cdot}10^4$, and at 300 ^{0}C Kp = $7{\cdot}10^2$. Therefore, when acetylene reacts with hydrogen chloride, vinyl chloride is formed from the beginning, and then 1.1-dichloroethane:

$$CH \equiv CH \xrightarrow{HCl} CH_2 = CHCl \xrightarrow{HCl} CH_3 - CHCl_2$$

Therefore, to obtain vinyl chloride by the first reaction, the HgCl2 and CuCl salts that accelerate the indicated reaction are a selective catalyst. When acetylene is hydrochlorinated, the following adverse reactions are possible:

$$CH_2 = CHCl + HCl \rightarrow CH_3 - CHCl_2$$

$$2CH \equiv CH \rightarrow CH_2 = CH - C \equiv CH$$

$$CH_2 = CH - C \equiv CH + HCl \rightarrow CH_2 = CHCl - CH = CH_2$$

Conclusion. Therefore, the hydrochlorination of acetylene and its homologues is carried out in the presence of selective catalysts that accelerate only the first stage of addition. For this purpose, salts of divalent mercury and monovalent copper are effective.

Of divalent mercury salts, mercuric chloride $HgCl_2$ is used. In addition to the main reaction, it greatly accelerates the hydration of acetylene with the formation of acetaldehyde. For this reason, and because of the deactivation of mercuric chloride in hydrochloric acid solutions, it is used in gas-phase process at 150-200 ^{0}C, using possibly drier reagents. In this case, acetaldehyde (due to a small admixture of moisture) and 1.1-dichloro-ethane are incidentally formed, but the yield of the latter does not exceed 1%. Vinyl chloride is currently mainly prepared in two ways: by hydrochlorination of acetylene with hydrogen chloride at 190-220 ^{0}C in the presence of a mercuric chloride supported on activated carbon and by dehydrochlorination of 1,2-dichloroethane. Chloroprene is mainly obtained by hydrochlorination of vinylacetylene in the presence of mercury and copper (at 50-60 ^{0}C in the presence of copper chloride) catalysts. The joint catalytic synthesis of vinyl chloride and chloroprene by hydrochlorination of acetylene is an urgent task of synthetic organic chemistry. In order to simultaneously produce vinyl chloride and chloroprene, we studied the gas-phase coupled.

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ВИНИЛ-ХОРИДИ ЖӘНЕ ХЛОРОПРЕНДЕР ГЕТЕРОГЕНДІ-КАТАЛИТИКАЛЫҚ СИНТЕЗІ

Аннотация. «Зол-гель» технологиясына арнап жергілікті шикізатқа негізделген бу фазасында ацетиленнің каталитикалық гидрохлорлану реакциясына белсенді және өнімділігі жоғары катали-заторды (ZnCl2) x * (FeCl3) y * (CuCl) z таңдап алдық, сонымен қатар түрлі факторлар әсерінен (ішінара қысым, температура, реактивтік қасиеттер қатынасы, байланыс уақыты, катализатор концентрациясы және т.б.) таңдалған катализатордың қатысуы негізінде шығым және реакция жылдамдығы зерттелді. Алынған нәтижелерге сүйене отырып, реакцияны қанағаттандыратын кинетикалық теңдеу ұсынылды, оның адекваттығы бағаланады және реакция механизмінің сұлбасы және кинетикалық модель негізі ұсынылады.

Масса ауысу (тасымалдау) коэффициентінің процесс өнімділігіне және басқа факторларға әсерін зерттеу нәтижесінде винилхлоридтің каталитикалық флокулянты және ацетиленнің хло-рофрен алу реакторының технологиялық параметрлері есептелді және экологиялық, экономикалық факторлардың технологиялық мүмкіндігі үйлесімділігінің негізгі көрсеткіштері негізделді. Зерттеу нәтижесінде винилхлорид пен хлоропренді біріктіріп қабылдаудың технологиялық сызбасы жасалды, үдерістің материалдық балансы есептелді.

Сондай-ақ, винилхлорид пен хлоропреннің бірлескен өндірісі, ацетиленнің сұйық фазадағы гидрохлорация үдерісі зерттелді. Ацетиленнің жоғары селективтілігі мен конверсиясымен винил-хлорид пен хлоропрен өндірісін қамтамасыз ететін үдеріс параметрлері анықталды. Ацетилен гидрохлорлаудың кейбір кинетикалық заңдылықтары да зерттелді. Сондықтан ацетилен мен оның гомологтарын гидрохлоризациялау тек қосудың алғашқы кезеңін жеделдететін селективті катали-заторлардың қатысуы негізінде жүзеге асырылады. Бұл үшін бөлінетін сынап пен моновалентті мыс тұзы тиімді.

Бөлінетін сынап тұзынан $HgCl_2$ сынап хлориді қолданылады. Негізгі реакциядан басқа ацетилдегид пайда болуы арқылы ацетилен гидратациясын едәуір жылдамдатады. Сондықтан тұз қышқылы ерітіндісінде сынап хлоридін залалсыздандыруға байланысты құрғақ реагенттерді пайдаланып, 150–200 ^{0}C температурадағы газ фазасында қолданылады. Бұл жағдайда ацетальдегид (ылғалды қоспаның аздығына байланысты) және 1,1-дихлороэтан кездейсоқ қалыптасады, бірақ соңғысының шығымы 1%-дан аспайды. Винилхлорид қазіргі кезде негізінен екі жолмен: активтендірілген көмірге қолдау көрсететін сынап хлоридінің қатысуы негізінде ацетиленді сутегі хлоридімен 190–220 ^{0}C-та гидрохлорлау және 1,2-дихлорэтанды дегидрохлорлау арқылы дайындалады. Хлорофрен негізінен сынап пен мыстың қатысуы арқылы (мыс хлоридінің қатысуы 50–60 ^{0}C) катализатор қосу негізінде винилацетилен гидрохлорлайды.

Қазіргі уақытта винилхлоридтің жыл сайынғы әлемдік өнімділігі 42 млн. тоннаны құрайды, оның 98% поливинилхлоридке жұмсалады. Винилхлоридтің ірі компаниялары – ацетиленнің каталитикалық гидрохлорациясы арқылы винилхлорид шығаратын Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult. Әдістерінің кемшілігі: улы затты ($HgCl_2$), тұрақсыз катализаторды, катализатордың төмен деңгейлі белсенділігін (0,5–1 жас) пайдаланады, сонымен қатар сынап хлоридінің құбылмалылығына байланысты үдеріс төмен температурада жүреді (150–180 °C), аталған әдістің тағы бір кемшілігі мынадай: активтендірілген көміртегі оның әлсіз механикалық беріктігіне сәйкес келетін катализатор тасымалдаушысы қызметін атқарады.

Винилхлорид алудың ыңғайлы әдісі – ацетиленнің каталитикалық гидрохлорациясы үшін отандық шикізат негізінде арзан, белсенді, селективті және жоғары өнімді катализатор дайындау.

Түйін сөздер: винилхлорид, синтез, ацетилен, поливинилхлорид, катализатор

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ГЕТЕРОГЕННО-КАТАЛИТИЧЕСКИЙ СИНТЕЗ ВИНИЛХЛОРИДА И ХЛОРОПРЕНА ИЗ АЦЕТИЛЕНА

Аннотация. Для реакции каталитического гидрохлорирования ацетилена в паровой фазе на основе местного сырья для «Зол–гель» технологии, нами был выбран активный и высокопроизводительный катализатор $(ZnCl_2)_x*(FeCl_3)_y*(CuCl)_z$ а также под влиянием различных факторов (парциальное давление, температура, соотношение свойств реагентов, время контакта, концентрации катализатора и.др) были исследованы выход и скорость реакции с участием выбранного катализатора. На основании полученных результатов было предложено кинетическое уравнение, удовлетворяющее реакции, оценена его адекватность и предложена схема механизма реакции, основания на кинетической модели.

В результате исследования влияния коэффициента массопередачи (транспортирования) на производительность процесса и влияния других факторов были рассчитаны технологические параметры каталитического флокулянта винилхлорида и хлоропренового экстракционного реактора ацетилена и обоснованы основные показатели совместности технологических возможностей экологических и экономических факторов.

В результате проведенных исследований создана технологическая схема совместного поступления винилхлорида и хлоропрена, а также рассчитан материальный баланс процесса.

Также изучен процесс совместного получения винилхлорида и хлоропрен, гидрохлорированием ацетилена в жидкой фазе. Найдены параметры процесса, обеспечивающие получение винилхлорида и хлоропрена с высокой селективностью и конверсией ацетилена. Изучены некоторые кинетические закономерности процесса гидрохлорирования ацетилена.

Поэтому гидрохлорирование ацетилена и его гомологов проводят в присутствии селективных катализаторов, ускоряющих только первую стадию присоединения. Для этой цели эффективными являются соли двухвалентной ртути и одновалентной меди.

Из солей двухвалентной ртути применяют сулему $HgCl_2$. Кроме основной реакции, она сильно ускоряет и гидратацию ацетилена с образованием ацетальдегида. По этой причине, а также из-за дезактивирования сулемы в солянокислых растворах ее используют в газофазном процессе при 150–200 ^{0}C, применяя возможно более сухие реагенты. При этом побочно образуются ацетальдегид (за счет небольшой примеси влаги) и 1,1-дихлорэтан, но выход последнего не превышает 1 %. Хлористый винил в настоящее время в основном получают двумя способами: гидрохлорированием ацетилена хлористым водородом при 190–220 ^{0}C в присутствии сулемы, нанесенного на активированный уголь и дегидрохлорированием 1,2-дихлорэтана. Хлоропрен в основном получается гидрохлорированием винилацетилена в присутствии ртутных и медных (при 50-60 ^{0}C в присутствии полухлористой меди) катализаторов.

В настоящее время ежегодная мировая производительность винилхлорида составляет 42 млн тонн, из них 98% расходуется на получение поливинилхлорида. Самые большие компании по производству винилхлорида – фирма Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult, которые при каталитическом гидрохлорирования ацетилена получают винилхлород. Недостатками их методов являются: применяют ядовитое вещество ($HgCl_2$), нестабильные катализаторы, низкая степень роботы катализатора (0,5–1 год), а также из-за летучести сулемы процесс-низкотемпературный (150–180 ^{0}C) ещё одним из недостатком данного метода заключается в том, что носителем катализатора служит активированный уголь, что соответствует его низкой механической прочности.

Самым удобным способом получения винилхлорида являются приготовление дешевого, активного, селективного и высокопроизводительного катализатора на основе отечественного сырья для каталитического гидрохлорирования ацетилена.

Ключевые слова: винилхлорид, синтез, ацетилен, поливинилхлорид, катализатор.

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CATALYTIC CONVERSION OF BIOGAS INTO SYNTHESIS GAS ON Ni, Co AND Ni-Co CATALYSTS

Abstract. The world's oil reserves are shrinking every day due to continuous production and processing using the most modern technologies. Scientists around the world are looking for different types of raw materials and ways to use the vast resources of natural gas as a substitute for oil. In this regard, considerable attention is paid to natural and associated gas as an alternative source of raw materials for the petrochemical industry. In this paper, Ni, Co and Ni-Co catalysts carried to θ-Al_2O_3 prepared by the traditional method of air impregnation for moisture capacity are studied. The developed compositions of monometallic and bimetallic compositions of catalysts were studied by the XRD method. The efficiency of the dry methane reforming reaction was investigated in a stationary reactor under the optimal process conditions found experimentally: T = 700 and 900°C, GHSV = 6000 h^{-1} and CH_4:CO_2: Ar = 1: 1: 1.

Key words: Dry reforming of methane, synthesis-gas, Ni, Co and Ni-Co catalyst, traditional method of air impregnation.

Introduction. After the industrial revolution, the widespread use of fossil fuels and the effects of greenhouse gases caused by massive CO_2 emissions gradually attracted the attention of people around the world. Reducing the impact of the greenhouse effect will be a very important issue. The greenhouse gases in the atmosphere are mainly composed of CO_2, CH_4, N_2O, CFCs and O_3. Two of the most important gases are CO_2 and CH_4. If we can effectively use these two gases, we can turn waste into treasure and realize the recycling of waste. The use of these two gases to synthesize H_2 and CO under the action of a catalyst is currently being studied by many researchers. At present, they are only in the laboratory research stage and have not achieved commercial research results. Mainly because the catalyst does not meet the standard, the activity and stability of the catalyst cannot meet the requirements of large-scale factory operation, and the cost is relatively high. A more important issue was how to use CO_2 efficiently and reduce greenhouse gas emissions. The process of methane reforming with carbon dioxide attracts a lot of attention due to its unique advantages. On the one hand, the process uses methane and carbon dioxide as reaction raw materials, which not only efficiently converts natural gas, but also effectively reduces carbon dioxide emissions. On the other hand, the methane reforming reaction can produce a volume ratio of H_2 to CO close to 1. The resulting synthesis gas can be used for the synthesis of dimethyl ether, oxygenates, Fischer-Tropsch synthesis, etc., and is of great importance for easing the chemical raw material and energy crisis, as well as for easing environmental problems [1-2]. There are two main types of methane reforming catalysts: catalysts based on noble metals and catalysts based on non-precious metals. Numerous catalysts based on noble metals such as Pt, Rh, Pd, Ir have been studied in works [3-8], which have high activity and good stability in the reforming reaction, but are expensive. Catalysts based on non-precious metals contain transition metals such as Ni, Cu, Fe, Co as main active components. Ni based catalysts have better productivity [9-12]. However, Ni-based catalysts deactivate faster and have low carbon accumulation compared to noble metal catalysts. Therefore, increasing the stability of non-precious metal catalysts and effective inhibiting of carbon deposition have become the main focus of research on methane reforming catalysts using carbon dioxide. Currently, Ni and Co based catalysts [13-19] are the most widely studied among the various types of studied catalysts. Typically, La_2O_3 and CeO_2 are used as additives, and Al_2O_3, ZrO_2, MgO and molecular sieves are used as carriers [20]. This paper describes research of the Ni- and Co-based catalysts for selective synthesis-gas production under the found optimal conditions of the methane reforming process with carbon dioxide.

Experimental

Catalyst preparation

The catalysts were prepared by the traditional method of air impregnation on moisture capacity. First, the aluminum oxide was dried at 110°C. Then the moisture content of carrier was determined. Titrated solutions of Ni and Co with a concentration of 0.15 g/ml of nitrate salts of $Ni(NO_3)\times6H_2O$ and $Co(NO_3)\times6H_2O$ were prepared. A certain amount of a titrated solution of Ni, Co or a mixture thereof is introduced into a porcelain cup, depending on the percentage of metals in the catalysts. Then a certain amount of distilled water is added, the whole mixture is well mixed and the dried carrier is poured into the solution. The resulting catalyst was stirred in air and dried at 250°C for 1 h, then calcined at 500°C for 2 h. The following catalysts were prepared: 10%Ni/θ-Al_2O_3, 9%Ni-1%Co/θ-Al_2O_3, 7%Ni-3%Co/θ-Al_2O_3, 5%Ni-5%Co/θ-Al_2O_3, 3%Ni-7%Co/θ-Al_2O_3, 1%Ni-9%Co/θ-Al_2O_3, 10% Co/θ-Al_2O_3.

Characterization techniques.

Analysis of the initial mixture and the reaction products was performed using "Chromos GC-1000" (Russia) chromatograph, which was equipped with packed and capillary columns. The packed column is used for the analysis of H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3-C_4 hydrocarbons, CO and CO_2.

The crystallinity of catalysts before and after reaction was measured by X-ray powder diffraction (XRD). The XRD was measured with PANalytical Empyrean diffractometer in Bragg-Brentano mode. Physico-chemical research was carried out at Institute of Biomedicine and Wihuri Physical Laboratory (Turku, Finland).

Catalyst activity.

The catalysts were tested in a fixed-bed quartz reactor with a diameter of 10 mm and a length of 40 cm at atmospheric pressure. The catalyst (2 ml) was placed between quartz granules in a tube reactor.

Results and discussion. Figure 1 shows the study of the effect of reaction temperature on the activity of 5%Ni-5%Co/θ-Al_2O_3 catalyst during the carbon dioxide conversion of methane into synthesis gas at CH_4:CO_2:Ar = 1:1 and GHSV = 6000 h^{-1}. It was found that the conversion increase from 500°C. The conversion of CH_4 and CO_2 were about 100% at 900°C.

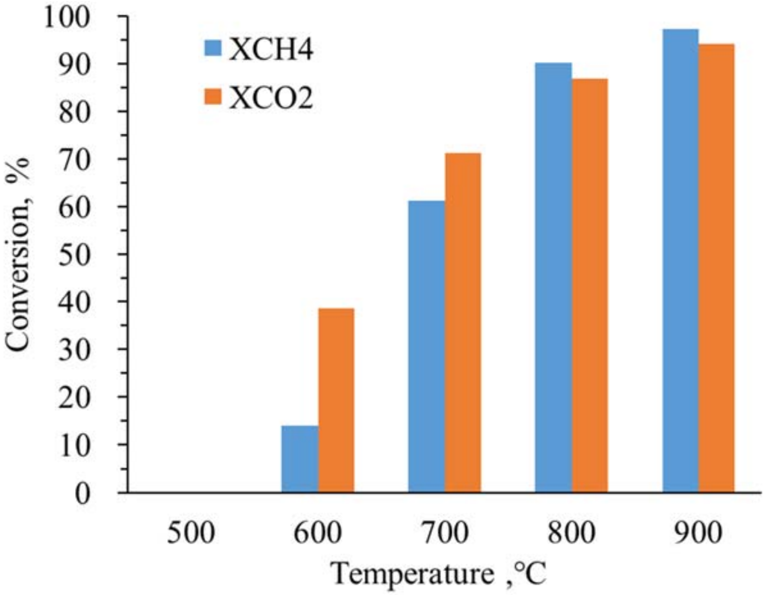

Figure 1 - Effect of the temperature on conversion of methane and CO_2 at CH_4:CO_2:Ar = 1:1:1 and GHSV = 6000 h^{-1} on the 5%Ni-5%Co/θ-Al_2O_3 catalyst

Figure 2 shows that the CH_4 conversion increases from 36.2% to 97.3%. The CO_2 conversion decreases after reaching a CH_4:CO_2:Ar = 1: 1: 1 ratio. Thus, it is determined that only when the ratio of CH_4:CO_2=1:1, the conversion of the two gases reaches its maximum.

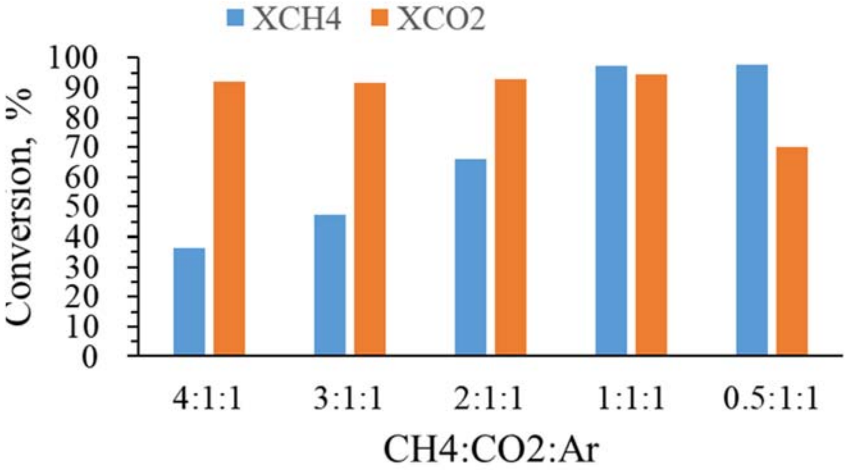

Figure 2 – Effect of the CH_4:CO_2:Ar ratio on conversion of methane and CO_2 at 900°C and GHSV = 6000 h^{-1} on the 5%Ni-5%Co/θ-Al_2O_3 catalyst

The study of variation of reaction space velocity showed that the conversion of CH_4 and CO_2 increase at rise of space velocity. It reaches the maximum at 6000 h^{-1} and then the conversion of CH_4 decreased from 97.3% to 93%, and CO_2 conversion decreased from 93% to 87%. Thus, it is determined that 6000 h^{-1} is optimal space velocity for conversion of CH_4 and CO_2 into synthesis gas, Figure 3.

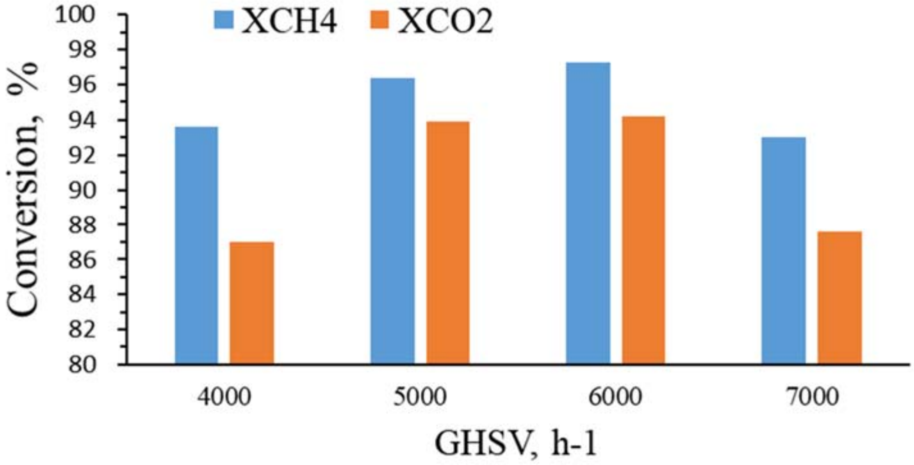

Figure 3 - Effect of the space velocity on conversion of methane and CO_2 at 900°C and CH_4:CO_2:Ar = 1:1:1 ratio on the 5%Ni-5%Co/θ-Al_2O_3 catalyst

Catalytic activity of the developed series of monometallic and bimetallic catalysts was investigated. It was found that the activity of investigated catalysts of the different compositions reached the highest value when the Ni:Co ratio (%) was 5:5. Figure 4 shows the data on activity of catalysts at a reduced temperature equal to 700°C, where it is shown that a decrease the temperature does not reduce the activity of the decomposed compounds in the reaction of the carbon dioxide conversion of methane to synthesis gas.

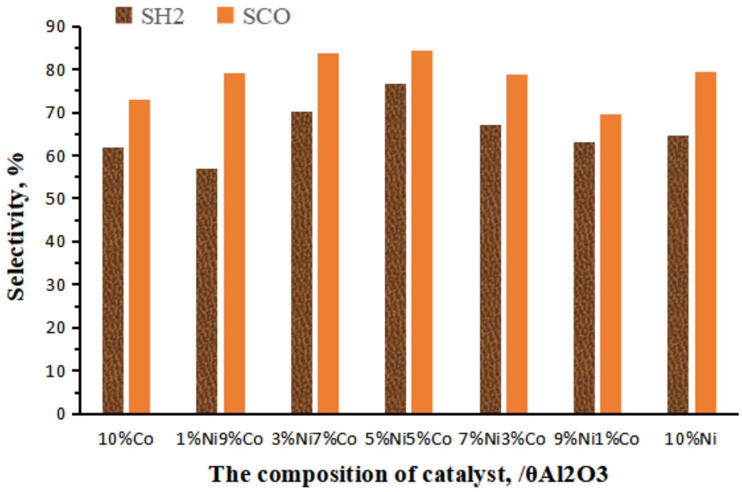

Figure 4 - Effect of the Ni and Co content in Ni-Co catalysts on θ-Al_2O_3 on the selectivity of H_2 and CO at 700°C, CH_4:CO_2:Ar = 1:1:1 ratio and GHSV = 6000h^{-1}

The XRD analysis of the developed catalyst compositions was performed. It was found that the size of catalyst particles varies with the composition of sample. It was determined that the minimum size of both fresh and spent samples was detected only on a bimetallic catalyst of the Ni:Co = 5:5 composition, which is assumed to be responsible for the activation of methane into synthesis gas, Figure 5. The obtained results are consistent with the catalytic activity of the developed catalysts in the reaction of carbon dioxide conversion of methane into synthesis gas. It was found that the bimetallic 5%Ni-5%Co/θ-Al_2O_3 catalyst is active and selective among the studied compositions.

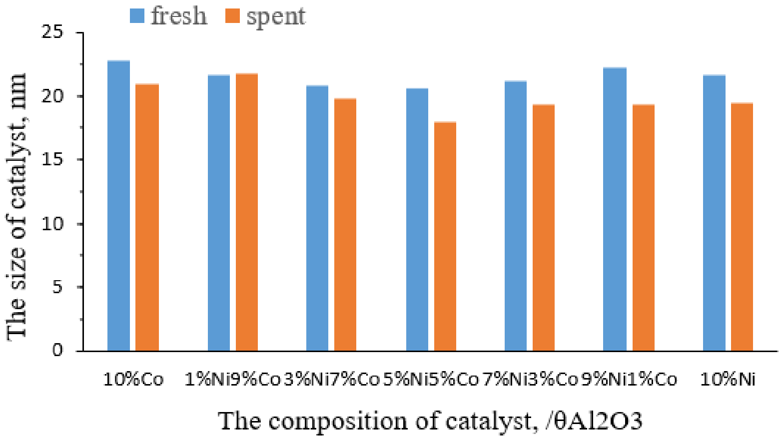

Figure 5 – Effect of the catalyst composition on catalyst particle sizes

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Conclusion. Thus, the smallest particles of catalysts were detected on the developed 5%Ni-5%Co catalyst over θ-Al_2O_3 by XRD method. It is assumed that they are responsible for the activity of developed catalytic composition in the reaction of carbon dioxide conversion of methane into synthesis-gas. It was found that a bimetallic catalyst with an equal content of Ni and Co is the most optimal among the developed catalyst compositions for the conversion of methane to synthesis gas. The conversion of CH_4 and CO_2 was 97.3 and 94.2%, respectively. The optimal process conditions were: T = 700 and 900°C, GHSV = 6000 h^{-1} and CH_4:CO_2:Ar = 1:1:1.

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Ni, Co және Ni-Co КАТАЛИЗАТОРЫНДАҒЫ БИОГАЗДЫҢ СИНТЕЗ ГАЗҒА ДЕЙІНГІ КАТАЛИТИКАЛЫҚ КОНВЕРСИЯСЫ

Аннотация. Өнеркәсіптік революциядан кейін қазбалы отынды кеңінен қолдану және CO_2 жаппай шығарындысынан пайда болатын парниктік газдың әсері біртіндеп әлем назарын аударды. Парниктік әсерді азайту – маңызды мәселе. Атмосферадағы парниктік газ негізінен CO_2, CH_4, N_2O, CFC және O_3-тен тұрады. Ең маңызды газдың екеуі – CO_2 және CH_4. Егер біз осы екі газды тиімді пайдалана алсақ, қалдықтарды қазынаға айналдырып, қайта өңдей аламыз. Осы екі газды H_2 және Co синтезіне катализатор әсерін қолдануды қазіргі уақытта көптеген зерттеуші қарастыруда. Қазіргі уақытта олар тек зертханалық зерттеулер сатысында және коммерциялық зерттеу нәтижелеріне қол жеткізе алмады. Негізінен, катализатор стандартқа сәйкес келмейтіндіктен, катализатордың белсенділігі мен тұрақтылығы зауыттың кең ауқымды жұмыс талаптарына сәйкес келмейді, ал құны салыстырмалы түрде жоғары шығады. Неғұрлым маңызды мәселенің бірі – CO_2 тиімді пайдалану және парниктік газ шығарындысын азайту. Көмірқышқыл газы бар метанды қайта құру процесінің ерекше артықшылығы назар аудартады. Бір жағынан, процесс метан мен көмірқышқыл газын реакциялық шикізат ретінде пайдаланады, бұл табиғи газды тиімді түрлендіріп қана қоймай, көмірқышқыл газының шығарылуын тиімді төмендетеді. Екінші жағынан, метан риформинг реакциясы H_2-нің Co-ға 1-ге жақын көлем қатынасына әкелуі мүмкін. Алынған синтез-газды диметил эфирін, оксигенаттарды синтездеу, Фишер-Тропш синтезі және т.б. үшін пайдалануға болады және химиялық шикізат пен энергетикалық дағдарыстарды жұмсарту, сондай-ақ экологиялық проблемаларды жұмсарту үшін үлкен маңызға ие [1-2]. Метан риформинг катализаторларының негізгі екі түрі бар: асыл металдарға негізделген катализатор және қымбат емес металдарға негізделген катализаторлар. Еңбектерде [3-8] PT, Rh, Pd, Ir сияқты асыл металдарға негізделген көптеген катализаторлар зерттелген, олар жоғары белсенділік пен риформинг реакциясында тұрақты, бірақ қымбат. Қымбат емес металдарға негізделген катализаторлар негізгі белсенді компоненттер ретінде Ni, Cu, Fe, Co сияқты өтпелі металдарды қамтиды. Никель негізіндегі катализаторлар өнімдірек [9-12]. Алайда Ni негізіндегі катализаторлар жылдам ажыратылады және асыл металл катализаторларымен салыстырғанда көміртек аз жиналады. Сондықтан қымбат емес металдардан жасалған катализаторлардың тұрақтылығын арттыру және көміртектің тұндырылу үдерісін тиімді тежеу көмірқышқыл газын қолдана отырып, метан риформинг катализаторларын зерттеудің негізгі бағытына айналды. Қазіргі уақытта Ni және Co негізіндегі катализаторлар [13-19] зерттелген катализаторлардың алуан түрлері арасында кеңінен зерттелген. Әдетте La_2O_3 және CeO_2 қоспалар ретінде қолданылады, ал тасымалдаушылар ретінде Al_2O_3, ZrO_2, MgO және молекулярлы електер қолданылады. Жұмысымызда метанды көміртегі диоксидімен қайта құру үшін оңтайлы жағдайдағы синтездік газды селективті өндіру үшін никель мен кобальт негізіндегі катализаторларды зерттеу жұмыстары сипатталған.

Заманауи технологияларды қолдана отырып, үздіксіз өндіру мен өңдеу арқылы әлемдік мұнай қоры күн сайын азайып келеді. Әлем ғалымдары шикізаттың алуан түрлерін және табиғи газдың ірі ресурстарын мұнай алмастырғыш ретінде пайдалану тәсілдерін іздейді. Осыған байланысты мұнай-химия өнеркәсібі үшін шикізаттың балама көзі ретінде табиғи және ілеспе газға көбірек көңіл бөлінеді. Бұл жұмыста ылғал сыйымдылығы бойынша ауа сіңірудің дәстүрлі әдісімен алынған θ-Al_2O_3-ке қондырылған Ni, Co және Ni-Co катализаторлары зерттелді.

Түйін сөздер: құрғақ метанды қайта құру, синтез газ, Ni, Co және Ni-Co катализаторлары, дәстүрлі ауа сіңіру әдісі.

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КАТАЛИТИЧЕСКАЯ КОНВЕРСИЯ БИОГАЗА В СИНТЕЗ ГАЗ НА Ni, Co и Ni-Co КАТАЛИЗАТОРАХ

Аннотация. После промышленной революции широкое использование ископаемых видов топлива и воздействие парниковых газов, вызванное массовыми выбросами CO_2, постепенно привлекли внимание людей во всем мире. Парниковые газы в атмосфере в основном состоят из CO_2, CH_4, N_2O, CFC и O_3. Двумя наиболее важными газами являются CO_2 и CH_4. Если мы сможем эффективно использовать эти два газа, мы сможем превратить отходы в сокровища и реализовать переработку отходов. Использование этих двух газов для синтеза H_2 и CO под действием катализатора в настоящее время изучается многими исследователями. В настоящее время они находятся только на стадии лабораторных исследований и не достигли результатов коммерческих исследований. В основном из-за того, что катализатор не соответствует стандарту, активность и стабильность катализатора не могут соответствовать требованиям крупномасштабной производственной эксплуатации, а его стоимость относительно высока. Более важным вопросом было то, как эффективно использовать CO_2 и сократить выбросы парниковых газов. Процесс риформинга метана с использованием диоксида углерода привлекает большое внимание благодаря своим уникальным преимуществам. С одной стороны, в этом процессе в качестве сырья для реакции используются метан и диоксид углерода, что не только эффективно преобразует природный газ, но и эффективно снижает выбросы диоксида углерода. С другой стороны, реакция риформинга метана может давать объемное отношение H_2 к CO, близкое к 1. Полученный синтез-газ можно использовать для синтеза диметилового эфира, оксигенатов, синтеза Фишера-Тропша и т.д. И он очень полезен для ослабления химического сырьевого и энергетического кризиса, а также для смягчения экологических проблем. Существует два основных типа катализаторов риформинга метана: катализаторы на основе благородных металлов и катализаторы на основе неблагородных металлов. В работах исследованы многочисленные катализаторы на основе благородных металлов, таких как Pt, Rh, Pd, Ir, которые обладают высокой активностью и хорошей стабильностью в реакции риформинга, но дороги. Катализаторы на основе неблагородных металлов содержат в качестве основных активных компонентов переходные металлы, такие как Ni, Cu, Fe, Co. Катализаторы на основе Ni обладают большей производительностью. Однако катализаторы на основе никеля дезактивируются быстрее и имеют низкое накопление углерода по сравнению с катализаторами из благородных металлов. Таким образом, повышение стабильности катализаторов из неблагородных металлов и эффективное ингибирование осаждения углерода стало основным направлением исследований катализаторов риформинга метана с использованием диоксида углерода. В настоящее время катализаторы на основе Ni и Co являются наиболее изученными среди различных типов катализаторов. Обычно La_2O_3 и CeO_2 используются в качестве добавок, а Al_2O_3, ZrO_2, MgO и молекулярные сита используются в качестве носителей. В данной работе описаны исследования катализаторов на основе никеля и кобальта для селективного получения синтез-газа в найденных оптимальных условиях процесса риформинга метана с диоксидом углерода.

Мировые запасы нефти сокращаются с каждым днем из-за непрерывной добычи и переработки с использованием самых современных технологий. Ученые всего мира ищут различные виды сырья и способы использования огромных ресурсов природного газа в качестве заменителя нефти. В связи с этим значительное внимание уделяется природному и попутному газу как альтернативному источнику сырья для нефтехимической промышленности. В данной работе исследованы Ni, Co и Ni-Co катализаторы, переносимые на θ-Al_2O_3, полученные традиционным методом воздушной пропитки по влагоемкости.

Ключевые слова: сухой риформинг метана, синтез-газ, Ni, Co и Ni-Co катализаторы, традиционный метод воздушной пропитки.

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FORMATION OF NANO-AND ULTRAFINE PALLADIUM POWDERS IN THE PRESENCE OF «RED-OX»SYSTEM«TITANIUM (III) - TITANIUM (IV)»

Abstract. The results of studies on the processes of obtaining ultra - and nanodispersed palladium powders from sulphate solutions by a combined chemical and electrochemical method in the presence of a "red-ox" system of titanium (III) - titanium (IV) are presented. It has been shown that when a titanium trivalent sulphate solution is added to a solution containing palladium (II) ions, palladium ions are immediately reduced to elemental state to form a nanodispersed powder. The completeness of the above-mentioned oxidizing-reducing reactions is established on the basis of calculating the equilibrium constant (K), which is 10^{34} and indicates that trivalent titanium ions completely reduce palladium ions to elemental state.

Effect of initial concentration of palladium ions on amount of formed palladium powder with addition of equivalent amount of trivalent titanium ions is investigated.

According to the authors, upon reduction of palladium ions, elemental palladium is formed in the atomic state, and over time, the atoms begin to combine with each other. Subsequently, atomic particles are combined into colloidal particles. It has been found that in the absence of coagulants, the colloidal palladium solution is stable for 2-3 hours, and in the presence of gelatin, the stability increases and remains for 36 hours.

It was shown that in all experiments powders with spherical particles are formed, the average sizes of which range from 0.116-0.240 microns.

Based on the results of the presented studies, a new technology for producing ultra - and nano-sized palladium powders is proposed.

Keywords: ultra-dispersed nanosized powders, palladium, titanium(III) ions, "red-ox" system, reduction, dispersion.

Introduction. Palladium is known to have special physical and chemical properties such as high corrosion resistance, heat resistance, mechanical strength, hardness, high catalytic activity and unique hydrogen sorption properties. In addition, palladium is much cheaper than other platinum metals. It is also known that the application of palladium on the contact surfaces significantly increases the service life of various radio and electrical equipment [1].

Palladium powder has been shown to have very high catalytic activity [2].

In the modern world, many industries, including machine-building, are developing in the direction of creating low-waste and waste-free technologies. Cutting of metals, which is one of the main methods of making parts, is economically disadvantageous because up to 60% of metal is lost.

The main method for making parts from metals, including parts of a complex configuration, is powder metallurgy, which allows to reduce the amount of waste by more than 10%.

The intensive development of modern technology for the production of non-ferrous, rare and noble metals requires the involvement of new modern methods. In recent years, much attention has been paid to the development and implementation of various non-reactive electrochemical processes, which is due to their significant capabilities in chemical, metallurgical and other remodeling.

Technologies of electrochemical extraction of metals, synthesis of their various compounds, as well as production of ultradisperse and nano-sized powders used in various industries and national economy are constantly developing.

The interest of many authors in metal powders is caused by the fact that in the modern world the demand for ultradisperse powders with nano-sized particles is growing. While previously palladium powder was used mainly only in the manufacture of the article, the scope of its application is now expanding more and more. One promising direction is the use of nanomaterials in the basis of the technology of creating new drugs, including those having wound healing effect [3-6]. It was found that when entering living organisms, nano-sized metal particles cause a biological response different from the action of the traditional ionic form of elements. It has been shown that nanoparticles of d-elements with parenteral administration are 7-50 times less toxic than metals in ionic form. Nanoparticles easily penetrate all organs and tissues and have a prolonged effect. In biotic doses, they stimulate metabolic processes and exhibit multifunctional effects.

There are data [4] that Acticoat, Nucryst brand dressings, which include silver nanoparticles, are widely used in the USA for the treatment of wounds, burns, trophic ulcers, eczema, acne rash. At the same time, in the practice of treating wounds of different etiologies, there remains a high need for soft dosage forms. In this regard, attention is drawn to the creation of metal nanoparticles, in particular palladium nanoparticles, which can serve as one of the components of soft dosage forms. The function of palladium in the body is well studied and its absolute need is proved at all stages of the process.

The antibacterial effect of certain metals and their compounds has been known since ancient times [2]. The study of the biological activity of copper and palladium nanoparticles, which differ in dispersion and phase composition to create a soft dosage form, is devoted to many studies conducted with the participation of medical workers. The dispersion of metal powders is a very important characteristic of them and in recent years the industry needs fine and nano-sized powders.

Experimental. Previously, palladium powders were prepared using chemical reducing agents such as hydrazine, formaldehyde and hydrogen, reduced with zinc, magnesium, as well as other metals having a more negative potential. An electrochemical method for producing palladium powders is also known. For example, [8] shows the possibility of cathodic deposition of palladium black from palladium (II) chloride solutions at certain pH values of the solution. From a palladium chloride solution at high cathode current densities at the cathode, palladium (II) ions are reduced to form palladium powders by the reaction:

$$Pd^{2+} + 2e \rightarrow Pd^0 \qquad (1)$$

The purpose of our work is to develop a new method for producing ultra-dispersed palladium powders in the presence of titanium (IV) ions. The objective of the study is to identify the conditions and regularities of the process of producing ultra-dispersed and nanosized palladium powders by chemical and electrochemical methods in the presence of the "red-ox" system of titanium (III) - titanium (IV).

The tests were carried out in a 50 ml thermostat cell at room temperature. To the sulphate solution containing palladium (II) ions was poured a titanium trivalent sulphate solution. At the same time, almost immediately palladium ions are reduced to elemental state with formation of metal powder by reaction:

$$Pd^{2+} + 2Ti^{3+} \rightarrow Pd^0 + 2Ti^{4+} \qquad (2)$$

It should be noted that by mixing solutions containing palladium (II) and titanium (III) ions in an equivalent ratio under certain conditions for ten seconds, the solution becomes colorless (note that the initial solution of titanium trivalent sulfate is violet and chloride falladium is reddish), i.e. clear. We presumably explain this phenomenon by the fact that at this moment palladium is in an atomic state, due to the very small particle sizes it becomes practically invisible.

After 2-3 minutes, palladium atoms begin to combine (group) with each other to a certain state, forming agglomerates in which the particle sizes depend on the experimental conditions. Further, colloidal particles of dark-colored palladium are formed throughout the volume of the solution, the stability depends on the conditions of the experiment. In the absence of coagulants, the colloidal palladium solutions remain stable for 2-3 hours and in the presence of gelatin for 36 hours.

In all experiments, powders with spherical particles are formed, the average sizes of which range from 0.116-0.240 microns. Figures 1a and b show micrographs of powders obtained from palladium chloride solution at different concentrations of palladium (II) ions. Micrographs obtained using an electron microscope.

Effect of initial concentration of palladium (II) ions on amount of formed palladium powders with addition of equivalent amount of trivalent titanium ions by reaction (2) was investigated. Table 1 shows the amount of palladium powder formed from the palladium chloride solution - 2 g/l, sulfuric acid - 100 g/l and with the addition of an equivalent amount of titanium (III) sulfate.

Table 1 - Influence initial concentrations of ions of palladium (II) on the mass of powder of palladium (V = 25 ml)

Palladium ion concentration, g/l	Weight of palladium in solution, mg	Weight of formed palladium powder, mg
0,25	6,25	6,0
0,50	12,50	12,2
0,75	18,75	18,5
1,00	25,00	24,1
1,25	31,25	30,9
1,50	37,50	37,0

As can be seen from Table 1, the reaction (2) is completely shifted to the right, the palladium ions contained in the solution are almost completely reduced to elemental state as ultradisperse powders. Palladium powder yield above 96%.

The completeness of the redox reaction in the reaction of the above two "red-ox" pairs is easily determined by calculating its equilibrium constant according to the known formula [9]. Reactions that are substantially complete must have a constant greater than 10^8 (with 99.99% of the starting materials being bound). To calculate the equilibrium constant of any reversible "red-ox" reaction, it is necessary to calculate lgK using the formula $\frac{n(E_1^0-E_2^0)}{0{,}059}=\lg K_{\text{red-ox}}$, and then K:

$$K_{\text{red}-\text{ox}} = 10^{\frac{(E_1^0-E_2^0)n}{0{,}059}} \qquad (3)$$

$$Pd^{2+} + 2Ti^{3+} \rightleftarrows Pd^0 + 2Ti^{4+} \qquad (4)$$

$$Pd^{2+} + 2e \rightarrow Pd^0 \; E^0 = +\,0.987 \text{ B } n = 2 \qquad (5)$$

$$2Ti^{3+} - 2e \rightarrow 2Ti^{4+} \; E^0 = -\,0.04 \text{ B} \qquad (6)$$

$$\lg K_{Pd^{2+}/Ti^{3+}} = \frac{(E_1^0-E_2^0)n}{0{,}059} = \frac{2(0.987+0.04)}{0.059} = \frac{2 * 1.027}{0.059} = \frac{2.054}{0.059} = 34.8 \qquad (7)$$

Equilibrium constant K ≅ $10^{34{,}8}$

The value of the constant of the above redox systems, equal to $K = 10^{34.8}$, suggests that both reactions go to the end from left to right and are practically irreversible. In addition, since the reaction constant represents the ratio of the product of the concentration of the final reaction products to the product of the concentrations of the starting products, the equilibrium of the above reaction occurs when $[2Ti^{3+}]^2 * [Pd(II)]$ becomes more than $[Ti^{4+}]^2 * [Pd]$ by 10^{34} times.

The results of our calculations show that trivalent titanium ions are completely spent on reducing palladium (II) ions to elemental state.

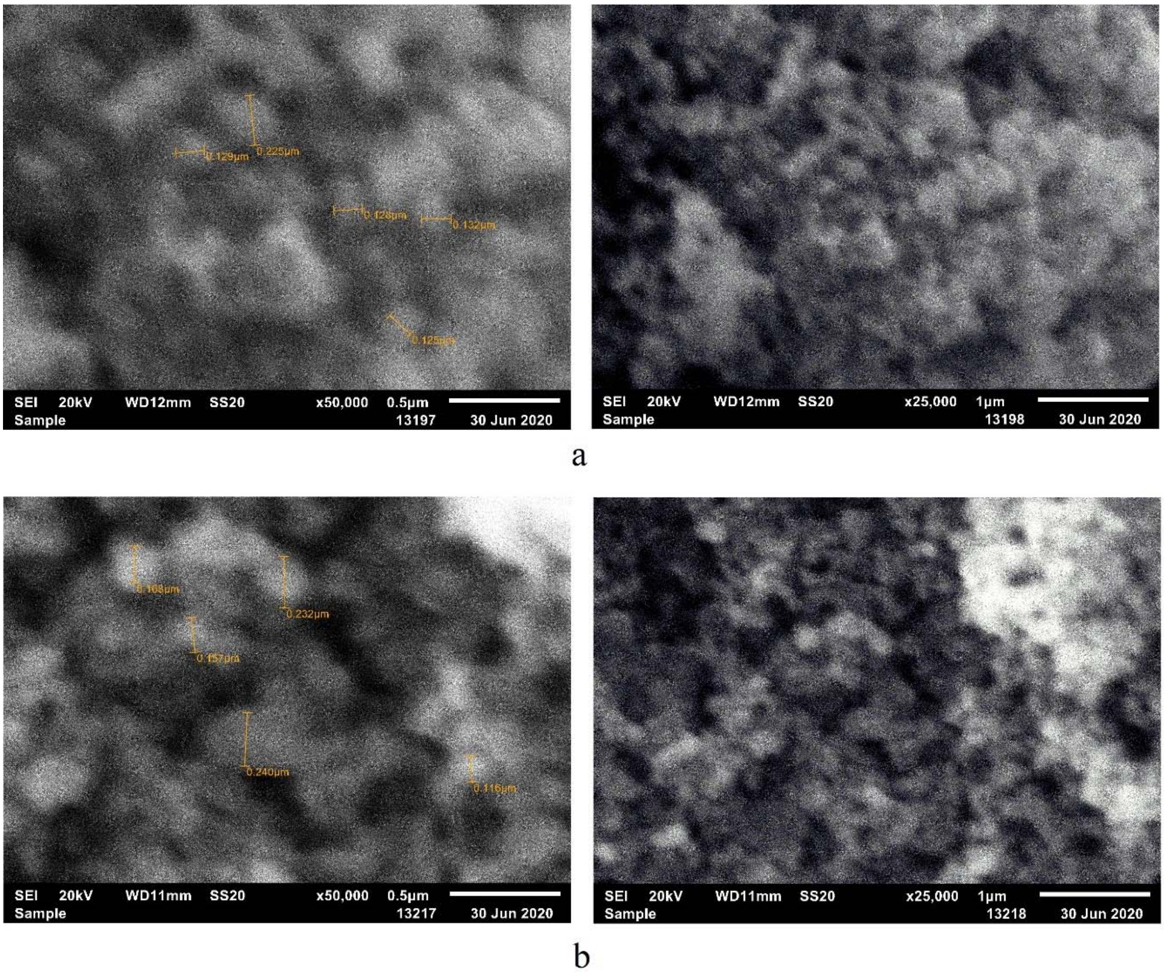

Figure 1 - Electron microscopic photographs of palladium powders obtained by reduction with titanium (III) ions: a - at initial content of palladium (II) ions - 0.1 g/l; b - at initial content of palladium (II) ions - 0.05 g/l

Based on the results of laboratory studies, we have proposed a new technological scheme for the production of ultra-dispersed palladium powders (figure 2).

We have previously shown [10-12] that in acidic solutions, when titanium electrodes are polarized by industrial alternating current under certain conditions, they are intensively dissolved to form trivalent ions colored purple. In carrying out such experiments, we have discovered a new phenomenon, which consists in the fact that after preliminary polarization of titanium electrodes with non-stationary currents, their further self-dissolution takes place in sulphate and hydrochloric acid solutions with the formation of titanium (III) sulfate and chloride, respectively. In this connection, it is very easy to obtain titanium trivalent salts. As can be seen from figure 2, by polarizing titanium electrodes (2) with industrial alternating current at a frequency of 50 Hz, titanium (III) ions are obtained in the electrolysis cell (1). In the reactor (2), a solution of titanium (III) sulfate was added to the palladium (II) chloride solution while stirring. In this case, elemental palladium is formed in the form of powder with particles of nanoscale values. In an electrolysis cell (3) in which the electrode spaces are separated by an anionite membrane, titanium (IV) ions are reduced in the cathode space to a trivalent state.

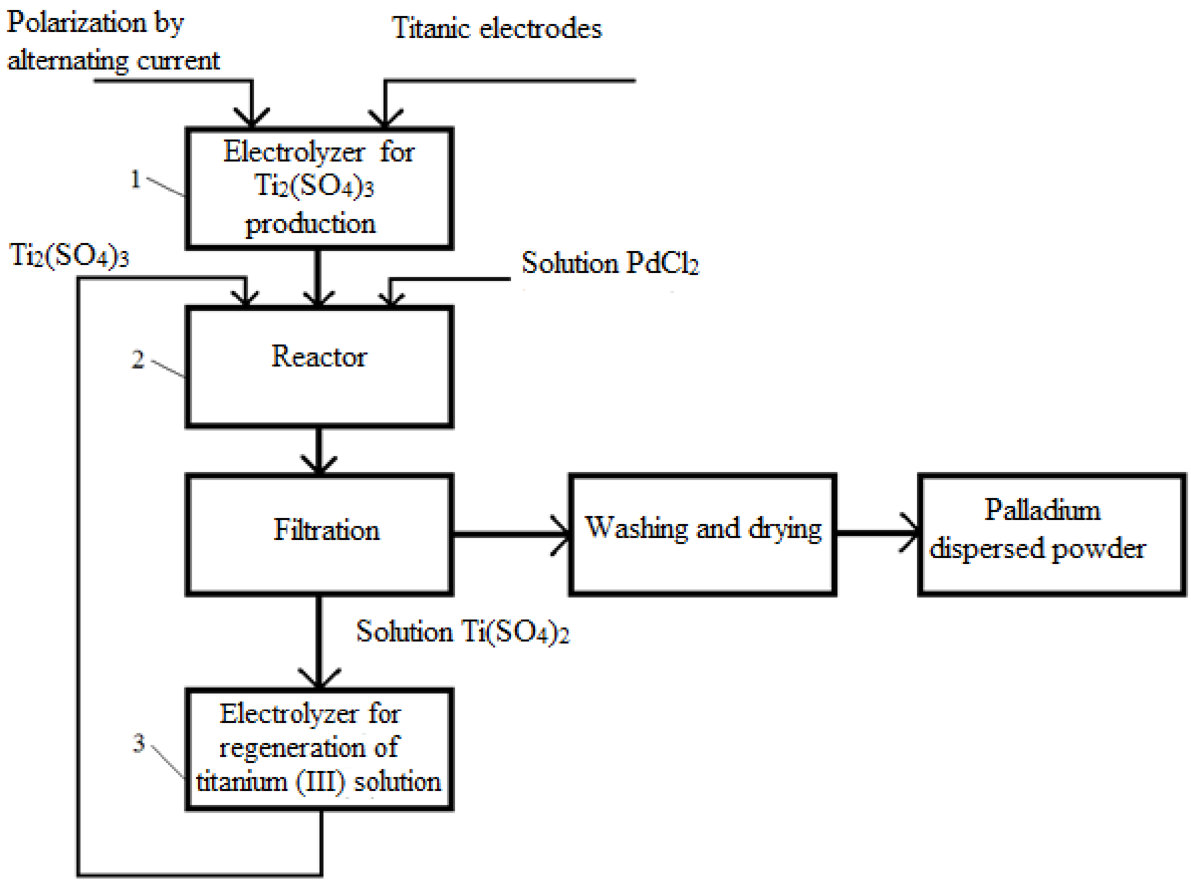

Figure 2 - Process flow diagram of production of ultra-dispersed palladium powders at cementation of palladium (II) ions with trivalent titanium ions: 1 - electrolyzer with titanium electrodes; 2 is a reactor for producing ultra-dispersed palladium powders; 3 shows an electrolytic cell with anionite membrane-separated electrode spaces for regeneration of titanium trivalent.

Palladium powders are separated by filtration, washed until there are no impurity ions, dried. All these processes are carried out in a box filled with inert gas (for example, carbon dioxide or argon). The obtained powder is placed in a sealed container.

When palladium powders are formed by reaction (1), trivalent titanium is converted to a quadrivalent state. Formed sulphate solution of tetravalent titanium is fed into cathode space (3) of electrolysis cell, in which electrode spaces are separated by anionite membrane. Titanium (IV) ions are reduced to trivalent state. A solution containing titanium (III) ions is sent to reactor (2) and reaction (1) is carried out again in this reactor to obtain palladium powder.

Thus, earlier we first showed the possibility of producing ultra - and nano-sized copper powders in the cathode, prianodic, as well as in interelectrode spaces [13-15], and in this work we first showed the possibility of producing nano- and ultradisperse palladium powders in the presence of the red-ox system "titanium (III) - titanium (IV)." On the basis of the conducted laboratory studies, a process scheme for producing ultra-dispersed palladium powders is proposed. It is shown that by this technology palladium powders of spherical shape with particle size 0.116 - 0.240 mcm are formed.

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НАНО- ЖӘНЕ УЛЬТРАДИСПЕРСТІ ПАЛЛАДИЙ ҰНТАҒЫНЫҢ «ТИТАН (III) – ТИТАН (IV)» RED-OX-ЖҮЙЕСІ ҚАТЫСЫНДА ТҮЗІЛУІ

Аннотация. Мақалада ультрадисперсті және наноөлшемдегі палладий ұнтағын «титан (III) – титан (IV) «red-ox» жүйесінің қатысында алудың біріктірілген химиялық және электрохимиялық әдісін жасауға арналған зерттеулер нәтижелері келтірілген.

Тәжірибелер бөлме температурасында көлемі 50 мл-ге тең термостатталған ұяшықта жүргізілді. Құрамында палладий (II) иондары бар күкіртқышқылды ерітіндіге үшвалентті титанның күкіртқышқылды ерітіндісі қосылды. Осы кезде палладий иондары бірден наноөлшемді ұнтақ түрінде элементті күйге дейін тотықсызданады.

Құрамында палладий (II) және титан (III) иондары бар ерітінділерді эквиваленттік арақатынаста белгілі жағдайда араластырған кезде он секунд ішінде ерітінді түссізденетіні, басқаша айтқанда, мөлдір болатыны анықталды (үшвалентті титан сульфатының ерітіндісі бастапқыда күлгін түсті, ал палладий хлоридінің түсі – қызыл). Бұл құбылыс былайша түсіндіріледі: бұл кезде палладий атомарлы күйде болады және бөлшек өлшемі өте кіші болғандықтан, көзге көрінбейді. 2-3 минуттан соң палладий атомдары құрамындағы бөлшек өлшемі тәжірибе жағдайына тәуелді болып келетін агломераттар түзе, белгілі бір күйге дейін бір-бірімен біріге (топтала) бастайды. Осыдан соң ерітіндінің бүкіл көлемінде палладийдің қоңыр түсті коллоидты бөлшектері түзіледі, олардың тұрақтылығы тәжірибе жағдайына тәуелді болып келеді. Коагулянттар жоқ болған кезде коллоидты палладий ерітінділері 2-3 сағат бойы тұрақты болады, ал желатин қосылғанда олар 36 сағат бойы тұрақты күйінде сақталады.

Электрондық микроскоп арқылы палладий (II) иондарының әртүрлі бастапқы концентрацияларында алынған ұнтақ микросуреттері түсірілді. Барлық тәжірибе нәтижесінде бөлшектері сфера тәріздес, орташа өлшемі 0,116-0,240 мкм аралығында ұнтақ түзілетіні анықталды.

Үшвалентті титан иондарын эквивалентті мөлшерде қосқанда палладий (II) иондарының бастапқы концентрациясының түзілетін палладий ұнтақ мөлшеріне әсері зерттелді. Бұл кезде палладий (II) иондарының бастапқы мөлшерінің 96%-тен астамы ультрадисперсті ұнтақ түрінде элементті күйге өтетіні анықталды.

Палладий және титан иондарының әрекеттесуі кезінде тотығу-тотықсыздану реакциясының толық өтуі «red-ox» жүйенің реакция константасын есептеу арқылы анықталды. Аталған тотығу-тотықсыздану жүйесі константасының шамасы $K \cong 10^{34}$ және бұл шама екі реакцияның екеуі де солдан оңға қарай толық жүретінін және іс жүзінде қайтымсыздығын болжаудың негізі болып саналады. Жүргізілген есептеу нәтижелері үшвалентті титан иондарының палладий (II) иондарын толық элементті күйге дейін тотықсыздануына жұмсалатынын көрсетті.

Жүргізілген лабораториялық зерттеулер негізінде палладийдің ультрадисперсті ұнтағын алудың жаңа технологиясының принципиалды сызба-нұсқасы ұсынылды. Сонымен қатар, мақалада тотықсыздандырғыш үшвалентті титан сульфатын алу жөнінде деректер келтірілген. Алынған деректер титан электродтарын қышқылды ерітінділерде өндірістік айнымалы токпен поляризациялау арқылы белгілі жағдайда палладий (II) иондарын тотықсыздандыратын үшвалентті титан иондарын түзе еритіні көрсетілді.

Түйін сөздер: ультрадисперсті наноөлшемді ұнтақтар, палладий, титан (III), иондар, «red-ox» жүйе, тотықсыздану, дисперстілік.

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ФОРМИРОВАНИЕ НАНО- И УЛЬТРАДИСПЕРСНЫХ ПОРОШКОВ ПАЛЛАДИЯ В ПРИСУТСТВИИ «RED-OX» СИСТЕМЫ «ТИТАН (III) – ТИТАН (IV)»

Аннотация. В статье приведены результаты исследований, посвященных разработке способа получения ультрадисперсных и наноразмерных порошков палладия комбинированным химическим и электрохимическим способом в присутствии «red-ox» системы «титан (III) – титан (IV).

Опыты проводились в термостатированной ячейке емкостью 50 мл при комнатной температуре. К сернокислому раствору, содержащему ионы палладия (II), добавляли сернокислый раствор трехвалентного титана. При этом практически сразу же происходит восстановление ионов палладия до элементного состояния в виде наноразмерных порошков.

Установлено, что при смешивании раствора, содержащего ионы палладия (II) и титана (III в эквивалентном соотношении при определенных условиях, в течение десяти секунд раствор становится бесцветным (исходный раствор сульфата трехвалентного титана имеет фиолетовый цвет, а хлорид палладия – красноватый цвет), т.е. прозрачным. Это явление мы предположительно объясняем тем, что в этот момент палладий находится в атомарном состоянии и из-за очень мелких размеров частиц становится практически невидимым. Показано, что после 2-3 минут атомы палладия начинают объединяться (группироваться) друг с другом до определенного состояния, образуя агломераты, в которых размеры частиц зависят от условий опыта. Далее, по всему объему раствора образуются коллоидные частицы палладия темноватого цвета, устойчивость зависит от условий опыта. В отсутствии коагулянтов коллоидные палладиевые растворы остаются устойчивыми в течение 2-3 часов, а в присутствии желатина – в течение 36 часов.

С помощью электронного микроскопа сняты микрофотографии порошков, полученных при разных исходных концентрации ионов палладия (II). Установлено, что во всех опытах формируются порошки с частицами сферической формы, средние размеры которых колеблются в пределах 0,116–0,240 мкм.

Исследовано влияние исходной концентрации ионов палладия (II) на количество образовавшихся порошков палладия при добавлении эквивалентного количества ионов трехвалентного титана. При этом более 96% исходного количества ионов палладия (II) переходит в элементное состояние в виде ультрадисперсного порошка.

Полноту протекания окислительно-восстановительной реакции при взаимодействии ионов палладия с ионами титана определили на основе расчета константы реакции «red-ox» системы. Величина константы вышеуказанных окислительно-восстановительных систем, равная $K \cong 10^{34}$, дает основание предположить, что обе реакции идут до конца слева направо и являются практически необратимыми. Результаты проведенных расчетов показывают, что ионы трехвалентного титана полностью расходуются на восстановление ионов палладия (II) до элементного состояния.

На основе проведенных лабораторных исследований предложена принципиально новая технологическая схема получения ультрадисперсных порошков палладия. В статье также приводятся данные о получении восстановителя – сульфата трехвалентного титана.

Приведенные данные показывают, что в кислых растворах при поляризации титановых электродов промышленным переменным током в определенных условиях они интенсивно растворяются с образованием трехвалентных ионов титана, являющихся восстановителем ионов палладия (II).

Ключевые слова: ультрадисперсные наноразмерные порошки, палладий, ионы титана (III), «red-ox» система, восстановление, дисперсность.

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PHYSICAL AND CHEMICAL STUDIES OF THE OIL SLUDGE HYDROCARBON COMPOSITION AND THE PROSPECTS FOR THEIR USE IN THE TECHNOLOGY OF EXPANDED CLAY PRODUCTION

Abstract. The article presents the results of gas chromatographic studies of the oil sludge hydrocarbon composition, physical and chemical and heat-producing properties, which enabled to assess the potential of oil sludge as raw materials, their assortment predisposition and possible manufacturability. It has been established that the main physical and chemical characteristics of the organic part from the averaged samples of oil sludge are similar in properties to raw materials for the production of kerosene-diesel fractions. The expediency of the use of oil sludge and weakly bloating clay materials in the production technology of the popular construction material – expanded clay is substantiated. The results of experimental studies on the development of light and porous heat insulating material by granulation method are presented herein. It is shown that oil sludge from a high viscous state is transferred to a loose conglomerate with a moisture content of 12–15% by co-mixing with finely dispersed sand dune, which ensures uniform distribution when mixed with the basic mass. The peculiarities of granules burning according to a specially developed mode without preliminary drying are considered. It has been established that the addition of oil sludge increases the organic content in the mixture, thereby intensifying the process of combustion, gas generation and bloating of the ceramic body, which will positively affect the technological parameters of obtaining a product. It is found that the proposed technology allows to obtain marketable products, which can be used efficiently. At the same time, the unconditional priority is given to waste-free technologies, as the most environmentally friendly.

Key words: oil sludge, expanded clay, loess-like loam, dune sand, porous microstructure.

Introduction. In the Republic of Kazakhstan, a leading role is given to the intensive development of the oil and gas industry, since it forms the basis of the modern economy. However, the commercial development of raw hydrocarbon deposits has a technological impact on the environment objects. For example, in the process of extracting, pumping, storing oil, operating a sewage treatment plants, a significant amount of oil wastes is generated, which belong to Grades 2-3 as per toxicity level and are dangerous pollutants of surface and undergroundwaters, soil and air. At the same time, the hydrocarbon part of the oil wastes is a valuable organic raw material [1] and it can be considered as a secondary raw material resource. One type of such oil wastes is oil sludge, which is a fairly stable suspension of highly-dispersive mineral particles, organic compounds and water. This is potentially a secondary oil resource that can be brought up to the appropriate parameters and returned to the turnover.Processing of this material can ensure profitability, which will allowconducting necessary environmental protection and rehabilitation measures and preserving the financial stability of the oil production enterprise.

Solving the problem of oil sludge disposal has been the subject of many papers [2-6]. This indicates, on the one hand, the importance and relevance of this problem, and on the other hand, its complexity and the impossibility of anunambiguous solution. Therefore, it can be said that despite the diversity of existing methods, the problem of processing and using oil sludge is one of the least developedonesaccording to the technology of their disposal.

It is known that the total area of existing and promising oil and gas fields in the Republic of Kazakhstan occupies more than 60% of the country's territory, and there are more than 200 existing oil and gas fields [7-10]. On the territory of each oil-producing complex, operating for decades, there are oil sludge tanks, the number of which is growing. Their capacity at most enterprises is currently overfilled. Therefore, the disposal of newly formed and accumulated oil sludge waste should be one of the priority areas thatstipulates a very heavy demand for the creation of modern technologies and effective methods of treatment and disposal.

Based on the above, the purpose of this paper is to study the oil sludge hydrocarbon composition and its physical and chemical, heat-producing properties; to analyze the effect of the oil sludge composition on the technological parameters of its processing as a bloating agent in the production of expanded clay.

Materials and methods. Oil sludges from the collectors of Kumkol, PetroKazakhstan Kumkol Resources JSC and Aschisay, KOR JSC based on the territory of Kyzylorda Region were taken as the objects of the study.

Oil sludges are extremely diverse in composition and are complex systems consisting of oil, water and mechanical impurities, the ratio of which varies within a very wide range [7-11].

Hydrocarbon composition of oil sludge has been studied using gas chromatograph-mass spectrometer Agilent 7890A/5975C (USA).

Gaschromatographicdetermination of the total hydrocarbon content in the oil sludge when programming the temperature of the partition column makes it possible to study in detail the composition of oil hydrocarbons.

Chromatographic conditions in analyzing hydrocarbons extracted from oil sludge are given in table 1.

Figures 1 and 2 show the chromatogram of the studied oil sludge and hydrocarbon composition is given in table 2.

Table 1 - Chromatographic conditions in analyzing hydrocarbons extracted from oil sludge

Indicators	Chromatographic conditions
moving phase (carrier gas)	helium
evaporator temperature	350^0C
flow vent (Split)	30:1
column thermostat temperature: beginning - temperature rise - end - retention time at this temperature -	 70^0C 4^0C per minute 290^0C 30 min
total analysis time	85 min
ion mode of mass detector	with electron impact method
Capillary chromatographic column	HP-5MS
column length	30 m
inner diameter	0,25 mm
stationary phase	dimethylpolysiloxane (95%)

Table 2 - Group composition of hydrocarbons by results of chromatography-mass spectrometric analysis

Hydrocarbon groups contained in oil sludge	Quantitative content, wt. %	
	Oil sludge from the collectors of Kumkol, PetroKazakhstan Kumkol Resources JSC	Oil sludge from the collectors of Aschisay, KOR JSC
Paraffins	46.38	45.12
Uncondensed cycloparaffins	27.71	28.25
Condensed cycloparaffins with 2 rings	8.45	7.85
Condensed cycloparaffins with 3 rings	6.92	7.14
Benzenes	2.74	3.79
Naphthenobenzenes	0.10	0.11
Dinaphthenobenzenes	0.10	0.10
Naphthalenes	3.66	3.59
Acenaphthenes	2.96	3.21
Phenanthrenes	0.98	0.84

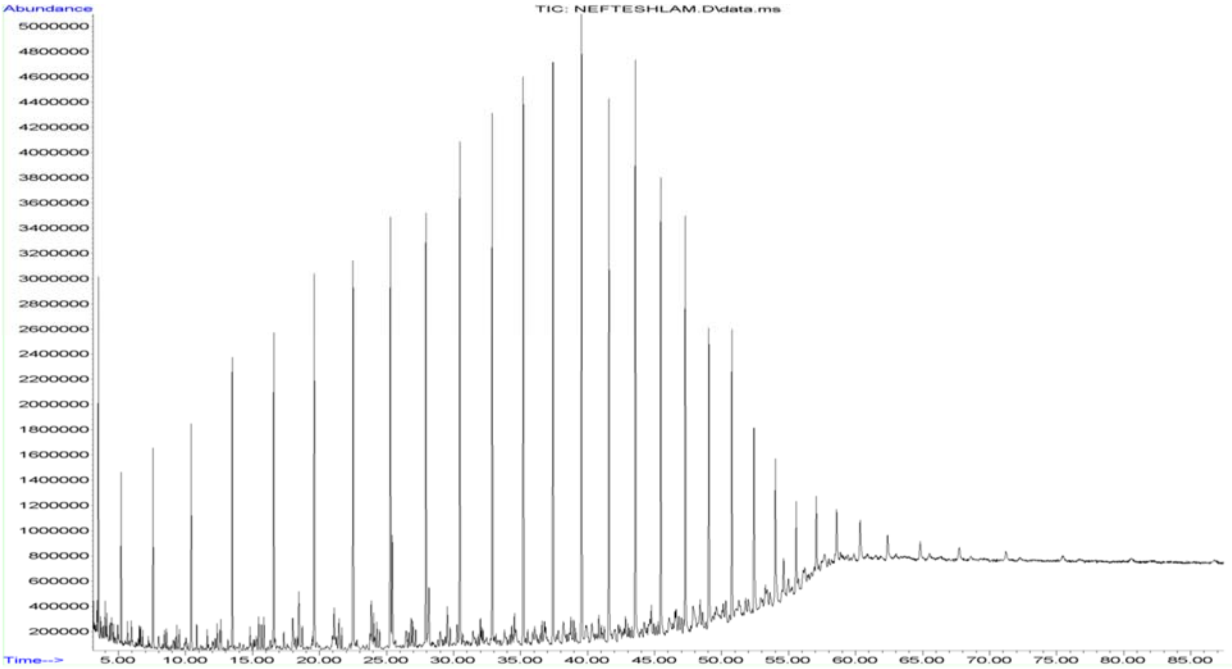

Figure 1 - Chromatogram of hydrocarbons extracted from the target oil sludge from the collectors of Kumkol, PetroKazakhstanKumkolResourcesJSC

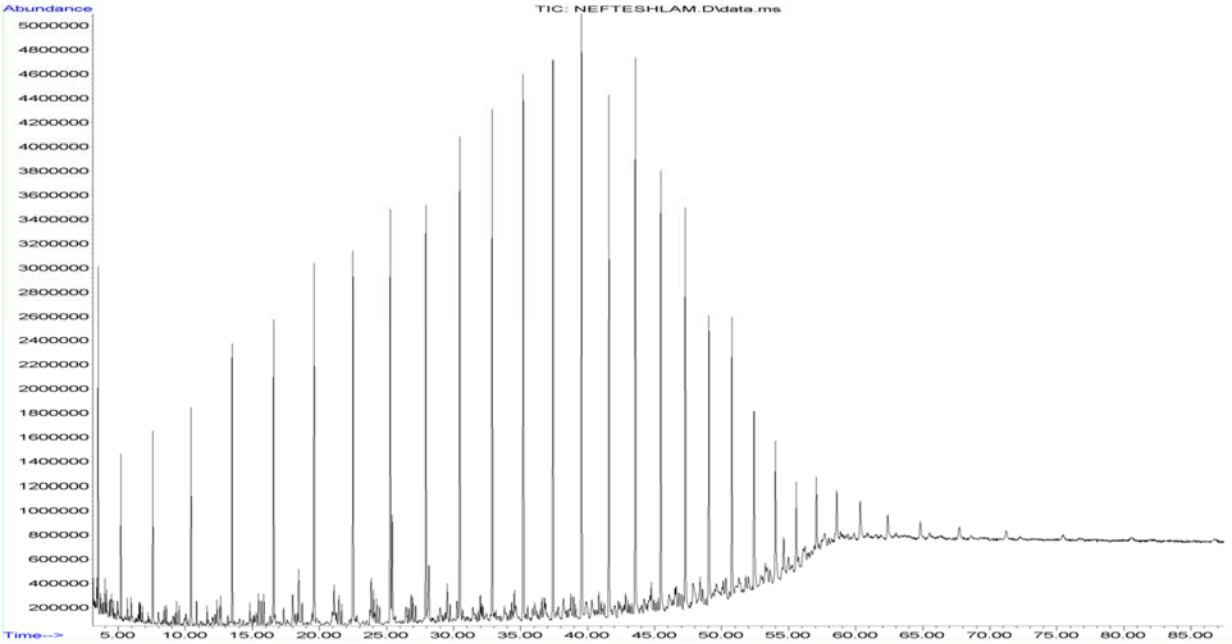

Figure 2 - Chromatogram of hydrocarbons extracted from the target oil sludge from the collector of Aschisay, KOR JSC

The physical and chemical properties, i.e. density, fractional composition, mass fraction of sulfur, combustion heat, content of mechanical impurities and chloride salts of the oil sludge under study were carried out according to known methods.

The mass fraction of sulfur in the oil sludge under studyhas been determined on the device Spectroscan-Max GF2E (Russia) by measuring the intensity of the sulfur fluorescence radiation excited under irradiation of the test sample with x-rays.

The combustion heat of the test samplehas been determined on the calorimeter S2000 of the company IKA-Werke (Germany) at the clean burning of a pre-weighed mass in the calorimetric bomb in a compressed oxygen environment andmeasurement of the amount of heat released at the combustion of auxiliary substances.

The results of the study of physical and chemical properties of oil sludge are given in table 3.

Studiesshow that the composition of oil sludge stored in sludge collectors for several years differs from the composition of fresh one. The high viscosity of oil sludge, high content of mechanical impurities and, most importantly, high aggregative stability are due mainly to the high content of asphaltenes, resins, paraffins and other high molecular components.

Table 3 - Properties of oil sludge

Descriptionof indexes	Indexes	
	Oil sludge from the collectors of Kumkol, PetroKazakhstan Kumkol Resources JSC	Oil sludge from the collectors of Aschisay, KOR JSC
Density, kg/m^{3}at20^{0}C	836.4	837.2
Fractional composition,% vol.		
200^{0}C	11	12
300^{0}C	39	38
350^{0}C	54	53
Mass fraction of sulfur, %	0.024	0.016
Combustion heat, kJ/g	44.987	45.546
Content of mechanical impurities, %	0.027	0.025
Content of chloride salts, mg / dm^3	28.46	32.95

Results and discussion. It has been established that according to the physical and chemical properties, oil sludge has a dual chemical function. On the one hand, there is its affinity to light oil products such as gasoil diesel oil products, on the other hand, as per the content of metalloporphyrin complexes, carbon radicals, colloidal structureand reactive capacity, it is close to heavy oil productssuch as fuel oil.

Previouslyin the papers [12,13], the affinity of the physical and chemical properties of the hydrocarbon part of oil sludgeswith heavy oil fractions has been described, and it has been determined that they belong to the category of highly flammable and combustible materials.

It is also known from literature sources that the multicomponent composition of the oil sludge pitproducts of oil production, the presence of various chemical compounds in it create many problems during the development of processing technologies, the extraction of commercial oil from them, the removal of solid residue from oil products.

Therefore, oil sludges, which, due to their composition, are difficult to burn and do not have resource valuefrom the practical and production standpoint, are most expedient to use in the production of construction materials, namely, in the production technology of the popular construction material – expanded clay. Oil sludge will play the role of a bloating agent in the composition of expanded clay. The addition of oil sludge increases the organic content in the mixture, which intensifies the process of combustion, gas generation and bloating of the ceramic body, respectively, which will positively affect the technological parameters of obtainingaproduct.

The studies of the authors [14-18] have assessed the possibility of using local clay materials, oil-contaminated wastes for the production of expanded clay granules, methods for producing expanded clay gravel, using it as a light fillerfor various construction applications, such as thermal insulation, lightweight structural concrete, and. etc.

In this light, we have given preference in this work to the use of noncritical raw materials. When justifying the need to adjust mixtures with additives and when choosing their type, the chemical, mineralogical and granulometric compositions of the clay raw materials; availability of local resources suitable for use of materials; technical and economic effect have been taken into account. For example, as clay raw materials – weakly bloating loess-like loams, which have reserves in all regions of the Republic of Kazakhstan. The use of expensive fuel materials as a bloating and thinning agent is excluded. Instead of this, bottom oil sludge from the collectors of Aschisay, KOR JSC, based on the territory of the Kyzylorda Region is proposed.

Such methods allow obtaining marketable products, which can be usedefficiently. At the same time, the unconditional priority is given to waste-free technologies, as the most environmentally friendly.

The main properties of raw materials were studied in the papers of the authors [19,20].

Raw materials were preliminarily milled in an MShL-1P laboratory ball mill to a specific surface of 1500-2000 cm^2/g. A sample of oil sludge obtained as the result oftank cleaning, was preliminarily subjected to averaging throughmechanical mixing. It is known that the oil sludge has an increased ductility and the use in such state in the compositions is difficult. Therefore, in the first stage, the oil sludge is transferred from a high viscous state to a capillary-porouscolloidal state by co-mixing with finely dispersed sand dune. This technological operation transfers the oil sludge into a loose conglomerate with a moisture content of 12-15% and provides a convenient position for subsequent technological operations, such as proportioning and uniform distribution when mixed with the basic mass. To determine the physical and mechanical properties of the raw material and the finished product, a set of standard techniques were used according to GOST 9757-90, GOST 22263-76 and GOST 530-2007. The measurement of the thermal conductivity of the samples was carried out using an ITP-MG-4 ZOND thermal conductivity meter. The examination of the surface microstructure was carried out on a JSM – 6510 LV scanning electron microscope manufactured by JEOL.

Raw material composition was prepared from the prepared components through weighing and proportioning. Specificcompositional analysis of the object under study is represented in table 4.

Table 4 - Compositional analysis of the ceramic composition

Components, wt. %	
Loess-like loam	Conglomeratemixture “sanddune - oilsludge”
85,0	15
83,0	17
80,0	20
78,0	22
75,0	25

Ceramic body with molding water content 18-20% was prepared from the compounds under study. Then granules with fractions of 5-10, 10-20, 20-40 mm, which were subjected to heat treatment at temperatures of 200-500ºC for 0.5-1.0 hours in a ShSP-0.5-70 drying cabinet, were manufactured. Granules for bloating were burned in a rotary kiln of the RSR120/1000/13 brand according to a specially developed mode in the temperature range of 1150–1180°C. Bloated granules were tested for the definition of physical and mechanical properties.The results of experimental studies are presented in table 5.

Table 5 - Physical and mechanical properties of the samples under study

Composition No.	Sensitivity coefficient to drying asper the Chizhsky rapid method, sec.	Burning temperature, ^0C	Bulk density kg/m^3	Cylindercrushing strength, MPa	Thermal conductivity W/mK
1	130	1170 ± 15	520	4.5	0.12
2	145		510	4.3	
3	166		480	3.9	0.08
4	180		475	3.7	
5	195		450	3.5	

According to the results of experimental studies, with an increase in the content of conglomerate mixture “sanddune - oilsludge” through a reduction of loam content, a decrease in the bulk density of the material from 520 to 450 kg/m^3 is observed. Low indicators of bulk density are seen in compositions No. 4 and No. 5 and they are in the range of 450-475 kg/m^3. Similar changes occur in respect of thermal conductivity and cylindercrushing strength. The minimum values of strength and thermal conductivity are also seenin compositions No. 4 and No. 5, while the cylindercrushing strength of these compositions is in the range of 3.5–3.7 MPa, and the thermal conductivity equals to 0.08 W/mK.

According to the qualification of heat insulating materials, samples of compositions No. 4 and No. 5 belong to class B (0.06–0.115 W/mK), and compositions No. 1, No. 2 and No. 3 belong to class C (0.1–0.175 W/mK). According to GOST 9757-90, samples of compositions No. 4 and No.5 belong to P200as per strengthgrade, and samples of compositions No. 1, No. 2 and No. 3 belong to P150. Analysis of the research results shows that the granular heat insulating material obtained has the best thermal-insulating and physical and mechanical properties as compared to the properties of typicalmontmorillonite-type expanded clay.

The most important value of chemical and mineralogical content of the raw material composition in the system “loess-like loam – oil sludge – sand dune”lies in the fact that it predetermines the complex physico-chemical processof structure formationof the finished product, including phase transformations at the main stages of thermal treatment.

Figure 3 shows the research results of the surface morphology, quantitative energy-dispersive microanalysis on the elemental constituentsof the sample of composition “loess-like loam 80% - conglomerate (sand dune-oil sludge) 20%” using a scanning electron microscope.

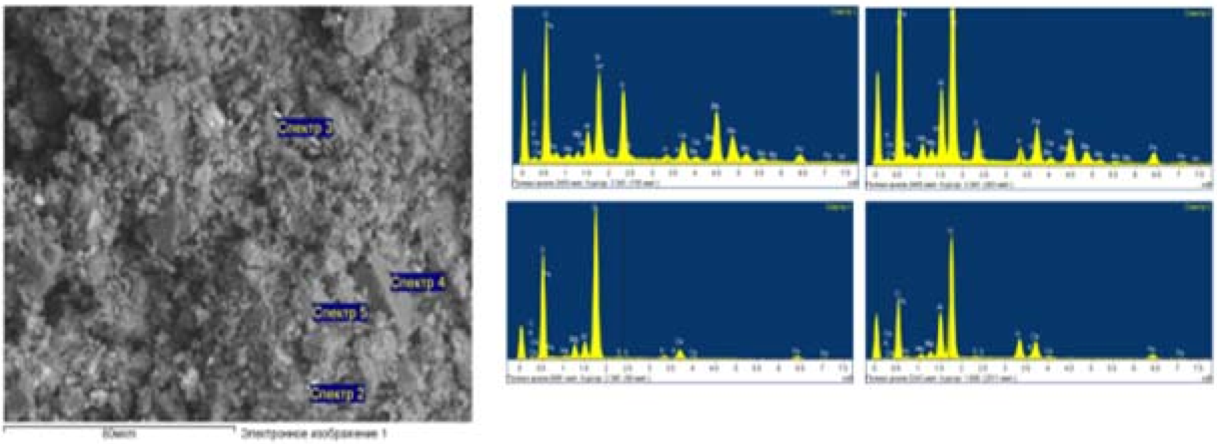

Figure 3 - Surface morphology, quantitative energy-dispersive microanalysis on the elemental constituentsof the sample of composition “loess-like loam 80% - conglomerate (sand dune-oil sludge) 20%”

The components of the system under consideration (clay minerals, oil sludge-basedorgano-mineral part) are directly involved and interact with each other in the formation of a porous structure with the release of a gaseous phasedue to combustion of oil sludge burning, without which pore formation and bloating are impossible.

It has been established that the addition of oil sludge increases the organic content in the mixture, which intensifies the process of combustion and gas generation, increases its capability to bloat, reduces the average density of the material; at the stage of drying, it acts as a thinning agent.

Organic impurities and iron oxides, increasing the intensity of oxidation-reduction processes, increase gas generation, reducing simultaneouslythe melting point and melt viscosity. The oxides of aluminium and silicon increase the viscosity, the burning temperature and as a result the strength of expanded clay. It is established that the combustion process of oil sludge in the composition of the conglomerate mixture allows raising the temperature inside the keln and speeding up the bloatingprocess of the ceramic body, and helps to reduce energy costs for the manufacture of products by 25-30%.

Bloating and formation of the structure in the composition under study is due to the optimum combination of components determining the rheological parameters of the pyroplastic body. This is due to the special nature of the structure and composition of the crystal lattices of the minerals of the constituent components included in the group of quartz, kaolinite, hydromica, and others. Lightweight heat insulating material such as “expanded clay” and its porous microstructure is shown in figure 4.

Figure 4 - Expanded clay and its porous microstructure

Conclusions. As can be seen from the above, the studies undertaken suggest that the use of oil sludge as abloating agenthas a positive impact on the technological parameters of the ceramic bodyprocessing, makes it possible to obtain granular material – expanded clay based on weakly bloating loess-like loams. It also solves the issues of rational use of natural resources, provides the construction industry with a competitive construction material.

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МҰНАЙ ШЛАМДАРЫНЫҢ КӨМІРСУТЕК ҚҰРАМЫН ФИЗИКА-ХИМИЯЛЫҚ ЗЕРТТЕУ ЖӘНЕ ОЛАРДЫ КЕРАМЗИТ ӨНДІРІСІ ТЕХНОЛОГИЯСЫНДА ПАЙДАЛАНУ ПЕРСПЕКТИВАЛАРЫ

Аннотация. Мақалада мұнай шламының шикізат ретіндегі ықтимал әлеуетін, ассортименттік бейімділігі мен өндірілу қабілетін бағалауға мүмкіндік тудырған мұнай шламының көмірсутек құрамын, физика-химиялық және калориялық қасиеттерін газды хроматографиялық зерттеу нәтижелері келтірілген. Мұнай шламының көмірсутек құрамын зерттеу Agilent 7890A / 5975C газды хромато-масс-спектрометр арқылы зерттелетін мұнай шламындағы күкірттің массалық бөлігі – Spectroscan-Max GF2E қондырғысы, ал калориялық мәні – IKA-Werke C2000 калориметрі арқылы жүргізілді. Араластырылып алынған сынамалардың органикалық бөлігінің негізгі физика-химиялық сипаттамалары қасиеттері бойынша керосинді-дизельдік фракцияларды өндіру үшін қолданылатын шикізатқа жақын екендігі анықталды. Мұнай шламын және Қазақстан Республикасының барлық өңірінде кездесетін нашар ісінетін сазды топырақты белгілі құрылыс материалы – керамзитті өндіру технологиясында пайдаланудың мақсаттылығы негізделген. Эксперименттік зерттеулер арқылы жеңіл және кеуекті жылу оқшаулағыш материалды түйіршіктеу әдісімен дайындау технологиясының нәтижелері анықталған. Мұнай шламын жоғары тұтқырлықтағы күйден негізгі қоспаға қосуға ыңғайлы 12-15% ылғалдықтағы конгломератты күйге барханды құммен араластыру арқылы қол жеткізуге болатындығы көрсетілген.

Зерттелетін құрам негізіндегі қалыпты ылғалдылығы 18-20% болатын керамикалық қоспа дайындалды. Осы қоспадан фракциялары 5-10, 10-20, 20-40 мм түйіршіктелген материал дайындап, арықарай 200-500°С, 0,5-1,0 сағат көлемінде ШСП-0,5-70 шкафында кептірілді. Сонан соң түйіршіктелген материал RSR120/1000/13 маркалы айналмалы пешінде дайындалған режимге сәйкес 1150-1180°С температура аралығында ісіру үшін күйдірілді. Ісінген түйіршікті материалдың физика-механикалық қасиеттері МЕМС 9757-90, 22263-76, 530-2007 кешенді стандартты әдістемелерді пайдалану арқылы жүргізілді. Үлгілердің жылу өткізгіш қасиеті ИТП-МГ-4 «ЗОНД» қондырғысы арқылы анықталды, беткі қабатының микроқұрылымы «JEOL» фирмасының JSM – 6510 LV растрлы электронды микроскопта жүргізілді. Яғни, ұсынылған технологияның тағы бір ерекшелігі керамикалық қоспадан дайындалған түйіршіктердің, алдын ала кептірілмей-ақ, арнайы жасалған режим бойынша айналмалы пеште күйдірілу мүмкіндігі қарастырылған. Мұнай шламын қосу шихтада органикалық зат құрамын жоғарылатады және осы арқылы керамикалық массаның жану, газ бөлу, ісіну үдерістерін белсендіре отырып, материал дайындаудың технологиялық параметрлеріне қолайлы әсер ететіндігі анықталған.

Жылусақтағыш материалдардың квалификациялық талабына сәйкес керамзиттің ұтымды құрамы Б (0,06–0,115Вт/мК) класына жататындығы және МЕМС 9757-90 сәйкес мықтылығы бойынша П200 маркасына сәйкестігі анықталды. Ұсынылған технология тиімді пайдалануға болатын тауарлы өнім өндіруге мүмкіндік береді. Жұмыста басымдық экологиялық тұрғыдан тиімді қалдықсыз технологиялар дайындауға бағытталған.

Қарастырылған құрылымдағы компоненттер, яғни, сазды минералдар, мұнай шламының органо-минералды бөлігі, бір-бірімен әрекеттесе отырып, мұнай шламының жану барысында бөлінген газды фаза әсерінен қуысты құрылымды түзуге қатысады. Бұл үдеріссіз қуыс түзбейді және ісінбейді.

Органикалық қоспалар және темір оксиді тотығу-тотықсыздану үдерістерінің қарқындылығын арттыра отырып, газ түзілісін жоғарылатады және балқу температурасы мен балқыма тұтқырлығын төмендетеді. Алюминиий оксиді мен кремний тұтқырлығын және күйдіру температурасын жоғарылатады, нәтижесінде керамзитті беріктендіруге үлес қосады. Сонымен қатар, конгломерат құрамында мұнай шламының жану үдерісі пеш ішіндегі температураны жоғарылатуға және керамикалық қоспаның ісіну жағдайын жылдамдатуға ықпал етеді. Нәтижесінде өндіру үдерісіне жұмсалатын энергияны 25-30 % үнемдеу мүмкіндігі туындайды.

Зерттелетін композициядағы ісіну және құрылым түзу үдерістері компоненттер құрамының ұтымдылығымен тікелей байланысты және пиропластикалық қоспаның реологиялық параметрлеріне де әсер етеді. Бұл кварц, каолинита, гидрослюда және т.б. тобына кіретін құрам компонент минералдары құрылымының және кристалл торының ерекшеліктері арқылы негізделеді.

Жүргізілген зерттеулер мұнай шламын ісіндіру компоненті ретінде пайдалану керамикалық қоспаны өңдеудің технологиялық параметрлеріне оңтайлы әсер ететіндігін, осы арқылы нашар ісінетін сары топырақты саздақтан түйіршектелген материал-керамзит алуға болатындығын дәлелдеді. Сонымен қатар, табиғи ресурстарды ұтымды пайдалануға болатындығын, құрылыс индустриясын бәсекеге қабілетті құрылыс материалымен қамтамасыз етуге болатындығын айқындады.

Түйін сөздер: мұнай шламы, керамзит, сары топырақты саздақ, барханды құм, кеуекті микроқұрылым.

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ФИЗИКО-ХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ УГЛЕВОДОРОДНОГО СОСТАВА НЕФТЯНЫХ ШЛАМОВ И ПЕРСПЕКТИВЫ ИСПОЛЬЗОВАНИЯ ИХ В ТЕХНОЛОГИИ ПРОИЗВОДСТВА КЕРАМЗИТА

Аннотация. В статье приведены результаты газохроматографического исследования углеводородного состава нефтешламов, физико-химических и теплотворных свойств, которые позволили оценить возможный потенциал нефтяного шлама как сырья, их ассортиментную предрасположенность, возможную технологичность. Изучение углеводородного состава нефтешлама проводили с помощью газового хромато-масс спектрометра Agilent 7890A/5975C, массовую долю серы в исследуемом нефтешламе – на приборе Спектроскан-Макс GF2E, теплоту сгорания – на калориметре С2000 фирмы IKA-Werke.

Установлено, что основные физико-химические характеристики органической части из усредненных проб нефтешламов по свойствам близки к сырью для производства керосино-дизельных фракции.

Обоснована целесообразность использования нефтяного шлама и слабовспучивающихся глинистых материалов, запасы которых имеются во всех регионах Республики Казахстан, в технологии производства популярного строительного материала – керамзит. Приведены результаты экспериментальных исследований по разработке технологии легкого и пористого теплоизоляционного материала методом гранулирования. Показано,что нефтешлам из высоковязкого состояния переводится в сыпучий конгломерат с влажностью 12–15% путем совместного перемешивания с тонкодисперсным барханным песком, что обеспечивает равномерность распределения при перемешивании с основной массой. Из исследуемых составов приготовлены керамическая масса с формовочной влажностью 18-20 %. Затем изготовлены гранулы с фракциями 5-10, 10-20, 20-40 мм, которые подвергались термообработке при температурах 200–500ºС в течении 0,5-1,0 часа в сушильном шкафу ШСП-0,5-70. Гранулы для вспучивания обжигались во вращающейся печи марки RSR120/1000/13 по специально разработанному режиму в интервале температур 1150-1180ºС. Вспученные гранулы подвергались испытанию по определению физико-механических свойств с использованием комплекса стандартных методик согласно ГОСТ 9757-90, ГОСТ 22263-76, ГОСТ 530-2007. Измерение теплопроводности образцов осуществили с помощью измерителя теплопроводности ИТП-МГ-4 «ЗОНД», изучение микроструктуры поверхности проведена на растровом электронном микроскопе JSM – 6510 LV фирмы «JEOL».

Таким образом, по предлагаемой технологии рассматриваются особенности обжига гранул по специально разработанному режиму без предварительной сушки. Установлено, что добавление нефтяного шлама повышает содержание органики в шихте, тем самым интенсифицирует процесс горения, газообразования и вспучивания керамической массы, что благоприятно повлияет на технологические параметры получения материала. Согласно квалификации теплоизоляционных материалов, оптимальные составы керамзита относятся классу Б (0,06 - 0,115 Вт/мК) и согласно ГОСТу 9757-90 относятся к марке по прочности П200.

Установлено, что предлагаемая технология позволяет получать товарную продукцию, находящую квалифицированное применение и при этом безусловный приоритет принадлежит безотходным технологиям как наиболее экологичным.

Компоненты рассматриваемой системы (глинистые минералы, органо – минеральная часть на основе нефтешлама) взаимодействуют с друг другом и участвуют непосредственно в образовании пористой структуры с выделением газообразной фазы за счет горения нефтешлама, без которой невозможно порообразование и вспучивание.

Органические примеси и оксиды железа, повышая интенсивность окислительно-восстановительных процессов, увеличивают газообразования, снижая одновременно температуру плавления и вязкость расплава. Оксиды алюминия и кремния повышают вязкость, температуру обжига и в конечном итоге – прочность керамзита. Установлено, что процесс горения нефтешлама в составе конгломератной смеси позволяет повысить температуру внутри печи и ускорить процесс вспучивания керамической массы. А также способствует снижению энергозатрат на производство изделий на 25-30 %.

Вспучиваемость и образование структуры в исследуемой композиции обусловлено оптимальным сочетанием компонентов, определяющим реологические параметры пиропластической массы. Это обуславливается особым характером строения и состава кристаллических решеток минералов, составляющих компонентов, входящих в группу кварца, каолинита, гидрослюды и других.

Проведенные исследования позволяют утверждать, что использование нефтяных шламов в качестве вспучивающей добавки благоприятно влияет на технологические параметры переработки керамической массы, дает возможность получить гранулированный материал – керамзит на основе слабовспучивающихся лессовидных суглинков. А также решает вопросы рационального использования природных ресурсов, обеспечивает строительную индустрию конкурентоспособным строительным материалом.

Ключевые слова: нефтешлам, керамзит, лессовидный суглинок, барханный песок, пористая микроструктура.

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PROSPECTS FOR CREATING A FULL CYCLE OF LITHIUM PRODUCTION IN KAZAKHSTAN – FROM ORE PROCESSING TO LITHIUM BATTERIES

Abstract. Today, lithium is becoming a new strategic material capable of influencing the sustainable development of the world economy. The results of developments in the production of innovative electrode materials from lithium carbonate on the basis of domestic lithium-containing raw materials with the creation of a full cycle of the technological line of lithium production: from ores to modern lithium batteries are pesented. Analysis of the explored reserves, mineral and material composition of domestic spodumene raw materials and lithium-containing dumps of the Belogorsk GOK indicate the prospects and expediency of their development for the production of the ever-increasing needs of the world market for lithium materials. As a result, the sulfuric acid technology for obtaining high-grade lithium carbonate directly from spodumene was optimized, bypassing the stage of obtaining a technical grade product, in a single technological process for processing spodumene with a reduction in the number of technological operations, excluding the expensive operation of concentrating a lithium sulfate solution by stripping. An efficient technology of purification and post-treatment of technical lithium carbonate to battery quality of 99.95% has been developed, including the processes of causticization of technical lithium carbonate, ultrafiltration and ion-exchange sorption of a solution of lithium hydroxide, followed by precipitation of lithium carbonate by ammonium carbonate. Cathode materials - lithium iron-phosphate , obtained from high-purity lithium carbonate by aerosol pyrolysis (MAP) and the sol-gel method (SGM), showed good electrochemical characteristics. The end result is innovative electrode materials for modern LIBs with significantly increased capacity and stability. The practical implementation of a full cycle of technologies from lithium-containing raw materials to modern lithium batteries opens up prospects for the creation in Kazakhstan of a high-tech lithium cluster according to the Scheme: Spodumene ores → Lithium concentrate → Lithium carbonate → Lithium cathode materials → Batteries

Keywords: lithium, extraction, ore, spodumene, battery grade lithium carbonate, li-ion battery, method, purification, technology, recycling, cathode material, lithium iron phosphate.

Introduction. Lithium-ion batteries (LIB) lead the market among all available battery technologies. They are widely used in portable electronic devices and electric vehicles [1]. LIBs have the advantages of high energy density, high potential, long shelf life and wide operating temperature range. The main part in the cost of LIB is made up of lithium-containing components (anode, cathode and electrolyte salt). Therefore, intensive work is underway to find new materials with better performance and low cost. This demand and the rapid development of the market for battery-powered devices, especially electric and hybrid vehicles and renewable energy, over the past 10 years has led to a sharp demand for higher capacity materials for LIB [2]. These batteries are also in demand in the market for military and space technology, medicine, etc. The growing consumption of LIB in electronic equipment has increased the demand for metals, especially lithium and lithium products. Lithium carbonate Li_2CO_3 is an important lithium salt that is widely used for the synthesis of cathode LIB materials due to its electrochemical reactivity and other unique properties [3,4].

EV developers are constantly exploring new sources of lithium carbonate in order to reduce dependence on its main suppliers - Chile and China. Today, the prospect of an "explosion" in the world lithium market associated with the aggravated raw material issue is becoming real. Increased investor interest in lithium products has led to dramatic changes in the lithium materials market. In May 2016, lithium carbonate prices rose sharply and reached $ 26.4/kg. Lithium metal prices also rose sharply from $ 100/kg to $ 400– $ 500/kg [5].

The rapid development of technologies in portable electronics (smartphones, laptops / tablets) and electric transport, led to the fact that lithium is becoming a new strategic material capable of influencing the sustainable development of the world economy [6, 7]. This led to its high demand in the international market and an increase in prices for it. Lithium demand is predicted to grow significantly over the coming years [8].

Currently, the sources for all commercial lithium production are mineral solutions and rich lithium ores. Solutions of continental origin are the largest resource (59%) in terms of lithium content, followed by hard rocks (25%). The largest known lithium deposits are found in Bolivia and Chile [9]. Australia and Chile are the leading producers and exporters of lithium ore materials. China and Chile have significant resources of lithium ore. Canada, Congo (Kinshasa), Russia and Serbia have lithium reserves of about 1 million tons each, while the same reserve for Brazil is 180,000 tons [10]. The distribution of lithium reserves in the world is uneven. Access to its reserves plays a significant role and influences technological development. Currently, lithium minerals are mined mainly from pegmatite. There are reserves of mineral raw materials containing mainly spodumene and petalite, which are intensively explored and mined in Canada, Finland and other countries. Spodumene is the main commercial lithium mineral containing about 8% lithium (in terms of Li2O oxide). About 50% of spodumene is mined in Australia and processed into lithium carbonate in China [11]. Another type of lithium deposits is the brines of some highly saline lakes. Chile and Argentina produce the largest part of the world's lithium from lake salts, together about 46% of all lithium production (companies FMC, Rockwood and S.Q.M.) [10, 11].

One of the main uses of spodumene is in the production of high purity lithium for lithium-ion batteries. Lithium obtained from spodumene has fewer impurities than lithium obtained from brines. These pollutants can degrade battery performance, making it the preferred raw material source for lithium battery. In this regard, there is currently growing interest in the development of lithium reserves concentrated in the pegmatite deposits of spodumene, the main lithium-containing mineral suitable for industrial processing. The problem of their development is the lack of efficient technologies for obtaining lithium concentrates, which can significantly reduce the cost of obtaining lithium carbonate [12].

The growth of areas and volumes of application of chemical power sources based on lithium compounds has led to the problem of developing a lithium raw material base due to the involvement of new, previously unused lithium sources.

Kazakhstan has large reserves of various rare earth metals and their accompanying lithium, mainly concentrated in Eastern Kazakhstan. According to the degree of readiness for development and development costs, the lithium deposits of the East Kazakhstan region can be divided into two groups.

The first group includes lithium mineral deposits in the East Kazakhstan region. The Akhmetkino deposit (vein 25), which has been explored and whose reserves have been approved, should be considered promising, and in which more than 23 thousand tons of lithium oxide and other useful components are concentrated [13, 14].

According to the US Geological Survey (USGS) at the beginning of 2013, the confirmed reserves of lithium in the subsoil of foreign countries show that even according to preliminary data of proven reserves, Kazakhstan is among the 10 world leaders.

The second group is represented by technogenic deposits, which are “tailings” formed due to the activities of the Belogorsk GOK during the Soviet period. This group of deposits requires the lowest development costs among the groups under consideration [15]. This group includes such concentrators as Belogorsk with tailings reserves of 1560.3 (lithium content 2800 g/t), BelogorskoeVerkhne-Baimurzinskoe with reserves of 4260 (lithium content 3200 g/t), Bakennoye with reserves of 1372 (lithium content 1500 g/t), Ak-Kezenskaya with reserves of 700 (lithium content 250 g/t), etc. In total, 15868 t of reserves with lithium content of 958.33 g/t. In total, for the Belogorsk GOK, there are more than 32 thousand tons of lithium in the dumps of the processing plants.

The purpose of this is to develop a technology for producing innovative electrode materials for modern lithium batteries with the creation of a full cycle of a technological production line from extracting lithium from domestic minerals and raw materials to science-intensive high-tech products - cathode and anode materials of modern lithium-ion batteries

Methods and Materials.

Feedstock: lithium-bearing, spodumene ore from the Ognevka deposit (East Kazakhstan region). Due to the fact that at present there is no production capacity for the production of spodumene concentrate from the ores of lithium deposits in the East Kazakhstan region, this work was carried out on the ore of manual disassembly. For this purpose, in the area of the exit of a powerful lithium-bearing, spodumene vein in the area of Ognevka (VKO), a technological sample weighing about 20 kg was taken. The processes of processing a technological sample for lithium carbonate were tested on the experimental laboratory equipment of the Central Scientific Research Laboratory of JSC Ulba Metallurgical Plant (UMP).

Additional purification of lithium carbonate to the quality of a battery grade of carbonization-decarbonization in combination with sorption processes. For this purpose, ion-exchange resins from Purolite and the appearance of ion exchangers Purolite S 930 plus, Purolite S 940, and Purolite S 950 were studied.

To prepare the cathode material by spray pyrolysis and the sol-gel method, lithium-iron phosphate and its modifications were synthesized. Syntheses of electrode materials were carried out on special equipment of the Institute of Accumulators.

Electrochemical cell preparation:

The cathode suspension is uniformly applied to the carbon surface covered with aluminum foil (CC Al) using a Micrometer Adjustable Film Applicator 150 mm with a Doctor Blade. A two-electrode electrochemical cell of the "coin cell 2032" type, where the anode is metallic lithium and the cathode is the synthesized material, lithium iron phosphate is collected in the glove box of the MBraun company. After assembling the cell, it is pressed on a hydraulic machine. To prepare the anode part of the button cell, spot welding of the Spot Welder brand (Japan) is used.

X-ray diffraction analysis of a lithium-iron-phosphate sample is performed on a Rigaku Smart Lab diffractometer. For electrochemical studies: cyclic voltammetry (reaction reversibility) and galvanostatic charge / discharge curves (determination of the cell capacity and cyclability, a VMP3 multichannel galvanostatpotentiostat (Biologic) was used.

Resuts. The full cycle of technology for producing lithium materials from spodumene raw materials includes the following main processing stages:

1. Sulfuric acid decomposition of spodumene concentrate and optimization of the technological process.

The sulfuric acid method includes decryption of the spodumene raw material at a temperature of 1100 °C, which ensures the transfer of spodumene to the acid-soluble β-modification and the subsequent processing of these media with sulfuric acid at a temperature of 250-300 ° C to obtain lithium sulfate [12, 16, 17].

$$\alpha\text{-Li (Na) Al [Si}_2\text{O}_6] \rightarrow \beta\text{-Li (Na) [AlSi}_2\text{O}_6] \quad (1)$$

$$\text{Li [AlSi}_2\text{O}_6] + \text{H}_2\text{SO}_4 \rightarrow \text{Li}_2\text{SO}_4 + \text{H[AlSi}_2\text{O}_6] \quad (2)$$

Treatment of the latter with a solution of soda ash makes it possible to obtain lithium carbonate as the final product [15].

The task of this stage is to develop a method for producing high-grade lithium carbonate by simplifying the process of purifying a lithium-containing solution from impurities. Optimization of sulfuric acid technology made it possible to obtain high-grade lithium carbonate directly from spodumene, bypassing the stage of obtaining a technical grade product, in a single technological process of processing spodumene with a reduction in the number of technological operations for purification from impurities, excluding the expensive operation of concentrating a solution of lithium sulfate by stripping.

A feature of the proposed technology is that the concentration of lithium is carried out by the membrane method of reverse osmosis, purification from impurities of metals and anions is carried out by the method of causticization of lithium sulfate, the precipitation of lithium carbonate is carried out with ammonium carbonate-UAS at a temperature of no more than 400 °C, followed by heating to 900 °C. Moreover, the concentration of lithium by the reverse osmosis method is carried out with the return of a part of the retentate stream to membrane filtration, and the proportion of the circulating retentate is calculated so that the total salt content of the lithium sulfate solution supplied to the membrane filtration does not exceed 35-40 g/l.

An essential feature of the method is the use of reverse osmosis membranes for concentrating a solution of lithium sulfate, which makes it possible to exclude from the technology a very laborious and expensive method of stripping off a solution of lithium sulfate. Concentration with the return of part of the retentate stream to membrane filtration leads to an increase in the degree of concentration of lithium in the retentate. Determination of the proportion of circulating retentate by the value of the salt content allows for optimal filtration modes by the reverse osmosis method. An increase in the salt content of the lithium sulfate solution supplied for filtration above 40 g/l is not advisable, since it will lead to a decrease in the membrane performance. The proposed method also differs in that the purification of metal impurities that form water-insoluble hydroxides and sulfate ion is carried out in one stage in the process of causticization - the conversion of lithium sulfate into lithium hydroxide. This technique allows further precipitation of lithium carbonate with a relatively cheap reagent, ammonium carbonate, and exclude the additional introduction of sodium ions into the technological process [17-18].

2. Additional purification of lithium carbonate to the quality of a battery grade of at least 99.5% of the content of the main component.

The technical problem posed is achieved due to the fact that in order to obtain high-purity lithium carbonate, the purification of technical lithium carbonate from impurities is carried out by converting it into lithium hydroxide monohydrate by the causticization method, since during the causticization process there is a partial purification of most of the normalized impurities, primarily calcium, magnesium, strontium, iron, due to the formation of poorly soluble hydroxides or carbonates of these elements at pH> 14. The total degree of purification from the analyzed impurities is 96.3%. However, in order to achieve the requirements of the quality specification of battery grade lithium carbonate, it is necessary to reduce the total content of impurities by about 2.7 times, for which finer methods of purification should be used - ion exchange sorption and / or ultrafiltration. The ultrafiltration method makes it possible to selectively remove most of the contaminants dissolved in it from the solution, to purify a larger number of impurities, and to reduce the load on sorption operations on synthetic cation-exchange resins based on phosphonic compounds, sulfonic acids, or complex chelate compounds. Further purification goes through the stages of ultrafiltration, ion-exchange sorption of a solution of lithium hydroxide and precipitation with ammonium carbonate (UAS) of purified lithium carbonate, the suspension of which is treated with carbon dioxide, and then after de-carbonization at a temperature of 75-900 °C, filtration and drying of the resulting precipitate of lithium carbonate, we obtain high-purity 99, 95% lithium carbonate. The bicarbonation is carried out at a pressure of 0.3 atm, which allows the use of conventional equipment that is not designed to work under pressure, which simplifies and reduces the cost of the process and the final product.

The technical result of the developed post-treatment technology is the production of high-purity lithium carbonate with a basic substance content of 99.95% [19].

3. Obtaining innovative electrode materials for LIB from battery-grade lithium carbonate based on domestic spodumene and technogenic raw materials

To date, the most promising cathode material for lithium-ion batteries is lithium iron phosphate $LiFePO_4$ with the olivine structure (hereinafter LFP). It has a number of important features: high theoretical capacity (170 mAh/g), charge/discharge potential (3.4 V relative to the lithium electrode), resistant to high temperatures (≤ 80 ° C) during charge/discharge, non-toxic and therefore widely used in the portable battery market. To obtain lithium iron phosphate by the sol-gel method, as well as by the spray pyrolysis method, powders of high-purity lithium carbonate (Li_2CO_3, obtained on the basis of the Kazakh mineral deposit Ognevka), 9-aqueous nitrate of iron (III) Fe $(NO_3)_3{\cdot}9H2O$ were taken as starting materials, ammonium dihydrogen phosphate $NH_4H_2PO_4$, which served as sources of Li, Fe, P (0.5:1:1 or 1:1:1 in a molar ratio) with stirring in distilled water. Citric acid is then added to form a homogeneous suspension. Citric acid was used as a carbon source. The acidity of the solution, equal to pH 2, was maintained by the addition of nitric acid. Then the solution is heated at 80 °C with constant stirring until a gel is formed. The resulting gel is dried at 100 °C overnight. Finally, it is annealed at 720 °C for 12 hours in an Ar/H2 atmosphere (95:5) to obtain lithium iron phosphate.

To study the synthesized powders ($LiFePO_4$), the methods of X-ray diffraction (determination of the phase composition) and scanning electron microscopy (determination of morphology) were used. To select the optimal temperature regime, synthesized samples were synthesized by spray pyrolysis at temperatures of 500, 550, 600 °C and the results of X-ray diffraction are shown in figure 10. For comparison, the X-ray diffraction pattern of a commercial $LiFePO_4$ sample is presented.

4. Electrochemical characteristics of a battery with a synthesized cathode material.

When studying the electrochemical properties of the synthesized materials, the following methods were used: cyclic voltammetry (VA) (reaction reversibility) and galvanostatic charge / discharge curves (determination of the cell capacity and cyclability).

Studies of the $Li/LiFePO_4$ system showed a stable potential for lithium deintercalation from the $LiFePO_4$ structure at 3.6 V and intercalation at 3.3 V for charge/discharge. No additional peaks were found, indicating the absence of impurities in the synthesized material. Based on the results of cyclic voltammetry, further galvanostatic testing was carried out within the voltage range of 2.5 - 4.2 V.

When analyzing the obtained charge-discharge curves, the initial discharge and charge capacities are about 145 and 138 $mAhg^{-1}$, respectively. Material capacity is over 81% of theoretical capacity. In addition, the sample has identical curves both during charging and discharging, which indicates a good reversibility of the reaction and the ability to deliver all the accumulated energy during the LIB discharge [20, 21].

Conclusion. Thus, a technology has been developed for obtaining innovative electrode materials for modern lithium batteries with the creation of a full cycle of a technological production line from extracting lithium from domestic mineral raw materials to science-intensive high-tech products - cathode and anode materials of modern lithium-ion batteries.

Creation of scientific and technological foundations for the development in Kazakhstan of a high-tech lithium cluster for the production of products with a high degree of readiness for the end user according to the scheme: Spodumene ores → Lithium concentrate → Lithium carbonate → Lithium cathode materials → Batteries. A business plan for the creation of a cluster-oriented lithium production was developed

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ҚАЗАҚСТАНДА ЛИТИЙ ӨНДІРІСІНІҢ КЕН ӨНДІРУДЕН ЛИТИЙ БАТАРЕЯЛАРҒА ДЕЙІНГІ – ТОЛЫҚ ЦИКЛІН ЖАСАУ ПЕРСПЕКТИВАЛАРЫ

Аннотация. Бүгінде литий әлемдік экономиканың тұрақты дамуына әсер етуге қабілетті жаңа стратегиялық материалға айналды. Литий-ионды батареялар (ЛИБ) қолданыстағы батарея технологиялары арасында нарықта көш бастап келеді. ЛИБ жоғары энергия тығыздығы, жоғары потенциал, ұзақ сақтау мерзімі және жұмыс температурасының ауқымы сияқты артықшылықтары бар. Электрондық жабдықтағы ЛИБ тұтынудың өсімі металдарға, әсіресе, литий мен литий өнімдеріне деген сұранысты арттырды. Литий карбонаты Li_2CO_3 – электрохимиялық реактивтілігі және басқа да ерекше қасиеттері арқасында ЛИБ катодты материалдарды синтездеу үшін кеңінен қолданылатын маңызды литий тұзы. Қазіргі кезде литийдің барлық өндірістік көзі минералды ерітінділері мен литий бай кен болып саналады. Литий минералдары негізінен пегматиттен өндіріледі. Құрамында сподумен және петалит бар минералды шикізат қоры бар. Сподумен – негізгі тауарлық литий минералы, құрамында (Li_2O оксиді бойынша) 8% литий бар. Литий шөгінділерінің тағы бір түрі – кейбір көл тұзы. Сподуменнің негізгі қолданысының бірі литий-иондық батериялар үшін жоғары таза литий өндірісі болып саналады. Қазақстанда әртүрлі сирек кездесетін металдардың және оларда ілеспе литийдің үлкен қоры кездеседі, негізінен қорлар Шығыс Қазақстанда шоғырланған. Бұл сақтау жүйелері мен энергия көзінің, жаңартылатын энергияның, электрониканың әлемдік нарығында маңызды орынға ие болу үшін Қазақстанда жаңа литий индустриясын құруға мүмкіндік тудырады. Бұл жұмыста литий өндірісінің кеннен қазіргі заманғы литий батареяларына дейінгі технологиялық желісінің толық циклын құра отырып, құрамында литий бар отандық минералды және техногенді шикізат негізінде литий карбонатынан инновациялық электродты материалдарды алудың өндіріс нәтижелері көрсетілген. Литий материалдарына әлемдік нарық сұранысын қанағаттандыру үшін отандық сподумен шикізатының және құрамында литий бар Белогор ГОК үйінділердің барланған қорларының минералды және материалды құрамының анализі олардың даму перспективалары мен мақсаттылығын көрсетеді. Нәтижесінде қымбат тұратын литий сульфаты ерітіндісін буландыру арқылы концентрациялау операциясын жойып, технологиялық операциялар санын азайту арқылы сподуменді қайта өңдеудің бірыңғай технологиялық процесінде жоғары сапалы литий карбонатын сподуменнен өндірудің күкірт қышқылы технологиясы оңтайландырылды. Техникалық литий карбонатын каустиктендіру, литий гидроксидінің ерітіндісін ультрафильтрациялау және ион алмастыру сорбциясы, содан кейін литий карбонатының аммоний карбонатымен тұндыру процестерінен тұратын техникалық литий карбонатын 99,95% батарея сапасына дейін тазарту және кейінгі өңдеудің тиімді технологиясы әзірленді. Аэрозольды пиролиз (МАП) және золь-гель әдісімен (SGM) тазалығы жоғары литий карбонатынан алынған катодты материалдар – литий темір фосфаты және оның модификациялары жақсы электрохимиялық сипаттамаларды көрсетті. Түпкілікті нәтиже – қуаттылығы мен тұрақтылығы едәуір артқан заманауи ЛИБ арналған инновациялық электродты материалдар болып саналады. Құрамында литий бар шикізаттан қазіргі заманғы литий батареяларына дейінгі технологиялардың толық циклін іс жүзінде жүзеге асыру схемасы бойынша соңғы пайдаланушыға дайындық деңгейі жоғары өнім өндіру үшін Қазақстанда жоғары технологиялық литий кластерін құру перспективаларын көрсетеді. Соңғы тұтынушыға дайындық деңгейі жоғары өнім өндіру үшін құрамында литий бар шикізаттан қазіргі заманғы литий батареяларына дейінгі технологиялардың толық циклін келесі сызба-нұсқа бойынша көрсетіледі: Сподумен кендері → Литий концентраты → Литий карбонаты → Литий катодының материалдары → Батареяларды іс жүзінде жүзеге асыру жұмыстары Қазақстанда жоғары технологиялық литий кластерін құрудың келешегін қалыптастырады.

Түйін сөздер: литий, экстракция, кен, сподумен, аккумуляторлы сапалы литий карбонаты, литий-ионды аккумулятор, әдіс, тазалау, технология, қайта өңдеу, катодты материал, литий темір-фосфаты.

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ПЕРСПЕКТИВЫ СОЗДАНИЯ ПОЛНОГО ЦИКЛА ПРОИЗВОДСТВА ЛИТИЯ В КАЗАХСТАНЕ – ОТ ПЕРЕРАБОТКИ РУД ДО ЛИТИЕВЫХ БАТАРЕЙ

Аннотация. Сегодня литий становится новым стратегическим материалом, способным влиять на устойчивое развитие мировой экономики. Литий-ионные батареи (LIB) лидируют на рынке среди всех доступных аккумуляторных технологий. LIB обладают такими преимуществами, как высокая плотность энергии, высокий потенциал, длительный срок хранения и широкий диапазон рабочих температур. Растущее потребление LIB в электронном оборудовании увеличило спрос на металлы, особенно на литий и литиевые продукты. Карбонат лития Li_2CO_3 является важной литиевой солью, которая широко используется для синтеза катодных материалов LIB из-за ее электрохимической реакционной способности и других уникальных свойств. В настоящее время источниками для всего коммерческого производства лития являются минеральные растворы и богатые литиевые руды. Литиевые минералы добываются в основном из пегматита. Сподумен - основной коммерческий литиевый минерал, содержит около 8% лития (в пересчете на оксид Li_2O). Одним из основных применений сподумена является производство лития с высокой степенью чистоты для литий-ионных батарей. Казахстан имеет большие запасы различных редкоземельных металлов и сопутствующего им лития, в основном сосредоточенные в Восточном Казахстане. Это дает возможность создать в Казахстане новую литиевую отрасль, чтобы стать важным игроком на мировом рынке систем хранения и источников энергии, возобновляемой энергетики, электроники. В настоящей работе представлены результаты разработок получения инновационных электродных материалов из карбоната лития на основе отечественного литийсодержащего минерального и техногенного сырья с созданием полного цикла технологической линии литиевого производства: от руды до современных литиевых батарей. Анализ разведанных запасов, минерального и вещественного состава отечественного сподуменового сырья и литийсодержащих отвалов Белогорского ГОК свидетельствуют о перспективности и целесообразности их освоения для производства всевозрастающих потребностей мирового рынка в литиевых материалах. В результате оптимизирована сернокислотная технология получения высокосортного карбоната лития непосредственно из сподумена, минуя стадию получения продукта технического сорта, в едином технологическом процессе переработки сподумена с сокращением числа технологических операций, исключением дорогостоящей операции концентрирования раствора сульфата лития методом упарки. Разработана эффективная технология очистки и доочистки технического карбоната лития до аккумуляторного качества 99,95%, включающая процессы каустификации технического карбоната лития, ультрафильтрации и ионообменной сорбции раствора гидроксида лития, с последующим осаждением углеаммонийной солькарбоната лития. Катодные материалы - фосфат лития, железа и его модификации, полученные из высокочистого карбоната лития аэрозольным пиролизом (МАП) и золь-гель методом (ЗГМ), показали хорошие электрохимические характеристики. Конечным результатом являются инновационные электродные материалы для современных LIB со значительно увеличенной емкостью и стабильностью. Практическое внедрение полного цикла технологий от литийсодержащего сырья до современных литиевых аккумуляторов открывает перспективы создания в Казахстане высокотехнологичного литиевого кластера для производства продукции с высокой степенью готовности для конечного потребителя по Схеме: Сподуменовые руды → Литиевый концентрат → Карбонат лития → Литиевые катодные материалы → Аккумуляторы.

Ключевые слова: литий, извлечение, руда. сподумен, карбонат лития аккумуляторного сорта, литий-ионный аккумулятор, метод, очистка, технология, переработка, катодный материал, литий-железо фосфат.

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FORMATION OF HYDROPHOBIZED NUTRIA VELOUR

Abstract. The formation of hydrophobized nutria fur velour has been carried out using the optimized alkenmalein acrylsyntane composition. Based on the implementation of the synthesized experimental plan “composition-properties of velour” by the modified McLean-Anderson method, the optimization of filling and hydrophobizing composition has been performed by Harrington method. The optimized composition involves the use of, wt. %: alkenmalein polymer – 54.1, polyacrylic emulsion Melio Resin A-821 – 18.8, reagent based on 2-naphtholesulfonic acid and dioxins-phenylsulfone – 27.1. The developed technology of forming hydrophobized nutria velour has been tested at the experimental production of leather enterprise (Chinbar Private Joint Stock Company, Kyiv, Ukraine). Nutria fur velour obtained by the developed technology is characterized by a significant increase in water resistance in dynamic conditions. The advantage of this technology is the production of fur velour with a higher yield of 5.4–5.6 % compared to the semi-finished chromium-aluminum tanning. The optimized filling and hydrophobizing composition can be effectively used in the technologies of manufacturing sheepskin and leather materials with high water resistance. According to the complex of properties, the obtained hydrophobized nutria velour is suitable for the production of uncovered items of various purposes, which will be used in extreme conditions.

Keywords: nutria velour, filling-hydrophobization, velour properties, McLean-Anderson method, multicriteria optimization, Harrington desirability function.

1. Introduction

The development of modern technologies for the production of new materials involves, first of all, the use of environmentally friendly chemical reagents, which allow expanding the range of products. At the same time, the use of such reagents also significantly improves existing technologies due to the application of new processes and operations. It concerns the production of fur materials, including velour, in particular the non-uniform structure obtained from natural raw materials. In this respect, an important aspect of the problem is the efficient use of fur raw materials that have not been used before for the manufacture of new uncovered products, namely nutria skins, which are not suitable for fur production because of the quality of hair covering.

The use of raw materials of nutria skin for velour resistant to the environment requires a significant modification of the porous structure of the skin tissue [1]. For this purpose it is necessary to carry out the processes of filling-hydrophobization of fur semi-finished products using the methods of mathematical modeling and multifactor optimization.

2. Literature analysis and problem statement

In technologies for the production of collagen-containing materials, including velour materials, scientifically sound processes of filling and modification of the fibrous porous structure of a semi-finished product are important. It stabilizes structural elements, which significantly affects the finite properties of the material. According to the analysis of research literature, a wide range of chemical reagents of different composition and structure is used for this purpose. In [2], the authors have investigated the effect of water-soluble polymers on the performance properties of natural materials. At the same time, there was an increase in the uniformity of physicochemical properties over the area of the semi-finished product, in particular thickness, density, strength, resistance to friction. In the formation of elastic natural materials, the authors of [3] have studied the effect of particle size of aqueous dispersions of acrylic acid copolymers on its strength and deformation properties. The dependence of physical and mechanical properties on the chemical composition of fluorine-containing aminopolymers has been explored [4]. Improved polishing quality of the semi-finished product is achieved. This will result in getting velour with a low even pile and necessary complex of physical and mechanical characteristics.

Alongside with the studies of the semi-finished product filling, they modify its porous structure, which is related, first of all, to the physicochemical blocking of hydrophilic groups of the filled structure of collagen, and can provide increased water resistance of the material. For this purpose, both monomeric and polymeric reagents of different molecular weights and chemical structures are used. This applies, in particular, to silanes, fluorocarbon and polydimethylsiloxane polymers, complex aluminum compounds [5]. For filling-hydrophobization of semi-finished products of chromium tanning copolymers of acrylic acid together with hydrophobic acryl monomers have also been used [6]. The result is a high degree of filling-hydrophobization of the natural material when using polymers, molecules of which contain straight hydrocarbon chains. The maximum effect of hydrophobization is observed at chain lengths above C16 [7]. In [8] the effect of fluorine-containing copolymer on the water resistance of natural material has been investigated. This results in an increase in the water resistance of the material, in particular dynamic waterlogging up to 55 min and a wetting angle of 155 ° with a fluorine content of 5 % in the copolymer. Hybrid polyfunctional polyurethanes are also known to improve water resistance and dirt repulsion of natural materials [9], but at the same time the exterior of the material deteriorates and its rigidity increases.

The authors of [10, 11] investigate the complex influence of polymers in combination with plasma treatment on the physical and chemical properties of the leather material. At the same time, the material strength was increased by 23 % and its water resistance by the duration of suction of water droplets by 86 %, while reducing its hygroscopicity by 76–87 % for semi-finished raw materials of cattle and sheepskin.

Thus, there are studies of the processes of filling the structure of tanned semi-finished products from natural raw materials of different origin and reduction of its hydrophilicity. The authors use monomeric and polymeric reagents of different molecular weights and chemical structures. This applies mainly to empirical studies. The formation of high quality natural materials from collagen-containing raw materials requires the development of scientifically sound technological processes and their computer optimization.

Taking into account the peculiarities of collagen-keratin structure, topographic unevenness of the skin tissue, features of its porosity and low durability in the formation of nutria skin velour, it is necessary to develop an optimized chemical composition of the filler-hydrophobic composition and determine the conditions for its effective use.

3. The purpose and objectives of the study

The purpose of the research is to study the process of hydrophobic velour formation from the skin of nutria by optimizing the structure of alkenmalein acrylsyntane composition. To achieve this goal, the following tasks have been set:

- synthesis of the experiment plan “structure of the composition-properties of velour” by the modified McLean-Anderson method;
- optimization of the structure of the filling and hydrophobizing composition by Harrington method;
- formation of hydrophobized nutria velour using the optimized structure of the filling and hydrophobizing composition.

4. Materials and methods of study of alkenmalein-acrylsynthan composition

The object of the study is the process of optimizing the filling and hydrophobizing alkenmalein-acrylsynthane (AM-AS) composition for the formation of high water resistance nutria velour. Raw materials of male nutria skins with coarse auburn hair of 24–25 dm^2 have been used after removing awn hair by epilation and chrome-aluminum finishing of a semi-finished product by technology [12] with obtaining temperature of hydrothermal stability (Γ_c) of skin tissue 90 °C. The studied composition AM-AC included alkenmaline (AM) polymer synthesized on the basis of α-alkenes $C_{20–24}$ and maleic anhydride with a mean molecular weight of $38 \cdot 10^3$, polyacrylic (PA) emulsion Melio Resin A-821 (Clariant, Germany) and the product of the synthesis of 2-naphtholesulfonic acid with dioxidiphenylsulphon (cyanant HC-DS). The composition has been dosed into the technological solution at a flow rate of 28 g/dm^3 for a ratio of water to the semi-finished product equal to 7.

Experimental studies of filled-hydrophobized nutria velour depending on the structure of AM-AC composition have been performed. Samples of the mined nutria semi-finished product have been selected by the method of proportional squares [13]. The effectiveness of using the composition for filling-extending the semi-finished fur velour has been determined in% by the difference of AM-AC composition used and its residue in the waste solution, water resistance of hydrophobized fur velour and its yield by area. Velour water resistance has been assessed by the dynamic method of the duration of water wetting on the device PVD-2 (Russia) when deforming the samples at a speed of 70 min – 1. Hydrothermal resistance of velour – at the initial reduction of the sample length when heated at a speed of 2.5–3.0 °C/min, porosity – the ratio of pore volumes and the original sample, physical and mechanical properties – using the bursting strength machine RT-250M, belt A (Russia) at a deformation rate of 80 mm / min according to the methods [13]. The yield of the velour area has been assessed by the ratio of the areas of hydrophobized and mined semi-finished product [12] under standard conditions.

The optimization of the structure of the filling and hydrophobizing composition consists in obtaining a D-optimal plan of the experiment, synthesized by a modified McLean-Anderson method [14], a mathematical model of the experiment “structure of the composition-property of velour” and determining the optimal content of the components of the composition by the Harrington method [15]. The optimum composition should correspond to the maximum duration for water wetting of the nutria velour, the maximum yield of its area and the effective use of the alkenmalein-acrylsynthan composition.

5. Obtaining a mathematical model “The structure of the filling and hydrophobizing composition – properties of nutria velour”

The influence of the components of the composition on the properties of nutria velour has been investigated during the formation of nutria velour. It is necessary to obtain a nonlinear mathematical polynomial model of “composition–properties”, which contains the components of the composition for each physicochemical indicator of hydrophobized nutria velour:

$$\hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j + \sum_{l=1}^{k-2} \sum_{i=l}^{k-1} \sum_{j=i+1}^{k} b_{l\,ij} x_i x_j , \tag{1}$$

Where $\hat{y}$ is the predictive value of the physicochemical indicator; b_i, b_{ij}, are model coefficients; x_i is the content of the components of the composition in a coded form (i = 1, 2,…, k); k is the number of components; l, i, j are the sequence numbers of the interaction of the components of the composition.

It should be noted that in the model (1) the condition of normalization of the composition structure must be kept:

$$\sum_{i=1}^{k} x_i = 1 \tag{2}$$

Based on the previous studies, the limits of changes in the components in the natural values of X_i,, wt. parts, in the structure of the filling and hydrophobic composition (table 1) has been set.

Table 1 – Component restrictions of filling-hydrophobized composition

Limits of changing the components of the composition, in values			
natural X_i		coded x_i	
min	*max*	*min*	*max*
0.84	10.36	0.03	0.37
3.92	13.44	0.14	0.48
3.08	12.32	0.11	0.44
5.88	11.20	0.21	0.40

Note. Restrictions of the components of the composition, respectively, at the lower and upper levels: $0 \le X_i^{\min} \le X_i \le X_i^{\max} \le 1$ (i = 1, 2, ..., k). In this case, the components X_1 and X_4 in chemical composition correspond to alkenmalein polymer, in particular X_1 is the amount of polymer introduced at the beginning of the technological process of filling, and X_4 – at the final stage of hydrophobization.

The general mathematical model of "composition–properties" (1) for the structure of the composition is:

$$\hat{y}_i = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4, \qquad (3)$$

where $\hat{y}_i$ is the predicted value of the physicochemical index of fur velour, $i = 1 \div 3$; in particular, the effectiveness of the influence of the structure of AM-AC composition on the physicochemical properties of nutria fur velour has been assessed by:
y_1 – the efficiency of use of the composition, wt. %; y_2 – duration of dynamic wetting of fur velour, s; y_3 – yield of fur velour area, %; x_1, x_2, x_3, x_4 – correspondingly encoded values of the components of the composition: AM polymer, PA emulsion, NS-DS synthant and AM polymer.

To determine the coefficients of the mathematical model (3), the experimental data have been approximated according to the synthesized plan. The task of planning the experiment was to obtain the most theoretically possible amount of information with a minimum number of experiments, taking into account the normalization of the composition of the mixture (2), as well as the important requirement of the presence of all components in the structure:

$$x_i > 0,\ i = 1,\ 2, \dots,\ k. \qquad (4)$$

The amount of experimental data can be substantially reduced by using the McLean-Anderson algorithm, which assumes that all possible combinations (more than 10^9) of N theoretical points of candidates selected by the McLean-Anderson algorithm [16] are provided, on condition that[1] $det|D| \to$min. In order to establish the coefficients of model (3), we select the minimum number of experimental points n = 10.

The synthesized optimal experiment plan in a restricted area of synthesis (table 1) during 23.86 h is shown in table 2.

Table 2 – Experiment plan

Composition components	The structure of the mixture at the experimental point									
	2	3	4	5	10	12	14	27	29	34
x_1	0.210	0.200	0.030	0.030	0.030	0.370	0.190	0.370	0.030	0.225
x_2	0.140	0.480	0.460	0.320	0.140	0.140	0.140	0.225	0.480	0.335
x_3	0.440	0.110	0.110	0.440	0.440	0.110	0.270	0.195	0.195	0.110
x_4	0.210	0.210	0.400	0.210	0.390	0.380	0.400	0.210	0.295	0.330

The implementation of the synthesized plan has made it possible to obtain experimental data characterizing the influence of the structure of the filling-hydrophobic AM-AS composition on the technological, physical and chemical properties of nutria velour (table 3).

Table 3 – Properties of hydrophobized fur velour

Metric	The value of the metric at the experimental points									
	2	3	4	5	10	12	14	27	29	34
y_1	79.2	88.5	73.4	78.6	65.3	87.1	89.4	88.3	79.1	93.0
y_2	1390.0	1260.0	1630.0	1370.0	1840.0	1565.0	1780.0	1353.0	1410.0	1560.0
y_3	106.2	102.4	103.8	101.5	102.3	104.3	105.3	104.7	104.5	106.1

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[1] The total number of combinations of points of N candidates can be assessed by probability theory: $C_N^n = \dfrac{N!}{n!(N-n)!}$.

Dispersion matrix of a combination of candidate points $D = \left(F^T F\right)^{-1}$, where F is the matrix of the experimental plan with dimension $n \times t$; t is the number of coefficients of the model.

The required coefficients of the mathematical model (3) have been determined by the approximation of the experimental data given in Table. 2 and 3 using the least squares method. Based on the obtained experimental data, the mathematical model (5) has been constructed according to the above-mentioned technological, physicochemical parameters of the properties of the nutria velour, depending on the structure of AM-AS composition:

$$\begin{cases} \hat{y}_1 = -117.2034906\,x_1 + 1.92375297x_2 - 8.67427379x_3 + 64.14648706x_4 \\ \quad + 444.6497106x_1x_2 + 467.4894979x_1x_3 + 374.8000603x_1x_4 + 437.5957898x_2x_3 \\ \quad + 87.20064507x_2x_4 + 146.8864982x_3x_4 \\ \hat{y}_2 = 402.3035289x_1 - 254.5017831x_2 + 494.9983683x_3 + 3368.948843x_4 \\ \quad + 3681.935211x_1x_2 + 1544.333049x_1x_3 - 1741.834756x_1x_4 + 2510.214516\,x_2x_3 \\ \quad + 761.5901424x_2x_4 + 700.4074566\,x_3x_4 \\ \hat{y}_3 = 62.55200238x_1 + 69.72480492x_2 + 74.7675243x_3 - 5.302538861x_4 \\ \quad + 36.20884176x_1x_2 + 95.63320238x_1x_3 + 251.4894287x_1x_4 + 23.05025504x_2x_3 \\ \quad + 264.0396943x_2x_4 + 230.9960487x_3x_4 \end{cases} \tag{5}$$

Thus, the obtained mathematical model "the structure of the composition - properties of nutria velour" can be subsequently used to optimize the alkenmalein-acrylsynthane composition in the manufacture of nutria fur velour.

6. Composition structure optimization by Harrington method

To find the optimal structure of AM-AC composition, a generalized Harrington D_f desirability function [14] has been used, according to which each techno-physicochemical indicator of nutria velour $\hat{y}_i$ is a partial function of the desirability of the technological indicator d_i,, can take corresponding dimensions y'_i from 0 to 1 depending on the component structure of the composition. The mathematical form of the desirability function for a three-component composition takes the form:

$$D_f = \sqrt[3]{d_1 d_2 d_3},$$

where; $d_i = \exp[-\exp(-y'_i)]$ $y'_i = b_0^{(i)} + b_1^{(i)} y_i$.

The coefficients are determined from the systems of equations:

$$\begin{cases} y_i'^{worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{cases}$$

where $y_i^{worse}, y_i^{better}$ is respectively, worse and better values of the indicators y_i set by the researcher; $y_i'^{worse} = -\ln(-\ln d_{worse})$, $y_i'^{better} = -\ln(-\ln d_{better})$ is worse and better dimensionless indicators; respectively, the partial desirability functions d_{worse} and $d\,better$ are assumed to be 0.2 and 0.8.

The maximum of the desirability function D_f corresponds to the optimal composition $\bar{x}^{opt}$ having the best compromise values of the physicochemical parameters y_i.

Due to the optimization of the composition its optimal component structure has been obtained, wt. parts: $x_1 = 0.149$, $x_2 = 0.188$, $x_3 = 0.271$, $x_4 = 0.392$. The expected values of the original variables acquired the following values: $y_1 = 89.7$ %, $y_2 = 1789.0$ c, $y_3 = 105.35$ %.

Therefore, for filling-hydrophobization of 100 kg of extracted and epilated nutria semi-finished product after removal of moisture by centrifugation it is necessary to use alkenmalein-acrylsynthane composition of 19.6 kg of optimum structure: PA-emulsion – 3.7, synthane – 5.3, A-MS – 10.6. In order to activate the filling process, it is necessary to use 2.92 kg of alkenmalein polymer.

7. Testing the technology of hydrophobized nutria velour production using alkenmalein-acrylsynthane composition

The optimized structure of alkenmalein-acrylsynthane composition was used in the manufacture of hydrophobized nutria velour at Chinbar Private Joint Stock Company (Kyiv, Ukraine) from raw materials of fresh and dry canning weighing 19 kg. The epilated semi-finished product of the nutria skins after chromaluminum tanning was processed with the composition at a ratio of the masses of the working solution and the semi-finished product 7. In this case, in order to obtain hydrophobized nutria velour the working semi-finished solution was successively dosed with the components of AM at the temperature of 40–43 °C. At first, the AM polymer was added in the container, 15–20 min later a filling mixture of Melio Resin A-821 polyacrylic emulsion and 2-naphtholsulfonic acid synth with dioxidiphenylsulfone were added. In one hour – the remaining hydrophobized AM polymer. The total duration of the filling-hydrophobization process was 2.5 hours. Then the semi-finished product was pressed in a centrifuge to a humidity of 52–53 % and performed drying and moistening processes and operations to a moisture content of 12–14 % and polishing the skin tissue. After keeping hydrophobized nutria velour under standard conditions [13], its physicochemical tests were carried out.

According to the benchmark technology of processing nutria velour differed from the developed one as it had no filling-hydrophobization processes. In this case, nutria velour drumming was performed with an electrolyte-resistant emulsion of Trupol DL (Trumpler, Germany) at a temperature of 38–40 °C with a fat consumption of 2.5 g / dm^3 during 1 hour.

The results of the study of physicochemical properties of hydrophobized nutria velour are shown in Table. 4. The efficiency of the process of nutria velour hydrophobization with the use of AM-AS composition lies in a significant increase in the duration of dynamic wetting, compared with the material obtained by the benchmark technology. This increases the efficiency of AM-AC composition, as well as the yeild area of the material. At the same time, there is an increase in the thickness of the skin tissue of hydrophobized nutria velour and, accordingly, the uniformity of the material in topographic areas, which contributes to a more efficient use of its area when manufacturing goods. At the same time, the deformation properties of the hydrophobized nutria velour are better than the ones obtained in the process of benchmark technology.

Table 4 – Physicochemical properties of nutria fur velour

Indicator	Nutria velour obtained by technology	
	developed	benchmark
Dynamic water wetting, p	1800±20	25±5
Performance of the composition,%	87.2±2.5	79.3±3.6
Yeild area,%	105.6±0.3	100.0±0.3
Thickness of the skin tissue, mm	1.22±0.4	1.06±0.7
Tensile strength, MPa	1.2±0.20	1.09±0.25
Elongation at break,%	62.0±5.0	59.0±5.0
Elongation of skin tissue at load of 4.9 MPa,%, complete	28.0±2.5	22.0±2.6
– elastic	17.5±1.6	13.0±1.2
– residual	10.5±0.9	9.0±0.8
Porosity of skin tissue,%	62.0±3.0	65.0±4.3

Based on the research conducted in semi-production conditions, it can be assumed that the technology developed for the formation of hydrophobized nutria velour can be used to expand the range of fur raw materials and velour materials for the manufacture of products operated in high humidity conditions. The proposed technology can also be used without significant changes to existing processing technologies of other types of fur raw materials for the production of velour materials with high performance.

8. Conclusions

1. The process of formation of hydrophobized nutria velour from a fur semi-finished product after removal of the ostium hair has been investigated using computer optimization of the structure of alkenmalein-acrylsynthan composition. In the optimization of the structure of the filling and hydrophobizing composition, a modified McLean-Anderson method has been used, taking into account the type of mathematical model "the structure of the composition – properties of the hydrophobized material" and Harrington's desirability function.

2. The optimal structure of the filling and hydrophobising composition, including components, wt. %: alkenmaline polymer – 54.1, Melio Resin A-821 polyacrylic emulsion – 18.8, HC-DS sulphate – 27.1 at their consumption, respectively, % of the mass of the squeezed sulphurous semi-finished product: 10.6, 3.7 and 5.3 for the ratio of semi-finished product / technological solution 1/7.

3. Having applied the developed technology, which involves the combination of processes of filling-hydrophobization, nutria velour has been obtained with a significant increase in the duration of dynamic water wetting and increase the yield of material area by 5.6 % compared with the semi-finished chromaluminic finishing. The effective use of the alkenmalein-acrylsynthane composition provides for the formation of more homogeneous elastic material from porous raw materials technologically unsuitable for fur production.

4. The developed technology of formation of hydrophobized nutria velour with optimization of the structure of the filling and hydrophobizing composition can be effectively used in the production of sheepskin coat and leather materials of high water resistance. According to the complex of properties, the obtained hydrophobized nutria velour is suitable for the manufacture of uncovered articles of various purposes, which will be used in extreme conditions.

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ГИДРОФОБТАЛҒАН НУТРИЯ ВЕЛЮРІН ҚАЛЫПТАСТЫРУ

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ФОРМИРОВАНИЕ ГИДРОФОБИЗИРОВАННОГО ВЕЛЮРА НУТРИИ

Аннотация. В работе проведено формирование гидрофобизированного мехового велюра нутрии с использованием оптимизированного состава алкенмалеиново-акрилсинтанной композиции.

Целью работы является исследование процесса формирования гидрофобизированного велюра со шкурок нутрии путём оптимизации состава алкенмалеиново-акрилсинтанной композиции. Для решения данной цели поставлены следующие задачи:

– синтез плана эксперимента «состав композиции – свойства велюра» по модифицированному методу Маклина-Андерсона;

– оптимизация состава наполнительно-гидрофобизирующей композиции методом Харрингтона;

– формирование гидрофобизированного велюра нутрии с использованием оптимизированного состава наполнительно-гидрофобизирующей композиции.

Объектом исследования был процесс оптимизации состава наполнительно-гидрофобизирующей алкенмалеиново-акрилсинтанной (АМ-АС) композиции для формирования велюра нутрии повышенной устойчивости к воде. В работе использовано сырьё самцов шкурок нутрии с грубым остевым волосом площадью 24–25 дм^2 после удаления остевого волоса путём эпилирования и хром-алюминиевого додубливания полуфабриката с получением температуры гидротермической устойчивости кожевой ткани 90 °С. Исследованная АМ-АС композиция содержала алкенмалеиновый полимер, синтезованный на основе α-алкенов $C_{20–24}$ и малеинового ангидрида со среднечисловым молекулярным весом $38 \cdot 10^3$, полиакриловую эмульсию Melio Resin A-821 фирмы «Clariant» (Германия) и продукт синтеза 2-нафтолсульфокислоты с диоксидифенилсульфоном. В технологический раствор композицию дозировали с расходом 28 г/дм^3 при соотношении вода / полуфабрикат равному 7/1.

В работе проведены экспериментальные исследования наполненно-гидрофобизированного велюра нутрии в зависимости от состава композиции АМ-АС. Образцы додубленного полуфабриката нутрии отбирали по методу пропорциональных квадратов. Эффективность использования композиции при наполнении-додубливании полуфабриката мехового велюра определяли в % по соотношению разницы между расходованной композицией АМ-АС и её остатком в отработанном растворе к расходованной композиции, водостойкости гидрофобизированного мехового велюра и его выходу по площади. Водостойкость велюра оценивали динамическим методом по продолжительности водопромокания на

приборе ПВД-2 (РФ) при деформировании образцов со скоростью 70 мин$^{-1}$. Гидротермическую устойчивость велюра – по начальному сокращению длины образца при нагревании со скоростью 2,5–3,0 °С/мин, пористость – отношением объёма пор к объёму начального образца, физико-механические свойства – на разрывной машине РТ-250М, пояс А (РФ) при скорости деформирования 80 мм/мин. Выход площади велюра оценивали отношением площадей гидрофобизированного и додубленного полуфабриката у стандартных условиях.

Оптимизация состава наполнительно-гидрофобизирующей композиции состояла в получении D-оптимального плана эксперимента, синтезированного по модифицированному методу Маклина-Андерсона, математической модели эксперимента «состав композиции-свойства велюра» и определении оптимального содержания ингредиентов композиции методом Харрингтона. Оптимальный состав должен отвечать максимальной продолжительности относительного водопромокания велюра нутрии, максимальному выходу его площади и эффективному использованию алкенмалеиново-акрилсинтанной композиции. На основании реализации синтезированного плана эксперимента «состав композиции–свойства велюра» по модифицированному методу Маклина-Андерсона выполнена оптимизация состава наполнительно-гидрофобизирующей композиции методом Харрингтона.

Оптимизированный состав композиции предусматривает использование: мас. %: алкенмалеинового полимера – 54.1, полиакриловой эмульсии Melio Resin A-821 – 18.8, реагента на основе 2-нафтолсульфокислоты и диоксидифенилсульфона – 27.1. Разработанная технология формирования гидрофобизированного велюра нутрии апробирована в условиях опытного производства кожевенного предприятия ПрАТ «Чинбар» (г. Киев, Украина). Эпилированный полуфабрикат шкурок нутрии после хромалюминиевого додубливания обрабатывали композицией оптимизированного состава при соотношении масс рабочего раствора и полуфабриката равному 7/1. При этом для получения гидрофобизированного велюра нутрии в систему «рабочий раствор-полуфабрикат» последовательно дозировали ингредиенты композиции АМ-АС при температуре 40–43 °С. Сначала в баркас добавляли АМ-полимер, через 15–20 мин – наполнительную смесь полиакриловой эмульсии Melio Resin A-821 и синтан 2-нафтолсульфокислоти з диоксидифенилсульфоном. Ещё через 1,0 час – остальную часть АМ-полимера. Общая продолжительность процесса наполнения-гидрофобизации составляла 2,5 часа. Затем полуфабрикат отжимали в центрифуге до влажности 52–53 %, проводили сушильно-увлажняющие процессы и операции до содержания влаги 12–14 % и шлифование кожевой ткани.

Полученный меховый велюр нутрии по разработанной технологии характеризуется значительным повышением устойчивости к действию воды в динамических условиях. Преимуществом такой технологии является получение мехового велюра с большим выходом площади на 5.4–5,6 % по сравнению с полуфабрикатом хромалюминиевого додубливания. Оптимизированный состав наполнительно-гидрофобизирующей композиции может эффективно использован в технологиях изготовления овчинно-шубных и кожевенных материалов повышенной гидростойкости. По комплексу свойств полученный гидрофобизированный велюр нутрии пригоден для изготовления нагольных изделий разного назначения для эксплуатации в экстремальных условиях.

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HYDROPROCESSING OF PETROLEUM FRACTIONS OVER MODIFIED ALUMINIUM OXIDE CATALYSTS

Abstract. The hydro processing of gasoline and diesel oil fractions over aluminum-nickel-molybdenum catalysts modified by additives HY, ZSM-5, phosphorus and rare earth elements were studied. At the hydro processing of straight-run gasoline over $NiO-MoO_3-Ce_2O_3-P_2O_5–ZSM(30\%)-Al_2O_3$ the content of isoalkanes increases in comparison with the initial from 26.3 to 35.7- 38.3% at 320-400°C. The octane number of refined gasoline at 400°C is 83.7 (RON) and 69.7 (MON). The sulfur content decreases from 0.037% (initial gasoline) to 0.0022%.

At hydro processing of straight-run gasoline over $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ in the range of 320–400 °C the content of isoalkanes is 30.7- 44.3%. The octane number of refined gasoline at 400°C is maximum and is equal to 91.8 (RON) and 72.4 (MON). Under these conditions the sulfur content decreases from 0.0092% to 0.0028%.

The optimal conditions for the hydro processing of straight-run gasoline were revealed: T=400˚C, V=2 h^{-1}, P = 4.0MPa. The catalyst $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-HY-Al_2O_3$ has the highest hydro desulfurizing activity, the residual sulfur content at 400°C is 0.0012%.

The catalyst $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ has the highest hydro desulfurizing activity. At hydro processing of straight-run diesel fraction on this catalyst under optimal conditions the sulfur content decreases from 0.6400 % to 0.0740 % and during hydro processing of a straight-run diesel fraction with a higher sulfur content 0.8042% - up to 0.053%, which, apparently, is associated with the presence in the feedstock of various types of organosulfur compounds. The lowest pour point and cloud point under optimal conditions reaches minus 39.6°C and minus 30.5°C respectively.

Thus, developed modified zeolite-containing catalysts for the hydro processing of gasoline and diesel fractions carry out hydro processing, hydro isomerization and hydrogenation in one stage. The developed catalysts make possible to obtain high-octane low-sulfur gasoline and low-solidification low-sulfur diesel fuel.

Key words: catalyst, straight-run gasoline, diesel oil fraction, zeolite, hydro processing.

Introduction. Currently, most petrochemical processes are carried out using catalysts. Further intensification of production depends on the creation of new, more active and selective catalysts. The development of new generations of catalysts for the processing of hydrocarbon raw materials is necessary for the creation of new efficient technologies in this area.

To obtain high-quality motor fuels from sulfurous, paraffinic oils, catalytic hydro processing processes are used: hydro processing, hydro isomerization and hydrogenation. As a result of hydro processing, sulfur, nitrogen compounds, unsaturated hydrocarbons are removed, thermal stability is increased, the corrosiveness of fuels is reduced, the formation of deposits during storage is reduced, and the color and smell of motor fuel are improved. Currently, there is a tendency to tighten requirements for the composition of motor fuels, the insufficiently high quality of which is one of the causes of environmental pollution, therefore, the main attention of many oil refineries is focused on increasing the depth of hydro desulfurization. In this regard, for the production of high-quality motor fuels at the present stage, the catalytic processes of deep hydro processing of oil fractions are of great importance [1-10].

Recently, in connection with the involvement of high-sulfur oil in the refining and the deepening of its refining, the requirements for the catalysts for the hydro processing of gasoline and diesel fractions of oil have increased. In the global production of motor fuels, there is a constant tendency to tighten their environmental characteristics. To increase the volume of production of petroleum products, expand their range and improve quality, changes in the existing technology of oil refining using highly efficient catalysts are required. In this regard, the creation of new highly efficient catalysts for the hydro processing of low-octane gasolines and diesel fractions is very important [11 - 21].

In this paper presents the results of hydro processing of gasoline and diesel oil fractions over new aluminum-nickel-molybdenum catalysts, modified with additives ZSM-5, HY, phosphorus and rare earth elements (REE).

Experimental part. New modified zeolite-containing alumina catalysts modified by the introduction of metals with variable valence and phosphorus were developed and prepared: $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(20%)-Al_2O_3, $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(30%)-Al_2O_3, $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 and $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3. The catalysts were prepared by impregnating a mixture of aluminum hydroxide with zeolites ZSM-5, HY and aqueous soluble salts of nickel, molybdenum, tungsten, cerium, lanthanum and phosphoric acid. After impregnation, the catalyst samples were molded and dried at 150^0C for 5 hours, then calcined at 550^0C for 5 hours. Using the synthesized modified zeolite-containing catalysts, a study of the hydro processing of gasoline and diesel oil fractions was carried out. The process was carried out in a high-pressure flow-through installation with a fixed catalyst layer at varying of temperature 320-400^0C, pressure of 2.5-4.0MPa and space velocity 1.0-3.0 h^{-1}.

The hydrocarbon composition of the reaction products was analyzed on chromatographs «Chromatek-Cristall». The analysis of sulfur content in the feedstock and products was carried out in LLP «OilSert International» (Almaty). Determination of the pour point and cloud point were carried out on a «LAZ M2» device.

Results and discussion. On synthesized new modified zeolite-containing alumina catalysts the study of the hydro processing of straight-run gasoline and diesel fractions of oil was carried out.

At hydro processing of straight-run gasoline over $NiO-MoO_3-Ce_2O_3-P_2O_5$-ZSM(20%)-Al_2O_3as the temperature increases to 350^oC isoalkane content increases from 26.3 to 32.8 % (table 1). The content of naphthenic hydrocarbons in the catalysis ranges from 22.5 to 31.8 %, olefins - 3.3-4.0 %. The yield of the liquid phase with an increase in temperature from 320 to 400 ^{0}C varies from 92.5 to 70.0%. The octane number of gasoline refined at 400 ^{0}C is 85.6 (RON). Under these conditions the sulfur content in the final product decreases from 0.037% (initial gasoline) to 0.0120 at 350 ^{0}C and up to 0.0102% at up to 400 ^{0}C.

Table 1 - Influence of temperature on the conversion of gasoline
over $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(20%)-Al_2O_3 at V = 2 h^{-1}, P = 4.0 MPa

Products, %	T,˚C				
	Initial	320	350	380	400
Paraffins C_5 -C_6	33.4	31.2	25.9	25.2	25.7
Iso-alkanes	26.3	26.1	32.8	31.9	22.1
Olefins	3.7	3.6	4.0	3.4	3.3
Aromatic hydrocarbons	5.6	7.3	11.8	17.0	19.3
Naphthenic hydrocarbons	31.0	31.8	25.5	22.5	29.6
Yield of liquid phase,%	-	92.5	80.0	70.0	70.0
Sulfur content,%	0.0375	0.0230	0.0120	0.0110	0.0102
Octane number(RON)	77.7	82.2	79.2	82.0	85.6
Octane number (MON)	53.8	60.9	62.5	66.1	63.9

Table 2 shows the results obtained in the hydro processing of the gasoline fraction on the $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(30%)-Al_2O_3. At hydro processing of straight-run gasoline at 320^0C isoalkane content increases from 26.3 to 38.3%. As the temperature increases to 400^0C isoalkane content decreases to 35.7 %. At varying the temperature in the range 320-400^0C the yield of aromatic hydrocarbons varies from 12.6 to 19.6 % and naphthenic hydrocarbons decreases from 26.5 to 21.8 %. The amount of olefins ranges from 3.7 to 4.2 %. The yield of the liquid phase with an increase in temperature from 320 to 400^0C varies from 70.0 to 50.0%. The octane number of gasoline at 400 ^{0}C is 83.7 (RON) and 69.7 (MON). The sulfur content in the final product decreases from 0.037% (initial gasoline) to 0.0022%.

Table 2 - Influence of temperature on the conversion of gasoline
on NiO-MoO$_3$-Ce$_2$O$_3$-P$_2$O$_5$–ZSM(30%)-Al$_2$O$_3$ at V = 2 h^{-1}, P = 4.0 MPa

Products , %	T,°C				
	Initial	320	350	380	400
Paraffins C$_5$-C$_6$	33.4	18.9	19.6	19.2	19.1
Iso-alkanes	26.3	38.3	37.8	36.7	35,7
Olefins	3.7	3.7	4.2	3.7	3.9
Aromatic hydrocarbons	5.6	12.6	12.6	18.1	19.5
Naphthenic hydrocarbons	31.0	26.5	25.8	22.3	21.8
Yield of liquid phase,%		70.0	65.0	57.5	50.0
Sulfur content,%	0.037	0.0125	0.0110	0.0091	0.0022
Octane number (RON)	77.7	79.6	81.5	82.7	83.7
Octane number (MON)	53.8	64.8	65.8	67.4	69.7

At hydro processing of straight-run gasoline at catalyst NiO-MoO$_3$-La$_2$O$_3$-P$_2$O$_5$-ZSM-HY-Al$_2$O$_3$ at 320^0C the content of isoalkanes increases as compared with the feedstock from 32.6 to 41.9%. However, with increasing temperature from 320 to 400°C contents of isoalkanes and naphthenic hydrocarbons reduced from 41.9 to 34.2% and from 26.3 to 22.3% respectively. The amount of aromatic hydrocarbons increases from 7.3 to 20.9 %, the content of olefins in the catalyzate is 3.6-3.9 %. Yield of the liquid phase as the temperature increases from 320 to 400^0 C is changed from 85.0 to 55.0%.The octane number of refined gasoline increases with temperature in the range of 320-400^0C: from 81.9 to 87.0 (RON) and from 63.2 to 68.9 (MON), while the sulfur content decreased from 0.0375 to 0.0012%.

At hydro processing of straight-run gasoline over NiO-MoO$_3$-La$_2$O$_3$-P$_2$O$_5$-ZSM-Al$_2$O$_3$ at 320^0C isoalkane content increased from initial of 36.8 to 44.3% (table 3). When the temperature rises to 400^0C is reduced and isoalkanes content equal to 30.7 %. When the temperature rises in the range 320-400^0C the yield of aromatic hydrocarbons varies from 10.4 to 28.3 %, naphthenic hydrocarbons is increased from 20.3 to 30.3 %. The amount of olefins depends little on the process temperature and is 4.3 - 5.8 %. The yield of the liquid phase with an increase in temperature from 320 to 400^0C decreases from 74.8 to 55.4%. The octane number of gasoline at 400^0C is maximum and is equal to 91.8 (RON) and 72.4 (MON). Under these conditions the sulfur content decreases from 0.0092% to 0.0028%.

Table 3 - Influence of temperature on the process of hydro processing
of straight-run gasoline on the catalyst NiO-MoO$_3$-La$_2$O$_3$-P$_2$O$_5$-ZSM-Al$_2$O$_3$ at V = 2 h^{-1}, P = 4.0 MPa

Products , %	T, °C				
	Initial	320	350	380	400
Paraffins C$_5$-C $_6$	27.3	20.7	10.0	8.5	5.0
Iso-alkanes	36.8	44.3	32.4	32.6	30.7
Olefins	4.8	4,3	5.4	5.6	5.8
Aromatic hydrocarbons	9.2	10.4	18.7	24.8	28.3
Naphthenic hydrocarbons	21.9	20.3	33.4	28.5	30.3
Yield of liquid phase		74.8	65.7	59.0	55.4
Octane number (RON)	78.9	84.3	89.8	90.0	91.8
Octane number (MON)	60.9	70.4	69.2	71.8	72.4
Mass fraction of sulfur,%	0.0092	0.0036	0.0033	0.0030	0.0028

The study of the effect of pressure on the process of hydro processing of straight-run gasoline over NiO-MoO$_3$-La$_2$O$_3$-P$_2$O$_5$-ZSM-Al$_2$O$_3$ showed that with an increase in pressure in the range of 2.5-4.0 MPa the maximum amount of isoalkanes observed at P=2.5 MPa and equal to 34.9% (table 4). With a further increase in pressure, their yield decreases to 30.7% at 4MPa, while the concentration of naphthenic hydrocarbons increases from 22.9 to 30.3%. The concentration of aromatic and olefinic hydrocarbons depends little on pressure and ranges from 27.3-29.7% and 4.6-5.8% respectively. The octane number of gasoline refined at 4.0 MPa is 91.8 (RON) and 72.4 (MON). The sulfur content decreases from 0.0092% (initial gasoline) to 0.0028% at 4.0 MPa.

Table 4 - Influence of pressure on the process of hydro processing of straight-run gasoline on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 at 400^{o}C and 2 h^{-1}

Products , %	P, MPa				
	Initial	2.5	3.0	3.5	4.0
Paraffins C_5-C_6	27.3	7.9	6.0	4.0	5.0
Iso-alkanes	36.8	34.9	34.3	30.6	30.7
Olefins	4.8	4.6	5.3	5.0	5.8
Aromatic hydrocarbons	9.2	29.7	27.3	28.4	28.3
Naphthenic hydro carb.	21.9	22.9	27.1	32.0	30.3
Liquid phase yield		52.0	50.4	53.2	55.4
Octane number (RON)	78.9	89.6	88.3	88.9	91.8
Octane number (MON)	60.9	72.9	71.8	70.1	72.4
Mass fraction of sulfur,%	0.0092	0.0047	0.0035	0.0033	0.0028

At hydro processing of straight-run gasoline fraction to the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 when changing the space velocity from 1.0 to 3,0 h^{-1}contents isoalkanes in catalyzate equals 30.1 - 30.7% (table 5). The amount of aromatic and naphthenic hydrocarbons in the resulting product also changes little with a change in the volumetric feed rate. The yield of olefinic hydrocarbons ranges from 4.9 to 5.8%. The octane number of the resulting gasoline increases compared to the original (78.9) to 90.9-91.8 (RON), the residual sulfur content decreases compared to the feedstock from 0.0092 to 0.0036.

Table 5 - Influence of the volumetric velocity of raw material on the process of hydro processing of straight-run gasoline on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 at 400^{o}C and 4.0 MPa

Products , %	V , h^{-1}				
	Initial	1.0	1.5	2.0	3.0
Paraffins C_5-C_6	28.0	5.0	4.9	5.0	4.1
Iso-alkanes	35.5	30.6	30.2	30.7	30.1
Olefins	4.8	4.9	5.4	5.8	5.2
Aromatic hydrocarbons	8.1	31.6	30.6	28.3	29.7
Naphthenic hydrocarbons	23.6	27.8	28.9	30.3	30.8
Liquid phase yield		50.1	48.0	55.4	43.0
Octane number (RON)	78.9	89.0	90.9	91.8	90.7
Octane number (MON)	60.6	71.3	70,7	72.4	72.1
Mass fraction of sulfur,%	0.0092	-	0.0019	0.0028	0.0036

Analysis of the obtained results shows that under optimal conditions during the processing of straight-run gasoline fraction, the highest octane number is characteristic of the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3: 91.8 (RON). The catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-HY-Al_2O_3 has the highest hydro desulfurizing activity, the residual sulfur content at 400 ^{0}C is 0.0012%.

Thus, modified zeolite-containing catalysts for the hydro processing of gasoline fractions have been developed and synthesized, which carry out hydro processing, hydro isomerization and hydrogenation in one stage. The developed catalysts make it possible to obtain high-octane low-sulfur gasoline.

Tests of the catalyst NiO-MoO_3-Ce_2O_3-P_2O_5–ZSM(30%)-Al_2O_3 were carried out in the process of hydro processing of the diesel fraction of oil % (table 6). The pour point of the diesel fraction after hydro processing at 320^{0}C and 4.0 MPa decreased from minus 18.3 to minus 35.9^{0}C. By increasing the temperature to 400^{0}C, pour point is reduced to minus 58.9 ^{0}C. The cloud point in these conditions falls from minus 11.3 to minus 30.7 - 57.7 ^{0}C. Yield of hydro finished diesel fuel is 90.0 -100.0 %. The sulfur content is reduced in comparison with the original diesel fraction from 0.560 0 % to 0.0536%.

Table 6 – Hydro processing of the diesel fraction over $NiO\text{-}MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{–}ZSM(30\%)\text{-}Al_2O_3Al_2O_3$

The main parameters of the process		Sulfur content,%	Pour point, ^{0}C	Cloud point, ^{0}C	Yield, %
Initial diesel fraction		0.560 0	-18.3	-11.3	
Process temperature, ^{0}C	320	-	-35.9	-30.7	100
	350	-	-51.3	-51.0	92.5
	380	-	-54.9	-48.1	91.0
	400	0.0536	-58.9	-57.7	90.0

During hydro processing of straight-run diesel fraction on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ with a sulfur content of 0.6400%, the pour point decreases from minus 13.6 to minus 39.6 ^{0}C, the cloud point temperature under these conditions varies from minus 12.4 to minus 30.5 ^{0}C. The yield of hydro finished diesel fuel is 92.0-97.5%. Under optimal conditions (400 ^{0}C, 2 h $^{-1}$, 4.0 MPa) the sulfur content decreases from 0.6400% in the initial fraction to 0.0740 (table 7). During the hydro processing of the diesel fraction of oil with a higher sulfur content (0.8042%) on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ in the range 320-400 ^{0}C, the sulfur content decreases from 0.8042% in the original fraction to 0.0530% at 400^{0}C.

Table 7- Hydro processing of straight-run diesel oil fraction on the $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$

Process temperature, ^{0}C	Cloud point, ^{0}C	Pour point, ^{0}C	Yield, %	Mass fraction of sulfur,%
Initial diesel fraction	-12.4	-13.6		0.6400
320	-24.1	-31.2	97.5	0.1900
350	-30.5	-35.4	95.8	0.1200
380	-33.0	-33.5	94.5	0.0760
400	-30.5	-39.6	92.0	0.0740

It should be noted that with the weighting of the fractional composition of the processed raw materials the proportion of hard-to-remove sulfur compounds increases. As a result, the higher activity of catalysts in the hydro desulfurization of the gasoline fraction compared to the diesel fraction is due to the predominance of mercaptans, disulfides of the gasoline fraction of oil, while in the diesel fraction sulfur is mainly found in the form of sulfides, thiophenes and benzothiophenes. In connection with the tightening of the permissible sulfur content in diesel fuel, the main attention of many oil refineries is focused on increasing the depth of hydro desulfurization. To obtain low-sulfur, environmentally friendly diesel fuel, technologies and catalysts for deep hydro desulfurizationare being developed to remove sulfur atoms contained in complex hydrocarbon molecules. When switching to the Euro-5 standard for sulfur content from 50 to 10 ppm, processing of low-reactive polyalkyldibenzothiophene is required [22-24].

Table 8 shows the results obtained in the study of the effect of pressure on the process of hydro processing of diesel oil fraction on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$. With an increase in pressure from 3.0 to 4.0 MPa, the pour point changes from minus 30.2 to minus 38.2^{0}C, the cloud point - from minus 29.1 to minus 37.9^{0}C, the sulfur content decreases compared to initial from 0.6400 to 0.0530%. With increasing pressure the yield of the target product practically does not change.

Table 8 - Influence of pressure on the process of hydro processing
of a diesel fraction of oil on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$

Pressure, MPa	Cloud point, ^{0}C	Pour point, ^{0}C	Yield, %	Mass fraction of sulfur,%
Initial diesel fraction	-12.4	-13.6		0.6400
3.0	-29.1	-30.2	95.0	0.1300
3.5	-28.3	-28.9	97.5	0.0980
4.0	-37.9	-38.2	94.2	0.0530

By increasing the space velocity of from 1.0 to 3.0 h $^{-1}$ at hydro processing of diesel fraction over catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ the cloud point decreases from minus 39.3 ^{0}C to minus 28.4 ^{0}C, a pour point also decreases from minus 39.6 ^{0}C to minus 28.7 ^{0}C. The yield of hydro finished fuel ranges from 94.2 to 97.1%. With a decrease in the space velocity of the feedstock, a decrease in the amount of residual sulfur is observed (table 9).

Table 9 - Influence of the space velocity on the process of hydro processing of the diesel fraction of oil on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$

Space velocity, h $^{-1}$	Cloud point, ^{0}C	Pour point, ^{0}C	Yield, %	Mass fraction of sulfur,%
Initial diesel fraction	-12.4	-13.6		0.6400
1.0	-39.3	-39.6	97.1	0.0510
2.0	-37.9	-38.2	94.2	0.0530
3.0	-28.4	-28.7	95.2	0.1200

Comparison of results shows that the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ has the highest hydro desulfurizing activity. When a straight-run diesel fraction is hydro processed on this catalyst under optimal conditions (400^{0}C, 2 h^{-1}, 4.0 MPa) the sulfur content decreases from 0.640% to 0.074%.When a straight-run diesel fraction with a higher sulfur content 0.8042% is hydro processed - up to 0.053%, which is due to the presence of various types of organosulfur compounds in the feedstock. The lowest pour point and cloud point under optimal conditions is observed during hydro processing of diesel fractions over $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ and reaches minus 39.6^{0}C and minus 30.5^{0}C respectively

Earlier, we found that when processing gasoline and diesel fractions on polyfunctional catalysts with dehydrogenating, hydrogenating and acidic capabilities, the *n*- alkane dehydrates first on the metal centers of the catalyst, the formed olefin on the acid center turns into a carbonium ion, which is easily isomerized [25, 26].

The results obtained when testing catalysts in the process of hydro processing of diesel oil fractions show that the greatest decrease in the pour point and cloud point occurs at a temperature of 380 - 400 ^{0}C. During the hydro processing of diesel and gasoline fractions, the lowest residual sulfur content is observed at a temperature of 400 ^{0}C. The studied catalysts make it possible to obtain winter grades of diesel fuels with a low sulfur content.

Thus, in the study of the process of hydro processing of straight-run gasoline and diesel fractions on modified alumina catalysts $NiO\text{-}MoO_3\text{-}$ $Ce_2O_3\text{-}P_2O_5\text{–}ZSM$ (20,0%)-Al_2O_3,$NiO\text{-}MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{–}ZSM$ (30,0%) -Al_2O_3, $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}HY\text{-}Al_2O_3$ and$NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$, it was found that the developed and synthesized catalysts have polyfunctional properties and in one stage they carry out hydro processing, hydro isomerization to obtain low-sulfur low-solidifying diesel fuel and low-sulfur high-octane gasoline.

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МОДИФИЦИРЛЕНГЕН АЛЮМООКСИДТІ КАТАЛИЗАТОРЛАРДА МҰНАЙ ФРАКЦИЯЛАРЫН ГИДРОӨҢДЕУ

Аннотация. ZSM-5, фосфор және СЖЭ қоспаларымен модификацияланған алюмоникелмолибден модификацияланған катализаторларында бензинді және дизельді мұнай фракцияларын гидроөңдеу процесі зерттелді. 320-400^{0}С температурада, 3,0–4,0 МПа қысымда және шикізатты берудің көлем жылдамдығы 1–3 сағ$^{-1}$ кезінде катализатордың стационарлық қабаты бар жоғары қысымды ағынды қондырғыда тура айдалған бензин мен мұнайдың дизельді фракцияларын гидроөңдеу процестері қарастырылды.

$NiO\text{-}MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{-}ZSM(20\%)\text{-}Al_2O_3$ катализаторында тура айдалған бензинді гидроөңдеу кезінде температураның 320-дан 400 ^{0}С-қа дейін өсуі арқылы сұйық фазаның шығымы 92,5-тен 70,0%-ға дейін өзгереді. 400^{0}С-та жақсартылған бензиннің октан саны 85,6 (З.Ә.) құрайды. Соңғы өнімдегі күкірт мөлшері 0,037%-дан (бастапқы бензин) және 400^{0}С-қа, 0,0102%-ға дейін төмендейді.

$NiO\text{-}MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{–}ZSM(30\%)\text{-}Al_2O_3$катализаторында тура айдалған бензинді гидроөңдеу кезінде 320-400^{0}С температурада изоалкандардың құрамы бастапқы 26,3-тен 35,7–38,3%-ға дейін артады. Температураның 320-дан 400^{0}С-қа дейін өсуі барысында сұйық фазаның шығымы 70,0-ден 50,0%-ға дейін өзгереді. 400^{0}С жақсартылған бензиннің октан саны 83,7 (З.Ә.) және 69,7 (М.Ә.) құрайды. Осы жағдайларда бензин фракциясын гидроөңдеу кезінде соңғы өнімдегі күкірт мөлшері 0,037%-дан (бастапқы бензин) 0,0022%-ға дейін төмендейді.

$NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 катализаторында тура айдалған бензинді гидроөңдеуде 320^{0}С температурада алынған катализаттағы изоалкандардың мөлшері бастапқы шикізатпен салыстырғанда 32,6-дан 41,9%-ға дейін өседі. 400^{0}С кезінде изоалкандардың құрамы 34,2%-ға дейін төмендейді. Температураның 320-дан 400^{0}С-қа дейін өсуі негізінде сұйық фазаның шығуы 85,0-ден 55,0%-ға дейін өзгереді. Тазартылған бензиннің октандық саны 320–400^{0}С аралығында артады: зерттеу әдісі бойынша 81,9-дан 87,0-ге дейін және мотор әдісі бойынша 63,2-ден 68,9-ға дейін, күкірттің құрамы 0,0375-тен 0,0012%-ға дейін төмендеді.

$NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 катализаторында тура айдалған бензинді гидроөңдеу кезінде 320-400^{0}С интервалында изоалкан мөлшері 30,7–44,3% құрайды. Температураның 400^{0}С-қа дейін өсуі арқылы изоалкан мөлшері төмендейді және 30,7%-ға тең болады. Температураның 320-дан 400^{0}С-қа дейін өсуі арқылы сұйық фазаның шығымы 74,8-ден 55,4% -ға дейін азаяды. 400^{0}С бензиннің октан саны максималды 91,8 (З.Ә.) және 72,4 (М.Ә.). Бұл жағдайда алынған бензиндегі күкірт мөлшері 0,0092%-дан 0,0028%-ға дейін төмендейді.

$NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 катализаторы негізінде тура айдалған бензинді гидроөңдеу процесіне шикізат берудің қысымы мен көлемдік жылдамдығының әсері зерттелді. Тура айдалған бензин фракциясын гидроөңдеу үшін келесі оңтайлы жағдайлар анықталды: 400^{0}С,V=2 сағ$^{-1}$, Р=4,0 МПа. Ең жоғары октандық сан $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 катализаторына тән екендігі анықталды: 91,8(З.Ә.). $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 катализаторы жоғары гидродесульфуризациялы белсенді болып келеді, 400^{0}С күкірттің қалдық мөлшері 0,0012% құрайды.

$NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 және $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(30%)-Al_2O_3 катализаторларын күкірттің әртүрлі мөлшері бар мұнайдың дизельді фракцияларын гидроөңдеу процесінде сынау жұмыстары жүргізілді.

Нәтижелерді салыстыру жұмыстары көрсеткендей, $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 катализаторы ең жоғары гидродесульфуризациялы белсенді. Оңтайлы жағдайларда (400 ^{0}С, 2 сағ$^{-1}$, 4,0 МПа) осы катализаторда тура айдалған дизель фракциясын гидроөңдеу кезінде күкірт мөлшері 0,6400%-дан 0,0740%-ға дейін төмендейді, ал күкірт мөлшері жоғары тура айдалған дизель фракциясын гидроөңдеу кезінде 0,8042%-дан 0,053%-ға дейін төмендейді, шамасы, бұл бастапқы шикізатта күкіртті органикалық қосылыстардың алуан түрлеріне байланысты болуы мүмкін. Оңтайлы жағдайларда қату және лайланудың ең төменгі температурасы $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 катализаторында дизель фракцияларының гидрожақ-сарғаны байқалады және сәйкесінше минус 39,6^{0}С және минус 30,5^{0}С жетеді.

Осылайша бір уақытта гидротазарту, гидроизомеризация және гидроизомерлеу жүргізетін бензин мен дизель фракцияларын гидроөңдейтін модифицирлен цеолитті катализаторлары жасалды. Дайындалған катализаторлар жоғары октанды, аз күкіртті бензин және төмен температурада қататын аз күкіртті дизель отынын алуға мүмкіндік береді.

Түйін сөздер: катализатор, тура айдалған бензин, дизельді мұнай фракциясы, цеолит, гидроөңдеу.

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ГИДРОПЕРЕРАБОТКА НЕФТЯНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМООКСИДНЫХ КАТАЛИЗАТОРАХ

Аннотация. Изучен процесс гидропереработки бензиновой и дизельных фракций нефти на модифицированных алюмоникельмолибденовых катализаторах, модифицированных добавками ZSM-5, фосфора и РЗЭ. Исследование процессов гидропереработки прямогонного бензина и дизельной фракций нефти проводилось в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400^{0}С, давлении 3,0–4,0 МПа и объемной скорости подачи сырья 1-3ч$^{-1}$.

При гидропереработке прямогонного бензина на катализаторе $NiO-MoO_3-Ce_2O_3-P_2O_5$-ZSM(20%)-Al_2O_3 выход жидкой фазы с ростом температуры от 320 до 400 ^{0}С меняется от 92,5 до 70,0%. Октановое число облагороженного при 400^{0}С бензина составляет 85,6 (И.М.), содержание серы в конечном продукте снижается с 0,037% (исходный бензин) до 0,0102% при 400^{o}С.

При гидропереработке прямогонного бензина на катализаторе $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(30%)-Al_2O_3 при температуре 320-400^{o}С содержание изоалканов повышается по сравнению с исходным от 26,3 до 35,7–38,3%. Выход жидкой фазы с ростом температуры от 320 до 400^{0}С меняется от 70,0 до 50,0%. Октановое число облагороженного при 400^{0}С бензина составляет 83,7 (И.М.) и 69,7 (М.М.). При гидропереработке

бензиновой фракции в этих условиях содержание серы в конечном продукте снижается с 0,037% (исходный бензин) до 0,0022%.

При гидропереработке прямогонного бензина на катализаторе $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 при температуре 320°С содержание изоалканов в получаемом катализате растет по сравнению с исходным сырьем от 32,6 до 41,9%. При 400°С содержание изоалканов снижается до 34,2%. Выход жидкой фазы с ростом температуры с 320 до 400 ^{0}С меняется от 85,0 до 55,0%. Октановое число облагороженного бензина увеличивается в интервале 320–400°С: по исследовательскому методу от 81,9 до 87,0 и моторному методу от 63,2 до 68,9, при этом содержаение серы снизилось 0,0375 до 0,0012%.

При гидропереработке прямогонного бензина на катализаторе $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 в интервале 320-400°С содержание изоалканов составляет 30,7–44,3%. При росте температуры до 400°С содержание изоалканов понижается и равно 30,7%. Выход жидкой фазы с ростом температуры от 320 до 400^{0}С уменьшается от 74,8 до 55,4%. Октановое число облагороженного при 400^{0}С бензина максимально и равно 91,8 (И.М.) и 72,4 (М.М.). В этих условиях содержание серы в получаемом бензине снижается с 0,0092% до 0,0028 %.

Изучено влияние давления и объемной скорости подачи сырья на процесс гидропереработки прямогонного бензина на примере катализатора $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3.

Выявлены оптимальные условия гидропереработки прямогонной бензиновой фракции: 400˚С, V=2 ч$^{-1}$, P=4,0МПа. Установлено, что наиболее высокое октановое число 91,8 (И.М) характерно для катализатора $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3. Катализатор $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 обладает наиболее высокой гидрообессеривающей активностью, остаточное содержание серы при 400^{0}С составляет 0,0012%.

Проведены испытания катализаторов $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 и $NiO-MoO_3-Ce_2O_3-P_2O_5$–ZSM(30%)-Al_2O_3 в процессе гидропереработки дизельных фракций нефти с различным содержанием серы. Сравнение полученных результатов показывает, что наибольшей гидрообессеривающей активностью обладает катализатор $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3. При гидропереработке прямогонной дизельной фракции на этом катализаторе в оптимальных условиях (400^{0}С, 2 ч$^{-1}$, 4,0 МПа) содержание серы снижается с 0,6400% до 0,0740%, а при гидропереработке прямогонной дизельной фракции с более высоким содержанием серы 0,8042% – до 0,053%, что, по-видимому, связано с присутствием в исходном сырье различных видов сероорганических соединений. Наиболее низкая температура застывания и помутнения в оптимальных условиях наблюдается при гидрооблагораживании дизельных фракций на катализаторе $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 и достигает минус 39,6^{0}С и минус 30,5^{0}С соответственно.

Таким образом, разработаны и синтезированы модифицированные цеолитсодержащие катализаторы гидропереработки бензиновых и дизельных фракций, которые в одну стадию проводят гидроочистку, гидроизомеризацию и гидрирование. Разработанные катализаторы позволяют получать высокооктановый малосернистый бензин и низкозастывающее малосернистое дизельное топливо.

Ключевые слова: катализатор, прямогонный бензин, дизельная фракция нефти, цеолит, гидропереработка.

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UTILIZATION OF HYDROGEN SULFIDE-CONTAINING REFINERY FLARE GASES

Abstract. Modern oil refinery flare does not provide the beneficial use of discharged hydrocarbon gases and vapors, which does not allow to reduce the volume of hydrocarbon gas burned in flare candles and reduce atmospheric pollution. To ensure a stable and trouble-free operation of the flare plant and to increase the efficiency of waste gas utilization, their preliminary compression using mechanical or jet compressors and the construction of gas treatment plants are required. A low-cost method of utilizing hydrogen sulfide-containing refinery gas is proposed, including two-stage gas compression by a liquid-ring compressor using an alkanolamine aqueous solution as a working fluid in the first stage of compression, separation of the compressor of first stage compression to produce desulfurized gas, hydrocarbon condensate and an alkanolamine saturated hydrogen sulfide. In the second stage, the compression of the desulfurized gas is carried out by a liquid-ring compressor using a hydrocarbon absorbent as the working fluid, cooling and separation of the compress of the second stage of compression produce lean gas, water condensate and absorbate. The aqueous condensate is mixed with saturated hydrogen sulfide alkanolamine absorbent and taken out for regeneration, the hydrocarbon condensate is mixed with the absorbate to produce BFLH, and the lean gas is subjected to membrane separation to produce hydrogen and fuel gas. Application of the method can partially cover the needs of refineries in hydrogen by reducing its losses, as well as return gas and hydrocarbon fractions for processing or to the fuel network of the plant.

Key words: flare plant, oil refining, waste gases, hydrogen sulfide, gas purification, gas compression, liquid-ring compressor, hydrogen utilization, fuel gas.

The relevance of the topic. Flare systems are designed to ensure the safety of permanent, periodic, and emergency discharges of flammable gases and vapors with their subsequent combustion. The most widely used method for gas utilization in flare plants is gas separation, which involves the separation of flare gases to produce hydrocarbon gas, which is utilized for combustion, and condensate that is pumped out of the plant. The modern flare facility of the oil refinery includes special installations for collection, short-term storage, and return of released hydrocarbon gases and vapors for further use. This method reduces the volume of irreversible losses of hydrocarbon gas (burned in flare candles), thereby reducing atmospheric pollution, and ensures stable and trouble-free operation of the flare plant [1-4]. Given that the emission of flare gas is one of the main sources of environmental pollution and global warming, it is of great importance to develop the methods for utilization of flare gases in the oil and gas industry, in particular in oil refineries of many countries [5-8]. One of the problems related to the utilization of low-pressure flare gases is the need to compress them to the pressure necessary for processing or transportation to external consumers [9-11].

Discussion of problems. For compression of hydrocarbon gas in flare plants, piston and screw compressors are usually used. To drive them, a large amount of energy resources (electricity or water vapor) is consumed, moreover, one could observe hydrogen sulfide corrosion of internal components, parts of the compressor, and other installation, pollution of the production environment due to leakage of the compressed medium [12-13]. As an alternative to a mechanical system for compressing flare gas, liquid-jet compressors are proposed. Water, petroleum products, and crude oil are used as the working fluid of a jet compressor (JC), and in the case of compression of aggressive gases, neutralizing liquids are used. For example, it is reported that light coking gasoil is used as a working fluid to compress the flare gas to a pressure of 0.5-0.6 MPa, which allows to send it to the fuel network of the plant. C3+ hydrocarbon fractions are released from the flare gas during compression due to their dissolution in gasoil and diverted to the catalytic cracking unit for utilization along with the balance excess [14].

The disadvantage of using gasoil or other petroleum products as a working fluid is that they practically do not absorb hydrogen sulfide during the gas compression process. The presence of its residual amounts in the compressor, which is used as fuel in process furnaces, leads to contamination of the production environment with toxic sulfur dioxide. To combine the processes of compression and purification of gas from hydrogen sulfide in a jet compressor, it is proposed to use an aqueous solution of amine as the working fluid [13]. However, as the practice has shown, the amine solution is contaminated with heavy hydrocarbon fractions contained in the compressed gas, which complicates the process of regeneration of the solution due to the foaming in the desorption column.

From both economic and operational points of view according to foreign companies, it is more appropriate to use low-pressure refinery gases for compression, including flare gases, and liquid-ring compressors (LRC). They successfully solve the problem of compressing explosive gases, as well as gases with a high content of hydrogen sulfide, hydrocarbon condensate, water, and gases containing mechanical impurities [15-17].

This type of compressor (LRC) supplied mainly by foreign manufacturers finds its application in the Russian oil and gas production and refinery [18-19]. For example, Garo and several other foreign companies supply compressors and installation based on them for the utilization of hydrogen sulfide-containing flare gases that use alkanolamine solutions as the working fluid. Due to the absorption properties of the working fluid in relation to hydrogen sulfide, these installations (see figure 1) reduce its content in the compressed fuel gas, which helps to solve the problem of environmental protection. When compressing the flare gas, heavy hydrocarbons of gasoline fractions are partially released from it because of condensation, which is usually carried with the gas to the flare. However, the use of an amine solution as a working fluid does not limit the loss of hydrogen contained in refinery flare gases in an amount of up to 60% vol., the loss of valuable hydrocarbon fractions C_{+4} of refinery flare gases reach up to 40% by mass. of the potential.

The analysis of scientific works of Kazakh scientists shows that many people were engaged in sulfur issues.

The paper shows the possibility of using sulfur as a vulcanizing agent of rubber mixtures. Thus, the authors of the work proposed one of the ways to utilize industrial sulfur in favor of production [20].

Materials and methods of research. We have proposed a method for compressing flare gas with a liquid-ring compressor, which reduces the loss of hydrocarbon fractions and hydrogen and increases the degree of purification from hydrogen sulfide (figure 1).

A special feature of the technical offer is that the process of compression of hydrogen sulfide-containing flare gas by a liquid-ring compressor is carried out in two stages: at the first stage, an amine solution is used as the working fluid, and at the second stage, the desulfurized gas is compressed with another working fluid - a hydrocarbon absorbent. The compressor of the second stage of compression is cooled and separated to obtain the lean gas, and the absorbent, which is mixed with hydrocarbon condensate and removed from the installation. The water condensate is mixed with an alkanolamine absorbent saturated with hydrogen sulfide, and removed from the installation, and the lean gas is subjected to membrane separation to produce hydrogen and fuel gas [21].

In the proposed method, compression of desulfurized gas at the second stage using a hydrocarbon absorbent as the working fluid allows the absorption of valuable hydrocarbon fractions contained in the desulfurized gas and reduction of their losses with the fuel gas. The membrane separation of the lean gas to produce hydrogen and fuel gas reduces the loss of hydrogen with the fuel gas and returns it to the production cycle and allows to obtain a fuel gas with a high volumetric calorific value.

The presence and quantity of hydrocarbon and water condensates released during compressor separation depend on the composition, temperature, and pressure of the refinery flare gases, on the flow rate and temperature of the alkanolamine and hydrocarbon absorbents, as well as on the compression pressure at each stage and the cooling temperature of the second stage compressor. Technological parameters of the process are set based on the requirements for the composition and characteristics of fuel gas and hydrogen (hydrogen-containing gas), as well as the acceptable level of losses of hydrocarbon fractions with fuel gas.

Gasoline, kerosene, diesel fuel, and any other hydrocarbon mixtures with low viscosity can be used as a hydrocarbon absorbent.

Research results. Based on the results of the pilot run and calculation studies, the technological regulations were developed for the design of the refinery's flare gas utilization unit with a capacity of 3000 nm3/h (2.4 t/h), including a compression unit based on the NAM-2500 liquid-ring compressor of the NASH company.

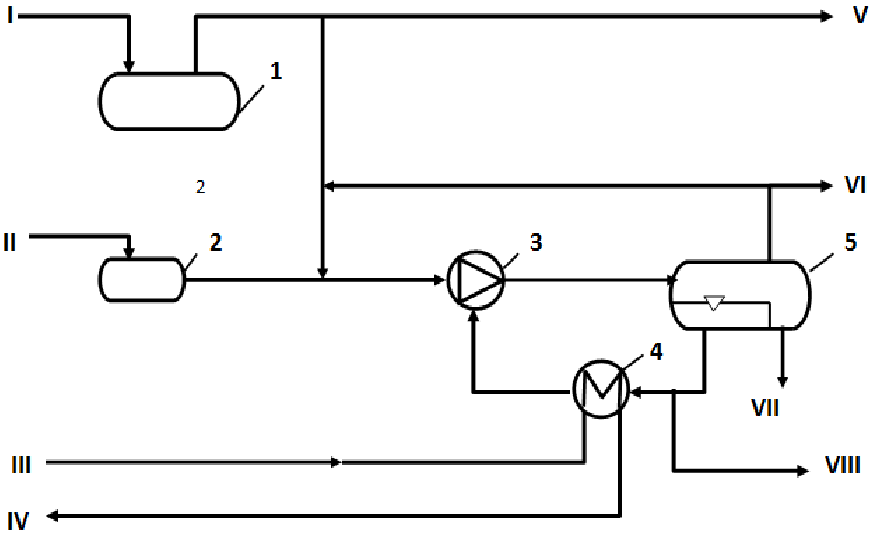

Figure 1 - The scheme of compression and purification of refinery flare gases [20]:
Flows: I – flare collector; II – fresh amine solution; III – cold coolant;
IV – hot coolant; VI – purified gas; VII – gas condensate; VIII - saturated amine solution for regeneration.
Devices: 1 – flare separator; 2 – gasoil tank; 3 – liquid-ring compressor;
4 – heat exchanger; 5 – three-phase separator.

According to the regulations, the oil refinery's flare gas, which contains 0.76% vol. of hydrogen sulfide and 45.9% vol. of hydrogen (see table 1) in the amount of 3000 nm3/h (2.4 t/h) at a temperature of 35 °C and a pressure of 0.15 MPa, is directed to the inlet of the NAM-2500 liquid-ring compressor of the NASH company. The compressor is supplied with a 15% aqueous solution of monoethanolamine in the amount of 8 m3/h as the working fluid. A compressor with a compression pressure of 0.4 MPa is sent to a separator to produce 3052 nm3/h of desulfurized wet gas containing 0.01% hydrogen sulfide and 7.99 t/h of an aqueous solution of monoethanolamine saturated with hydrogen sulfide. Hydrocarbon condensate is not released under experimental conditions, and there is no change in the hydrocarbon composition of the gas after the first stage of compression as can be seen from table 1.

Table 1 - Results of compression of flare gas with a liquid-ring compressor

No.	Components	The content of components, % vol.			
		Flare gas	Gas after the 1st compression stage	Gas after the 2nd compression stage	Fuel gas
1	Methane	25,34	24,9	27,18	44,0
2	Ethane	6	5,9	5,89	7,19
3	Propane	6,63	6,52	5,22	12,2
4	Isobutane	2,43%,	2,39	1,37	3,18
5	N-butane	3,84%	3,77	1,83	4,23
6	Isopentane	1,89	1,86	0,5	1,13
7	N-pentane	0,77	0,76	0,17	0,37
8	Propylene	2,18	2,14	1,79	4,19
9	Butylenes	0,13	0,13	0,07	0,16
10	Pentenes	0,34	0,33	0,09	0,19
11	Hydrogen sulphide	0,76	0,01	0,01	0,02
12	Nitrogen	3,77	3,71	4,11	9,66
13	Hydrogen	45,9	45,1	50,77	12,4
14	Carbon dioxide	0,02%	-	-	-
15	Water	-	2,48	1,0	1,08

Further, the desulfurized gas is sent for compression to the inlet of a liquid-ring compressor, where 8 t/h of raffinate from the aromatic hydrocarbon extraction unit is used as working fluid and compressed to 0.8 MPa. After that, the compressor is cooled to 40 °C and separated to produce 2730 nm3/h of lean gas and 8.6 t/h of absorbate, which is sent to pyrolysis, and 37.9 kg/h of water condensate, containing dissolved monoethanolamine vapor, which is mixed with an aqueous solution of monoethanolamine saturated with hydrogen sulfide and sent for regeneration. An increase in the mass of the absorbate by 0.6 t/h (8.6 t/h against the initial mass of the working fluid of raffinate, 8.0 t/h) is associated with the absorption of valuable C4+ hydrocarbon fractions contained in the initial flare gas. It allows to reduce their content in the gas, as can be seen from Table 1, and by this reduce their losses due to combustion in the fuel gas

Then, to separate the hydrogen, the lean gas is sent to a membrane gas separation unit, which produces 1.35 t/h (1160 nm3/h) of fuel gas and 0.45 t/h (1570 nm3/h) of hydrogen-containing gas with a content of 79% vol. of hydrogen. The resulting hydrogen concentrate is compressed for short-cycle adsorption (SCA) process, which produces 1240 nm3/h of pure hydrogen, as well as 330 nm3/h of fuel gas. After mixing the fuel gas from the membrane unit and the SCA, the gas is sent to the fuel network of the refinery in the amount of 1490 nm3/h, the composition of which is shown in Table 1.

Conclusions. Thus, the proposed method of gas processing can be used in the oil and gas, oil refining, and petrochemical industries for the utilization of hydrogen- and hydrogen sulfide-containing refinery flare gases. The application of the method can partially cover the demand of the oil refinery in hydrogen by reducing its losses, as well as return valuable hydrocarbon fractions to processing, and the gas purified from hydrogen sulfide - to the fuel network of the plant.

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ҚҰРАМЫНДА КҮКІРТТІ СУТЕГІ БАР ЗАУЫТТЫҚ МҰНАЙ АЛАУ ГАЗЫН КӘДЕГЕ ЖАРАТУ

Аннотация. МӨЗ-дің қазіргі заманғы алау шаруашылығы тасталатын көмірсутекті газ бен будың пайдаға асырылуын қамтамасыз ете алмайды, нәтижесінде, алау шамдарында жағылатын көмірсутекті газдың көлемі азайтылмайды және атмосфераның ластануын азайтуға мүмкіндік болмайды. Алау шаруашылығының жұмысын тұрақты және апатқа ұшырамайтындай қамтамасыз ету үшін және төгінді газды кәдеге жарату тиімділігін арттыру үшін механикалық немесе ағынды компрессорларды пайдалана отырып, оларды алдын ала компримирлеу және газ тазалау қондырғыларын салу талап етіледі.

Құрамында күкіртсутегі бар зауыттық мұнай алау газын кәдеге жаратудың аз шығынды тәсілі ұсынылды, бұл тәсілдің құрамында алканоламиннің су ерітіндісін сығудың бірінші сатысында жұмыс сұйықтығы ретінде пайдалану арқылы сұйықты-сақиналы компрессормен екі сатылы газды сығу, сондай ақ сығудың бірінші сатысы бойынша компрессатты сепарациялау арқылы күкіртсіздендірілген газ алу және көмірсутекті конденсат пен күкірт сутегімен қаныққан алканоламин абсорбентін алу қарастырылған.

Техникалық ұсыныстың негізгі ерекшелігі – құрамында күкіртсутегі бар факельді газды сұйықты-сақиналы компрессормен сығу процесі екі сатыда жүзеге асырылуында: бірінші сатыда жұмыс сұйықтығы ретінде амин ерітіндісі пайдаланылады, ал екінші сатыда күкіртсіздендірілген газды сығу басқа жұмыс сұйықтығымен, яғни, көмірсутекті абсорбент арқылы жүргізіледі.

Екінші сатыда күкіртсіздендірілген газды сығуды жұмыс сұйықтығы ретінде көмірсутекті абсорбентті пайдалану арқылы сұйық-сақиналы компрессормен жүргізеді, сығудың екінші сатысы бойынша компрессатты салқындату және сепарациялау арқылы бензинденбеген газды, су конденсатын және абсорбатты алады. Су конденсатын қаныққан күкіртсутекпен, алканоламин абсорбентімен араластырады және регенерацияға шығарады, көмірсутегі конденсатын ЖККФ-ды (жеңіл көмірсутектердің кең фракциясы) алатындай етіп абсорбатпен араластырады, ал бензинделген газ сутегі мен отын газын алу арқылы мембраналық бөлуге ұшырайды.

Компрессаттарды сепарациялау кезінде бөлінетін көмірсутекті және су конденсаттарының болуы және олардың мөлшері, зауыттық мұнай алау газдарының құрамына, температурасына және қысымына, алканоламин және көмірсутекті абсорбенттердің шығыны мен температурасына, сондай-ақ, екінші сатылы компрессаттың әрбір сатыдағы сығылу қысымынан және оның салқындату температурасына байланысты болады. Үдерістің технологиялық параметрлері отын газы мен сутегінің (құрамында сутегі бар газ) құрамы мен сипаттамаларына, сондай-ақ отын газы бар көмірсутек фракциялары шығынының рұқсат етілген деңгейіне қойылатын талаптарға сүйене отырып беріледі.

Көмірсутекті абсорбент ретінде бензиндер, керосиндер, дизель отындары және тұтқырлығы төмен кез келген басқа да көмірсутекті қоспалар пайдаланылуы мүмкін.

Тәжірибелік жүріс және есептік зерттеулер нәтижелері бойынша NASH фирмасының NAM-2500 маркалы сұйықтықты-сақиналы компрессор негізіндегі компримирлеу блогын қамтитын өнімділігі 3000 нм^3/сағ (2,4 т/сағ) МӨЗ-ның факелді газын кәдеге жарату торабын жобалауға технологиялық регламент әзірленді.

Ұсынылған әдісті қолдану МӨЗ-нің сутегідегі қажеттілігін оның шығынын азайту есебінен ішінара жабуды, сондай-ақ газды және көмірсутекті фракцияларды қайта өңдеуге немесе зауыттың отын желісіне қайтаруды қамтамасыз етуі мүмкін.

Түйін сөздер: алау қондырғысы, мұнайды қайта өңдеу; төгінді газ; күкіртті сутегі; газдарды тазарту; газдарды компримирлеу; сұйықтықты-сақиналы компрессор; сутекті кәдеге жарату; отын газы.

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УТИЛИЗАЦИЯ СЕРОВОДОРОДСОДЕРЖАЩИХ НЕФТЕЗАВОДСКИХ ФАКЕЛЬНЫХ ГАЗОВ

Аннотация. Современное факельное хозяйство НПЗ не обеспечивает полезное использование сбрасываемых углеводородных газов и паров, что не позволяет уменьшать объем сжигаемых в факельных свечах углеводородного газа и снижать загрязнение атмосферы. Для обеспечения устойчивой и безаварийной работы факельного хозяйства и для повышения эффективности утилизации сбросных газов требуется их предварительное компримирование с использованием механических или струйных компрессоров и сооружение газоочистных установок.

Предложен малозатратный способ утилизации сероводородсодержащих нефтезаводских факельных газов, включающий двухступенчатое сжатие газов жидкостно-кольцевым компрессором с использованием на первой ступени сжатия водного раствора алканоламина в качестве рабочей жидкости, сепарацию компрессата первой ступени сжатия с получением обессеренного газа, углеводородного конденсата и насыщенного сероводородом алканоламинового абсорбента.

Особенностью технического предложения является то, что процесс сжатия сероводородсодержащего факельного газа жидкостно-кольцевым компрессором осуществляют в две ступени: на первой ступени в качестве рабочей жидкости используют аминовый раствор, на второй ступени сжатие обессеренного газа проводят другой рабочей жидкостью ─ углеводородным абсорбентом.

На второй ступени сжатие обессеренного газа проводят жидкостно-кольцевым компрессором с использованием в качестве рабочей жидкости углеводородного абсорбента, охлаждением и сепарацией компрессата второй ступени сжатия получают отбензиненный газ, водный конденсат и абсорбат. Водный конденсат смешивают с насыщенным сероводородом алканоламиновым абсорбентом и выводят на регенерацию, углеводородный конденсат смешивают с абсорбатом с получением ШФЛУ, а отбензиненный газ подвергают мембранному разделению с получением водорода и топливного газа.

Наличие и количество углеводородного и водного конденсатов, выделяемых при сепарации компрессатов, зависит от состава, температуры и давления нефтезаводских факельных газов, от расхода и температуры алканоламинового и углеводородного абсорбентов, а также от давления сжатия на каждой из ступеней и температуры охлаждения компрессата второй ступени. Технологические параметры процесса задаются исходя из требований, предъявляемых к составу и характеристикам топливного газа и водорода (водородсодержащего газа), а также к допустимому уровню потерь углеводородных фракций с топливным газом.

В качестве углеводородного абсорбента могут быть использованы бензины, керосины, дизельные топлива и любые другие углеводородные смеси с невысокой вязкостью.

По результатам опытного пробега и расчетных исследований разработан технологический регламент на проектирование узла утилизации факельного газа НПЗ производительностью 3000 нм^3/час (2,4 т/час), включающий блок компримирования на основе жидкостно-кольцевого компрессора марки NAM-2500 фирмы NASH.

Применение способа может частично покрыть потребности НПЗ в водороде за счет снижения его потерь, а также возвратить газ и углеводородные фракции на переработку или в топливную сеть завода.

Ключевые слова: факельная установка, переработка нефти; сбросный газ; сероводород; очистка газов; компримирование газов; жидкостно-кольцевой компрессор; утилизация водорода; топливный газ.

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PROBLEMS AND SOLUTIONS OF THE SILT SLUDGE UTILIZATION ISSUES AT WASTE TREATMENT FACILITIES OF NUR-SULTAN CITY

Abstract. Effective management of wastewater sludge is currently one of the most pressing environmental problems in Nur-Sultan city, which becomes more acute year by year and requires immediate solution. Wastewater sludge is almost completely stored at the treatment facilities, which turns them into a source area of bacteriological and toxicological hazard. For this reason, the most urgent problem now is the development of new sustainable and zero waste technologies that can effectively expedite the reduction of silt sludge and lead to a significant decrease in their final volume. This article analyzes various methods of sludge disposal. It is shown that of all possible technology options with admissible environmental impact and the best economic indicators, the most acceptable is the method of thermo-catalytic oxidation of wastewater sludge in a semi fluidized bed of the catalyst, the use of which can fundamentally change the situation with the sludge disposal. Also, the article studied the composition and carried out measurements of silt sludge contamination with heavy metals and oil products at wastewater treatment plants of Nur-Sultan city. It is pointed out that the LOC for the TPH-in-soil is 1.5 g/kg, from which it can be concluded that there is a significant excess in the wastewater sludge for this indicator, and studies for the heavy metals presence in the wastewater sludge showed that sediments can have a toxic effect and are classified as 4 class of hazard.

Key words: composition, silt sludge, landfill, waste treatment facilities, utilization.

The development of new resource saving and zero waste technologies to efficiently clean human waste with the possibility of their reutilization, is one of the most critical tasks in the field of environmental protection [1].

Self-restoration of natural ecosystems is slow, which is mainly due to the high concentration of xenobiotics, which are not included in the biotic cycle, and their high resistance to decomposition.

As a rule, an increase in the environment of xenobiotics concentration is directly or indirectly associated with human economic activities, which generates industrial and agricultural waste, pollution of water resources, soil, and atmosphere with toxic substances. Therefore, special attention is required to the issues of environmental reclamation, in particular rehabilitation and restoration of land fertility, sustainable processing of municipal waste, aqueous effluents treatment and wastewater sludge utilization of treatment facilities.

As a result of human household and industrial activities, liquid waste is generated in the form of wastewater, which is mainly discharged into the sewage collection system. In the process of wastewater undergoing all stages of treatment at the waste treatment facilities, a silt sludge is generated, which for the most part is resistant to, or difficult to process by any kind of treatment, except for dehydration and storage, which causes the spread of negative air and gas pollution, contamination of soil and underground water with toxic components included in their composition [2]. The composition of silt sediments may include substances with general toxic, toxicogenetic, embryotoxic, carcinogenic and other negative properties. They may contain heavy metals, pathogens, excess nitrates, toxic substances, pesticides, polychlorinated biphenyls, aliphatic compounds, esters, mono- and polycyclic aromatic substances, phenols, nitrosamines, etc.

Thus, the silt sludge utilization from wastewater is one of the most major problems of modern cities. Common methods for treating silt sediments in sludge digesters or dumping them on silt landfills are not effective enough and require the alienation of significant land plots near pollution sources [3]. The territories provided for the storage of silt sludge are overflowing quickly and cannot cope with continuous sludge flows. Besides that, silt storage facilities pose a threat to environmental compartments due to the high content of dangerous viruses, bacteria, harmful gases, hazardous chemical compounds. Additionally, in the process of fermentation in vivo offensive odors are produced, which causes great inconvenience to the townspeople. On the flip side, due to the presence of a high concentration of phosphorus and nitrogen, the wastewater sludge can serve as a good fertilizer. Due to this, the main focus in the disposal of silt sludge should have been its use as a local fertilizer. However, the question of the use of silt sludge in agriculture, and especially the matter of the accumulation of toxic substances in soil and plants when applied as fertilizer, is not well understood. As a result, the practical use of silt sludge as a fertilizer can be a source of pollution, since, in addition to various organic substances, it can contain heavy metals, the migration of which in the biosphere have an extremely negative impact on the environment.

This is one of the reasons why methods of sludge incineration have become more widespread in recent years. That process also makes it possible to obtain a positive energy balance and use the calorific value of silt sediment efficiently[4]. The main factor that encourages the use of this method is the fact that the amount of sludge generated at urban wastewater treatment facilities is enormously large compared to the free areas where the sludge can be disposed of or otherwise treated (composting, for instance).

In a number of cities and large settlements of Kazakhstan, dehydrated raw sludge is collected and placed in urban silt landfills, worsening the already tense ecological situation. Thus, the accumulation of a huge amount of off grade sediments - production waste after the biological treatment of wastewater.

Currently, about 89 thousand tons of dehydrated wastewater sludge are taken annually to the landfill of Nur-Sultan city, with a moisture content of 68-73% (initial moisture content of wastewater sludge is 93-97%), for dry solids (estimated value) about 32-33 thousand tons. There is a tendency to its substantial increase with the city's population growth. Sediments of urban wastewater treatment facilities are organic (up to 72%) and mineral (about 28%) impurities isolated from water as a result of mechanical, biological, and physical and chemical treatment. It was determined that silt sediments of Nur-Sultan city contain a significant amount of organic matter, that is, fats, proteins, carbohydrates, etc. Through the analysis it was found that the ash content of the dehydrated sludge from the wastewater treatment facility of MSE Astana Su Arnasy is 27-32%.

In modern conditions, the protection of soil from pollution appears to be important, since any harmful compounds in it sooner or later enter the human body [5,6]. Silt landfills are one of the major and largest in terms of environmental pollutants with harmful and hazardous substances, in particular heavy metals.

Silt landfills operation involves:

1. The washing out of contaminants in open bodies of waters and groundwater;
2. The ingress of contaminants through the food chains into the human body;
3. Many compounds have the ability to accumulate in tissues, and especially in bone tissues.

Heavy metals and their compounds make up a significant group of toxicants [7]. A distinctive feature of heavy metals is their inaptness to break down in the natural environment, instead, they are able to accumulate in ecosystems, causing long-term harm. Following the links of the migration chain (soil - plants - animals - people), heavy metals have toxic and carcinogenic effects on all living organisms. The greatest harm is caused by metals, which are used in significant quantities in human production activities and, as a result of accumulation in the environment, pose a major hazard in terms of their biological activity and toxic properties. These include metals such as lead, mercury, cadmium, zinc, bismuth, cobalt, nickel, copper, tin, antimony, vanadium, manganese, chromium, molybdenum and arsenic. An additional source of heavy metals in wastewater sludge is industrial effluents from electronic, instrument making and other industries. Heavy metals in wastewater are contained in the form of ions and complexes with inorganic and organic substances [8]. They can be in suspended colloidal and dissolved forms in untreated wastewater. Dissolved forms of metal compounds are the most toxic [9].

However, there are no large industrial enterprises in Nur-Sultan city, the activity of which leads to significant pollution of industrial wastewater with heavy metals. Effluents entering the wastewater treatment facilities of Nur-Sultan city are 80% household pollution greywater and the concentration of heavy metals is low in them. Heavy metal ions are contained in coarse dispersed mineral suspended solids and undissolved organic impurities that are trapped in the preliminary settling tanks of treatment facilities and make up wastewater sludge. Metal compounds are almost non-degraded during biological oxidation. Partially, metal compounds are sorbed by active sludge, and then, through a series of biochemical processes, they are converted into an inactive form. The other part of heavy metal ions create complexes with activated sludge protein. The accumulation of metal compounds in activated sludge occurs in both cases [9]. Excess active sludge is a part of a wastewater sediments and is subject to utilization.

The measurements of the heavy metals mass content in raw dehydrated wastewater sludge (gross content) are presented in table 1. The data show that the concentration of heavy metals in dried sludge is higher than in raw sludge.

Table 1 - The content of heavy metals in silt sludge

Sampling Location	S, mg/kg				
	Zn	Pb	Cr	Cd	Ni
raw sludge before dehydration	789	24.4	74.0	1.9	51.3
Dried sludge	1021	23.4	67.8	2.5	59.9
Sediment from deposit sites	618	23.1	63.9	2.4	56.0
Soil APC	220	130	-	2.0	80

The data of Table 1 on heavy metals in wastewater sludge showed that wastewater sludge can have a toxic effect and belong to the 4th class of hazard [10].

Silt sediments were also examined for the content of oil products in them. Given that the MAC for the content of oil products in the soil is 1.5 g/kg, we can conclude that there is an excess for this marker in the wastewater sludge (table 2).

Table 2 - The content of petrochemicals in the sludge

Sample name	Unit	Concentration of petrochemicals
Raw sludge of wastewater dehydration	mg/dm^3	105.4
Dehydrated wastewater sludge	mg/kg	4105
Wastewater sludge from deposit sites	mg/kg	2429

Most sediment is stored at silt sites and landfills, leading to pollution of surface and groundwater, soil and vegetation. When entering subsurface and groundwater, the aqueous extract of wastewater sludge gives them color and flavors, which negatively affects the quality of such waters [10].

Effective management of wastewater sludge is at present one of the severe environmental issues in Nur-Sultan city, which is aggravated every year and requires urgent solutions. Wastewater sludge is almost completely stored in the landfill of treatment facilities, which turns them into a hot spot of bacteriological and toxicological hazard. At the same time, the use of sediment from wastewater sludge will solve the current need to search for alternative energy sources, which wastewater silt sludge may become one.

There are many methods for wastewater sludge utilization. As a rule, the choice of recovery method is determined by the availability of appropriate equipment. The most promising in regards to the processing of sludge are thermal methods.

Due to the high content of volatile solids and colloidal substances generated during fermentation, excess active sludge is hard to treat with mechanical types of dehydration. Wastewater sludge generated at the sewage treatment facility of Nur-Sultan city, is subjected to a dehydration process using flocculants prior to utilization. In turn, the use of flocculants obstructs the processing of the resulting wastewater sludge after dehydration into compost and fertilizer.

The resource of silt sediment deposition on the maps of landfills is significantly limited or exhausted, and recycling methods that radically reduce the initial volumes of silt sediments logically come to the forefront, and, of course, thermal ones are among them; those are divided into two large groups -

incineration and thermal breakdown (drying by the pyrolysis). However, the disadvantage of thermal methods for utilizing sludge is the formation of flue gases, which requires the use of modern and effective methods for their purification and careful monitoring of exhaust gases.

Sludge sediments are traditionally burned in pseudo-boiling-layer furnaces, which, although being an efficient environmental equipment, are quite temperamental to the process conditions, and require capital investments for operation, and input for expensive spare and wear parts. Additionally, due to the high content of heavy metal salts in the sludge, the generation of tar during combustion, and also due to a general lack of technology - the generation of dioxins - sludge incineration cannot be considered as the optimal solution, as it requires a powerful and expensive gas cleaning unit. The search for alternative solutions in the field of thermal technologies leads to thermal breakdown or drying of sediments [11,12].

Pyrolysis technologies are also known and used in various industries [13]. They are about heating the feed materials in an oxygen-free atmosphere that prevents combustion. The manufacture of pyrolysis equipment for the utilization of silt sludge (a crucible updraft furnace) with a couple of operating cycles per day that meets the needs of industrial production will be a rather ergonomic and technologically intensive process. The process product will be carbonized hydrophobic dry residue of hazard class V (not hazardous), which is confirmed by the results of a number of tests [14]. The pyrolysis disadvantage is the increased fire and explosion hazard of the pyrolytic plants. The implementation of sludge utilization by pyrolysis is the most expensive methods. The process of sludge disposal by pyrolysis is less common than utilization by burning, and it is not widespread in the CIS countries.

The most relevant of all the possible technology options with acceptable environmental impact and the best economic factors is the method of thermo-catalytic oxidation of wastewater sludge in a fluidized bed of catalyst. The introduction of sludge incineration technology and the construction of a heating module for thermo-catalytic oxidation of wastewater sludge from sewage treatment facilities are described in the literature [15]. This pilot project allows to solve the problem with large savings of investment costs compared with foreign counterparts and fundamentally turn the situation with the silt sludge utilization, significantly improving the environmental situation in different regions through technological scaling.

There are no technologies used for the thermal utilization of wastewater silt sludge in Kazakhstan. However, such facilities operate in a number of cities of the Russian Federation, such as: St. Petersburg, Novocheboksarsk, and a plant in Omsk was also tested in pilot mode [15].

In summary, there aren't any industrialized options for the use of final products of the silt sludge utilization in Kazakhstan today. All alternative options come down only to theoretical assumptions and experiments, and the implementation of the methods of thermal utilization discussed in this article can quite effectively manage the reduction of silt sludge, and lead to a significant decrease in its final volume.

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НҰР-СҰЛТАН ҚАЛАСЫНДАҒЫ КӘРІЗ ТАЗАРТУ ҚОНДЫРҒЫЛАРЫНДАҒЫ ТҰНБА ШЛАМЫН КӘДЕГЕ ЖАРАТУ МӘСЕЛЕЛЕРІ МЕН ШЕШУ ЖОЛДАРЫ

Аннотация. Ағынды су тұнбасын тиімді басқару қазіргі таңда жыл сайын шиеленісіп келе жатқан және жедел шешуді қажет ететін Нұр-Сұлтан қаласындағы ең маңызды экологиялық мәселелердің бірі болып саналады. Ағынды су тұнбасы толығымен дерлік тазарту қондырғы полигондарының аумағында сақталған, бұл оларды бактериологиялық және токсикологиялық қауіпті ошаққа айналдырады. Тұнба шөгінін сақтауға арналған алаңдар тез толып, тұнба ағынына төтеп бере алмайды. Сонымен қатар, тұнба шөгінінің жиналуы мен сақталуы кезінде ашыту үдерісі табиғи жағдайда жағымсыз иістің пайда болуына орай жүреді (аэрация мәселесіне байланысты мәселе), бұл қала тұрғындарына үлкен қолайсыздық тудырады.

Осылайша қазіргі кездегі ең өзекті мәселенің бірі – тұнба шөгінділерінің азаюына тиімді әсер ете алатын және көлемін азайтатын жаңа инновациялық, тиімді, ресурстарды үнемдейтін және қалдықсыз технологияларды дамыту.

Мақалада авторлар бірқатар қолданбалы мәселелерді шешуге қабілетті, тұнба шламын кәдеге жаратудың түрлі әдісіне талдау жасаған. Барлық мүмкін нұсқалардың ішінен қоршаған ортаға қолайлы әсер ететін технологиялардың ең тиімді экономикалық көрсеткіштері неғұрлым қолайлы болып саналатын әдісі көрсетілген, ол катализатордың сұйылтылған қабатында ағынды судың термокаталитикалық тотығу әдісі. Мақалада қарастырылған аталған пилоттық жоба шетелдік аналогтармен салыстырғанда күрделі шығынды үнемдеу мәселесін шешуге және тұнба шөгінділерін кәдеге жарату жағдайын түбегейлі өзгертуге мүмкіндік береді, түрлі аймақтардағы экологиялық жағдайды технологиялық масштабтау арқылы едәуір жақсартады.

Сондай-ақ, жұмыста Нұр-Сұлтан қаласының кәрізді тазарту қондырғыларында тұнба шөгінділерінің ауыр металдармен және мұнай өнімдерімен ластану жағдайы өлшенді. Жер қыртысындағы мұнай өнімдерінің шекті рұқсат етілген концентрациясы (ШРК) мөлшері 1,5 г / кг екенін ескерсек, ағынды суда бұл көрсеткіштен асып кету мүмкіндігі бар деп қорытынды жасауға болады, ал зерттеулер ағынды су тұнбасында ауыр металдар болғандықтан, тұнбалар уытты әсер етуі мүмкін және қауіптіліктің 4 тізіліміне енгізілген. Сондықтан, ауыл шаруашылығында тұнба шламын тыңайтқыш ретінде практикалық қолдану мәселесі ластану көзі болып саналады, өйткені оның құрамындағы ауыр металдар қоршаған ортаға теріс әсер етеді.

Осылайша бүгінде Қазақстанда ағынға қойылған тұнба шламын кәдеге жарату кезіндегі дайын өнімдерді пайдалануға арналған нұсқалар жоқ. Барлық балама нұсқалар тек теориялық болжамдар мен эксперименттерге ғана сүйенеді, ал осы мақалада қарастырылған термиялық кәдеге жарату әдісін жүзеге асыру арқылы шөгіндіні азайтумен тиімді күресуге болады.

Түйін сөздер: құрам, тұнба шламы, полигон, кәріз тазарту қондырғылары, кәдеге жарату.

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ПРОБЛЕМЫ И ПУТИ РЕШЕНИЯ УТИЛИЗАЦИИ ИЛОВОГО ШЛАМА НА КАНАЛИЗАЦИОННЫХ ОЧИСТНЫХ СООРУЖЕНИЯХ Г. НУР-СУЛТАН

Аннотация. Эффективное управление иловым осадком сточных вод в настоящее время является одной из наиболее острых экологических проблем г. Нур-Султан, которая с каждым годом обостряется и требует безотлагательного решения. Осадки сточных вод практически полностью хранятся на территории полигонов очистных сооружений, что превращает их в очаг бактериологической и токсикологической опасности. Территории, предусмотренные для хранения иловых осадков, быстро переполняются и не справляются с непрерывными иловыми потоками. Кроме того, при скоплении и хранении иловых осадков происходит процесс брожения в естественных условиях с образованием неприятных запахов (проблема, связанная с вопросом аэрации), что доставляет большие неудобства населению городов.

Таким образом, актуальнейшей проблемой в настоящее время является разработка новых, инновационных, экономичных, ресурсосберегающих и безотходных технологий, позволяющих эффективно справиться с сокращением иловых осадков и привести к существенному уменьшению их конечного объема.

В данной статье были проанализированы различные способы утилизации илового шлама, которые способны решить ряд прикладных задач. Показано, что из всех возможных вариантов технологий с допустимым воздействием на окружающую среду с наилучшими экономическими показателями, наиболее приемлемым является способ термокаталитического окисления осадков сточных вод в псевдожиженном слое катализатора. Данный пилотный проект, рассмотренный в статье позволяет решить проблему с большой экономией капитальных затрат по сравнению с зарубежными аналогами и принципиальным образом изменить ситуацию с утилизацией иловых осадков, улучшив существенным образом экологическую ситуацию в различных регионах путем технологического масштабирования.

Также в настоящей работе изучен состав и проведены измерения загрязненности иловых осадков тяжелыми металлами и нефтепродуктами на канализационных очистных сооружениях г.Нур-Султан. Учитывая то, что ПДК по содержанию нефтепродуктов в почве составляет 1,5 г/кг, можно сделать вывод о том, что в осадках сточных вод наблюдается значительное превышение по данному показателю, а исследования на наличие тяжелых металлов в осадках сточных вод показали, что осадки могут оказывать токсическое действие и относятся к 4 кассу опасности. Поэтому вопрос о практическом использовании илового шлама в сельском хозяйстве в качестве удобрений может представлять собой источник загрязнения, так как содержащиеся в нем тяжелые металлы оказывает крайне отрицательное воздействие на окружающую среду.

Таким образом, на сегодняшний день в Казахстане отсутствуют какие –либо поставленные на поток варианты использования конечных продуктов утилизации иловых осадков. Все альтернативные варианты сводятся лишь к теоретическим предположениям и экспериментам, а реализация рассмотренных в данной статье методов термической утилизации может довольно эффективно справиться с сокращением иловых осадков.

Ключевые слова: состав, иловый шлам, полигон, канализационные очистные сооружения, утилизация.

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DIRECTIONAL PROTEOLYSIS OF SECONDARY RAW MATERIALS

Abstract. For the food industry, technologies for processing secondary raw materials are of interest. Curd whey is a typical complex secondary bioproduct. It has a high acidity, so it is difficult to recycle. The scope of use of curd whey is limited.

There are technologies for processing whey from cheese. In the manufacture of rennet cheese, whey is formed, which is successfully processed. The technology for processing whey from cheese can only partially be applied for processing whey from cottage cheese. In particular, the use of ultrafiltration can be used for the concentration of curd whey protein. The whey protein concentrate from cottage cheese can be hydrolyzed. Curd whey after proteolytic biocatalysis has a higher potential for use in the food industry

The use of hydrolyzed whey rather than native is promising. According to studies of domestic and foreign scientists, peptides of medium length (3-10 kDa) have the highest biological value. However, during hydrolysis, a proteolytic process occurs, the consequence of which is the appearance of a bitter taste due to the formation of bitter amino acids. The aim of the study was to obtain a whey protein hydrolyzate with minimally altered sensory characteristics.

The problem with whey protein hydrolysis is that a bitter taste appears during hydrolysis. The aim of the study was to obtain a whey protein hydrolyzate of curd whey. The resulting hydrolyzis should not have a bitter taste, and the length of its peptides should be medium.

To obtain curd whey hydrolysates with harmonized sensory characteristics, an enzyme preparation from the group of fungal proteases produced by Aspergillus oryzae was selected. The experimental data made it possible to optimize the parameters of the hydrolysis process.

The results of the study and analysis confirm that the whey protein hydrolyzate has minimal changes in organoleptic characteristics compared to native serum. In the hydrolyzate there is no bitterness in the taste and aftertaste. It has been proven that the resulting peptides are of medium size.

Key words: hydrolysates, curd whey, enzymes, peptides, secondary raw materials.

Summary. Whey is a by-product of high-protein dairy products, such as cheese and cottage cheese. Whey from cheese and whey from cottage cheese have a rich chemical composition, but the use of whey in other dairy products is limited.

As a result of comprehensive studies, the process of biocatalytic conversion of curd whey ultrafiltrate was developed and optimized. A whey hydrolyzate with a high potential for dairy products was obtained. The hydrolyzate has a high biological value and a pleasant organoleptic range. It can be used to enrich other dairy products, such as cottage cheese desserts.

Introduction. The world entered the 21st century under the auspices of progressive biotechnology. Biotechnological approaches open up a space of opportunities in the modern world, in particular in the food sector. Many approaches and methods allow solving complex problems. Such a problem is, for example, the processing of whey. Among secondary dairy resources, whey processing is the most difficult.

Numerous studies of whey treatment options are based on extracting the maximum amount of benefical components from whey [1,2]. Research in this area in Russia was carried out by famous scientists: A.G., Gavrilov GB, Evdokimov I.A., Ostroumov L.A., Prosekov A.Yu., Kharitonov V.D. ect.

In their research, they expressed the prospect of using whey proteins as ingredients for other dairy products. Serum hydrolysates can be used to create preventative and functional products [3-6].

Currently, there are approaches and technologies for processing cheese whey. But these technologies cannot be used to process curd whey. Due to the fact that the acidity of curd whey is very high, it is much more difficult to process. It is difficult to use curd whey in the technology of other products [7].

A promising direction for the processing of curd whey is ultrafiltration, after which hydrolytic bioconversion occurs [8-10]

In connection with the above, the current research area is the development of a biocatalytic conversion process using Russian hydrolytic enzymes suitable for biocatalysis of curd whey. The resulting hydrolyzate can be used to enrich curd products.

The aim of our study was to develop an optimized process for the preparation of curd whey hydrolyzate with confirmed biological value and minimally altered organoleptic characteristics. The hydrolyzate should have the potential of application as an enrichment for curd products [11].

Methods. To study the molecular weight distribution of the ultrafiltration concentrate and protein hydrolyzate of curd whey, the method of high performance liquid chromatography was used.

Chromatographic analysis was performed on a Gilson high performance liquid chromatograph (Gilson Medical Electronics, Villiers le Bel, France), and a Gilson 118 variable wavelength spectrophotometric detector was also used. Detection was carried out at a wavelength of 214 nm. In the obtained chromatograms, the relative content of the high molecular weight protein fraction larger than 10 kDa, the average molecular fraction from 3.5 to 5 kDa and from 5 to 10 kDa, as well as free amino acids less than 3.5 kDa were identified.

As the main proteomic technology, two-dimensional electrophoresis (DEF) according to O'Farrell with isoelectric focusing in ampholine (IEF-PAGE) was used. The detection of proteins on two-dimensional electrophoregrams was performed by staining with Coomassie blue R-250 (CBB R-250) and then sequentially with silver nitrate. For computer densitometry, two-dimensional electrophoregrams were used, which were in a wet state. Their complete digital images and / or images of individual fragments were obtained by scanning on an Epson Expression 1680 scanner. Mass spectra ("peptide fingerprints") were decrypted using traditional bioinformation technologies. The analysis of the obtained mass spectra of tryptic peptides was performed using the Mascot program, option Peptide Fingerprint (Matrix Science, USA), with an accuracy of determining the mass of MH + equal to 0.01%.

Organoleptic studies were carried out in accordance with GOST ISO 6658-2016 and GOST ISO 10399-2015.

Results. Curd whey contains a relatively low mass fraction of protein, on average 0.5%. With such a low protein content, the efficiency of proteolysis decreases, so the ultrafiltration method was chosen to concentrate the protein fraction. Using this method, a concentration coefficient of 3.6 was achieved. Thus, the mass fraction of protein ultrafiltrate averaged 3.3%.

At the stage of choosing the hydrolytic enzyme, we evaluated the proteolytic activity declared by the manufacturer against milk proteins. The selected enzyme should hydrolyze the whey protein ultrafiltrate. Enzymes produced by Aspergillus niger and Aspergillus oryzae cultures were selected for the study. These enzymes are proteins characterized as aspergillopepsin, aspartate pepA protease.

When using the enzyme preparation Aspergillus niger, a significant intensification of the process was noted in comparison with the process carried out under the same conditions, but using the enzyme preparation Aspergillus oryzae.

So, when using the first enzyme, with a minimum enzyme-substrate ratio of (0.5), the degree of hydrolysis was 1.2%, and the maximum degree of hydrolysis was observed with an enzyme-substrate ratio of 8.5 and amounted to 8.43%. Whereas, with a minimal activity of the enzyme in the second case, the degree of hydrolysis was 7.03%, and with a maximum of 13.8%.

The duration of the hydrolysis process was varied to determine the conditions for achieving the maximum degree of hydrolysis from 1 to 5 hours. After hydrolysis, the samples were pasteurized at a temperature of 80 ° C with an exposure of 15 minutes to inactivate the enzyme.

When choosing an enzyme preparation, the most important requirement was to obtain a curd whey hydrolyzate with minimal changes in sensory characteristics. To select an enzyme preparation, a mandatory organoleptic assessment was carried out in parallel with other studies. Hydrolysates obtained under various conditions of the hydrolysis process were subjected to organoleptic analysis.

Sensory characteristics studies have shown that when using the enzyme preparation Aspergillus niger, the first signs of damage were noted with an enzyme-substrate position of 3.5 and a degree of hydrolysis of 4.5%. Aspergillus oryzae mountain taste sensation with enzyme activity of 7.5 u / cm^3 and increased hydrolysis. Comparative sensory characteristics evaluation (table 1) allowed us to choose an enzyme preparation. As a control sample, native curd whey was used to evaluate changes in the organoleptic gamut. According to the results, an enzyme preparation produced by Aspergillus oryzae was selected.

Table 1 - Sensory evaluation of the curd whey protein hydrolyzate

Indicator name	Sensory characteristic of native curd whey	Sensory characteristic of curd whey hydrolyzate obtained using enzyme preparation	
		by Aspergillus oryzae	by Aspergillus niger
Appearance and consistency	Homogeneous translucent liquid with insignificant protein precipitate	Homogeneous opaque liquid with suspended protein particles	Homogeneous opaque liquid with suspended protein particles
Colour	Pale green	Pale green with a cream tint	Pale green with a cream tint
Taste	Typical characteristic of curd whey	Typical characteristic of curd whey	Bitter, acid, uncharacterist ic for curd whey
Smell	Sour-milk, whey, characteristic without extraneous tones	Peculiar to curd whey, without extraneous smacks and odors	Uncharacteristic for curd whey, with extraneous tones

When analyzing expert assessments of sensory characteristics, the concordance coefficient was 1, which confirms the unity of opinion of the expert commission.

According to the results of a set of studies, the process of hydrolytic bioconversion is optimized. As a result of process optimization [12], the following conditions were determined: temperature 46.4°C; the duration of the process is 180 minutes; enzyme-substrate ratio of 9.5. These parameters make it possible to achieve a maximum degree of hydrolysis of 13.2%.

The selected process conditions allow targeted biocatalysis of curd whey proteins. As a result, we obtain a hydrolyzate with the desired sensory characteristics.

According to published data, the preparation of hydrolysates with a degree of hydrolysis of 5–20% with a high content of medium-length peptides (3–10 kDa), which can be used in specialized and functional nutrition, is of practical interest [13, 14].

To determine the molecular mass distribution of peptide fractions, they were studied using high performance liquid chromatography and two-dimensional electrophoresis (figure 1).

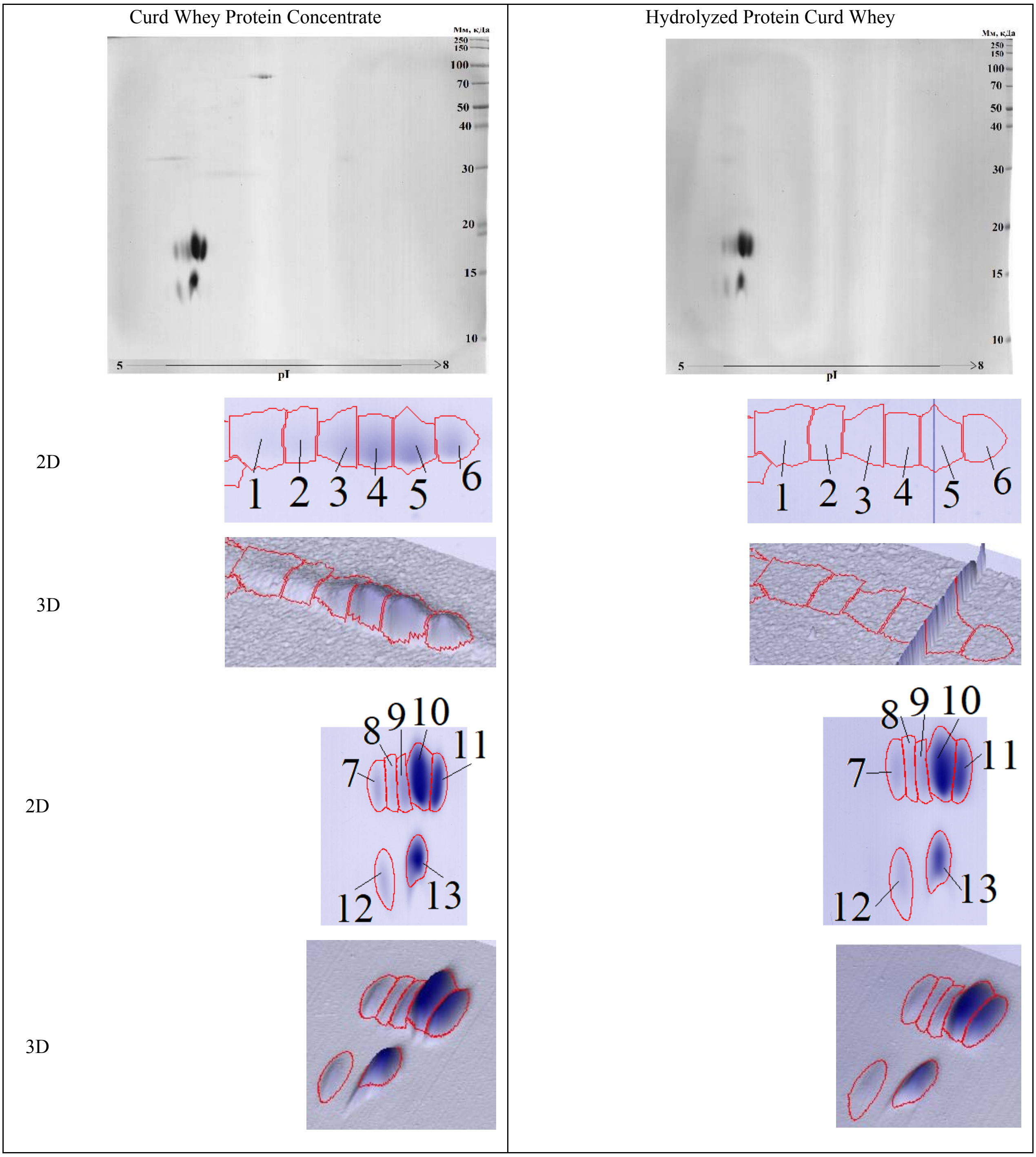

Figure 1 - Electrophoregram of the concentrate and hydrolyzed protein curd whey

Summarizing the obtained experimental results, we concluded that the content of high molecular weight peptide compositions in the obtained hydrolyzed protein of curd whey approximately halved compared to the concentrate (ultrafiltrate). The content of peptides with a molecular weight of 3.5 - 5 kDa increased by almost 10 times. The content of components with a molecular weight of less than 3.5 kDa increased by about 1.5 times. Visualization of the results is presented as a graphical interpretation of the molecular weight distribution of peptide compositions in the concentrate and hydrolyzate of curd whey proteins (figure 2).

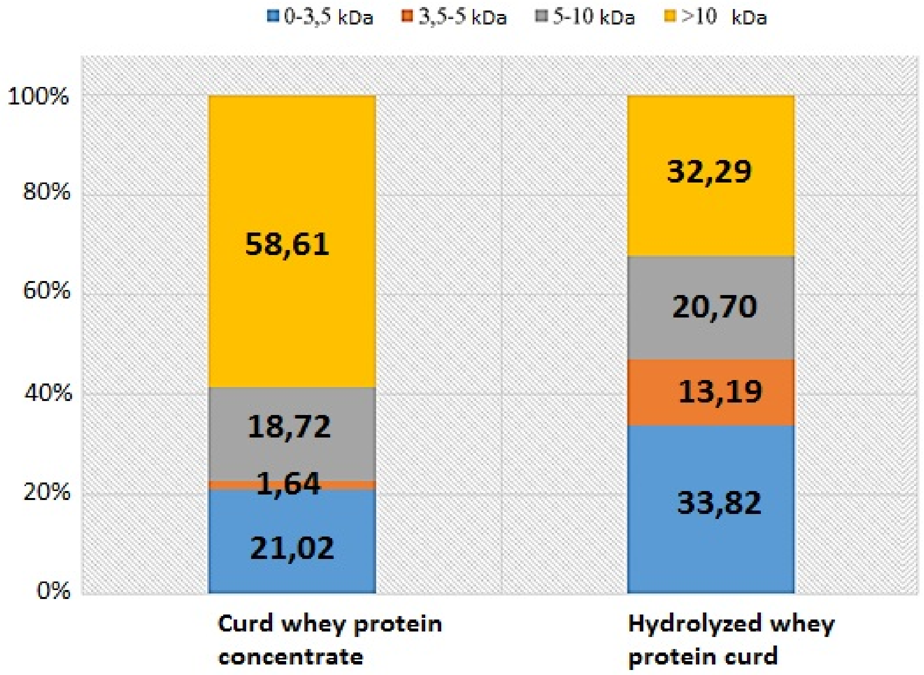

Figure 2 - Molecular mass distribution of peptide compositions
in a concentrate and hydrolyzed protein of curd whey

The obtained results of electrophoretic analysis and molecular mass distribution prove that as a result of targeted biocatalysis using the enzyme preparation Aspergillus oryzae, a degree of hydrolysis is achieved, which provides medium-length peptides with predictable functional properties.

Conclusion. The biocatalysis of curd whey ultrafiltrate was carried out using an enzyme preparation produced by Aspergillus oryzae. As a result of the work, it was proved that the obtained hydrolyzate possesses the necessary sensory characteristics. Namely, it lacks bitterness in taste and aftertaste. Peptides of medium length (3-10 kDa) prevail in the obtained hydrolyzate. This indicates the feasibility of using the hydrolyzate as an enriching agent in the production of specialized nutrition and functional products.

Discussion. Curd whey contains more than 250 compounds with unconditional biological and nutritional value [15]. According to A.G. Khramtsov and I.A. Evdokimov deep processing of whey will solve several problems. Among them are the synthesis of new composites that can be used to enrich other dairy products. Curd whey can be used biologically active or enriching component [16,17].

The use of serum concentrations is not innovative. To date, technologies have been developed for processing whey from cheese. These technologies include various types of concentration. Using concentration and separation, you can get by-products from whey from cheese [18].

Membrane filtration is applied to cheese whey to obtain demineralized whey and its subsequent drying [19].

Ultrafiltration allows you to save most of these substances. According to G. B. Gavrilov and A. G. Khramtsov, the use of membrane separation of serum fractions is the most promising industry [20].

The use of hydrolytic bioconversion is the most sparing method of biotransformation of whey proteins. In addition, targeted limited proteolysis yields medium-sized peptides. They have minimally altered organoleptic characteristics. Therefore, the resulting hydrolyzate has a high potential for use both in the dairy industry and in other food industries.

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ЕКІНШІЛІК ШИКІЗАТ РЕСУРСТАРЫНДАҒЫ БАҒЫТТЫ ПРОТЕОЛИЗ

Аннотация. Тамақ өнеркәсібі үшін екіншілік шикізат ресурстарын қайта өңдеу үлкен қызығушылық тудырады және бүкіл тамақ өнеркәсібі үшін жоғары әлеуетке ие. Сүт сарысуы – бірқатар жоғары ақуызды сүт өнімдерін өндірудің жанама өнімі, мысалы, ірімшік (ірімшік сарысуы) немесе сүзбе (сүзбе сарысуы). Сарысудың құрамы химиялық бай болғанымен, оны сүт өнімдер технологиясында қолдану шектеулі. Ірімшік сарысуы – жоғары қышқылды болғандықтан, шектеулі қолданылуына байланысты өңдеуге арналған күрделі биологиялық жүйе.

Ірімшік сарысуын өңдеудің қолданыстағы тәсілдері (мәйекті ірімшік өндіру кезінде пайда болған қайталама өнім) сүзбе сарысуын өңдеу технологиясында жартылай ғана қолданылады. Атап айтқанда, ақуыз компонентінің шоғырлануы үшін фракциялардың мембраналық бөлінуін және одан кейінгі биокатализді ірімшік сарысуына қолданады және ірімшік сарысын өңдеуге қолдану мүмкіндігі бар.

Кешенді зерттеулер нәтижесінде ультрафильтрацияланған сүзбе сарысуы концентратын биокаталитикалық конверсиялау үрдісі жасалды және оңтайландырылды, нәтижесінде жоғары биологиялық құндылығы мен қанағаттанарлық органолептикалық диапазонына байланысты сүт өнімдеріне байытатын ингредиент ретінде қолдануға жоғары әлеуеті бар гидролизат алынды. Сүзбе сарысуынан ақуыз концентратына қол жеткізілді.

Табиғи емес гидролизденген сарысуды қолдану перспективті деп саналады. Отандық және шетелдік ғалымдардың зерттеулері бойынша орташа ұзындықтағы пептидтер (3-10 кДа) биологиялық құндылыққа ие. Алайда гидролиз кезінде протеолитикалық үрдіс жүреді, ащы аминқышқылдары пайда болатындықтан ащы дәмнің болуы салдарына жатады. Зерттеу мақсаты – аз мөлшерде өзгертілген органолептикалық қасиеттері бар сарысу ақуызының гидролизатын алу.

Үйлесімді органолептикалық сипаттамалары бар сұрыпталған ірімшік сарысуы гидролизатын алу үшін *Aspergillus oryzae* бөліп шығаратын саңырауқұлақ протеазалар тобынан ферментті препарат таңдалды. Гидролиз үрдісі оңтайландырылды және сүзбе сарысуы ақуызының гидролизаты концентратының қажетті қасиеттерінің жиынтығына қол жеткізілетін параметрлер анықталды.

Алынған гидролизаттың органолептикалық сипаттамалары аз өзгеретіні, ащы дәмі әрі дәмсіздігі тәжірибе жүзінде расталды. Молекулалық салмақтың таралуын зерттеу орта ұзындықтағы пептидтердің гидролиз нәтижесінде түзілетінін дәлелдейді.

Гидролитикалық биоконверсияны қолдану сарысуы бар ақуыздарды биотрансформациялаудың ең тиімді әдісі болып саналады. Сонымен қатар, бағытталған шектеулі протеолиз құрамы органолептикалық профилі аз өзгеретін орташа мөлшерлі пептидтерді алуға мүмкіндік береді. Сондықтан оны сүт өнеркәсібінде де, басқа тамақ өнеркәсібінде де қолданудың мүмкіндігі жоғары.

Түйін сөздер: гидролизаттар, сүзбе сарысуы, ферменттер, пептидтер, екіншілік шикізат.

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НАПРАВЛЕННЫЙ ПРОТЕОЛИЗ ВТОРИЧНЫХ СЫРЬЕВЫХ РЕСУРСОВ

Аннотация. Для пищевой промышленности переработка вторичных сырьевых ресурсов представляет большой интерес и обладает высоким потенциалом для всей пищевой отрасли. Молочная сыворотка представляет собой побочный продукт производства ряда высокобелковых молочных продуктов, например, сыра (подсырная сыворотка) или творога (творожная сыворотка). Сыворотка имеет богатый химический состав, однако её применение в технологии молочных продуктов ограничено. Творожная сыворотка является сложной для переработки биологической системой в связи с тем, что обладает высокой кислотностью, и, следовательно, ограниченным применением.

Существующие подходы переработки подсырной сыворотки (вторичного продукта, образующегося при выработке сычужных сыров) лишь отчасти могут быть применены в технологии переработки творожной сыворотки. В частности, применение мембранного разделения фракций для концентрирования белковой составляющей и последующий биокатализ применяются для подсырной сыворотки и имеют потенциал применения для переработки творожной сыворотки.

В результате проведенных комплексных исследований разработан и оптимизирован процесс биокаталитической конверсии ультрафильтрационного концентрата творожной сыворотки, в результате которого получен гидролизат, обладающий высоким потенциалом применения как обогащающего ингредиента для молочных продуктов за счет подтвержденной высокой биологической ценности и удовлетворительной органолептической гаммы. Получен концентрат белков нативной творожной сыворотки.

Перспективно использование не нативной, а гидролизованной сыворотки. Согласно исследованиям отечественных и зарубежных ученых, наибольшую биологическую ценность имеют пептиды средней длины (3-10 кДа). Однако при гидролизе происходит протеолитический процесс, последствием которого является появление горького вкуса вследствие образования горьких аминокислот. Целью исследования являлось получение гидролизата сывороточных белков с минимально измененными органолептическими свойствами.

Для получения гидролизатов творожной сыворотки с гармонизированными органолептическими показателями выбран ферментный препарат из группы грибных протеаз, продуцируемый Aspergillus oryzae. Оптимизирован процесс гидролиза и определены параметры, при которых достигается комбинация требуемых свойств гидролизата концентрата белков творожной сыворотки.

Экспериментально подтверждено, что полученный гидролизат имеет минимально измененные органолептические показатели, не обладает горьким вкусом и послевкусием. Исследование молекулярно-массового распределения доказывает, что в результате гидролиза образуются пептиды средней длины.

Применение гидролитической биоконверсии является наиболее щадящим методом биотрансформации сывороточных белков. Кроме того, направленный ограниченный протеолиз позволяет получить пептиды среднего размера, композиции которых обладают минимально измененным органолептическим профилем. Следовательно, имеет высокий потенциал использования как в молочной отрасли, так и в других пищевых отраслях.

Ключевые слова: гидролизаты, творожная сыворотка, ферменты, пептиды, вторичное сырье.

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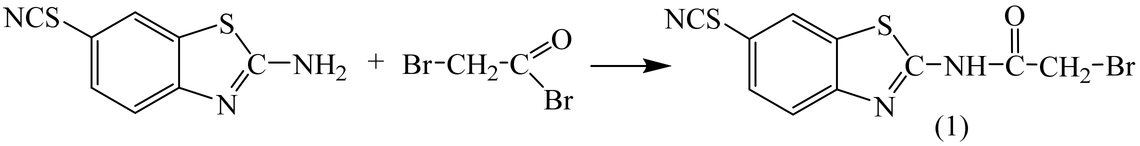
SOME DIRECTIONS IN THE MODIFICATION OF AZOLES

Abstract. This article presents studies on the targeted search for new derivatives of azoles, such as benzthiazole, 3,5-dimethylpyrazole, 1,3,4-oxadiazole-2-thione, 1,3,4-thiadiazole. The possibility of combining in one molecule of the azole ring with other cyclic compounds: the alkaloid cytisine, morpholine, furan and some arenes has been studied. To obtain new compounds, the reactions of bromination, acylation, and interaction with isothiocyanates were studied. Optimal synthesis conditions were studied for all reactions. It was found that the reaction of 4-bromo-3,5-dimethylpyrazole with isothiocyanates, in contrast to the previously written derivatives of anilines, takes a longer time and requires heating the reaction mixture. The combination of a pirasol fragment with halide substituents often results in an enhanced therapeutic effect. The synthesized 2-bromine-N-(6-rodanbenzo[d]thiazole-2-yl)acetamide, due to the alkylbromide group, is an important synth in the synthesis of new benzthiazole derivatives. Its derivatives combine in one molecule the rest of rhodanbenzthiazole with alkaloid cytisine and biogenic amine morpholine and are potentially biologically active compounds, since the molecule structure contains several pharmacophoric fragments: benzthiazole and alkaloid (amine) heterocycles, rhodane and urea groups. The mechanism of formation of 1,3,4-oxadiazole-2-tyons from hydrazides under action on them by carbon disulfide was studied and assumed. It was shown that dithiocarbamates in acidic medium decompose with the release of hydrogen sulfide and the formation of highly reactive isothiocyanate group. Then, intra-molecular cyclization occurs, with the formation of end products - 1,3,4-oxadiazole-2-thions. The structures of the synthesized compounds were studied by ^{1}H and ^{13}C NMR spectroscopy. All synthesized substances are potentially biologically active compounds, since they contain several pharmacophore fragments in their structure.

Key words: azoles, benzothiazole, 3,5-dimethylpyrazole, 1,3,4-oxadiazole-2-thione, heterocyclization.

Condensed nitrogen-containing heterocycles with various heteroatoms are widely used in medical practice as drugs with various therapeutic effects [1-5]. However, practically available benzothiazoles are of limited use due to their incomplete and comprehensive research, including through further chemical modification.

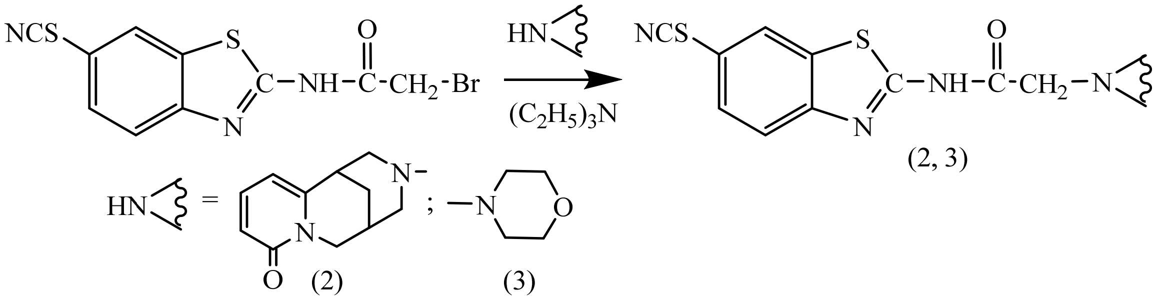
Thus, 2-amino-6-rhodanebenzothiazole is a by-product in the preparation of 4-rhodananiline. In order to use it as a starting reagent for the synthesis of various derivatives, we carried out its acylation with bromoacetic acid bromide. Due to its poor solubility in common organic solvents, acylation was performed in anhydrous DMF.



The resulting 2-bromo-N- (6-rhodanebenzo [d] thiazol-2-yl) acetamide (1) was further used in nucleophilic substitution reactions with the alkaloid cytisine and morpholine [4-8].

The synthesis was carried out by boiling the desired reagents in toluene, in the presence of an acceptor of hydrogen bromide – triethylamine. The obtained compounds (2, 3) are yellowish powdery substances soluble in hot polar solvents.

The composition, structure, and individuality of the synthesized compounds (2, 3) were confirmed using elemental analysis and IR spectroscopy. Physicochemical constants and elemental analysis data are presented in table 1.



In the IR spectra of the synthesized compounds (2, 3) there is an intense absorption band of the amide carbonyl C(O)NH in the region of 1703-1646 cm^{-1}, the NH group in the region of 3400-3200 cm^{-1}, in the region of 2150-2160 cm^{-1} the absorption band of the rhodane group –S–C≡N.

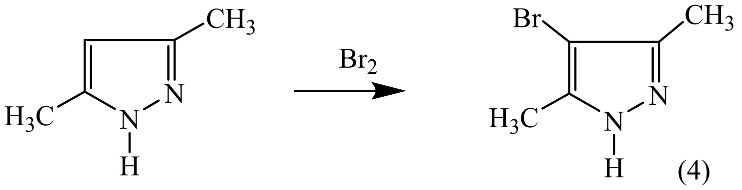
Table 1 – Physicochemical constants and data of elemental analysis of compounds (1-3)

№ of compounds	Yield, %	M.p., °C	Found, %			Molecular formula	Calculated, %		
			C	H	N		C	H	N
1	37.2	204-205	32.36	1.92	11.03	$C_{20}H_{13}Br_3N_6O_2S_4$	32.58	1.78	11.40
2	93.2	193-195	57.42	4.51	15.91	$C_{21}H_{19}N_5O_2S_2$	57.65	4.38	16.03
3	83.8	120-122	50.42	4.01	16.51	$C_{14}H_{14}N_4O_2S_2$	50.28	4.22	16.75

Compound (1), due to the presence of an alkyl bromide group, is an important synthon in the synthesis of new benzothiazole derivatives. Compounds (2, 3) combine in one molecule the rodanebenzthiazole residue with the alkaloid cytisine (2) and with the biogenic amine morpholine (3). Substances (2, 3) are potentially biologically active compounds, since they contain several pharmacophore fragments in the structure of the molecule: benzthiazole and alkaloid (amine) heterocycles, rodane and urea groups [6-9].

Another representative of azoles is pyrazole, whose derivatives have established themselves as the oldest drugs with antipyretic and analgesic properties [10-13]. At the same time, practically no data are available in the literature on the basis of the basic pyrazole moiety of compounds containing thiourea or thioamide groups. The combination of the pyrazole moiety with halogen substituents can lead to an increase in the therapeutic effect.

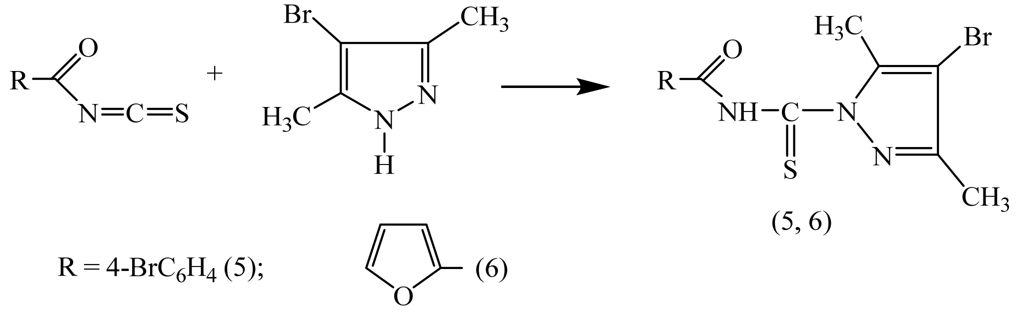
It should also be noted that pyrazole derivatives are practically available compounds. In this regard, we have carried out the synthesis of 4-bromo-3,5-dimethylpyrazole (4) by bromination of the corresponding derivative.



(4)

Further, on the basis of 4-bromo-3,5-dimethylpyrazole (4), we carried out the interaction with 4-bromobenzoyl isothiocyanate and 2-furancarbisothiocyanate.

The synthesis of the starting isothiocyanates was carried out in situ (without isolation) by heating the corresponding acid chlorides (4-bromobenzoyl chloride and 2-furancarboxylic acid chloride) with potassium thiocyanate in acetone for 2 hours. Next, the obtained solutions of isothiocyanates were added to acetone solutions of 4-bromo-3,5-dimethylpyrazole.



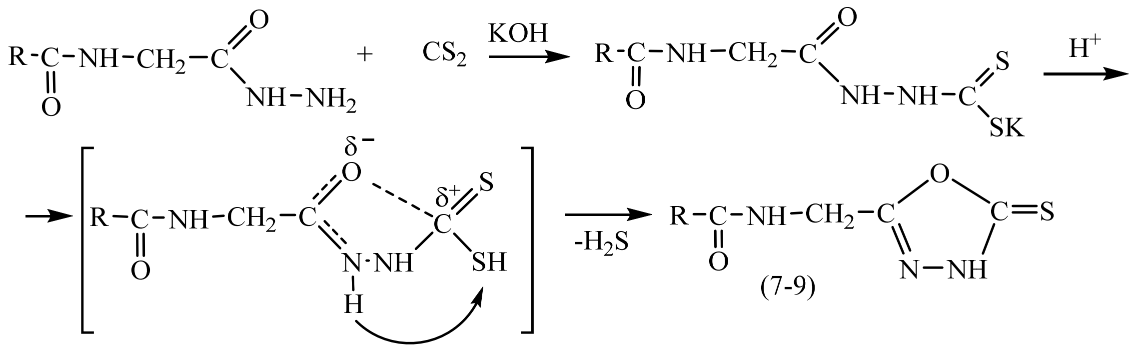
It was found that the reaction of 4-bromo-3,5-dimethylpyrazole with isothiocyanates, in contrast to the above-described aniline derivatives, takes longer and requires heating the reaction mixture to 50°C. In this case, almost all the reaction products are released from the reaction acetone medium in the form of yellow or slightly yellowish acicular crystalline substances.

The composition, structure, and individuality of the synthesized compounds (5, 6) were confirmed by the data of elemental analysis, IR, and PMR spectroscopy. Physicochemical constants and elemental analysis data for thiourea derivatives (5, 6) are presented in Table 2.

Table 1 – Physicochemical constants and data of elemental analysis of compounds (5, 6)

№ of compounds	Yield, %	M.p., °C	Found, %			Molecular formula	Calculated, %		
			C	H	N		C	H	N
5	30	147-150	37,86	3,04	10,55	$C_{13}H_{11}Br_2N_3OS$	37,43	2,66	10,07
6	50	120-122	40,65	3,32	13,21	$C_{11}H_{10}BrN_3O_2S$	40,26	3,07	12,80

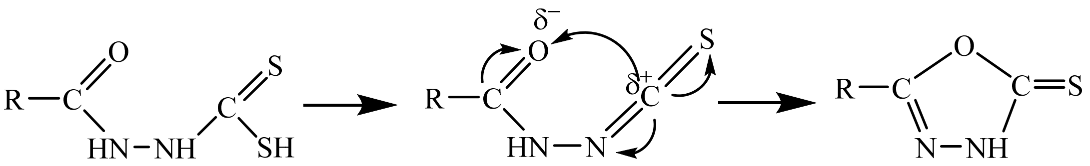
Derivatives of oxadiazole-2-tines are of undoubted interest in the search for new antibacterial drugs, since they contain a number of pharmacophore groups [14-16]. In this regard, in order to search for new anti-tuberculosis drugs and study the structure-activity relationship [17-21], we studied the interaction of acylglycine hydrazides with carbon disulfide in the presence of potassium hydroxide. Further acidification of the resulting potassium salt of dithiocarbamic acid with 0.1 N HCl solution leads to the formation of cyclic products - 1,3,4-oxadiazole-2-thiones. Product yields (7-9) were 70-80%.



R= C_6H_5 (7), *м*-$CH_3C_6H_4$ (8), *o*-BrC_6H_4 (9).

As can be seen from the equation, the cyclization reaction is promoted by the formation of dithiocarbamic acid, which is an unstable compound.

Based on this, we can assume the following mechanism for the formation of 1,3,4-oxadiazole-2-thiones from hydrazides when exposed to carbon disulfide. Dithiocarbamates in an acidic medium decompose with the release of hydrogen sulfide and the formation of a highly reactive isothiocyanate group. Further, intramolecular cyclization occurs due to the attack by the electron-deficient carbon atom of the isothiocyanate group of the nucleophilic center - the carbonyl oxygen atom with a further redistribution of the electron density, with the formation of the final products - 1,3,4-oxadiazole-2-thiones



The synthesized compounds (7-9) are white crystalline substances, readily soluble in polar organic solvents. The resulting 1,3,4-oxadiazole-2-thiones are heterocyclic compounds containing a thion-thiol group capable of tautomeric transformations. IR spectral data indicate that compounds (7-9) in the crystalline state have the structure of thions (thioamides).

In the IR spectra of compounds (7-9), vibrations of the SH-group are absent and characteristic bands appear for stretching vibrations of the thioamide group at 1510-1460 cm^{-1}, there is also a peak of average intensity at 1230-1210 cm^{-1}, referred to C=S - group.

When analyzing the PMR spectrum of compound (7), recorded in D2O, a group of lines at 7.31 ppm. and 7.59 ppm. represents the signals of the protons of the aromatic ring in the form of complex multiplets. Singlet at 4.44 ppm. assigned to the methylene proton CH_2–NH. The physicochemical constants of the synthesized compounds (7-9) are shown in Table 3.

Table 3 – Physicochemical constants and data of elemental analysis of compounds (7-9)

№ of compounds	Yield, %	M.p., °C	R_f*	Found, %			Molecular formula	Calculated, %		
				C	H	N		C	H	N
7	82	175 (decomp.)	0,47	51,17	3,79	17,96	$C_{10}H_9N_3O_2S$	51,06	3,82	17,87
8	78	149-150	0,72	53,11	4,31	16,92	$C_{11}H_{11}N_3O_2S$	53,01	4,41	16,86
9	69	148-149	0,68	51,33	3,33	18,01	$C_{10}H_8N_3O_2SBr$	51,28	3,41	17,94
* Note: eluent – propanol-2 : ammonia : water (7:2:1)										

Thus, based on the review of the literature and experimental data, it can be concluded that azole derivatives have high chemical and physiological activity, their derivatives are low-toxic and are promising in the creation of new drugs with antibacterial, insecticidal, antitumor and other effects.

Experimental part. The IR spectrum was recorded on a Vertex 70V spectrophotometer (Bruker) in KBr pellets. UV spectra were recorded on a Lambda 750 spectrophotometer (PerkinElmer). The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d6 on a JNM-ECA 400 spectrometer of the Jeol company from Japan. The survey was carried out at room temperature using a DMSO-d6 solvent. Chemical shifts are measured relative to the signals of residual protons or carbon atoms of a deuterated solvent.

N-(6-rhodanobenzothiazol-2-yl)-2-(cytisine-1-yl)acetamide (2) To a solution of 1 g (0.003 mol) 2-bromo-N- (6-rhodanebenzo[d]thiazol-2-yl)acetamide in 10 ml of dioxane was poured into 1.12 g of triethylamine and 0.57 g (0.012 mol) of cytisine was added. Heated under reflux for 5 hours. Was filtered hot from the precipitate of triethylamine hydrobromide. The solvent was distilled off. The oily product was triturated and crystallized with hexane. It was recrystallized from a benzene-hexane mixture. Yield 1.24 g (93.2%), mp. 193-195°C.

N-(6-rhodanebenzothiazol-2-yl)-2-morpholinoacetamide (3) Synthesized similarly to compound (2) from 2-bromo-N- (6-rhodanebenzo[d]thiazol-2-yl)acetamide and morpholine. Yield 0.42 g (83.8%), mp. 120-122°C.

N-(4-bromo-3,5-dimethyl-1H-pyrazole-1-carbamothioyl)-4-bromobenzamide (5). To a solution of 1.55 g (0.007 M) of p-bromobenzene chloride in 5 ml of acetone with stirring on a magnetic stirrer was added 0.69 g (0.007 M) of potassium thiocyanate. Stirred at reflux for two hours, then filtered through a paper filter to a solution of 1.23 g (0.007 M) of 4-bromo-3,5-dimethylpyrazole in 10 ml of acetone. Then the mixture was stirred at a temperature of 45-50°C for 2-3 hours. The precipitated crystalline product was filtered off, washed with 2-propanol. The product was recrystallized with a mixture of organic solvents isopropyl alcohol and hexane. Received 0.45 g (30%) of a crystalline substance with mp. 147-150°C.

N-(4-bromo-3,5-dimethyl-1H-pyrazole-1-carbamothioyl) furan-2-carboxyamide (6) was synthesized similarly to compound (2.20), from 1.37 g (0.01 M) acid chloride 2-furancarboxylic acid, 1.10 g (0.011 M) potassium thiocyanate and 1.75 g (0.01 M) 4-bromo-3,5-dimethylpyrazole. Received 1.54 g (50%) of crystalline substance with mp 120-122°C.

5-(Benzoylaminomethylene)-3,4-dihydro-1,3,4-oxadiazole-2-thione (7). To a solution of 1.90 g (0.01 mol) of N-benzoylglycine hydrazide in 20 ml of ethanol was added with constant stirring 0.56 g (0.01 mol) of potassium hydroxide. Then 0.76 g (0.01 mol) of carbon disulfide dissolved in 10 ml of alcohol was added slowly. Stirred at 35-40°C for 1.5 hours. The reaction mixture was cooled to room temperature, acidified with 0.1 N hydrochloric acid solution to pH = 5-6. The precipitate that formed was filtered off. 1.92 g (82%) of a powdery substance was obtained, mp 175-176°C.

5-(*m*-Methylbenzoylaminomethylene)-3,4-dihydro-1,3,4-oxadiazole-2-thione (8) was synthesized similarly to compound (119) from 2.07 g (0.01 mol) of hydrazide N-m- methylbenzoylglycine, 0.56 g (0.01 mol) of potassium hydroxide and 0.76 g (0.01 mol) of carbon disulfide. 1.94 g (78%) of a powdery substance with a melting point of 149-150°C was obtained.

5-(*o*-Bromobenzoylaminomethylene)-3,4-dihydro-1,3,4-oxadiazole-2-thione (9) was synthesized similarly to compound (119) from 2.86 g (0.01 mol) of hydrazide N-o- bromobenzoylglycine, 0.56 g (0.01 mol) potassium hydroxide and 0.76 g (0.01 mol) carbon disulfide. Received 1.27 g (69%) of a powdery substance with a melting point of 140-141°C.

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АЗОЛ МОДИФИКАЦИЯСЫНДАҒЫ КЕЙБІР БАҒЫТТАР

Аннотация. Мақалада бензтиазол, 3,5-диметилпиразол, 1,3,4-оксадиазол-2-тион, 1,3,4-тиадиазол сияқты азолдардың жаңа туындыларын мақсатты іздеу бойынша эксперименттік зерттеу нәтижелері келтірілген. Азолды сақина молекуласының басқа циклдік қосылыстармен, мысалы, цитизин алкалоидымен, морфолин, фуран және де кейбір арендермен араласу мүмкіндігі зерттелген. Жұмыста қолданылған түрлендіруші заттар биологиялық белсенділіктің әртүрінің тасымалдаушысы болып саналады. Бір зат құрылымындағы бірнеше химиялық қосылыстар әрекеті олардың әрқайсысының биологиялық әсерін өзгерте алады. Бұл жұмыста азолдардың жаңа туындыларын алу үшін түрлі бромдау, ацилдеу, 4-бромбензойл изотиоцианатпен және 2-фуранкарбизотиоцианатпен әрекеттесу реакциялары зерттелді. Олардың оңтайлы реакциядағы жүру шарттары анықталды. Бұл жағдайда реакция өнімдерінің барлығы дерлік реакциялық ацетонды еріткіштік ортадан сары немесе сәл сарғыш сары түсті кристалды заттар түрінде бөлініп алынады. 4-Бромо-3,5-диметилпиразолдың изотиоцианаттармен реакциясы, анилиндердің бұрыннан белгілі туындыларынан айырмашылығы, көп уақытты алатындығы және реакция қоспасын қыздыруды қажет ететіндігі анықталды. Пиразол бөлігінің галогенді алмастырғышпен үйлесуі көбінесе олардың бактерияға қарсы терапиялық әсерін жоғарылатады. 4-Бромо-3,5-диметилпиразолдың изотиоцианаттармен реакциясы, жоғарыда сипатталған анилин туындыларынан айырмашылығы, көп уақытты алатындығы және реакция қоспасын ұзақ уақыт қыздыруды қажет ететіндігі анықталды. 2-Амин-6-роданебензотиазолды бром-сірке қышқылы бромидімен ацилдеу әртүрлі ортада жүргізілді. Өнімділік пен тазалық бойынша ең жақсы нәтижелер диметилформамид (ДМФА) еріткіші ортасында алынды. Синтезделген 2-бром-N-(6-роданебензо[д]тиазол-2-ил) ацетамид, алкил бромид тобына байланысты жаңа бензотиазол туындыларын синтездеуде маңызды синтон болып саналады. Оның туындылары бір молекулада роданебензтиазол қалдықтарын өсімдіктен алынатын цитизин алкалоиды мен биогенді амин морфолинмен біріктіреді. Синтезделген жаңа қосылыстар потенциалды биологиялық белсенді заттар болып саналады, өйткені олардың құрамында молекула құрылымында бірнеше маңызды фармакофорлы фрагменттер: бензотиазолды және алкалоидты (амин) гетероциклдер, родан және мочевина топтары бар. Көміртекті дисульфидтің әсерінен гидразидтерден 1,3,4-оксадиазол-2-тиондардың түзілу реакциялары зерттелген және ұсынылған. Алынған эксперименттік мәліметтер негізінде 1,3,4-оксадиазол-2-тиондардың түзілу механизмі ұсынылды. Дитиокарбаматтар қышқылды ортада күкіртсутек бөліп, нәтижесінде жоғары реакциялық қабілеті бар изотиоцианат тобы түзіліп ыдырайтыны көрсетілген. Арықарай молекулааралық циклизация реакциясы жүреді де, соңғы өнімдер пайда болады. Алынған 1,3,4-оксадиазол-2-тиондар таутомерлі түрлендіруге қабілетті маңызды гетероциклді қосылыстар болып саналады. Барлық зерттелген реакцияларға оңтайлы синтез шарттары жасалды. Бұл жұмыста алынған түрлі биофрагментті қосарландырылған азотты гетероциклдарды түрлі терапиялық әсері бар жаңа биологиялық белсенді заттарды іздеуде маңызды синтондар ретінде пайдалануға болады. Синтезделген қосылыстардың құрылымы қазіргі заманғы физикалық-химиялық ИК, ^{1}Н ЯМР және ^{13}С спектроскопия әдістерін қолдана отырып зерттелді. Барлық синтезделген заттар потенциалды биологиялық белсенді қосылыстар болып саналады, өйткені олардың құрылысында бірнеше фармакофорлық фрагменттер бар.

Түйін сөздер: азол, бензтиазол, 3,5-диметилпиразол, 1,3,4-оксадиазол-2-тион, гетероциклизация

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НЕКОТОРЫЕ НАПРАВЛЕНИЯ В МОДИФИКАЦИИ АЗОЛОВ

Аннотация. В данной статье представлены результаты экспериментальных исследований по направленному поиску новых производных азолов, таких как бензтиазол, 3,5-диметилпиразол, 1,3,4-оксадиазол-2-тион, 1,3,4-тиадиазол. Изучена возможность совмещения в одной молекуле азолового цикла с другими циклическими соединениями, такими как алкалоид цитизин, морфолин, фуран и некоторыми аренами. Использованные в работе модифицирующие вещества являются носителями различных видов биологической активности. Одновременное действие нескольких химических соединений может изменить биологическое действие каждого из них. Для получения новых производных азолов исследованы разнообразные реакции бромирования, ацилирования, взаимодействие с 4-бромбензоилизотиоцианатом и 2-фуранкарбизотиоцианатом в различных средах. Определены оптимальные условия проведения реакции. При этом практически все продукты реакции выделяются из реакционной ацетоновой среды в виде желтых или слегка желтоватых игольчатых кристаллических веществ. Установлено, что реакция 4-бром-3,5-диметилпиразола с изотиоцианатами, в отличие от ранее писанных производных анилинов, протекает продолжительнее и требует нагрева реакционной смеси. Комбинация пиразольного фрагмента с галоидными заместителями зачастую приводит к усилению их антибактериального терапевтического эффекта. Установлено, что реакция 4-бром-3,5-диметилпиразола с изотиоцианатами, в отличие от вышеописанных производных анилинов, протекает продолжительнее и требует продолжительного нагрева реакционной смеси. Осуществлено ацилирование 2-амино-6-роданбензотиазол бромангидридом бромуксусной кислоты в различных средах. Показано, что наилучшие результаты по выходу и чистоте продуктов получаются в среде ДМФА. Синтезированный 2-бром-N-(6-роданбензо[d]тиазол-2-ил)ацетамид, благодаря наличию алкилбромидной группы, является важным синтоном в синтезе новых производных бензтиазола. Его производные совмещают в одной молекуле остаток роданбензтиазола с растительным алкалоидом цитизин и с биогенным амином морфолином. Синтезированные новые соединения являются потенциально биологически активными веществами, так как содержат в структуре молекулы несколько фармакофорных фрагментов: бензтиазоловый и алкалоидный (аминный) гетероциклы, родано- и карбамидную группы. Изучен и предположен механизм образования 1,3,4-оксадиазол-2-тионов из гидразидов при действии на них сероуглеродом. На основании полученных экспериментальных данных предложен механизм образования 1,3,4-оксадиазол-2-тионов. Показано, что дитиокарбаматы в кислой среде распадаются с выделением сероводорода и образованием высокореакционной изотиоцианатной группы в их составе. Далее в реакционной среде происходит внутримолекулярная циклизация, с образованием конечных продуктов. Полученные 1,3,4-оксадиазол-2-тионы относятся к важным гетероциклическим соединениям, способным к таутомерным превращениям. Для всех изученных реакций установлены оптимальные условия синтеза. Все полученные в работе конденсированные азотсодержащие гетероциклы с различными биофрагментами могут быть использованы в качестве исходных синтонов в поиске новых биологически активных веществ с разнообразным терапевтическим эффектом. Структуры синтезированных соединений изучены с применением современных физико-химических методов ИК, ЯМР ^{1}Н и ^{13}С-спектроскопии. Все синтезированные вещества являются потенциально биологически активными соединениями, так как содержат в своей структуре по несколько фармакофорных фрагментов.

Ключевые слова: азолы, бензтиазол, 3,5-диметилпиразол, 1,3,4-оксадиазол-2-тион, гетероциклизация.

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BINDING d-ELEMENT OF THE 4TH PERIOD OF V-GROUP OF THE PERIODIC SYSTEM OF D.I. MENDELEYEV AND ITS PARAMAGNETIC PROPERTIES

Abstract. Vanadium is a connecting element between the main subgroup VA and the subgroup VB. In the opinion of B.V. Nekrasov, if we compare the VB group of vanadium elements with the valence states of P and As VA main subgroup, then in the oxidation states of -3, 0, +3 arsenic is an analogue of phosphorus, and in the oxidation state +5, it will not be an analogue of phosphorus. In contrast, in the low oxidation degrees of vanadium, it differs from phosphorus, and in the oxidation state of +5 vanadium is not a complete analogue of phosphorus.

The similarity of the electronic configuration of atoms for vanadium and phosphorus in the +5 oxidation state specifies the similarity of the properties of their chemical compounds.

When comparing vanadium and its compounds with elements of the VA subgroup, we conclude that vanadium is a binding element between the VA subgroup and the VB subgroup and the compounds have similar properties.

As a result of many years of work, it was found that vanadium in the penta- and tetravalent states has paramagnetic properties. In crude oil, it is in a tetravalent state.

In order to improve the standard photocalorimetric method for determining vanadium in oil and petroleum ashes, a more rapid method was proposed for estimating the total concentration of vanadium based on the interaction of V_2O_5 with concentrated hydrochloric acid.

Studies of the EPR spectra of porphyrin complexes with transition metals such as copper were of great importance in the identification of natural porphyrin complexes.

In the course of comparison of experimental works of paramagnetic properties of vanadium and phosphorus with each other, it can be said that their application is of great practical importance in different fields of science.

Summing up the results of studying the reduction of triphenylphosphine with an alkali metal, we proposed a scheme for the splitting of triphenylphosphine, including the formation of radical anions.

Keywords: binding d-element, vanadium, incomplete analogue, electronic structure, paramagnetism.

Vanadium is a connecting element between the main subgroup VA and the subgroup VB. It is the first d-element of the VB subgroup, its analogues are niobium and tantalum. Their electronic structure and valence states are equal. The VB element group resembles the IVB group of elements. In normal conditions, vanadium in the cold dissolves in “aqua regia” and when heated in nitric and concentrated sulfuric acids. Upon fusion with alkalis, anionic oxo complexes are formed. The oxidation degree of niobium and tantalum in the form of a halide is +4 [1-3]. Vanadium in the form of vanadyl - VO^{2+} ion enters into many chemical reactions and is found in complex compounds [4].

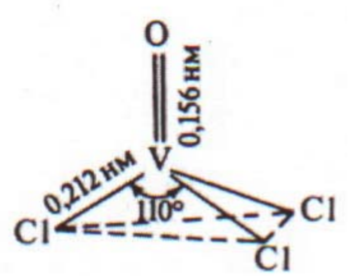
In the opinion of B.V. Nekrasov [5], if we compare the VB group of vanadium elements with the valence states of P and As VA main subgroup, then in the oxidation states of -3, 0, +3 arsenic is an analogue of phosphorus, and in the oxidation state +5, it will not be an analogue of phosphorus. In contrast, in the low oxidation degrees of vanadium, it differs from phosphorus, and in the oxidation state of +5 vanadium is not a complete analogue of phosphorus (Table 1).

The 3d orbital of the phosphorus atom makes phosphorus chemistry deeply different from the nitrogen properties. The similarity of the electronic configuration of atoms for vanadium and phosphorus in the +5 oxidation state specifies the similarity of the properties of their chemical compounds.

Table 1 - Comparison of the valence states of vanadium, phosphorus, and arsenic

Valence	Electron arrangement by energy levels in atoms of elements		
	V (VB)	P (VA)	As (VA)
-3	-	2,8,**8**	2,8,18,**8**
0	2,8,11,**2**	2,8,**5**	2,8,18,**5**
+3	2,8,**10**	2,8,2	2,8,18,**2**
+5	2,8,**8**	2,**8**	2,8,**18**

Vanadium (V) oxychloride - a liquid (mp. -77^{0}C, bp. 127^{0}C). $VOCl_3$ has the form of a distorted tetrahedron with a vanadium atom in the center [2].



Vanadium (V) halogenide reacts with the main halogenide to form an anionic complex:

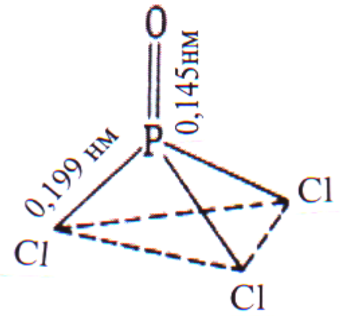
$$KF + VF_5 = K[VF_6]$$

Phosphorus oxotrichloride (V) - a liquid (mp 1°C, bp 107 °C) formed by heating the mixture of P_2O_5 and PCl_5 :

$$P_2O_5 + 3PCl_5 = 5POCl_3$$

$POCl_3$ has the form of the distorted tetrahedron [2] (see Fig.). In non-aqueous solutions, PF_5 interacts with basic fluoride:

$$PF_5 + KF = K\,[PF_6]$$



The coordination number in the vanadium (V) and phosphorus (V) complex compounds is 6. For the compounds under consideration, in which these elements are in the valence state 5, the chemical properties are similar.

When comparing vanadium and its compounds with elements of the VA subgroup, we conclude that vanadium is a binding element between the VA subgroup and the VB subgroup and the compounds have similar properties.

It is known that vanadium (V) oxide in an acidic environment exhibits oxidizing properties:

$$V_2O_5 + 6HCl = 2VOCl_2 + Cl_2 + 3H_2O$$

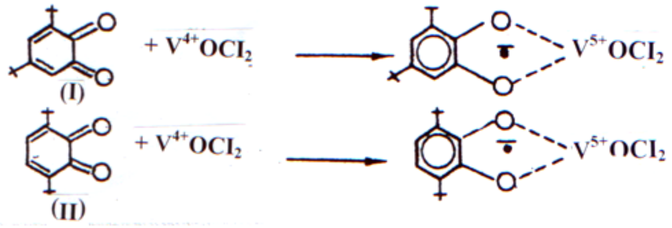
At present, in many research laboratories, the methods of neutron activation analysis (NAA) and X-ray fluorescence analysis (XRF) are used to determine vanadium and other trace elements in oils and petroleum products. The use of neutron activation analysis for these purposes is associated with several known technological difficulties. The main drawback of X-ray fluorescence analysis is the superimposition of the titanium spectral line on the vanadium spectral line in the X-ray fluorescence spectra.

Due to the existing shortcomings of these methods in the geological calculation of vanadium reserves and mass laboratory analyzes, GOST 10364-63 is used to determine the content of vanadium in oils and petroleum products, the essence of which is the photometry of the phosphoric-tungsten-vanadium complex formed after cineration of the test sample of the oil and petroleum product as well as after the processing of the ash by hydrochloric and phosphoric acids and sodium tungstate. However, the photocolorimetric method does not always have the necessary sensitivity and selectivity. Also, one analysis takes a lot of time, and analytically requires many operations.

To improve the common photocolorimetric method for determining vanadium in petroleum ashes, a more rapid method is proposed for estimating the total amount of vanadium in petroleum ashes based on the interaction of V_2O_5 with concentrated hydrochloric acid. The vanadium concentration in the studied petroleum ashes of the Caspian Sea region was determined by the anisotropic electron paramagnetic resonance (EPR) spectrum of the resulting vanadyl chloride [6]. The advantages of the EPR method for determining total vanadium in petroleum ash are its performance, selectivity, high accuracy, and reliability compared to traditionally used photocolorimetric methods.

In this work, we propose the EPR method for estimating the total vanadium concentration in petroleum ashes based on the ability of vanadium d-elements to form stable paramagnetic complexes with sterically hindered quinones [7]. This was facilitated by the forming complexes of o-semiquinones with metal chlorides of group III [8].

In this regard, we attempted to study the interaction of vanadyl chloride with 3,5-di-tert-butylorthobenzoquinone and 3,6-di-tert-butyl-orthobenzoquinone in toluene. This type of redox process reduces to the oxidation of V^{4+} to V^{5+} with the formation of a vanadium-containing complex with a paramagnetic o-benzosemiquinone ligand [7]:



where —+ = $C(CH_3)_3$

The analysis of the vanadium content in oil and petroleum products plays a significant role in oil refining and identifying promising deposits for the extraction of valuable metal.

In the natural porphyrin complexes identification, studies of the EPR spectra of porphyrin complexes with transition metals such as copper were of great importance [9]. If we compare the EPR spectrum of the VO – EP complex (figure 1a) and the Cu^{2+}– EP obtained from it, we receive very interesting data.

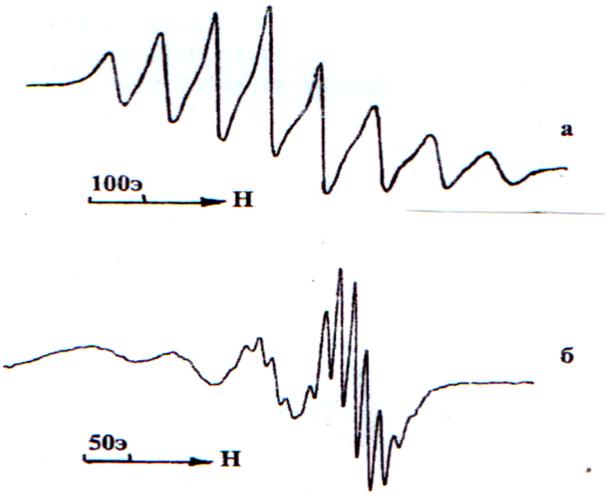


Figure 1 - EPR spectrum of the VO - EP (a) complex from the Karazhanbas oil and obtained Cu^{2+} - EP (b)

Cu^{2+}– EP has a square - planar structure in which a copper ion lies in the plane of four equivalent nitrogen atoms of the porphyrin ligand (Fig. 1b). The isotropic spectrum of this complex, recorded in solution, consists of four hyperfine structure (HFS) lines due to the interaction of an unpaired copper electron with a $^{63.65}Cu$ nucleus; HFS constant is a_{Cu} =102.5 Gs with $g_{изо}$ =2.101.

An additional hyperfine structure is observed near the band in a strong field due to the interaction of an unpaired electron with ligand nitrogen nuclei. The line intensity of the additional HFS is expressed by the ratio 1:4:10:16:19:16:10:4:1. Nine lines of the hyperfine structure with splitting between the lines a_N = 12.5 Gs are due to the interaction of the unpaired electron with the magnetic moments of four united nitrogen atoms (I_N=1) of the porphyrin macrocycle. Thus, the homologues of all VOP VO^{2+} extracted from oils coordinate with the four nitrogen atoms of the pyrrole nuclei.

Summing up the study of the recovery of triphenylphosphine with an alkali metal, Brit and Kaiser [10] proposed a triphenylphosphine splitting scheme that does not include the formation of an anion radical (AR).

When reducing triphenylphosphine with alkali metals (K and Na) in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) at -70 °C with EPR method, we found almost the same EPR spectrum [11] as Ilyasov [12] during electrochemical recovery. In DME, the spectrum is described by the following hyperfine structure constants:

$$a_p = a_н^{para} = 2.5\ гс,\ a_н^{ortho} = 1.25\ Gs$$

The analysis of the spectrum hyperfine structure shows that an unpaired electron is regularly delocalized throughout the molecule. Figure 2 shows the quantum numbers under the spectrum corresponding to the projections of the resultant spin of 3 pairs of protons (I_H=1/2) and one phosphorus nucleus (I_P=1/2). As follows from the experimental data, the triphenylphosphine reaction network in the interaction with alkali metals should include the stage of single electron transfer from the metal and the formation of the primary triphenylphosphine anion radical

$$Ph_3P \xrightarrow{M} Ph_3P^{\overline{\cdot}}M^+$$

triphenylphosphine
anion radical

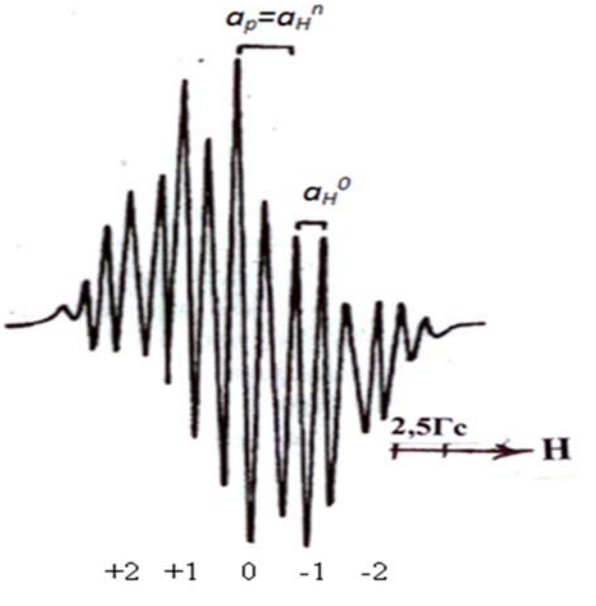


Figure 2 - EPR spectrum of triphenylphosphine-potassium anion radical in DME at -60°C

Therefore, during the organic elements chemistry course [13–15] for students of chemical specialties in universities, it should be noted that upon the preparation of organic alkali metal derivatives from triphenylphosphine, the very first-stage triphenylphosphine anion radical is formed.

In recent years, the intensive development of the homolytic chemistry of phosphorus has aroused interest in the phosphorus centric and, in particular, phosphonyl radicals [16,17].

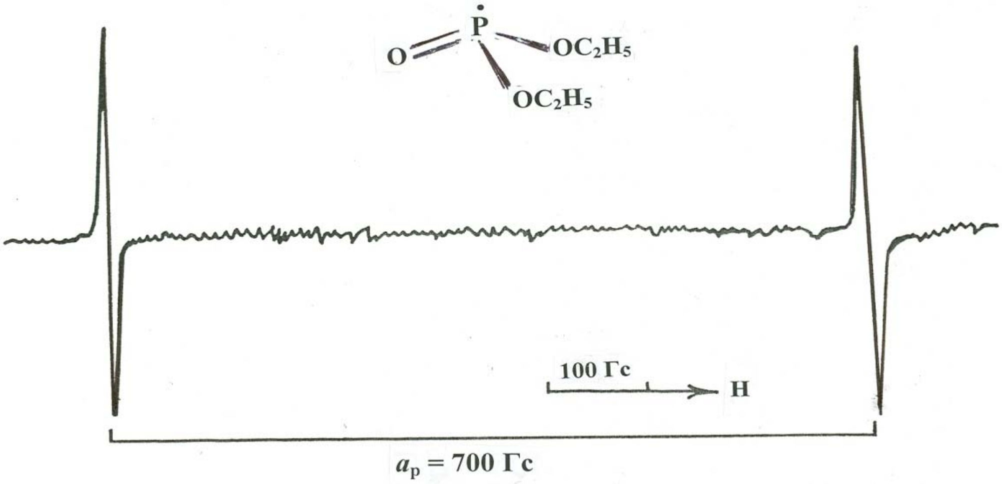


Figure 3 - EPR spectrum of phosphonyl radicals

Phosphonyl radicals (figure 3) are easily formed during the photolysis of the corresponding hydrophosphoryl compounds into di-tert-butyl peroxides.

$$(C_2H_5)_2POH + \bullet OCMe_3 \longrightarrow (C_2H_5)_2\dot{P}{=}O + Me_3COH$$

In this case, the unpaired electron is delocalized mainly in the phosphorus atom. The same spin as the proton, i.e., ½, is possessed by ^{31}P nuclei that are part of various phosphonyl compounds. The hyperfine interaction of the unpaired electron with this magnetic core in radicals leads to doublet splitting in the EPR spectrum as in the case with a proton.

Experimental part. The triphenylphosphine anion radical was received in DME by the common method on metal mirrors of K and Na at -70^{0}C in a vacuum. The EPR spectrum was recorded with a Varian E-12 spectrometer.

Using the methods of demetallization and chromatographic separation, etioporphyrin was obtained from vanadyl porphyrin concentrates of the Karazhanbass oil. Bivalent copper complexes were prepared by reacting of the anhydrous salt $CuCl_2$ with etioporphyrin in dry chloroform at room temperature.

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Д.И. МЕНДЕЛЕЕВТІҢ ПЕРИОДТЫҚ ЖҮЙЕСІНІҢ 4-ПЕРИОДЫ V ТОБЫНЫҢ БАЙЛАНЫСТЫРУШЫ D-ЭЛЕМЕНТІ ЖӘНЕ ОНЫҢ ПАРАМАГНИТТІК ҚАСИЕТТЕРІ

Аннотация. Ванадий VA негізгі тобы мен VB кіші тобы арасындағы байланыстырушы элемент ретінде әрекет етеді.

Б.В. Некрасовтың ұсынысына сәйкес, егер ванадий элементі VB тобын негізгі топтың P және As VA валентті күйімен салыстырсақ, онда тотығу дәрежесінде -3, 0, +3 күшала фосфордың аналогы болып саналады, ал тотығу дәрежесі +5 болса, күшала фосфордың аналогы болмайды. Керісінше, ванадий тотығуының төменгі дәрежесінде фосфордан ерекшеленеді, ал тотығу дәрежесі + 5 ванадий фосфордың толық емес аналогы болып есептеледі.

Ванадий мен фосфор атомдарының электрондық конфигурациясының тотығу дәрежесі +5 болуы олардың химиялық қосылыстары ұқсастық қасиеттерін тудырады.

Ванадий мен оның қосылыстарын VA негізгі топ элементтерімен салыстыру барысында біз ванадий – VA кіші топшасы мен VB негізгі топшасы арасындағы байланыстырушы элемент, ал қосылыстары ұқсас қасиеттерге ие деген қорытындыға келдік.

Көпжылдық жұмыстың нәтижесінде ванадий бес және төрт валентті күйінде парамагнетизм қасиетінің бар екендігі анықталды. Шикі мұнайда ол төрт валентті күйде болады.

Мұнай және мұнай өнімдері күлдеріндегі ванадийді анықтаудың стандартты фотокалориметрлік әдісін жетілдіру мақсатында жұмыста ванадийдің жалпы мөлшерін бағалау үшін ванадийдің бес валентті оксидін (V_2O_5) концентрлі тұз қышқылымен өзара әрекеттестіруге негізделген неғұрлым жылдам анықтау әдістемесі ұсынылған.

Табиғи текті порфирин кешендерін сәйкестендіруде мыс сияқты өтпелі металдармен порфирин кешендерінің ЭПР спектрлерін зерттеу үлкен маңызға ие болды.

Ванадий мен фосфордың парамагнитті қасиеттерін бір-бірімен салыстыра отырып, оларды ғылымның түрлі салаларында қолдану зор практикалық маңызға ие деп айтуға болады.

Трифенилфосфиннің сілтілі металмен тотықсыздануын зерттеу нәтижесінде анион радикалдар түзетін трифенилфосфиннің ыдырау схемасын ұсындық.

Түйін сөздер: байланыстырушы d-элемент, ванадий, толық емес аналогы, электрондық құрылысы, парамагнетизм.

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СВЯЗУЮЩИЙ d-ЭЛЕМЕНТ 4-го ПЕРИОДА V- ГРУППЫ ПЕРИОДИЧЕСКОЙ СИСТЕМЫ Д.И.МЕНДЕЛЕЕВА И ЕГО ПАРАМАГНИТНЫЕ СВОЙСТВА

Аннотация. Ванадий выступает как бы связующим элементом между главной подгруппой VA и подгруппой VB.

Согласно представлениям Б.В.Некрасова, если сопоставить VB группу элементов ванадия с валентными состояниями P и As VA главной подгруппы, то в степенях окисления -3, 0, +3 мышьяк является *аналогом* фосфора, а в степени окисления +5 мышьяк не будет аналогом фосфора. Напротив, в низких степенях окисления ванадий отличается от фосфора, а в степени окисления +5 ванадий является *не полным аналогом* фосфора.

Аналогичность электронной конфигурации атомов для ванадия и фосфора в степени окисления +5 обусловливает сходства свойств их химических соединений.

В ходе сравнения ванадия и его соединений с элементами VA подгруппы мы пришли к выводу, что ванадий- связующий элемент между подгруппой VA и подгруппой VB, а соединения обладают аналогичными свойствами.

В результате многолетней работы было установлено, что ванадий в пяти и четырехвалентном состоянии обладает парамагнетизмом. В сырой нефти он находится в четырехвалентном состоянии.

С целью усовершенствования стандартного фотокалориметрического метода определения ванадия в золах нефтей и нефтепродуктах в работе предложена более экспрессная методика для оценки общего количества ванадия, основанная на взаимодействии V_2O_5 с концентрированной соляной кислотой.

В идентификации порфириновых комплексов природного происхождения большое значение имели исследования спектров ЭПР комплексов порфиринов с такими переходными металлами, как медь.

В ходе сравнения экспериментальных работ парамагнитных свойств ванадия и фосфора друг с другом, можно сказать, что их применение имеет большое практическое значение в разных областях науки.

Подводя итоги изучения восстановления трифенилфосфина щелочным металлом, мы предложили схему расщепления трифенилфосфина, включающую образование анион радикалов.

Ключевые слова: связующий d-элемент, ванадий, неполный аналог, электронная структура, парамагнетизм.

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HYDROTREATING AND HYDROISOMERIZATION OF OIL FRACTIONS ON MODIFIED ALUMINUM-COBALT-MOLYBDENUM CATALYSTS

Abstract. In this work we are given results and research of hydro refining of gasoline and diesel oil fractions on alumina catalysts $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5$- AAC-ZSM -Al_2O_3. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolites ZSM-5, HY with aqueous solutions of salts Co, Mo, La and phosphoric acid. Large-scale laboratory tests of the synthesized catalysts were carried out in the process of hydro processing of various types of gasoline and diesel fractions.

At hydro treating of straight-run gasoline over $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ shows that in the temperature range 320 - 350°C the maximum amount of isoalkanes is formed 33.4-40.4%. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). The sulfur content of catalysate with increasing temperature up to 400°C decreased to 0.0012 %.

At hydro processing of catalytic cracking gasoline on $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ the octane number of refined gasoline is slightly reduced. The sulfur content of catalysate with increasing temperature up to 400°C decreased from initial with from 0.0134 to 0 0014 %.

It was found that the lowest pour point and cloud point of hydro-refined diesel fuel is observed on the catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$. After hydro treating on this catalyst the pour point and cloud point are equal to minus 52.7°C and minus 40.8°C accordingly. This same catalyst has the highest hydro desulfurization activity: the sulfur content decreases from 0.5600% to 0.104%.

Thus, the developed modified zeolite-containing catalysts $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3$, exhibiting high activity at hydro treating of gasoline and diesel fractions and is able in one stage deep hydro treating, hydro isomerization and hydrocracking which allows to obtain low-sulfur, high-octane gasoline and low-sulfur and low solidifying diesel fuel which is important for operation of vehicles in winter conditions.

Key words: straight-run gasoline, diesel fraction of oil, zeolite, catalyst, hydro treating.

Introduction. Recently, due to the necessity of deep processing heavy sour crude oil significantly increased requirements for the process of hydrotreating petroleum oil fractions. The efficiency of hydrotreating processes is mainly determined by the properties of the catalysts used. To carry out deep hydrotreating of petroleum fractions, it is necessary to use new efficient catalysts and technologies. According to international standards, a significant limitation of the content of sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is required. At present, environmental requirements for the quality of motor fuels are being tightened, which requires their deep hydrotreating and refining. In many countries, catalysts are being searched to increase the depth of removal of sulfur-containing compounds and the technology for the production of motor fuels is being improved. Existing catalysts for the hydroprocessing of petroleum fractions in Kazakhstan and the CIS countries do not always meet the increased requirements for the quality of motor fuels. To improve the quality of motor fuels, to reduce the cost of their production, an urgent and priority task is the creation of highly effective polyfunctional catalysts for processing petroleum fractions. In this case great importance is the development of catalysts for hydrotreatment of a certain type of oil [1-20].

This paper presents results and research hydrorefining gasoline and diesel oil fractions on new aluminum-cobolt-molybdenum catalysts, modified with additives of zeolite ZSM-5 and HY, lanthanum and phosphorus.

Experimental part. Enlarged batches of catalysts CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3, CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3, CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 were prepared. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolites ZSM-5, HY, with aqueous solutions of cobalt, molybdenum, lanthanum, and phosphoric acid salts. Then granulation and shaping were carried out. Thereafter, the catalysts pellets were dried at 150°C and calcined at 550°C. Enlarged laboratory tests of the synthesized catalysts were carried out in the process of hydroprocessing of various types of gasoline and diesel fractions. Tests performed in high-pressure flow installation with a stationary catalyst layer at 320-400°C, pressure 2.5 - 4.0 MPa and the space velocity 1.0 - 3.0 h^{-1}.

The hydrocarbon composition of the reaction products was analyzed on chromatographs «Chromatek-Crystal». The analysis of the sulfur content was carried out in «Oilsert International» LLP (Almaty) and the laboratory of physicochemical methods of ITKE. The determination of the pour point and cloud point was carried out on a «LAZ M2» device.

The physicochemical characteristics of the synthesized catalysts were investigated by electron microscopy «EM-125K» transmission electron microscope using microdiffraction [21]. To determine the number of acid sites, the method of temperature-programmed desorption of ammonia was used [22].

Results and its discussion. During the hydroprocessing of straight-run gasoline on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 in the temperature range 320-350°C (table 1) the maximum amount of isoalkanes is formed 33.4-40.4%. At higher temperatures the yield of isoalkanes is reduced to 32.2% at 400°C. The content of aromatic hydrocarbons in the catalyzate under these conditions increases from 14.9 to 20.1 %. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). The sulfur content of catalysate with increasing temperature up to 400°C decreased to 0.0012 %.

Table 1 - Influence of temperature on the hydroprocessing of straight-run gasoline
on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 at V = 2 h^{-1}, P = 4.0 MPa

Products , %	T, °C				
	Initial	320	350	380	400
Paraffins C_5-C_6	27.3	14.5	7.1	4,3	14.7
Iso-alkanes	36.8	39.3	40.4	33.4	32.2
Olefins	4.8	6.8	7.0	7.4	4.0
Aromatic hydrocarbons	9.2	14.9	17.8	23.1	20.1
Naphthenic hydrocarbons	21.9	24.5	27.7	31.8	23.0
Yield of the liquid phase		77.0	49.0	44.5	55.0
Octane number (RON)	78.9	81.4	84.9	88.3	89.3
Octane number (MON)	60.9	66.3	69.4	69.2	73.4
Weight fraction of sulfur, %	0.0092	0.0072	0.0062	0.0056	0.0012

The influence of pressure on the process of hydro-processing of straight-run gasoline on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 was studied. It can be seen that the yield of the liquid phase with an increase in pressure from 2.5 to 4.0 MPa decreases from 95.0 to 55.0% (table 2). The content of isoalkanes changes little with increasing pressure and ranges from 30.8 to 36.2%. The amount of aromatic hydrocarbons increases from 14.3 to 20.1%, the yield of olefins slightly increases in comparison with the original from 4.8 to 6.3%. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). With increasing pressure the sulfur content decreased in comparison with the initial from 0.0092 to 0.0012 %.

Table 2 - Effect of pressure on the process of hydrorefining
of straight-run gasoline over a catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ at 400^{o}C and 2 h $^{-1}$

Products , %	P, MPa				
	Initial	2,5	3.0	3,5	4.0
Paraffins C_5 -C_6	27.3	22.1	20.1	20.8	16.7
Iso-alkanes	36.8	34.4	36.1	30.8	36.2
Olefins	4.8	6.2	4.6	6.3	4.0
Aromatic hydrocarbons	9.2	14.3	13.2	15.9	20.1
Naphthenic hydrocarbons	21.9	20.8	25.9	26.1	23.0
Yield of the liquid phase		95.0	91.7	88.0	55.0
Octane number (RON)	78.9	81.4	81.4	82.7	89.3
Octane number (MON)	60.9	64.5	63.2	63.5	73.4
Weight fraction of sulfur, %	0.0092	0.0025	0.0020	0.0013	0.0012

The hydroprocessing of catalytic cracking gasoline on the catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ has been investigated. Yield of the liquid phase as the temperature increases from 320 to 400 ^{o}C decreases from 95.0 to 90.0%. In the temperature range 320 - 400 ^{o}C maximal content of isoalkanes observed at 320 ^{o}C and is equal to 44.5 %. The amount of isoalkanes in the range of 350 - 400 ^{o}C ranges from 37.2 to 42.7%. The amount of aromatic hydrocarbons is increased from 28.7 to 37.4% with increasing process temperature to 400 ^{o}C. Yield olefins falls significantly compared to initial (31.2%), decreasing from 13.3 to 3.9% with increasing temperature from 320 to 400 ^{o}C. The amount of naphthenic hydrocarbons in the resulting catalysis ranges from 6.9-8.3%. The octane number of refined gasoline changes in comparison with the original from 88.7 to 85.8 (RON) and from 80.1 to 79.5 (MON). The sulfur content with increasing temperature up to 400 ^{o}C decreased from initial from 0.0134 to 0 0014 %.

The effect of pressure on the process of hydroprocessing of catalytic cracking gasoline on the catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ was studied (table 3). When the pressure is varied from 2.5 to 4.0 MPa, the amount of isoalkanes in the resulting product is 38.9-41.3%. The concentration of naphthenic hydrocarbons decreases with increasing pressure in the range of 2.5-4.0 MPa from 10.3% to 8.0%. The amount of aromatic hydrocarbons is 35.8-37.4%. The yield of the liquid phase ranges from 90.0-97.0%. The octane number of gasoline refined at 4.0 MPa is 85.8 (RON) and 79.5 (MON). The sulfur content in the final product is reduced from 0.0134% (initial gasoline) to 0.0014% at 4.0MPa.

Table 3 - Influence of pressure on the process of hydroprocessing of catalytic cracking gasoline
on the catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$

Products , %	P, MPa				
	Initial	2,5	3.0	3,5	4.0
Paraffins C_5 -C_6	6.3	8.9	9.3	10.1	9,4
Iso-alkanes	25,4	40.9	38.9	39.5	41.3
Olefins	31.2	4.0	4.2	4.9	3.9
Aromatic hydrocarbons	30.1	35.8	37.1	36.6	37.4
Naphthenic hydrocarbons	7.0	10.3	10,4	9.0	8.0
Yield of the liquid phase		97.0	95.5	93.0	90.0
Octane number (RON)	88.7	85.6	86.0	84.8	85.8
Octane number (MON)	80.1	78.9	79.7	78.9	79.5
Weight fraction of sulfur, %	0.0134	0.0019	0.0018	0.0015	0.0014

In hydroprocessing of catalytic cracking gasoline using catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ when changing the feed space velocity of from 1.0 to 3.0 h $^{-1}$ the content of isoalkanes changes little - 41.3 - 41.5%, the concentration of aromatic hydrocarbons is 36.1 - 38.2%, the yield of naphthenic hydrocarbons ranges from 7.2 to 8.9%. The yield of olefinic hydrocarbons is significantly reduced compared to the original (31.2%) and at a feed space velocity of 3.0 h^{-1} is 3.0%. The octane number of the resulting gasoline is 85.0-85.8 (RON) and 79.0 -79.5 (MON). Gasoline with the lowest sulfur content – 0.0006% was obtained at a feed rate of 1.0 h^{-1}.

In testing the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 in the process of hydrorefining of diesel oil found that with increasing temperature from 320 to 400 ^{o}C pour point and cloud point of the diesel fraction is reduced by 36.7 and 37.1^{o}C, respectively. The yield of diesel fuel is 92.0-100%. The sulfur content after the hydrorefining of diesel fraction at 380- 400^{o}C decreases from 0.560 to 0.104% (table 4).

Table 4 - Influence of temperature on the hydroprocessing of the diesel fraction
on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 at V = 2 h^{-1}, P = 4.0 MPa

Process temperature, ^{o}C	Cloud point, ^{o}C	Pour point, ^{o}C	Weight fraction of sulfur,%	Yield, %
Initial diesel fraction	-11.3	-18.3	0.560	-
320	-42.8	-47.5	0.448	100
350	-48.4	-49.0	0.323	96.0
380	-44.7	-50.0	0.296	94.0
400	-40.8	-52.7	0.104	92.0

At P=4.0 MPa, V = 2.0 h^{-1} the hydroprocessing of straight-run gasoline fraction on the catalyst CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 was investigated (table 5). Yield of the liquid phase as the temperature increases from 320 to 400 ^{o}C decreases from 77.0 to 60.0%. In the temperature range 320-400 ^{o}C maximal content isoalkanes observed at 320^{o}C and is equal to 41.3 % . At higher temperatures, their number is 36.9-41.3%. The content of aromatic hydrocarbons increases from 12.9 to 19.7% with an increase in the process temperature up to 400 ^{o}C. The amount of olefins and naphthenic hydrocarbons ranges from 5.6 to 6.3% and 20.1-25.3%, respectively. The octane number of refined gasoline increases in comparison with the initial one from 79.2 to 87.3 (RON) and from 61.1 to 72.7 (MON). The sulfur content with increasing temperature up to 400^{o}C decreased from initial with from 0.0080 to 0.0016 %.

Table 5 - Influence of temperature on the hydroprocessing
of straight-run gasoline catalyst CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 at V = 2 h^{-1} and P = 4.0 MPa

Products , %	T, ^{o}C				
	Initial gasoline	320	350	380	400
Paraffins C_5-C_6	27.5	17.0	12.7	12.8	14.2
Iso-alkanes	39.8	41.3	40.0	36.9	39.8
Olefins	5.8	5,6	6.3	5,6	6.2
Aromatic hydrocarbons	8.7	12.9	15.7	22.8	19.7
Naphthenic hydrocarbons	18.2	23,2	25.3	21.9	20.1
Yield of the liquid phase		77.0	67.0	65.0	60.0
Octane number (RON)	79.2	84.0	86.4	85,2	87.3
Octane number (MON)	61.1	68.7	71.0	70.8	72.7
Weight fraction of sulfur, %	0.0080	0.0036	0.0027	0.0023	0.0016

In hydroprocessing gasoline of catalytic cracking on CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 with increasing temperature up to 320-350 ^{o}C content of isoalkanes increases from 25.4 to 47.5 % (table 6) . With a further increase in temperature, there is a decrease in the amount of formed isoalkanes to 40.3% (400 ^{o}C). Under these conditions, the amount of aromatic hydrocarbons in the produced gasoline increases from 25.5 to 35.0 %. The content of naphthenic hydrocarbons in the catalysis is low and ranges from 6.1 to 8.3 %. The concentration of olefins in the catalyzate decreases from 31.2 % to 8.0 %. Yield of the liquid phase with increasing temperature in the range 320-400 ^{o}C varies between 95.0-100%. The octane number of ennobled at 400 ^{o}C catalytic cracking gasoline is 86.1 (RON) and 79.6 (MON). The sulfur content in the final product is reduced from 0.0134% (original gasoline) to 0.0029%.

Table 6 - Influence of temperature on the hydroprocessing of catalytic cracking gasoline on the catalyst CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 at V = 2 h^{-1}, P = 4.0 MPa

Products , %	T, °C				
	Initial gasoline	320	350	380	400
Paraffins C_5-C_6	6.3	8.8	9.2	10.6	8.1
Iso-alkanes	25,4	47.5	47.3	43.0	40.3
Olefins	31.2	12.1	7.6	5,0	8.0
Aromatic hydrocarbons	30.1	25.5	29.4	32.6	35.0
Naphthenic hydrocarbons	7.0	6.1	6.6	8.1	8.3
Yield of the liquid phase		100	97.5	95.5	95
Octane number (RON)	88.7	86.2	85,2	85,4	86.1
Octane number (MON)	80.1	81.0	79.0	78.0	79.6
Weight fraction of sulfur, %	0.0134	0.0048	0.0047	0.0035	0.0029

The hydroprocessing of straight-run gasoline on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 has been investigated. When hydroprocessing the gasoline fraction in the temperature range of 320-400 °C, the content of isoalkanes ranges from 30.9-37.1 %. Under these conditions, the amount of aromatic hydrocarbons decreases from 33.2 to 8.7 %. The yield of naphthenic hydrocarbons is growing from 13.6 to 26.9 %. Yield of the liquid phase as the temperature increases from 320 to 400 °C decreases from 91.3 to 70.2%. The octane number of gasoline after hydroprocessing increases from 83.7 (IM) and 58.9 (MM) in the initial to 79.1 (RON) and 78.9 (MON) at 400 °C. The sulfur content of catalysate with increasing temperature decreases from 0.0088 to 0.0001 % with 400 °C.

In testing the catalyst CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 in the hydrorefining of straight-run diesel fractions shown that the process temperature is raised from 320 to 400 °C pour point decreases from minus 28.5 to minus 40.0 °C. The cloud point under these conditions varies from minus 28.2 °C to 39.7 °C. The yield of hydrorefined diesel fuel is 80.0-87.5%. Sulfur content with increasing temperature up to 400 °C decreases from 0.6400 to 0.0671% (table 7).

Table 7 - Hydroprocessing of straight-run diesel oil fraction on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 at V = 2 h^{-1}, P = 4.0 MPa

Temperature, °C	Cloud point, °C	Pour point, °C	Yield, %	Weight fraction of sulfur, %
Initial	-16.1	-16.4	-	0.6400
320	-28.2	-28.5	80.0	0.0659
350	-32.4	-32.7	83.5	0.0553
380	-33.1	-33.4	87.5	0.0888
400	-39.7	-40.0	80.0	0.0671

Comparison of the results obtained in the study of the hydroprocessing of straight-run gasoline shows that the catalysts CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3, CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 and CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 have high hydrodesulfurizing activity. Under optimum conditions (P=4,0MPa, V = 2h^{-1} and 400°C) the hydrodesulfurization degree of CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 is 98.86%, on CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 - 80.0% and on CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 - 86.9% (residual sulfur content is 0.0001%, 0.0016 and 0.0012% respectively).

In the hydroprocessing of straight-run gasoline on catalysts CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3, CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 and CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3 there is an increase in the octane number compared to the original from 78.9 to 89.3, from 79.2 to 87.3 and from 79.1 to 88.4, respectively. This is mainly due to an increase in the content of isoalkanes and aromatic hydrocarbons in hydro-refined gasoline.

In gasoline hydroprocessing catalytic cracking was shown that under optimal conditions (p = 4,0MPa, V = 2h^{-1} and 400 °C) the degree of hydrodesulfurization catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 is 89.5%, on CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3 - 78.4%, the residual sulfur content is 0.0014 and 0.0029% respectively. The initial sulfur content in catalytic cracked gasoline is 0.0134%.

It has been established that among the developed catalysts the lowest pour point and cloud point of hydro-refined diesel fuel is observed on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3. After hydroprocessing at this catalyst pour point and cloud point are minus 52.7 °C and minus 40.8°C respectively. The same catalyst has the highest hydrodesulfurization activity: the sulfur content decreases from 0.5600% to 0.104% (the degree of hydrodesulfurization is 81.4%).

It should be noted that with the weighting of the fractional composition of the processed raw materials, the proportion of hard to remove sulfur compounds increases. As a result, the higher activity of catalysts in the hydrodesulfurization of the gasoline fraction in comparison with the diesel fraction is due to the predominance of mercaptans, disulfides of the gasoline fraction of oil, while in the diesel fraction sulfur is mainly found in the form of sulfides, thiophenes and benzothiophenes [6, 9, 23]

The activity of catalysts is related to the surface structure, composition and state of active sites. The physicochemical characteristics of the catalysts have been studied using various methods (EM, BET). The BET method has shown that the developed catalysts are characterized by pores with $d \approx 1.5–2.5$ nm.

Using temperature-programmed ammonia desorption, the acid-base characteristics of the catalysts were determined. On the surface of the catalyst $CoO-MoO_3-Ce_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 the acid sites with $T_{des} = 250$ °C prevail, their number is $8.57 \cdot 10^{-4}$; mol/g catalyst. The temperature of desorption of ammonia from the surface of the catalyst $CoO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 shifts to the region of lower temperatures up to 230 °C, its amount is $8.05 \cdot 10^{-4}$ mol/g catalyst. Number more weakly acid sites at desorbed 150 °C on the catalysts $CoO-MoO_3-Ce_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 and $CoO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 is small and amounts to 1.88 and $2.33 \cdot 10^{-4}$ mol/g of catalyst, respectively. The total amount of ammonia desorbed from the surface of the catalysts $CoO-MoO_3-Ce_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 and $CoO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 practically the same: 10.45 and $10.38 \cdot 10^{-4}$ mol/g of catalyst.

Electron microscopic studies of the dispersion, structure and state of active centers allowed to establish that on the surface of the catalyst $CoO-MoO_3-Ce_2O_3-P_2O_5$-ZSM-HY-Al_2O_3 there are clusters with $d \approx$ 4.0-5.0 nm composed of smaller particles, identifying x as the Ce_2O_3. There are structures with $d \leq$ 10.0 nm, which include Ce_6O_{11}, CoMoP, $Ce(MoO_4)$, $CoAIO_4$, $Ce_8Mo_{12}O_{49}$, $AI_5Co_2Ce_4$, CoSi, $Ce_2Mo_3O_{12}$ и $Ce_4(P_2O_7)_3$. In addition, single dense particles were found, consisting of $Co(H_2PO_3)_2 \cdot 6H_2O$, AIP and $MoPO_4$ with $d \leq 10.0$ nm.

The catalyst $CoO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 is characterized by extensive accumulations of small particles with $d \approx$ 3.0-5.0 nm, corresponding to a mixture of phases $MoOPO_4$, La_2O_3, MoO_5, and La_2MoO_3. Also, small accumulations of highly dispersed particles with a size of ≈ 8.0-10.0 nm were found, which can be attributed to $La_4(P_2O_7)_3$. There are small transparent aggregates with $d \leq$ 20.0 nm related to $LaAIO_3$ in a γ- La^0 mixture. The appearance of γ- La^0 can be associated with redox processes occurring between the components of the active phase.

It should be noted that the detected structures $AlMo_3$, CoSi, $LaAIO_3$ and $MoSi_2$ indicate the incorporation of metals-components of the active phase into the structure of the zeolite with the formation of new centers that can function as Lewis acid centers [24].

The studied catalysts are characterized by the presence of both metal and acid-base centers. The acid sites can include metals in various oxidation states, fixed both inside the zeolite cavities and on their outer side [24 - 26]. Electron microscopy studies made it possible to establish that on the surface of the studied catalysts there are several types of surface structures that differ significantly both in size and in the chemical state of the components. The catalysts are highly dispersed, the metal components of the active phase are predominantly in an oxidized state, forming associate clusters on the surface, the dispersion, structure and state of which is determined by the nature of the catalyst components.

Thus, modified zeolite-containing catalysts $CoO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3, $CoO-MoO_3-Ce_2O_3-P_2O_5$-ZSM-HY-Al_2O_3, $CoO-MoO_3-La_2O_3-P_2O_5$-AAC-ZSM-Al_2O_3 exhibiting high activity in the hydrorefining of gasoline and diesel fractions, capable of one-stage deep hydrotreating, hydroisomerization and hydrocracking [23, 27] , which makes it possible to obtain low-sulfur, high-octane gasoline and low-sulfur and low-solidifying diesel fuel, which is important for the operation of vehicles in winter conditions .

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МОДИФИЦИРЛЕНГЕН АЛЮМОКОБАЛЬТМОЛИБДЕНДІ КАТАЛИЗАТОРЛАРДА МҰНАЙ ФРАКЦИЯЛАРЫН ГИДРОТАЗАЛАУ ЖӘНЕ ГИДРОИЗОМЕРЛЕУ

Аннотация. Жұмыста мұнайдың бензин және дизель фракцияларын алюмоксидті катализаторларда $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3$. гидроөңдеуді зерттеу нәтижелері келтірілген.

Катализаторлар алюминий гидроксиді мен ZSM-5 цеолит қоспасын, кобальт, молибден, лантан және фосфор қышқылы тұздарының HY су ерітінділерімен сіңдіріп дайындады. Түйіршіктеу мен қалыптаудан кейін катализаторларды 150°C-та кептіріп, 550°C-та қыздырды.

Әртүрлі бензин және дизель фракцияларды гидроөңдеу процесінде синтезделген катализаторлардың ірілендірілген зертханалық сынақтар жүргізілді. Сынақтар 320-400 С температурада, 2,5-4,0 МПа қысымда және шикізат берудің көлем жылдамдығы 1,0-3,0 сағ$^{-1}$ кезінде катализатордың стационарлық қабаты бар жоғары қысымды ағынды қондырғыда жүзеге асырылды.

Реакция өнімдерінің көмірсутегі құрамы «Хроматэк-Кристалл» хроматографында талданды. Күкірт құрамын «Oilsert International» ЖШС-да (Алматы қ.) талдау жүргізілді. Қату және лайлану температурасын анықтау Лаз М2 аспабында жүзеге асырылды.

$CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторында тура айдалған бензинді гидроөңдеу кезінде 320–350^{0}С температура аралығында изоалкалардың көп саны 33,4-40,4% пайда болатынын көрсетеді. Жоғары температурада изоалкалар шығыны 400С кезінде 32,2%-ға дейін төмендейді. Катализаттағы ароматты көмірсутек құрамы 14,9-дан 20,1%-ға дейін артады, нафтендік көмірсутектердің шығуы 24,5-23,0% шегінде ауытқиды. Бензиннің октан саны бастапқы көрсеткішпен салыстырғанда 78,9-дан 89,3-ке (З.Ә) және 60,9-дан 73,4-ке (М.Ә.) дейін артады. Температураны 400С-қа дейін арттырғанда катализаттағы күкірт мөлшері 0,0012%-ға дейін төмендеді.

$CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторында каталитикалық крекинг бензинін гидроөңдеу кезінде жақсартылған бензиннің октандық саны шамалы төмендейді. Температураның 400°С-қа дейін өсуі арқылы катализаттағы күкірттің құрамы бастапқы көрсеткішпен салыстырғанда 0,0134-тен 0, 0014%-ға дейін төмендеді. $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторында каталитикалық крекинг бензинін гидроөңдеу кезінде шикізатты көлемдік беру жылдамдығы 1,0-ден 3,0 сағ$^{-1}$-ға дейін өзгергенде катализаттағы изоалкалар құрамы шамалы өзгереді: 41,3-41,5% , ароматты көмірсутек концентрациясы 36,1-38,2% құрайды, нафтенді көмірсутектер шығымы 7,2-ден 8,9% құрайды. Олефинді көмірсутектердің шығымы бастапқы (31,2%) және шикізат көлем беру жылдамдығы 3,0 сағ$^{-1}$ тең болғанда 3,0%-ды көрсетті. Құрамында 0,0006% күкірті ең аз бензин көлем беру жылдамдығы 1,0 сағ$^{-1}$ тең болғанда алынған.

Гидрожақсартылған дизель отынының қату және лайланудың ең төмен температурасы $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторында байқалады. Гидроөңдеуден кейін осы катализаторда қату және лайлану температурасы тиісінше минус 52,7 °С және минус 40,8 °С-қа тең. Бұл катализатор ең жоғары гидрокүкіртсіздендіру активтілігін көрсетті: күкірт мөлшері 0,5600%-дан 0,104%-ға дейін төмендейді. Дайындалған модифицирленген цеолитті катализаторлар $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3$ бензин мен дизель фракцияларын гидро-өңдеу кезінде жоғарғы белсенді болып келеді, бір сатыда терең гидротазалауға, гидроизомеризациялауға және гидрокрекингке қабілетті, бұл қыста көлік құралдарының жұмысына маңызды болып саналатын төмен күкірт, жоғары октанды бензин мен аз күкіртті және төмен температурада қататын дизель отынын алуға мүмкіндік береді.

Мұндай зерттеулер $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$ және $CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3$ катализаторларында жүргізілді.

Түйін сөздер: тура айдалған бензин, мұнайдың дизель фракциясы, цеолит, катализатор, гидротазалау.

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ГИДРООЧИСТКА И ГИДРОИЗОМЕРИЗАЦИЯ НЕФТЯНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМОКОБАЛЬТМОЛИБДЕНОВЫХ КАТАЛИЗАТОРАХ

Аннотация. В данной работе приведены результаты исследования гидропереработки бензиновых и дизельных фракций нефти на алюмооксидных катализаторах $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5$- $AAC-ZSM-Al_2O_3$.

Катализаторы готовили пропиткой смеси гидрооксида алюминия и цеолитов ZSM-5, HY водными растворами солей кобальта, молибдена, лантана и фосфорной кислоты. После гранулирования и формования катализаторы сушили при 150°С и прокаливали при 550°С.

Были проведены укрупненные лабораторные испытания синтезированных катализаторов в процессе гидропереработки различных видов бензиновых и дизельных фракций. Испытания осуществляли в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400ºС, давлении 2,5-4,0 МПа и объемной скорости подачи сырья 1,0–3,0 ч$^{-1}$.

Углеводородный состав продуктов реакции анализировали на хроматографах «Хроматэк-Кристалл». Анализ содержания серы проводился в ТОО «Oilsert International» (г. Алматы). Определение температуры застывания и помутнения проводились на приборе ЛАЗ М2.

При гидропереработке прямогонного бензина на катализаторе $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ показано, что в интервале температур 320 - 350ºС образуется максимальное количество изоалканов 33,4-40,4%. При более высоких температурах выход изоалканов снижается до 32,2% при 400ºС. Содержание ароматических углеводородов в катализате возрастает от 14,9 до 20,1%, выход нафтеновых углеводородов колеблется в пределах 24,5-23,0%. Октановое число облагороженного бензина повышается по сравнению с исходным от 78,9 до 89,3 (И.М.) и от 60,9 до 73,4 (М.М.). Содержание серы в катализате с ростом температуры до 400ºС снизилось до 0,0012%.

При гидропереработке бензина каталитического крекинга на катализаторе $CoO -MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ октановое число облагороженного бензина незначительно снижается. Содержание серы в катализате с ростом температуры до 400ºС снизилось по сравнению с исходным с 0,0134 до 0, 0014%.

При изменении объемной скорости подачи сырья от 1,0 до 3,0 ч$^{-1}$ содержание изоалканов в катализате мало меняется – 41,3–41,5%, концентрация ароматических углеводородов составляет 36,1–38,2%, выход нафтеновых углеводородов колеблется в пределах от 7,2 до 8,9%. Выход олефиновых углеводородов значительно снижается по сравнению с исходным (31,2%) и при объемной скорости подачи сырья, равной 3,0 ч$^{-1}$, составляет 3,0%. Бензин с наиболее низким содержанием серы –0,0006% получен при скорости подачи сырья, равной 1,0 ч$^{-1}$.

При испытании катализатора $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ в процессе гидропереработки дизельной фракции нефти установлено, что наиболее низкая температура застывания и помутнения гидрооблагороженного дизельного топлива наблюдается на катализаторе $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$. После гидропереработки на этом катализаторе температура застывания и помутнения равны минус 52,7ºС и минус 40,8ºС соответственно. Этот же катализатор обладает наиболее высокой гидрообессеривающей активностью: содержание серы понижается с 0,5600% до 0,104%

Таким образом, разработаны модифицированные цеолитсодержащие катализаторы $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$, $CoO-MoO_3-La_2O_3-P_2O_5-AAC-ZSM-Al_2O_3$, проявляющие высокую активность при гидроперереботке бензиновых и дизельных фракций, способные в одну стадию проводить глубокую гидроочистку, гидроизомеризацию и гидрокрекинг,ч то позволяет получать малосернистый, высокооктановый бензин и малосернистое низкозастывающее дизельное топливо, что важно для работы автотранспорта в зимних условиях.

Аналогичные исследования были проведены на катализаторах $CoO-MoO_3-Ce_2O_3-P_2O_5-ZSM-HY-Al_2O_3$ и $CoO-MoO_3-La_2O_3-P_2O_5$- AAC-ZSM -Al_2O_3.

Ключевые слова: прямогонный бензин, дизельная фракция нефти, цеолит, катализатор, гидроочистка.

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SYNTHESES OF CATION EXCHANGER WITH MACROPOROSITY AND INVESTIGATING SPECIFIC PROPERTIES

Abstract. Obtained new strongly acid cation exchanger of macroporous structure based on furfural and dipheniloxide. The optimal amount of the poreformed agent and the molar ratio of the reacting substances were determined. Initially results showed that the polymer matrix using camphor as pore forming agent present a uniform surface with inter-connected pores and adding camphor into the polymer matrix could attain more abundant pores than adding n-heptane. We studied the components, surface and pore structures of the cation exchanger by Fourier transform infrared spectroscopy and scanning electron microscopy (SEM). SEM observations showed that the resin abounded in macropores as large as 7.4 to 22.6 μm both in the surface and the interior. The parameters of the porous structure of the samples are calculated using by equation BET (Brauner., at al.) and the total pore volume of ion exchangers and the radius of submicroscopic capillaries were determined. Finally dates testing prototypes under application conditions, allow us to recommend this cation exchanger for sorption of small radius ions at high speed, as fundamentals upon receipt of ion exchangers, etc.

Keywords: cation exchanger, furfural, pore-forming agent, exchange capacity, bulk density, specific volume, porosity, selectivity.

Introduction. The areas of use of ion exchangers are expanding annually, which determines the range of research and technological work on the synthesis of ion exchangers following sorption properties. [1-5]. The issue of improving the kinetic and mechanical properties of ion-exchange polymers that has recently become particularly acute has found a rather successful solution due to the creation of macroporous structures. In the literature, there are a large number of reports on the methods of obtaining copolymers of macroporous structure by copolymerizing vinyl derivatives in the presence of various additives, and the number of works on the preparation of macroporous ion exchangers on polycondensation matrices is very limited [6-7].

It is known that in a conventional copolymer, the gaps in the molecular network formed during the crosslinking process are micropores. When swelling in aromatic and chlorinated hydrocarbons, the solvent penetrates into them, greatly expanding the molecular network. The mechanism of swelling of the macroporous copolymer is different. Its porosity is similar to that of a sponge. The blowing agent fills the free space in the copolymer, which is accompanied by only a slight expansion of the molecular network.

Scientist of work (8-9) reported dyes were immobilized under mild conditions by a sol–gel process which generates a high porosity for easy analyte access.

Methods. Three-necked flask equipped with a reflux condenser and a mechanical stirrer with a bolt and a thermometer. Diphenyloxide putted into flask and 45% solution of sulfuric acid added. The mechanical stirrer speed of 120 round a minute into the flask during the reaktion. After a few time at 30-40°C furfural added drop by drops. Pore-forming agents (n-heptane, camphor) added to the reaction environment from 20 to 60% by the total weight of monomers. The temperature was raised to 70-80°C and at this temperature, during 90–100 minutes gel was formed. Product transferred to a porcelain dish and dried in the air at ambient temperature. The dried polymer was milled to a grain diameter d_g = 0.25-0.5 mm. Following the granules of obtaining polymer spread to the lawn covered by blanket for distilling over from pore-formed substances using steam. The duration of process 3 hours. Later dry process carried out in two stages; initially at 80-90° C, then at 100°C until it reached the air – dry state.

The finished polymer exposed to the sulfonation. The polymer swelled in concentrated sulfuric acid was placed in a three-neck flask with a mechanical stirrer and reflux condenser. The sulfonation conducted with 92-95% sulfuric acid, the molar ratio of polymer and acid was 1:6. The sulfonation temperature 70°C for 6 hours. To avoid deformation of the polymer matrix after sulfonation, the cooled polymer was washed with sulfuric acid, decreasing the concentration successively to 75, 50, 25 and 10% and then washed with distilled water until neutral wash water, then the resulting cation exchanger was dried at 80-90°C in a drying cabinet [10-13].

The microstructure and morphological studies of the surface were carried out using a scanning electron microscope 10(Carl Zeiss) and the compositions of the ion exchangers were determined using an energy-dispersive elemental analyzer brand EDS (Oxford Instrument)– Aztec Energy Advanced X-act SDD. Investigation of the dimension of microporous cation exchanger was performed using SEM device (Quanta 3D 200i) [14-15]

Strong acid cation exchangers adsorption isotherms were measured on a high-vacuum installation with mercury valves and Mac-Ben quartz weights in the range of 0–100% relative humidity at 25 ± 0,3°C. **C**alculated absolute adsorption isotherms of porous bodies to determine the specific surface and pore distribution over the radius at low temperature using by BET equation [16-17].

Results and discussion. By polycondensation of diphenyloxide and furfural in the presence of pore-forming agents, n-heptane and camphor, copolymers of macroporous structure were obtained [18-19]. Properties of obtained ion exchanger depends on degree of crosslink agent and the amount of pore-forming agents. Studied the molar ratio of furfural range from 1 to 2 moles per mole of dypheniloxide and the amount of pore-forming agent varies from 20 to 60% of the total weight of monomers.

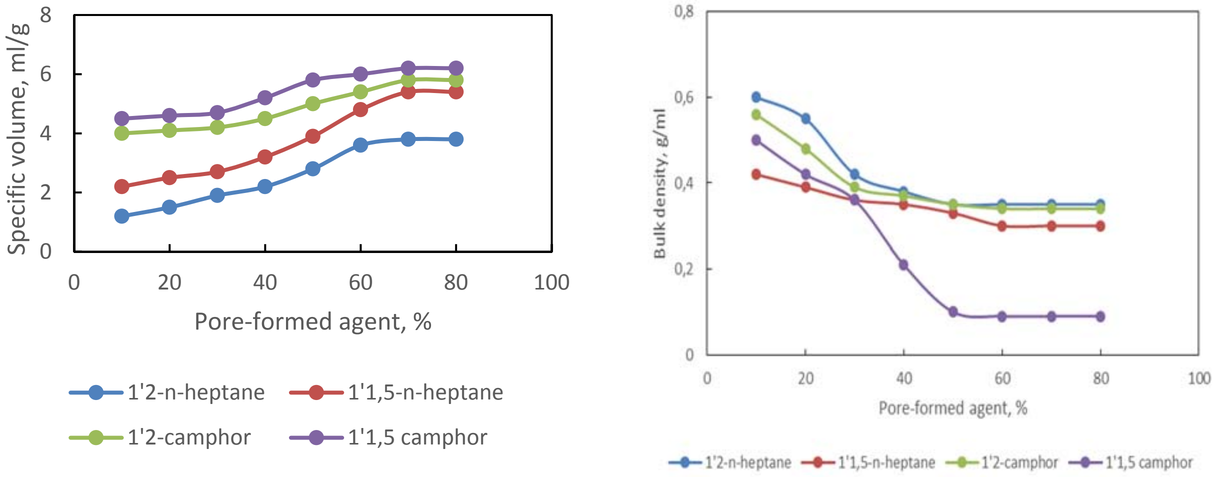

Figure 1. Dependence of bulk density and specific volume on the content
of the pore-formed agent at various molar ratios of dyheniloxide and furfural

Figure 1 shows that with an increase in the amount of pore-formed agent present during polycondensation, the bulk density of polymers decreases and the specific volume increases. In our opinion, the case of this situation is the transition from the gel to the macroporous structure depends on the content of the cross-agent in the copolymer and on the amount of the pore-formed agent entered into the reaction environment. The optimal molar ratio of the polycondensation reaction between dyheniloxide and furfural are 1'1,5 and amount of pore-formed agent is 60%.

The study of changes in the specific volume and amount of solvent absorbed by the copolymer during swelling suggests that the swelling mechanism changes from a conventional structure to a macroporous one: the solvent fills the free space in the copolymer, which is accompanied by a relatively small expansion of the molecular network. It had founded that macroporous copolymers swelled not only in conventional “swelling” agents, but also in solvents in which conventional copolymers do not swell. Figure 2 demonstrate the dependences of the amount of toluene and cyclohexane absorbed during swelling by the ion exchanger on the inserted pore-forming agent.

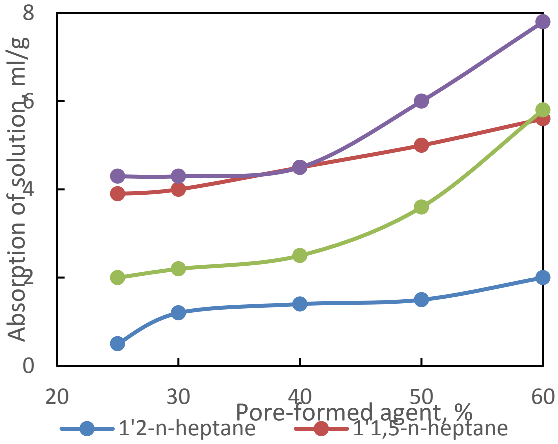

Figure 2 - Dependence of absorption of solution
on the content of the pore-formed agent at various molar
ratios of dyheniloxide and furfural

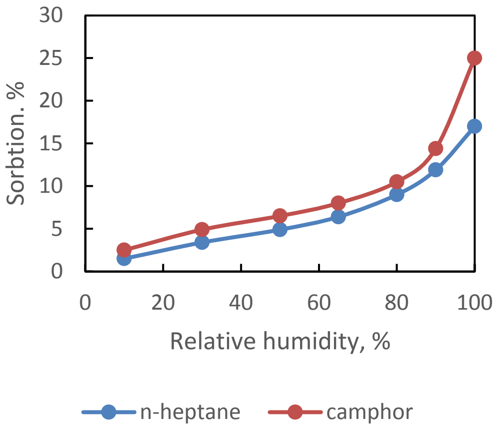

Figure 3 - The influence of the nature
of the pore-formed agent on the sorption
of water vapor by cation exchanger at 25 ° C

The direction of the curves figure 2 shows that as the amount of the blowing agent increases, the amount of absorbed toluene and cyclohexane increases; at the same time, the degree of swelling decreases in toluene and increases in cyclohexane. This again shows that the structure of the cation exchanger influenced simultaneously by the degree of crosslinking and the amount of introduced pore-forming agent.

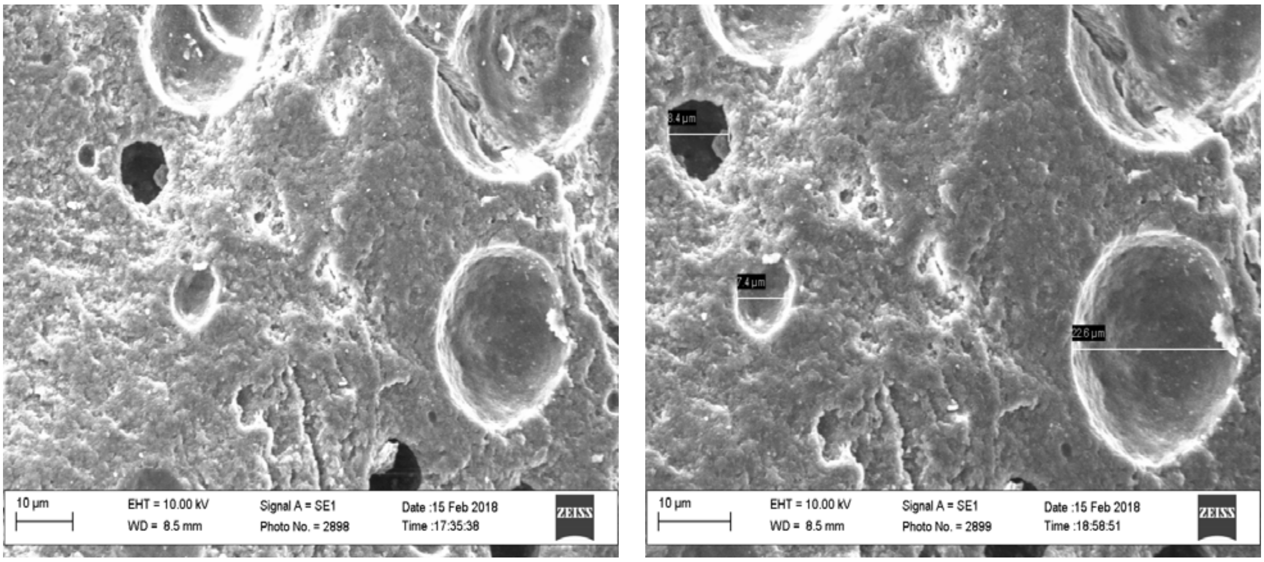

Figure 4 - Electronic images pores of obtaining cation exchanger

Further studied the influence of the nature of the pore-forming agent on the sorption of water vapor by cation exchanger in figure 3. The results of water vapor sorption by ion exchanger predicated once again that camphor as pore-formed agent suitable for polymer matrix and given the better dates than n-heptane.

Using by scanning electronic microscopy equipment investigated high accuracy poros sizes of obtaining cation exchanger, which containing poros from 7.4 to 22.6 µm. Once again, the results confirmed that for macroporous cation exchanger reasonable pore-formed agent is camphor.

Determining of specific surface area and pore distribution over the radius at low temperature is an important indicator for comparison obtaining macroporous cation exchanger with existing cation exchangers. Depending on the porosity and pore size distribution of the particle, the specific surface area is influenced by size, shape, and roughness. When the particle structure presents nil or low porosity, the specific surface area of the particle is a function of these other attributes. Under these circumstances the specific surface area typically presents a stronger correlation with dissolution rate of the particle if the dissolution rate is controlled by external mass transfer.

The specific surface area is typically characterized by the physical adsorption of a gas (argon, krypton, or nitrogen) on the surface of the sample at cryogenic temperature. Gas adsorption can be determined by volumetric, gravimetric, or flux methods. The volume of gas adsorbed on a monolayer over the surface of the particles is determined according to the BET equation (Brunauer et al.), and the specific surface area is calculated based on molar volume of the gas and the average area occupied by the gas molecule [18].

For this aim calculated absolute adsorption isotherms of porous bodies using by BET equation. The capacity of the monolayer determined by the equation:

$$\frac{P_i}{x(P_1^0-P_i)}=\frac{1}{x_m \cdot C}+\frac{C-1}{x_m \cdot C}\cdot\frac{P}{P_0}$$

where: P – is the equilibrium vapor pressure of the sorbate over the sorbent; P_0 – is the saturated vapor pressure of sorbate at the same temperature; X – is the amount of the sorbed substance, g/g; Xm is the amount of a substance in a continuous monomolecular layer, g/g; C – is a constant representing the ratio of the lifetime of the molecules in the first layer and the liquid, respectively.

According to the equation, the dependence of $\frac{P}{(P_0-P)}$ P on $\frac{P}{P_0}$ should have the form of a straight line with the slope $S=\frac{C-1}{x_m \cdot C}$ and cut off the ordinate segment $i=\frac{1}{x_m \cdot C}$ Solving the system of equations gives the value of the monolayer capacity: $x_m=\frac{1}{S+i}$ and energy constants $C=\frac{S}{i}+1$

Based on results of applying equation BET obtained following dates, which presented in table 1.

The ion exchange resins are macroporous, have a surface area of at least 50 m^2/g, and an average particle size of at least 20 micrometers [19]. As you see that obtaining macroporous cation exchanger contained high specific surface area about 150 m^2/g and up to 20 micrometers respectively.

Table 1 - Effect of the nature of the pore-forming agent on the capillary-porous structure of the samples

Sample	Pore-forming agent	
	n-heptane	camphor
Monolayer capacity, X_m, g/g	0.0325	0.0420
Specific surface area, S_{sp}, m^2/g	114.24	147.63
Total pore volume, W_0, sm^3/g	0.17	0.25
Radius of submicroscopic capillaries, r_c, Å	29.76	33.87

Researches related to investigation of structure synthesis polymers (PI) involved by scientists [20]. Crosslinked sulfonated polymer (Pl) types have been developed for use as cation exchange membranes. The sulfonated PIs have excellent proton conductivity and a low cost of preparation. Therefor in the process of regeneration of ion exchange resin, it is necessary to achieve the most complete desorption of both noble metals and impurities. [21]. However, there are significant differences between ion-exchange membranes and ion-exchange resins concerning the polymer structures which are primarily due to the differences in size and shape between ion-exchange beads and ion-exchange membrane sheets. In both cases the fixed ion-exchange groups lead to a swelling of the polymer when it is in contact with an aqueous solution. The degree of swelling depends on the ionic strength of the solution and on the degree of cross-linking of the polymer [22].

The main properties and requirement for cation exchangers are cation exchange capacity. In our case, entered pore-formed agents in the several quantities into polymer matrix following this exchange capacity differed each other depending on form of cation exchanger. In table, 2 presented dates of sorption properties of obtained macroporous cation exchangers depending on the nature of the pore-forming agent and its quantity.

Table 2 - Exchange capacity of macroporous cation exchangers depending on ion form

Pore-formed agent	Amount of Pore-formed agent, %	Exchange capacity, meq/l							
		NaCl 0.1N	NaOH 0.1N	0.1N $CaCl_2$		0.1N $MgSO_4$		0.1N $CuSO_4$	
				Ion form					
				H-	Na-	H-	Na-	H-	Na-
n-heptane	30	0.72	3.2	0.55	1.75	0.65	1.75	0.4	1.1
	60	0.84	3.8	0.8	1.2	0.8	1.85	0.6	1.4
camphor	30	0.95	3.8	0.95	2.0	1.0	2.0	1.2	1.2
	60	1.32	4.8	1.45	2.35	1.45	2.35	1.4	1.5

Its value depends on the number of acid groups of the ion exchanger, the degree of their dissociation, as well as the nature and concentration of the exchanging ions. The exchange capacity of sodium form higher than hydronium forms. This process explained with radius of exchanging ions, as they activity properties.

Conclusion. Thus, as a result of the research, obtained strong acid cation exchangers and investigated the dependence of their properties on the degree of macroporosity. The presence of macropores explains the ability of the copolymer to absorb also aliphatic and cyclic compounds in which the usual copolymer does not swell. This also explains the increased mechanical strength of ion exchangers based on macroporous copolymers under operating conditions, since during sorption and desorption their volume remains almost constant. At the same time, macroporosity creates a large exchange surface, contributes to the rapid diffusion of ions and the sorption.

Based on the data obtained, it is possible to conclude that when polycondensation is present in the presence of the selected type of pore formers, cation exchangers are obtained with a macroporous structure that approaches the structure of rigid sorbents, and the degree of macroporosity increases in the investigated interval with increasing cross-agent content and the amount of pore-forming agent.

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МАКРОСАҢЫЛАУЛАРМЕН КАТИОНАЛМАСТЫРҒЫШТАҒЫ СИНТЕЗ ЖӘНЕ ЕРЕКШЕ ҚАСИЕТТЕРДІ ЗЕРТТЕУ

Аннотация. Иониттегі макросаңылаулар оған қалыпты жағдайда сополимерлерде болмайтын алифатикалық және циклді қосылыстарды сіңіруге мүмкіндік береді. Сонымен қатар, жұмыс барысында макросаңылаулы сополимерлерге негізделген иониттердің механикалық беріктігінің арту жағдайын түсіндіреді, сорбция және десорбция барысында олардың көлемі өзгермейді. Онда үлкен макросаңылаулық алмасу бетін қалыптастырады, иондардың жылдам диффузиясына және ірі молекулалар сорбциясына әсер етеді.

Белгілі болғандай, қарапайым сополимерде тігілу үдерісі барысында түзілетін молекулалық торда аралық микросаңылау ретінде қарастырылады. Ароматты және хлорланған көмірсутекте ісіну кезінде еріткіш оларға өтіп, молекулалық торды нақты шамада кеңейтеді. Макросаңылаулы сополимердің ісіну механизмі әртүрлі. Оның саңылаулығы серпімділік кеуектігіне ұқсас. Саңылау түзуші сополимердегі бос кеңістікті толтырады, ол молекулалық тордың шағын кеңеюі арқылы жүзеге асады. Макросаңылау қарапайым сополимер ісінбейтін сополимердің алифатты және циклді қосылыстарды сіңіру қабілетін түсіндіреді.

Жоғарыда келтірілгенді ескеріп, түрлі саңылау түзуші заттардың (н-гептан және камфара) қатысуымен дифенил оксиді мен фурфурол поликонденсациясы арқылы макросаңылаулы құрылымның сополимерлері алынады. Саңылау түзуші заттың оңтайлы мөлшері және реакцияға түсетін заттардың молярлық қатынасы анықталады. Бастапқыда нәтижелер көрсеткендей, камфора қолдану негізінде полимерлі матрица саңылау түзуші агент ретінде байланыстырылған саңылауы бар біртекті жоғарғы бет түрінде алынады, ал полимер матрицасына камфорды қосу н-гептанды қосуға қарағанда көп мөлшерде саңылау түзеді.

Макросаңылаулы ион алмастырғыш кеуектің негізгі сипаттамалары, оның ішінде саңылаудың жалпы көлемі (см^3/г), саңылаудың орташа тиімді радиусы, олардың радиусы бойынша саңылаудың таралуы, меншікті жоғарғы беті (м^2/г) 25 ± 0,3 °С температурада 0-100% салыстырмалы ылғалдылық аралығында сынап қақпағы мен Мак-Бен кварц таразымен жоғары вакуумды қондырғыда зерттеледі. Фурье түрлендіргіш ИК-спектроскопиясы мен сканерлеуші электронды микроскоп (СЭМ) арқылы катионит құраушылары, жоғарғы беті және саңылаулы құрылымы зерттеледі. СЭМ арқылы бақылау жұмыстары көрсеткендей, шайыр құрамының жоғарғы бетінде, ішінде 7,4 тен 22,6-ға мкм дейінгі өлшемде макросаңылаудың мөлшері көп байқалады.

Үлгілердің саңылаулы құрылымының параметрлері БЭТ (Браунэр-Эммит-Теллер) теңдеуі бойынша есептеледі және ионалмастырғыш саңылаудың жалпы көлемі мен субмикроскопиялық капиллярлар радиусы анықталады. БЭТ теңдеуінің координаталарындағы су буының адсорбциялық изотермалары төмен қысымды аймақта түзу сызықты сипатқа ие. Бұл алынған СКДФ-МП макросаңылаулы катиониттің су буының сорбциялық изотермаларын сипаттайтын БЭТ теңдеуінің қолданылу тиімділігін айқындайды. Өнеркәсіпте жасалатын макросаңылаулы иониттерде саңылау көлемінің қосындысы 0,2-1,0 см^3/г, меншікті жоғарғы беті 30-дан 200 м^2/г дейін, саңылаулардың үлкен радиусы 5-60 нм құрайды. Өндірістік иониттермен салыстырғанда, біз алған мәліметтер оның көрсеткіштерінен төмен емес. Нәтижесінде пайдалану жағдайындағы тәжірибелік үлгілерді сынау күндері бұл катионитті ионалмастырғыштар алуға негіз ретінде жоғары жылдамдықта аз радиусты иондарды сорбциялауға ұсынуға мүмкіндік береді.

Сорбциялық изотермалар негізінде таңдалған типтегі саңылау түзушілердің қатысуы арқылы полимер алуда байқалатын саңылау сипаттамалары есептеледі, макросаңылаулы құрылымды катионит түзіледі, ол қатты сорбенттер құрылымына ұқсас, ал зерттелетін аралықта саңылауды түзу мөлшерін арттырумен макросаңылау дәрежесі жоғарылайды.

Түйін сөздер: фурфурол, катионит, саңылау түзуші зат, алмасу сыйымдылығы, көлем тығыздығы, меншікті көлем, кеуектік, селективтік.

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СИНТЕЗ КАТИОННООБМЕННИКА С МАКРОПОРИСТОСТЬЮ И ИССЛЕДОВАНИЕ ОСОБЫХ СВОЙСТВ

Аннотация. Наличие макропор в ионите позволяет ему поглощать алифатические и циклические соединения, что недоступно обычным сополимерам. Этим же объясняется повышенная механическая прочность ионитов на основе макропористых сополимеров в условиях эксплуатации, так как при сорбции и десорбции их объем остается почти постоянным. Вместе с тем макропористость создает большую поверхность обмена, способствует быстрой диффузии ионов и сорбции молекул большого размера.

Известно, что в обычном сополимере промежутки в молекулярной сетке, образующиеся в процессе сшивания, являются микропорами. При набухании в ароматических и хлорированных углеводородах растворитель проникает в них, значительно расширяя молекулярную сетку. Механизм набухания макропористого сополимера иной. Его пористость подобна пористости губки. Порообразователь заполняет свободное пространство в сополимере, что сопровождается лишь незначительным расширением молекулярной сетки. Наличие макропор объясняет способность сополимера поглощать также алифатические и циклические соединения, в которых обычный сополимер не набухает. Этим же объясняется повышенная механическая прочность ионитов на основе макропористых сополимеров в условиях эксплуатации, так как при сорбции и десорбции их объем остается почти постоянным.

Учитывая вышесказанное, поликонденсацией дифенилоксида и фурфурола в присутствии различных порообразователей (н-гептана и камфары), были получены сополимеры макропористой структуры. Определяли оптимальное количество порообразователя и молярное соотношение реагирующих веществ. Первоначально результаты показали, что полимерная матрица с использованием камфоры в качестве порообразующего агента представляет собой однородную поверхность со связанными порами, и добавление камфоры в полимерную матрицу может дать более обильные поры, чем при добавлении н-гептана.

Основные характеристики пористости макропористого ионообменника такие, как суммарный объем пор (в см^3/г), средний эффективный радиус пор, распределение пор по их радиусам, удельная поверхность (в м^2/г) изучена на высоковакуумной установке с ртутным затвором и кварцевыми весами Мак-Бена в интервале относительных влажностей 0-100% при 25±0,3°C. Мы изучили компоненты, поверхностную и поровую структуры катионита с помощью ИК-спектроскопии с Фурье-преобразованием и сканирующей электронной микроскопии (СЭМ). Наблюдения с помощью СЭМ показали, что смола содержала большое количество макропор размером от 7,4 до 22,6 мкм как на поверхности, так и внутри.

Параметры пористой структуры образцов рассчитывали по уравнению БЭТ (Браунэр-Эммит-Теллер) и определяли общий объем пор ионообменников и радиус субмикроскопических капилляров. Изотермы адсорбции паров воды в координатах уравнения БЭТ имеет прямолинейный характер в области низких давлений. Это подтверждает применимость уравнения БЭТ для характеристики изотерм сорбции водяного пара полученного макропористого катионита СКДФ-МП. В производимых промышленностью макропористых ионитов суммарный объем пор составляет 0,2-1,0 см3/г, удельная поверхность от 30 до 200 м2/г, преимущественный радиус пор составляет 5-60нм. Полученными нами данные по сравнению производственных ионитов не уступает своими показателями. Наконец, даты испытаний опытных образцов в условиях применения позволяют нам рекомендовать этот катионит для сорбции ионов малого радиуса на высокой скорости, в качестве основы при получении ионообменников и т. д.

На основании изотерм сорбции были рассчитаны поровые характеристики, показывающие при получении полимера в присутствии порообразователей выбранного типа, образуются катиониты, обладающие макропористой структурой, которая приближается к структуре жестких сорбентов, причем в исследованном интервале с увеличением количества порообразователя степень макропористости увеличивается.

Ключевые слова: фурфурол, катионит, порообразующий агент, обменная емкость, насыпная плотность, удельный объем, пористость, селективность.

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BEHAVIOUR OF SULFUR, ARSENIC AND ORGANIC CARBON IN A GRAVITY CONCENTRATION OF GOLD FROM REFRACTORY ORE

Abstract. The results of assay-gravimetric, chemical, mineralogical analyzes of gold ore are presented. According to the content of sulfide sulfur and the degree of oxidation of sulfur gold-bearing ore is assigned to the poor sulfide type of ore in the primary zone. Gold ore refers to refractory carbonaceous arsenic-containing sulfide ores. The gravity concentration of ore was assessed using a laboratory 3-inch Knelson KC-MD3 centrifugal concentrator. According to the results of the GRG test, the total gold extraction was 39.58% with the total concentrate yield of 3.96%. The extraction of gold in the first stage is lower than in the subsequent stages. This indicates the absence of large gold in the ore. The behavior of sulfur and arsenic during gravity concentration is similar to the behavior of gold. These data confirm that the main amount of gold is associated with arsenopyrite (arsenic pyrite) and pyrite. The behavior of organic carbon during gravity is significantly different. Only 3.39% of organic carbon passes into the gravity concentrate from ore, which reduces the persistence of the concentrate. Most of the organic carbon (96.61%) remains in the tails of gravity. The content of components in the total gravity concentrate was: Au 21.63 g/t, S 6.40%, As 0.82%, C(organic) 0.58%. The extraction of the components in the total concentrate is as follows, %: Au 39.58; S 34.52; As 27.27; C(organic) 3.39.

Key words: refractory ores, preg-robbing, double-refractory ores, gravity concentration method, GRG test, gold ore, carbon-arsenic sulfide ores.

Introduction. The most common reason for the technological persistence of gold-bearing ores is the thin impregnation of gold, which is closely associated with sulfide minerals. Such minerals are most often iron and arsenic sulfides: pyrite and arsenopyrite [1–3]. Direct cyanide leaching of such ore is not effective, the cyanide solution is not accessible to gold even when leaching finely ground (less than 40 μm) raw materials. This type of ore belongs to refractory ores that require preliminary destruction (oxidation) of sulfide minerals and the release of gold from them for its further dissolution [4–7].

Some refractory gold-bearing ores also contain an organic carbonaceous substance that has sorption activity in relation to the gold-cyanide complex (the "preg-robbing" effect), which gives the raw material additional persistence. Therefore, such raw materials are often called double stubborn raw materials. The presence of carbonaceous substances in ores not only complicates the cyanidation process, but also makes it unprofitable due to the low extraction of a valuable component [7–15]. To reduce the sorption activity of the carbonaceous substance that is part of the ore, various methods and techniques are used, which include gravity concentration, flotation, hydrochemical oxidation of chlorine, autoclave and bacterial oxidation, etc. [10–21].

One of the primary methods for processing carbonaceous-arsenic sulfide gold-bearing ores is gravity concentration method. To assess the enrichment of ores by gravity methods, a special GRG test (Gravity recoverable gold test) is most often used in production [22–24]. The methodology for performing the GRG test consists in the stage-by-stage grinding of ore with a gradual reduction in its size and the extraction of gold at each stage as it is released [25–28].

The aim of this work is to study the behavior of sulfur, arsenic and organic carbon during gravity concentration of refractory gold-bearing ore.

Object and method of research. The object of research is the gold-containing ore from one of the deposits of Kazakhstan in the East Kazakhstan region. According to the results of assay-gravimetric analysis, the average gold grade in the ore is 2.29 g/t.

The chemical composition of the ore by main components is shown in table 1.

Table 1 – The results of chemical analysis of the sample

Components	Content, %	Components	Content, %
Copper	0.004	Aluminium oxide	11.52
Nickel	0.01	Arsenic	0.17
Cobalt	0.001	Antimony	undefined
Zinc	0.008	Common carbon	2.59
Lead	0.02	Organic carbon	0.61
Iron	3.77	Carbonate carbon	1.98
Calcium oxide	4.06	Common sulfur	0.80
Magnesium oxide	3.20	Sulphate sulfur	0.04
Sodium oxide	0.72	Sulphide sulfur	0.76
Potassium oxide	2.80	The degree of sulfur oxidation	5.00
Silicon oxide	57.88		
Ore type: *– according to the degree of oxidation of sulfur: primary ore range;* *– by the amount of sulfide sulfur: poor sulfide type.*			

The industrially valuable component in the sample is only gold. The remaining metals, due to their low content, do not represent industrial value. The arsenic content in the sample was 0.17%. Almost all sulfur is represented by a sulfide form. According to the content of sulfide sulfur, the sample is classified as a poor sulfide type. According to the phase composition of sulfur, the sample is assigned to the primary ore range.

Visually and by analysis confirms the presence of carbonaceous shales in the sample. Carbon schists are natural sorbents of gold dissolved in cyanide. Such ores are classified as refractory ores, the extraction of gold from which is difficult. The organic carbon content in the sample was 0.61%.

Complex mineralogical analysis was carried out using x-ray phase, microscopic and optical analyzes. Samples were examined under a microscope in transparent thin sections, and polished sections, artificial briquettes and immersion environment. Gold grains were studied on an electronic microanalyzer of the JEOL JXA – 8230 Electron Probe Microanalyzer brand.

X-ray diffractometric analysis of medium samples was carried out on a DRON-4 diffractometer with Cu - radiation, β-filter. Conditions for recording diffractograms: U = 35 kV; I = 20 mA; survey θ-2θ; detector 2 deg/min.

The identification of the mineral phases according to X-ray diffraction analysis is shown in the diffraction pattern in figure 1.

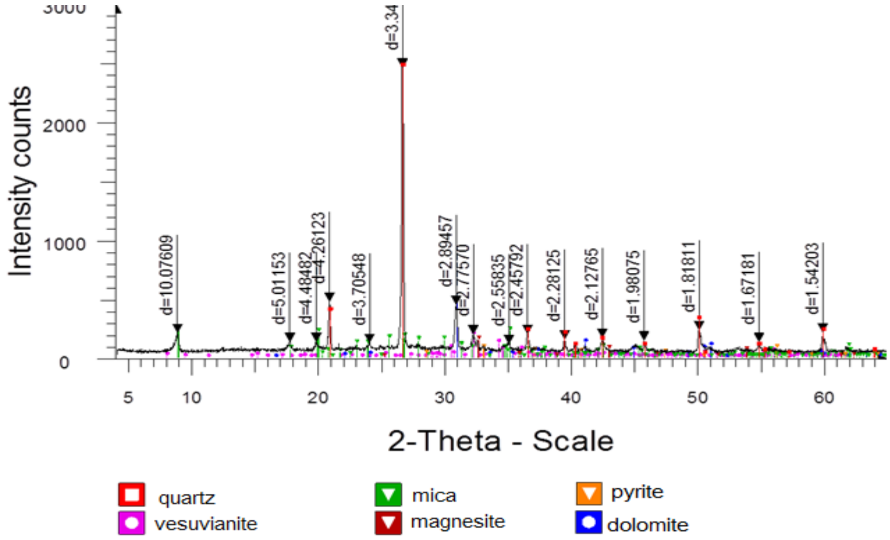


Figure 1 – The diffraction pattern of an average sample

The mineral composition of the average sample, calculated according to x-ray phase analysis using chemical analysis and studying the products under a microscope, the following (%): *ore* – pyrite 1.5–2.0; arsenopyrite 0.4–0.5; iron hydroxides and galenite – significant values; *rock-forming* – quartz 54–55; muscovite 21–22; magnesite 8–10; dolomite 12–13; carbonaceous substance 1; others 1–2.

Methodology for conducting the GRG test. The GRG test was conducted on a 10 kg ore sample at the Knelson concentrator KC-MD3. This test is performed in three stages. At the first stage, the ore weighing 10 kg was crushed to a particle size of 100% of –1.2 mm class and crushed ore was passed through the Knelson concentrator. Next, the tails of the first stage were grinded to a particle size of 80% of –0.3 mm class and passed through the Knelson concentrator. In the third stage, the tails of the second stage were grinded to a particle size of 80% of –0.071 mm class and passed through the Knelson concentrator. During the process, at all stages, samples were taken from the tailings for analysis and preparation of the technological balance. The resulting enrichment products - concentrates and tails were analyzed for gold, sulfur, arsenic and carbon.

The scheme of the GRG test is given in figure 2.

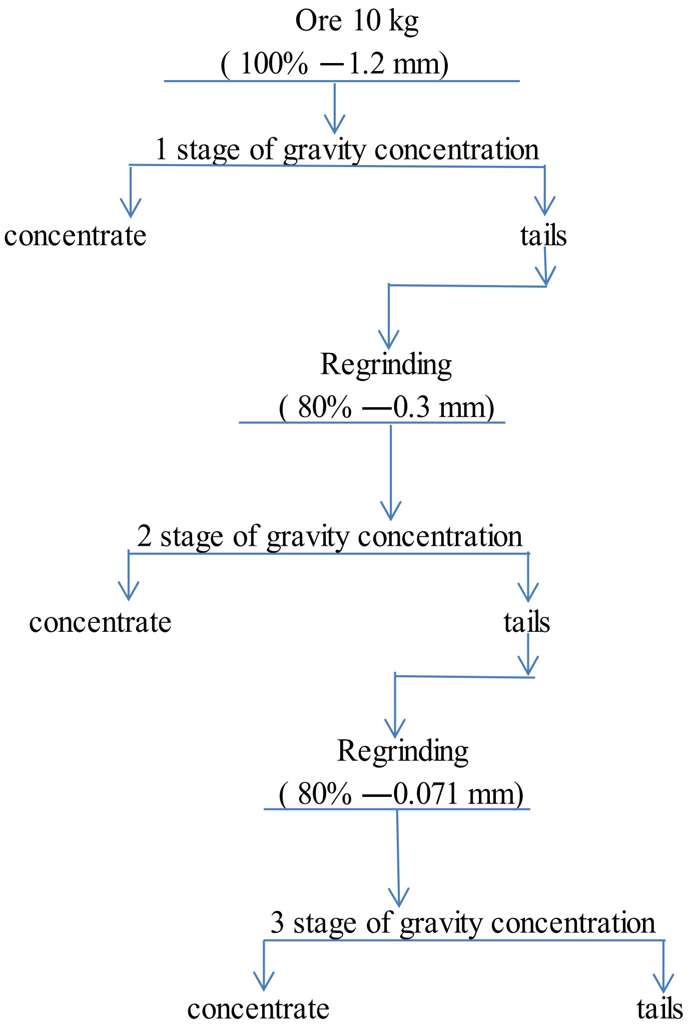


Figure 2 – Scheme of the GRG test

Results and discussion. According to the results of assay, chemical and mineralogical analyzes, only gold is an industrially valuable component.

A GRG test was performed to assess the gravity concentration of gold-containing ore. The results of the GRG test are shown in table 2.

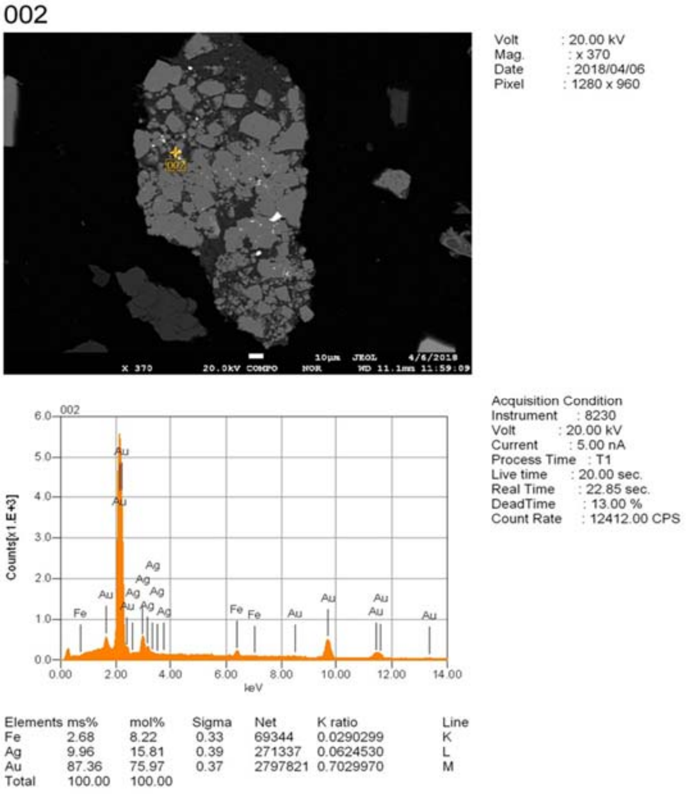
Table 2 – The results of the GRG test

Product	Output		Au content, g/t	Au extraction, %
	g	%		
1 Stage 100 % –1.2 mm				
Concentrate 1	114.8	1.15	23.00	12.33
Tails 1	9885.2	98.85	1.90	87.67
Ore	10000.0	100.00	2.14	100.00
2 Stage 80% –0.3 mm				
Concentrate 2	141.4	1.43	18.87	14.30
Tails 2	9743.8	98.57	1.64	85.70
Tails 1	9885.2	100.00	1.89	100.00
3 Stage 80% –0.071 mm				
Concentrate 3	139.5	1.43	23.30	19.92
Tails 3	9604.4	98.57	1.36	80.08
Tails 2	9743.8	100.00	1.67	100.00
Total				
Concentrate 1	114.80	1.15	23.00	12.21
Concentrate 2	141.36	1.41	18.87	12.34
Concentrate 3	139.46	1.39	23.30	15.03
Concentrate 1+2+3	395.62	3.96	21.63	39.58
Tails 3	9604.38	96.04	1.36	60.42
Ore	10000.00	100.00	2.16	100.00

The total extraction of gold during three-stage enrichment was 39.58 % with a total concentrate yield of 3.96 %. The gold content in the combined concentrate is 21.63 g/t.

According to electron-probe analysis, gold in the ore is present as thin (microns or less) inclusions in pure pyrite and arsenic-containing pyrite. The maximum size of detected gold grains is 4-5 µm. It is possible that smaller gold is part of the crystal lattice of sulfide minerals. The content of the main elements in the composition of native gold, established by electron-probe analysis, varies in the following ranges (%): Au 82–92; Ag 6–10; Fe 1.6–4.9 (figure 3). Electrum has the following composition (%): Au 67.12; Ag 23.70; Fe 9.19 (figure 4).

The GRG test indicators for related components are shown in table 3.

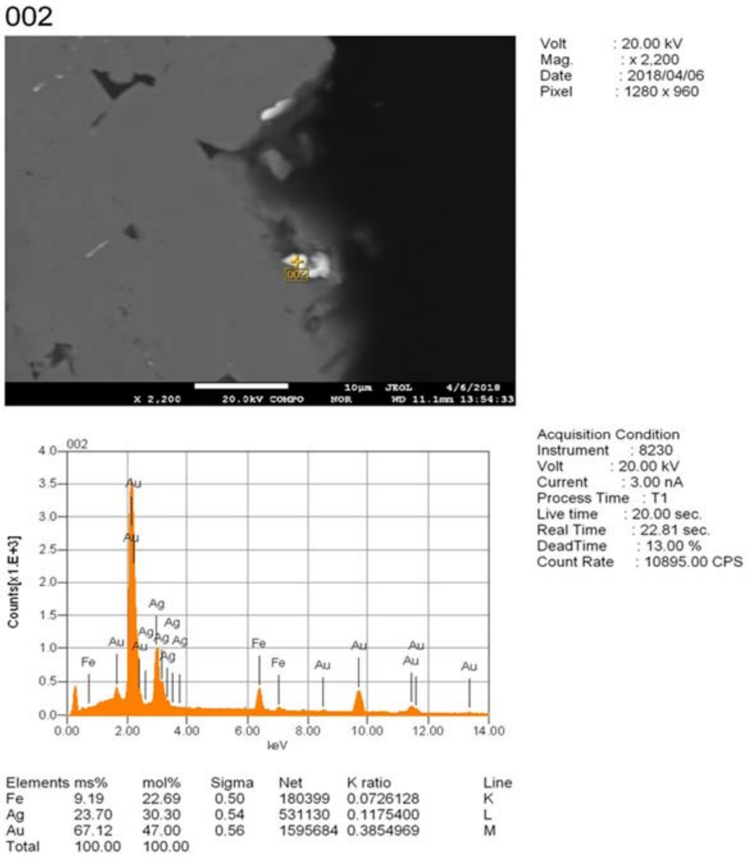


Volt : 20.00 kV
Mag. : x 370
Date : 2018/04/06
Pixel : 1280 x 960

Acquisition Condition
Instrument : 8230
Volt : 20.00 kV
Current : 5.00 nA
Process Time : T1
Live time : 20.00 sec.
Real Time : 22.85 sec.
DeadTime : 13.00 %
Count Rate : 12412.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
Fe	2.68	8.22	0.33	69344	0.0290299	K
Ag	9.96	15.81	0.39	271337	0.0624530	L
Au	87.36	75.97	0.37	2797821	0.7029970	M
Total	100.00	100.00				

Figure 3 – The high-grade gold in pyrite. The size of gold particles 3–4 µm, EDS mode, x370



Volt : 20.00 kV
Mag. : x 2,200
Date : 2018/04/06
Pixel : 1280 x 960

Acquisition Condition
Instrument : 8230
Volt : 20.00 kV
Current : 3.00 nA
Process Time : T1
Live time : 20.00 sec.
Real Time : 22.81 sec.
DeadTime : 13.00 %
Count Rate : 10895.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
Fe	9.19	22.69	0.50	180399	0.0726128	K
Ag	23.70	30.30	0.54	531130	0.1175400	L
Au	67.12	47.00	0.56	1595684	0.3854969	M
Total	100.00	100.00				

Figure 4 – Electrum (2 grains) in arsenic pyrite. The size of the analyzed grain is about 2 µm, EDS mode, x2200

Table 3 – The GRG test results for sulfur, arsenic and carbon

Product	Output, %	Content,%			Extraction, %		
		S	As	C	S	As	C
1 Stage 100 % –1.2 mm							
Concentrate 1	1.15	8.32	0.94	0.38	12.77	9.03	0.61
Tails 1	98.85	0.66	0.11	0.72	87.23	90.97	99.39
Ore	100.00	0.75	0.12	0.72	100.00	100.00	100.00
2 Stage 80% –0.3 mm							
Concentrate 2	1.43	6.08	0.79	0.77	11.19	10.28	1.83
Tails 2	98.57	0.70	0.10	0.60	88.81	89.72	98.17
Tails 1	100.00	0.78	0.11	0.60	100.00	100.00	100.00
3 Stage 80% –0.071 mm							
Concentrate 3	1.43	5.14	0.75	0.55	12.99	10.79	1.16
Tails 3	98.57	0.50	0.09	0.68	87.01	89.21	98.84
Tails 2	100.00	0.57	0.10	0.68	100.00	100.00	100.00
Total							
Concentrate 1	1.15	8.32	0.94	0.38	13.02	9.08	0.65
Concentrate 2	1.41	6.08	0.79	0.77	11.72	9.40	1.61
Concentrate 3	1.39	5.14	0.75	0.55	9.77	8.80	1.13
Concentrate 1+2+3	3.96	6.40	0.82	0.58	34.52	27.27	3.39
Tails 3	96.04	0.50	0.09	0.68	65.48	72.73	96.61
Ore	100.00	0.73	0.12	0.68	100.00	100.00	100.00

The content of components in the total gravity concentrate was: Au 21.63 g/t, S 6.40%, As 0.82%, C(organic) 0.58%. The extraction of the components in the total concentrate is as follows, %: Au 39.58; S 34.52; As 27.27; C(organic) 3.39.

The extraction of gold in the first stage is lower than in the subsequent stages. This indicates the absence of large gold in the ore. This is more clearly seen in Figure 5, which shows the change in the extraction of gold and related components by stages.

Figure 6 shows the total extraction of gold, sulfur, arsenic, and organic carbon extracted by gravity at various sizes.

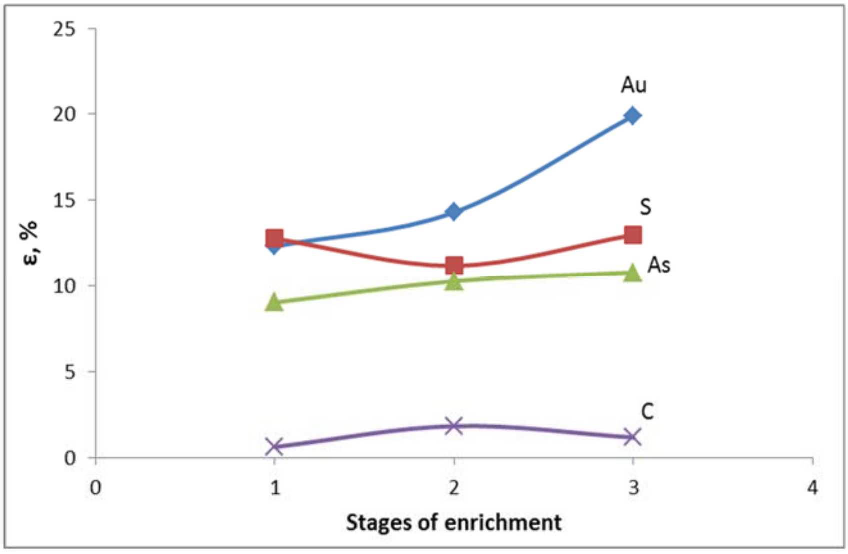


Figure 5 – Extraction of gold, sulfur, arsenic and organic carbon by stages of enrichment (from operation)

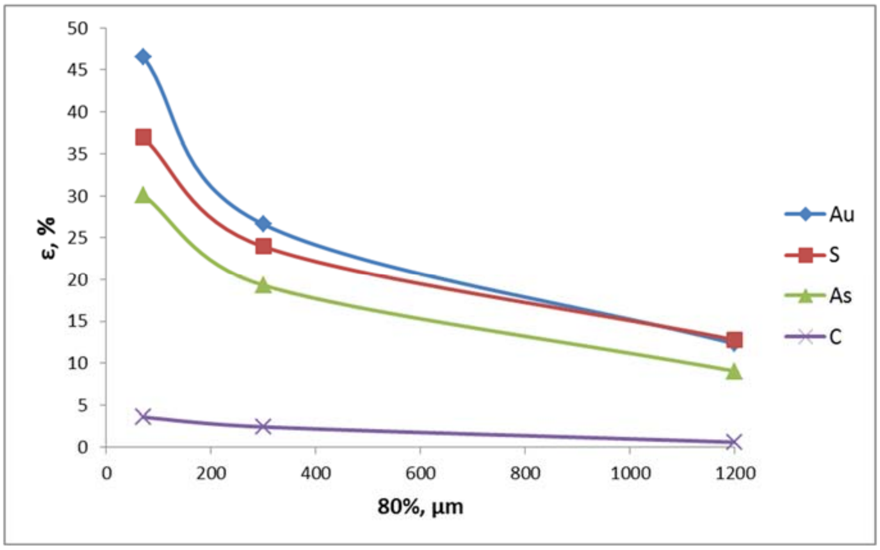


Figure 6 – The total percentage of gold, sulfur, arsenic and organic carbon extracted by gravity at different ore sizes

The nature of the curves for the total extraction of gold and related components (especially sulfur) is identical, which once again confirms the close relationship of gold with these components, which is confirmed by mineralogical analysis (figures 3–4).

First of all, free gold passes into gravity concentrate, if it is present in ore. In the absence of free gold, those sulfide minerals with which gold is associated are transferred to the gravity concentrate, i.e. pyrite and arsenopyrite. The sizes of pyrite grains are mainly from thousandths to 0.05 mm, in some cases up to 0.1 and 0.4–0.5 mm (figure 7), and the sizes of arsenopyrite are 0.02 mm.

The behavior of sulfur and arsenic during gravity concentration is similar to the behavior of gold. These data once again confirm that the main amount of gold is closely associated with arsenopyrite (arsenic pyrite) and pyrite.

The behavior of organic carbon during gravity concentration is significantly different. Only 3–4% of organic carbon passes into the gravity concentrate from ore, which reduces the persistence of the concentrate. The most (96–97%) of organic carbon remains in the tails of gravity.

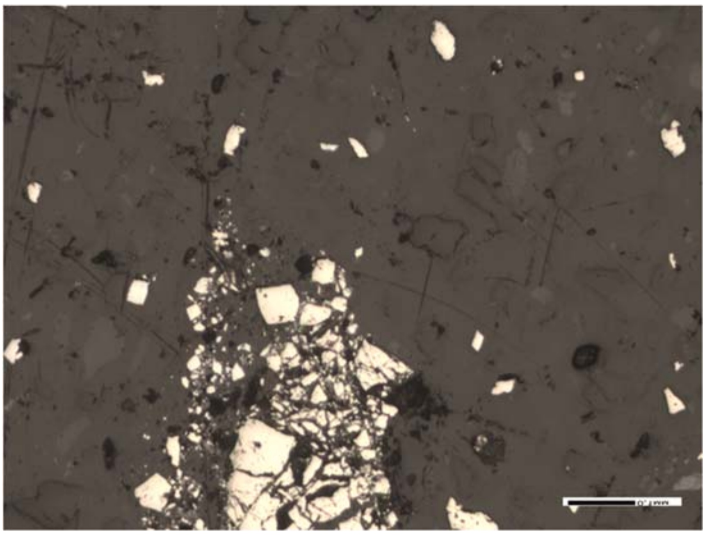


Figure 7 – Gravity concentrate. In the field of view are single crystals of pyrite and its accumulations. Polished artificial briquette, x100

Conclusion. In the gravity concentration of refractory carbonaceous arsenic-containing sulfide ore, gold and sulfide minerals (arsenopyrite, pyrite) with which it is associated are effectively extracted into the gravity concentrate. The extraction of gold and sulfur reached 34–39%, arsenic 27%. The extraction of organic carbon in the gravity concentrate amounted to only about 3.5%. Thus, the gravity concentration method can significantly reduce the content of organic carbon in the enriched product and, accordingly, reduce the persistence of the obtained product during further processing.

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КҮРДЕЛІ БАЙЫТЫЛАТЫН КЕННЕН АЛТЫНДЫ ГРАВИТАЦИЯЛЫҚ БАЙЫТУ КЕЗІНДЕГІ КҮКІРТ, КҮШАЛА ЖӘНЕ ОРГАНИКАЛЫҚ КӨМІРТЕКТІҢ ӘСЕРІ

Аннотация. Күрделі байытылатын алтынқұрамды технологиялық кеннің кеңірек таралу себебі – алтынның сульфидті минералдармен тығыз байланыстылығында. Мұндай минералдар көбінесе темір мен күшала сульфидтері: пирит және арсенопирит.

Күрделі байытылатын алтынқұрамынды кенде алтын-цианидті кешенге қатысты сорбциялық белсенді органикалық көміртекті зат бар («preg-robbing» әсері), бұл шикізатқа қосымша беріктік сипат береді. Сондықтан мұндай шикізат көбінесе екі есе берік шикізат деп аталады. Кенде көміртекті заттардың болуы цианирлеу үдерісін күрделендіріп қана қоймай, бағалы компоненттің төмен бөліну салдарынан оны тиімсіз етеді. Кен құрамына кіретін көміртекті заттардың сорбциялық белсенділігін төмендету үшін гравитация, флотация, хлормен гидрохимиялық тотықтыру, автоклавтық және бактериялық тотықтыру және т.б. қамтитын әртүрлі әдістер мен технологиялық тәсілдер қолданылады. Көміртекті-күшала сульфидті алтынқұрамды кен өңдеудің бастапқы әдістерінің бірі гравитациялық байыту болып саналады. Гравитациялық әдістермен кеннің байытылу үдерісін бағалау үшін өндірісте жиі арнайы GRG тест (Gravity recoverable gold test) қолданылады.

Жұмыстың мақсаты – күрделі байытылатын алтынқұрамды кенді гравитациялық байыту кезіндегі күкірт, күшала және органикалық көміртектің әсерін зерттеу.

Зерттеу нысаны – Шығыс Қазақстан облысындағы алтынқұрамынды кен. Сынамалы-гравиметрлік талдау нәтижелері бойынша кендегі алтынның орташа құрамы тоннасына 2,29 г құрайды. Сынамадағы күшала мөлшері 0,17 % құрады. Кенде барлық күкірт сульфид түрінде ұсынылған. Сульфидті күкірттің құрамы бойынша сынама аз сульфидті типке жатқызылған. Күкірттің фазалық құрамы бойынша сынама кеннің сульфидті типіне жатады.

Визуалды түрде де және талдау нәтижесінде де сынамада көмірлі сланцтердің болатыны расталады. Көмірлі сланцтер цианидте еріген алтынның табиғи сорбенттері болып саналады. Мұндай кен күрделі байытылатын кенге жатады, олардан алтынды алу қиын. Сынамадағы органикалық көміртек мөлшері 0,61 % құрады. Зертеуге берілген алтын құрамынды кен күрделі байытылатын көміртекті-күшала типтес сульфидті кенге жатады.

Кеннің гравитациялық байыту жұмысын бағалау үшін Нельсон KC-MD3 зертханалық 3 дюймдік центрден тепкіш концентраторы қолданылды. GRG сынағының нәтижелері бойынша алтынның жалпы бөлінуі 39,58 %, концентраттың жалпы шығымы 3,96 % құрады. Бірінші сатыдағы алтынның жалпы бөлінуі кейінгі сатыларға қарағанда азырақ. Бұл кенде ірі алтынның жоқтығын көрсетеді. Гравитациялық байыту кезінде күкірт және күшаланың бөлінуі алтынның бөлінуіне ұқсас. Бұл деректер алтынның арсенопиритпен (күшала пиритімен) және пиритпен байланысты екенін растайды. Гравитация кезіндегі органикалық көміртектің бөлінуі айтарлықтай ерекшеленеді. Гравитациялық концентратқа кеннен органикалық көміртектің небәрі 3,39 % өтеді, бұл концентрат беріктігін төмендетеді. Органикалық көміртектің көп бөлігі (96,61 %) гравитация қалдықтарында қалады. Жиынтық гравитациялық концентраттағы компоненттердің құрамы Au – 21,63 г/т, S – 6,40 %, As – 0,82 %, C (органикалық) – 0,58 % құрады. Компоненттерді жиынтық концентратқа бөлінуі, %: Au – 39,58; S – 34,52; As – 27,27; C (органикалық) – 3,39. Осылайша, гравитациялық байыту байытылған өнімдегі органикалық көміртек мөлшерін айтарлықтай азайтуға және одан әрі өңдеу кезінде алынған өнімнің беріктігін төмендетуге мүмкіндік береді.

Түйін сөздер: күрделі байытылатын кен, preg-robbing, күрделі байытылатын қос кен, гравитациялық байыту әдістері, GRG тест, алтынқұрамды кен, көміртекті-күшала сульфидті кен.

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ПОВЕДЕНИЕ СЕРЫ, МЫШЬЯКА И ОРГАНИЧЕСКОГО УГЛЕРОДА ПРИ ГРАВИТАЦИОННОМ ОБОГАЩЕНИИ ЗОЛОТА ИЗ УПОРНОЙ РУДЫ

Аннотация. Наиболее распространенной причиной технологической упорности золотосодержащих руд является тонкая вкрапленность золота, тесно ассоциированного с сульфидными минералами. Такими минералами чаще всего являются сульфиды железа и мышьяка: пирит и арсенопирит.

В некоторых упорных золотосодержащих рудах содержится также органическое углистое вещество, обладающее сорбционной активностью по отношению к золотоцианидному комплексу (эффект «preg-robbing»), что придает сырью дополнительную упорность. Поэтому такое сырье часто называют сырьем двойной упорности. Наличие в рудах углеродистых веществ не только затрудняет процесс цианирования, но и делает его нерентабельным вследствие низкого извлечения ценного компонента. Для снижения сорбционной активности углеродистого вещества, входящего в состав руды, применяют различные методы и технологические приемы, которые включают гравитацию, флотацию, гидрохимическое окисление хлором, автоклавное и бактериальное окисление и т.д. Одним из первичных методов переработки углисто-мышьяковистых сульфидных золотосодержащих руд является гравитационное обогащение. Для оценки обогатимости руд гравитационными методами чаще всего в производстве используют специальный GRG тест (Gravity recoverable gold test).

Целью работы является изучение поведения серы, мышьяка и органического углерода при гравитационном обогащении упорной золотосодержащей руды.

Объектом исследований является золотосодержащая руда одного из месторождения Казахстана в Восточно-Казахстанской области. По результатам пробирно-гравиметрического анализа среднее содержание золота в руде составляет 2,29 г/т. Промышленно ценным компонентом в пробе является только золото. Содержание мышьяка в пробе составило 0,17 %. Практически вся сера представлена сульфидной формой. По содержанию сульфидной серы проба отнесена к убогосульфидному типу. По фазовому составу серы проба отнесена к первичному типу руды.

Визуально и анализом подтверждается наличие в пробе углистых сланцев. Углистые сланцы являются природными сорбентами растворенного в цианиде золота. Такие руды относят к упорным рудам, извлечение золота из которых затруднено. Содержание органического углерода в пробе составило 0,61 %. Золотосодержащая руда относится к упорным углистым мышьяксодержащим сульфидным рудам.

Проведена оценка гравитационной обогатимости руды на лабораторном 3-х дюймовом центробежном концентраторе Нельсона KC-MD3. По результатам GRG теста суммарное извлечение золота составило 39,58 % при выходе суммарного концентрата 3,96 %. Извлечение золота на первой стадии более низкое, чем на последующих стадиях. Это указывает на отсутствие в руде крупного золота. Поведение серы и мышьяка, при гравитационном обогащении аналогично поведению золота. Эти данные подтверждают, что основное количество золота ассоциировано с арсенопиритом (мышьяковистым пиритом) и пиритом. Поведение органического углерода при гравитации существенно отличается. В гравитационный концентрат из руды переходит всего 3,39 % органического углерода, что снижает упорность концентрата. Большая часть (96,61 %) органического углерода остается в хвостах гравитации. Содержание компонентов в суммарном гравитационном концентрате составило: Au – 21,63 г/т, S – 6,40 %, As – 0,82 %, C(органическая) – 0,58 %. Извлечение компонентов в суммарный концентрат следующее, %: Au – 39,58; S – 34,52; As – 27,27; C(органическая) – 3,39. Таким образом, гравитационное обогащение позволяет существенно снизить содержание органического углерода в обогащенном продукте и, соответственно, снизить упорность полученного продукта при дальнейшей переработке.

Ключевые слова: упорные руды, preg-robbing, руды двойной упорности, гравитационные методы обогащения, GRG тест, золотосодержащая руда, углисто-мышьяковистые сульфидные руды.

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SYNTHESIS OF CARBON NANOTUBES BY THE ELECTRIC ARC-DISCHARGE METHOD

Abstract. The paper presents the synthesis of carbon nanotubes (CNTs) by the method of electric arc-discharge. To obtain CNTs, the process of an electric arc-discharge of graphite was carried out; the current strength at a constant voltage of 50 V was 120, 150, 170, 200 A (inert medium - argon). Using the methods of electron microscopy, BET and Raman scattering, the chemical composition, specific surface area were determined, and the surface morphology of the obtained samples was studied. The results of determining the specific surface area and pore volume show that with increasing current strength, the specific surface area and specific pore volume increase from 25.450 to 159.737 m^2/g and from 0.011 cm^3/g to 0.068 $cm^3/$ g, respectively. Electron microscopic images show CNT particles with a diameter of 58 to 370 nm, which are rolled into a single, seamless, cylindrical shape.

Keywords: CNT, graphite, electric arc-discharge, specific surface area, graphitization.

Introduction. Analysis of the state and development trends of nanoindustry objects at present allows us to conclude that one of the most promising areas of nanotechnology is the synthesis of carbon nanomaterials (CNM) - graphene, graphene oxide, MWCNT, SWCNT, fullerene-like structures, which are a new allotropic form of carbon in the form of closed, framework, macromolecular systems. Among these materials, a special place is occupied by carbon nanotubes (CNTs), which with diameters from 1 to 50 nm and lengths up to several micrometers form a new class of quasi-one-dimensional nanoobjects. CNTs have a number of unique properties due to the ordered structure of their nanofragments: good electrical conductivity and adsorption properties, the ability to cold electron emission and gas accumulation, diamagnetic characteristics, chemical and thermal stability, high strength combined with high values of elastic deformation. Materials created on the basis of CNTs can be successfully used as structural modifiers of structural materials, hydrogen accumulators, electronic elements, additives to lubricants, varnishes and paints, high-performance adsorbents, gas distribution layers of fuel cells. The use of carbon nanostructures in fine chemical synthesis, biology, and medicine is widely discussed [1].

The developed surface and structure of CNTs determines their unique electrochemical and sorption properties when the conditions for their filling with gaseous or liquid substances are realized. CNTs can be considered as a unique capacity for storing substances in a gaseous, liquid or even solid state [2-4], since the graphite shell provides a fairly good protection of the material contained in it from external chemical or mechanical stress. They have found application for obtaining high-temperature heat-insulating composite materials [5,6], modified electrodes [7,8], sorbents [9], nanofibers [10] of catalytic systems [11-12], as well as in medicine, security and defense devices , devices for the generation and storage of electricity, transport, communications, computer technology, building materials [13]. Among the most important properties of CNTs, the relationship between the geometric structure of a nanotube and its electronic characteristics should be mentioned first of all [14-16]. The widespread use of CNTs requires the production of a large amount of material at a low cost. Therefore, the development of low-cost methods for the synthesis of CNTs is urgent.

Among the advantages of carbon nanotubes are:

1. Many unique and truly useful properties that can be used in the implementation of energy efficient solutions, photonics, electronics, and other applications;

2. It is a nanomaterial that has a high coefficient of strength, excellent thermal and electrical conductivity, and fire resistance.

3. Improving the properties of other materials by incorporating a small amount of carbon nanotubes into them;

4. Carbon nanotubes with an open end exhibit a capillary effect, that is, they can draw in molten metals and other liquid substances;

5. Nanotubes combine the properties of solids and molecules, which opens up significant prospects.

The predominant methods currently used to synthesize CNTs from coal are based on thermal plasma, chemical vapor deposition (CVD) and arc discharge methods.

Currently, the synthesis of CNTs is based on the methods of thermal plasma [17], chemical vapor deposition (CVD) [18] and arc discharge [19]: Tian et al. [14] were the first to develop a thermal plasma method for obtaining multi-walled CNTs (MWCNTs) from coal, the second one based on the thermal decomposition of carbon-containing gases (chemical vapor deposition), accompanied by gas-phase chemical deposition (GPCD) of crystalline nanocarbon on metal catalysts. The third method of synthesis consists in the evaporation of graphite and the subsequent condensation of the product when the vapor is cooled in an arc discharge.

The most widespread method for producing CNTs is using thermal sputtering of a graphite electrode in the plasma of an arc-discharge burning in a helium atmosphere. The method used in 1991 by the Japanese scientist S. Ijima [20] differed from the method of obtaining fullerenes in that the electrodes did not come into contact with each other, but were at some distance from each other during the arc burning. Under these conditions, carbon evaporating from the anode is condensed on the cathode in the form of a deposit of a predominantly cylindrical shape. Carbon nanotubes were obtained in the form of sharp needles with a diameter of 4 to 30 nm and a length of 1 μm at the negative end of a carbon electrode at a constant arc discharge current. Graphite electrodes were placed in a volume filled with argon atmosphere..

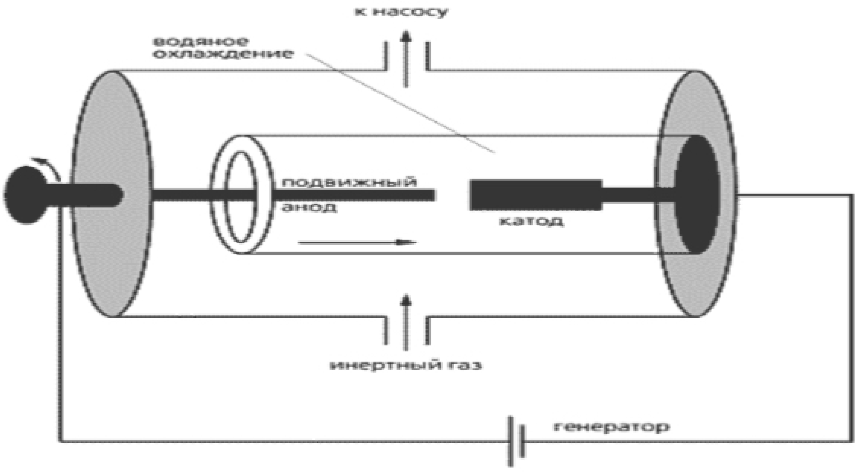


Figure 1 - Scheme of graphite sputtering in an electric arc plasma

Studying the structure of needles consists of coaxial tubes nested within each other, which, in turn, consist of hexagonal graphite networks, in the nodes of which carbon atoms are located. The winding angle can vary from tube to tube, as well as within a single tube. The tops of carbon nanotubes are closed with caps consisting of hexagons and pentagons, as is the case in the structure of the C_{60} fullerene molecule.

Carbon nanotubes combine the properties of molecules and solids and can be regarded as an intermediate state of matter. This feature attracts constant attention of researchers studying the fundamental features of the behavior of such an exotic object in various conditions. These features, which are of significant scientific interest, can form the basis for the effective applied use of nanotubes in various fields of science and technology [21].

The purpose of this work is to synthesize carbon nanotubes (CNTs) by the electric arc-discharge method and to study the physicochemical properties of the samples obtained.

We have chosen the method of electric arc-discharge to obtain CNTs, since this method is acceptable in laboratory conditions. The electric arc method is currently the most common method for obtaining defect-free CNTs. The essence of the method consists in thermal sputtering of a graphite electrode in the plasma of an arc discharge burning in an inert gas atmosphere.

To obtain CNTs, the process of an electric arc-discharge of graphite was carried out, the current strength at a constant voltage of 50 V was 120, 150, 170, 200 A (in an inert atmosphere of argon) (figure 1).

Figure 1 - Installation for producing CNTs by electrophysical method

The elemental composition, structure, and dimensions of the samples were studied by energy dispersive X-ray spectroscopy on an SEM device (Quanta 3D 200i) with an EDAX attachment for energy dispersive analysis.

The study of the type of carbon modification was carried out using Raman spectroscopy using the method of Raman light scattering (RS). The Raman spectra of the samples were recorded on a HORIBA Jobin Yvon instrument and an Integra Spectra scanning probe microscope using a laser with a radiation wavelength of 473 nm. Installation parameters: power - 35 mW, solid-state laser, grating –600/600.

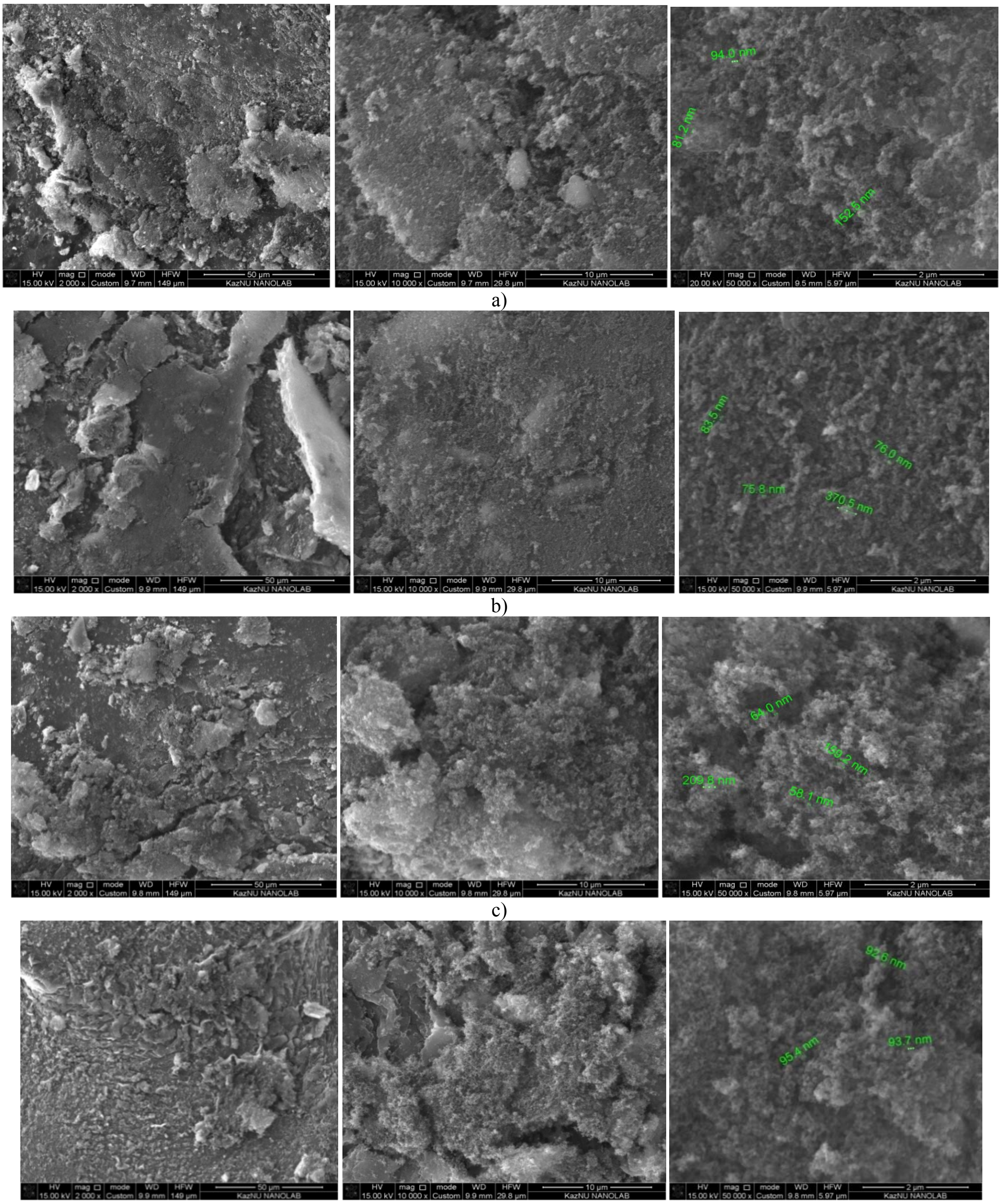
Specific surface area, specific pore volume by limiting filling were studied by the Brunauer-Emmett-Teller (BET) method. The measurements were carried out on a KATAKON Sorbtometer M.

The results of the performed elemental analysis and determination of the specific surface area and pore volume presented in Table 1 show that with an increase in the current strength, the specific surface area and specific pore volume increase from 25.450 to 159.737 m^2/g and from 0.011 cm^3/g to 0.068 cm^3/g, respectively.

Table 1 - Physicochemical characteristics of CNTs obtained from graphite by electric arc-discharge

Current strength, A	Elemental composition, %					Specific surface, m^2/g	Specific pore volume, cm^3/g
	C	O	Si	Fe	Cl		
120	86,64	12,19	0,90	-	0,26	25,450	0,011
150	88,42	11,14	0,44	-	-	56,203	0,024
170	87,04	12,48	-	0,48	-	159,737	0,068
200	85,04	13,19	0,50	1,27	-	140,143	0,060

As can be seen from the research data, the highest specific surface area - 159.737 m^2/g is observed where the current strength was 170 A, at a constant voltage of 50 V (in an inert argon atmosphere).



a)

b)

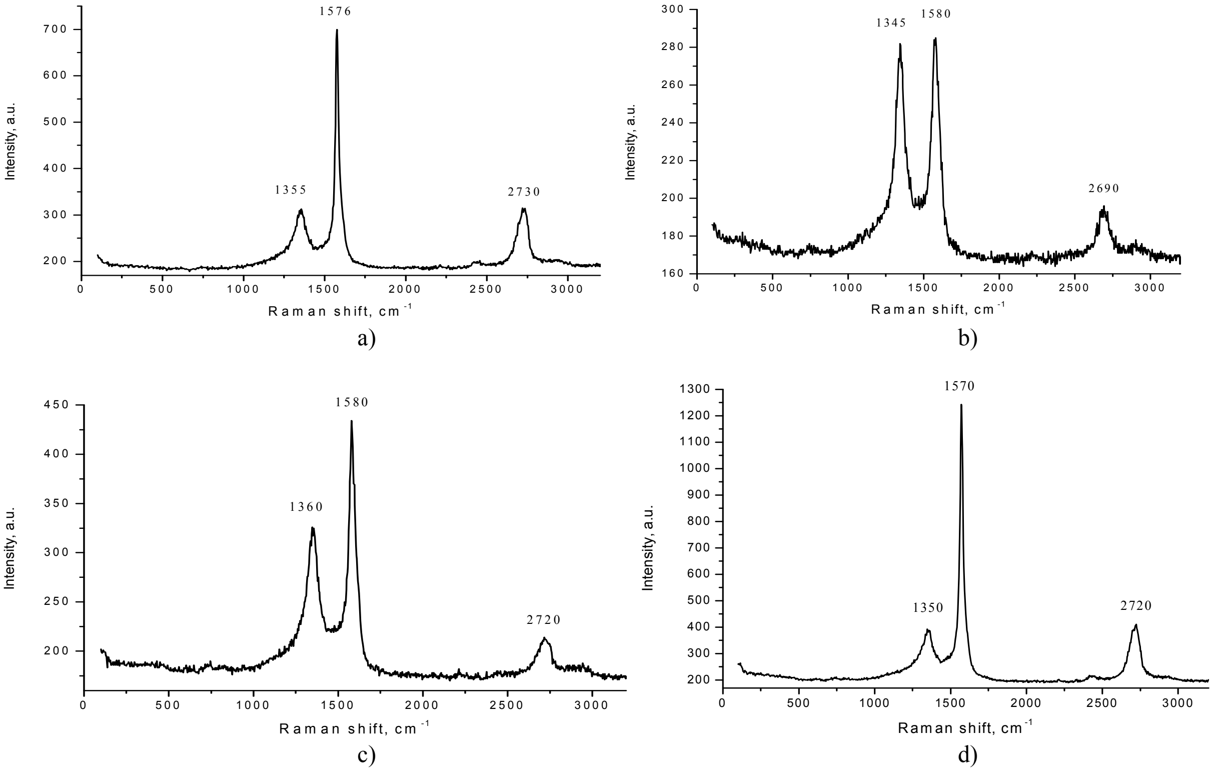
c)

d)

Figure 2 - Electron microscopic images of CNTs at current strength: a) 120; b) 150; c) 170; d) 200 A

The electron microscopic images shown in Figures 2 show that CNT particles with a diameter of 58 to 370 nm are rolled into a single, seamless, cylindrical shape. The length of nanotubes can reach tens of micrometers; the end of such a tube can be open or closed by a fullerene-like hemisphere. The cylindrical surface of the tubes is formed by hexagons. In real nanotubes [22], due to the existence of pentagons and heptagons and structural defects, the formation of bridges and the curvature of the cylindrical surface are observed.

Figure 3 shows the Raman spectra of CNTs obtained after an electric arc-discharge at 120, 150, 170, 200 A, which contain graphite-like carbon of varying degrees of crystallinity and order.



a) b) c) d)

Figure 3 - Raman spectra of CNTs after an electric arc-discharge at a current strength of:
a) 120; b) 150; c) 170; d) 200 A

We have determined the ratio of the intensity of the peak G to D (IG / ID) in order to assess the quality of carbon-based materials in terms of the presence of defects [23-26]. The higher the ratio of G to D, the higher the quality of the materials. The Raman spectra (figure 3a) of the obtained materials showed three peaks at 1355 and 2730 cm^{-1}, corresponding to peaks D and 2D (signal with a defect) and 1576 cm^{-1} signal G (graphite order), respectively. Increasing the current at a constant voltage of 50 V and a current of 120 A showed an IG / ID ratio of 2.33, which is indicated by the presence of defects. Increasing the current, increases the temperature in the arc, i.e. between the two electrodes and the process of carbonization of the carbon material is accelerated. With an increase in the current of 170 A (figure 3 (c)), the process proceeds with the formation of graphite at 1580 cm^{-1} and graphene at 2720 cm^{-1}, as well as CNTs, as indicated by the high ratio IG / ID = 1.271. With an increase in the current strength of 200A (figure 2 (d)), the carbonization process proceeds with the formation of predominantly graphite-like materials. As shown by the Raman spectrum, a weak peak at 1350 cm^{-1} and a high signal intensity at 1570 cm^{-1} G, as well as a weak 2D peak at 2720 cm^{-1} indicate a high IG / ID ratio of 3.25.

A narrow intense peak G at 1582 cm^{-1} together with a weakly pronounced peak D at 1365 cm^{-1} are characteristic of rather large (on the order of several micrometers) graphite particles. The appearance of a peak in the region of ~ 2700 cm^{-1} (2D peak) indicates a certain ordering of the structure under study. The broadening of the peaks, as well as an increase in the intensity of the 2D defect peak, indicate the presence of the formation of carbon nanotubes. Broadening of peaks in Raman spectra, as well as an increase in the intensity of the defect peak D, indicate the presence of the presence of finely dispersed graphite particles and the formation of carbon nanotubes.

Thus, the method for producing carbon nanotubes is based on the electric arc-discharge of graphite, which is the most promising method for the industrial production of CNTs and provides a product with a relatively high multilayer fraction and uniformity of the fraction, which determines the achievement of the strength characteristics required for structural materials.

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ЭЛЕКТРДОҒАЛЫ ӘДІС БОЙЫНША КӨМІРТЕКТІ НАНОТҮТІКШЕ СИНТЕЗІ

Аннотация. Мақалада электрдоғалы әдісімен көміртекті нанотүтікшелер (КНТ) синтезі ұсынылған. КНТ алу үшін графитті электрдоғалы разрядтау үдерісі жүргізілді, 50 В тұрақты кернеудегі ток күші 120, 150, 170, 200 А құрады (инертті орта – аргон). Электронды микроскопия, БЭТ және Раман - спектроскопия әдістері арқылы үлгілердің химиялық құрамы, бетінің меншікті ауданы анықталды, алынған үлгілердің беткі морфологиясы зерттелді. Беттің меншікті ауданы мен кеуек көлемін анықтау нәтижелері көрсеткендей, ток күштің артуымен беттің меншікті ауданы және кеуек көлемі 25,450 ден 159,737 м^2 / г дейін және сәйкесінше 0,011 см^3/г-ден 0,068 см^3/г дейін артады. Электронды микроскопиялық суреттерде диаметрі 58-ден 370 нм-ге дейінгі КНТ бөлшектері көрсетілген, олар біртекті, цилиндрлік пішін құрайды. Нанотүтікшелердің ұзындығы ондаған микрометрге жетуі мүмкін, мұндай түтіктің соңы фуллеренге ұқсас жарты шармен ашылуы немесе жабылуы мүмкін. Раман спектрінде тар қарқынды G шыңы 1582 см$^{-1}$-де және ірі (бірнеше микрометр) графит бөлшектеріне тән 1365 см$^{-1}$-де D айқын емес шыңы байқалады. ~ 2700 см$^{-1}$ (шыңы 2D) аймақта шыңның пайда болуы зерттелетін құрылымның белгілі бір реттілігін айқындайды. Шыңның кеңеюі, сондай-ақ 2D шыңының қарқындылығының артуы көміртекті нанотүтікшелердің пайда болуын көрсетеді.

Жұмыста көміртекті нанотүтікшелерді (КНТ) электрдоғалы тозаңдату әдісімен синтездеу ұсынылған. Электрдоғалы әдісі қазіргі уақытта ақаусыз КНТ алудың көп таралған әдісі болып саналады. Әдістің мәні – инертті газ атмосферасында жанатын доға разрядты плазмадағы графит электродының термиялық шашырауы.

Үлгілердің элементтік құрамын, құрылымын және өлшемін зерттеу EDAX-тен энергия дисперсиясын талдауға арналған префиксі бар СЭМ (Quanta 3D 200I) құрылғысында энергияны дисперсиялық рентгендік спектроскопия әдісімен жүргізілді. Көміртекті модификациялау түрін зерттеу Раман спектроскопиясы арқылы жарықтың комбинациялық шашырау әдісін (ЖКШ) қолдану арқылы жүргізілді. ЖКШ спектрлері HORIBA Jobin Yvon аспабында және Integra Spectra зондты сканерлеу микроскопында, толқын ұзындығы 473 нм болатын лазерді қолдана отырып жазылды. Орнату параметрлері: қуаты – 35 мВт, қатты күйдегі лазер, тор – 600 / 600. Бетінің меншікті ауданы, шекті толтыру бойынша меншікті кеуек көлемі Брунауэр-Эммет-Теллер (БЭТ) әдісімен зерттелді. Өлшеу Sorbtometer m катаконында жүргізілді. Беттің меншікті ауданы мен меншікті кеуек көлемін анықтау нәтижелері ток күшінің ұлғаюы кезінде нақты беті мен меншікті кеуек көлемі сәйкесінше 25,450-ден 159,737 м^2/г-ға дейін және 0,011 см^3/г-ден 0,068 см^3/г-ге дейін ұлғаятынын көрсетеді. Электронды микроскопиялық суреттерде диаметрі 58-ден 370 нм-ге дейінгі КНТ бөлшектері көрінеді, олар тұтас, тігіссіз, цилиндрлік пішінге оралған. Нанотүтікшелердің ұзындығы ондаған микрометрге жетуі мүмкін, мұндай түтіктің ұшы ашық немесе жабық фуллерен тәрізді жарты шар болуы мүмкін. ЖКШ спектрінде 1582 см$^{-1}$ кезіндегі G тар қарқынды шыңы, 1365 см-^{1} кезіндегі d сәл айқын шыңымен бірге графит бөлшектеріне тән (бірнеше микрометрге жуық). ~2700 см$^{-1}$ (2D шыңы) аймағындағы шыңның көрінісі зерттелетін құрылымның белгілі бір реттілігін көрсетеді. Шыңның кеңеюі, сондай-ақ ақаулы 2D шыңының қарқындылығының артуы көміртекті нанотүтіктердің пайда болуын көрсетеді. Біз ақаулардың болуы тұрғысынан көміртегі негізіндегі материалдардың сапасын бағалау үшін G шыңының D (IG/ID) қарқындылығының арақатынасын анықтадық. G-нің D қатынасы неғұрлым жоғары болса, материалдардың сапасы соғұрлым жоғары болады. Алынған материалдардың комбинациялық шашырау спектрлері сәйкесінше D және 2D шыңдарына (ақауы бар сигнал) сәйкес келетін 1355 және 2730 см$^{-1}$ және 1576 см$^{-1}$ G сигналына (графит реті) сәйкес келетін үш шыңды көрсетті. 50 В және 120А тұрақты кернеулердегі ток күшінің жоғарылауы IG/ID 2,33 қатынасын көрсетті, бұл ақаулардың болатынын білдіреді. Ток күшінің жоғарылауы доғадағы температураны жоғарылатады, яғни екі электрод арасында көміртекті материалды карбонизациялау үдерісі жеделдейді. 170 А ток күшінің жоғарылауымен (2 (в) сурет) үдеріс графит 1580 см$^{-1}$ және графен 2720 см$^{-1}$, сондай-ақ КНТ түзумен жүреді, бұл IG / ID = 1,271 жоғары қатынасын көрсетеді. 200А ток күшінің жоғарылауымен (2-сурет (г)) карбонизация үдерісі негізінен графит тәрізді материалдардың пайда болуы негізінде жүреді. ЖКШ көрсеткендей, облыстағы әлсіз шың 1350 см$^{-1}$ және сигналдың үлкен қарқындылығы 1570 см$^{-1}$ G, сондай-ақ 2720 см$^{-1}$ саласындағы әлсіз шың 2D IG / ID-нің 3,25-ке тең жоғары арақатынасын көрсетеді. Осылайша, көміртекті нанотүтікшелерді алу әдісі графиттің

электрдоғалы тозаңдануға негізделген, ол КНТ өнеркәсіптік өндірісінің ең перспективті әдісі болып саналады және салыстырмалы түрде жоғары қабатты және фракцияның біртектілігі бар өнім алуды қамтамасыз етеді, бұл құрылымдық материалдарға ұсынылған беріктік сипаттамаларына қол жеткізуді анықтайды.

Түйін сөздер: КНТ, графит, электрдоғалы шашырау, меншікті бет, графитизация

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СИНТЕЗ УГЛЕРОДНЫХ НАНОТРУБОК ЭЛЕКТРОДУГОВЫМ МЕТОДОМ

Аннотация. В работе представлен синтез углеродных нанотрубок (УНТ) методом электродугового распыления. Электродуговой способ в настоящее время является наиболее распространенным методом получения бездефектных УНТ. Суть метода состоит в термическом распылении графитового электрода в плазме дугового разряда, горящего в атмосфере инертного газа. Для получения УНТ проводился процесс электрического дугового разряда графита, сила тока при постоянном напряжении 50 В составила 120, 150, 170, 200 А (инертная среда-аргон). С использованием методов электронной микроскопии, БЭТ и комбинационного рассеяния определен химический состав, удельная поверхность и изучена морфология поверхности полученных образцов. Исследование элементного состава, структуры и размерности образцов проводили методом энергодисперсионной рентгеновской спектроскопии на приборе СЭМ (Quanta 3D 200i) с приставкой для энергодисперсионного анализа от EDAX. Изучение типа модификации углерода проводили с помощью Рамановской спектроскопии с использованием метода комбинационного рассеяния света (КРС). Спектры КРС образцов записывали на приборе HORIBA Jobin Yvon и зондовом сканирующем микроскопе Integra Spectra с использованием лазера с длиной волны излучения 473 нм. Параметры установки: мощность - 35 мВт, твердотельный лазер, решетка –600/600.Удельная площадь поверхности, удельный объем пор по предельному заполнению изучали методом Брунауэра-Эммета-Теллера (БЭТ). Измерения проводили на приборе КАТАКОН Sorbtometer M. Результаты определения удельной площади поверхности и объем пор показывают, что при увелечении силы тока удельная поверхность и удельный объем пор увеличиваются от 25,450 до 159,737 м^2/г и от 0,011 см^3/г до 0,068 см^3/г соответсвенно. На электронно-микроскопических снимках видны частицы УНТ с диаметром от 58 до 370 нм, которые свернуты в цельный, без швов, цилиндрческой формы. Длина нанотрубок могут достигать десятков микрометров, конец такой трубки может быть открытым или закрытым фуллереноподобной полусферой. На КРС спектрах обнаружен узкий интенсивный пик G при 1582 см$^{-1}$ вместе со слабовыраженным пиком D при 1365 см$^{-1}$ характерны для довольно крупных (порядка нескольких микрометров) графитовых частиц. Проявление пика в области ~2700 см$^{-1}$ (2D пик) указывает на определенную упорядоченность исследуемой структуры. Уширение пиков, а также увеличение интенсивности дефектного пика 2D свидетельствуют о наличии формирования углеродных нанотрубок. Нами определено соотношение интенсивности пика G к D (IG / ID) с целью оценки качество материалов на основе углерода с точки зрения наличия дефектов. Чем выше отношение G к D, тем выше качество материалов. Спектры комбинационного рассеяния полученных материалов показали три пика при 1355 и 2730 см$^{-1}$, соответствующим пикам D и 2D (сигнал с дефектом) и 1576см$^{-1}$ сигнал G (графитовый порядок), соответственно. Повышение силы тока при постоянном напряжении 50 В и тока 120А показало отношение IG/ID 2,33, на что указывает на наличие дефектов. Повышение силы тока повышает температуру в дуге, т.е. между двумя электродами и ускоряется процесс карбонизации углеродного материала. С повышением силы тока 170 А (рисунок 2 (в)) процесс идет с образованием графита 1580 см$^{-1}$ и графена 2720 см$^{-1}$, а также УНТ, на что указывает высокое отношение IG / ID = 1,271. С повышением силы тока 200А (рисунок 2 (г) процесс карбонизации протекает с образованием преимущественно графитоподобных материалов. Как показал КРС, спектр слабый пик в области 1350 см$^{-1}$ и большая интенсивность сигнала 1570 см$^{-1}$ G, а также слабый пик 2D в области 2720 см$^{-1}$ указывают на высокое соотношение IG / ID равной 3,25. Таким образом, способ получения углеродных нанотрубок построен на основе электродугового распыления графита, который является наиболее перспективным способом промышленного производства УНТ и обеспечивает получение продукта с относительно высокой многослойностью и однородностью фракции, что определяет достижение прочностных характеристик, предъявляемых к конструкционным материалам.

Ключевые слова: УНТ, графит, электродуговое распыление, удельная поверхность, графитизация.

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OPTIMIZATION OF TECHNOLOGICAL PARAMETERS OF HYDRAGENERATION PROCESS OF ACETYLENE USING A PILOT CATALYTIC PLANT

Abstracts. A pilot plant was launched and the modes of acetylene hydrogenation on cobalt catalysts were worked out. It has been found that the modified 7% Co/ SiAl cobalt catalyst is active in the process of hydrogenating acetylene into ethylene. Optimal conditions of acetylene hydrogenation on 7% Co/ SiAl catalyst were determined. The effects of temperature, space velocity and the ratio of initial components in the hydrogenation of acetylene to ethylene were investigated.

The textural characteristics of cobalt catalysts before and after the hydrogenation of acetylene were investigated by the SEM method. The structure of cobalt catalysts after the hydrogenation of acetylene does not lose catalytic activity and selectivity. It has been found that catalyst samples have channels of different sizes, flaky particles and fibers located in the gaps between large aggregates are also present on the surface.

The optimum temperature was 180 ° C in the hydrogenation of acetylene into ethylene at conversion 73.0%. Conversion of acetylene increases to 81.2% when temperature rises to 200°C, acetylene conversion decreases to 68% with further temperature exceeding to 220°C. Acetylene conversion again increases from 68 to 73.6% at 140°C in the ratio of acetylene to hydrogen 1:2. The selectivity of the catalyst 7%Co/SiAl to ethylene was studied depending on the temperature in the acetylene hydrogenation reaction. The selectivity to ethylene decreases with increasing temperature, since an increase in temperature activates side reactions.

Key words: catalytic unit, hydrogenation, acetylene, ethylene, catalysts.

Indruction. The main factor of large-scale production of light unsaturated compounds such as ethylene, propylene, butenes and other aromatic compounds (benzene, toluene, xenones etc.) is a pyrolysis of petrol content such as naphtha and liquefied petroleum gases, at thermal conversion with olefins forms acetylene and diene hydrocarbons in small amounts. Their selection is often economically ineffective. Their presence as an impurity in product disable further use of olefins for polymerization processes [1-4]. Thus, acetylene hydrocarbons have a poison effect on polymerization catalysts of ethylene, and their content in ethylene fraction supplied to polymerization should be below 1 ppm. In this regard, one of the most important tasks when preparing raw materials in order to produce various polymers is a hydrogenation of diene and acetylene hydrocarbons without complete hydrogenation of olefins, which contain only one double bond in their composition to alkanes. In industry, for selective hydrogenation, there are used precious metal based catalysts, predominantly palladium. The price of such catalysts has been high for a long time due to significant metal content (1-5%). At present, it has been shown that it is possible to create heterogeneous catalysts for selective hydrogenation of diene and acetylene hydrocarbons with a low metal content and a narrow distribution in size [5, 6].

Experimental part. The basic process flow diagram of the plant for hydrogenation of acetylene is shown in figure 1. The plant for hydrogenation of acetylene includes a stainless steel reactor; rector heating system (oven with thermo regulator), gas supply unit, gas supply system and measurement of gas consumption; means of regulation and control of pressure, made in the form of solenoid valve, a gas pressure guard and a pressure gauge; gas mixer (evaporator) and heater with thermostat, separator with cold water circulation system and gas chromatograph.

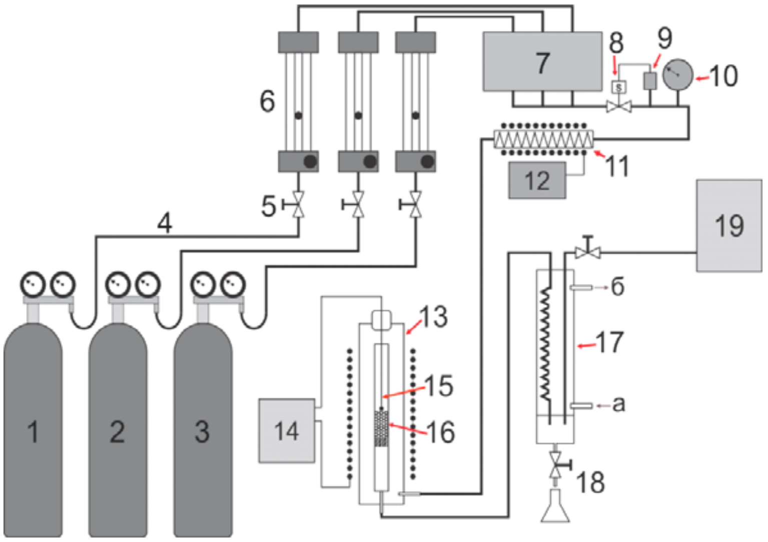

Figure 1 - Scheme of catalytic plant for selective hydrogenation of acetylene

1, 2, 3 - gas cylinder; 4 - gas pipelines; 5 - needle valve; 6 - gas rotameters; 7 - gas flow meter IRG; 8 - solenoid valve; 9 - gas pressure preserver; 10 - gauges; 11 - gas mixer (evaporator) and heater; 12 - thermostat; 13 - reactor; 14 - thermocontroller, 15 - thermocouple; 16 - container for catalyst; 17 - separator (a, b - cooling water); 18 - tap for draining and condensate collection; 19 - chromatograph

The plant for study of hydrogenation of acetylene to ethylene contains a gas supply unit, consisting of cylinders with argon, hydrogen and acetylene (1-3), gas pipelines (4), needle valves (5), flowmeter (6), supply system and gas flow metering containing of IRG-3 (7), units for regulation and pressure control, like a solenoid valve (8), a gas pressure regulator (9), manometer (10),gas mixer (vaporization device) heater (11), with thermostate (12), catalytic reactor (13), with a heating system, consisting of furnace and thermocontroller (14), thermocouple (15), container for a catalyst (16), a separator (17), with circulation system of cold water (a), (b) dump cock and condensate collection (18), gas chromatograph (19).

The plant has 3 independent channels for measuring of flow rate by means of rotameters (6) that determines the current volumetric flow rate, which is important to maintain the performance and efficiency for further usage. The flow rate measurement can be carried out simultaneously using all three channels. The measurement data for each channel is given in digital form with reduction to standard conditions.

Results and discussions. A certain sample of catalyst is loaded into container and placed to the reactor. The temperature of reaction zone is measured using a chromel-alumel thermocouple which was placed to catalyst layer, and target temperature with accuracy of ± 1 ° is kept due to temperature controller.

In order to reach a temperature, the developed catalysts are purged with argon. Heat treatment is carried out at a temperature of 100-120 ° C for 60 minutes under argon (10 ml / min), after that the catalyst is restored with hydrogen (10 ml / min) for 60 minutes. When target temperature is reaching reactor, a reaction mixture flow with different rations is fed into reactor using IRG-3 flowmeter through a mixer (evaporator), and during passing there is formed uniformly mixed gas. Acetylene and hydrogen were used as reaction raw materials in a volume ratio of 1: 3. The setting and maintenance of gas flow rate is carried out in automatic mode using computer. In mixer there is occurred a heating of gas mixtures to a temperature of 200 ° C. Then the gas-vapor steam came from outlet of the reactor and directed to the separator. In separator, the hot flow of gas-vapor steam is initially cooled up to operating temperature, and after that the liquid reaction products enter the condensate collector, but gaseous products are analyzing using a gas chromotograpg «Chrome-3700» and Gas Chromatography with mass spectrometric detection (Agilent 7890A / 5975C).

The separator is connected to chromatograph through a pipeline where a needle valve is installed. Helium was used as a gas carrier. Reaction products were identified by comparing of their retention time and reference substances in the same conditions, increasing the corresponding picking intensity with addition of reference substances to reaction product mixture. Almost all studies have shown a relative error of chromatographic analysis which is no more than 3%.

By using proposed plant, there is a possibility to carry out various sample tests with catalysts keeping operating conditions such as (temperature from 25 to 500 ° C, pressure from 0 to 10 atm, gas consumption from 5 to 2500 cm^3/ min) in order to produce hydrogenation of hydrocarbon, the yield of target products and selectivity of technological parameters.

In this work, a cobalt catalyst 7% Co/SiAl was chosen in order to optimize the technological parameters of hydrogenation process of acetylene using a pilot catalytic plant.

The study of volumetric velocity effect was carried out at different temperatures from 180 to 220 °C and ratio of C_2H_2:H_2=1:2. Figure 2 shows the effect of volumetric reaction rate to ethylene yield during hydrogenation process of acetylene using 7% Co/SiAl catalyst.

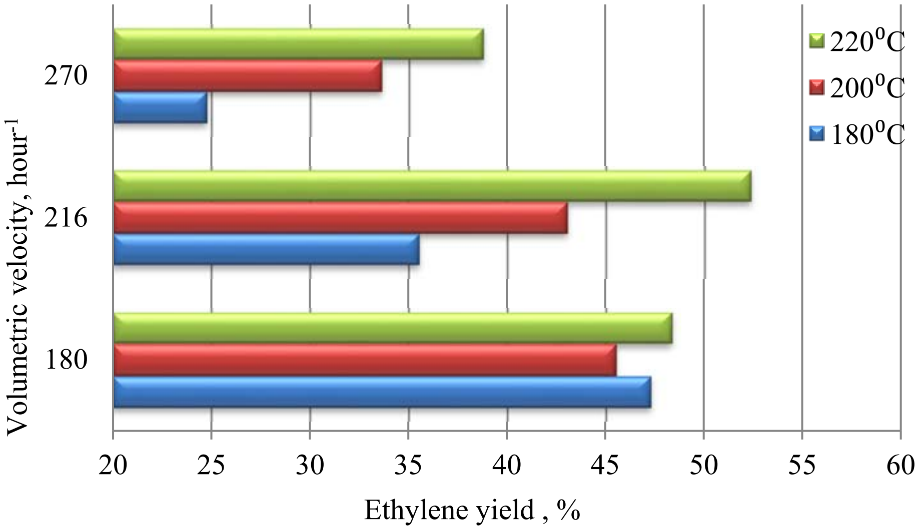

Figure 2 – An influence of volumetric velocity on ethylene yield during hydrogenation process of acetylene using 7% Co/SiAl catalysts

From figure 2 it can be seen that best results in formation of target products when output from reactor are equal to the volumetric velocity and corresponding to 216 h^{-1}, at a temperature of 220 ° C, it reaches the maximum value. At this rate, the ethylene yield increases from 48.37 to 52.38%. A further increase in volumetric velocity leads to decrease in ethylene yield. From obtained data it can be seen that the optimal volumetric flow rate of ethylene formation is 220 $hours^{-1}$.

There was studied an effect of reaction temperature and raw material ratio on ethylene yield in the process of acetylene hydrogenation using cobalt-containing catalyst 7% Co/SiAl. Figure 3 shows the results of ethylene yield depending on reaction temperature.

On cobalt-containing catalyst 7% Co/SiAl at reaction temperature of 180 ° C, the ratio C_2H_2:H_2 (1: 2), and ethylene yield is 42.9%, but at a ratio of (1:3), the ethylene yield increases to 66.7%. A further increase of a temperature up to 200 °C at a ratio of C_2H_2:H_2 (1:2), the ethylene yield increases from 42.9 to 62.2%, but at a ratio (1:3), the ethylene yield increases to 62.9%. An increase of reaction temperature up to 100-120 ° C leads to a decrease in target product from 62.9 to 52.9%.

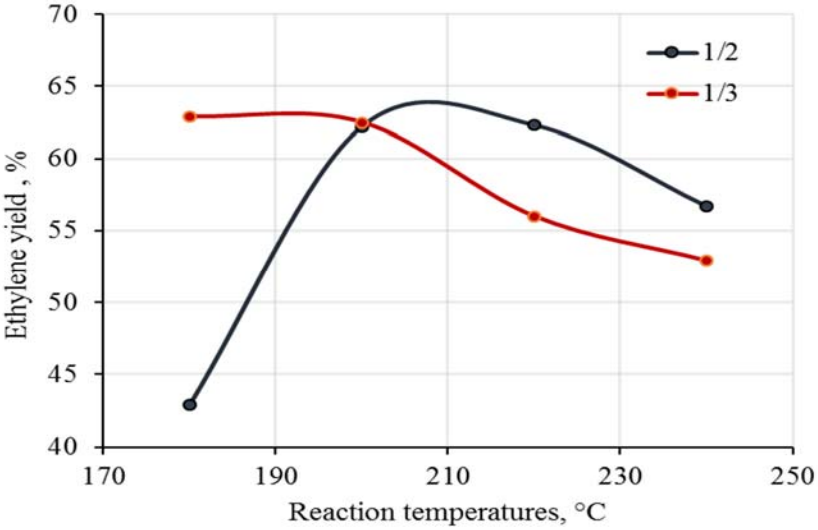

Figure 3 - Influence of reaction temperature and raw material ratio on ethylene yield
in the process of acetylene hydrogenation by 7% Co/SiAl

Thus, for this process, an optimal reaction temperature is 180°C in a ratio of raw material (1:3) is positive, where the ethylene yield is 62.9%.

With an increase of hydrogen flow during hydrogenation process of acetylene 1:3 at reaction temperature of 180°C, the conversion of acetylene was 73.0%, at increasing of a temperature up to 200°C, the conversion of acetylene has increased to 81.2%, with a further increase in temperature to 220 ° C, the conversion of acetylene is reduced to 68%. At 140°C in the ratio of acetylene to hydrogen 1: 3, the conversion of acetylene increases again from 68 to 73.6%.

Figure 4 shows the selectivity data during hydrogenation process of acetylene to ethylene using 7% Co/SiAl catalyst. The selectivity of catalyst 7% Co/SiAl catalyst was studied depending on temperature in acetylene hydrogenation reaction.

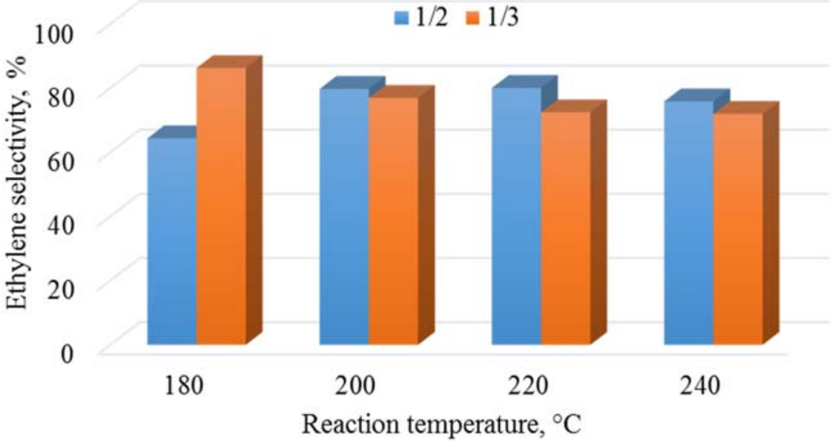

Figure 4 - Influence of reaction temperature on selectivity
during hydrogenation process of acetylene using 7% Co / SiAl

As can be seen from Figure 4, with increasing of temperature the selectivity of ethylene decreased, because increase of a temperature activates side reactions.

The properties of applied catalysts are determined not only by composition and nature, but also by texture features of a carrier and the particle size of active component. The most important strategic factor is a choice of carrier and method of catalyst preparation. Although the clays do not possess a large amount of acidic centers, but due to resistance to high temperatures and ease of surface modification, it is possible to enhance the catalytic properties [5].

The texture and morphological characteristics of obtained catalysts were studied by employees of Xinjiang University, Institute of Chemistry and Chemical Engineering (Ürümqi city, PRC), using scanning electron microscope JEOL JSM-6390 LA with an energy dispersive X-ray detector JED 2300. figure 5 shows SEM photomicrographs on 7% Co / SiAl cobalt catalysts.

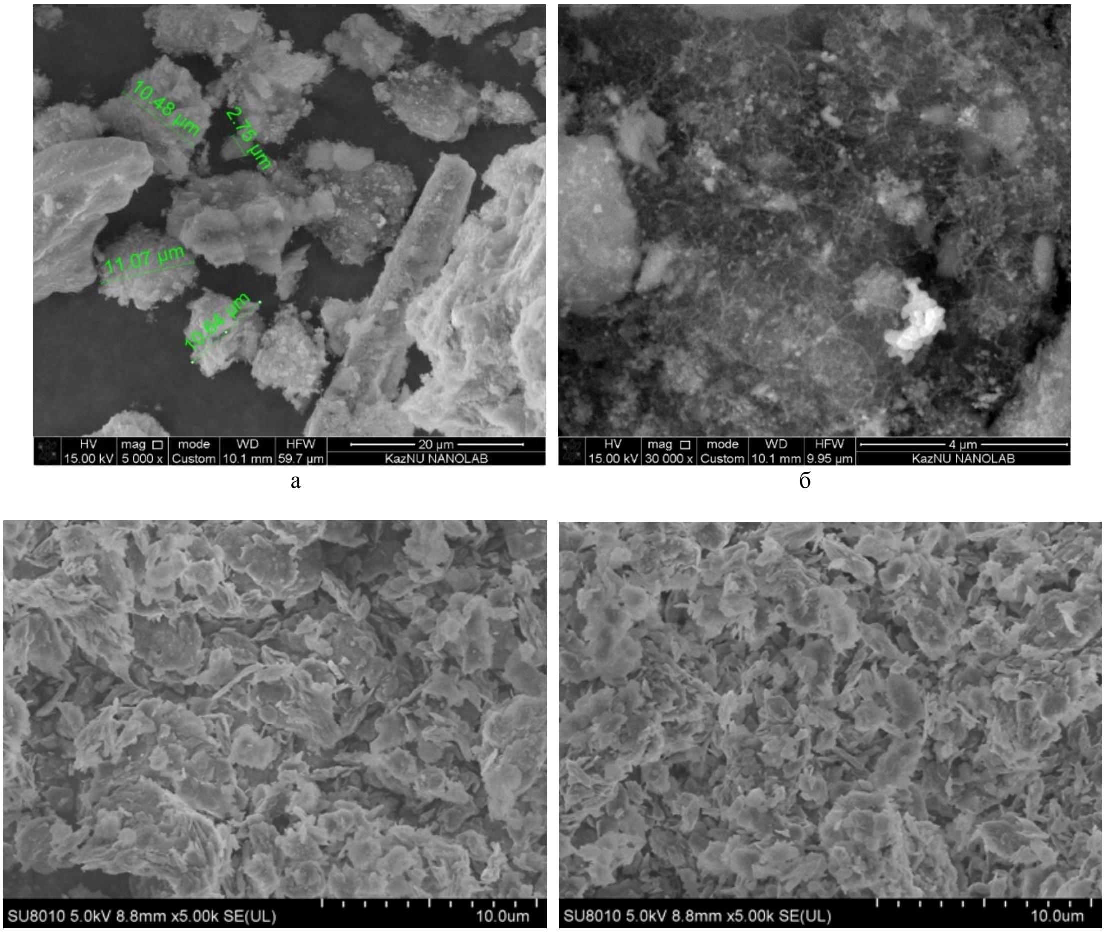

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Figure 5 - Micrographs of 7% Co / SiAl cobalt catalysts

According to electron microscopy data, in samples 7% Co/SiAl there are presented microparticles of different sizes, moreover, with an increase of it up to 1000 times, a lot of scaled particles and fibers are becoming visible, that located in spaces between large areas (figure 5 (a, b)). The structure of samples before (5b) and after (5g) hydrogenation of acetylene does not change and not lose catalytic and selective activity. Samples of catalysts have channels of different sizes, and there are also scaly particles and fibers at the surface, located in the intervals between large aggregates.

According to elemental analysis results, there is no any change in composition of 7% Co/SiAl catalyst; this catalyst worked for 62 hours without losing a catalytic activity in the process of acetylene hydrogenation.

Conclusions. As the results of experiments there are obtained following results:

1. A pilot plant was launched and the modes of acetylene hydrogenation using cobalt catalysts were tested;
2. When studying the effect of volumetric velocity at different temperatures, a ratio is C_2H_2:H_2= 1:2 on 7% Co/SiAl catalyst, it can be seen that best results on target products formation are equal to volumetric velocity and corresponds to 216 h^{-1}, at the temperature of 220°C and reaches maximum value. At this rate, the ethylene yield rises from 48.37 to 52.38%;
3. The study of cobalt catalysts 7% Co / SiAl on scanning electron microscope - JEOL JSM-6390LA have shown that in sample 7% Co / SiAl there are presented microparticles with different sizes, when

increasing 1000 times there are appeared many scaled particles and microfibers located in spaces between large aggregates. The structure of samples before (5c) and after (5d) hydrogenation of acetylene does not change and not lose catalytic activity and selectivity. Samples of catalysts have channels with different sizes; there are also scaly particles and fibers at the surface that located in the spaces between large aggregates.

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ПИЛОТТЫҚ КАТАЛИТИКАЛЫҚ ҚОНДЫРҒЫДА АЦЕТИЛЕНДІ ГИДРЛЕУ ҮДЕРІСІНІҢ ТЕХНОЛОГИЯЛЫҚ ПАРАМЕТРЛЕРІН ОҢТАЙЛАНДЫРУ

Аннотация. Пилоттық қондырғы іске қосылды және кобальт катализаторларында ацетиленді гидрлеу режимдері өңделді. Модификацияланған 7% Co/SiAl кобальт катализаторы ацетиленді этиленге гидрлеу үдерісінде белсенді болатыны анықталды. 7%Co/SiAl катализаторында оңтайлы гидрирлеу шарттары анықталды. Ацетиленді этиленге гидрирлеуге температураның, көлемді жылдамдықтың және бастапқы компоненттер қатынасының әсері зерттелді.

СЭМ әдісімен кобальт катализаторларының текстуралық сипаттамалары ацетиленді гидрлеуге дейін және кейін зерттелді. Ацетилен гидрирлеуден кейін кобальт катализаторларының құрылымы каталитикалық белсенділікті және селективтілігін жоғалтпайды. Катализатор үлгілері түрлі көлемдегі арналарға ие, сондай-ақ бетінде үлкен агрегаттар арасында орналасқан қабыршақты бөлшектер мен талшықтар бар екендігі анықталды.

Ацетиленді этиленге гидрлеу үдерісінің оңтайлы температурасы 180°C, ацетиленнің конверсиясы 73,0% құрайды. Температура 200°С-қа дейін көтерген кезде ацетилен конверсиясы 81,2%-ға дейін жоғарылайды, одан әрі температураны 220°С-қа дейін арттырғанда ацетилен конверсиясы 68%-ға дейін төмендейді. 140°С кезінде ацетилен мен сутегі қатынасы 1:2 болғанда ацетилен конверсиясы 68-ден 73,6%-ға дейін артады.

Ацетиленді гидрлеу реакциясы температурасына этилен бойынша катализатордың 7%Co/SiAl селективтілігінің тәуелділігі зерттелді. Температураның жоғарылағанда этилен бойынша селективтілік төмендейді, өйткені температураның жоғарылауы жанама реакцияларды белсендендіреді.

Түйін сөздер: каталитикалық қондырғы, гидрлеу, ацетилен, этилен, катализаторлар.

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ОПТИМИЗАЦИЯ ТЕХНОЛОГИЧЕСКИХ ПАРАМЕТРОВ ПРОЦЕССА ГИДРИРОВАНИЯ АЦЕТИЛЕНА НА ПИЛОТНОЙ КАТАЛИТИЧЕСКОЙ УСТАНОВКЕ

Аннотация. Была запущена пилотная установка и отработаны режимы гидрирования ацетилена на кобальтовых катализаторах. Установлено, что модифицированный 7%Co /SiAl кобальтовый катализатор является активным в процессе гидрирования ацетилена в этилен. Определены оптимальные условия гидрирования ацетилена на 7%Co /SiAl катализаторе. Исследованы влияния температуры, объемной скорости и соотношение исходных компонентов в гидрировании ацетилена в этилен.

Методом СЭМ исследованы текстурные характеристики кобальтовых катализаторовдо и после гидрирования ацетилена.Структура кобальтовых катализаторов после гидрирования ацетилена не теряют каталитическую активность и селективность. Обнаружено, что образцы катализаторов обладают каналами разных размеров, также присутствуют на поверхности чешуйчатые частицы и волокна, расположенные в промежутках между крупными агрегатами.

Оптимальная температура процесса гидрирования ацетилена в этилен составляет 180°C, конверсия ацетилена – 73,0 %. При повышении температуры до 200°C конверсии ацетилена увеличиваются до 81,2 %, при дальнейшем превышении температуры до 220°C конверсия ацетилена уменьшается до 68 %. При 140°C в соотношении ацетилена и водорода 1:2 конверсия ацетилена снова увеличивается от 68 до 73,6 %.

Изучена селективность 7%Co/SiAl катализатора по этилену в зависимости от температуры в реакции гидрирования ацетилена. Селективность по этилену с повышением температуры падает, так как повышение температуры активизирует побочные реакции.

Ключевые слова: каталитическая установка, гидрирование, ацетилен, этилен, катализаторы.

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POLYMER ADDITIVE EFFECT ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF THE ORGANIC PART OF OIL BITUMINOUS ROCK

Abstract. The article presents the results of gas chromatographic analysis method of the organic part of oil bituminous rock and the results from the analysis of the molecular weight distribution of atactic polypropylene carried out using reverse gel-permeation chromatography. The research results of the structural and mechanical properties of the bitumen part of oil bituminous rock (OBR) of the Iman-Kara deposit, atactic polypropylene (APP) and compositions based on them, carried out on the instrument Reotest 2.1, are also presented herein.

It has been determined that the organic part of OBR of the Iman-Kara deposit mainly consists of oxygen-containing organic compounds with additions of heteroatomic structures (sulfur, haloids and nitrogen) with a weight fraction of 53.97%.

According to the chromatogram of the molecularly-mass distributed atactic polypropylene, it is found that the average time of fraction maximum yield is 11.4 minutes, the corresponding value of logarithm of the average molecular weight Lg(M) equals to 5.5. Accordingly, the average molecular weight of fraction M is 400.

The change patterns of the rheological properties of the organic part of OBR, atactic polypropylene and compositions based on them are described. It has been established that the addition of APP to the organic part of OBR creates a disperse system in which the particles of a polymer additive that are swollen due to oily components are dispersed in the bitumen medium. At the same time, mechanical properties such as elasticity and heat resistance of the organic part of oil bituminous rock are improved. These properties can be shown only with the optimum quantity of APP, when their concentration is such that they form an uninterrupted net structure. The influence patterns of APP on the structure of the organic part of OBR defined in the process of experiments can also be used in further experiments during development of various types of waterproofing materials and coatings.

Key words: oily bituminous rocks, asphaltenes, atactic polypropylene, rheology, structure formation, heat resistance, composition.

Introduction. It is known that oil bitumen is a material widely used in all countries of the world in various building technologies.

In the context of limited crude oil production and price volatility in world markets, the issues of processing not only the main mineral raw materials, but also the search for the use of secondary resources, production wastes for the real sector of economy is most relevant. From this perspective, resource saving is one of the priority tasks of the economy for many countries.

The papers of authors[1-12]are dedicated to the issue of processing oil-containing raw materials, methods for evaluation and calculation of the economic effect of investment on the processing of unused, cheaper and affordable types of raw materials, secondary material resources, including production wastes, and to determine the profitability and search for the break-even production capacity of various technologies.

Given that in the foreseeable future, the need for resources of oil products, namely, oil bitumen will undoubtedly grow, the importance of oil bituminous rocks (OBR) will perhapsrise steadily. Considerable reserves of OBR are concentrated in Kazakhstan and it can be considered as a multi-purpose raw material, as a complex raw material of the third millennium [13].

In this regard, of continuing interest is the study of curing processes of OBR with various modifying additives and production wastesand their physical and mechanical properties research, for the purpose of further use as components in the composition of waterproofing construction materials.

The study object in this paperareOBRs of the Iman-Kara deposit (Atyrau Oblast) and atactic polypropylene (APP).

It is known from literary sources [13] that the organic part of oil bituminous rock of the Iman Kara deposit is heavy and viscous. Gasoline and light kerosene fractions are practically absent inOBR. Perhaps it depends on the oxidation of OBRs themselves, since they embed shallow. The saturation with bitumen of OBRof the Iman-Kara deposit is on average 18.9 wt%. The organic part of OBR of the Iman-Kara contains asphaltenes 12.5 wt %, resin – 36.4%, and the oil content is 51.1 wt %.

Atactic polypropylene is a material obtained when producingpolypropylene as a co-product. According to its characteristics, this type of polypropylene belongs to thermoplastics. The ring-and-ball softening point is 112ºC, the depth of needle penetration at 25ºC,0.1 mm – 40.0, the density is 850 kg/m^3.

Atactic polypropylene has a number of useful properties and can be used in various production spheres. Although atactic polypropylene is considered waste material, it has many useful properties that can be used in various industrial fields. It is a soft, plastic and elastic material similar to rubber. It has high flow state – it can take different forms: from liquid buttery to thicker waxy. According to the authors [14-16], polypropylene is well combined with bitumen in almost all proportions, has high impact resistance and gives these properties to bitumen-polymer compositions, therefore, to the obtained construction materials. Bitumen-polymer compositions obtain the best properties, when atactic polypropylene forms a continuous networkin the composition, which is achievedwith its optimal content.

Based on the above, it follows that the use of APP as components in the compositions of various waterproofing construction materials wouldavoid disposal and convert it from wastes into useful raw material.

Materials and methods. The organic composition of oil bituminous rock has been analyzed on an Agilent 7890A/5975C chromatograph/mass spectrometer (USA). Before analysis, the organic part of the rock has been extracted using hexane.

Chromatographic conditions: gas chromatograph 7890A with mass-selective detector 5975C of Agilent company; mobile phase (carrier gas) – helium; evaporator temperature is 3500°C, flow discharge (Split) is 500:1; column thermostat temperature, beginning 70°C, temperature rise is 4°C per minute, final temperature is 290°C, kept at this temperature for 30 minutes, total analysis time is 80 minutes; ion mode of the mass detector is by electron impact method. A capillary chromatographic column HP-5MS has been used, the column length is 30 m, the internal diameter is 0.25 mm, the stationary phase – dimethylpolysiloxane (95%) and phenyl polysiloxane (5%).

According to the results of chromatographic analysis, it can be judged that the main part of oil bituminous rock mainly consists of oxygen-containing organic compounds with additions of heteroatomic structures (sulfur, haloids and nitrogen) with a weight fraction of 53.97% (table 1, figure 1).

Table 1 - Results of gas chromatographic analysis of the organic part of oil bituminous rock

Alkanes, wt %	Naphthenes, wt %	Arenes, wt %	Other compounds, wt %
16.50	10.85	18.68	53.97

The molecular weight distribution of atactic polypropylene has been studied using reverse gel-permeation chromatography on a Shimadzu HPLC Prominence-20 (Japan).

A sample of atactic polypropylene was dissolved in tetrahydrofuran at a concentration of 1 wt %. The obtained solution was filtered off on a syringe filter.

Chromatographic conditions: stationary phase – Shim-pack GPC-80M Shimadzu, column size – 300x8 mm, mobile phase - tetrahydrofuran, elution rate 1.0 ml/min, detection – refraction, thermostat temperature – 30°C, injection volume – 20 μl. The chromatogram is shown in figure 2.

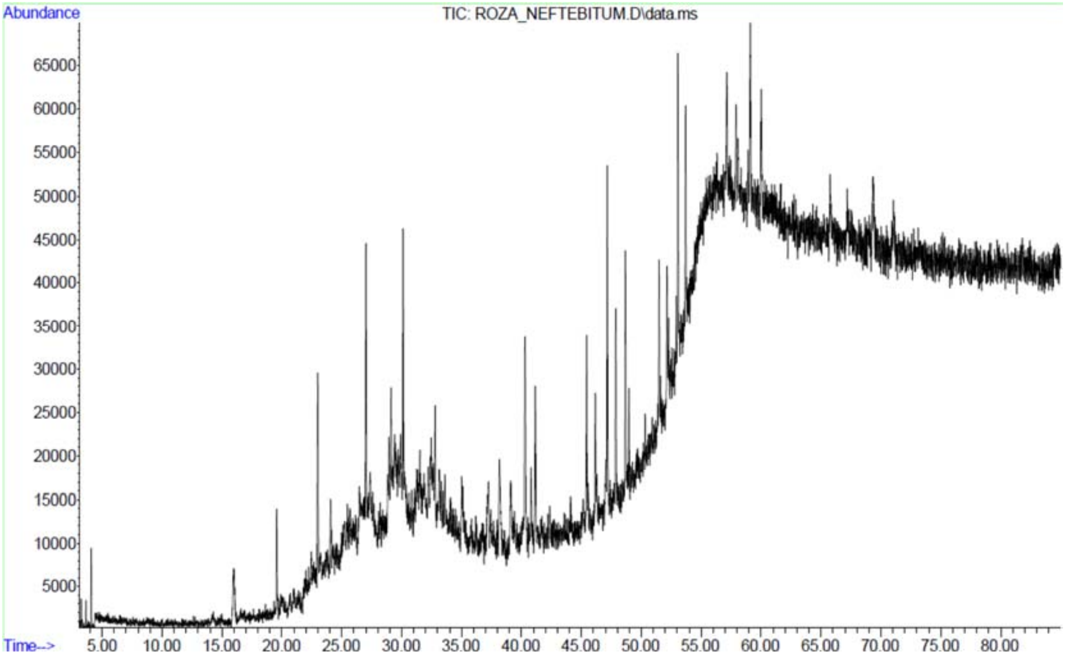

Figure 1 - Chromatogram of the organic part of oil bituminous rock

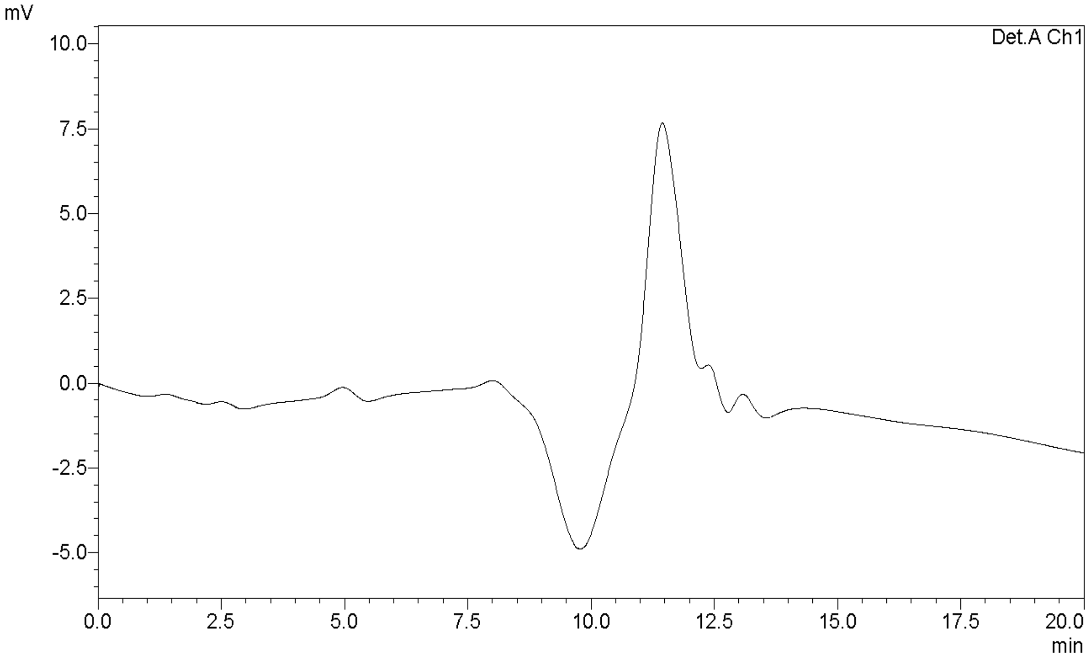

Figure 2 - Chromatography of molecularly-mass distributed atactic polypropylene

The average molecular weight has been determined by defining the corresponding value at an average time of fraction maximum yield. According to the chromatogram, the average time of fraction maximum yieldis 11.4 minutes, the corresponding value of logarithm of the average molecular weight Lg (M) was 5.5 (figure 3). Accordingly, theaveragemolecularweightoffractionMis 400.

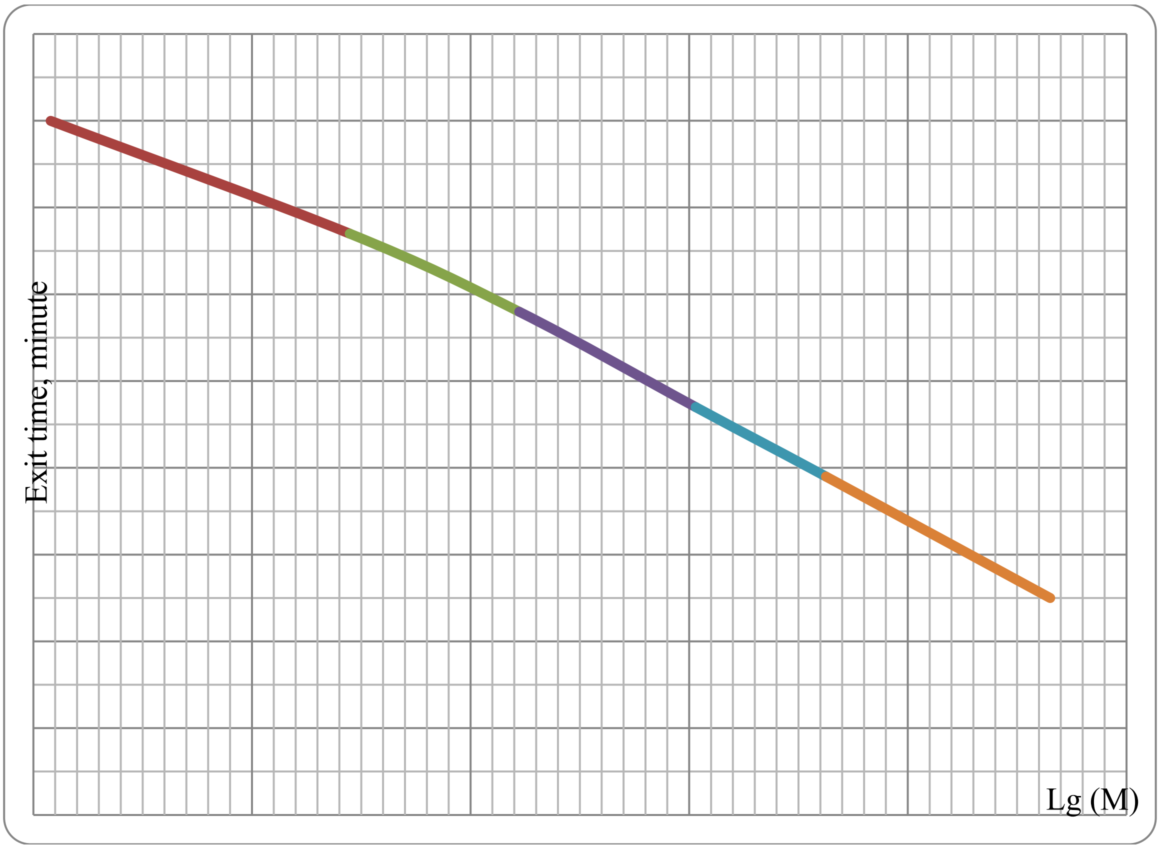

Figure 3 - Defining the corresponding value at an average time of fraction maximum yield

Thus, taking into account that the materials studied belong to rheologically complex, elastoplastic systems, which are characterized both by strength and viscosity properties, further studies were directed to:

- justification of the structuring role of atactic polypropylene, significantly expanding the range of physico-chemical and physico-technical properties of the organic part of OBR;
- change patterns of the rheological properties of the organic part of oil bituminous rock when they are combined with polymer additives.

On the instrument Reotest 2.1, the structural and mechanical characteristics for the organic part of OBR of the Iman-Kara deposit, APP, have been determined according to the pure shear scheme at temperatures of 20°C, 60°C, 90°C.

Results and discussion. As a result of experimental work, complete rheological flow curves were obtained) $lgD = f(p)$, $lg\eta = f(p)$,which made it possible to determine the rheological characteristics for describing the structural and mechanical properties of primary components (Table 1).

The organic part of OBR of the Iman-Kara deposit at 20°C has η_0 - 590.1, η_m – 14.5 Pa·s.

It is known that an increase in the amount of oils reduces the bitumen viscosity, and with an increase in the amount of asphaltenes in bitumen, its viscosity and heat resistance increase.

At a temperature of 90°C, the organic part of OBR of the Iman-Kara deposit has a viscosity equal to η_0=3.1 P·s and it is a Newtonian liquid, which is apparently caused by the maximum dissolution of individual particles and the almost complete destruction of the structural network due to the kinetic energy of thermal motion. The high sensitivity of OBRbitumen to elevated temperature is due to the high content of oils and resins. In contrast to the organic part of oil bituminous rock, atactic polypropylene has a higher degree of structuredness and its viscosity at a temperature of 90°C isη_0 =114.6 Pa·s, η_m=1.35 Pa·s,, which allows using it as a structure forming additive, strengthening the structure of the organic component of OBR and the obtaining composition.

Selection of the optimal ratio between the components of the “organic part of OBR:APP” has been carried out using the second-order rotabledesign for two variables: X_1 – consumption of the organic part of OBR and X_2 – consumption of APP. The variation levels of technological factors under study are given in table 2.

Table 2 – Variation levels of technological factors

Name of factors under study	Code	Variation levels				
		-1.41	-1	0	+1	+1,41
Consumption of the organic part of OBR, %	X1	83.3	62.8	55.5	48.1	45.4
Consumption of APP, %	X2	16.7	37.2	45.5	51.9	54.6

The softening point, viscosity and depth of needle penetration are taken as the optimization parameters. Theexperimentation plan and the results obtained during its implementation are presented in Table 3. As a result of statistical processing of experimental data obtained during the implementation of the plan, the quantitative dependence of the studied properties of the “organic part of OBR:APP” system is derivedfrom the variable factors under examination.

Table 3 – Rheological characteristics of the organic part of OBR and atactic polypropylene

Item No.	Components	t, ^{0}C	P_{k1}, Pa	P_{k2}, Pa	η_0, Pa•s	η_m,Pa•s	$1/\eta_0 \cdot 10^{-2}$	$1/\eta_m$	η_0/η_m	$\eta_0-\eta_m$	$K_t \cdot 10^{-2}$
1	Organic part of OBR, Iman-Kara	20 60 90	399 576 16	70309 - -	590.1 18.7 3.1	14.50 3.20 0.40	0.200 5.360 32.700	0.609 0.309 2.281	49.7 5.8 7.3	575.6 15.4 2.6	8.35
2	APP	60 90	1683 269	13441 471	671.0 114.6	1.50 1.30	0.649 0.872	435.710 0.740	669.5 84.9	113.3	9.15

Table 4 – Plan and results of experimentation the results of mathematical planning were verified by experimental studies.

Item No.	Variation level				Organic part of OBR, g	APP, g	Organic part of OBR:APP ratio	Softeningpoint, ^{0}C	η_0, Pa·s	η_m, Pa·s	$K_{t\,60\text{-}90} \cdot 10^{-2}$	Depth of needle penetration ,mm
	Incodedvariables		Innaturalvariables									
	X1	X2	X1	X2								
1	+1	+1	48.1	51.9	48.1	51.9	1 : 1.1	126	1010	2.57	9.48	21
2	-1	+1	62.8	51.9	62.8	51.9	1 : 0.83	122	898	1.94	9.49	23
3	+1	-1	48.1	37.2	48.1	37.1	1 : 0.77	120	791	1.70	9.35	23
4	-1	-1	62.8	37.2	62.8	37.2	1 : 0.6	110	751	1.35	9.06	27
5	+1.41	0	45.4	45.5	45.4	45.5	1 : 1	126	1009	2.30	9.48	20
6	-1.41	0	83.3	45.5	83.3	45.5	1 : 0.55	90	730	1.2	9.08	29
7	0	+1.41	55.5	54.6	55.5	54.6	1 : 1	126	1003	2.25	9.48	20
8	0	-1.41	55.5	16.7	55.5	16.7	1 : 0.4	45	724	1.35	9.10	39
9	0	0	55.5	45.5	55.5	45.5	1 : 0.8	121	993	1.94	9.49	23
10	-1.41	-1.41	83.3	16.7	83.3	16.7	1 : 0.2	24	147	2.09	7.04	51

The study of APPeffect on the bitumen structure of OBR was carried out on compositions prepared according to the ratios given in Table 3, where the content of APP varied from 0.2 to 1.1 wtfr. %.

The study of the physical and mechanical properties of the composition show that adding APP to the organic part of OBR from 0.2 to 1.1wtfr. %increases the softening point of the asphalt-binder from 24 to 121°C, the depth of needle penetration decreases from 51 to 21 mm (Figure 4, Figure 5).

A further increase in the content of APP in the system changes the abovementioned figures slightly. To identify the advantages of the structure of the two-component "bitumen OBR:APP" system, rheological studies have been conducted at temperatures of 60°C.The rheological characteristics presented in Table 3 show that with the addition of APP into OBR bitumen, the strength of the system structure increases.

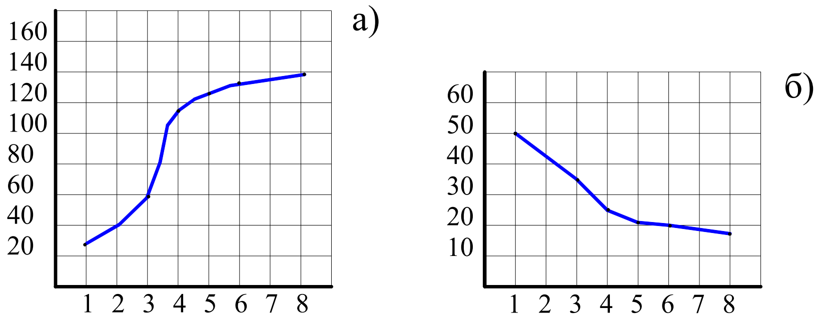

Figure 4 – The effect of the amount of atactic polypropylene additives on standard properties of the organic part of OBR (Iman-Kara):
Abscissa axis – the content of APP,% (x10); ordinate axis: on a – softening point, ^{0}C, on b – depth of needle penetration, mm

The viscosity of the undestroyed structure "η_0" for all systems under study changes more sharply than the viscosity of the destroyed structure "η_m" in the same temperature range. The strongest structure is formed at the ratios of "OBRbitumen:APP" system – 1:0.8 and 1:1. At the same time, the obtained composition has the best structure compared to the structure of OBR bitumen and its viscosity approaches the viscosity of oil bitumen BN 90/10, as indicated by the following data. For the composition of OBRbitumen:APP"η_0 = 993 Pa·s for OBR bitumen (Iman-Kara) η_0 =18.66 Pa s, while for bitumenBN 90/10 it equals η_0 = 1073 Pa s.

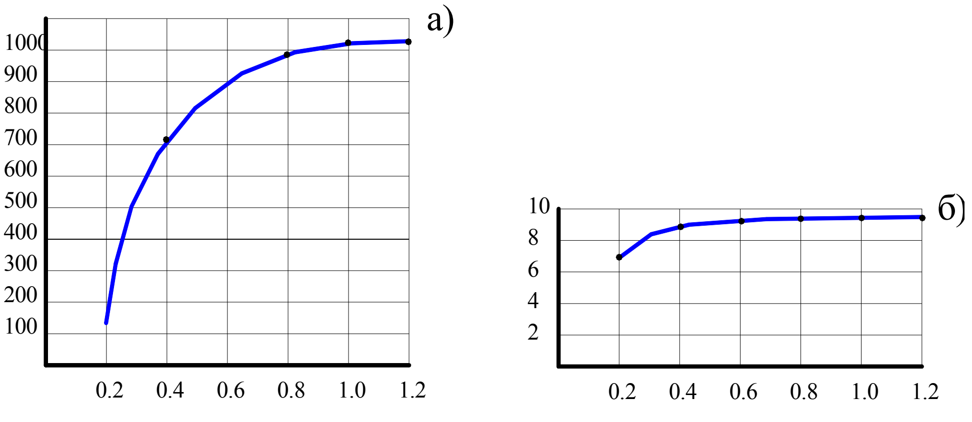

Figure 5 – The change in viscosity (a) and heat resistance (b) of the organic part of OBR depending on the content of APP:
Abscissa axis – the content of APP, wtfr.%; ordinate axis: on a – viscosity, Pa·s, on b – coefficient of heat stability(x10^{-2}), °C

The almost constant value of theheat sensitivity coefficient (9.1×10^{-2} - 9.49×10^{-2}) in the temperature range 60-90^{0}C indicates the thermal stability of the obtained system. The rise of the elastic limit Pk_1 and the yield limit Pk_2 with an increase in APP concentration indicates the existence of stronger links in the system that form the spatial structure, that is, about the stability of the systemstructure. With the increase of APP concentration, the structurednessdegree of the system increases, that is characterized by the ratio η_0/η_m and the difference η_0/η_m.

The formation of strong structure in the compositions is associated with the development in the volume of OBR bitumen of the structural network, the nodes or centers of origin of which are the APP particles.

At the same time, it is believed that with an increase in the degree of volumetric filling of the bitumen disperse medium with a polymer additive,the formation of the structure takes place in two stages:

- the first – an intensive change in the properties of the system and, as a rule, its hardening;
- the second – stabilization of the hardened structure and the elastoplastic properties of the system.

Conclusions. Thus, the conducted studies allowed to characterize the structural and mechanical properties of the organic part of oil bituminous rock of the Iman-Kara deposit and atactic polypropylene, which could become components of the predicted compositions of waterproofing materials. The patterns of effect of APP on the structure of the organic part of OBR defined during the experiments can also be used in further experiments during development of various types of waterproofing materials and coatings.

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ПОЛИМЕРЛІ ҚОСПАНЫҢ МҰНАЙ-БИТУМДЫ ЖЫНЫСТАРДЫҢ ҚҰРЫЛЫМДЫҚ-МЕХАНИКАЛЫҚ ҚАСИЕТІНЕ ӘСЕРІ

Аннотация. Мақалада мұнай-битумды жыныстардың (МБЖ) органикалық құрамын газды-хроматографиялық әдіспен зерттеудің нәтижелері және атактикалық пропиленнің молекулярлы-массалық бөлінуін кері гель-өткізу хроматография арқылы анықтау нәтижелері келтірілген. Хроматогрфиялау жағдайы: Agilent фирмасының 5975C масс-селективті детекторлы 7890A газды хроматографы; қозғалмалы фаза – гелий; буландырғыш температурасы 350^{0}С, ағынның бөлінуі (Split) 500:1; баған термостанының температурасы, басталуы 70^{0}С, температура минутына 4^{0}С-ге көтеріледі, соңғы температура 290^{0}С, бұл температурада 30 мин ұсталады, анализдің жалпы уақыты 80 мин.; масс-детектордың ионизация режимі – электрондық соққы әдісі. HP-5MS капиллярлы хроматографиялық бағанасы қолданылды, баған ұзындығы 30 м, ішкі диаметрі 0,25 мм, қозғалмайтын фаза – диметилполисилоксан (95%), фенилполисилоксан (5%).

Иман-Қара кенішіндегі мұнай-битумды жыныстарының органикалық құрамы, негізінен, гетероатомды құрылымды қоспалары бар оттекті қосылысты органикалық қоспалардан тұрады (күкірт, галоидтар, азот). Бұл қоспаның массалық үлесі – 53,97%.

Shimadzu HPLC Prominence-20 (Жапония) қондырғысында қайтымды гель-өткізгіш хроматография көмегімен жүргізілген атактикалық полипропиленнің (АПП) молекулалы-массалық таралуды зерттеу нәтижелері келтірілген. Атактикалық полипропиленнің молекулярлы-массалық бөлінуінің хроматограммасына сәйкес төмендегі көрсеткіштер анықталды: фракциялардың максималды шығуының орташа уақыты 11,4 мин. Бұл көрсеткішке сәйкес фракциялардың орташа молекулалық массасының Lg(M) логарифмі 5,5 тең болады. Сәйкесінше, «М» фракциясының орташа молекулярлық массасы 400-ді құрайды.

Атактикалық полипропилен қоспасының мұнай-битумды жыныстың органикалық бөлігінің физика-механикалық қасиетіне әсерін зерттеу нәтижелері келтірілген. 0,2 мен 1,1 массалық үлес аралығында полимерлік қоспаны қосқанда мұнай-битумды жыныс битумды құрамының жұмсару температурасын, тұтқырлығын, температураға тұрақтылығын арттырады, иненің ену тереңдігі төмендейді.

Сонымен қатар, «Реотест 2.1» қондырғысы арқылы Иман-Қара кенішінің мұнай-битумды жыныстары органикалық құрамының, атактикалық пропиленнің құрылымдық-механикалық қасиетін зерттеу нәтижелері және мұнай-битум жыныстарының битумдық бөлігінің полимер қоспасымен араластырғаннан кейінгі реологиялық қасиеттерінің өзгеру заңдылықтарын анықтау нәтижелері келтірілген. Бастапқы компоненттер мен олардың негізінде алынған композициялар үшін толық реологиялық қисықтары келтірілген $lgД=f(p)$, $lg\eta = f(p)$.

Мұнай-битумды жыныстардың органикалық құрамының, атактикалық полипропиленнің және осы материалдардың негізінде дайындалған композициялардың реологиялық қасиеттерінің өзгеру заңдылықтары сипатталған.

Реологиялық сипаттамаларға қарай отырып, мұнай-битумды жыныстың органикалық бөлігіне атактикалық полипропиленді ендіру жүйе құрылымының беріктігін арттыратынын байқауға болады. Ең мықты құрылым МБЖ:АПП - 1:0,8 және 1:1 қатынастағы жүйесінде түзіледі. Бұл жағдайда алынған композиция мұнай-битумды жыныс битумына қарағанда жоғары құрылымға ие және оның тұтқырлығы БН 90/10 мұнай битумының тұтқырлығына жақындайды.

Мұнай-битумды жыныстың органикалық бөлігіне атактикалық полипропиленді қосқанда полимерлі қоспаның бөлшектері майлы компоненттердің есебінен ісініп битумды жүйеге дисперсияланып дисперсті жүйе түзеді. Бұл жағдайда мұнай-битумды жыныстың органикалық бөлігінің серпімділік, термотұрақтылық тәрізді механикалық қасиеттері жақсарады. Бұл қасиеттер тек атактикалық полипропиленнің оңтайлы құрамында байқалады, өйткені бұл концентрацияда олар үздіксіз торлы құрылым түзеді.

60-90^{0}С температура аралығында термотұрақтылық коэффицентінің тұрақты шамасы (9.1x10^{-2}-9,49x10^{-2}) алынған композицияның термиялық тұрақтылығын көрсетеді. Атактикалық полипропилен концентрациясын жоғарылатқанда Рк$_1$ серпімділік және Рк$_2$ аққыштық шегінің жоғарылауы жүйеде кеңістіктік құрылым түзетін берік байланыстардың түзілгендігін, яғни жүйе құрылымының тұрақтылығын көрсетеді. Атактикалық полипропилен концентрациясы өскен сайын жүйенің құрылымдалуы да жоғарылай түседі, ол η_0/η_m қатынасымен және $\eta_0 - \eta_m$ айырмашылығымен сипатталады.

Атактикалық полипропиленді мұнай-битумды жыныстардың органикалық құрамымен араластыру нәтижесінде полимер түйіршіктері органикалық заттың құрамындағы май компонентімен қанықтырыла отырып, дисперстік жүйе құрайды және осы арқылы битумды материалдың ыстыққа төзімділігін, қаттылығын жақсартады. Бұл қасиеттерге атактикалық полипропиленнің ұтымды қатынасында, яғни ұтымды құрылым түзетін концентрациясында ғана қол жеткізуге болады. Эксперимент нәтижесінде анықталған заңдылықтарды, яғни атактикалық полипропиленнің мұнай-битум жыныстарының органикалық бөлігімен құрылымтүзгіштік рөлін алдағы уақытта әртүрлі гидроизоляциялық материалдар мен жабын алу технологиясында қолдануға болады.

Түйін сөздер: мұнай-битум жыныстары, асфальтендер, майлар, атактикалық полипропилен, хроматография, тұтқырлық, жұмсару температурасы, реология, құрылымтүзгіштік, жылуға төзімділік, композиция.

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ВЛИЯНИЕ ПОЛИМЕРНОЙ ДОБАВКИ НА СТРУКТУРНО-МЕХАНИЧЕСКИЕ СВОЙСТВА ОРГАНИЧЕСКОЙ ЧАСТИ НЕФТЕБИТУМИНОЗНОЙ ПОРОДЫ

Аннотация. В статье приведены результаты газо-хроматографического метода анализа органической части нефтебитуминозной породы и результаты анализа молекулярно-массового распределения атактического полипропилена, проведенной с помощью обратной гель-проникающей хроматографии. Условия хроматографирования: газовый хроматограф 7890А с масс-селективным детектором 5975С фирмы Agilent; подвижная фаза (газ носитель) – гелий; температура испарителя 350^{0}С, сброс потока (Split) 500:1; температура термостата колонки, начало 70^{0}С, подъем температуры 4^{0}С в минуту, конечная температура 290^{0}С, при этой температуре удерживается 30 мин, общее время анализа 80 мин; режим ионизации масс-детектора методом электронного удара. Использовали капиллярную хроматографическую колонку HP-5MS, длина колонки 30 м, внутренний диаметр 0,25 мм, неподвижная фаза – диметилполисилоксан (95%), фенилполисилоксан (5%).

По результатам хроматографического анализа можно судить, что основная часть нефтебитуминозной породы (НБП) в основном состоит из кислородсодержащих органических соединений с примесями гетероатомных структур (сера, галоиды и азот) с массовой долей 53,97.

Приведены результаты исследований молекулярно-массового распределения атактического полипропилена (АПП), который проведен с помощью обратной гель-проникающей хроматографии на приборе Shimadzu HPLC Prominence-20 (Япония). Согласно хроматограмме молекулярно-массово распределенного атактического полипропилена установлено, что среднее время выхода максимума фракции является 11,4 мин, соответствующее значение логарифма средней молекулярной массы Lg(M), составила 5,5. Соответственно, средняя молекулярная масса фракции М составляет 400.

Приведены результаты исследования влияния добавки атактического полипропилена на физико-механические свойства органической части нефтебитуминозной породы. Отмечено, что с добавлением полимерной добавки от 0,2 до 1,1 мас. долей % повышается температура размягчения, вязкость, теплоустойчивость битумной составляющей нефтебитуминозной породы, снижается глубина проникания иглы.

Также приведены результаты исследований структурно-механических свойств битумной части нефтебитуминозной породы месторождения Иман Кара, атактического полипропилена и композиций на их основе, проведенной на приборе «Реотест 2.1». Для исходных компонентов и композиций на их основе получены полные реологические кривые течения $lgД=f(p)$, $lg\eta = f(p)$.

Реологические характеристики показывают, что с введением атактического полипропилена в органическую составляющую нефтебитуминозной породы повышается прочность структуры системы. Наиболее прочная структура образуется при соотношениях системы "битум НБП:АПП" – 1:0,8 и 1:1. При этом полученная композиция имеет наилучшую структуру по сравнению со структурой битума нефтебитуминозной породы и вязкость его приближается к вязкости нефтяного битума БН 90/10.

Установлено, что добавление атактического полипропилена в органическую часть нефтебитуминозной породы создает дисперсную систему, в которой частицы полимерной добавки, набухшие за счет масляных компонентов, диспергируют в битумной среде. При этом улучшаются механические свойства, как упругость, термостойкость органической части нефтебитумнозной породы. Эти свойства могут проявляться только при оптимальном количестве атактического полипропилена, когда их концентрация такова, что они образуют непрерывную сетчатую структуру.

Практически постоянная величина коэффициента термочувствительности ($9.1x10^{-2}$ - $9,49x10^{-2}$) в интервале температур $60\text{-}90^0C$ свидетельствует о термической устойчивости полученной композиций. Повышение предела упругости $Pк_1$ и предела текучести $Pк_2$ с увеличением концентрации атактического полипропилена указывает на существование в системе более прочных связей, образующих пространственную структуру, то есть об устойчивости структуры системы. С увеличением концентрации атактического полипропилена повышается и степень структурированности системы, характеризуемая соотношением η_0/η_m и разностью $\eta_0 - \eta_m$.

Проведенные исследования позволили охарактеризовать структурно-механические свойства органической части нефтебитуминозной породы месторождения Иман-Кара и атактического полипропилена, которые могли бы стать составляющими компонентами прогнозируемых составов гидроизоляционных материалов. Установленные в процессе экспериментов закономерности влияния атактического полипропилена на структуру органической части нефтебитуминозной породы также могут быть использованы в дальнейших экспериментах при разработке различных видов гидроизоляционных материалов и покрытий.

Ключевые слова: нефтебитуминозная порода, асфальтены, атактический полипропилен, реология, структурообразование, теплостойкость, композиция.

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Кроме того, в журналах «Известия НАН РК. Серия физико-математическая», «Известия НАН РК. Серия химии и технологий» и «Известия НАН РК. Серия геологии и технических наук» также указаны отрасли науки, по которым будут приниматься научные статьи для экспертизы и дальнейшего опубликования:

III. Научный журнал **«Известия НАН РК. Серия физико-математическая»** посвящен исследованиям в области математики, физики и информационной технологии.

Редакционная коллегия принимает статьи по следующим отраслям науки:

1. Математика.
2. Информатика.
3. Интеллектуальный анализ данных и распознавание образов.
4. Математическое моделирование социальных и экономических процессов.
5. Механика.
6. Механика машин и роботов.
7. Теория управления и космические исследования.
8. Физика.
9. Ядерная физика.
10. Теоретическая физика.
11. Астрономия.
12. Ионосфера.

Адрес сайта «**Известия НАН РК. Серия физико-математическая**» –
http://physics-mathematics.kz/index.php/en/archive

IV. Научный журнал **«Известия НАН РК. Серия химии и технологий»** посвящен исследованиям в области химии и технологий новых материалов.

Редакционная коллегия принимает статьи по следующим отраслям науки:

1. Органическая химия.
2. Неорганическая химия.
3. Высокомолекулярные соединения.
4. Физическая химия (катализ, электрохимия).
5. Технология новых материалов.
6. Технология органических веществ.
7. Технология неорганических веществ.
8. Технология химических удобрений.
9. Технология полимерных и строительных материалов и силикаты.
10. Технология пищевых продуктов.
11. Фармацевтическая химия.

Адрес сайта **«Известия НАН РК. Серия химии и технологии»** –

http://chemistry-technology.kz/index.php/en/arhiv

V. Научный журнал «**Известия НАН РК. Серия геологии и технических наук»** посвящен исследованиям в области геологии и технических наук:

Редакционная коллегия принимает статьи по следующим отраслям науки:

1. Геология.
2. Региональная геология.
3. Петрология.
4. Геология нефти и газа.
5. Геология и генезис рудных месторождений.
6. Гидрогеология.
7. Горное дело и геомеханика.
8. Фундаментальные проблемы обогащения минерального сырья.
9. Инженерная геология.
10. Геофизика и сейсмология.
11. География.

Адрес сайта **«Известия НАН РК. Серия геологии и технических наук»** –
http://www.geolog-technical.kz/index.php/en/archive