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Д.В.Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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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.

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CATALYTIC CONVERSION OF METHANE INTO SYNGAS AND ETHYLENE

Abstract. The object of research is development technology of the new composite materials synthesis for the processing of light alkanes into syngas and ethylene. The study varying technological parameters of the reaction (temperature, volumetric rate, reaction mixture composition) oxidative conversion of methane into syngas and ethylene. Paper presents data of developed methods of synthesis were developed and the catalysts physicochemical characteristics were established. Optimized technological parameters of the process in an integrated automated laboratory setup. It has been established that the active in syngas and ethylene formation in mixture oxidative transformation of CH_4+O_2+Ar on 10%K-30%Mn-10%Nb/50% glycine catalyst prepared by the SHS (solution combustion synthesis) method and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation method.

Key words: methane, catalytic oxidation, syngas, ethylene.

Introduction

The world's oil reserves are decreasing every day due to the continuous production and their processing using the most modern technologies. Scientists all over the world are looking for various raw materials and methods to use the vast resources of natural gas as a substitute for petrochemicals. In this regard, great attention is drawn to natural gas as an alternative source of raw materials for petrochemical industries.

According to the annual Statistical Review of World Energy – 2018, published by British Petroleum (BP) at the end of 2017 proven natural gas reserves in the world are estimated at 193.5 trillion cubic meters.

Kazakhstan ranks 15th in the world and 4th in the CIS of natural gas reserves. The prospects for the development of the global gas processing industry are associated with the creation and introduction of new catalytic environmentally friendly technologies for producing of olefins, based on production of polymers, alcohols and motor fuels. Gas processing plants in Kazakhstan are currently engaged mainly in the purification of gases from water, impurities of carbon dioxide and hydrogen sulfide for their use for domestic purposes. This situation is associated with the lack or absence of new catalytic technologies for the directed processing of light C_1-C_4 alkanes. There are no production facilities for the production of olefins, plastics, motor fuels and other products whose demand is met by imports. Therefore, an important task is the intensive development of the industrial processing of light hydrocarbon raw materials, the reserves of which far exceed oil reserves.

It is known that natural gas is 90% methane. Oxidative dimerization of methane to ethylene, which allows to obtain a number of petrochemical products, such as polyethylene, polystyrene and many other chemical products, is of considerable interest. This is primarily due to the low cost of methane compared to other hydrocarbons [1]. Development of new efficient catalysts for the selective oxidation of light alkanes is still at the research and development stage [2-8].

In the work of Karakaya [9] the $Mn/Na_2WO_4/SiO_2$ catalyst was studied for the oxidative dimerization of methane. The catalyst was prepared by impregnation methods. The influence of temperature, volume velocity and the ratio of reaction gases were investigated. It is determined that methane conversion is 38% at a volume rate of 390 h^{-1}. The maximum ethylene yield was 16% at 750°C and a gas ratio of $CH_4/O_2 = 2$.

In [10] Sr-Al, La-Sr-Al and Na_2WO_4–Mn/SiO_2 series of catalysts were prepared by solution combustion synthesis (SCS). The activity of catalysts was investigated at 450-850°C and $CH_4:O_2:N_2 = 32:8:10$ ratio, the linear velocity of gases was 50 ml/min. During the experiments it was determined that catalysts were not active in the temperature range of 450-600°C. The Sr-Al series of catalysts, where Sr/Al = 1.25, were active. It was found that the maximum yield of C_2 hydrocarbons on the Sr/Al = 1.25 catalyst was 11.5% at ~ 800°C and $C_2H_4/C_2H_6 = 4.5$ ratio. For each catalyst of the La-Sr-Al series, the C_2 hydrocarbons yield and ethylene/ethane ratio were measured over a wide temperature range. The highest ethylene yield of 12.3~13.0% was achieved at 720°C, and the $C_2H_4/C_2H_6 = 1.7$ and 1.6 ratio, respectively. It was found that the 10% Na_2WO_4–5% Mn/SiO_2 catalyst providing the maximum yield of C2 hydrocarbons ~ 21% at 750°C and the ethylene / ethane = 2 ratio is the most highly active and selective.

In [11] the Mn-Ce-Na_2WO_4/SiO_2 catalysts prepared by the impregnation method were investigated for oxidative dimerization of methane. In particular, due to the double advantages of the tubular membrane reactor, a high methane conversion of 60.7% with selectivity of C_{2+} 41.6%, ethylene/ethane ratio of 5.8% and ethylene yield of 19.4% at a space velocity of GHSV= 6050 $ml \cdot g^{-1} \cdot h^{-1}$ was achieved.

We have developed polyoxide catalysts based on molybdenum, chromium and gallium, applied to natural clays for catalytic oxidation of propane butane mixture into oxygenates and olefins [12-14] and developed of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas [15-17].

Methods for synthesis of catalysts were presented in paper the physicochemical characteristics of catalysts were established, as well as the optimization of technological parameters for the process of synthesis of syngas and ethylene from methane in an integrated automated installation.

Experimental

Catalyst preparation

Paper presents results of the study of activity of developed following catalysts:

1.5% K - 3.5% Mn/AlSi;

10% K - 30% Mn - 10% Nb/50% glycine;

10% K - 30% Mn - 10% Nb/ceramic block;

The catalytic systems were synthesized by the method of impregnation in air and by solution combustion synthesis.

The developed compositions of catalysts were prepared by capillary impregnation of mixed aqueous solutions of metal nitrate salts supported on carriers by moisture capacity, followed by drying at T = 473 K for 2 h. Calcinations of samples at T = 773 K for 2 h in air was carried out for decomposition of supported metal salts and corresponding volatilization of nitrates from the catalyst surface.

The catalysts with using the SCS method were prepared [18-20]. Thus, certain amounts of nitrates of the corresponding salts were weighed to prepare a catalyst. These salts are pre-ground in an agate mortar and then mixed in a porcelain dish. Then 10 ml of distilled water is gradually added to this mixture of salts, the mixture is stirred in air for several minutes until complete dissolution.

The muffle furnace was previously turned on to the required temperature (in our case, up to 500°C). The prepared mixture from a porcelain cup is transferred to a 200 ml heat-resistant glass beaker and placed in a heated muffle furnace. After 2-3 minutes with an incomplete opening of the door of the muffle furnace, it is visually possible to observe burning in the solution, at which this mixture rises along the walls of the glass during rapid boiling. Urea and glycine were added to the composition of SCS catalysts to improve the combustion process. The presence of glycine or urea in the composition of catalyst contributes to a change in the color of solution into brown color during combustion. Then the glass is cooled in air and the finished catalyst is placed in glass cups.

The specific surface area and measurement of the pore distribution of the developed catalysts were studied by the BET method (Bronauer-Emmett-Teller) on a GAPP V-Sorb 2800 analyzer (China). Nitrogen with helium was used as carrier gas. BET method was carried out at Advanced Ceramics and

Composites Laboratory, Institute of Nanoscience and Nanotechnology NCSR “Demokritos” (Athens, Greece).

Characterization techniques

The analysis of the initial mixture and reaction products was carried out using a chromatograph "Chromos GC-1000" with the "Chromos" software and on a chromatograph "Agilent Technologies 6890N" (USA) with computer software. Chromatograph "Chromos GC-1000" is 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. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. Carrier gas velocity Ar = 10 ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve V = f (S) was constructed, where V - amount of substance in ml, S - peak area in cm^2. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was ± 3.0%.

Results and discussion

The paper presents data of activity of 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation for the oxidative conversion of the 34% CH_4+17% O_2+49% Ar mixture at 6500 h^{-1} space velocity. As can be seen from figure 1, the yield of the reaction products also increases with increasing the reaction temperature from 650 to 900°C. The formation of products of partial oxidation - H_2 and CO, complete oxidation - CO_2, and the target reaction products - C_2H_6 and C_2H_4 are observed in the oxidative conversion of methane.

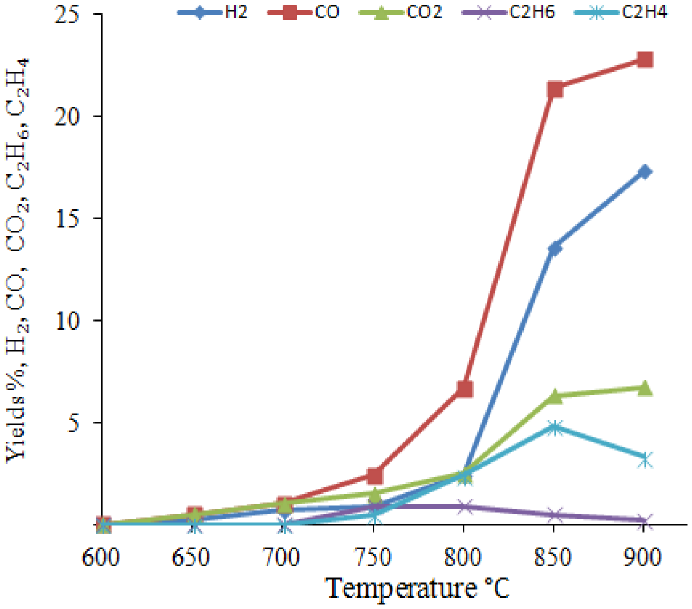

Figure 1 - Effect of a reaction temperature on the product yield of the oxidative conversion of methane on 1.5 % K - 3.5 % Mn/AlSi catalyst

It should be noted that the process goes towards the formation of H_2 and CO. The yields of products increase with increasing reaction temperature. CO_2 is produced in smaller amounts, the yield of which also increases with increasing temperature. The yield of ethylene does not exceed 5% at all temperatures.

Data on the activity of the developed three-component 10%K-30%Mn-10%Nb/50%glycine catalyst prepared by the SCS method for oxidative conversion of 41.8% CH_4 + 16.2% O_2 + 42.% Ar mixture at a space velocity of 3500 h^{-1} and CH_4:O_2 = 2.5:1.0 ratio will be given. As can be seen from figure 2, the three-component composition with the addition of niobium showed good activity in relation to the formation of ethylene compared with the two-component compositions of catalyst. The yield of ethylene also increases with an increase in the reaction temperature from 600 to 800°C. At a temperature of 800°C, the ethylene yield passes through a maximum and decreases again with increasing temperature to 900°C. The yields of H_2, CO and CO_2 slightly change with increasing temperature and vary within 2-3%.

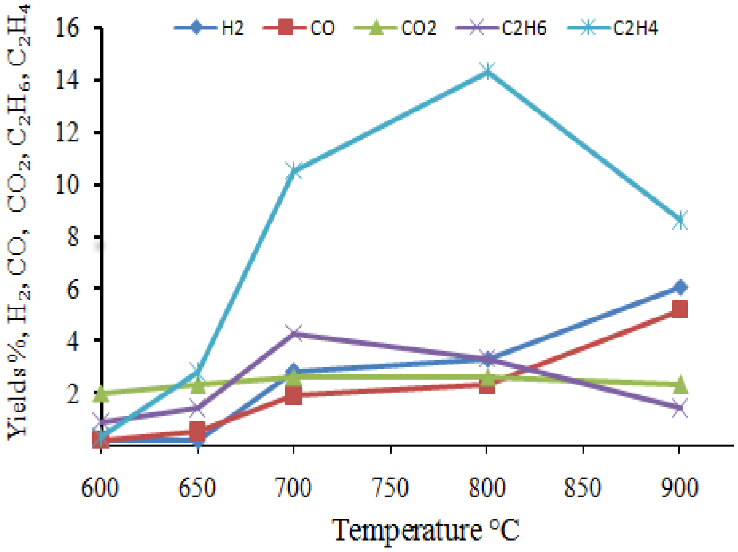

Figure 2 - Effect of reaction temperature on the product yield of oxidative conversion of methane on 10%K-30%Mn-10%Nb/50% glycine catalyst

Thus, the optimal temperature for the formation of ethylene is 800°C at which the ethylene yield is 14.3%.

Developed active phase of 10% K -30% Mn - 10% Nb of catalyst was supported on ceramic block (Fig. 3). The activity of this catalyst composition

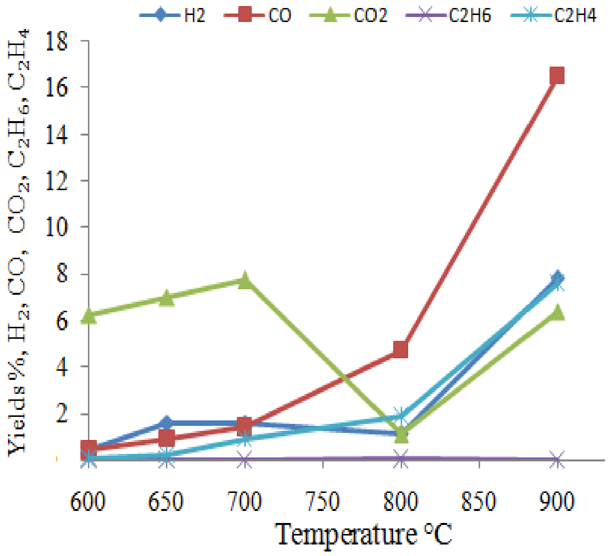

Figure 3 - Effect of reaction temperature on the product yield of the oxidative conversion of methane on 10 % K – 30 % Mn – 10 % Nb/ceramic block

CH_4 + 16.2% O_2 + 42% Ar mixture with a ratio of $CH_4:O_2 = 2:1.5$ and at 6500 h^{-1} space velocity. Under these conditions, the catalyst was less active with respect to the formation of both ethylene and H_2. As the temperature rises, only the yield of CO increases.

Thus, the activity of the developed two- and three-component catalytic systems prepared by impregnation and SCS method in the oxidative conversion of the methane of natural gas was investigated.

It was established that 10%K-30%Mn-10%Nb/50%glycine catalyst prepared by the SCS method is the most active in formation of ethylene and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation for the oxidative conversion of methane into syngas.

In addition, the methods for synthesis of the developed catalysts were determined and the physicochemical characteristics of the catalysts were established. Developed applied K-Mn catalyst was studied by G. Kaumenova, a 3-year doctoral student at al-Farabi Kazakh National University during an overseas internship (Fig. 4,5). Nitrogen with helium was used as carrier gas.

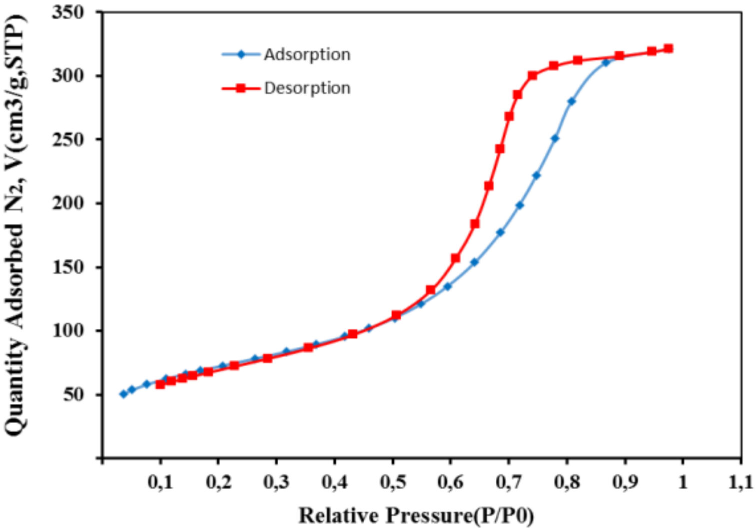

Figure 4 – Isotherm of adsorption and desorption of applied K-Mn catalyst

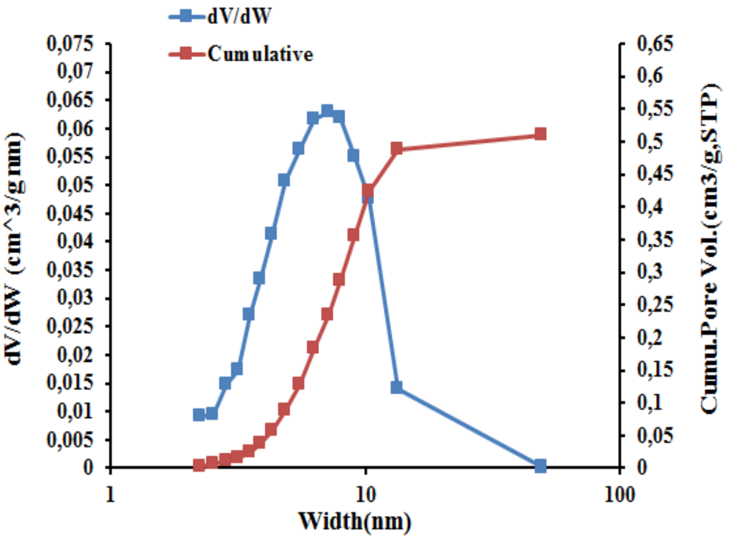

Figure 5 – Differential dependence of pore size distribution
on applied K-Mn catalyst

From the data of Figure 5, it can be seen that a significant amount of pores have a size of up to 10 nm. This, in turn, is an important characteristic of catalyst, on the basis of which it can be concluded that the developed catalyst is nanoscale.

Thus, the influence of technological parameters of reaction on the yield of target products was established. The study of catalytic oxidative conversion of the main components of natural gas is methane was carried out on the developed catalytic systems by varying the reaction temperature, space velocity and ratio of the main gases in reaction mixture in order to obtain the optimal amount of desired reaction products. Process parameters on an effective catalyst in an integrated plant were optimized.

Conclusion

Thus, synthesis methods were developed and physicochemical characteristics of catalysts were established. Technological parameters of the process in an integrated automated laboratory setup were optimized.

It was established that 10% K - 30% Mn - 10% Nb/50% glycine catalyst prepared by SCS method is active for production of 14.3% C_2H_4 in oxidative conversion of 41.8% CH_4 + 16.2% O_2 + 42% Ar at 800°C and space velocity of 3500 h^{-1} and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation method is active for obtaining of 17.3% H_2 and 23.8% CO in the oxidation of 34% CH_4+17% O_2+49% Ar at space velocity of 6500 h^{-1}.

From the above results, it follows that it is possible to optimize the process of oxidative conversion of methane by selecting the reaction technological parameters and improving the composition of inserted catalysts.

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МЕТАННЫҢ СИНГАЗ ЖӘНЕ ЭТИЛЕНГЕ ДЕЙІН КАТАЛИТИКАЛЫҚ КОНВЕРСИЯСЫ

Аннотация. Зерттеу нысаны табиғи газ метанды олефиндерге қайта өңдеуде жаңа композитті материалдарды синтездеу болып табылады. Олефиндерге тотыға айналу реакциясының технологиялық параметрлерінің (температура, көлемдік жылдамдық, реакциялық қоспаның құрамы) өзгерістері зерттелінді.

Мақалада дайындалған катализаторлардың синтездеу әдістері мен физика-химиялық қасиеттері ұсынылған. Автоматтандырылған зертханалық қондырғыда үрдістің технологиялық параметрлері оңтайландырылған.

Ерітіндіде ӨЖС әдісімен 10%K-30%Mn-10%Nb/50% глицин дайындалған катализаторда және сіңіру әдісімен дайындалған 1,5%K-3,5%Mn/AlSi катализаторы бастапқы реакциялық қоспа CH_4+O_2+Ar сингаз және этилен түзуде белсенділігі анықталынды.

Түйін сөздер: метан, каталитикалық тотығу, сингаз, этилен.

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КАТАЛИТИЧЕСКАЯ КОНВЕРСИЯ МЕТАНА В СИНГАЗ И ЭТИЛЕН

Аннотация. Объектом исследования является разработка технологии синтеза новых композиционных материалов для переработки природного газа метана в олефины. Было изучено варьирование технологических параметров реакции (температура, объемная скорость, состав реакционной смеси) окислительного превращения метана природного газа в олефины.

В статье представлены данные разработанных методов синтеза и установлены физико-химические характеристики катализаторов. Оптимизированы технологические параметры процесса в автоматизированной лабораторной установке.

Установлено, что активным по образованию сингаза и этилена при окислительном превращении смеси CH_4+O_2+Ar являются 10%K-30%Mn-10%Nb/50%глицин катализатор, приготовленный методом СВС в растворе и 1,5%K-3,5%Mn/AlSi катализатор приготовленный метождом пропитки.

Ключевые слова*:* метан, каталитическое окисление, сингаз, этилен.

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REFERENCES

[1] Gambo Y, Jalil AA, Triwahyono S, Abdulrasheed AA (2018) Journal of Industrial and Engineering Chemistry 59:218-229. DOI: 10.1016/j.jiec.2017.10.027

[2] Dury F, Gaigneaux EM, Ruiz P (2003) Applied Catalysis A: General 242:187-203. DOI: 10.1016/S0926-860X(02)00516-1

[3] Ozkan US, Watson RB (2005) Catalysis Today 100:101-114. DOI: 10.1016/j.cattod.2004.12.018

[4] Dimitratos N, Vedrine JC (2006) Journal Mol Catal A Chem, 255:184-192. DOI: 10.1016/j.molcata.2006.03.075

[5] Routray K, Reddy KRSK, Deo G (2004) Applied Catalysis A: General, 265:103-113. DOI: 10.1016/j.apcata.2004.01.006

[6] Wang J., Chou L., Song H., Yang J., Zhao J., Li S. (2006) Catal. Commun, 7:59-63. DOI: https://doi.org/10.1016/j.catcom.2005.08.013 (in Eng)

[7] Aubakirov YA, Sassykova LR, Starikov EB (2016) International Journal of Biology and Chemistry DOI: 10.26577/2218-7979-2016-9-2-45-50

[8] Aubakirov YA, Sassykova LR, Nalibayeva AM, Dossumov KD, Tashmukhambetova ZK, Zhumakanova AS (2017) Oriental journal of chemistry DOI **:**http://dx.doi.org/10.13005/ojc/330655

[9] Karakaya C, Zhu H, Loebick C, Weissman JG, Kee RJ (2018) Catalysis Today 312:10-22. DOI: 10.1016/j.cattod.2018.02.023

[10] Ghose R, Hwang HT, Varma A (2013) Applied Catalysis A: General 452:147-154. DOI: 10.1016/j.apcata.2012.11.029

[11] Liu K, Zhao J, Zhu D, Meng F, Kong F, Tang Y (2017) Catalysis Communications 96:23-27. DOI: 10.1016/j.catcom.2017.03.010

[12] Baizhumanova TS, Tungatarova SA, Xanthopoulou G, Zheksenbaeva ZT, Kaumenova G.N, Erkibaeva MK, Zhumabek M, Kassymkan (2018) News of the NAS RK. Series chemistry and technology, 431:132–138 https://doi.org/10.32014/2018.2518-1491.17 (in Eng).

[13] Massalimova BK, Jetpisbayeva GD, Altynbekova DT, Nauruzkulova SM, Atakozhaeva AA, Sadykov VA (2019) News of the NAS RK. Series chemistry and technology, 434:5-11. https://doi.org/10.32014/2019.2518-1491.11 (in Eng).

[14] Baizhumanova T, Tungatarova S, Kaumenova G, Zhumabek M, Kassmkhan K (2019) Oriental journal of chemistry, 35:404:408. http://dx.doi.org/10.13005/ojc/350151 (in Eng).

[15] Tungatarova SA, Xanthopoulou G, Kaumenova GN, Zhumabek M, Baizhumanova TS, Grigorieva VP, Komashko LV, Begimova GU (2018) News of the NAS RK. Series chemistry and technology, 432:6-15. https://doi.org/10.32014/2018.2518-1491.20 (in Eng).

[16] Xanthopoulou G, Karanasios K, Tungatarova S, Baizhumanova T, Zhumabek M, Kaumenova G, Massalimova B, Shorayeva K (2019) Reaction Kinetics, Mechanisms and Catalysis 126: 645-661. https://doi.org/10.1007/s11144-019-01541-9 (in Eng).

[17] Tungatarova S, Baizhumanova T, Zheksenbaeva Z, Zhumabek M, Kaumenova G, Aubakirov Y, Begimova G. (2019) Chemical Engineering and Technology, 42: 918:924. https://doi.org/10.1002/ceat.201800522 (in Eng).

[18] Tungatarova SA, Xanthopoulou G, Karanasios K, Baizhumanova TS, Zhumabek M, Kaumenova G (2017) Chemical Engineering Transactions 61:1921-1926. DOI: 10.3303/CET1761318

[19] Tungatarova SA, Zheksenbaeva ZT, Baizhumanova TS, Zhumabek M, Sarsenova RO, Kaumenova G, Massalimova B, Shorayeva KA (2018) Chemical Engineering Transactions 70:1927-1932. DOI: 10.3303/CET1870322

[20] Xanthopoulou G, Karanasios K, Tungatarova S, Baizhumanova T, Zhumabek M, Kaumenova G, Massalimova B, Shorayeva K (2019) Reaction Kinetics, Mechanisms and Catalysis DOI: 10.1007/s11144-019-01541-9.

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CHEMICAL CONSTITUENTS OF *LIGULARIA NARYNENSIS*

Abstract. In this work, the quantitative and qualitative analysis of phytochemical constituents of medicinal plant *Ligularia narynensis* from Kazakhstan have been made for the first time. Total bioactive components of *L. narynensis* such as organic acids (0.58 %), flavonoids (0.64 %) and together with moisture content (5.98 %), total ash (7.58 %), and extractives content (25.1 %) were determined. Eleven macro-, microelements from the ash of plant were identified, main contents of them were K (1308.25 µg/ml), Ca (1312.77 µg/ml), and Mg (231.18 µg/ml) by using method of multi-element atomic emission spectral analysis. In addition, the ethyl acetate extract from the aerial part of *L. narynensis* was analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS).

Key words: *Ligularia narynensis,* bioactive constituents, macro-, microelements, LC-MS.

Introduction

Ligularia is a medicinally important genus of the family Compositae that comprises about 180 Eurasian species, 17 species growing in mountains of Kazakhstan [1]. They grow in a great variety of habitats from riverine to high-mountain rocky places, ranging from sea level to 5000 m altitude [2]. More than 27 *Ligularia* species have been used as traditional Kazakh and Chinese medicinal herbs for the treatment of fever, pain, inflammation, intoxication, cough phlegm, removing blood stasis, emetic, diuresis, cholagogue and removing jaundice [3-10]. Phytochemical investigations of various *Ligularia* species showed the presence of monoterpenes, sesquiterpenes, diterpenes, triterpenes, alkaloids, steroids, flavonoids, lignans, and other skeleton type compounds, as well as some of these compounds showed various biological activities such as anticancer, antibacterial, antihepatotoxicity, antioxidant, and antithrombus [11-13].

L. narynensis is a perennial herb growing in Almaty region of Kazakhstan and in Xinjiang province of China. Scientist Xue Gao determined the structures of oplopane-type sesquiterpenes, a new 8-O-4'-type neolignan, oplopane and guaiane type sesquiterpenoids, monoterpenoids from the roots of *L. narynensis* [3, 9, 14, 15].

Our previous phytochemical investigations have reported the total bioactive components from the root part of *L. narynensis* such as organic acids, flavonoids, moisture content, total ash, and extractives content. By using method of multi-element atomic emission spectral analysis eleven macro-, microelements from the ash of plant were determined. Concurrently, twenty amino and eight fatty acids were analyzed from this plant [16]. Additionally, fifty nine liposoluble constituents in chloroform extract from the root part of *L. narynensis* have been identified by GC-MS method [17].

In present study has been made the investigation of the chemical constituents for the aerial part of medicinal plant *L. narynensis* grown in Almaty region of Kazakhstan for the first time. Total bioactive components of *L. narynensis* such as organic acids, flavonoids together with moisture content, total ash, and extractives content were determined. Eleven macro-, microelements from the ash of plant were identified by using method of multi-element atomic emission spectral analysis. In addition, the ethyl acetate extract from the aerial part of *L. narynensis* has been analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS).

Materials and methods

Plant material. The aerial part of plant *L. narynensis* was collected in September 2018 from the Zailiysky Alatau Mountains of Almaty region and identified by Dr. Alibek Ydyrys. Specimens (1217-БН-17) were deposited in the Herbarium of Laboratory Plant Biomorphology, Faculty of Biology and Biotechnology, Al-Farabi Kazakh National University, Almaty, Kazakhstan. The air dried aerial part of *L. narynensis* were cut into small pieces and stored at room temperature.

Extraction. The air-dried plant *L. narynensis* (8.5 kg) were pulverised and extracted with 95% ethanol (EtOH) three times (seven days each time) at room temperature. After evaporation of the solvent under reduced pressure, 420 g of the residues were mixed and suspended in water and then successively partitioned with petroleum ether (PE), dichloromethane (DCM), and ethyl acetate (EA) to afford the corresponding extracts.

Experimental part

The quantitative and qualitative analysis. The quantitative and qualitative contents of biologically active constituents from the aerial part of the plant were determined according to methods reported in the State Pharmacopeia XI edition techniques [18].

Analysis of macro-, microelements. In the «Center of Physico-Chemical methods and analysis», Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* was analyzed elemental constituents. To determine the mineral composition of ashes was used Shimadzu 6200 series spectrometer [16].

Liquid chromatography-mass spectrometry. Analytical LC-MS spectra perform on a Waters 2695 instrument coupled with a Waters 2998 PAD, a Waters 2424 ELSD and a Waters 3100 SQDMS detector [19]. The EA fraction were analyzed by LC-MS using water-acetonitrile in increasing non-polarity until 100% acetonitrile (Table 1).

Table 1 – The method of LC-MS

H_2O, %	ACN, %	Time, min
90	8	5
90	10	5
80	20	7
70	30	8
5	95	10
0	100	10

Results and discussion

Extraction. Powdered the aerial part of *L. narynensis* plant (8.5 kg) was extracted (30 L x 3) for twenty one days in total at room temperature. The combined extract was evaporated under reduced pressure to give a residue (420 g) which was dissolved in water and partitioned with solvents of increasing polarity to give PE (195 g), DCM (20 g), and EA (11 g) (Figure 1**)**.

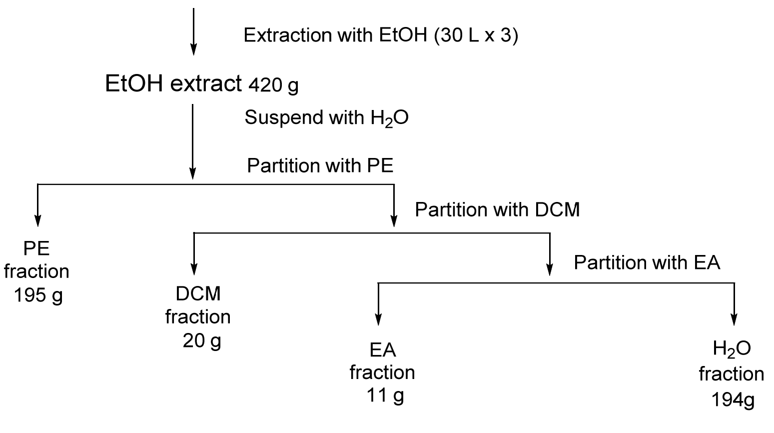

Figure 1 – Flow-chart of partition of the aerial part of *L. narynensis*

The quantitative and qualitative analysis. The quantitative and qualitative analysis of biologically active constituents together with moisture content, total ash, and extractives contents were determined from the aerial part of *L. narynensis*. The results shown in Table 2.

Table 2 – Quantitative analysis of bioactive constituents of *L. narynensis*

Content, %				
Moisture content	Ash	Extractives	Organic acids	Flavonoids
5.98	7.58	25.1	0.58	0.64

Analysis of macro-, microelements. In «Center of Physico-Chemical methods of analysis», Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* were determined eleven macro- and microelements, showed in Table 3 and major of them was K (2214.13 μg/ml), Ca (391.31 μg/ml), Mg (231.18 μg/ml), Fe (80.61 μg/ml). Potassium, magnesium and calcium are macroelements. Typically, each of the macroelements performs several functions.

Potassium is the main intracellular ion, while the main extracellular ion is sodium. The interaction of these ions is important in maintaining cell isotonicity. Potassium contributes to better brain activity, improving its oxygen supply. It has a positive effect in many allergic conditions.

Calcium is the most common macroelement in the human body. Being one of the main components of bones, calcium is necessary for mineralization of new bone tissue. It is also a cofactor for the activation of many enzymes or the formation of a number of enzyme complexes in multi-stage blood clotting processes.

Magnesium is a universal regulator of biochemical and physiological processes in the body, participating in energy, plastic and electrolyte metabolism. As a cofactor of many enzymes, magnesium is related to more than 300 biochemical reactions.

Iron is the most important microelement, which is necessary for the normal functioning of the body. It plays a very important role in the oxidation and reduction processes. Iron is part of the red blood cell hemoglobin, myoglobin and many enzymes involved in hematopoiesis. Consequently, iron provides reversible binding of oxygen to red blood cells and its transport to all organs and tissues of the human body [20].

Table 3 – Composition of macro-micro elements in the ash of plant *L. narynensis*

Element	**Cu**	**Zn**	**Cd**	**Pb**	**Fe**	**Ni**	**Mn**	**K**	**Na**	**Mg**	**Ca**
μg /ml	0.90	2.34	0.15	1.54	80.61	0.10	6.39	1308.25	20.98	231.18	1312.77

Liquid Chromatography-Mass Spectrometry. The results of the spectral analysis of the studied extract of *L. narynensis* obtained by LC-MS are shown in Figures 2. On UV spectra of the fraction has an intense absorption bands, which supposedly indicates the presence in the extract of flavonoids and flavonoid glycosides. These components can be identified with the peaks at retention time of 7.31 min, 383 m/z, 8.39 min, 447 m/z, 9.11 min, 427 m/z, 9.58 min, 535 m/z, 12.55 min, and 327 m/z, respectively.

Variety of flavonoids found in the nature possesses their own physical, chemical, and physiological properties. Structure function relationship of flavonoids is epitome of major biological activities. Medicinal efficacy of many flavonoids as antibacterial, hepatoprotective, anti-inflammatory, anticancer, and antiviral agents is well established [21]. A wide spectrum of biological activities has been documented for flavonoid glycosides, including antioxidant, immunomodulatory, anticancer activities [22].

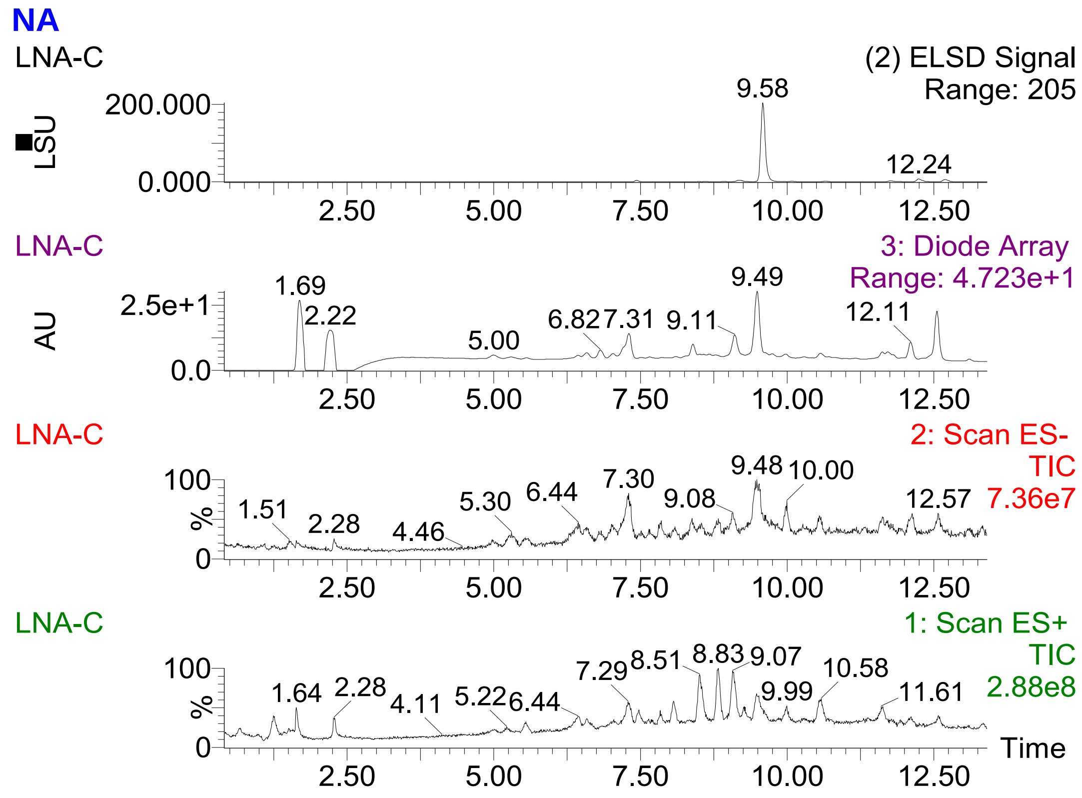

Figure 2 – LC-MS chromatogram of the EA fraction from the aerial part of *L. narynensis*

Comparative review. The contents of the investigated biological active compounds and macro-, microelements from the aerial and the root parts of the *L. narynensis* are similar [16].

Conclusion

In summary, the quantitative and qualitative analysis of phytochemical constituents from the aerial part of *L. narynensis* of Kazakhstan have been made for the first time. As the results of this study, the dried and powdered plant was extracted three times with 95% ethanol, the extract was evaporated in vacuo to give a residue, which was suspended in water and partitioned successively with petroleum ether, dichloromethane, ethyl acetate; total bioactive components of *L. narynensis* were determined; eleven macro-, microelements from the ash of plant were identified; the ethyl acetate fraction of the aerial part presumably rich by flavonoids and flavonoid glycosides was analyzed by LC-MS. Flavonoids and flavonoid glycosides have important pharmacological activities such as anticancer, antibacterial, hepatoprotective, anti-inflammatory, antioxidant, immunomodulatory activities. These results suggest that *L. narynensis* is recommended as plant with pharmaceutical importance. However, further studies are needed to undertake its bioactivity and toxicity profile.

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LIGULARIA NARYNENSIS ӨСІМДІГІНІҢ ХИМИЯЛЫҚ ҚҰРАМДАРЫ

Аннотация. Бұл жұмыста Қазақстанда өсетін дәрілік өсімдіктің *Ligularia narynensis* фитохимиялық құрамының сандық және сапалық талдауы бірінші рет жүргізілді. Өсімдіктің ылғалдылығы (5.98 %), күлділігі (7.58 %) және экстрактивтілігі (25.1 %), сонымен бірге органикалық қышқыл (0.58 %), флавоноидтар (0.64 %) сияқты биологиялық активті компоненттер құрамы анықталды. Атомдық эмиссия спектральды талдау әдісін қолдана отырып, өсімдіктің күліндегі он бір макро- және микроэлементтері зерттелді және оның негізгі құрамы K (1308.25 мкг/мл), Ca (1312.77 мкг/мл), Mg (231.18 мкг/мл). Бұдан басқа, *L. narynensis* жер үсті бөлігінің этилацетат сіріндісі сұйықты хроматография–масс-спектрометрияның (ЖХ-МС) әдісімен талданды.

Түйін сөздер: *Ligularia narynensis*, биоактивті құрамдастар, макро-, микроэлементтер, ЖХ-МС.

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ХИМИЧЕСКИЕ СОСТАВЛЯЮЩИЕ РАСТЕНИЯ *LIGULARIA NARYNENSIS*

Аннотация. В данной работе впервые был сделан количественный и качественный анализ фитохимических составляющих лекарственного растения Казахстана *Ligularia narynensis*. Определены биологически активные компоненты *L. narynensis,* такие как органические кислоты (0,58 %), флавоноиды (0,64 %) вместе с содержанием влаги (5,98 %), общей золы (7,58 %) и экстрактивных веществ (25,1 %). При использовании метода многоэлементного атомно-эмиссионного спектрального анализа в золе растения были идентифицированы одиннадцать макро-, микроэлементов, основными из которых являются K (1308.25 мкг/мл), Ca (1312.77 мкг/мл), Mg (231.18 мкг/мл). Кроме того, этилацетатный экстракт надземной части *L. narynensis* был проанализирован методом жидкостной хроматографии–масс-спектрометрии (ЖХ-МС).

Ключевые слова: *Ligularia narynensis*, биоактивные компоненты, макро-, микроэлементы, ЖХ-МС.

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REFERENCES

[1] Baitenov MS (**2001**) Flora of Kazakhstan [Flora Kazahstana]. Gylym, Kazakhstan. ISBN 9965 – 07 – 036 – 9 (In Russian).

[2] Ponomarenko LP, Ermolaeva SD, Doudkin RV, Dyshlovoy SA, Gorovoy PG (**2017**) Phytochemistry Letters 21:264-268. https://doi.org/10.1016/j.phytol.2017.07.013 (In English).

[3] Gao X, Lin CJ, Xie WD, Shen T, Jia ZJ (**2006**) Helvetica Chimica Acta 21:1387-1394. https://doi.org/10.1002/hlca.200690138 (In English).

[4] Wang Q, Chen TH, Bastow KF, Morris-Natschke SL, Lee KH, Chen DF (**2013**) J Nat Prod 76:305–310. https://doi.org/10.1021/np300532p (In English).

[5] Saito Y, Taniguchi M, Komiyama T, Ohsaki A, Okamoto Y, Gong X, Kuroda C, Tori M (**2013**) Tetrahedron 69:8505–8510. https://doi.org/10.1016/j.tet.2013.06.104 (In English).

[6] Wu YX, Chen YJ, Liu CM, Gao K (**2012**) J Asian Nat Prod Res 14:1130–1136. https://doi.org/10.1080/10286020.2012.733002 (In English).

[7] Xu X, Konirhan B, Zakaria B, Jenis J et al (**2009**) The Kazakh Herbal Medicine. Ethnic publishing house, Beijing, China. Book 1, P.39. ISBN 978-7-105-10066-8 (In Chinese).

[8] Wang Ren (**2012**) The Kazakh Herbal Medicine. Xinjiang Science and Technology press, Urumqi, China. Book 3, P.58. (In Chinese).

[9] Gao X, Jia ZJ (**2008**) Chinese Chemical Letters 19:71–72. https://doi.org/10.1016/j.cclet.2007.10.039 (In English)

[10] Gong Y, Meng XH, Zhu Y (**2018**) Biochemical Systematics and Ecology 80:122–127. https://doi.org/10.1016/j.bse.2018.07.006 (In English).

[11] Yang JL, Wang R, Shi YP (**2011**) Nat Prod Bioprospect 1:1-24. https://doi.org/10.1007/s13659-011-0003-y (In English)

[12] Wang YM, Zhao JQ, Yang JL, Tao YD, Mei LJ, Shi YP (**2017**) Biochemical Systematics and Ecology 72:8-11. https://doi.org/10.1016/j.bse.2017.03.007 (In English).

[13] Wu L, Liao ZX, Liu C, Jia HY, Sun JY (**2016**) Chem. Biodivers 13:645-671. https://doi.org/10.1002/cbdv.201500169 (In English).

[14] Gao X, Xie WD, Jia ZJ (**2008**) J Asian Nat Prod Res 10:185-192. https://doi.org/10.1080/10286020701394431 (In English).

[15] Gao X, Shen T, Xie WD, Jia ZJ (**2006**) Chinese Chemical Letters 17: 341-343. (In Chinese).

[16] Utegenova LA, Nurlybekova AK, Duysebaeva MA, Jenis J (**2019**) News of the National Academy of Sciences of the Republic of Kazakhstan. Series chemistry and technology. Volume 1, Number 433 (2019), PP 32-38. https://doi.org/10.32014/2019.2518-1491.5 ISSN 2518-1491 (Online), ISSN 2224-5286 (Print) (In English).

[17] Nurlybekova AK, Ye Y, Jenis J (**2018**) International Journal of Biology and Chemistry 11: 189-197. (In English).

[18] Tulegenova AU et al (**2008**) State Pharmacopoeia of the Republic of Kazakhstan [Gosudarstvennaya farmakopeya Respubliki Kazakhstan]. Publishing house «Zhibek Zholy», Almaty, Kazakhstan. ISBN 9965-759-97-9 (In Russian).

[19] Li L, Liu H, Tang C, Yao S, Ke C, Xu C, Ye Y (**2017**) Phytochemistry Letters 20:177-180. http://dx.doi.org/10.1016/j.phytol.2017.04.038 (In English).

[20] Gorbachev VV, Gorbacheva VN (**2002**) Vitamins, micro- and macro elements [Vitaminy, mikro- i makroelementy]. Interpresservis, Belorussia. ISBN 985-428-547-2 (In Russian).

[21] Shashank Kumar, Abhay K. Pandey (**2013**) The Scientific World Journal 2013:1-16. http://dx.doi.org/10.1155/2013/162750 (In English).

[22] Yang B, Liu H, Yang J, Gupta VK, Jiang Y (**2018**) Trends in Food Science & Technology 79:116-124. https://doi.org/10.1016/j.tifs.2018.07.006 (In English).

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THE OPTIMAL FREEZING TEMPERATURE OF COW MILK AND CAMEL MILK

Abstract. In the freezing process of cow milk and camel milk, three areas of temperature variations were identified. Specifically, on the first period, both types of milk cooled, then supercooled and further the formation process of ice crystals a taken place. On the second area, it was observed the isothermal area and the phase transformation of water into ice was present. On the third stage, the weakly bound water contained in cow milk and camel milk completely transited into ice. Based on a study of the pattern of changes in the amount of frozen moisture, it was found that, at the minis temperature of t=-15 °C, more than 95% of the water consisted in both types of milk are frozen, and further reducing of temperature had monotonously insignificantly increasing behaviour of the freezing. Therefore, from the point of view of energy savings and maximum preservation of the initial qualities during the shelf-life of cow milk and camel milk, the optimal freezing temperature range is recommended.

Key words: freezing, milk, frozen moisture, isothermal process, free and bound water.

Introduction

One of the most consumed groups of products in Kazakhstan households and abroad is milk and dairy products [6]. However, storage of raw milk by energy saving benefits with a prolonged shelf-life is actual problem for the dairy technology specialists.

There are several advantages of using freeze-drying instead of conventional sensory characteristics within the food product. These advantages make freeze-drying an adequate technology among the new trends of functional and nutraceutical products in the food industry [4].

Freeze drying method is used for the increasing a shelf-life of dried milk as one of the significant parameters and to maximize the amount of preserved nutrients [10, 14].

Review of the available literature shows that currently among researchers engaged in the field of vacuum freeze-drying of the food products, there is no consensus regarding of a selection of the freeze-drying temperature of milk [3]. For example, according to the authors' opinion [8], for the maintenance of the original quality during of the freeze-drying of the product, a lower value of the freezing temperature is sufficiently within t= -45 °C. However, the authors [12] consider that the initial quality of the dried milk can be achieved at the temperature range: t= -10...- 13 °C, where until 90-92% of water in milk are frozen, residual water content is not available for the spoilage of food. (in remain, it will be 8% of water that has an insignificantly value)

As a result of freezing of mare and camel milk, powder remains, which when re-diluted with water retain practically all the beneficial properties of milk [9].

On average camel milk contains 81.4-87% water, 10.4% dry matter, 1.2-6.4% milk fat, 2.15-4.90% protein, 1.63-2.76% casein, 0.65-0.80% whey protein, 2.90-5.80% lactose and 0.60-0.90% ash [1].

The fat content in camel milk varies in a fairly wide range, which depends on the species, season, forage, individual and other factors [13].

Water of cow milk and camel milk is a weakly bound and with its dry framework, besides the forms and energy of bond of this moisture are various [8].

Within a temperature dropping below $T=0^0C$, i.e. below the cryoscopic temperature, a part of water of cow milk and camel milk is frozen [5]. In the refrigeration technology, water that has turned into a solid state is called frozen. The amount of frozen water is presented as a fraction of its total mass in the product [11].

In accordance with the existing classification of the food products there are available a free and bound water [3]. At the freezing of camel milk a tightly bound water is not involved in phase transformations.

It is known that at a temperature below of cryoscopic value, free water is gradually transformed into ice. At the vacuum freeze-drying, in the initial drying period, firstly a frozen part of the free moisture and then the associated part of the water are outlets. In our opinion, on the base of the foregoing statement, by using the parameter of frozen water amount, as a parameter that describes the state of water in the drying process and reveals qualitative changes when camel milk is frozen. Objectively, it is possible to set a lower limit temperature during a vacuum freeze-drying of camel milk [12].

The purpose of this work is a determination of the lower limit of the freeze-drying temperature by amount of frozen water in cow milk and camel milk.

Materials and methods

As the study objects, cow milk and camel milk of the “Gulmaira” farm (Turkestan region, Kazakhstan) were used.

To study of the physico-chemical properties of cow milk and camel milk, the following analytical devices were applied:

- Water content in milk was determined by the standard method of drying at a temperature of 105 °C.
- pH was measured by the ionomer SCHOTT Instrument Lab 850 (Germany) device.
- For the determination of density, proteins and fats content the Lactan-4 of “Sibagropribor NPP” (Russia) device was used.

Both milks were frozen in the freezer device at a temperature of −18 ° C in the form of a cylinder: diameter 30 mm, height 50 mm. Previously, a thermometer sensor was installed in the center of the cylinder, fixed on all sides, and then placed in a refrigerator/

The electronic LCD thermometer TE-850 brand was used for the measuring a temperature.

The amount of water in milk was determined by the standard method of drying in the ALTO SHAAM VECTOR VMC-H2 3F convection multifunctional oven, according to the GOST 3626-73, until constant weight at the temperature of 105 ° C.

A quantity of frozen water in the milk was determined by the formula of G.B.Chizhov [2] that is widely used in practice:

$$\omega=1-\frac{t_{cryos}}{t}$$

where ω – a quantity of frozen water at cryoscopic temperature t_{cryos}; t – start temperature, °C.

Results and discussion

Physico-chemical properties

The quality of milk depends on its chemical composition, i.e. protein, lipids, lactose, etc. In this regard, the studies were carried out on the physicochemical properties of cow milk and camel milk. The results of the physico-chemical properties are shown in Table 1.

Table 1 - Physico-chemical properties of cow milk and camel milk

№	Indicator	Cow milk	Camel milk
1	Mass fraction, %: - dry matter	8,5	12,6

	- fats - proteins - lactose	3,00 3,10 4,50	4,38 4,25 4,32
2	Density, kg/m^3	1027	1029
3	pH	6,70	6,80

The obtained results meet the standards for raw milk. The value of dry matter of camel milk is more than for cow milk. The contents of protein, lipids and lactose in camel milk are high then in cow milk. The values of density and pH are equal for both milks.

Studyoftheprocessoffreezing cow and camel milk

It was experimentallyfound that a water content in camel milk W = 84.7%, and in cow milk W = 87.0%. Water in both milks can be represented as a medium in that other components are dissolved. Lactic acid and it salts that contained in water basically form true solutions; proteins and other high-molecular compounds transform to the colloidal solutions in water. Fats and other poorly soluble compounds form emulsions when dispersed with water [8]. Based on the above mentioned, it can be concluded that the composition of cow milk and camel milk have a complex colloidal solution.

The results of the study of the freeze-drying process of cow milk and camel milk are presented in Figure 1.

Thermogram's analysis shows that in the freeze-drying process of the cow milk and camel milk there are three areas of temperature variations. On the first section, both types of milk are not only cooled, but also supercooled till a cryoscopic temperature. The duration of this period for camel milk is 46 minutes, and for cow milk is 72 minutes. Further it was observed the isothermal area that has a long duration, particularly the phase transformation of water into ice. The duration of this second area for camel milk is 70 minutes or in the range from 46 minutes to 116 minutes, and for cow milk is 44 minutes or in the range from 72 minutes to 116 minutes. As known from the refrigeration technology, the freezing process is considered as a complete when the centre frozen product temperature reached T=-8°C. In this regard the third area is a short, and on this stage water containing in camel and cow milk transforms into ice. The duration of this area for both types of milk is 15 minutes, or in the range from 116 minutes to 135 minutes.

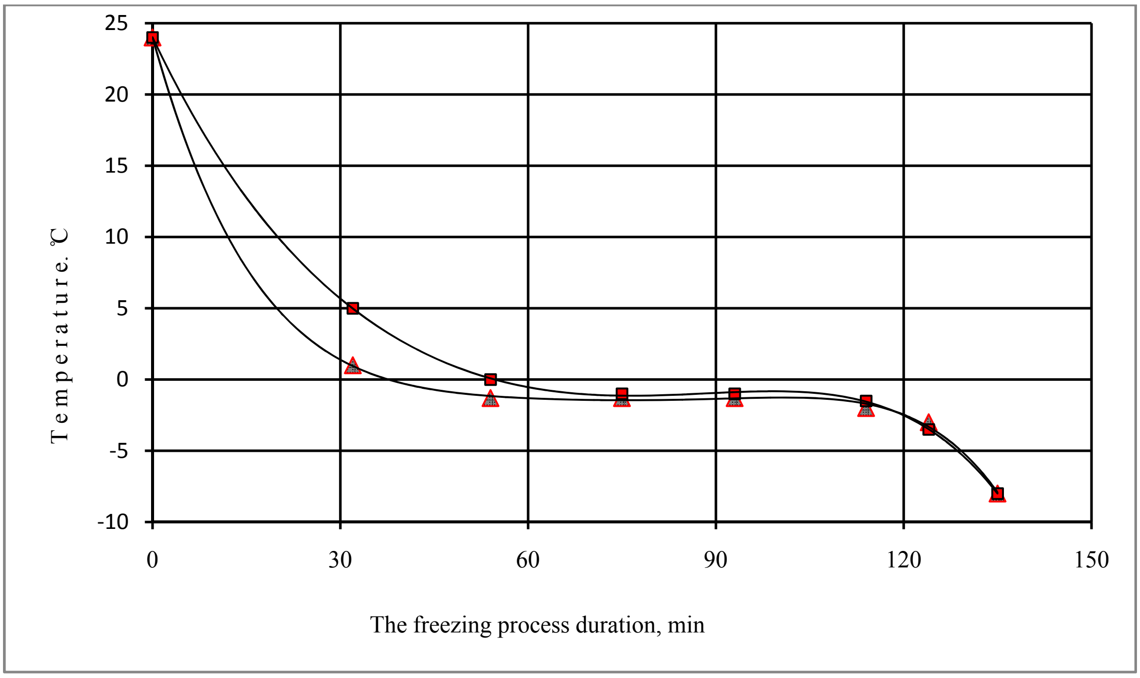

Figure 1 - Thermograms of the freezing of cow milk (□) and camel milk (Δ)

The kinetics dependence of the freezing process of cow milk and camel milk

For a more detailed analysis of the phase transition process of water contained in cow milk and camel milk, its freezing thermograms (Figure 1) were differentiated by time, and the dependence of cooling rate of both milks by time were obtained. The kinetics dependence of the freeze-drying process of cow milk and camel milk are presented in Figure 2.

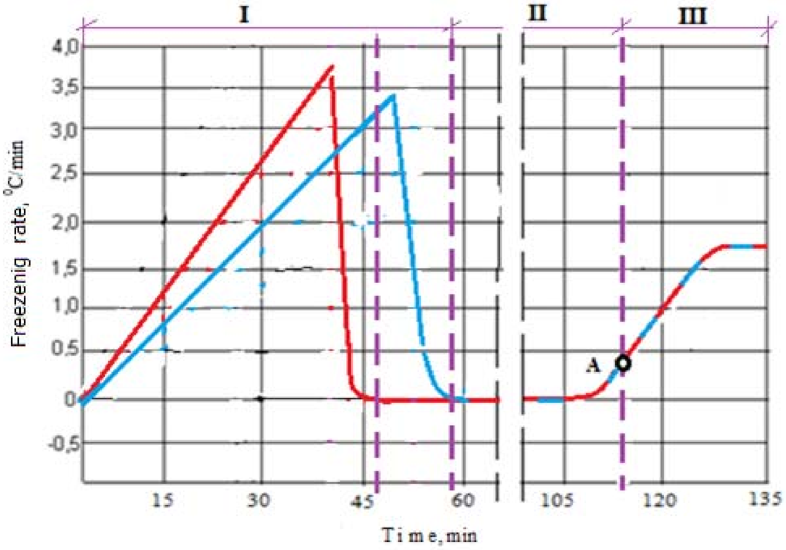

Figure 2 – Kinetics dependence of the freezing process of cow milk (a red curve) and camel milk (a blue curve)
I – cooled and supercooled phase, II - isothermal area and a phase transformation of water into ice,
III – ice forming phase

Figure 2 shows availability of an area with a zero cooling rate that corresponding to the isothermal field of moisture crystallization beginning in cow milk and camel milk. In addition, it can be determined the end point of the crystallization process of free and bound moisture: it corresponds to the inflection point on the cooling rate curve (point A) or t=-3^{0}C.

Study of the amount of frozen water in cow milk and camel milk

The following step in our study was a research of the amount of frozen water in cow milk and camel milk. The obtained results are presented in Figure 3.

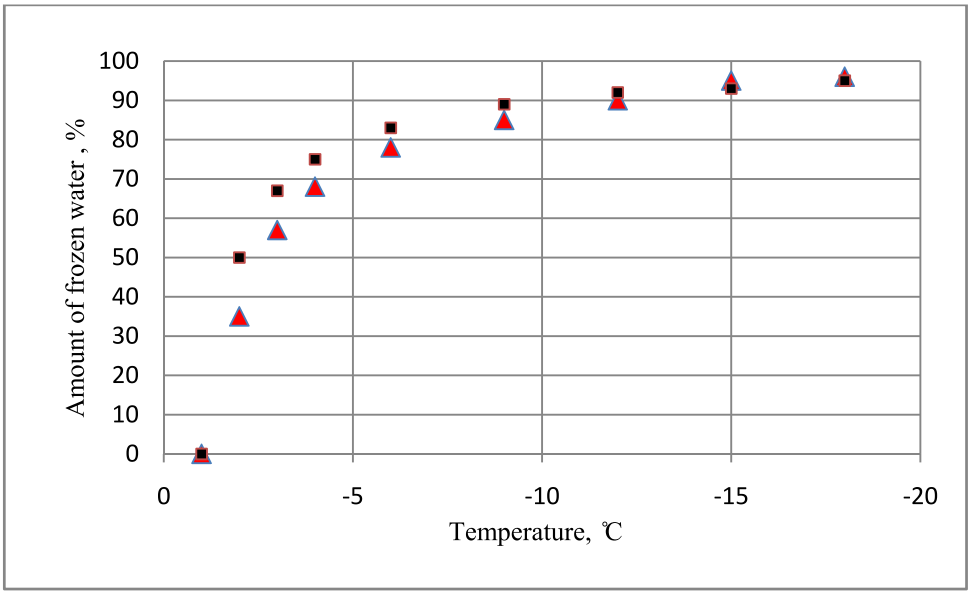

Figure 3 - The amount of frozen water in cow milk (□) and camel milk (Δ)

Analysis of Figure 3 shows that in the range from the cryoscopic temperature till -5 °C in the composition of camel milk, over 70% of the moisture freezes. However, over 80 % of water is frozen in cow milk. At the subsequent temperature decreasing a dependence on the amount of frozen water by a temperature for both types of milks have a monotonously increasing behaviour.

For example, in camel milk, at the temperature range from -5 °C till -10 °C 88% of water is frozen, then at the temperature range from-10 °C till -15 °C, up to 95% of moisture is frozen, and at temperature -20 °C 96% of water is frozen. In cow milk at the temperature range from -5 °C till -10 °C freezes 91 % of moisture, then at the temperature range from -10 °C till -15 °C freezes like in camel milk up to 95% moisture, and at temperature -20 °C 96% of water is frozen.

Based on the above mentioned, it can be concluded that from the point of view of energy savings, lowering the minus temperature below t=-15 °C is economically unprofitable. Because if it is considered a refrigeration machine, where a cold is produced, for the lowering of the temperature in one ^{0}C, the power consumption for the production of cold increases for 4,5%.

Conclusion

In the freeze-drying process of cow milk and camel milk, three areas of temperature variations were identified. The first freezing period for camel milk duration is 46 minutes, and for cow milk is 72 minutes. At the second area the phase transformation of water contained in cow milk and camel milk into ice is present. For cow milk duration is 44 minutes, i.e. from 72 minutes to 116 minutes, and for camel milk is 70 minutes, i.e. from 46 minutes to 116 minutes. The third area has a comparably short time for both milks, and the weakly bound water completely transforms into ice. The duration of this area for both types of milk is 15 minutes, i.e. from 116 minutes to 135 minutes.

The kinetics dependence of the freeze-drying process indicates the inflection point of the cooling rate at the temperature t=-0,5^{0}C. The study of patterns of the freeze-drying process shows the major part of the water contained in the cow milk and camel milk, frozen till a temperature of t=-10 °C. From the point of view of energy savings, lowering the minus temperature below t=-15 °C is economically disadvantageous. Therefore, in the case of using of vacuum - freeze drying process of cow milk and camel milk, the lower limit of the sublimation temperature, a temperature of -13 °C ...- 15 °C is recommended.

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СИЫР МЕН ТҮЙЕ СҮТІНІҢ МҰЗДАТУНЫҢ ОҢТАЙЛЫ ТЕМПЕРАТУРАСЫ

Аннотация. Сиыр сүті мен түйе сүтін мұздату кезінде температураның өзгеруінің үш аймағы анықталды. Атап айтқанда, бірінші кезеңде сүттің екі түрі де салқындатылады, содан кейін аса салқындатылады және одан әрі мұз кристалдарының пайда болу процесі жүреді. Екінші учаскеде изотермиялық аймақ байқалып, судың мұзға фазалық айналуы байқалды. Үшінші кезеңде сиыр және түйе сүтіндегі әлсіз байланысқан су толығымен мұзға өтті. Қатып қалған ылғал мөлшерінің өзгеру сипатын зерттеу негізінде минус Т=-15°С температурада сүттің екі түрлерінде болатын судың 95% - дан астамы мұздатылады және температураның одан әрі төмендеуі бірқалыпты азырақ өсіп келе жатқан сипатқа ие болды. Демек, сиыр сүті мен түйе сүтін мұздату кезінде энергияны үнемдеу және бастапқы қасиеттерін барынша сақтау тұрғысынан сублимация температурасының оңтайлы диапазоны ұсынылды.

Кілт сөздер: сүт, мұздатылған ылғал, изотермиялық процесс, еркін және байланысқан су.

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ОПТИМАЛЬНАЯ ТЕМПЕРАТУРА ЗАМОРАЖИВАНИЯ КОРОВЬЕГО МОЛОКА И ВЕРБЛЮЖЬЕГО МОЛОКА

Аннотация. В процессе замораживания коровьего молока и верблюжьего молока были выявлены три области изменения температуры. В частности, в первый период оба типа молока охлаждаются, затем переохлаждаются и далее происходит процесс образования кристаллов льда. На втором участке наблюдалась изотермическая область, и присутствовало фазовое превращение воды в лед. На третьем этапе слабосвязанная вода, содержащаяся в коровьем молоке и верблюжьем молоке, полностью переходила в лед. На основании изучения характера изменений количества замерзшей влаги было установлено, что при температуре минус T=-15°C более 95% воды, содержащейся в обоих типах молока, замораживается, и дальнейшее снижение температуры имело монотонно незначительно возрастающее поведение. Следовательно, с точки зрения экономии энергии и максимального сохранения первоначальных качеств, при замораживании коровьего молока и верблюжьего молока, рекомендуется оптимальный диапазон температур сублимации.

Ключевые слова: молоко, замороженная влага, изотермический процесс, свободная и связанная вода

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REFERENCES

[1] Brezovečki A., Čagalj M., Dermit Z.F., Mikulec N., Ljoljić D. B., Antunac N. (2015).Camel milk and milk products. Mljekarstvo/Dairy, 65(2), 81-90 http://dx.doi.org/10.15567/mljekarstvo.2015.0202

[2] Chizhov G. B. (1979). Teplofizicheskie process v holodil'nojtehnologiipishhevuhproduktov[Thermophysical processes in refrigeration technology of food products]. Moscow, 1979, 271 (in Russian)

[3] Chomanov U.Ch., Shingisov A.U. (2016). Sovershenstvovanijatehnologiivakuum-sublimacionnojsushkikumysaishubata (Improving of the vacuum freeze-drying technology of koumiss and shubat). Monography, Almaty: TOO «378», 272 (in Russian)

[4] Garcia-Amezquita LE, Welti-Chanes J, Vergara-Balderas FT, Bermúdez-Aguirre D. (2016). Freeze-drying: the Basic Process. Reference Module in Food Science from Encyclopedia of Food and Health, Academic Press Oxford, 104-109 http://dx.doi.org/10.1016/B978-0-12-384947-2.00328-7

[5] Kamerbaev A.J. (2001). The role of water in food products and its function. Almaty, 203 (in Russian)

[6] Orymbetova G.E., Conficoni D., Kassymova M.K., Kobzhasarova Z.I., Orymbetov E.M., Shambulova G.D.(2018) Risk assessment of lead in milk and dairy products. News of the National Academy of Sciences of the Republic of Kazakhstan-Series Chemistry and Technology, 6(432), 23-28https://doi.org/10.32014/2018.2518-1491.22

[7] SemenovG.V., KasianovG.I. (2002). Sushkasyr'ja: mjaso, ryba, ovoshhi, frukty, moloko. (Drying of raw: meat, fish, vegetables, fruits, milk). Rostov-on-Don: TOO «MarT», 112 (in Russian)

[8] Semenov G.V., Krasnova I.S. (2013).Vakuumnajasublimacionnajasushka (Vacuum freeze-drying). Moscow: DeLipljus, 264 (in Russian)

[9] Kantureeva G.O., Defrancesco E, Alibekov R.S., Urazbayeva K.A., Efimova I.E. (2018). New trends in the identification of the traditional food products of Kazakhstan. News of the National Academy of Sciences of the Republic of Kazakhstan-Series Chemistry and Technology, 5(431), 6-12 http://dx.doi.org/10.32014/2018. 2518-1491.1

[10] Myrkalykov B., Shingisov A., Ospanov A., Simov Z., Latif A., Aripbaeva A. (2018). Freeze Drying of Sheep Milk: Calculating Process Duration. European Online Journal of Natural and Social Sciences; 7(2), 460-470 http://european-science.com/eojnss/article/view/5281

[11] Olenev Y.A. (1983). Energy outage moisture during the hardening ice cream. Refrigeration technics, 1(5), 41-42 (in Russian)

[12] Shingisov A.U., Alibekov R. S. (2017). Analysis of the moisture evaporation process during vacuum freeze-drying of koumiss and shubat. Heat and Mass Transfer, 53(5), 1571-1578 http://dx.doi.org/10.1007/s00231-016-1920-4

[13] Shingisov A., Alibekov R., Nurseitova Z., Orymbetova G., Kantureeva G., Mailybaeva E. (2015). Desorption isotherms of the koumiss and shubat clots enriched by various additives. Modern Applied Science, 9(8), 409 http://dx.doi.org/10.5539/mas.v9n8p409

[14] Sulieman A.M.E., Elamin O. M., Elkhalifa E. A., Laleye L.A. (2018). Comparative Study of Physicochemical Properties of Freeze-dried Camel's Milk and Cow's Milk Powder.Discourse Journal of Agriculture and Food Sciences, 6(2), 11-16 http://www.resjournals.org/JAFS/PDF/2018/March/Sulieman%20et%20al.pdf

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CATHODE RESTORATION OF SELONIUM ANIONS WITH THE FORMATION OF ITS POWDERS

Abstract. The article shows the possibility of obtaining selenium powders by cathodic reduction of its anions in acidic and alkaline solutions. It has been established that in alkaline medium it is impossible to obtain selenium powders by reducing selenite ions. However, it is shown that selenium powders can be obtained by cathodic reduction of these ions in a sulfate medium.The main results of the conducted research are the production of selenium powders by cathodic reduction of “hardly recoverable”, and cathode “non-renewable” selenite-ions and determination of the regularities of this process.

It has been shown for the first time that in sulfate solutions in the presence of titanium (IV) ions by cathodic reduction of selenite-ions, selenium powders can be obtained. The effect of the concentration of titanium (IV) ions, selenite-ions, and cathode current density on the formation of selenium powders was studied.It has been established that in the absence of titanium (IV) ions, selenium powders are not formed, and at their concentration equal to 5.0 g/l, the current yield for selenium powder formation reaches 70%. It has been proven that titanium (IV) ions have a catalytic effect on the cathode formation of selenium powders. It is shown that the formation of selenium powders proceeds in two stages, i.e. consists of an electrochemical and chemical reaction, namely, tetravalent titanium is reduced at the cathode to the trivalent state.It has been established that the titanium (III) ions formed in this case interact in the cathode space with selenium (VI) anions, reducing them to elemental selenium as an ultrafine powder.

It is shown that an increase in the current density at the cathode leads to a decrease in the current efficiency for the formation of selenium powders. With an increase in the concentration of selenite-ions, the yield of selenium powders increases.It is established that with selenium (VI) concentration equal to 10.0 g/l, the yield of selenium powder formation is 68.1%, and at 30 g/l - 94.9%.The shapes and sizes of the obtained selenium powders were determined using an electron microscope.

Keywords: selenium powder, selenite and selenate ions, sulphuric acid, electrolysis, cathode, current output.

Introduction. The electrochemical properties of selenium ions in aqueous media are studied in detail [1-10].

Selenium powders can be obtained by the reduction of selenium ions with sulfur dioxide [11]:

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se\downarrow + 2H_2SO_4 \quad (1)$$

Sulfur dioxide (SO_2) is a toxic gas so this method is not widespread.

In our first study, we considered the possibility of obtaining selenium powders by the reduction of tetravalent selenium ions in an alkaline medium. According to the literature, selenite ions can be reduced according to the following cathodic reactions in an alkaline medium [12, 13]:

$$SeO_3^{2-} + 3H_2O + 4e \rightarrow Se^o + 6\ OH^- \quad (2)$$

$$SeO_3^{2-} + 3H_2O + 6e \rightarrow Se^{2-} + 6\ OH^- \quad (3)$$

From the literature, the newly formed element reacts with hydroxide ions at the moment, and a disproportion reaction occurs [14]:

$$3Se^o + 6OH^- \rightarrow 2\ Se^{2-} + SeO_3^{2-} + 3H_2O \quad (4)$$

According to these data, selenite ions can be reduced at one stage simultaneously to selenide-ions or elemental selenium.

Procedure of work execution. In our initial studies, electrolysis was carried out in a solution containing 15 g/l of selenium (IV) ions and 40 g/l of NaOH. The electrolysis was carried out by a 100 ml electrolyzer and an unseparatedinterelectrode space. Titanium was used as a cathode, non-oxidizable iron electrodes (IX18H10T) were used as an anode.

The results of electrolysis at a current density of 50–350 A/m^2 on the electrodes showed that selenium powders did not form at the cathode, mainly the formation of red-brown polyselenide-ions.

The restoration of the cathode in an alkaline medium by six valence selenate ions (SeO_4^{2-}) was also investigated.The electrolysis results show that this ion is not recovered.There was no formation of selenium powders in the cathode, and the color change of the electrolyte did not occur in the cathode space.

Since the main goal of our research is the production of selenium powders, we did not consider it necessary to continue research further.

Subsequent studies of selenium powders were carried out in a solution containing sulfuric acid and tetravalent selenite-ions.Our preliminary studies have shown that selenium powders are formed on the cathode in an acidic environment.

The presented studies were carried out in the above-mentioned electrolyzer only when using a graphite electrode as an anode.Our subsequent studies showed that cathodic reduction of hexavalent selenium ions ($SeO^{4-}{}_2$) does not occur in a solution with sulfuric acid, and adding titanium (IV) ions to the electrolyte, it was found that the formation of ultrafine selenium powders takes place at high speed.

Theoretical. According to the literature, hexavalent selenium ions can be reduced by strong reducing agents only in alkaline media at temperatures above 200 ° C and only at high pressures. Hydrogen, sulfides, elemental sulfur or organic reducing agents are used as reducing agents.[11-13]. In acidic environments by boiling the selenium ion to the tetravalent state in concentrated hydrochloric acid, and then gaseous sulfur dioxide restores to the elemental state. In this case, the recovery of six valence selenium ions occurs in two stages[11]. These processes significantly aggravate the working condition.Since this is a very complex process, the above steps are not available for the production of elemental selenium from six valence selenium ions.

However, the selenate ions with an octahedral shape are surrounded by oxygen atoms (shielded) that cannot penetrate into the double electrode layer on the cathode surface, which leads to kinetic difficulties. Information on the non-recoverability of selenate ions in the cathode is given in the literature.[1, 11-13].

From the point of view of thermodynamics, selenate ions should be restored at the cathode, and their standard potentials are given below:

$$SeO_4^{2+} + 3H^+ + 2e \rightarrow HSeO_3^- + H_2O \qquad E^o = + 1.075V \qquad (5)$$

$$HSeO_3^- + 5H^+ + 4e \rightarrow Se + 3H_2O \qquad E^o = +0.77\ V \qquad (6)$$

$$SeO_4^{2-} + 8H^+ + 6e \rightarrow Se + H_2O \qquad E^o = +0.877\ V \qquad (7)$$

The current output for the formation of selenium powder is determined depending on its weight. During electrolysis, the formation of red was found dispersed amorphous selenium on the surface and area of the cathode.

The effect of the concentration of sulfuric acid and titanium (IV) ions, as well as the effect of the current density of cathode electrodes in the solution on the current output for the formation of selenium powders was investigated.

Experimental. The results of the study showed that tetravalent titanium ions have a significant effect on the current efficiency of the direct reduction of selenium powder with selenate ions.For example, when the current density on the cathode electrode is 100 A/m^2 and the concentration of titanium in the solution is 2.5 g/l, then the current for the formation of selenium powder will be 44.1%, at 5.0 g/l - 68.5%, and at 10 g/l will be equal to 79.8%. Table 1 shows the effect of current density on the current output of selenium powder.

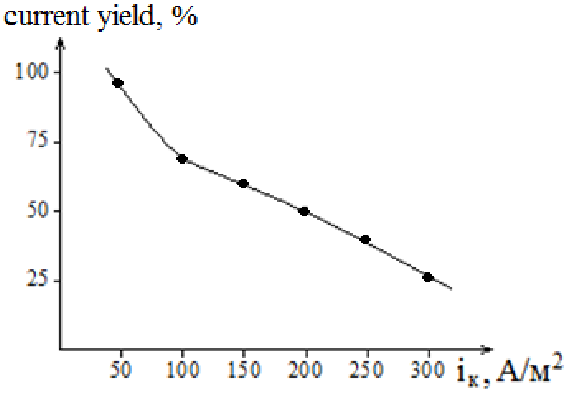
Table 1 -Influence of titanium (IV) ions present in the solution on the formation of selenium powders:
Se (IV) = 10 g/l, H_2SO_4 – 100 g/l, i_c = 100 A/m^2, τ = 1 hour

Ti (IV), g/l	0.5	1.0	2.5	5.0	7.5	10.0
Current output, %	20.9	30.5	44.1	68.5	72.1	79.8

If we take into account that the value of selenium ions (VI) is lower than the value of the limiting current - at 100 A/m^2 completely restores selenium powders. This phenomenon indicates that selenium (VI) ions are not restored on the cathode surface in a direct way, and their recovery occurs with the help of intermediate titanium (III) ions.Consequently, titanium (IV) ions can be reduced to three valence states at the cathode, and then the subsequent reduction of the selenite-ions to selenium powder is observed.

With an increase in the concentration of sulfuric acid in the solution (in the presence of titanium ions), a slight decrease in the current yield of selenium powder is observed.

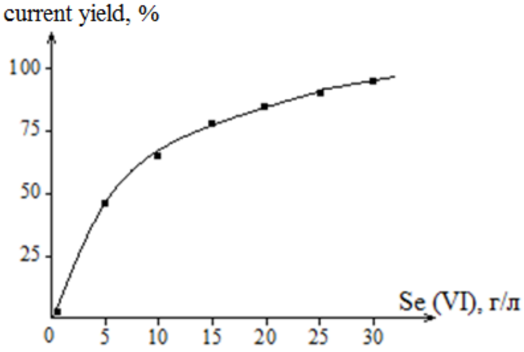
The increase in cathode current density leads to a decrease in the current for the formation of selenium powders (Fig. 1), this phenomenon can be explained by an increase in the proportion of hydrogen gas in the cathode layer, and it can be traced by the smell of hydrogen sulfide at high cathode densities. However, it was found that when the cathode current density is 50-175 A/m^2 and the concentration of selenium (VI) ions exceeds 10 g/l, the formation of hydrogen gas does not occur.



Se (VI) – 10 g/l, H_2SO_4 – 100 g/l, Ti (IV) – 5 g/l

Figure 1 –The effect of cathode current density on the current output for the formation of selenium powder

Changes in the concentration of selenium ions in solution have a significant effect on the current efficiency of the formation of selenium powder at the cathode. For example, while the current density is 100 A/m^2 and the concentration of selenium ions is 5 g/l, the current efficiency will be 45.5%, and at 10 g/l it will be 68.1%, at 30 g/l it will be 94.9%. Figure 2 shows the effect of the current density on the titanium cathode on the current efficiency for the formation of selenium powder.



Ti (VI) – 5.0 g/l, i_c – 100 g/l, H_2SO_4 – 100 g/l

Figure 2 – The effect of the concentration of selenium (VI) ions in solution
on the current output for the formation of selenium powders

The aforementioned research results show that in the presence of titanium (IV) ions in solution, hexavalent selenium ions cause a direct reduction of their own powders.This phenomenon can be explained by the catalytic effect of the Ti (IV) –Ti (III) redox system.

Tetravalent titanium ions are reduced at the cathode to trivalent:

$$TiO^{2+} + e + 2H^{+} \rightarrow Ti^{3+} + H_2O \qquad E^{o} = -0{,}04\ V \qquad (8)$$

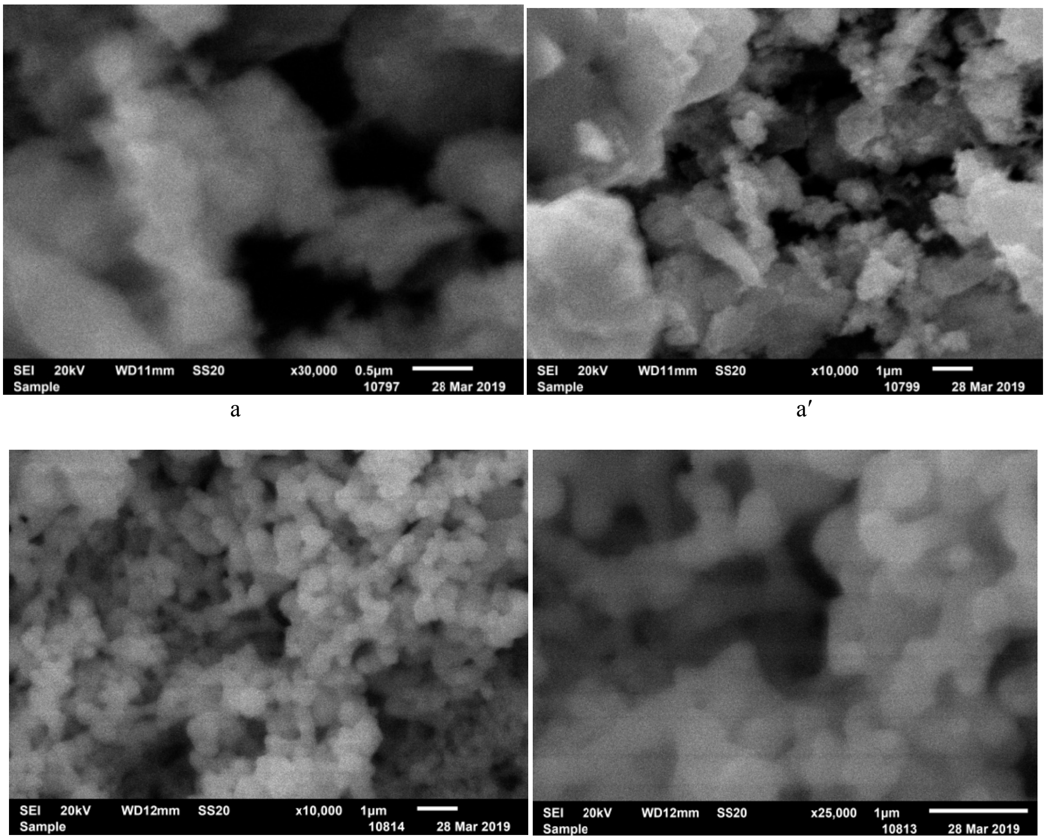
According to the literature [15], the standard potential of the Se (VI) -Se system is +0.86 V, and Ti (IV) -Ti (III) is +0.04 V.

Titanium (III) ions react with selenite-ions in the cathode region, and as a result of the redox reaction, selenium powder is formed:

$$6Ti^{3+} + SeO_4^{2-} + 2H_2O \rightarrow Se^{o} + 6TiO^{2+} + 4H^{+} \qquad (9)$$

As a result, tetravalent titanium ions are regenerated, then they are re-reduced at the cathode to the trivalent state and restore selenium (VI) ions in the cathode region. This process is repeated cyclically.Therefore, in this case, the reduction of selenate ions to selenium powders is a catalytic process. In our earlier works, we mentioned that titanium (IV) ions act as a catalyst in the formation of copper powders.[16-22].

The shape and size of selenium powder obtained by electrolysis were obtained using electron microscopy (JSM-6610 LV).The results of the study showed the formation of selenium powder in its mostly round shape, not exceeding 1-2 microns in size. No significant changes are observed in the shape and size of selenium powders formed on the cathode at a current density in the range of 100-150 A/m^2.



a a′

b b′

Se (VI) – 10g/l, H_2SO_4 – 100 g/l, Ti (IV) – 5.0 g/l, τ =1hour

a, a$^{'}$ -i=100 A/m^2; b, b$^{'}$ - i=150 A/m^2

Figure 3 – Micrographs of selenium powder obtained by reducing selenate ions at the cathode in the presence of titanium (IV) ions

In conclusion, we showed for the first time that selenium ions “non-reducible” at the cathode are reduced in the presence of titanium (IV) ions, and we also obtained pink amorphous selenium powder. Titanium (IV) ions have been shown to have a catalytic effect. Under optimal conditions, it was found that the current for the formation of selenium powder exceeds 90%.

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СЕЛЕН АНИОНДАРЫН КАТОДТА ТОТЫҚСЫЗДАНДЫРУ АРҚЫЛЫ ОНЫҢ ҰНТАҚТАРЫН АЛУ

Аннотация. Мақалада қышқылды және сілтілі ерітінділерде селен аниондарын катодты тотықсыздандыру арқылы селен ұнтақтарын алу мүмкіншіліктері көрсетілген. Сілтілі ортада селенит-иондарын тотықсыздандыру арқылы селен ұнтақтарын алуға болмайтындығы көрсетілген. Ал ббірақ бұл иондарды күкірт қышқылы ерітіндісінде катодты тотықсыздандыру арқылы селен ұнтақтарын алуға болатындығы анықталған. Жүргізілген ғылыми зерттеулердің негізгі нәтижелерінде қиын тотықсызданатын, ал катодты «тотықсызданбайтын» селенат-иондарын катодты тотықсыздандыру арқылы селен ұнтақтарын алу мүмкіншіліктері көрсетіліп, бұл процестің заңдылықтары анықталған.

Алғаш рет селенат-иондарын күкірт қышқылы ерітіндісінде титан (IV) иондары қатысында катодты тотықсыздандырып селен ұнтақтарын алуға болатындығы көрсетілген. Селен ұнтақтарының түзілу процесіне титан (IV) иондарының, селенат-иондарының концентрацияларының, катодтағы ток тығыздығының әсері зерттелді. Титан (IV) иондары қатысынсыз селен ұнтақтарының түзілмейтіндігі, ал оның мөлшері 5,0 г/л болғанда селен ұнтақтарының түзілуінің ток бойынша шығымы 70 %-ке жақындайтындығы анықталды. Селен ұнтағының катодты түзілуінде титан (IV) иондарының каталитикалық әсер көрсететіндігіне көз жеткізілді. Селен ұнтақтарының түзілуі екі стадияда, яғни электрохимиялық және химиялық реакциялардан құралатыны анықталды. Дәлірек айтатын болсақ, катодта төрт валентті титан үш валенттіге дейін тотықсызданып, катод аумағында селен (VI) иондарын элементті ультрадисперсті ұнтақ түріне дейін тотықсыздандыратындығы анықталды.

Катодтағы ток тығыздығының өсуі, селен ұнтақтарының түзілуінің ток бойынша шығымын төмендететіндігі көрсетілді. Алты валентті селенат-иондарының концентрациясының өсуімен, селен ұнтақтарының түзілуінің ток бойынша шығымының өсетіндігі анықталды. Селен ұнтақтарының түзілуінің ток бойынша шығымы селеннің (VI) концентрациясы 10,0 г/л болғанда – 68,1 % болса, ал 30 г/л-де – 94,9 % тең болатындығы көрсетілді.

Алынған селен үнтақтарының размері мен формасы электронды микроскоп арқылы анықталды.

Түйін сөздер: селен ұнтағы, селенит-, селенат-иондары, күкірт қышқылы, электролиз, катод, ток бойынша шығым.

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КАТОДНОЕ ВОССТАНОВЛЕНИЕ АНИОНОВ СЕЛЕНА С ОБРАЗОВАНИЕМ ЕГО ПОРОШКОВ

Аннотация. В статье показана возможность получения порошков селена катодным восстановлением его анионов в кислых и щелочных растворах. Установлено, что в щелочной среде невозможно получить порошки селена восстановлением селенит-ионов. Однако показано, что путем катодного восстановления этих ионов в сернокислой среде можно получить порошки селена. Основными результатами проведенных научных исследований является получение порошков селена катодным восстановлением «трудновосстанавливаемых», а катодно «невосстанавливаемых» селенат- ионов и определение закономерностей данного процесса.

Впервые показано, что в сернокислых растворах в присутствии ионов титана (IV) катодным восстановлением селенат-ионов можно получить порошки селена. Исследовано влияние концентрации ионов титана (IV), селенат-ионов, катодной плотности тока на процесс образования порошков селена. Установлено, что в отсутствии ионов титана (IV) порошки селена не образуются, а при их концентрации, равной 5,0 г/л, выход по току образования порошков селена достигает 70%. Доказано, что на катодное формирование порошков селена ионы титана (IV) оказывают каталитическое действие. Показано, что образование порошков селена протекает в две стадии, т.е. состоит из электрохимической и химической реакции, а именно, четырехвалентный титан восстанавливается на катоде до трехвалентного состояния. Установлено, что образовавшиеся при этом ионы титана (III) взаимодействуют в катодном пространстве с анионами селена (VI), восстанавливая их до элементного селена в виде ультрадисперсного порошка.

Показано, что увеличение плотности тока на катоде приводит к снижению выхода по току образования порошков селена. С возрастанием концентрации селенат-ионов происходит повышение выхода по току образования порошков селена. Установлено, что при концентрации селена (VI), равной 10,0 г/л выход по току образования порошков селена составляет 68,1%, а при 30 г/л – 94,9%. Формы и размеры полученных порошков селена определены с помощью электронного микроскопа.

Ключевые слова: порошок селена, селенит-, селенат-ионы, серная кислота, электролиз, катод, выход по току.

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REFERENCES

[1] Baeshov A., Zhurinov M.Zh., Zhdanov S.I. (1989) Electrochemistry of selenium, tellurium and polonium. [Jelektrohimija selena, tellura i polonija] Science KazSSR [Nauka KazSSR] P.172. (in Russian).

[2] Baeshov A., Daribaev Zh.E., Baeshova A.K. (1999**)** The method of obtaining elemental selenium **[**Sposob poluchenija jelementarnogo selena] Provisional patent of the Republic of Kazakhstan № 7299 from 11.07.97 published in the bulletin № 3. (in Russian).

[3] Baeshov A., Sarbaeva K.T., Baeshova S.A. i dr. (2007) The method of producing sodium polyselenide [Sposob poluchenija poliselenida natrija] Provisional patent of the Republic of Kazakhstan № 18451 from 17.10.05. Published in the bulletin № 5. (in Russian).

[4] Baeshov A., Sarbaeva K.T., Baeshova S.A., Zhurinov M.Zh. (2007) The method of obtaining sodium selenite [Sposob poluchenija selenita natrija] Provisional patent of the Republic of Kazakhstan № 18325 from 13.09.05. Published in the bulletin № 3. (in Russian).

[5] Baeshov A., Serazitdinova G., Baeshova S.A. i dr. (2007) The method of producing sodium polyselenide [Sposob poluchenija poliselenida natrija] Provisional patent of the Republic of Kazakhstan № 18452 from 17.10.05. Published in the bulletin № 5. (in Russian).

[6] Baeshov A., Baeshova A.K., Buketov E.A. (1985) Anodic behavior of selenium (VI) in solutions of lithium, sodium, and potassium hydroxides [Anodnoe povedenie selena (VI) v rastvorah gidroksidov litija, natrija, kalija] Non-ferrous metallurgy, University news. [Cvetnaja metallurgija, Izv. VUZov]. № 2, P.66-69. (in Russian).

[7] Bayeshov A., Ivanov N., Myrzabekov B. (2014) Electrochemical behavior of Selenium as Part of Composite Electrode in Sulfuric Acid Medium. Journal of Advances in Chemistry, Vol.7, №3. P.1378-1385. DOI: https://doi.org/10.24297/jac.v7i3.2373 (in English).

[8] Speranskaja E.F. (1967) Polarographic recovery of selenites and tellurites on amalgam drip electrodes. [Poljarograficheskoe vosstanovlenie selenitov i telluritov na kapel'nyh amal'gamnyh jelektrodah] Electrochemistry [Jelektrohimija] T. 3, V.2. P.1405-1507. (in Russian).

[9] Baeshov A., Kozhakov B.E., Buketov E.A. (1984) Electrocatalytic reduction of selenium (VI) in hydrochloric acid [Jelektrokataliticheskoe vosstanovlenie selena (VI) v soljanoj kislote] Reports of the Academy of Sciences of the USSR. [DAN SSSR], T.278, № 3, P.646-650. (in Russian).

[10] Baeshov A., Bejbitova A.D. (1986) Electrochemical reduction of selenite and selenate ions in hydrochloric acid solution [Jelektrohimicheskoe vosstanovlenie selenit- i selenat-ionov v soljanokislom rastvore] Physical and chemical bases of mineral processing in Kazakhstan. [Fiziko-himicheskie osnovy pererabotki mineral'nogo syr'ja Kazahstana] Alma-ata. P.271-276. (in Russian).

[11] Chizhikov D.M., Schastlivyj V.P. (1964) Selenium and selenides [Selen i selenidy] Moscow: Science [M.: Nauka] P.56 (in Russian).

[12] Grejver T.N., Zajceva I.G., Kosover V.M. (1977) Selenium and tellurium [Selen i tellur] Moscow [M.] 296 p. (in Russian).

[13] Kudrjavcev A.A. (1968) Chemistry and technology of selenium and tellurium [Himija i tehnologija selena i tellura] Moscow [M.] 339 p. (in Russian).

[14] Buketov E.A., Ugorec M.Z. (1975) Hydrochemical oxidation of chalcogens and chalcogenides. [Gidrohimicheskoe okislenie hal'kogenov i hal'kogenidov] Alma-Ata. –326 P. (in Russian).

[15] Handbook of Electrochemistry edited by A.M. Suhotin [Spravochnik po jelektrohimii. Pod red. A.M. Suhotina], L.Himija (1981), 488 p. (in Russian).

[16] Baeshov A., Kozhakov B.E., Buketov E.A. (1982) The method of producing copper powder [Sposob poluchenija poroshka medi] USSR author's certificate № 1082066 from 12.07.82. (in Russian).

[17] Baeshov A., Dauletbaev A.S., Baeshova A.K. (2010) Electrochemical method of producing copper powder [Jelektrohimicheskij sposob poluchenija mednogo poroshka] Innovative patent of the Republic of Kazakhstan № 22669 from 24.06.09. Published in the bulletin №7. (in Russian).

[18] Baeshov A., Gaipov T.Je., Baeshova A.K. (2018) The method of obtaining ultrafine copper powders [Sposob poluchenija ul'tradispersnyh poroshkov medi] Patent of the Republic of Kazakhstan for a utility model № 3364 from 04.07.18. (in Russian).

[19] Baeshov A., Kozhakov B.E., Buketov E.A., Kremko E.G. (1984) Electrochemical production of copper powder [Jelektrohimicheskoe poluchenie mednogo poroshka] Collection of works in chemistry [Sbornik rabot po himii], V.8, Alma-Ata, P.283-290. (in Russian).

[20] Baeshov A., Piskova N.I., Dospaev M.M. (1988) Cementation of copper (II) from sulphate solutions in the presence of titanium (IV) [Cementacija medi (II) iz sernokislyh rastvorov v prisutstvii titana (IV)] In the book: Collection of Chemistry [V kn.: Sbornik po himii], Alma-Ata, V. II.-P. 144-148. (in Russian).

[21] Bayeshov A., Gaipov T.E. etc., (2018) Production of nano- and ultrafine copper powders by cementation of copper (II) ions by trivalent titanium ions/ News NAS RK, a series of chemistry and technology, № 6. P. 87-95. DOI.org/10.32014/2018.2518-1491.30 (in Eng).

[22] Bayeshov A., Myrzabekov B.EH., Kolesnikov A.V. (2018) Patterns of formation of dispersed copper powders in the electrolyte volume when using a copper anode in a solution of sulfuric acid containing titanium (IV) ions/ News NAS RK, a series of chemistry and technology. № 6. –P.96-101. DOI.org/10.32014/2018.2518-1491.31 (in Eng).

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DATA ON ANTIOXIDANT ACTIVITY OF HUMIC SUBSTANCES OF LOW-MINERALIZED SLUDGE SULPHIDE MUD (PELOIDS) AND THEIR CLASSIFICATION

(Review)

Abstract. In this work, an overview of the antioxidant activity of humic substances of low-mineralized sludge sulphide muds (peloyds). Though these substances show the greatest biological and therapeutic activity, in comparison with similar substances of other sources (keonardits, coals, etc.) they are insufficiently studied. Formed in the reduction conditions, molecules of humin substances ща low-mineralizedof silt sulphidic mud possess a unique structure, and excludes a possibility of education in the course of receiving carcinogenic the alkilnic the halogenderivants and thereof urgent is a research in given the directions.

Key words: antioxidatic properties, activity, humin substances, peloida.

Peloid therapy or mud cure is one of the earliest methods of therapy using natural components, which have the biggest adaptogene potential Being customary stimulants, they have an expressed curative influence [1,2].

The peloid therapy can be considered as a unique method for sanitation, since the range of deceases, on which it has positive influence, is quite wide [3]. Peloids have immunomodulatory effect, they cause natural adaptive reactions of human body [4,5], produce anti-inflammatory, desensitizing, antineoplastic [2,6,7], anaesthetic and absorbable effect, improve hemodynamics and lymphdynamics, reduce the activity of exudative and infiltrative processes, soften commissural structures [9]. The mud cure is applied when treating various pathologies: arthritis, respiratory illness, dermatological deceases, gastrointestinal problems, gynaecological deceases, trophic ulcers, hepatitis, inflammatory diseases of lungs, paradontium [10].

The therapeutic effects of mud are based on the combination of actions of closely related thermal, mechanical, chemical and biological factors. Depending on physical and chemical composition of the mud, the severity of the biological reactions of each of them is different. The literature sources describe studies devoted to the study of the peloid composition, but they all characterize mineral component of the mud, and almost do not include functional ability of the organic component. The insufficient knowledge of the organic substances of peloids caused their underestimation in the mechanism of effect on the body [11].

The peloids are divided into the following groups basing on the content of organic substances: peat, sapropelic, sludge sulphide [12]. A number of studies [10] has showed a high biological effect of sludge sulphide mud, which is associated with the components of the composition of the organic fraction. Ё

Sludge sulphide mud are dividing into the following categories basing on the content of sulphides: weakly sulphide (0.01–0.15 % of wet mud), medium sulphide (0.15–0.5 %), heavy sulphide (exceeding 0.5 %). Depending on the salinity of mud solution, low-mineralized (1.0–15.0 g/l), medium-mineralized (15.0–35 g/l), highly mineralized (35–150 g/l), saline-saturated (exceeding 150 g/l) sulphide muds [13] are distinguished.

The therapeutic significance of sludge sulphide mud is related to high viscous-plastic and thermal properties, content of large amounts of sulphides (exceeding 0.2 %) and organic substances (approximately 5 % on dry basis), including humic acids and their salts, lipids and hemicellulose, and presence of vitamins, enzymes and hormones [14]. Groups of nonspecific and specific compounds are distinguished from the composition of organic substances of peloids. Non-specific compounds include lipids, carbohydrates, amino acids, enzymes, keratinoid pigments, vitamin complexes, and others [10, 15-17].

A higher content of organic substances in peloids is represented by specific organic components – humic substances [16, 18, 19], which content is equal to 45–90 %.

Scientists of all countries are making attempts to isolate and study properties of organic components of peloids to use them independently as biologically active natural compounds and introduce them into public health practice. The study of fractions of humic substances of peloids: himatomelanic, humic, fulvic acids is a considerable interest for creating innovative pharmacotherapeutic drugs based on them, including those with high antioxidant activity [20-24].

Humic substances are a combination of biothermodynamically stable compounds that form, plant and animal residues having no analogues in living organisms in the process of decomposition and biotransformation, which are distinguished by dark color, polydispersity, high molecular weights [25-27]. All humic substances are formed as a result of the postmortal transformation of organic humification residues, process of transformation of decomposition products having different composition and origin of organic residues into humic substances [28].

The difference of this group of natural organic substances from others lies in their pestoichiometric structure and stochastic nature related to the peculiarities of formation resulting from the selection of biothermodynamically stable structures. The variaty of molecular forms of humic substances is determined by the mechanism of biochemical reactions that accompany formation and conditions of geochemical transformation [28, 29].

Classification of humic substances is based on various solubility of these substances in acids and alkalis. According to this classification, they are divided into the following fractions: fulvic, himatomelanic, humic, humus acids and humin-conglomerate of esters of acids and their organo-mineral sorption complexes with clay minerals, insoluble in most solvents [28-30].

Humic acids are insoluble at pH <2, in a dissolved state they have a dark brown colour, in dry state – black powder or flakes [27]. They consist of aromatic core and peripheral part formed by specific chains.

The himatomelanic acids are an alcohol-soluble fraction, which have a cherry-red colour in solution and were first isolated in 1889 and described by the German biochemist, doctor Ernst Felix Hoppe-Zeiler [25].

Fulvic acids are soluble in the whole range of medium acidity, have a variable colour in the range from straw-yellow to orange colour. They vary from humic and himatomelanic acids by greater oxidation and lower carbon content, as well as greater hydrophilicity [27].

Humus acids are the sum of humic, hymatomelanic, and fulvic acids. They have more folded, complex, stochastic structure. Presumably, being supramolecular structures, humus acids are destroyed during classic fractionation of humic substances. Besides, mechanical mixing of already obtained fractions following separation does not have the same set of properties, that humus acids have [14, 25].

Free radical activity is a fundamental property of humic substances [31, 32]. Studying the structure of various natural biopolymers, we can judge the reactivity of the specified substances and their possible transformations in one or another environment. The nature and properties of stable organic free radicals of humic substances has been investigated in a large number of works [32-33]. The content of aromatic structures in the composition of humic substances determines their low solubility in water and high stability during transformation. Electrophilic substitution reactions occur mainly at benzene nuclei, and side chain alkyl are primarily subjected to oxidation.

It is known that one of the most important characteristics of humic substances is high content of paramagnetic centers in them, which presence may be related to free radicals. Presence of paramagnetic centers increases, if the aromaticity of the humic series compounds increases [26]. Paramagnetism of hmus acids and their fractions consists of at least three types of paramagnetic components: radicals with a predominant localization of the unpaired electron on the heteroatomic peripheral groups; high-molecular systems with a sufficiently developed poly-conjugation chain with structural defects; as well as complexes of metals with variable valence [26].

The effect of humic substances on the intensity of biochemical processes is explained by their participation in reductive-oxidative reactions due to the presence of polyphenolic and quinoid groups. During the enzymatic oxidation of polyphenols, quinones are generated through seven quinones-type intermediate compounds [28].

In a similar manner, the electrons of reactive oxygen species and electrons in the molecules of humic substances are blocked.

The study of the antioxidant activity of humic substances obtained from various sources, today is an important task. The reductive-oxidative properties of soil humic substances [26], peat [34] under the influence of various chemical and physical and chemical factors have already been determined. At the same time, the study of the reductive-oxidative properties of humic substances of peloids is not well understood. Although these substances exhibit the greatest biological and therapeutic activity, compared with similar substances of other sources (keonardites, coals, etc.). Formed under reductive conditions, molecules of humic substances of low-mineralized sludge sulphide have a unique structure, and it excludes the possibility of generation when obtaining carcinogenic alkyl halogen derivatives. It means that the research in this field becomes improtant.

The methods for determining the antioxidant activity are based on the principles of direct or indirect measurement of the rate or completeness of reaction of antioxidants with appropriate reagents, among which amperometry and manometry have the greatest interest. For the quantitative determination of antioxidants, the amperometric method seems to be the most reliable, since it allows directly measuring the content of all antioxidants in a sample. It is based on the measurement of the electric current that is generated during the electrochemical oxidation of the investigated substance (or mixture of substances) on the surface of the work electrode at a certain potential. Under conditions of amperometric detection, compounds containing a hydroxyl group are well oxidized, the limit of their detection lies in the range of 10^{-9}–10^{-12} g, and under favourable conditions, some compounds are determined at a level of 10^{-15}.

The antioxidant activity of humic acid solutions with various concentrations of 1 %, 0.1 %, 0.01 %, 0.001 % was measured in works [35-39] (Table 1). Quercetin was used as a reference material ($C_{15}H_{10}O_7$). To build an analytical curve of quercetin, recommended as a standard for this device, the All-Russia Scientific Research Institute of Metrological Service sequentially recorded signals of standard solutions of quercetin in the order of their concentrations increasing. According to the obtained results, curves of the peak area (signal value) dependence on quercetin concentration were built.

An arithmetic average of five measurements was taken as a result (relative standard deviation no more than 5 %), and a calibration curve was built (Figure 1).

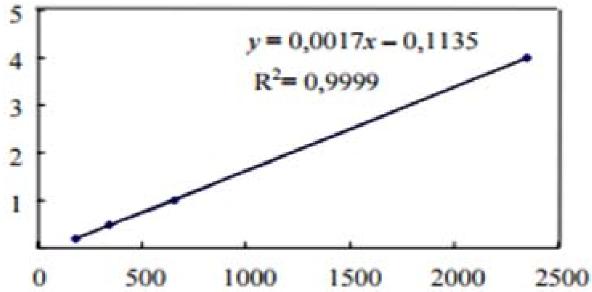

Figure 1 - Dependence of the peak area on the concentrations of quercetin

Table 1 - The value of the total content of antioxidants.

Name	Concentration	Signal value (area), нАс	CCA, mg / ml (standard quercetin)
Humic acid	0.001%	516	Менее 0.0001
Humic acid	0.01%	3602	0.00058
Humic acid	0.1%	14571	0.00387
Humic acid	1%	44177	0.043

The value of the humic acid signal of 0.001 %, concentration – 516 nAc indicates that the total content of antioxidants is less than 0.0001 mg/ml. Increasing the concentration of humic acids, the value of digital signals, and total content of antioxidants increases. When the concentration of humic acids is 0.01 %, the total content of antioxidants is 0.00058 mg/ml, at a concentration of 0.1 % – 0.00387 mg/ml, and when the concentration of humic acids is equal to 1 %, the value of the total content of antioxidants reaches 0.043 mg/ml. The obtained data suggests that humic acids have antioxidant activity, which value increases, if the concentration is increased.

If several years ago humic substances were used mainly in agriculture and animal farming, today their use has proven to be in demand in pharmacy. The research of their physical, chemical and pharmacological properties will improve the effectiveness and accessibility of peloid therapy for patients, and will allow making dosed treatment. Peloid preparations are easier packed and transported, do not require special conditions for their storage. Waste material (mud) is disposed in the mud baths, but it still keep valuable substances. The active components isolated from these “wastes” can later be used to isolate humic substances and produce peloid drugs.

The Kazakhstan market of medicines is filled with foreign antioxidant drugs, and this affects their final price paid by the consumer. The country needs domestic drugs that can generate high competition. Therefore, the research related to the creation of innovative medicines based on humic substances of peloids has particular importance and relevance.

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ЛАЙ СУЛЬФИДТІ БАТПАҚТАН АЛЫНҒАН ГУМИНДІК ЗАТТАРДЫҢ АНТИОКСИДАНТТЫ БЕЛСЕНДІЛІГІ МЕН ОЛАРДЫҢ КЛАССИФИКАЦИЯСЫ ТУРАЛЫ

(Шолу)

Аннотация. Бұл мақалада лай сульфидті батпақтан алынған (пелоид) гуминді заттардың антиоксиданттық белсенділігіне шолу жасалды. Бұл заттар басқа да көздерден алынған ұқсас заттармен салыстырғанда (кеонардит, көмір және т.б.) ішіндегі ең биологиялық және терапевтік белсенділікке ие болғанымен, олар аз зерттелген. Қалыптасу жағдайында туындаған лай сульфидті батпақтардағы гуминді заттардың молекулалары бірегей құрылымға ие және оларды алу барысында канцерогенді алкил галоген туындыларының пайда болу мүмкіндігін жоққа шығарады, нәтижесінде осы саладағы зерттеулердің маңыздылығы зор екендігі қалыптасады.

Түйін сөздер: антиоксиданттық белсенділік, гуминді заттар, пелоид.

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О АНТИОКСИДАНТНОЙ АКТИВНОСТИ ГУМИНОВЫХ ВЕЩЕСТВ НИЗКОМИНЕРАЛИЗОВАННЫХ ИЛОВЫХ СУЛЬФИДНЫХ ГРЯЗЕЙ (ПЕЛОИДОВ) И ИХ КЛАССИФИКАЦИЯ

(Обзор)

Аннотация. В данной работе сделан обзор об антиоксидантной активности гуминовых веществ низкоминерализованных иловых сульфидных грязей (пелойдов). Хотя данные субстанции проявляют наибольшую биологическую и терапевтическую активность, по сравнению с аналогичными субстанциями других источников (кеонардитов, углей и др.) они недостаточно изучены. Образованные в восстановительных условиях, молекулы гуминовых веществ низкоминерализованных иловых сульфидных грязей обладают уникальным строением, и исключает возможность образования в процессе получения канцерогенных алкильных галогенопроизводных, и вследствие этого актуальным становится исследование в данном направлений.

Ключевые слова: антиоксидантная активность, гуминовые вещества, пелоиды.

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REFERENCES

[1] Dubishev A.V., Men'shich L.V. Minor Study of humic substances influence on peloids renal excretory function // Bulletin of Samara Scientific Center RAN. Samara, 2010, vol.12, №1 (8). P.2023-2026 (in Russ.).

[2] Leshynski A.F, Zuza Z.I. Mud and pharmacotherapy in inflammatory diseases / Kiev, 1985.184 p. (in Russ.).

[3] Kalenini S.V. Physiology of mud as a special case of non-specific adaptation of the organism // Vopr.kurortologii. 2003. №4. P.52-53 (in Russ.).

[4] Mechuperenko O.N. Mud - natural biogenic stimulators, healing mechanisms of action / Provizor. 1998. №6. P.54-57(in Russ.).

[5] Suramfer M.J. Smoking, estrogen and prevention of hear disease in women / Mayo elin, proc.-1989. Vol.84. P.1553-1557 (in Russ.).

[6] Semionova M.A. Chemical and pharmaceutical, organizational and economic feasibility of application of humic acids of peloids:. Avtoref.diss.kand.farm.nauk / Samara, 2006, 20 p.

[7] Shustov L.P. Extracts of silt sulfide mud and the rationale for their use in clinical practice / Vopr.kurortologii. 1999. №6. P.35-37 (in Russ.).

[8] Ulashchik V.S., Lukomsky I.V. Total fizitoterapiya: textbook / Minsk, 2004. 327 p. (in Russ.)

[9] Shustov L.P. Extracts of silt sulfide mud and healing of use, Tomsk, 1996. 182 p. (in Russ.)

[10] Agaplov A.I., Mezhevalova N.I.,Avvakumova N.P. Peloidopreparaty humic series as a means of increasing the efficiency of ieloidoterapii under new conditions / Actual problems of organization of children's and family-san. kur.lecheniya and recreation in resort areas. Tez.nauch.-praktich.konf., Dedicated to the 100th anniversary of the resort Anan.-Anan, 1998, P.29-31 (in Russ.).

[11] Chukov S.N. Structural and functional parameters of soil organic matter under conditions of anthropogenic impact / St. Petersburg:. St. Petersburg State University, 2011. 216 p. (in Russ.).

[12] Adilov V.B., Berezhnov E.S., Trebukhova T.M., Trebukhov J.A. Natural curative resources Samara Region / Vopr.kurortologii, physical therapy and exercise therapy, 2008. №2. P. 45-47 (in Russ.)

[13] Adilov V.B., Gusarev I.I. (Et al.) // On the question of the permissible content of radionuclides in mineral waters, curative mud, clay / Vopr.kurortologii, physiotherapy and LFK. 2011. №3. P. 30-33 (in Russ.)

[14] Puntus F.A. The study of the chemical nature of humic acids of sapropel:. Avtoref.diss.kand.nauk / M., 1976, 18 p. (in Russ.)

[15] Agapov A.I. Specific organic substances as a source of medicinal mud peloidopreparatov humic series: avtoref.dis.d Mr. biol.nauk / -Samara, 1999.-58 P. (in Russ.)

[16] Bachmann V.I., Ovsyannikov K.A., AD-Vadkovsky method of analysis of therapeutic mud (peloitdov) / M: TsNIIKiF, 1965. 217 P. (in Russ.).

[17] Cherepanov M.N. The group composition of organic compounds of therapeutic mud / Vopr.izucheniya medicinal mineral water, mud and klimata. M., 1976. T.31. P.142-146 (in Russ.).

[18] Kosyanova Z.F. Chemical characterization and biological activity of humic acids of some therapeutic muds: avtoref.dis.kand.biol.nauk / M., 1985, 20 p. (in Russ.).

[19] Krechetova E.V., Humic acid oil shale. Their properties and structure: avtoref.diss.kand.biol nauk / M., 1994, 20 p. (in Russ.).

[20] Kan S., Tyurin A., Kurmangaliyeva Sh. Physical and chemical sduies of therapeutic mud Arasan-Kundyzdy fugs // Proceedings of the NAS RK, Series of geology and engineering sciences. Almaty, Volume 5. Number 431(2018), 12-14, ISSN 2224-5278, https:doi.org/10.32014/2018.2518-170X.3(in Eng.).

[21] Dospaev M. M., Bayeshov A., Zhurinov M. Z., Zhumakanova A.S., Bayeshova A.K., Syzdykova B.B., Dospaev D.M., Kakenov K.S. Physical-and-chemical regulirities of forming Chrysocolla mineraling in metasilicate solution // Proceedings of the NAS RK, Series of geology and engineering sciences. Almaty, Volume 5. Number 431(2018), 107-113., ISSN 2224-5278, https:doi.org/10.32014/2018.2518-170X.15 (in Eng.).

[22] Bazhirov N.S., Dauletiyarov M.S., Bazhirov T.S., Serikbayev B.E., Bazhirova K.N. Research of waste of aluminium production as the raw components in technology of composite cementing materials // Proceedings of the NAS RK, Series of geology and engineering sciences. Almaty, Volume 1, Number 427 (2018), 93 – 98, ISSN 2224-5278.

[23] Omarov B.T., Moldabekov Sh.M., Zhantasov K.T., Bolysbek A.A., Baiysbay O.P., Suigenbayeva A.Zh., Bekzhigitova K.A., Kenzhibayeva G.S., Tleuova A.B., Shapalov Sh.K. Study of the Yuild of humic acids in a hydrodynamic rotary-pupulsating apparatus // Proceedings of the NAS RK, Series of geology and engineering sciences. Almaty, Volume 2, Number 428 (2018), 167 – 171. (In Eng.), ISSN 2224-5278 (in Eng.).

[24] Zholtayev G.Zh., Zhukov N.M., Bespayev Kh.A. The theolory of forecasting and evaluating the minerals and raw materials dase of the Republic of // Proceedings of the NAS RK, Series of geology and engineering sciences. Almaty, Volume 2, Number 428 (2018), 193-200. ISSN 2224-5278 (in Russ.)

[25] Katunina V.V. Ecological and biochemical activity gimatemelanovyh acids of peloids: avtoref.dis.kand.biol.nauk / Samara, 2007.-20 p. (in Russ.).

[26] Lodygin V.D., Bezosikov V.A., Chukov S.N. Structural and functional parameters of humic substances podzonistyh bog soils podzonistyh / SPB:. Science, 2077.- P. 5-8. (in Russ.).

[27] Popov A.I., pod.red. Ermakov E.I. Humic substances: properties, structure, education / St. Petersburg, 2004.-248p. (in Russ.).

[28] Koponova M.M. Soil organic matter, its nature, properties, and methods of study / M.; 1963. 292 p. (in Russ.).

[29] Kairbekov Zh., Toktamysov M.T., Zhalgasuly N., Eshova Zh.T.. Complex processing of brown coal in central Kazakhstan / Monograph. Almaty: Kazakh University, 2014. 278 p. (in Russ.).

[30] Kairbekov Zh.K., Yermoldina E.T., Jeldybayeva I.M., Kairbekov A.Zh. Complex processing of brown coal of South Kazakhstan / Monograph: Almaty - Kazakh University, 2018. 454 b. (in Russ.)

[31] Koponova M.M. Soil organic matter, its nature, properties and methods of study / M., 1963-292 p. (in Russ.).

[32] Nikopova S.I., Chukov S.N. Application of the EPR method to the study of model humus-ferrous compounds / Modeling of soil-forming processes of the humid zone.-L.: Leningrad. Publishing House, 1984, P.115-128. (in Russ.)Black M.C. and McCarthy L.F. Dissolved organic matter reduces the uptake of hydrophobie organic contaminants by gills of the rainbow trout, Salrno gairdneri Environ/ Toxicol.Chem.7,p.593-600. (in Eng.).

[33] Black M.C. and McCarthy L.F. Dissolved organic matter reduces the uptake of hydrophobie organic contaminants by gills of the rainbow trout, Salrno gairdneri Environ/ Toxicol.Chem.7,p.593-600.

[34] Maltsev V.V. Physico-chemical properties of humic acids modified by the method of mechanical activation of caustobilot, and their interaction with biocides: Abstract. Cand. Chemical Science-Tomsk, 2010. 23 c. (in Russ.).

[35] Avvakumova N.P., Glubokova M.N., Katunina E.E. Investigation of the antioxidant properties of peloids humic acids / Minerals.-Samara State Medical University, 2013.-C.1160-1162. (in Russ.)

[36] Kairbekov Zh.K., Jeldybayeva I.M., Yermoldina E.T., Suymbaeva S.M. The modern view of the antioxidant activity of humic substances of peloids and their classification // Trudy IX inter. Beremzhanovsky Congress on Chemistry and Chemical Technology, Almaty. - December 9-10, 2016 - p. 315-321 (in Russ.).

[37] Kalzhapparova I., Sabitova A., Jeldybayeva I.M. Improving the method of obtaining humic substances from peloids // International Scientific Conference of Students and Young Scientists "Ul-Farabi Elemi", Almaty, 2017, p.14 (in Russ.).

[38] Baymold J.A., Abilmazhinova D., Jeldybayeva I.M., Kishibaev K.O. Practical application of silt sulfide mud (peloids) // Materials of the Int. Scientific-practical conference "Modern directions of development of education and science in the field of chemistry, biology, ecology and geography", Almaty, October 27, 2017, P.92-94 (in Russ.).

[39] Abilmazhinova, DZ, Jeldybayeva, IM, Yermoldina, E.T., Kairbekov Zh.K. Method of obtaining humic substances from low-mineralized silt sulfide muds (peloids) // 4th Inter. Russian-Kazakhstan scientific practical. conference "Chemical tech. of functional materials ”Almaty, April 12-13, 2018, p. 133-135 (in Russ.).

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LIQUEFIED PETROLEUM GAS AS RAW MATERIALS FOR THE PRODUCTION OF LIQUID OXYGEN-CONTAINING ORGANIC COMPOUNDS

Abstract. Studies on the air oxidative transformation of the propane-butane mixture to oxygen-containing compositions have been carried out. The optimum temperatures of the process, as well as the ratios of the initial components of the reaction mixture and the content of the active phase on the carrier and volumetric rates have been determined. Physical and chemical studies of the initial and treated catalysts under experimental conditions were carried out. When changing the content of the active component on the carrier from 1 to 10%, it was found that the most optimal is the catalyst 5% MoCrGa/TC, on which up to 22% acetone was obtained. As a result of varying the composition of the catalyst, the content of the active phase, the ratio of reactants, up to 35–40% of acetone was obtained. In addition, in some cases, CH3OH was obtained, with the maximum yield 22%, as well as 35% of methyl ethyl ketone. As a result of EM and XRD studies, it was shown that under reaction conditions a new Cr_2O_5 phase (corresponding to the Cr^{2+} and Cr^{3+} transition to Cr^{5+}) is formed on the catalyst surface, as well as joint phases of Mo and Cr in various valence states, the physical meaning and role of which are to be determined.

Key words: natural clay, acetone.

Introduction. Natural and petroleum gases are the most important alternative sources of raw materials that can in the long run compete with oil. Of particular relevance for countries rich in this type of raw material is the problem of the rational use of alkanes in their composition [1-5]. Kazakhstan has significant oil and gas reserves. Unfortunately, there is currently no industrial organic synthesis based on alkanes in Kazakhstan, with the exception of gas processing plant in Zhanauzen, the nitrogen-fertilizer plant in Atyrau (which uses the low-profitable process of steam reforming of methane into synthesis gas) and ethylene production in Aktau (by non-catalytic pyrolysis of ethane with the addition of other hydrocarbons and petroleum fractions). Kazakhstan is entering a new era in hydrocarbon processing. Gas processing is the most promising direction of petrochemistry is. This sphere will help Kazakhstan to integrate faster in the world market. The partial oxidation of liquefied petroleum gas to ketones and aldehydes is relevant from the of ecological and economical point of view, since about 100 billion cubic meters of associated petroleum gas are burned annuallyand pollutant emissions to the atmosphere amount to thousands of tons [6-11]. The combustion process due to oxygen consumption and heat release contributes to the greenhouse effect. In addition, the economy is suffering losses due to the combustion of far from cheap petroleum gas, especially if we consider that it would be possible to get petrochemical products from the liquefied petroleum gas which are much more expensive than the original product.

A large number of studies have been carried out on the oxidation of propane and butane to unsaturated aldehydes and acids /12-16/, but there are few works on the production of ketones /17-20/.

Methods. This paper presents the results of oxidative transformation study of liquefied petroleum gas (propane-butane mixture) by air into oxygen-containing compositions in reaction mixtures with a propane-butane content 14- 80% and oxygen 4-18% at T = 300-600 °C and W=330-15000h^{-1}. Polyoxide catalysts of different composition, containing 1-10% Mo, Ga, Cr in various proportions, deposited on natural Torgai clay (TC), having the structure of kaolinite (in some cases with the addition of hematite and α-quartz) were tested. Automated analysis of initial materials and reaction products were carried out on Agilent Technologies 6890N chromatograph. Physical and chemical studies of the initial and treated catalysts under experimental conditions (XRD, EM, elemental analysis, determination of acidity) were carried out [9-10].

It is established that the main reaction products are acetone, methanol, acetaldehyde, methyl ethyl ketone (MEK). The optimum process temperature is 350-400 °C. C_2H_4, H_2, CO, and CO_2 were detected in the reaction products when temperature increased. It was shown that the yield of oxygen-containing products on catalysts pretreated with 10% HCl exceeds similar yields on untreated catalysts. Acid treatment of sorbents contributed to the development of the surface and an increase in the pore radius, which led to an increase in oxygen-containing compounds in catalyzate [8-9]. Varying the reaction conditions on a number of catalysts (two-component - CrGa/TC and three-component - MoCrGa/TC) leads to a change in the content of the active phase and has a significant impact on the yield of the main products. When varying the content of the active component on the carrier from 1 to 10%, it was shown that the most optimal was 5% MoCrGa/TG catalyst, on which up to 22% acetone was obtained, the three-component catalyst being more active than the two-component catalyst (Figure 1).

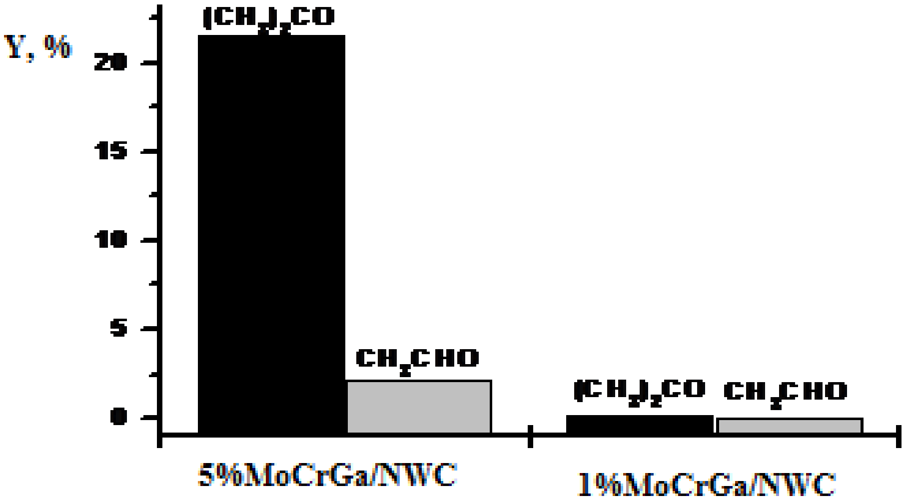

Figure 1 - The effect of active phase content of the catalysts on the yield of acetone and acetaldehyde.

Tests of the above catalysts at space velocities from 330 to 15000 h^{-1} showed that for the synthesis of acetaldehyde and acetone on the 1% CrGa / TC catalyst, the optimal rate is W = 1200 h^{-1}, and for the 5% CrGa/TC catalyst - 9000 h^{-1} for acetaldehyde and 330h^{-1} for acetone (acetone yield is 32%), Figure 2 and 3. Optimal space velocities were also determined for three-component MoCrGa/TC catalysts with different content of the active phase on the carrier. At W=1350 h^{-1} , up to 23% of acetone and 35% of methyl ethyl ketone on 5% MoCrGa/TC were produced, whereas 22% of acetone on 5% MoCrGa/TC catalysts was produced.

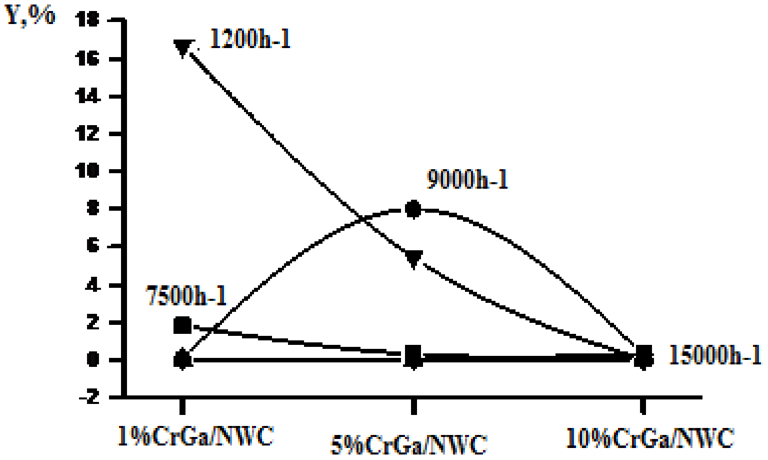

Figure 2 - The effect of space velocities on the yield of acetaldehyde
on 1% -, 5% - and 10% CrGa/TC catalyst at 400 °C

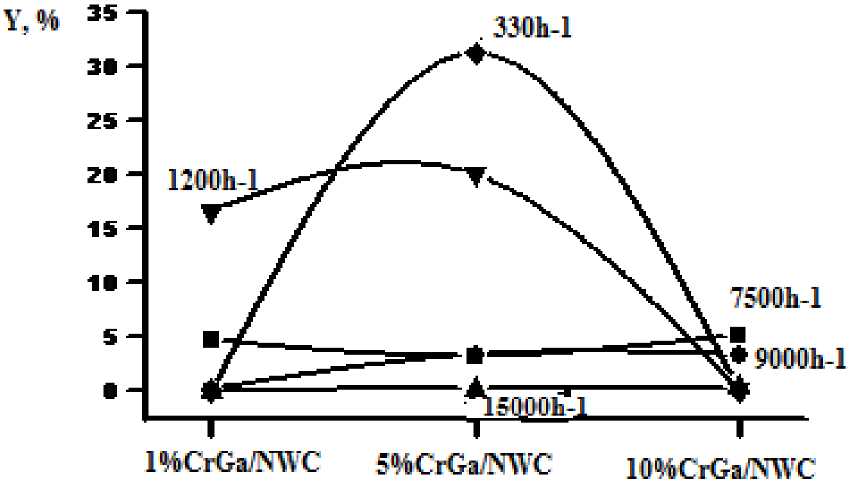

Figure 3 -The effect of space velocities on the yield of acetone
on 1% -, 5% - and 10% CrGa/TC catalyst at 400 °C

Studies on variation of the initial components ratio in the reaction mixture allowed to determine the most optimal compositions for the process implementation. By varying the concentration of O2 from 3.8 to 8.4% in the mixture, it was shown that when the content of O_2 is 5.3% and the propane-butane mixture is ~ 60-66%, the yield of acetone is 23% and methanol is 22%. When the content of the propane-butane mixture is 33-36% with the same O_2 content, 31% acetone and 35% MEK are obtained. By varying the composition of the catalyst, the content of the active phase, the ratio of reactants up to 31% acetone and 35% MEK were produced. In addition, in some cases CH_3OH was produced with the maximum yield 22%.

The microstructure and morphology of the catalysts were determined by X-ray phase analysis and electronic microscopy (EM) [14].

Results and discussion. The experiment was carried out on the electron microscope EM-125K by single-stage coal replicas method with extraction, using microdiffraction, as well as the method of survey through the lumen (suspension preparations). The survey was carried out at different magnifications depending on the particle size []. The carrier was dissolved in concentrated HF. The X-ray phase analysis was performed on a DRON-4-07 X-ray diffractometer. EM method provides observation of electron diffraction on individual crystals and accumulation of particulate matter, while the XRD method gives the total diffractogram of all phases [8-9].

In addition, for the manifestation of the phase in XRD it must have a large enough size. Therefore, many phases detected by EM method may not be observed in X-ray phase analysis, but this does not mean their absence in the catalyst.

For microdiffraction in electron microscopy, the transparency of the material for the electron beam is important. Sometimes well crystallized phases stably observed in XRD may be not transparent to the EM.

Both methods complement each other and provide a more complete picture of the catalyst changes under the influence of the environment.

The presence of a large number of insoluble components that make it difficult to decipher the deposited phases is characteristic of the carrier (Torgai clay). For the original clay sample MoCrGa / Torg. large particles and aggregates of large dense particles are characteristic, the microdiffraction pattern of which is represented by individual rare reflexes attributed to Cr2O3 (JCPDS, 6-508) and CrO (JCPDS, 6-532), as well as translucent particles of lamellar type, the microdiffraction image from which reflexes, located on the hexagonal motif, referred to CrMoO4 (JCPDS, 34-474).

The phase related to Ga, were not detected. Mo-containing phase is characterized by dense large crystals of 500–1000 Å with signs of a rectangular motif of cut, corresponding to Mo4O11 (JCPDS, 13-142). For the Cr-containing phase, large semitransparent lamellar particles α-Cr2O3 (JCPDS, 6-503), small clusters made up of dispersed particles ~ 30 Å in size, referred to Cr2O5 (JCPDS, 36-1329), aggregates of translucent particles with minimal size 200-400Å and larger, characteristic for CrO2 (JCPDS, 9-332), a cluster of translucent lamellar particles Cr5O12 (JCPDS, 18-390) 300-600 Å in size with a rectangular cut motif.

Furthermore, we detected small clusters characteristic for joint phases consisting of particle 30-50Å in size and large plate-type particles. Microdiffraction is represented by a mixture of rings and individual reflexes. The rings correspond to the phase of disperse particles CrMoO4 (JCPDS, 29-452), and large plate crystals correspond to Cr2MoO6 (JCPDS, 33-401). Ga-containing phase is characterized by different phases of Ga oxidation up to the metal phase: α-Ga2O3 (JCPDS, 6-503), φ-Ga2O3 (JCPDS, 20-426), ε-Ga2O3 (JCPDS, 6-509) mixed with Ga (JCPDS, 31-539), Ga (JCPDS, 25-345).

Comparison with the EM pictures of the initial samples of catalysts allowed to state that as a result of their treatment under the reaction conditions, a new Cr2O5 phase appears, corresponding to the Cr2 + and Cr3 + transition to Cr5 +, as well as the combined Mo- Cr phases in different valence states, the physical meaning and role of which are to be determined

Conclusion. Source of research funding. Initiative project "Conversion of hydrocarbon raw materials of Kazakhstana" Department of «Chemistry and Chemical Technology" of M.Kh.Dulaty Taraz State University.

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СЫҒЫЛҒАН МҰНАЙ ГАЗЫ - СҰЙЫТЫЛҒАН ОТТЕКҚҰРАМДАС ОРГАНИКАЛЫҚ ҚОСЫЛЫСТАР ӨНДІРІСІ ҮШІН ШИКІЗАТ РЕТІНДЕ

Аннотация. Пропан-бутан қоспасының құрамында оттегі бар органикалық қосылыстарға каталитикалық тотығуы бойынша зерттеулер жүргізілді. Сондай-ақ үрдістің оптимальді технологиялық температуралары, бастапқы компоненттердің жәнетасымалдағыштың белсенді фаза құрамы жәнекөлемдік жылдамдықтары анықталды. Бастапқы және реакциядан кейінгі (өңделген) катализаторларға физика-химиялық зерттеулер жүргізілді. Зерттеулер нәтижесі бойынша тасымалдағыштағы белсенді компоненттердің құрамын 1% -дан 10% дейін өзгерту нәтижесінде ең тиімді катализатор 5% MoCrGa / ТСБ екені анықталып, 22% ацетон алынды. Катализатордың және тасымалдағыштағы белсенді заттардың құрамын, әрекеттесуші реагенттердің қатынасын өзгерту нәтижесінде 35-40% дейін ацетоналынды. Сонымен қатар, кейбір жағдайларда CH_3OH максималды 22% шығымы және 35% метилэтилкетон алынды. ЭМ және РФА зерттеулерінің нәтижесінде реакция жағдайында катализатордың бетінде жаңа Cr_2O_5 фазасы (Cr^{2+} және Cr^{3+} -ға Cr^{5+} -ге көшу), сондай-ақ әртүрлі валенттік күйлердегі Mo және Cr біріккен фазалары пайда болатыны анықталды.

Түйін сөздер: табиғи сазбалшық, ацетон, .

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СЖИЖЕННЫЙ НЕФТЯНОЙ ГАЗ КАК СЫРЬЕ ДЛЯ ПРОИЗВОДСТВА ЖИДКИХ КИСЛОРОДСОДЕРЖАЩИХ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

Аннотация. Проведены исследования по окислительному превращению пропан-бутановой смеси в кислородсодержащие компоненты,а также определены оптимальные температуры, пропорции исходных компонентов, содержание активной фазы носителя и объемные скорости процесса.Были проведены физико-химические исследования исходных и обработанных катализаторов в условиях эксперимента. Было обнаружено, что при изменении содержание активных фаз в носителе от 1 до 10%, наиболее эффективным катализатором является 5% MoCrGa/ТГ, при котором было получено 22% ацетона. В результате варьирования состава катализатора, содержания активной фазы, соотношения реагентов, было получено до 35-40% ацетона. Кроме того, в некоторых случаях были получены CH_3OH с максимальным выходом 22%, а также 35% метилэтилкетона. В результате исследований ЭМ и РФА было показано, что в условиях реакции на поверхности катализатора образуется новая фаза Cr_2O_5 (соответствующая переходу Cr^{2+} и Cr^{3+} в Cr^{5+}), а также совместные фазы Mo и Cr в разных валентных состояниях, физический смысл и роль которых должны быть определены.

Ключевые слова: природная глина, ацетон.

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REFERENCES

[1] X.Li, J.Zhao, W.Ji, Zh.Zhang, Y.Chen et. al. (**2006**) Effect of vanadium substitution in the cesium salt of Keggin-type heteropolyacids on propane partial oxidation. J. Catal. .237:58-66.

[2] J.Xu, B.L.Mojet, J.G.Ommen, and L.Lefferts. (**2005**) Effect of Brönsted acidity in the mechanism of selective oxidation of propane to acetone on CaY zeolite at room temperature. J. Catal. 232:411-423.

[3] Zakarina N, Volkova L, Kim A, Akulova G, Chanysheva I, Latypov I, Grigorieva V. (**2010**) Industry of Kazakhstan, 6 :83-85.

[4] Tungatarova S.A., Xanthopoulou G., Kaumenova G.N., Zhumabek M., Baizhumanova T.S., Grigorieva V.P., Komashko L.V., Begimova G.U. (**2018**) Development of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas. NEWS of the national academy of sciences of the republic of kazakhstan serieschemistry and technology ISSN 2224-5286 https://doi.org/10.32014/2018.2518-1491.20 Volume 6, Number 432 (2018), 6 – 15. (in Eng).

[5] Baizhumanova T.S., Tungatarova S.A., Xanthopoulou G., Zheksenbaeva Z.T., Kaumenova G.N., Erkibaeva M.K., Zhumabek M., Kassymkan K. (**2018**) Catalytic conversion of methane into olefins. N E W sof the national academy of sciences of the republic of kazakhstan serieschemistry and technology ISSN 2224-5286 https://doi.org/10.32014/2018.2518-1491.17 Volume 5, Number 431 (2018), 132 – 138542.973.7; 547.211. (in Eng).

[6] N.A. Zakarina, N.A. Kornaukhova, R. Toktassyn. (**2019**) Pt- and Pd-catalysts on modified kaolinites in the reaction of n-hexane isomerization. N E W S of the national academy of sciences of the republic of kazakhstan series chemistry and technology. ISSN 2224-5286. https://doi.org/10.32014/2019.2518-1491.7. Volume 1, Number 433 (2019), 47 – 56. (in Eng).

[7] A.K. Bayeshova , S.Molaigan , A.B. Bayeshov (**2018**) Hydrogen energetics current state and hydrogen production methods. N E W S of the national academy of sciences of the republic of kazakhstan series chemistry and technology. № 5. 2018 107 ISSN 2224-5286 https://doi.org/10.32014/2018.2518-1491.14. Volume 5, Number 431. P.107 – 116. (in Eng).

[8] Dosumov K, Tungatarova SA, Kuzembaev KK, Masalimova BK (**2005**) Oxidative C3-C4 hydrocarbon conversion to olefins and oxygen-containing compounds in the presence of molybdenum and tungsten polyoxometalates, Petroleum Chemistry, 45:261-263. (in Eng).

[9] Massalimova B.K. (**2019**) Partial oxidation C3-C4 hydrocarbons. Kazakhstan. ISBN 978-601-7300-69-2. (in Kaz).

[10] Massalimova B.K. (**2019**) Partial oxidation C3-C4 hydrocarbons. Kazakhstan. ISBN 978-601-7300-69-2.

[11] Tungatarova S.A., Xanthopoulou G., Kaumenova G.N., Zhumabek M., Baizhumanova T.S., Grigorieva V.P., Komashko L.V., Begimova G.U. (**2018**) Development of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas. News of the NAS RK. Series chemistry and technology 432:6–15. https://doi.org/10.32014/2018.2518-1491.20 (in Eng)

[12] Baizhumanova T.S., Tungatarova S.A., Xanthopoulou G., Zheksenbaeva Z.T., Kaumenova G.N., Erkibaeva M.K., Zhumabek M., Kassymkan K. (**2018**) Catalytic conversion of methane into olefins News of the NAS RK. Series chemistry and technology 431:132 – 138542.973.7; 547.211. https://doi.org/10.32014/2018.2518-1491.17 (in Eng)

[13] Dosumov K., Tungatarova S.A., Kuzembaev K.K., Masalimova B.K. (**2005**) Oxidative C3-C4 hydrocarbon conversion to olefins and oxygen-containing compounds in the presence of molybdenum and tungsten polyoxometalates, Petroleum Chemistry, 45:261-263. (in Eng).

[14] Massalimova B.K. (**2016**) Oxidative conversion of C3-C4 hydrocarbons over polycomponent oxide catalysts. XII International Conference on Reactors CHEMREACTOR-22, London, UK. PP.51. (In Eng.).

[15] Arutyunov V.S., Strekova L.N. and Nikitin A.V. (**2013**). Partial Oxidation of Light Alkanes as a Base of New Generation of Gas Chemical Processes. Eurasian Chemico-Technological Journal15 (2013) 265-273.

[16] Zakarina N, Volkova L, Kim A, Akulova G, Chanysheva I, Latypov I, Grigorieva V. (**2010**) Industry of Kazakhstan, 6 :83-85.

[17] Tungatarova S.A, Xanthopoulou G, Kaumenova G.N, Zhumabek M, Baizhumanova T.S, Grigorieva V.P, Komashko L.V, Begimova G.U (**2018**) Development of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas. News of the NAS RK. Series chemistry and technology, 432:6-15. https://doi.org/10.32014/2018.2518-1491.20 (in Eng).

[18] Baizhumanova T.S, Tungatarova S.A, Xanthopoulou G, Zheksenbaeva Z.T, Kaumenova G.N, Erkibaeva M.K, Zhumabek M, Kassymkan K (**2018**) Catalytic conversion of methane into olefins. News of the NAS RK. Series chemistry and technology, 431:132– 138542.973.7; 547.211. https://doi.org/10.32014/2018.2518-1491.17 (in Eng).

[19] Zakarina N.A, Kornaukhova N.A, Toktassyn R (**2019**) Pt- and Pd-catalysts on modified kaolinites in the reaction of n-hexane isomerization. News of the NAS RK. Series chemistry and technology, 433:47-56. https://doi.org/10.32014/2019.2518-1491.7 (in Eng).

[20] Bayeshova A.K, Molaigan S, Bayeshov A.B (**2018**) Hydrogen energetics current state and hydrogen production methods. News of the NAS RK. Series chemistry and technology, 431:107-116. https://doi.org/10.32014/2018.2518-1491.14 (in Eng).

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TERPENOIDS OF *MATRICARIA CHAMOMILLA* L. FROM DIFFERENT PLACES OF GROWTH

Abstract. In this work, a comparative gas chromatography-mass spectrometry analysis of the component composition of CO_2-extracts from *Matricaria chamomilla* L. raw materials collected at the site of medicinal plants of the International Research and Production Holding "Phytochemistry" (Karaganda region, Republic of Kazakhstan), Mozheikovo agro-town (Grodno Region, Belarus) and in the vicinity of Sarkand (Almaty region, Republic of Kazakhstan) was undertaken. As a result of the research conducted, it was revealed that the major components of the obtained CO_2-extracts of *Matricaria chamomilla* L. are: bisabolol oxide A, bisabolol oxide B and en-in-dicycloether. Meanwhile, in the CO_2-extract of *Matricaria chamomilla* L. collected at the site of medicinal plants of JSC "IRPH "Phytochemistry"the quantitative content of matricarin and chamazulene are prevailed.Thus, thecontent of matricarin exceedthree times, and the content of chamazulene five and two times, in comparison with extracts obtained from the Belarusian and Almaty raw materials.

The prospect of using *Matricaria chamomilla* L. raw material that grows on the medicinal plants site of JSC "IRPH "Phytochemistry" in the production of the anti-inflammatory ointment "Matripin-Dent" has been established.

Key words:*Matricaria chamomilla* L., CO_2-extraction, chromato-mass spectrometry, chamazulene, matricarin.

Introduction

In modern medicine, herbal medicines occupy a special place, as they have a wide range of biological activity, which allows them to be used for the prevention and treatment of many diseases.

Phytopreparations are included in more than 85 pharmaceutical groups of medicines and most of them do not have equivalent synthetic substitutes [1].

Flowers of *Matricaria chamomilla* L., which have been used in medical practice for a long time as an anti-inflammatory, antiseptic and antispasmodic medicines [2] and are used as raw materials for obtaining fees, extracts, medicines "Romazulan" (Romania), "Rotokan" (Russia), "Rekutan" (Ukraine), "Camillozan" (Germany), "Alorom" (Russia), "Stomatofit" (Poland) [3-5] should be included among the types of plant raw materials that are widespread in the foreign and domestic pharmaceutical market.

The annual public health need for *Matricaria chamomilla* L.inflorescences is quite large and the amounts are about 250 tons [6]. At the same time, its main part is provided due to cultivation in specialized farms and only insignificant volumes - due to the harvesting of wild-growing raw materials [7].

Therefore, it is a relevant task to study of plant resources and to evaluate stock of herbs for the rational use of them and expansion of the range domestic drugs in the pharmaceutical market[8].

The pharmacological effect of *Matricaria chamomilla* L.flowers is due to the presence of a whole complex of biologically active substances with a broad spectrum of biological activity in their composition [9-17], primarily essential oils, flavonoids, coumarins, and sesquiterpene lactones of matricarin and matricin, which are the initial compounds in the biosynthesis of chamazulene possessing anti-inflammatory and antiallergic action.

Matricaria chamomilla L.raw materials are also used in the manufacture of cosmetics and pharmaceuticals. Recent studies show that the use of raw *Matricaria chamomilla* L. for cosmetic preparations is due to the high content of phenolic compounds [18-21].

An analysis of recent studies shows that for the production of high-quality extracts from *Matricaria chamomilla* L. raw materials, it is advisable to use compressed and liquefied gases as solvents. According to the literature [22, 23], supercritical CO_2-extraction is preferable.

Despite the existing range of medicines, extracts of *Matricaria chamomilla* L.continue to be a promising object for further study and the creation of new medicines with a number of pharmacological and therapeutic activity.

JSC "International Scientific and Production Holding "Phytochemistry" on the basis of "Karaganda Pharmaceutical Plant" LLP develops and introduces into production the original drug "Matripin-Dent", which consists of carbon dioxide extracts of *Populus balsamifera* and *Matricaria chamomilla* L. In order to determine the suitable raw materials of *Matricaria chamomilla* L. and to obtain high-quality CO_2-extracts with a quantitative content of biologically active substances, we studied 3 types of *Matricaria chamomilla* L. raw materials growing in various places.

The purpose of the work is a chemical study of the component composition of CO_2-extracts of *Matricaria chamomilla* L. depending on the place of growth.

Experimental part

Materials and research methods

The materials used for the study were *Matricaria chamomilla* L. inflorescences collected in the flowering phase in various places: at the medicinal plant site of the JSC "International Research and Production Holding "Phytochemistry" (Karaganda, Kazakhstan), in the Mozheikovo agro-town(GrodnoRegion, Belarus) and Sarkand (Almaty region, Republic of Kazakhstan).

Drying of the raw material was carried out by the airily-shadow method at a temperature of 25-30°C.

CO_2-extraction of all types of raw materials was carried out under the same supercritical conditions: pressure - 250 bar, temperature: 50°C, extraction time: 180 min.After that, a three-fold water-alcohol treatment of the obtained CO_2-extracts was carried out to precipitate and separate the lipophilic components. For each stage, the mass of ethanol was used; the mass of ethanol is three times the mass of the extract, and the mass of water, one and a half times the mass of the extract. The extract was dissolved in alcohol, heated to 70°C. After that, water heated to 70°C was immediately added to the resulting solution. The solution was stirred and left in a dark place for a day, then filtered. The precipitate was re-treated with alcohol and water. The filtrate obtained after three processing steps was evaporated on a rotary evaporator.

The qualitative and quantitative content of essential oil components in CO_2-extracts was determined by gas chromatography-mass spectrometry on a gas chromatograph with an Agilent 7890/5975C mass-selective detector. A 5% Phenyl Methyl Silox HP-5MS column (30 mm×250 mm×0.25 mm) was used with a helium carrier gas velocity of 1 ml/min. Evaporator temperature - 230°C. The gas chromatography column was kept at 40°C for 5 min; with temperature programming up to 240˚C with a rate of temperature change of 5˚C/min, and then kept in isothermal mode for 50 min. Sample entry mode with flow division. The sample volume is 0.1 μl. The conditions for recording mass spectra are 70 eV, the mass range is m/z 10-400. The percentage of components was calculated automatically based on the peak areas of the total ion chromatogram. Components were identified by mass spectra and retention times using the Wiley GC/MS library.

Results and discussion

According to the analysis by the GC/MS method, it is established that the main components of the CO_2-extracts of *Matricaria chamomilla* L. are: bisabolol oxide A (21.51%, 17.90% and 18.57%), bisabolol oxide B (17.11%, 5.71% and 14.32%) and en-in-dicycloester (18.93%, 43.58% and 21.17%) (table 1).

Meanwhile, the quantitative content of matricarin and chamazulene in the CO_2-extract of *Matricaria chamomilla* L., collected in the area of medicinal plants of JSC "IRPH "Phytochemistry", prevailsas opposed places of growth. Thus, the content of matricarin exceed three times, and the content of chamazulene five and two times, in comparison with extracts obtained from the Belarusian and Almaty raw materials. Also, the quantitative content of the en-in-dicycloester in the CO_2-extract obtained from the Belarusian raw materials of *Matricaria chamomilla* L. should be noted, its content is 2 times higher than from the Kazakh raw materials.

Table 1 - Comparative component composition of CO_2-extracts of *Matricaria chamomilla* L., depending on the place of growth

Component name	CO_2-extract of *Matricaria chamomilla L.*					
	JSC “International Research and Production Holding “Phytochemistry” (Karaganda, Kazakhstan)		Mozheikovo (Grodno Region, Belarus)		Sarkand (Almaty region, Republic of Kazakhstan)	
	RT, min	Content, %	RT, min	Content, %	RT, min	Content, %
β-farnesene	26.882	2.01	26.876	3.50	26.830	1.83
Spathulenol	29.903	1.30	29.897	1.49	29.846	0.18
Bisabolol oxide B	**31.666**	**17.11**	**31.643**	**5.71**	**31.585**	**11.87**
Bisabolol oxide	32.289	8.50	32.278	5.85	32.226	5.84
Herniarin	33.159	4.50	33.147	7.13	-	-
Chamazulene	33.331	4.78	33.319	0.88	33.262	1.80
Bisabolol oxide A	**33.668**	**21.51**	**33.645**	**17.90**	**33.582**	**14.36**
En-in-dicycloester	**36.438**	**18.93**	**36.443**	**43.58**	**36.346**	**21.17**
N-hexadecanoic acid	37.845	1.07	-	-	38.446	0.47
9,12-octadecadienoic acid	41.410	0.42	41.193	1.50	41.513	1.61
Matricarin	45.885	2.71	45.867	0.90	45.872	0.94

At the same time, chamazulene and sesquiterpene lactone matricarin are relatively valuable biologically active substances in the studied extracts, both components have an anti-inflammatory effect and are the main components of *Matricaria chamomilla* L. raw material [24, 25].

Conclusion

On the basis of the obtained results, it was established that the main components of the isolated CO_2-extracts are bisabolol oxides A and B and en-in-dicycloester. Due to the comparative study of the component composition of extracts of *Matricaria chamomilla* L. it was revealed that the quantitative content of matricarin and chamazulene in the extract of *Matricaria chamomilla* L. collected at the medicinal plants site of JSC “International Scientific and Production Holding “Phytochemistry” (Karaganda region, Republic of Kazakhstan) are prevailed in comparison with extracts selected from the Belarusian and Almaty raw materials.

Thus, to obtain a CO_2-extract of *Matricaria chamomilla* L. with a quantitative content of pharmacologically active components for the drug “Matripin-Dent”, it is advisable to use raw materials growing on the medicinal plants site of “International Scientific and Production Holding “Phytochemistry”, since this raw material has a quantitative content of basic pharmacologically active compounds with a wide range of pharmacological activity.

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«Фитохимия» халықаралық ғылыми-өндірістік холдингі» АҚ, Қарағанды қ., Қазақстан Республикасы

ӘРТҮРЛІ АЙМАҚТАРДА ӨСЕТІН ДӘРІЛІК ТҮЙМЕДАҚТЫҢ (*MATRICARIA CHAMOMILLA* L.) ТЕРПЕНОИДТАРЫ

Аннотация. Осы жұмыста «Фитохимия» халықаралық ғылыми-өндірістік холдингінің дәрілік өсімдіктер учаскесінде (Қарағанды облысы, Қазақстан Республикасы), Можейково агроқалашығында (Гродно облысы, Беларусь Республикасы) және Сарқанд төңірегінде (Алматы облысы, Қазақстан Республикасы) жиналған дәрілік түймедақ шикізатынан алынған CO_2-сығындыларының компоненттік құрамына салыстырмалы хроматографиялық масс-спектрометриялық талдау жүргізілді. Жүргізілген зерттеулер нәтижесінде дәрілік түймедақтан алынған CO_2-сығындыларының мажорлы компоненттері бисабололоксид А, бисабололоксид Б және ен-ин-дициклоэфир болып табылатыны анықталды. Сонымен қатар «Фитохимия» ХҒӨХ» АҚ дәрілік өсімдіктер учаскесінде жиналып алынған дәрілік түймедақтың CO_2-

сығындыларында матрикарин мен хамазуленнің мөлшері басым болып келетіні анықталды, атап айтқанда, белорустық және алматылық шикізаттан алынған сығындылармен салыстырғанда матрикарин мөлшері үш есе, ал хамазулен бес және екі есе артық.

«Фитохимия» ХҒӨХ» АҚ дәрілік өсімдіктер учаскесінде өсетін дәрілік түймедақ шикізатын қабынуға қарсы «Матрипин-Дент» жақпамайының өндірісінде қолдану келешегі анықталды.

Түйін сөздер: дәрілік түймедақ, *Matricaria chamomilla*L.,CO_2-экстракциялау, хроматографиялық масс-спектрометрия, хамазулен, матрикарин.

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ТЕРПЕНОИДЫ РОМАШКИ АПТЕЧНОЙ (MATRICARIA CHAMOMILLA L.) ИЗ РАЗЛИЧНЫХ МЕСТ ПРОИЗРАСТАНИЯ

Аннотация. В данной работе проведен сравнительный хромато-масс-спектрометрический анализ компонентного состава CO_2-экстрактов из сырья ромашки аптечной, собранной на участке лекарственных растений Международного научно-производственного холдинга «Фитохимия» (Карагандинская область, Республика Казахстан), агрогородка Можейково (Гродненская область, Республика Беларусь) и в окрестности Сарканда (Алматинская область, Республика Казахстан). В результате проведенных исследований выявлено, что мажорными компонентами полученных CO_2-экстрактов ромашки аптечной являются: бисабололоксид А, бисабололоксид Б и ен-ин-дициклоэфир. Между тем, количественное содержание матрикарина и хамазулена в CO_2-экстракте ромашки аптечной, собранной на участке лекарственных растений АО «МНПХ «Фитохимия» преобладает, так содержание матрикарина превосходит в три раза, а хамазулена в пять и два раза, в сравнении с экстрактами, полученными из белорусского и алматинского сырья.

Установлена перспективность использования сырья ромашки аптечной, произрастающей на участке лекарственных растений АО «МНПХ «Фитохимия» в производстве противовоспалительной мази «Матрипин-Дент».

Ключевые слова: ромашка аптечная,*Matricariachamomilla*L.,CO_2-экстракция, хромато-масс-спектрометрия, хамазулен, матрикарин.

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REFERENCES

[1] Leonova M.V., Klimochkin Y.N. (**2012**) Extraction methods for the manufacture of medicinal products from vegetable raw materials: a teaching aid [Jekstrakcionnye metody izgotovlenija lekarstvennyh sredstv iz rastitel'nogo syr'ja: uchebno-metodicheskoe posobie] Samara State Technical University, Russia. [Samarskij gosudarstvennyj tehnicheskij universitet, Rossija] ISBN: 5-7964-0707-4. (In Russian).

[2] Pervyshina G.G., Efremov A.A., Gordienko G.P., Agafonova E.A. (**2002**) Chemistry of plant materials. [Himija rastitel'nogo syr'ja] 3:21-24. (In Russian).

[3] Samylina I.A., Kochergina N.V. (**2007**) Ways of use and standardization of *Matricaria chamomilla* raw materials in homeopathy and allopathy [Puti ispol'zovanija i standartizacija syr'ja romashki aptechnoj v gomeopatii i allopatii]. Collection of scientific works of the congress: "Traditional Medicine -2007" [Sbornik nauchnyh trudov kongressa: «Tradicionnaja Medicina - 2007»]. Moscow, Russia. P.87-92. (In Russian).

[4] Mironov S.E., Fetisova A.N. (**2013**) Health & education millennium, 15:385-389. ISSN: 2226-7425 (In Russian)

[5] Unanko B.B., Karasavidi A.O. Sakanyan E.I. (**2008**) Pharmacy. [Farmacija] 6:19-24. (In Russian).

[6] Terekhin A.A. (**2008**) The technology of cultivation of medicinal plants [Tehnologija vozdelyvanija lekarstvennyh rastenij]. RUDN, Moscow 201 p. (In Russian).

[7] Atlas of medicinal plants of Russia (**2006**) [Atlas lekarstvennyh rastenij Rossii]. Rus. Acad. sciences. ARSR IMAP Moscow. ISBN: 5-87019-067-3. (In Russian).

[8] Adekenov S.M.,Gabdullin E.M., Khabarov I.A.,Bekeev B.B.,Shaushekov Z.K. (**2019**) News of the National Academy of Sciences of the Republic of Kazakhstan. SERIES OF BIOLOGICAL AND MEDICAL ISSN 2224-5308 Volume 2, Number 332 (2019), PP. 42–48 https://doi.org/10.32014/2019.2519-1629.19 (in Eng).

[9] Konovalova O.A., Rybalko K.S. (**1982**) Plant resources. [Rastitel'nye resursy] 18:116-127. (In Russian).

[10] Khare C.P. (**2007**) Indian medicinal plants-an illustrated dictionary, Springer, Verlag, New York. ISBN: 978-0-387-70638-2.

[11] Kobayashi Y., Nakano Y., Inayama K., Sakai A., Kamiya T. (**2003**) Dietary intake of the flower extracts of German chamomile (*Matricaria recutita* L.) inhibited compound 48/80-induced itch-scratch responses in mice, Phytomedicine, 10:657-664. DOI: 10.1078/0944-7113-00283 (In Eng).

[12] Cemek M., Kağa S., Simşek N., Büyükokuroğlu M.E., Konuk M. (**2008**) Antihyperglycemic and antioxidative potential of *Matricaria chamomilla* L. in streptozotocin-induced diabetic rats, Journal of natural medicines, 5:284-293. DOI: 10.1007/s11418-008-0228-1 (In Eng).

[13] Srivastava J.K., Gupta S. (**2007**) Antiproliferative and apoptotic effects of chamomile extract in various human cancer cells, Journal of Agricultural and Food Chemistry. 55:9470-9478. DOI: 10.1021/jf071953k (In Eng).

[14] Ramos M.F., Santos E.P., Bizarri C.H., Mattos H.A., Padilha M.R. (**1996**) Preliminary studies towards utilization of various plant extracts as antisolar agents, International Journal of Cosmetic Science. 18:87-101. DOI: 10.1111/j.1467-2494.1996.tb00140.x (In Eng).

[15] Macchioni F., Perrucci S., Cecchi F., Cioni P.L., Morelli I., Pampiglione S. (**2004**) Acaricidal activity of aqueous extracts of camomile flowers, *Matricaria chamomilla*, against the mite *Psoroptes cuniculi*, Medical and Veterinary Entomology. 18:205-207. DOI: 10.1111/j.0269-283X.2004.00488.x (In Eng)

[16] Kassi E., Papoutsi Z., Fokialakis N., Messari I., Mitakou S., Moutsatsou P. (**2004**) Greek plant extracts exhibit selective estrogen receptor modulator (SERM)-like properties, Journal of Agricultural and Food Chemistry. 52:6956-6961. DOI: 10.1021/jf0400765 (In Eng).

[17] Al-Hindawi M.K., Al-Deen I.H., Nabi M.H., Ismail M.A. (**1989**) Antiinflammatory activity of some Iraqi plants using intact rats, Journal of Ethnopharmacology. 26:163-168. DOI: 10.1016/0378-8741(89)90063-9 (In Eng)

[18] Maschi O., Dal C.E., Galli G.V., Caruso D., Bosisio E., Dell' A.M. (**2008**) Inhibition of human cAMP-phosphodiesterase as a mechanism of the spasmolytic effect of *Matricaria recutita* L., Journal of Agric Food Chem. 56: 5015-5020. DOI: 10.1021/jf800051n (In Eng).

[19] McKay D.L., Blumberg J.B. (**2006**) A review of the bioactivity and potential health benefits of chamomile tea (*Matricaria recutita* L.), Phytotherapy Research. 20:519-530. DOI: 10.1002/ptr.1900 (In Eng)

[20] Bozorgmehr B., Mojab F., Faizi M. (**2012**) Evaluation of sedative-hypnotic effect of ethanolic extract of five medicinal plants; Nepeta menthoides, *Matricaria chamomilla*, *Asperugo procumbens*, *Lippiacitriodora* and *Withania somnifera*, Research in Pharmaceutical Sciences. 7:831. (In Eng).

[21] Darvishpadok A., Azemi M., Namjoyan F., Khodayar M., Ahmadpour F., Panahi M. (**2012**) Effect of *Matricaria chamomilla* L. on blood glucose and glycosylated hemoglobin in female fertile diabetic rats. Proceeding of 13th Iranian Pharmaceutical Sciences Congress, Iran. P. 19.

[22] Molnar M., Mendešević N., Šubarić D., Jokić S. (**2016**) High pressure extraction techniques of chamomile and determination of antioxidant activity and umbelliferone content in obtained extracts. In book of abstracts from 22nd International Congress of Chemical and Process Engineering CHISA, Praga, Češka Republika. P. 485.

[23] Kotnik P., Škerget M., Knez Ž. (**2007**) Supercritical fluid extraction of chamomile flower-heads: Comparison with conventional extraction, kinetics and scale-up, The journal of supercritical fluids. 43:192-198. DOI: 10.1016/j.supflu.2007.02.005 (In Eng).

[24] Safayhi H., Sabieraj J., Sailer E.R., Ammon H.P. (**1994**) Chamazulene: an antioxidant-type inhibitor of leukotriene B4 formation, Planta Medica. 60:410-413. DOI: 10.1055/s-2006-959520 (In Eng).

[25] Parvez M., Ahmad, V.U., Farooq U., Jassbi A.R., Raziullah H.S. (**2002**) Matricarin, Acta Crystallographica. 58:324-325. DOI: 10.1107/S1600536802002982 (In Eng).

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PROPANE-PROPYLENE OLIGOMERIZATION OVER MODIFIED PILLARED CLAY CATALYSTS

Abstract. Metal supported pillared clay catalysts were used in propane-propylene oligomerization. In the article was shown that the pillaring process has a significant impact on the carrier's nature. That is, specific surface area and porosity of the pillared clay were significantly increase compared with natural clay. The natural clay has lost its porosity at a temperature of 140 °C, reduce surface area from 62 to 20 m^2/g. After pillaring this value increased to 110 m^2/g. The catalysts exhibited good thermal stability at the calcination of 500 to 600 °C as indicated by its specific surface area. As well as, all synthesized catalysts showed selectivity to C_6 and C_9 olefins. The resulting mixtures of isoolefins provide a high-octane product that can be used as a mixture of environmentally friendly gasoline, jet and diesel fuel through hydrogenation.

Key words: pillared clay, propane-propylene fraction, fuel blending component, conversion, selectivity.

1. Introduction

According to the British Petroleum outlook report in 2016, the dependence of energy on crude oil will decrease to 30% by 2035 [1]. This means that in the future, alternative energy sources are more used. Oligomerization of light olefins is one direction of utilize residual gases from the oil refining processes (light FCC, Fisher-Tropsch synthesis of naphtha, etc.). In the oligomerization reaction it is more effective to use acid catalysts, like zeolites, ionic liquids and ion exchange resins. As well as, this reaction is also possible to perform in clay catalysts. Clay catalysts are natural, low cost and reusable, as well as does not cause any harm to the environment. Due to these advantages clay catalysts are widely used in oil refining [2-4].

Although, the most studied light olefin is ethylene, demand for propylene continues to grow. Propylene is a dissymmetric molecule, double bond on the carbon 1 (C1) or 2 (C2) allows it to obtain large amounts of dimer in the coordination of olefins to the catalytic metal center (see Fig. 1) [5]. Further, oligomerization is also developed with this mechanism. In propylene oligomerization products, linear oligomers are use for in diesel fuel additives, aromatics are use for solvents and detergents precursors. Recent years, demand for branched olefins is growing. The highly branched olefins (2,6-dimethylheptan-3, 2,6-dimethylheptan-2, 4,6-dimethylheptan-3, 2-methyloxan-2, 7-methyloctane-3) which obtained from the trimerization of propylene, are widely demanded for production of polymers. These products can be used in the production of plasticizers for plastics, especially the development of plastics with specific properties which will replacement of metal to plastic in aviation, automotive and military industries. And the tetramers of propylene are used in the production of lubricating oil additives. Research on this subject is more common in scientific literature of the last century [6-10]. Paul et al. the first reported that oligomerization of C_3 - C_4 olefins on nickel-substituted synthetic mica-montmorillonites (Ni-SMM). The Ni-SMM catalyst was extremely selective to high-octane products and showed corrosion and sulfur resistance [11]. Khamzin et al. reported pillared clay based super acidic catalysts use for oligomerization of propane –propylene fractions. The catalysts which were prepared by intercalation of montmorillonite with zirconium, then modified with nickel. The 2.5% nickel modified pillared clay catalyst exhibited the best activity and selectivity in propylene trimerization[12]. Presently, Ni-exchanged pillared clays used as selective ethylene oligomerization. Hulea et al. elaborated the synthesis of acid washed (K10) and Al-pillared clays exchanged with nickel and tested them ethylene oligomerization reaction. They believed that the obtained results related to the textural and acid characteristics of the catalyst. The catalyst Ni-K10 exhibited superior catalytic behavior and higher selectivity to C_4 and C_6 liner olefins [13]. However, there are no publishing data on bimetal supported pillared clay catalysts use for propane-propylene oligomerizaton. In our previous publication, we reported investigation of the conversion of butane-butylene fractions on ruthenium and cobalt modified pillared clay catalysts [14]. Therefore, our present study was aimed to investigating catalytic properties of ruthenium and nickel supported pillared clay catalysts for propane-propylene oligomerization.

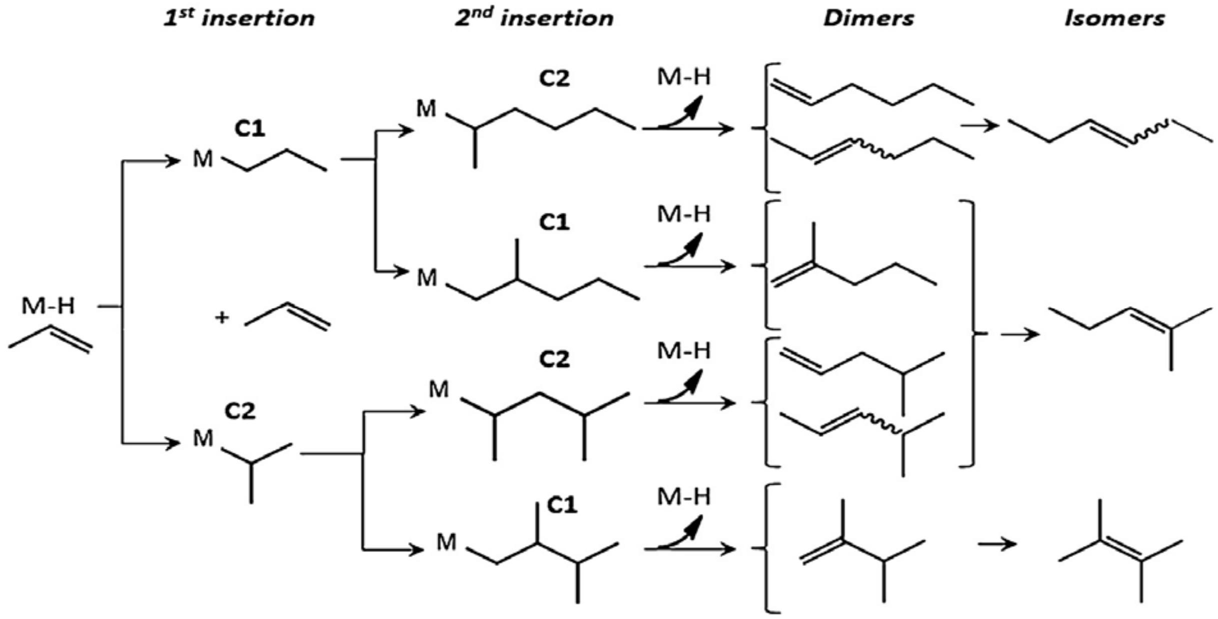

Figure 1 - Dimerization mechanism of propylene [5](M-H being a metal hydride)

Table 1 - Composition of Feedstock

Component	Quantity, %
Ethylene	2.1
Propane	19.2
Propylene	74.8
Total content of C_4	3.8

2. Experimental

2.1. Materials

Bentonit (from South Kazakhstan, rich in montmorillonite > 90%). The cation exchange capacity is 66.4 mmol/100.0 g. clay. $CrCl_3$ (99%, Sigma-Aldrich), NaCl, Ruthenium (III) chloride ($RuCl_3 \cdot 3H_2O$, 99.99%, Alfa-Aesar) and hexahydrate of nickel (II) nitrate ($Ni(NO_3)_2 \cdot 6H_2O$). Materials in this experiment were used without further purification.

2.2. Catalyst preparation

For preparation of RuNi/MMC* catalyst system the aqueous solutions of ruthenium (III) chloride - $RuCl_3 \bullet 3H_2O$ and hexahydrate of nickel (II) nitrate - Ni $(NO_3)_2 \bullet 6H_2O$ were used. Pillared clay preparation carried out by method proposed in [15, 16]. Prior to pillaring process, the clay was saturate with sodium ions through exchange with 1M NaCl for 8 h., and then washed with deionized water. The residue NaCl determined by the solution of $AgNO_3$. Then 0.1M NaOH solution was added to 0.1M $CrCl_3$ solution under vigorous stirring at room temperature. Concentration of chromium chloride change from 4.0 to 20.0 mmole Cr^{3+} per gram of clay. Then this mixture was added to aqueous clay suspension and stirred 4h. Obtained mass undergoes to drying in an air at ambient temperature and left for a few days, dryed in air at 80 °C 8 hour, then calcined 450 °C with heating rate of 2 °C/min during 6h. Finally a certain mass of this sample is impregnated by nickel and ruthenium salts. The obtained mass was dried in the air (2 °C/min) at 80 °C for 8 hour and calcined at 450 °C during 6 h.

2.3. Characterization techniques

Chemical compositions of starting and modified clays were determined by XRF analysis. The textural properties of the samples were obtained from nitrogen adsorption-desorption isotherm, measured at 77K using an ASAP 200 Micrometric instrument. The specific surface area and porosity were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) - methods respectively.

2.4. Catalytic tests

The oligomerization of propane-propylene mixture was carried out in a stainless steel continuous flow fixed-bed reactor (inner diameter 5 mm). The temperature was monitored by using a K-type thermocouple that was inserted directly into the fixed bed and reaction pressure was controlled digitally using a Tescom back-pressure regulator. The reaction temperature and gas pressure are 110-170 °C and 4.0 MPa respectively. The crushed quartz was placed inside the reactor along with the catalyst. Prior to experiment the catalyst (1g) was pre-treated with stream of hydrogen (50 cm^3/min) at 300 °C for 2 h. Then the reactor was cooled to reaction temperature with a flow of argon (Ar, 50 cm^3/min) and the propane-propylene mixture were fed to the reactor and increasing the pressure to reaction conditions. Determination of feedstock (Table 1) and reaction products are analyzed by DANI Master GC Fast Gas Chromatograph equipped with a flame ionization detector (FID).

3. Results and discussion

The chemical compositions of starting and modified clays determined by XRF are listed in Table 2. The starting clay is composed of (by mass %): 59.15% SiO_2, 17.9% Al_2O_3, 6.41% Fe_2O_3, 1.03% MgO, 0.07% CaO and 2.56% Na_2O. After pillaring treatment, the exchangeable cations (Na^+) were completely displaced by polyhydroxy complex of Cr^{3+}, while Mg^{2+} content remained almost constant, not act as exchangeable cation.

The chemical, structural and textural characteristics of the modified clay and catalysts from its derived were widely examined in our previously report. They are belonging to type of pillared clay catalysts, with well ordered pillar and mesopore structure [17]. The main features of the catalysts prepared on this basis are shown in Table 3. In the table structural and adsorption characteristics of natural bentonite clay and the clay pillared with polyhydroxy complexes of chromium are summarized. The polyhydroxy complex of Cr, when modifying the natural clay led to the formation of columnar structures and give them a thermal stability at temperature of 500-600 °C.

Table 2 - Chemical composition (wt. %) of starting and pillared clays

Samples	Bentonite	Cr/Bentonite
SiO_2	59.15	52.74
Al_2O_3	17.9	15.98
Fe_2O_3	6.41	6.30
MgO	1.03	1.0
CaO	0.07	-
Na_2O	2.56	0.02
Cr_2O_3	-	10.63

Table 3 - Main properties of the starting and pillared clays

Amount of chromium, mmol/g clay	SSA, m^2/g	d_{001}, nm	Total pore volume, cm^3/g	SSA at calcinations temperature	
				ºC	m^2/g
-	62	0.9	0.10	140	20
4.0	160	1.82	0.36	300	130
8.0	220	1.96	0.42	450	190
12.0	250	2.38	0.46	500	220
16.0	270	2.6	0.47	600	240
20.0	250	2.15	0.43	600	230

*SSA-specific surface area

In our study, bentonite was modified with polyhydroxy complexes of chromium, which leads to a change in some physicochemical characteristics of this system. The non modified bentonite clay was loses its porosity at temperature 140 °C with the surface area reduced from 62 to 20 m^2/g. After pillaring, this value increased to 110 m2/g. The value of specific surface area of chromium pillared clay depends on amount of the polyhydroxy complex which give them a thermal stability at temperature of 500-600 °C. specific surface area of samples containing 12-20 mmol Cr^{3+} determined after heat treatment at 180 °C are 250-270 m^2/g. The temperature increased 500 to 600°C was observed slightly reduces the value of their specific surface to 220-240 m^2/g, respectively.

Pillared bentonite has a total pore volume of 0.36-0.47 cm^3/g and interlayer distances of 1.82-2.6 nm. Compared with natural bentonite, where these values are - 0.10 cm^3/g and 0.9 nm respectively. The highest values are corresponds to a chromium concentration about 12-16 mmol per gram of clay, where the polyhydroxy complexes of chromium are located between the layers. An increase in concentration of chromium above 20 mmol per gram of clay does not lead to further growth of the interlayer distance. This is probably due to the fact that in the solution non hydrolyzed forms of chromium salt do not affect the formation of layered-columnar structure.

The dependence of active metals in the catalyst on the product selectivity at different temperatures range shown in Figure 2. The reaction were conducted with different metal loading catalysts ranging from 0.5 to 2.0 wt.%. As you seen from the figure, almost all synthesized catalysts have shown good selectivity to C_6 and C_9 olefins. When the amount of active metal in the catalyst increases from 0.5 to 2.0% the selectivity of C_6 and C_9 decreases and selectivity of C_{12} and C_{15+} increases. The highest selectivity catalyst for C_6 (170 °C, 59 %) and C_9 (150 °C, 35 %) was 1.0%RuNi/MMC and the highest selectivity catalyst for C_{12} (110 °C, 16 %) and C_{15+} (170 °C, 3.1%) was 1.5%RuNi/MMC. Increase in the yield of C_{12} and C_{15+} olefins is due to the increase of the hydrogen spillover by increasing the concentration of nickel and ruthenium onto the surface of the catalysts, which leads to cracking and other related reactions - disproportion of seal products. Additionally, taking into account the effect of the temperature to the product selectivity, in Fig. 2A and 2D can be seen, the increase in temperature was directly proportional to the formation of C_6 and C_{15+} olefins. In Fig. 2B and 2C, the temperature increase from 110 to 150 °C, the selectivity for C_9 increased, and the selectivity for C_{12} decreased. Selectivity was opposite when the temperature continued rise to 170 °C.

The dependence of active metals on the conversion of C_3 fractions in various temperature ranges is shown in Figure 3. While the temperature rises from 110 to 170 °C, the conversion reaches a maximum value of at 150 °C (Fig. 3). Further increase in temperature had a negative effect on conversion. Also, it should be noted that the content of ruthenium and nickel is not directly proportional to the catalytic activity of the catalyst. When the content of ruthenium and nickel were 0.5-1.5 %, occurred an increase in conversion with increasing temperature, maximum attained with a 1.0 % content. Further increase to 2.0%, there was a decrease in conversion compared to others due to the transition of nanoscale particles to cluster structures.

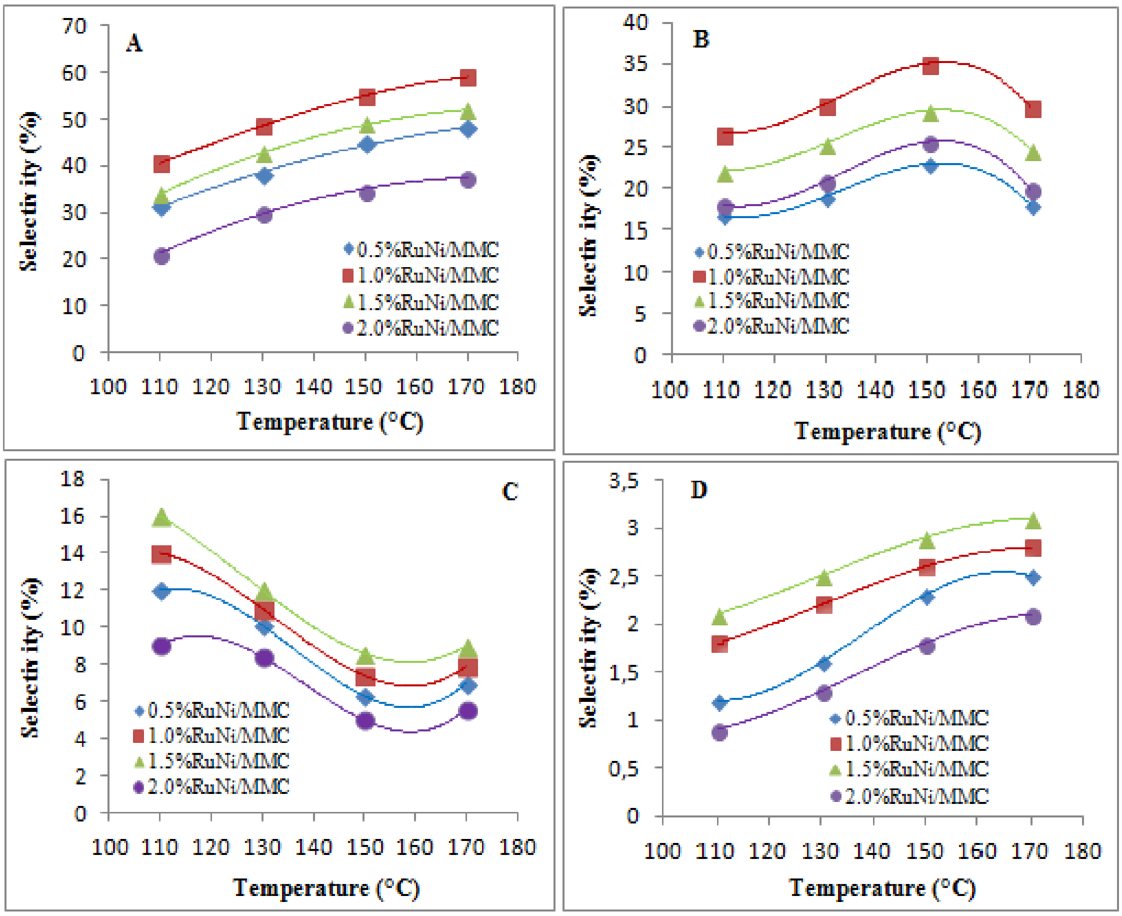

Figure 2. Dependence of isoolefin compositions (A – C_6; B – C_9; C – C_{12}; D – C_{15+}) from the process temperature on the catalyst samples: (0.5 ~ 2.0 %) RuNi/MMC

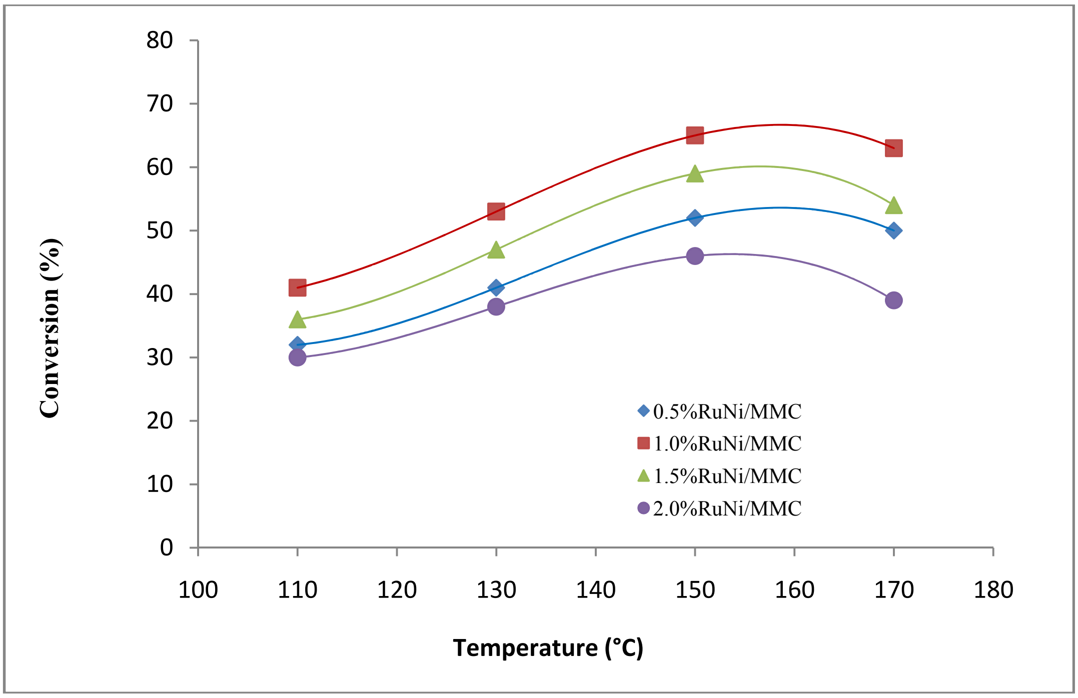

Figure 3 - Dependence of conversion of propane-propylene fractions to isoolefins from the process temperature on the catalyst samples: (0.5 ~ 2.0 %)RuNi/MMC

Conclusion

In propane-propylene oligomerization reaction were used metal supported pillared clay catalysts. It was found that the modified pillared clay catalyst samples had an optimal process temperature of 150 °C. The nature of the carrier was investigated by the role of pillaring agent and the active metal to be supported to the carrier. As a result of experiment, the pillaring of natural clay has significantly improved its textural properties and has shown good thermal stability at high temperatures (500-600 °C). The catalyst maintained its textural properties when further modified with active metals. As a result, synthesized all the catalysts were selective to C_6 and C_9 olefins. The resulting catalytic systems are of interest for simplicity of synthesis, the ability to widely vary the textural properties of the catalyst and the availability of raw materials - deposits of bentonite clay with a high content of montmorillonite exist in Kazakhstan.

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МОДИФИЦИРЛЕНГЕН ҚАБАТТЫҚ ҚҰРЫЛЫМДЫ САЗ БАЛШЫҚТЫ КАТАЛИЗАТОРЛАРДА ПРОПАН-ПРОПИЛЕНДІ ОЛИГОМЕРЛЕУ

Аннотация. Пропан-пропилен олигомеризациясында металл отырғызылған тірек сазды катализаторлар қолданылды. Мақалада қабаттық құрылымдау процесінің тасымалдаушы сипатына айтарлықтай әсер ететіндігі көрсетілген. Яғни, табиғи саз балшыққа қарағанда қабаттық құрылымданған саз балшықтың арнайы беті мен кеуектілігі айтарлықтай артты. Табиғи саз балшық 140 °С температурада кеуектілігін жоғалтып, меншікті бетінің ауданы 62-ден 20 $м^2$/г-ға төмендетеді. Бұл мән қабаттық құрылымдаудан кейін 110 $м^2$/г дейін өсті. Меншікті бетінің ауданымен көрсетілгендей, катализаторлар 500-600 °С температурада кальцинация кезінде жақсы термиялық тұрақтылықты көрсетті. Сондай-ақ, барлық синтезделген катализаторлар C_6 және C_9 олефиндеріне біршама селективтілік көрсетті. Алынған изоолефин қоспасы гидрлеу арқылы экологиялық таза бензин, реактивті және дизель отыны қоспасы ретінде пайдаланылуы мүмкін жоғары октанды өніммен қамтамасыз етеді.

Түйін сөздер: қабаттық құрылымданған саз балшық, пропан-пропилен фракциясы, отынды араластыру компоненті, конверсия, селективтілік.

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ОЛИГОМЕРИЗАЦИЯ ПРОПАН-ПРОПИЛЕНОВАЯ ФРАКЦИЯ НА МОДИФИЦИРОВАННЫХ ГЛИНИСТЫХ КАТАЛИЗМАХ

Аннотация. В пропан-пропиленовой олигомеризации применяли катализаторы на основе глины, нанесенный металлом. Было показано, что процесс пилларирование оказывает существенное влияние на природу носителя. То есть удельная площадь поверхности и пористость столбчатой глины значительно увеличились по сравнению с природной глиной. Природная глина потеряла свою пористость при температуре 140 °С, уменьшила площадь поверхности от 62 до 20 $м^2$/г. После пилларирование это значение увеличилось до 110 $м^2$/г. Катализаторы демонстрировали хорошую термическую стабильность при прокаливании от 500 до 600 °С, как указано ее удельной поверхностью. Все синтезированные катализаторы показали селективность по отношению к олефинам C_6 и C_9. Полученные смеси изоолефинов обеспечивают высокооктановый продукт, который можно использовать в качестве смеси экологически чистого бензина, реактивного и дизельного топлива посредством гидрирование.

Ключевые слова: столбчатая глина, пропан-пропиленовая фракция, компонент для смешивания топлива, конверсия, селективность.

REFERENCES

[1] https://www.bp.com/.../bp/.../energy.../energy-outlook-2016/

[2] N.A. Zakarina, O. Dolelkhanuly, D.A. Jumadullaev, A.K. Akurpekova, L.S. Djumabaeva. (2018) News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology. Volume 5, Number 431 (2018), 117 – 124. https://doi.org/10.32014/2018. 2518-1491.15

[3] B.K.Massalimova, G.D.Jetpisbayeva, D.T.Altynbekova, S.M.Nauruzkulova, A.A.Atakozhaeva, V.A.Sadykov. (2019) News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology. Volume 2, Number 434 (2019), 5 – 11. https://doi.org/10.32014/2019.2518-1491.11

[4] M.E. Gyftopoulou, M. Millan , A.V. Bridgwater , D. Dugwell , R. Kandiyoti , J.A. Hriljac. (2005) Applied Catalysis A: General 282: 205–214. https://doi.org/10.1016/j.apcata.2004.12.012

[5] Anna Paula, Rodrigues Ehlert, Eduardo Miraglia Carvalho, Daniel Thiele, Cristiano Favero, Isabel Vicente, Katia Bernardo-Gusmão, Rafael Stieler, Roberto Fernando de Souza, Michèle Oberson de Souza (2017) Catalysis Today 296: 272–276. https://doi.org/10.1016/j.cattod.2017.04.005

[6] M. Kojima, J.C.Q. Fletcher and C.T. O᾽Connor, (1986) Applied Catalysis, 28: 169-179. https://doi.org/10.1016/S0166-9834(00)82501-4

[7] J.C.Q. Fletcher, M. Kojima, C.T. O᾽Connor, (1986) Applied Catalysis, 28: 181-191. https://doi.org/10.1016/S0166-9834(00)82502-6

[8] C.T. O᾽Connor, L.L. Jacobs and M. Kojima, (1988) Applied Catalysis, 40: 277-290. https://doi.org/10.1016/S0166-9834(00)80442-X

[9] A.P. Vogel, C.T. O᾽Connor, M. Kojima, (1990) Clay Minerals, 25: 355-362. DOI: 10.1180/claymin.1990.025.3.10

[10] J.C.Q. Fletcher, A.P. Vogel, C.T. O᾽Connor, (1992), New Frontiers in Catalysis, 1731-1734. https://doi.org/10.1016/S0167-2991(08)64521-8

[11] Paul G. Berclk, Kirk J. Metzger and Harold E. Swlft, (1978) Ind. Eng. Chem. Prod. Res. Dev., 17(3): 214-219. **DOI:** 10.1021/i360067a007

[12] Yu. A. Khamzin, R.R. Shiriyazdanov, A.R. Davletshin, F.Sh. Vil'danov, E.A. Ipatova, M.N. Rakhimov, E.G. Telyashev, R.R. Abdyushev, and L.S. Doinitsyna, (2015) Chemistry and Technology of Fuel and Oils, Vol. 15, №5, 458-463.

[13] Asma Aid, Radu Dorin Andrei, Samira Amokrane, Claudia Cammarano, Djamel Nibou, Vasile Hulea, (2017) Applied Clay Science 146: 432–438. http://dx.doi.org/10.1016/j.clay.2017.06.034

[14] Utelbaev B.T., Toktassyn R., Michele O. de Souza, Myrzahanov M. Study of the butane-butylene fraction on modified Ru-Co supported clay catalysts, (2017) News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology. Volume 1, Number 421 (2017), 5 – 11. https://doi.org/10.32014/2018.2518-1491

[15] Georgescu A., Brabie G., Nistor I. D., Penot C., Nardou F (2015) J Porous Mater 22: 1009–1019. https://doi.org/10.1007/s10934-015-9975-z

[16]. Korili, S.A., Gill, A., Korili, A., Trujillano, R., Vicente, M.A. Pillared clays and related catalysts. Springer: 2010, p. 225. ISBN: 978-1-4419-6669-8

[17] Toktassyn R., Utelbayev B.T., Michele O. de Souza, Suleymenov E.N (2016) Bulletin of Chemical Reaction Engineering & Catalysis 11 (3): 431-437. http://dx.doi.org/10.9767/bcrec.11.3.495.431-437.

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HYDROPROCESSING OF DIZEL OIL FRACTIONS ON MODIFIED ALUMINA CATALYSTS

Abstract. The paper presents the results of a study of hydroforming diesel oil fractions on alumina catalysts modified with metals of variable valency, the addition of phosphorus and lanthanum. The study of the process of hydroprocessing of the diesel fractions was carried out in a high-pressure flow unit with a stationary catalyst bed at temperature of 320-400^{0}C, a pressure of 3 - 4.0 MPa and a volume feed rate of 1-3 h^{-1}. The results obtained during the tests of catalysts in the process of hydroprocessing of diesel oil fractions show that the greatest decrease in the pour point and turbidity occurs at a temperature of 380–400^{o}C. During the hydroprocessing of the diesel fraction, the lowest residual sulfur content is observed at a temperature of 400^{o}C.

During the hydroprocessing of the diesel fractions of oil, the catalyst $CoO-WO_3$- La_2O_3 - P_2O_5-ZSM- Al_2O_3, has the greatest hydrodesulfurizing activity. The sulfur content of the catalysate with increasing temperature up to 400^{o}C decreased from 0,560 to 0,0229%. The greatest decrease in the pourpoint and cloudpoint, during the hydroprocessing of the diesel oil fraction is observed on the catalyst $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3: minus 58.9 and minus 57.7^{o}C, respectively.

Physical and chemical characteristics of catalysts are studied. The method of temperature–programmed desorption of ammonia found that the highest concentration of acid centers has a catalyst $NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3 (31.3•10^{-4}mol NH_{3des} /g cat) with T_{des}= 215^{0}C, which determines its high hydroisomerizing activity in the processes of hydroprocessing of diesel fractions.

The developed catalysts make it possible to obtain winter grades of diesel fuels with low sulfur content.

Key words: diesel fraction of oil, zeolite, catalyst, hydropurification.

Introduction

Recently, due to the involvement in the processing of high-sulfur oil and the deepening of its processing, the requirements for catalysts for hydroprocessing gasoline and diesel oil fractions have increased. According to international standards, a significant restriction of the content of sulfur, benzene, aromatic and olefin hydrocarbons in motor fuels is required. Existing industrial catalysts for hydroprocessing of oil fractions in many countries of the world do not meet the increased requirements for the quality of motor fuels.

In the oil refining industry, hydroprocessing and hydroisomerization processes are increasingly used to produce high-quality diesel fuels. As a result of hydroprocessing, sulfur, nitrogen compounds, unsaturated hydrocarbons are removed, thermal stability is increased, the corrosion activity of fuels is reduced, the formation of sludge during storage is reduced, and the color and smell of motor fuel is improved. At present, there is a tendency to tighten the requirements for the composition of motor fuels, the insufficient quality of which is one of the causes of environmental pollution, so the main attention of many refineries is focused on increasing the depth of hydrodesulfurization. In this regard, catalytic processes of deep hydroprocessing of oil fractions are of great importance for the production of high-quality motor fuels at the present stage.

The practical implementation of this direction is associated with the creation of new multifunctional catalysts that can effectively carry out deep hydroprocessing of diesel fractions in one stage. Catalysts based on high-silica zeolites, the activity and selectivity of which is determined by the unique acid-base and molecular-sieve properties, are very promising in this regard. One of the possible ways to regulate catalytic properties is the introduction of elements with variable valence into the catalyst and the use its as modifiers.

At the same time, more attention is paid to the development of a hydroprocessing catalyst for a certain type of oil product. [1 - 20].

In this work the results of research of catalytic hydroprocessing gasoline and diesel fractions of crude oil on the new aluminonickel(cobalt),tungsten, molybdenum catalysts supported on Al_2O_3 and modified with additives of zeolite ZSM-5, phosphorus and lanthanum.

Experimental part

New zeolite-containing aluminum oxide catalysts modified by the introduction of metals with variable valence and phosphorus were developed and prepared. The catalysts were prepared by simultaneous impregnation of a mixture of aluminum hydroxide with high-silica zeolite HZSM-5, water-soluble salts of Nickel, cobalt, molybdenum, tungsten, lanthanum and phosphoric acid. After impregnation, the catalyst samples were molded at 150^0C for 5 hours, then dried at 550^0C for 5 hours.

The activity of the synthesized catalysts was studied in the processes of hydroprocessing of diesel oil fractions. The process was carried out in a flow unit with a stationary catalyst bed at temperatures of 320-400^0C, a volume feed rate of 1-3 hour^{-1}, a pressure of 3.0-4.0 MPa.

Analysis of sulfur content in raw materials and products was carried out on the SPECTROSCAN device. Determination of pour point and cloud point was carried out on the device LAZ M2.

Physical and chemical characteristics of catalysts were studied using BET electron microscopy [21] and temperature-programmed desorption of ammonia [22].

Results and discussion

The catalyst $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$was tested in the process of hydroprocessing of diesel oil fraction (table 1). With an increase in the process temperature from 320 to 400°C, the pour point of the diesel fraction after its hydroprocessing decreased from minus 18.3 to minus 37.6°C. Cloud point in these conditions varies from minus 11.3 to minus 36.1°C. The yield of hydro-refined diesel fuel is 95.0-100.0%. The sulfur content after hydroprocessing of the diesel fraction at 380-400°C on the catalyst $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$decreases from 0.560 to 0.0229%.

Table 1 - Hydroprocessing of diesel oil fraction on the catalyst $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, V=4 h^{-1}, P=4.0 MPa

Process temperature, ^{0}C	Sulphur content,%	Pourpoint, ^{0}C	Cloudpoint, ^{0}C	Yield, %
Initial diesel fraction	0,560	-18,3	-11,3	-
320	-	-36,1	-28,5	100
350	-	-33,8	-32,0	97,5
380	0,0266	-37,6	-36,1	95,0
400	0,0229	-36,2	-34,6	95,0

When testing the catalyst $NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$during the hydroprocessing of the diesel fraction of oil, it is shown that the pour point of the diesel fraction at 400°C decreased to minus 38.8°C, while the pour point of the feedstock is minus 18.3°C. Cloud point in these conditions varies from minus 11.3 to minus 28.8°C. The yield of hydro-refined diesel fuel is 96.1-100.0%. The sulfur content is reduced from 0.560% in the initial fraction to 0.102% (table 2).

Table 2 - Hydroprocessing of diesel oil fraction on the catalyst $NiO-WO_3$- La_2O_3- $P_2O_5-ZSM-Al_2O_3$, V=2 hour^{-1}, P=4.0 MPa

Process temperature, ^{0}C	Sulphur content,%	Pourpoint, ^{0}C	Cloudpoint, ^{0}C	Yield, %
Initial diesel fraction	0.560	-18,3	-11,3	-
320	0,453	-30,2	-21,9	100
350	0,367	-35,1	-25,0	99,6
380	0,245	-38,1	-27,2	98,5
400	0,102	-38,8	-28,2	96,1

In the process of hydroprocessing diesel oil fraction at the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3pour point of the diesel fraction with 320°C decreased from minus 18,3 to minus 35,9°C. When the process temperature rises to 400°C, the pour point decreases to minus 58.9°C. Cloud point in these conditions falls from minus 11.3 to minus 57.7°C. The yield of hydroprocessing diesel fuel is 90.0-100.0% (table 3). Sulfur content is reduced to 0.0536%.

Table 3 - Hydroprocessing of diesel oil fraction
on the catalyst NiO-MoO_3- La_2O_3 - P_2O_5-ZSM- Al_2O_3, $V=4\ h^{-1}$, P=4.0 MPa

Process temperature, ^0C	Sulphur content,%	Pourpoint, ^0C	Cloudpoint, ^0C	Yield, %
Initial diesel fraction	0,560	-18,3	-11.3	-
320	0,367	-35,9	-30,7	100
350	0,251	-51,3	-51,0	92,5
380	0,135	-54,9	-48,1	91,0
400	0,0536	-58,9	-57,7	90,0

Table 4 presents the results obtained in the study of the effect of the bulk feed rate on the process of hydroprocessing of the diesel fraction of oil on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3at P=4.0 MPa, 400C. When the volume velocity decreases from 3.0 and 1.0 h^{-1}, the amount of sulfur in the catalyst decreases from 0.1942% to 0.0536%. The greatest decrease in pour point and cloud point on this catalyst - to minus 58, 9 and minus 57.7, respectively - is observed at an optimal volumetric feed rate of 2.0 h^{-1}. Reducing the activity of the catalyst with increasing feed rate is due to a decrease in the contact time of reacting substances with the active centers of the catalyst.

Table 4 - The effect of the volumetric feed rate of raw materials in the process of hydroprocessing the diesel fraction on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3, with P=4,0 MPa, 400°C

V, h^{-1}	Cloudpont, ^0C	Pourpoint, ^0C	Yield, %	Sulphur content, %
Initial diesel fraction	-11,3	-18,3	-	0,560
1,0	-57,7	-58,9	84,0	0,0536
2,0	-60,5	-60,7	88,0	0,1848
3,0	-30,8	-31,4	100,0	0,1942

From the data presented in table 5, it can be seen that with an increase in pressure in the range of 3.0-4.0 MPa during the hydroprocessing of the diesel fraction of oil on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3, the pour point and turbidity with an increase in pressure to 4.0 MPa decrease from minus 18.3°C to minus 58.9°C, and minus 11.3°C to minus 57.7°C, the sulfur content decreases from 0.560 to 0.0536%.

Table 5 –The pressure effect on the process of hydroprocessing of the diesel fraction
on the catalyst NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3, $V=2\ h^{-1}$, 400°C

P, MPa	Cloudpoint, ^0C	Pourpoint, ^0C	Sulphur content, %	Yield, %
Initial diesel fraction	-11,3	-18,3	0,560	-
3,0	-32,1	-36,1	0,1110	93,0
3,5	-42,9	-43,1	0,0917	88,0
4,0	-57,7	-58,9	0,0536	84,0

When testing the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3in the process of hydroprocessing the diesel oil fraction, it was found that with an increase in the process temperature from 320 to 400°C, the pour point and turbidity of the diesel fraction decreases by 36.7 and 37.1°C, respectively. The yield of hydroprocessing diesel fuel is 92.0-100.0%. The sulfur content after hydroprocessing of the diesel fraction at 380-400°C on the catalyst CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3decreases from 0.560 to 0.104% (table 6).

Table 6 - Effect of temperature on the process of hydroprocessing of the diesel fraction on the catalyst $CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$at P=4.0 MPa, V=2.0 h^{-1}

Process temperature, ^0C	Cloudpoint, ^0C	Pourpoint, ^0C	Sulphur content,%	Yield, %
Initial diesel fraction	-11,3	-18,3	0,560	-
320	-42,8	-47,5	0,448	100,0
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

During the hydroprocessing of the diesel fraction of oil containing 0.64% sulfur on the catalyst $CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}Fe_2O_3\text{-}ZSM\text{-}Al_2O_3$in the range of 320-400°C, A decrease in the pour point from minus 13.5 to minus 38.4°C(table 7) the cloud point under these conditions varies from minus 12.0 to minus 38.1°C. The yield of hydroblagged diesel fuel is 94.0-99.0%. The sulfur content is reduced from 0.64 % in the initial fraction to 0.0310% in the resulting catalyst.

Table 7 -Hydroprocessing of the diesel fraction of oil containing 0.64% sulfur on the catalyst $CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}Fe_2O_3\text{-}ZSM\text{-}Al_2O_3$at P=4.0 MPa, V=2.0 h^{-1}

Process temperature, ^0C	Cloudpoint, ^0C	Pourpoint,^0C	Sulphur content, %	Yield, %
Initial diesel fraction	-12,0	-13,5	0,64	-
320	-16,0	-16,3	0,39	97
350	-21,2	-21,5	0,28	99
380	-33,0	-33,3	0,11	99
400	-38,1	-38,4	0,031	94

The analysis of the test results of the developed catalysts in the process of hydroprocessing of diesel oil fractions shows that the greatest decrease in the pour point and cloud point of hydroblagged fuel occurs at temperature of 380 – 400°C. During the hydroprocessing of the diesel fraction, the lowest residual sulfur content is observed at temperature of 400°C.

In the study of the process of hydroprocessing of diesel oil fractions on the studied catalysts, it was established that the greatest decrease in the pour point and turbidity is observed on the catalyst $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$and is equal to minus 58.9 and minus 57.7°C, respectively, at an experiment temperature of 400°C. The hydrodesulfurizing activity of $CoO\text{-}WO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$is significantly higher than that of other catalysts studied: the sulfur content decreases to 0.0229%.

During the hydroprocessing of the diesel fraction at 400°C and the bulk speed of the raw material from 2.0 h^{-1}, the greatest hydrodesulfurizing activity varies in a number of catalysts (%): $CoO\text{-}WO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ (0,0229%) <$CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}Fe_2O_3\text{-}ZSM\text{-}Al_2O_3$ (0,031%)< $NiO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}HZSM\text{-}Al_2O_3$ (0,0536%) <$CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}ZSM\text{-}Al_2O_3$ (0,104%)

The studied catalysts make it possible to obtain winter grades of diesel fuels with low sulfur content.

The activity of catalysts is associated with the size of their surface and acid-base characteristics. Physical and chemical characteristics of catalysts were studied using BET methods and temperature–programmed desorption of ammonia. By the BET method it is established that the surface of the developed catalysts fluctuates within 211,0-274,0 m^2/g of the catalyst. The catalysts are characterized by pores with d ≈ 1.5-2.5 nm and d ≈ 7.0 nm. The total volume of catalyst pores does not exceed 0.28-0.41 ml/g of catalyst.

Acid-base characteristics of catalysts are essential for the processing of hydrocarbons. Acid characteristics of catalysts were investigated by temperature–programmed desorption of ammonia (table 8).

Table 8 - Acid-base characteristics of catalysts

The catalysts	Temperature of the high peaks, ^0C		Amount of desorbed ammonia, 10^{-4} mol/gcat.		ΣNH_3 desorbed 10^{-4} mol/gcat.
	1	2	1	2	
$NiO-WO_3- La_2O_3- P_2O_5-ZSM- Al_2O_3$	—	195	—	21,0	21,0
$CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$	—	210	—	26,0	26,0
$NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$	—	215	—	31,3	31,3
$CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$	175	220	10,2	9,5	19,7
$CoO-MoO_3-La_2O_3-P_2O_5-Fe_2O_3-ZSM-Al_2O_3$	150	265	4,5	5,5	10,0

From the data presented in table 8, it can be seen that on the surface of the catalysts $NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$, there are strong acid centers with T_{des} equal to 195 , 210 , 215°C, respectively. The amount of ammonia desorbed from the surface of $NiO-WO_3-La_2O_3-P_2O_5-ZSM- Al_2O_3$ is $21.0 \bullet 10^{-4}$molNH_{3des}/g cat. The number of acid centers of $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$catalyst is $26.0 \bullet 10^{-4}$mol NH_3 $_{des}$/g cat. The concentration of acid centers on the catalyst $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ above – $31.3 \bullet 10^{-4}$molNH_{3des}/g cat. Two forms of adsorbed ammonia with T_{des} equal to 175 and 220°C were found on the surface of the catalyst $CoO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$. Their number is close to 10.2 and 9.5 mol NH_{3des}/g cat, respectively. The total amount of NH_{3des} = 19.7 10^{-4}molNH_{3des}/g cat. The total amount of ammonia desorbed from the surface of $CoO-MoO_3-La_2O_3-P_2O_5-Fe_2O_3-ZSM-Al_2O_3$ is significantly lower than $10.0 \bullet 10^{-4}$mol NH_3 $_{des}$/g cat. This catalyst is characterized by the presence of the most loosely bound and most strongly bound forms of ammonia in comparison with other studied catalysts: with T_{des} equal to 150°C and 265°C.

It should be noted that the highest concentration of acid centers has the catalyst $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$($31,3 \cdot 10^{-4}molNH_3$ $_{des}$/g cat) T_{des}= 215°C, which determines its high hydroisomerized activity in the processes of hydroprocessing diesel fractions.

Thus, the developed multifunctional modified alumina catalysts of hydroprocessing diesel oil fractions, which are simultaneously in one step carry out hydroprocessing, hydrocracking and hydroisomerization, which allows to obtain low-sulfur waxy diesel fuel.

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МҰНАЙДЫҢ ДИЗЕЛЬДІК ФРАКЦИЯЛАРЫН МОДИФИЦИРЕНГЕН АЛЮМООКСИДТІ КАТАЛИЗАТОРЛАРДА ГИДРОӨҢДЕУ

Аннотация Жұмыста мұнайдың дизельдік фракцияларын ауыспалы валентті металдармен, фосфор және лантан қоспаларымен модифицирленген алюмооксидті катализаторында гидрожақсарту процесін зерттеу нәтижелері көрсетілген. Дизельдік фракцияларды гидроөңдеу процестерінде зерттеулер 320-400^{0}С температурада, қысымы 3-4,0 МПа және шикізат берілудің көлемдік жылдамдығы 1-3 сағ$^{-1}$ болып катализатордың тұрақты қабатында ағымды қондырғыда жүргізілді. Катализаторларды сынау нәтижесінде мұнайдың дизельдік фракцияларын гидроөңдеу процестерінде лайлану және қату температураларының ең көп төмендеуі 380 - 400^{0}С температураларда болатыны көрсетілді. Дизельдік фракцияларды гидроөңдегенде ең аз күкірт мөлшері 400˚С температурада байқалды. Мұнайдың дизельдік фракциясын гидроөңдегенде ең үлкен гидрокүкіртсіздендіру активтілігін $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторы көрсетті. Температура 400С-қа дейін өскенде катализаттағы күкірттің мөлшері 0,560-тан 0,0229%-ға кеміді. Мұнайдың дизельдік фракцияларын гидроөңдегенде қату және лайлану температуралары ең көп төмендеуі $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ катализаторында байқалды: минус 58,9 қату және минус 57,7^{0}С лайлану.

Катализаторлардың физика-химиялық қасиеттері зерттелді. Аммиактың температура-бағдарламалы десорбция әдісі бойынша қышқылдық орталықтардың ең үлкен мөлшері $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$

катализаторында ($31,3\cdot10^{-4}$ моль $NH_{3дес}$ /г кат. $T_{дес}$= 215^0C) болып , олар дизель фракцияларын гидроөңдегенде жоғары гидроизомерлеу активтілігін анықтайды.

Жасалынған катализаторлар күкірті аз қыстық сортты дизель отындарын алуға мүмкіндік береді.

Түйін сөздер: мұнайдың дизельдік фракциясы, цеолит, катализатор, гидротазарту

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ГИДРОПЕРЕРАБОТКА ДИЗЕЛЬНЫХ ФРАКЦИЙ НЕФТИ НА МОДИФИЦИРОВАННЫХ АЛЮМООКСИДНЫХ КАТАЛИЗАТОРАХ

Аннотация В работе приведены результаты исследования гидрооблагораживания дизельных фракций нефти на алюмооксидных катализаторах, модифицированных металлами с переменной валентностью, добавками фосфора и лантана. Исследование процесса гидропереработки дизельных фракций проводилось в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400^0C, давлении 3-4,0 МПа и объемной скорости подачи сырья 1-3 $ч^{-1}$. Результаты, полученные при испытаниях катализаторов в процессе гидропереработки дизельных фракций нефти, показывают, что наибольшее снижение температуры застывания и помутнения происходит при температурах 380 - 400^0C. При гидропереработке дизельных фракций наименьшее остаточное содержание серы наблюдается при температуре 400˚С.

При гидропереработке дизельных фракций нефти наибольшей гидрообессеривающей активностью обладает катализатор $CoO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$. Содержание серы в катализате с ростом температуры до 400^0C снизилось с 0,560 до 0,0229%. Наибольшее снижение температуры застывания и помутнения при гидропереработке дизельных фракций нефти наблюдается на катализаторе $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$: минус 58,9 и минус $57,7^0C$ соответственно.

Изучены физико-химические характеристики катализаторов. Методом температурно–программированной десорбции аммиака установлено , что наибольшей концентрацией кислотных центров обладает катализатор $NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$ ($31,3\cdot10^{-4}$ моль $NH_{3дес}$ /г кат-ра) с $T_{дес}$= 215^0C, что и определяет его высокую гидроизомеризующую активность в процессах гидропереработки дизельных фракций.

Разработанные катализаторы позволяют получать зимние сорта дизельных топлив с низким содержанием серы.

Ключевые слова: дизельная фракция нефти, цеолит, катализатор, гидроочистка

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REFERENCES

[1] Havkin V.A. ,Chernysheva E.A., Guljaeva L.A. Hydrogenation processes of obtaining motor fuels [Gidrogenizacionnye processy poluchenija motornyh topliv], Ufa, 2013, 259 p. (In Russian).

[2] Mirimanjan A.A., Vihman A.G., Mkrtychev A.A. On reduction of the benzene content of gasoline and the reformed [O snizhenii soderzhaniya benzola v benzinah i riformatah] Refining and petrochemicals [Neftepererabotka i neftehimija] – 2006, 8:11-14. (In Russian).

[3] Tailleur R.G. Deep hydrotreating diesel fractions for low-sulfur fuel production using gas-phase and trickle bed reactors system operating in parallel, Catalysis Today, 220-222:133-152.DOI: 10.1016/j.cattod.2013.10.006 (In Eng).

[4] Babich, I. V., Moulijn, J. V. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, Fuel, 2003,82,6:607–631. (In Eng).

[5] Gavrilov N.V., Durov O.V. Production of environmentally friendly gasoline corresponding to European standards [Poluchenie ekologicheski chistyh benzinov, sootvetstvuyushchih evrostandartam] Chemistry and technology of fuels and oils [Himija i tehnologija topliv i masel] 2008, 6:9-13.(In Russian).

[6] Rodrıguez-Castellon E., Jimenez-Lopez A., Eliche-Quesada D. Nickel and cobalt promoted tungsten and molybdenum sulfide mesoporous catalysts for hydrodesulfurization, Fuel, 87:1195-2006.DOI: 10.1016/j.fuel.2007.07.020. (In Eng).

[7] Dengqian Zhang, AijunDuan, Zhen Zhao, ChunmingXu. Synthesis, characterization and catalytic performance of NiMo catalysts supported on hirrarchically porous Beta-KIT-6 material in the hydrodesulfurization of dibenzothiophen , J. of catalysis, 2010, 274, 2:273-286. (In Eng).

[8] YoussefSaih, KohichiSegawa. Catalytic activity of CoMo catalysts supported on boron-modified alumina for the hydrodesulphurization of dibenzothiophene and 4,6- dimethyldibenzothiophene, Applied. Catalysis, 353: 258-265.DOI:10.1016/j.apcata.2008.10.037 (In Eng).

[9] Nefedov B.K. Technologies and catalysts of deep Hydrotreating of motor fuels for ensuring requirements of the new Euro-4 standard [Tekhnologii i katalizatory glubokoj gidroochistki motornyh topliv dlya obespecheniya trebovanij novogo standarta Evro-4] Catalysis in the industry [Kataliz v promyshlennosti] 2003, 2:20-27. (In Russian).

[10] Talisman E.L., Trofimov O.V., Smirnov V.K., Irisova K.N. Production of diesel fuel components with ultra-low sulfur content in the conditions of domestic refineries [Poluchenie komponentov dizel'nyh topliv s ul'tranizkim soderzhaniem sery v usloviyah otechestvennyh NPZ] oil Refining and petrochemistry [Neftepererabotka i neftehimija] 2008, 11:13-17. (In Russian).

[11] Kashin O.N., Ermolenko A.D. Problems of production of high-quality gasoline and diesel fuels [Problemy proizvodstva vysokokachestvennyh benzinov i dizel'nyh topliv] oil Refining and petrochemistry [Neftepererabotka i neftehimija] 2005, 5:32-38. (In Russian).

[12] Onoychenko S.N., Emelyanov V.E., Krylov I.F. Modern and perspective fuels and automobile gasoline [Sovremennye i perspektivnye topliva i avtomobil'nye benziny] Chemistry and technology of fuels and oils [Himija i tehnologijatopliv i masel] 2003, 6:3-6. (In Russian).

[13] Konovalchikov O.D., Melik-Ahnazarov T.H., Khavkin V.A. i dr. etc. Polyfunctional zeolite catalysts for the processes of oil refining // Oil Refining and petrochemistry [Polifunkcional'nye ceolitsoderzhashchie katalizatory dlya processov neftepererabotki] Oil Refining and petrochemistry [Neftepererabotka i neftehimija] 2000, 9:12-16. (In Russian).

[14] Tomina N. N., Pimerzin A. A., Loginova L. N., Sharygina M. A. Zhilkina E. A., Eremin Yu. V. The catalytic hydroforming of petroleum fractions on modified alyumonikelmolibden catalysts [Kataliticheskoe gidrooblagorazhivanie neftyanyh frakcij na modificirovannyh alyumonikel'molibdenovyh katalizatorah] Petrochemicals [Neftehimija] 2004, 44, 4:274-277.(In Russian).

[15] Toledo-Antonio, J.A., Cortés-Jácome, M.A., Angeles-Chávez, C., Escobar, J., Barrera, M.C., López-Salinas, E., Highly active CoMoS phase on titania nanotubes as new hydrodesulfurization catalysts, Appl. Catal., B, 2009, 90:213-223. (In Eng).

[16] Dumond, F., Marceau, E., Che, M., A Study of Cobalt Speciation in Co/Al_2O_3 Catalysts Prepared from Solutions of Cobalt−Ethylenediamine Complexes // J. Phys. Chem. C. - HZSM-5 (Nitrate) and Zn-HZSM-5 (Acetate) Catalyst, Revista de Chimie, 2007, 67:1523-1528. (In Eng).

[17] Plantenga F.L, Leliveld R.G. Sulfur in fuels: more stringent sulfur specifications for fuels are driving innovation, Appl. Catal. A: General, 2003, 248:1-7. (In Eng).

[18]Morales-Ortuño J.C., Klimova T.E. . Development of New Hydrodesulfurization NiMo Catalysts Supported on Al_2O_3-TiSBA-15 Hybrid Materials, Fuel, 2005, 198: 99-109. (In Eng).

[19] Qiherima, Li, H., Yuan, H., Zhang, Y., Xu, G., Effect of Alumina Support on the Formation of the Active Phase of Selective Hydrodesulfurization Catalysts Co-Mo/Al_2O_3 ,Chin. J. Catal,2011, 32: 240-249. (In Eng).

[20] Smirnov V.K., Irisova K.N, Talisman E.L. [Novye katalizatory gidrooblagorazhivanija neftjanyh frakcij i opyt ih ekspluatacii] Catalysis in industry [Kataliz v promyshlennosti], 2003, 2:30-36. (In Russian).

[21] WilliamsD.B., CarterC.B. TransmissionElectronMicroscopy, 2009. Springler. 760p. (In Eng).

[22] Yushchenko V. V., Zakharov A. N., Romanovsky B. V. On the application of the method of temperature-programmed desorption to the study of acidic properties of high-silica zeolites [O primenenii metoda temperaturno-programmirovannoj desorbcii k issledovaniyu kislotnyh svojstv vysokokremnezemistyh ceolitov] Kinetics and catalysis [Kinetika i kataliz], 1986, 27, 2:474-478. (In Russian).

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SORPTION ABILITY OF MODIFIED NANO-CARBON MATERIALS

Abstract. In this work expanded graphite (EG) and carbonized rice husk (CRH) were obtained by heat treatment at different temperatures and by using different activating conditions.The samples were tested as sorbent for oil in water. The oil removal efficiency of carbonized rice husks and expanded graphite, were studied as an adsorbent for the removal of emulsified oils from wastewater. Results showed that the oil removal efficiency increased to 10-15 % in the case ofEG samples after base leaching.As concerns as the carbonized rice husk samples the adsorption capacities are similar and no particular variation with the activation temperature are detected. As a general result the carbonization process induced an increase of the adsorption capacities.Samples were purified and characterized by SEM-EDAX, FTIR, elemental analysis, Proximate analysis and ICP MS.

Keywords: Carbonized rice husk;expanded graphite; Oily wastewater; Adsorbent; Oil removal efficiency.

Introduction

Oil and oil-derivative are the most dangerous water contaminants in Kazakhstan. The oil pollution causes serious environmental problems to aquatic organisms and humans due to the high toxicity of many oil components[8]. The removal of oil and oil-derivative from wastewater by adsorption on solid sorbents is one feasible option to purify waters. To this aim we have prepared solid carbon-based sorbents by heat treatment of natural graphite and rice husk[1]. The aim of my internship at IRC-CNR was the characterization of these materials and the collection of preliminary data about their oil adsorption capacity.

1. MATERIALS AND METHODS

Sample preparation

Natural graphite (NG) of the Zavalievsky deposit of Ukraine has been used (Zavalievsky Graphite Ltd., Ukraine, Kiev). Natural flake graphite, grade GTO-92, consist of 92.8 wt.% in carbon. Rice husk (RH) has been recovered from a deposit of the filed Kyzylorda in Kazakhstan. EG has been produced at al-Farabi University of Kazakhstan by a heat treatment method (Fig. 1). This is a very simple method in which a mechanical mixture of natural graphite and crystalline zinc nitrate hydrate ($Zn(NO_3)_2$ x $6H_2O$) has been heated in air in a muffle furnace for 20 minutes at variable final temperature. The experimental conditions are listed in the Table 1.

Figure 1 - Scheme of the synthesis of the expanded graphite

Table 1 - Experimental conditions for expanded graphite synthesis

Samples labels	Percentage of components, wt. %		Final temperature, °C
EG350(80/20)	20% NG	80% $Zn(NO_3)_2$ x 6 H_2O	350
EG 400(80/20)	20% NG	80% $Zn(NO_3)_2$ x 6 H_2O	400
EG 600 (80/20)	20% NG	80% $Zn(NO_3)_2$ x 6 H_2O	600
EG 800(80/20)	20% NG	80% $Zn(NO_3)_2$ x 6 H_2O	800
EG 500(70/30)	30% NG	70% $Zn(NO_3)_2$ x 6 H_2O	500
EG 600 (70/30)	30% NG	70% $Zn(NO_3)_2$ x 6 H_2O	600
EG 1000(80/20)	20% NG	80% $FeCl_3$ x 6 H_2O	1000

The RH carbonization has been performed at the Institute of Combustion Problems in Kazakhstan. 15 g of RH were carbonized in a home-made reactor (Fig. 2) under argon atmosphere at different temperatures for 1 h (Table 2.).

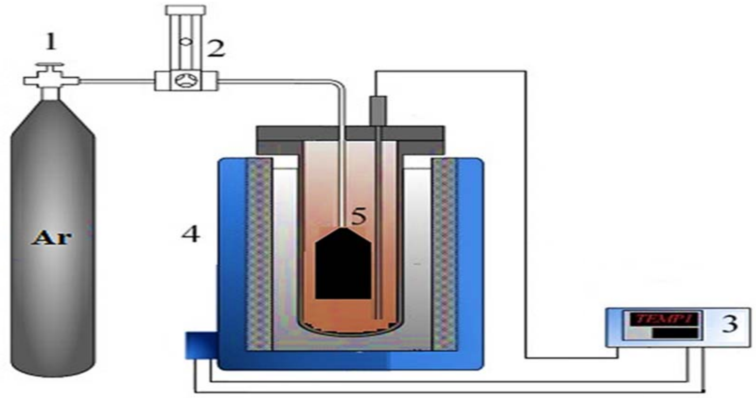

Figure 2 - Schematic diagram the RH carbonization setup. 1. argon cylinder, 2. mass flowmeter, 3. temperature controller, 4. carbonization rector, 5. iron crucible

Table 2 - Experimental condition for carbonized RH synthesis

Samples labels	Carbonization temperature, ^{0}C	Carbonization time, hour
CRH 600	600	1
CRH 700	700	1
CRH 800	800	1
CRH 900	900	1

Washing. The samples have been purified at the IRC-CNR of Naples. 0.3 g of EG 600(70/30) and CRH 600 have been stirred with 50 mL of distilled water for 30 minutes and filtered on a Millipore FHUP 0.45 μm filter membrane. The solid has been recovered and allowed to dry at 105 °C overnight[2,8].

Base leaching. Base leaching treatment was performed in order to remove Zn oxide impurities from the graphitic surface. This treatment was performed on the two EG samples obtained with 70:30 ratio at 500 and 600 °C. These samples have been selected since they exhibited the highest carbon content among the EG samples obtained by using zinc nitrate as activation agent. The base treatment was performed on 0.4 g of material by adding 50 mL of 5M sodium hydroxide (NaOH) solution under stirring at the temperature of 90 °C for 2 h. After cooling to room temperature, the solid was recovered by filtration and washed until neutrality (about 200 ml of water)[3,8].

2. RESULTS AND DISCUSSION

Oil adsorption test.

Oil adsorption tests have been performed accordingly to the procedure reported in [5]. To this aim small boxes with a capacity of ~2 mL have been prepared by using a stainless steel metal grid (~100 μm pore dimensions) (Fig.3a). Each box has been filled with 0.1 g of sample (sample granulometry above 300 μm) and dipped for 5 minutes in a 100 mL beaker containing 50 mL of water and 1 g of oil (Figs. 3 b,c). After the oil adsorption, the box was allowed dripping for 24 hours (Fig. 3d). After that time the box with the sample was dried at 60 °C overnight. In the oil absorption tests a commercial carbon black (CB N110 type) was also used for comparison[4,5].

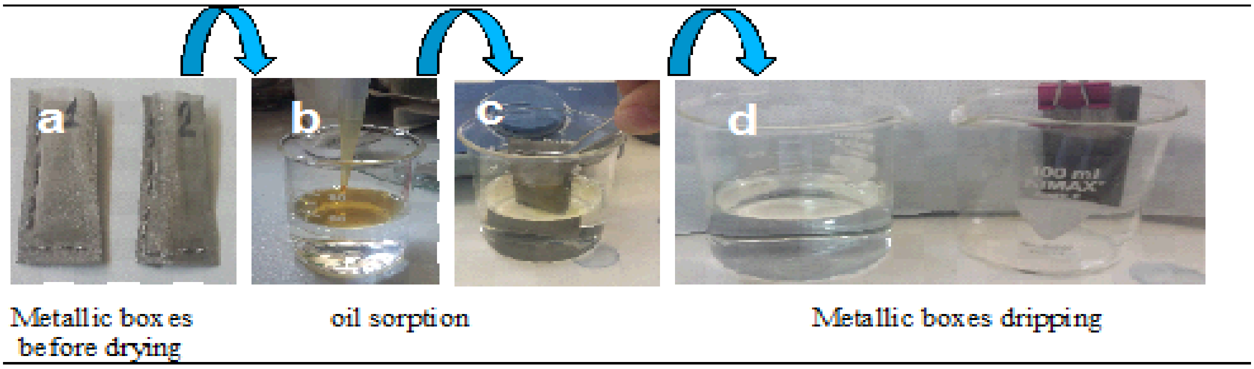

Figure 3 - Oil adsorption procedure

The oil sorption capacity was calculated as follows [7]:

Oil sorption capacity (g/g) = $(S_{st}-S_0)/S_0$

Where S_0 is the initial mass of the sorbent, $S_{st}$is the weight of the spent sorbent (sorbent containing adsorbed oil at the end of the sorption test).

The results of the washing process are reported in Table 3.

Table 3 - Washing results

Name of samples	Water, ml	Time of mix, min	Yield, %
EG600(70/30)	50	30	93.5
CRH 600	50	30	94.2

The results of ICPMS analyses of the liquids recovered after washings are reported in the table below (Table 4).

Table 4 - ICP-MS results (quantities are expressed in ppm)

sample	EG 600(70/30)	CRH600
Na	67.45	165.8
Mg	522.1	936.6
K	236.3	15830
Ca	707.5	1047
Mn	13.82	46.6
Fe	<10	<10
Co	<10	<10
Ni	<10	<10
Cu	<10	<10
Zn	1636	5.648
As	<10	<10
Sr	4.096	11.64
Zr	<10	<10
Mo	0.6923	0.6515
Cd	0.7217	0.6565
Ba	1.515	0.703

The results of base leaching are reported in Table 5. It is worth of note that after this purification step about 40% of material (inorganic matter) was removed.

Table 5 - base leaching results

Name of samples	NaOH, mL	Time of stirring, h	Yield, %
EG500 (70/30)	50	2	62.6
EG600(70/30)	50	2	61.0

2.1 Materials morphology

SEM images in **Fig.** 4 show the typical structure of NG and of EG sample obtained at temperature 350 ºC (EG350 (80/20)). As a result of thermal expansion graphite increases in volume due to the salts intercalation which leads to the formation of multilayer thermally expanded graphite.

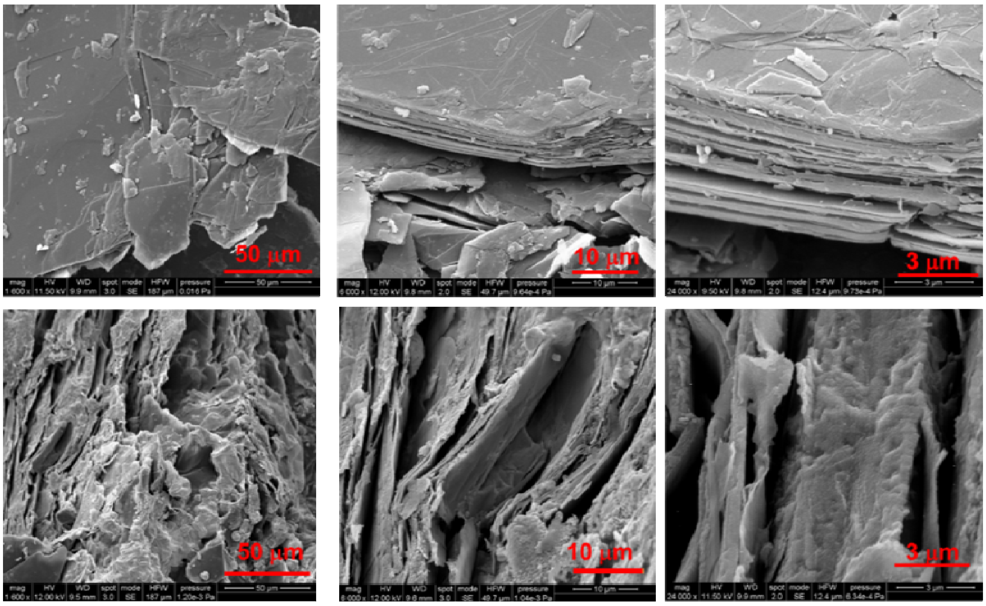

Figure 4 -SEM images of natural graphite (NG, upper row) and expanded graphite obtained at the temperature of 350 °C (lower row) at different magnifications

The SEM imaging revealed that inorganic matter is present in EG350(70/30) sample, probably zinc or iron oxides (Fig. 5).

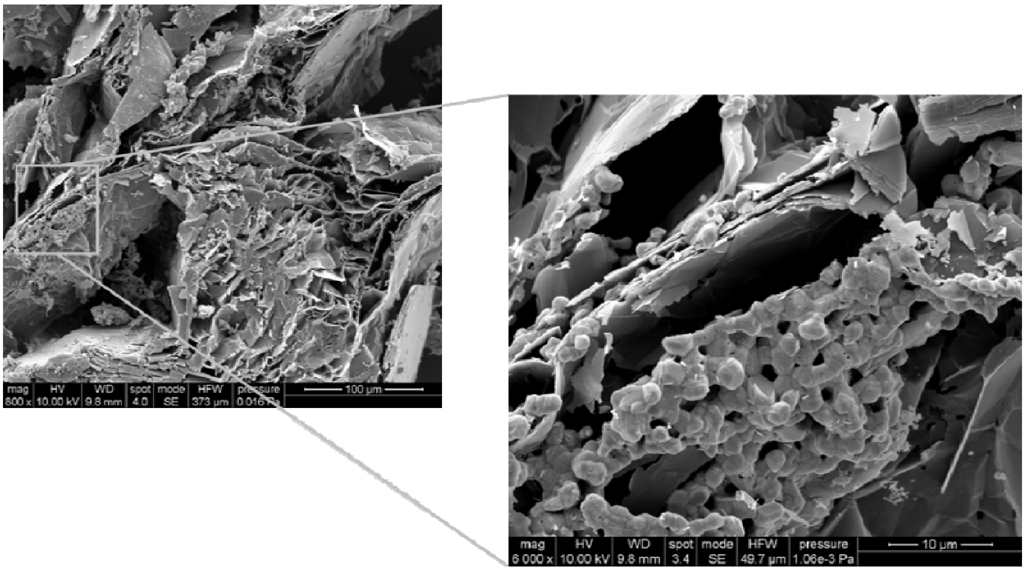

Figure 5 - SEM images of expanded graphite (EG350(70/30) before NaOH treatment

SEM imaging was also performed on the expanded graphite after base leaching. The samples appear overall more homogeneous (Fig. 6).

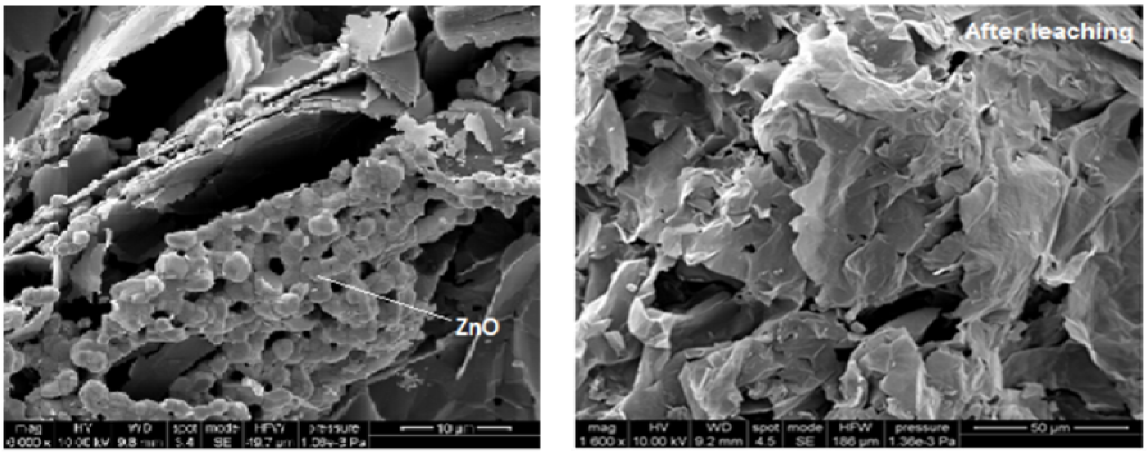

Figure 6 - SEM images of expanded graphite (EG350(70/30) before (left panel) and after (right panel) leaching by NaOH

SEM imaging on raw rice husk and carbonized rice husk at 600 °C (CRH600) are reported in figure 7.

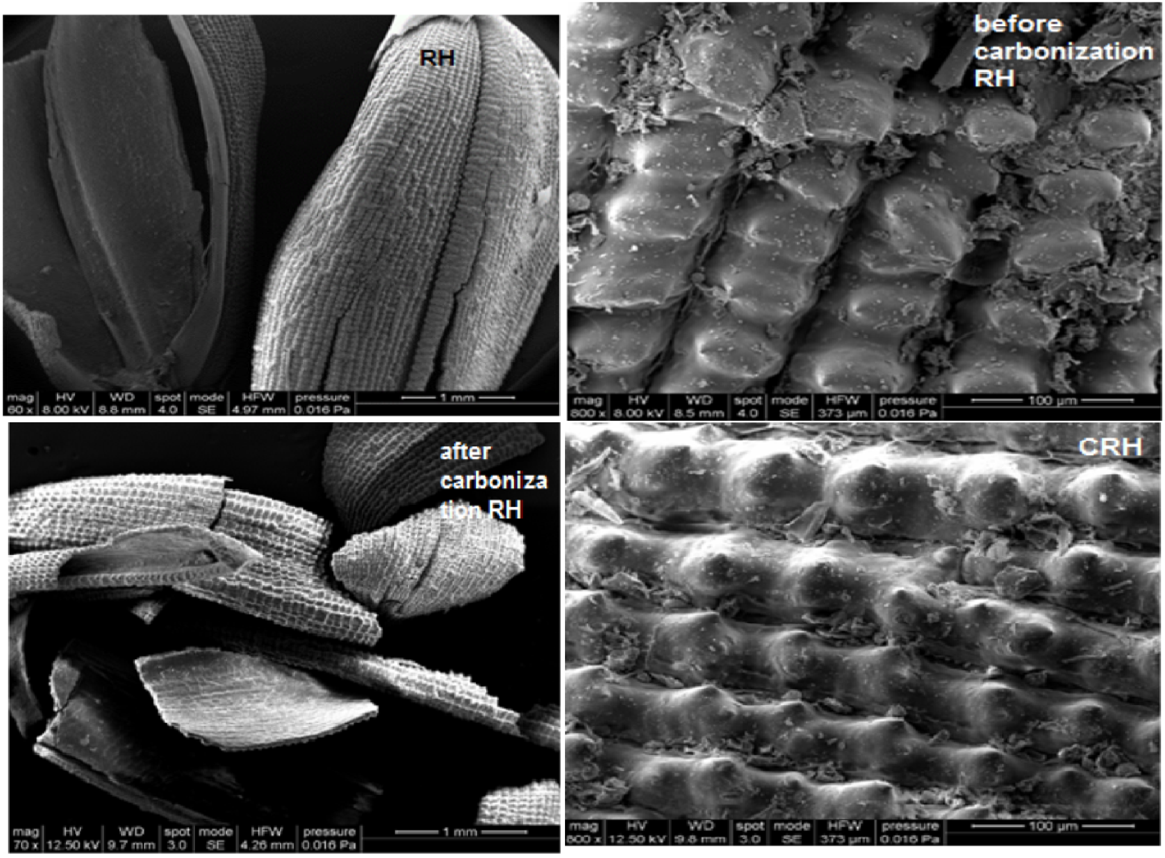

Figure 7 - SEM images Rice husk (RH) and carbonized Rice husk (CRH600) at different magnifications

Overall it can be observed that the carbonization process does not significantly alter the macroscopic morphology of the RH.

The results of oil sorption capacity are shown in Table 6 and Fig. 8.

Sorbent	S_{St}, Mass of the spent sorbent (sorbent+oil), g	S_0, mass of sorbent, g	Oil sorption capacity, g/g
NG	0.42	0.10	1.8
EG 500(70/30) before leaching	0.99	0.10	6.0
EG 500(70/30) after leaching	0.87	0.10	7.1
EG 600(70/30) before leaching	1.1	0.10	5.6
EG 600(70/30) after leaching	0.78	0.10	6.2
RH	0.35	0.10	1.2
CRH 600	0.73	0.10	3.1
CRH 700	0.67	0.10	3.3
CRH 800	0.69	0.10	3.7
CRH 900	0.66	0.10	3.2
CB	0.56	0.10	2.6

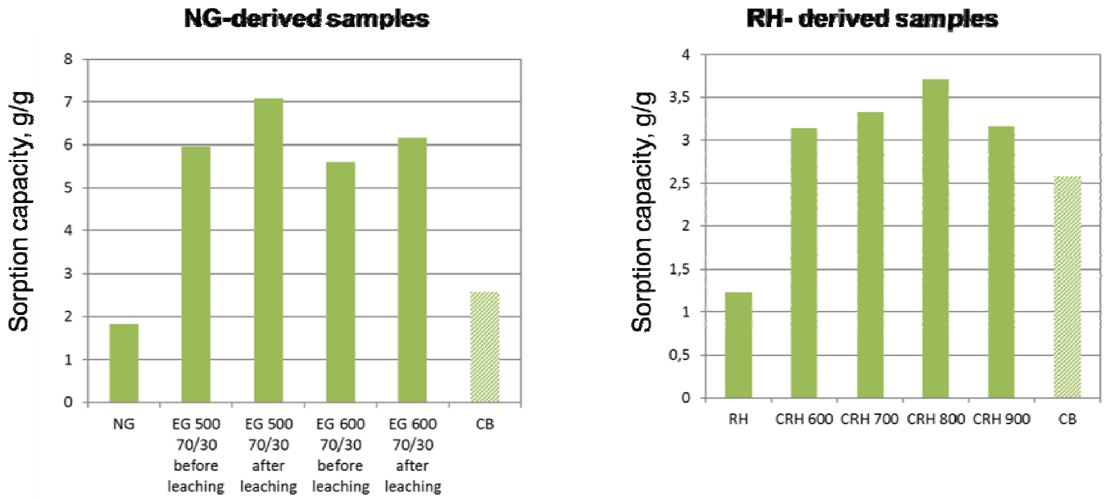

Figure 8.Comparison between NG-derived samples (left)
and RH – derived samples (right). CB is also reported for comparison.

The oil adsorption results indicated that EG samples after base leaching are the best adsorbents with an increase of 10-15 % compared to the not purified samples. It is noteworthy that as a general trend all the EG samples exhibit an adsorption capacity at least three-fold higher than NG.

As concerns as the CRH samples the adsorption capacities are similar and no particular variation with the activation temperature are detected. As a general result the carbonization process induced an increase of the adsorption capacities[6].

It is worth to note that the adsorption capacities estimated for the all heat-treated samples are quite higher compared to available literature data [7,8], as reported in Fig. 9 where oil absorption performances of acetic anhydride treated corncobs, an abundant biodegradable agricultural waste, are reported.

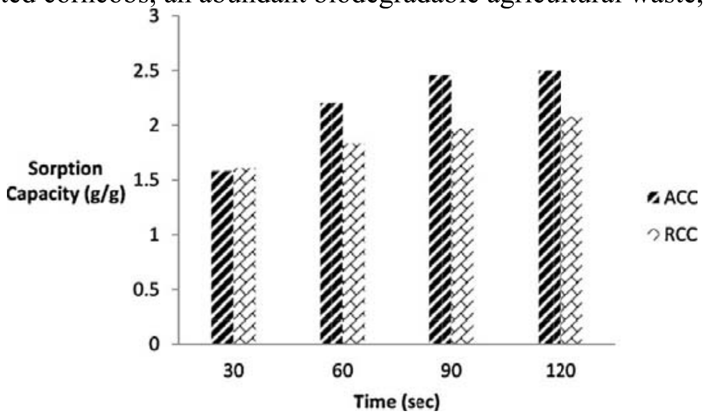

Figure 9 - Crude oil sorption capacity (g/g) of corncobs ad different sorption time

3.Conclusions

In this work expanded graphite (EG) and carbonized rice husk (CRH) were obtained by heat treatment at different temperatures and by using different activating conditions. Samples were purified and characterized by SEM-EDAX, FTIR, elemental analysis, Proximate analysis and ICP MS. The samples were tested as sorbent for oil in water.

EG samples after base leaching are the best oil sorbents with an increase of 10-15 % compared to the not purified samples. It is noteworthy that as a general trend all the EG samples exhibit an adsorption capacity at least three-fold higher than NG.

As concerns as the carbonized rice husk samples the adsorption capacities are similar and no particular variation with the activation temperature are detected. As a general result the carbonization process induced an increase of the adsorption capacities.

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СОРБЦИОННАЯ СПОСОБНОСТЬ МОДИФИЦИРОВАННЫХ НАНО-УГЛЕРОДНЫХ МАТЕРИАЛОВ

Аннотация. В этой работе расширенный графит (РГ) и карбонизированная рисовая шелуха (КРШ) были получены термической обработкой при различных температурах и с использованием различных условий активации. Образцы были испытаны в качестве сорбента для нефти в воде. Эффективность удаления масла из карбонизированной рисовой шелухи и вспененного графита изучалась в качестве адсорбента для удаления эмульгированных масел из сточных вод. Результаты показали, что эффективность удаления масла увеличилась до 10-15% в случае образцов РГ после основного выщелачивания. Что касается образцов карбонизированной рисовой шелухи, адсорбционные способности аналогичны, и никаких особых изменений в зависимости от температуры активации не обнаружено. Как общий результат, процесс карбонизации вызвал увеличение адсорбционной емкости. Образцы были очищены и охарактеризованы с помощью SEM-EDAX, FTIR, элементного анализа, проксимального анализа и ICP MS.

Ключевые слова:Карбонизованная рисовая шелуха, расширенный графит, масляные сточные воды, адсорбент, эффективность удаления масла.

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МОДИФИЦИРЛЕНГЕН НАНО-КӨМІРТЕКТІ МАТЕРИАЛДАРЫНЫҢ СОРБЦИЯЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Бұл жұмыста кеңейтілген графит (EG) және карбонизацияланған күріш қаузы (CRH) әр түрлі температурада термиялық өңдеу және әр түрлі белсендіру жағдайлары арқылы алынды. Сынамалар судағы мұай үшін сорбент ретінде сыналды. Карбонизацияланған күріш қаузы мен кеңейтілген графиттың сулардан эмульгирленген майларды алу үшін адсорбент ретінде зерттелді. Нәтижелер көрсеткендей, мұнай сіңірудің тиімділігі базалық шаймалаудан кейін КГ үлгілерінде 10-15% -ға дейін артты. Карбонизацияланған күріш қаузы үлгілерінде адсорбциялық ұқсастығы бар және белсендіру температурасы анықталған жоқ.

Жалпы нәтиже ретінде карбонизациялау процесі адсорбциялық мүмкіндіктерді арттырды. Үлгілер тазартылды және SEM-EDAX, FTIR, элементальды талдау, Шамамен талдау және ICP MS сипатталды.

Түйін сөздер: Карбонизделген күріш қаузы, кеңейтілген графит, су бетіндегі мұнай, адсорбент, эффективтілікті жою.

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REFERENCES

[1] S. Azat, Zh.Ye. Sartova, Z.A. Mansurov, R.L.D. Whitby Utilization of rice husk ash as an alternative source for the production silica nanoparticles//News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology 10 (422), 2017 P.38-44.

[2] A.L. Ahmad. S. Sumathi. B.H. Hameed Residual oil and suspended solid removal using natural adsorbents chitosan. bentonite and activated carbon: A comparative study. Chemical Engineering Journal 108 (2005) P.179-185.

[3] Khaled Okiel. Mona El-Sayed. Mohamed Y. El-Kady Treatment of oil-water emulsions by adsorption onto activated carbon. bentonite and deposited carbon. Egyptian Journal of Petroleum (2011) P.9-15.

[4] MdShahinoor Islam. Kerry N. McPhedran. Selamawit A. Messele. Yang Liu. Mohamed Gamal El-Din Isotherm and kinetic studies on adsorption of oil sands process-affected water organic compounds using granular activated carbon. Chemosphere 202 (2018) P.716-725.

[5] Abba Chetima. Abdoul Wahabou. Gaston Zomegni. AbdoulNtieche Rahman. Divine BupNde Bleaching of neutral cotton seed oil using organic activated carbon in a batch system: Kinetics and adsorption isotherms. MDPI journal (2018) P.6-22.

[6] Y. Zhao. C. Zhang. Pollution control and Resource Reuse for Alkaline Hydrometallurgy of Amphoteric metal hazardous wastes. (2017) P.405.

[7] J.O. Nwadiogbu. V.I.E.Ajiwe. P.A.C. Okoye Removal of crude oil from aqueous medium by sorption on hudrophobic corncobs: Equilibrium and kinetic studies // Journal of TaibahUnivesity for Science 10 (2016) P.56-63.

[8] M. A. Mukhamedzhanov, Jai Sagin, L. M. Kazanbaeva, I. K. Rakhmetov Influence ofanthropogenic factors On hydrogeochemical conditions Of underground drinking Waters of kazakhstan //News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences. Volume 3(429) 2018, P.6-11https://doi.org/10.32014/2018.2518-170X.1ISSN 2518-170X (Online), ISSN 2224-5278 (Print).

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THE USAGE OF VEGETABLE RAW MATERIALS IN THE PRODUCTION OF COTTAGE CHEESE PRODUCTS

Abstract. In the present work the technology of production of cottage cheese products based on the use of herbal supplements is considered. Fiber and stevia are used as products that increase the nutritional value of the product. The results of experimental studies show that the addition of plant components have a positive effect on the quality and nutritional value of the product.

Key words: cottage cheese, cottage cheese products, fiber, stevia.

Milk and dairy products are obligatory and irreplaceable food of the person. Kazakhstan is one of the twenty world consumers of milk and dairy products and is a large dairy market. The volume of consumption of milk and dairy products in natural terms in Kazakhstan annually increases by an average of 9% per year over the past five years [1].

In order to increase agricultural production with an emphasis on the most popular types of food and the development of exports of processed agricultural products, in the coming period it is necessary to provide maximum coverage of agricultural producers with state support by creating favorable conditions and infrastructure for the production of primary processing, storage and marketing of competitive products[2].

Also, Government of Kazakhstan has been done a larger work in developing strategic framework regarding safety of organic food, that are aiming to get an healthy and functional food products[3].

One of the leading ingredients among food processors, including dairy products, are dietary fibers. Diets that rich in dietary fiber have a positive impact on human health, as their consumption reduces the risk of cancer. The use of dietary fiber in the form of fiber and bran can enrich the product with insoluble dietary fiber, reduce the deficit of their consumption. The influence of vegetable additives on the properties and chemical composition of cottage cheese products was studied. According to the study, the protein content increased by 1.92% [4].

The state program of development of agro-industrial complex of the Republic of Kazakhstan for 2017 - 2021, in accordance with the strategic objectives of the development of Kazakhstan, outlined in the National Plan "100 concrete steps" and the Strategy "Kazakhstan-2050" will be aimed at ensuring the internal needs of the population by popular types of agricultural products, the definition of a targeted export policy.

According to statistics for 11 months of 2018, Kazakh companies have provided demand for milk and cream by 96.2%, against 94% in the same period a year earlier; for cheese and cottage cheese — by 56.5%.

There was a significant increase of exports of milk and cream: just 47.6% per year. Export of cheese and cottage cheese products also increased by 4.2% [5]. The dynamics of growth in demand for dairy products in the Republic of Kazakhstan is shown in figure 1.

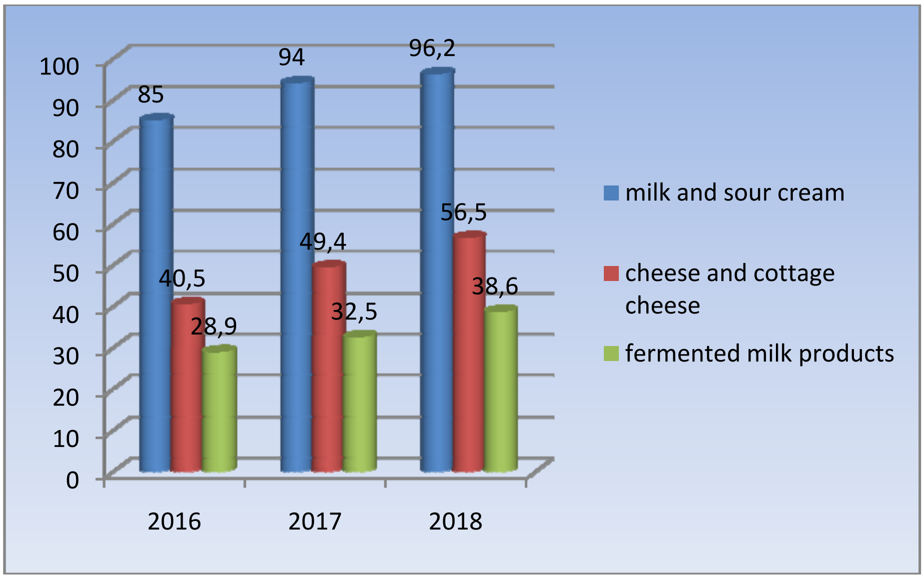

Figure 1 - Demand for dairy products

Cottage cheese production in Kazakhstan is concentrated mainly in the following regions: Almaty region: 26.7%, East Kazakhstan region (12.7%) and Almaty (11.7%).The data are shown in figure 2.

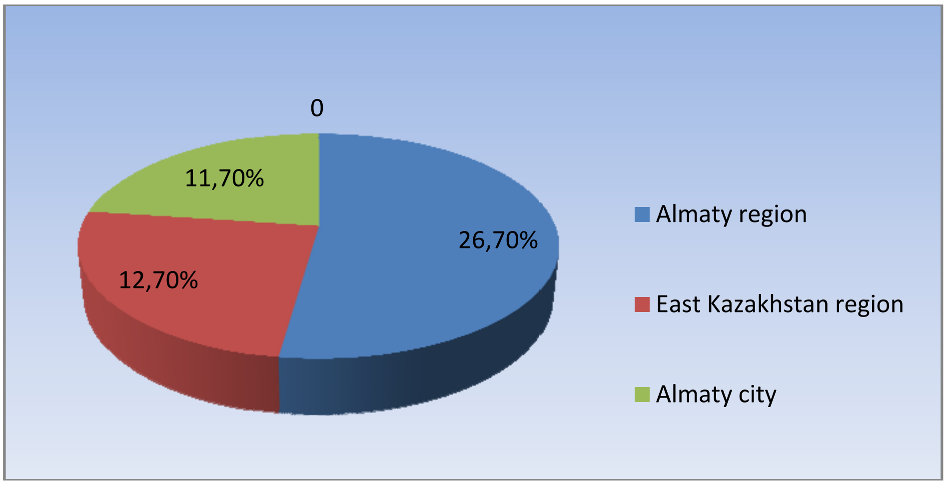

Figure 2 - Leaders of cheese and cottage cheese production

Among the producers of milk and cream Almaty region is also among the leaders: 113.7 thousand tons, production growth by 13% per year. In addition, North Kazakhstan (140,8 thousand tons, +20% for the year) and Kostanay (78,3 thousand tons, -1% for the year) regions entered the top three "dairy" regions.

As noted, at the end of 2017 Almaty region was the leader in the production of dairy products, but the data for 2018 in the regional context were not provided [6].

The current level of human nutrition is unsatisfactory both quantitatively and qualitatively. The qualitative aspect of nutrition is associated with a deficiency in the diet: a full protein, polyunsaturated fatty acids, vitamins, minerals, dietary fibers. In accordance with the changes in the structure of nutrition of the population and the existing protein deficiency, special attention is paid to the creation of new biologically valuable protein products, including dairy products.

Dairy products have long been considered one of the most popular foods in the diet of mankind. New products in this industry have a number of advantages and demand. The use of non-traditional methods in production will make it possible to save resources[7,8].

According to modern concepts of nutrition science, cottage cheese as a protein product is of great importance for a balanced diet of people. In this regard, the question of expanding the range of cottage cheese is relevant. In this regard, various fillers are added to the cottage cheese, which has a complex of taste, medical,dietary and nutritional properties. One of the promising directions of expanding the range is the production of various types of functional products based on milk with the addition of plant ingredients [9].

With the passage of circumstances and the modern rhythm of life, the factors depleting the human body has increased markedly. Therefore, the enrichment of cottage cheese products with vegetable additives, with higher nutritional properties and immuno-enhancing actions are an important factor. Biologically active additives are ingredients of non-dairy origin, but the development of current technology allows to enrich the composition of food by any methods.

Analysis of the market of protein foods shows increasing consumer interest in cottage cheese and cottage cheese products as the most affordable for all segments of the population.

The high nutritional value of cottage cheese is due to the increased content of amino acids important for the body, especially methionine, lysine. The high content of mineral substances in cottage cheese has a positive effect on the construction of tissues and bone formation[10].

Cottage cheese— fermented milk product obtained by fermentation of milk with subsequent removal of whey.

Cheese contains protein, minerals, lactose (milk sugar), fat, enzymes, vitamins a, D, C and b vitamins are Also in large quantity are calcium, iron, phosphorus. The vitamin composition of cottage cheese is shown in table 1.

Table 1– vitamin Content in cottage cheese.

Vitamins	Content in cottage cheese	Daily norms of vitamins	The percentage of content in 100 gr. cottage cheese from the daily rate (%)
Vitamin C (ascorbic acid)	0.5 mg	75 mg	0.66
Vitamin B1 (thiamine)	0.04 mg	2.25 mg	1.7
Vitamin B2 (riboflavin)	0.31 mg	2.50 mg	12.4
Vitamin B3 (PP, niacin)	3.17 mg	15 mg	21.1
Vitamin A (retinol)	0.08 mg	1 mg	8

Useful properties of cottage cheese are caused by its curative structure. Milk protein – casein, contained in cottage cheese, has a high nutritional value and can replace animal proteins.

Cottage cheese products enriched with cereals and berries, improve the activity of the gastrointestinal tract, normalize intestinal peristalsis. It regulates the functions of the nervous, digestive, cardiovascular and muscular systems [11]. For the effective solution of actual problems in the field of nutrition and health of residents of the Republic of Kazakhstan, the production of cottage cheese enriched with cereals is a promising direction.

In this aspect, the actual task is to develop the technology of cottage cheese products characterized by high levels of nutritional and biological value with a given composition and properties based on the addition of natural components of plant origin.

The developed technology of cottage cheese enriched with wheat bran is a source of fiber, essential macro-and microelements, b vitamins, vitamins E and A. Fiber is especially important for the good functioning of the intestine and the normal functioning of the digestive system as a whole[12].

Regular inclusion of fiber in the diet contributes to the maintenance of normal intestinal microflora, prevents the development or exacerbation of diabetes, significantly reduces the risk of cardiovascular disease, normalizes the functions of the liver and gallbladder, radionuclides and slags, is powerful prevention of cancer, in particular, colon cancer [13,14].

According to medical research, almost the entire population of the world suffers from fiber deficiency to one degree or another. In the average person uses from 5 to 15 g of fiber per day, while the body needs much more – about 40 g per day (for people with diabetes, - 50 g) with the energy value of the diet of 2500 kcal. It is this amount of dietary fiber that ensures the normal functioning of all organs and systems of the body [15]. Given that a significant part of the population prefers to consume cottage cheese with sugar, it is advisable to develop a cottage cheese with fiber and the addition of sugar substitutes.

The market for low-calorie sweeteners has developed very rapidly over the past 30 years, and there is no doubt that some developments in the field of food ingredients have recently been very important. The range, composition, and quality of foods that use sweeteners, especially in the dietary and low-calorie sector, have undergone significant changes in recent years [16,17]. Currently, manufacturers have the opportunity to offer a large part of the population food products that are fully consistent with or even superior to similar types of products made on sugar and have additional functional properties. One of such possibilities is the replacement of high-calorie sugars with low-calorie sweetening additives of plant origin – a natural sweetener from stevia [18,19,20].

It is necessary to note an important property of stevia – its high antioxidant activity [21].

The purpose of this study is to develop the technology of cottage cheese products of increased biological value. As plant additives, wheat fiber and a substitute for sugar of plant origin –stevia were used.

During the experimental study, standard methods of analysis were used:

- determination of acidity by titrimetric method;
- definition of protein by the method of formoltitration;
- determination of moisture cottage cheese and cottage cheese products by drying to constant weight;
- determination of lactose by refractometric method;
- determination of pH by potentiometric method;

In the proposed work as the main objects of the study were taken:

1) Normalized, pasteurized 3,2% fat whole milk, taken from the dairy plant of S.Seifullin university.
2) Cottage cheese, that was made in the dairy plantof S. Seifullin university.
3) Dry starter culture for cottage cheese.
4) Wheat fiber
4) Stevia leaves

Experimental studies were conducted on the basis of the laboratory and dairy plant of S. Seifullinuniversity, a pilot batch of finished products obtained in the production and experimental plantof S.Seifullin university.

For the analysis, 6 samples of cottage cheese were prepared: a control sample, samples with fiber and dry stevia leaves, samples with fiber and stevia extract in different ratios. Also, cottage cheese with the addition of fiber and stevia in a dry, crushed form during fermentation, and cottage cheese with the addition of fiber and stevia extract during fermentationwere studied. These options were excluded, since the acidity index in milk with the addition of stevia extract exceeded the norm, and in milk with the addition of dry stevia leaves, the taste of the resulting cottage cheese was not expressive, as in cottage cheese with the addition of stevia extract after fermentation [22].

To assess the organoleptic properties of the developed cottage cheese product, an organoleptic evaluation was carried out. According to the results of the tasting evaluation and the data of physical and chemical analyses, there was a sample (6) with fiber and stevia extract in a ratio of 1:3. Data of physical and chemical analyses are given in table 2.

Table 2 - Data of physical and chemical analysis of samples

Parameter	pH	Acidity, °T	Moisture, %	Mass fraction of lactose, %	Mass fraction of protein, %,
Control sample (C)	4,7	160	43,52	3,42	6,528
Version 2	4,6	160	23,86	3,36	6,528
Version 3	4,7	138	45,88	3,82	6,528
Version 4	5,0	140	28,66	3,72	8,448
Version 5	5,1	144	25,38	3,77	6,528
Version 6	5,1	150	20,2	3,70	8,546

These analyses show that the resulting cottage cheese product meets the standards. The data of organoleptic evaluation are given in table 3.

Table 3 – Organoleptic characteristics of cottage cheese products with vegetable additives

Parameter	Consistency	Taste and aroma	Color
Pure cottage cheese	Soft, crumbly	Pure	White
Cottage cheese with fiber and stevia	Soft, crumbly	Pure, slightlysweet	White with brown grains of fiber

On the basis of theoretical and experimental studies, an optimal way to improve the quality of traditional cottage cheese was developed, which allows to increase the shelf life of cottage cheese, increase its biological value and increase the amount of cottage cheese from a unit of raw materials.

The improved technology of cottage cheese, which allows increasing the biological value of the product by including in the structure of cottage cheese biologically active components such as fiber and stevia.

Taking into account the results of the research, the new cottage cheeseproduct can be recommended as dietary and therapeutic and preventive nutrition to the General population.

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ӨСІМДІК ШИКІЗАТЫН СҮЗБЕ ӨНІМДЕРІН ӨНДІРУДЕ ПАЙДАЛАНУ.

Аннотация. Осы жұмыста өсімдік қоспаларын қолдануға негізделген ірімшік өнімдерін өндіру технологиясы қарастырылады. Өнімнің тағамдық құндылығын арттыратын зат ретінде жасұнық пен стевия пайдаланылады. Эксперименттік зерттеулердің нәтижелері өсімдік компоненттерінің қосылуы өнімнің сапасы мен тағамдық құндылығына оң әсерін тигізетіндігін көрсетеді.

Түйін сөздер: ірімшік, ірімшік өнімдері, жасұнық, стевия.

УДК637.146.32:664.76 (043.3)

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ИСПОЛЬЗОВАНИЕ РАСТИТЕЛЬНОГО СЫРЬЯ В ПРОИЗВОДСТВЕ ТВОРОЖНЫХ ИЗДЕЛИЙ

Аннотация. В представленной работе рассматривается технология производства творожных изделий на основе применения растительных добавок. В качестве продуктов, повышающих пищевую ценность продукта используются клетчатка и стевия. Результаты экспериментальных исследований показывают, что добавление растительных компонентов оказывают положительное влияние на качество и пищевую ценность продукта.

Ключевые слова: творог, творожные изделия, клетчатка, стевия.

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REFERENCE

[1] Gosudarstvennai aprogramma razvitiia agropromyshlennogo kompleksa Respubliki Kazakhstanna 2017-2021 gody. Astana, 2017 (InRussian).

[2] Korneva, ER, Butina EO, Gerasimenko VV, Kuznetsova ON(2011) New technologies [Novyetekhnologii] 2:26-30.

[3] G.O. Kantureeva, E. Defrancesco, R.S. Alibekov, K.A. Urazbayeva, I.E. Efimova (2018) New trends in the identification of the traditional food products of Kazakhstan. News of the academy of sciences of the Republic of Kazakhstan. Series chemistry and technology. Volume 5, number 431(2018), PP.6-12. https://doi.org/10.32014/2018.2518-1491.1 ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

[4] DautkhankyzyZhD, Tomashinova SM (2018) X international student scientific conference “Student scientific forum” [Xmezhdunarodnaiastudencheskaianauchnaiakonferentsiia «Studencheskiinauchnyi forum»]

[5] ApsaliamovN(2018) Transiteconomy [Tranzitnaiaekonomika] 5 (44):248.

[6] Kharitonov VA, Zobkova ZS, Shove ZhV(1995) Dairy industry [Molochnaiapromyshlennost'] 3:7-8.

[7] Kol'iashkin MA, PolushkinaNN (2009) 254

[8] Ospanov A, Zhakupova G, Toxanbayeva B (2018) International Journal of Engineering & Technology, 7 (3.19):200-205

[9] Spirechev VB, Shatniuk LN (2000) Food industry [Pishchevaiapromyshlennost'] 7.

[10] Mel'nikova EI, Skryl'nikova ES, Rudnichenko ES(2012) Proceedings of the universities [Izvestiiavuzov] 4:52

[11] Ipatova LG(2007) Food industry [Pishchevaiapromyshlennost'] 5:425

[12] Van Mourik SV(2015) Food industry [Pishchevaiapromyshlennost'] 5:48-50

[13] Maiorov AA, BuzoverovSIu,Surai NM (2016)Equipment and technology of food production [Tekhnikaitekhnologiiapishchevykhproizvodstv]2: 222

[14] Zobkova ZS, Shcherbakova SA (2006)Dairy industry [Molochnaiapromyshlennost'] 7:47-49

[15] ZankievaBG, TsugkievaVB, TsugkievBG (2010) 12:32-34.

[16] PodporinovaGK, VerzilinaND, Rudakova, LV (2005) Food industry[Pishchevaiapromyshlennost'].9:97.

[17] Lukashevich VM(1979) Theoretical basis of chemical technology [Teoreticheskieosnovykhimicheskoitekhnologii] 6:839-845.

[18] Podporinova GK, Verzilina ND(2005) Food industry[Pishchevaiapromyshlennost'] 7:68.

[19] Pavlova GN, ErashovaLD, ArtiukhLV, ErmolenkoRS (2005) Food industry[Pishchevaiapromyshlennost']5:59.

[20] MerzlikinaAA, Podporinova GK, PolianskiiKK(2006) Food industry[Pishchevaiapromyshlennost'] 11:24-25.

[21] Polianskii KK (2005)Food industry [Pishchevaiapromyshlennost']5:58.

[22] Russkikh VM (2006) Food industry [Molochnaiapromyshlennost']5:.63-64.

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DISSOLUTION BEHAVIOR OF BRASS POLARIZED BY ALTERNATING CURRENT IN SODIUM PHOSPHATE AQUEOUS SOLUTION

Abstract. The electrochemical behavior of Cu-Zn alloy (brass) polarized with industrial - frequency alternating current has been studied for the first time in aqueous sodium phosphate solution. The effects of current density in brass (200-1200 A/m^2) and titanium (20-120 kA/m^2) electrodes, sodium phosphate solution concentration (0,5-2,0 M), alternating current (AC) frequency (30-180 Hz) and electrolysis duration (0,25-1,5 h) on the alloy dissolution current efficiency were considered.

Intensive brass dissolution by forming copper (II) and zinc (II) ions during the electrolysis in alternating current mode was shown for the first time. In the case of direct current (DC) electrolysis, the current output value of alloy electrochemical dissolution was very low. As the current density of the alternating current polarized brass electrode was increased, the current output rate of the alloy dissolution increased initially and decreased to 400 A/m^2, where (400 A/m^2) alternating current value comprised 80% in an optimal condition. When the titanium electrode current density was increased, the brass dissolution current efficiency showed a maximum value; the current output of Cu (II) and Zn (II) ions formation at current 60 кA/m^2 density was 50% and 30%, respectively. As the electrolysis duration and the AC frequency are increased, the brass electrode current efficiency is reduced.

On the basis of obtained results, the potential of copper and zinc phosphate synthesis was shown.

Key words: brass, alternating current, electrolysis, sodium phosphate, titanium electrode.

At present, the use of alternating current in studying alloy electrochemical properties and in the synthesis of its important compounds is of great interest. Electrochemical processes are used to solve various topical issues in the field of production. Rather than direct current, alternating current allows to create simple, yet rational technological processes [1].

Alloys electrochemical dissolution is a very complicated process. An alloy of copper with zinc is called brass; by composition they may be red brass (containing less than 20% zinc), yellow brass (20-50% zinc), white brass (50-80% zinc) and special brass (containing lead, nickel manganese, iron, silicon, beryllium, etc. alongside with copper and zinc). The alloy electrochemical dissolution depends on dimensional ratio of its components and nature of the solution [2]. The more copper-based alloys are used, the more their residuals size in the environment increases as well. Digestion of metals from solid alloy wastes is an important source of production, since it reduces load on the environment [3, 4]. Subsequently, the demand for copper alloys, especially for brass (C38500) is great due to the development of automobile industry and the construction industry. Therefore, a thorough study of copper alloy properties is one of the main tasks today [5].

In this regard, it is important to develop different methods of processing solid alloy residuals on the basis of copper and zinc.

As the copper contains Cu 87%, Zn 13.67% and other impurities 0.33%, the brass electrochemical dissolution is similar to the copper electrochemical dissolution properties. Therefore, the copper electrochemical properties can be applied to the Cu-Zn alloy [2].

A.B. Bayeshov and et al. developed a method of obtaining copper (II) sulfate by the industrial alternating current polarization [6]; while the method of obtaining copper (I) chloride and copper bromide, inorganic copper and zinc compounds was developed by A.S. Kadirbayeva and R.N. Nurdillayeva [7-9].

With a view of obtaining copper salts, the electrochemical properties of copper were studied in sodium carbonate, sulfuric acid, potassium iodide, potassium bromide, and sodium sulfate, neutral and acidic media [10-15].

Corrosive [16-17] and electrochemical [18-21] properties of brass in aqueous solutions have been studied in a number of works. The electrochemical dissolution of brass was investigated by potentiodynamic polarization and cyclic voltammetry methods with and without the presence of Cl^- ions in $NaHSO_3$ solution. The results of this work indicated that brass dissolution was accelerated by increasing HSO_3^- concentration [18]. The electrochemical properties and passivation of Cu-30Zn alloy in the alkaline medium have been considered, increasing the NaOH concentration on the potentiodynamic curves basis has led to an increase in corrosion current density [19]. In the following study, the electrodisolution brass (60.8Cu-36.3Zn-2.9Pb) and pure copper were comparatively studied in 0.1 M HCl using cyclic voltammetry and a rotating ring-disc electrode and similarity of dissolution mechanism of copper and pure copper in the brass composition was discovered [20]. The electrochemical properties of α, β'-brass ($CuZn_{40}Pb_2$) were investigated at different pH values in basic nitrate solutions. The study indicated that the extent of the dezincification was affected by presence of Pb in the alloy but the pH value was determined to be a key parameter [21].

Literature data show that brass electrode electrochemical properties in aqueous sodium phosphate solution have not been investigated.

Results and discussion

In the present work, the brass electrode electrochemical properties were studied in aqueous sodium phosphate solution polarized with industrial-frequency alternating current. Due to the slow electrochemical reactions in the polarization of the brass electrode by direct current, an alternating current was used in our study. The achievement of using alternating current during the electrolysis was noted by the authors of [22] work.

During the alternating current polarization, the electrochemical dissolution of Cu-Zn alloy in the sodium phosphate aqueous solution was investigated at the range of 200 to 1200 A/m^2 (Fig. 1). When the current density is increased up to 400 A/m^2, the current efficiency in Cu (II), Zn (II) ions formation and brass dissolution gradually increases. When the current density increased up to 1200 A/m^2, the decrease in the alloy dissolution current output occurred. This can be explained by the increase in the additional reactions rate due to the current density increase.

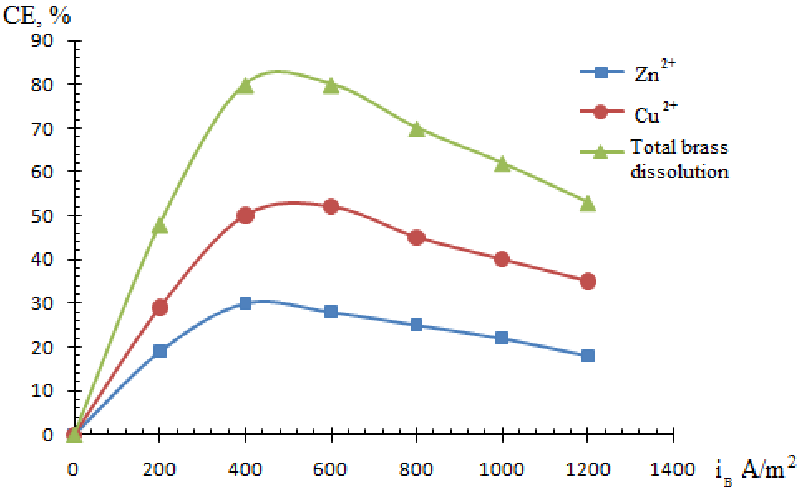

Figure 1 - The effect of the brass electrode current density on the current efficiency of the AC polarized Cu-Zn alloy dissolution: i_{Ti}=60 kA/m^2, [Na_3PO_4]=1.0 M, τ=0.5 h.

The effect of the additional titanium electrode current density on the electrochemical dissolution of the brass electrode polarized with alternating current in a neutral medium was investigated (Figure 2). An increase in the current efficiency rate of Cu (II) ions formation and the total brass dissolution by increasing the current density of titanium electrods from 20 kA/m^2 to 60 kA/m^2 can be explained by an occurrence of an oxide layer with a valve property on the titanium electrode surface in the anodic half-period. Further increase in the titanium electrode current density has led to a reduction in the current output. This is because the oxide layer surface structure in the titanium electrode changes due to the current density increase and its current correction property decreases.

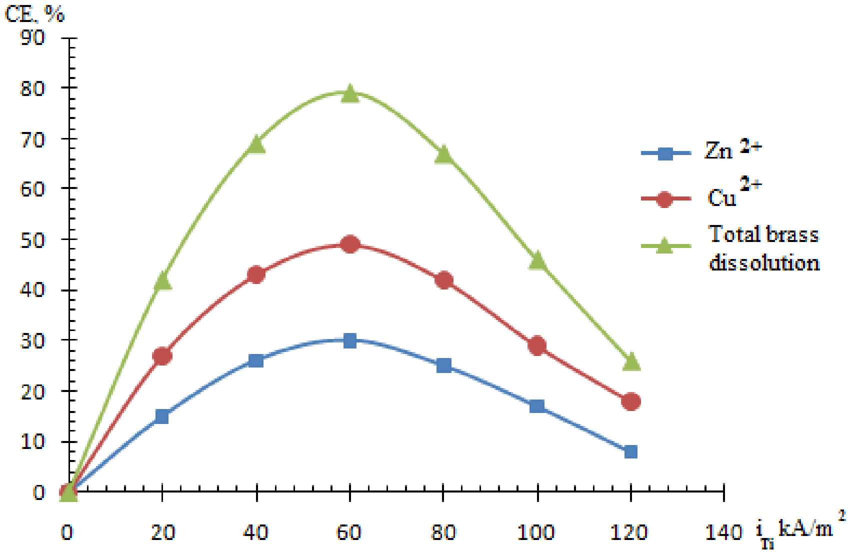

Figure 2 - Effect of titanium electrode current density on the current efficiency of the brass electrode dissolution polarized with alternating current: i_B=400 A/m^2, [Na_3PO_4]=1.0 M, τ=0.5h.

The effect of sodium phosphate solution concentration on the current efficiency of brass electrode dissolution polarized with alternating current was studied in a range 0.25 and 1.5 M (Fig. 3). As the sodium phosphate concentration increases, the current output of the brass electrode dissolution increases, but it decreases from 1.0 M. The reason is that as the electrolyte concentration increases, the brass electrode surface area is covered with saline coating and the brass electrode passivation takes place.

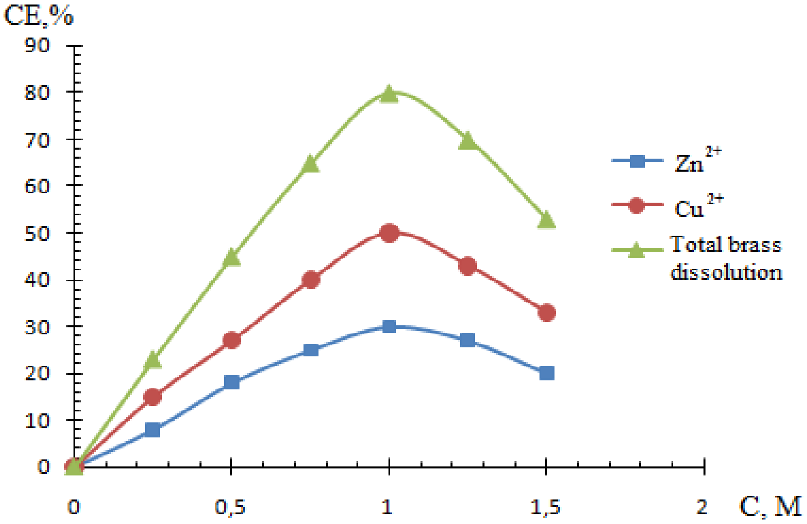

Figure 3 - Effect of sodium phosphate concentration on the current efficiency of brass electrode dissolution polarized with alternating current: i_{Ti} = 60 kA/m^2, i_B = 400 A/ m^2, τ = 0.5h.

The current efficiency decrease of copper, zinc ions formation and brass electrode dissolution due to the alternating current frequency increase can be observed in Figure 4. It can be assumed that the required time for the occurrence of the alloy oxidation reaction by forming copper and zinc ions can not be provided due to the rapid periods changes at high current frequencies.

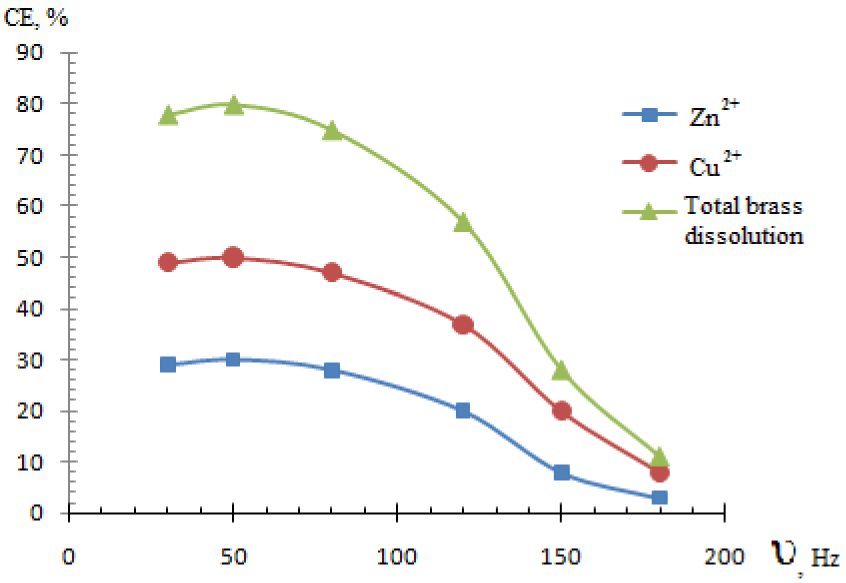

Figure 4 - AC frequencies effect on the current efficiency of brass electrode dissolution polarized with alternating current: i_{Ti}=60 kA/ m^2, i_B=400 A/m^2, [Na_3PO_4]=1.0 M, τ=0.5 h.

Figure 5 shows the electrolysis duration effect on the brass electrode current current efficiency. As the, electrolysis duration increases, the brass electrode current output decreases. As the electrolysis duration increases, electrodes electrolysis products begin to passivate with poorly soluble copper and zinc products. It is explained by the formation of blue saline coat on the electrode surface.

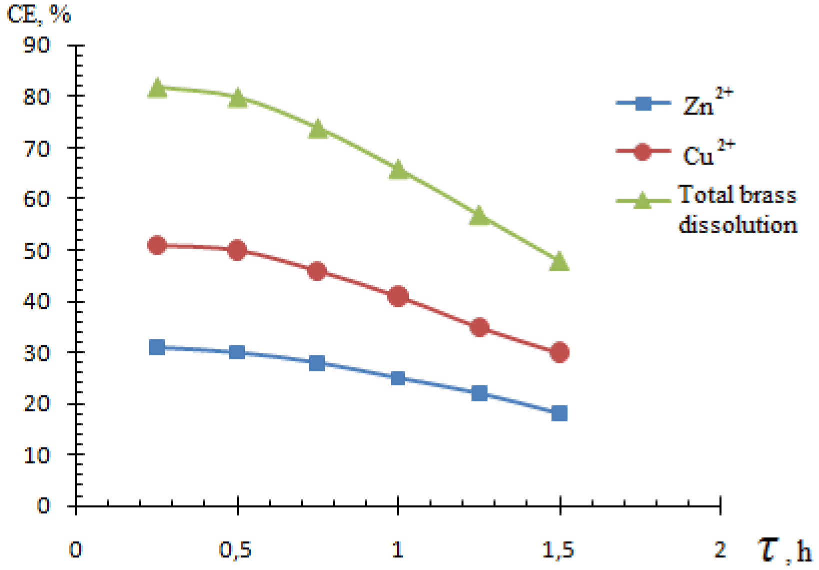

Figure 5 - The electrolysis duration effect on the current efficiency of brass electrode dissolution polarized with alternating current: i_{Ti}=60 A/ m^2, i_B=400 A/m^2, [Na_3PO_4]=1.0 M

Figure 6 shows the solution temperature effect on the brass electrode current efficiency. In our study, a decrease in current efficiency value of Cu (II) ions formation beginning from 30 °C was observed due to the increase in electrolyte temperature and the linear increase in the current efficiency value of Zn (II) ions formation took place. As the solution temperature increases, zinc chemically interacts with the hydrogen ions and thereby its ionization potential is facilitated. The total current output of the alloy dissolution increased up to 40 °C and slowed down at higher temperatures.

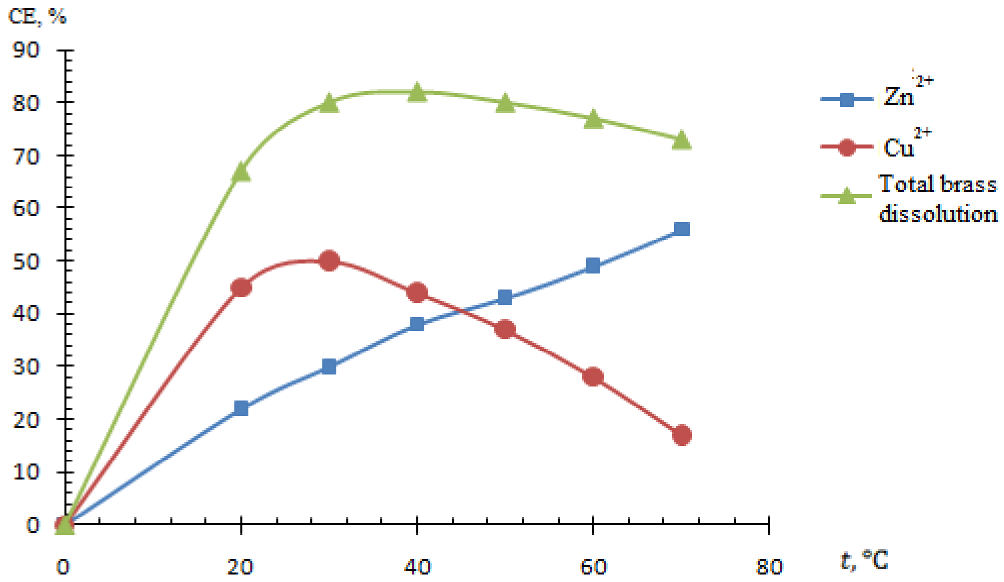

Figure 6 - The electrolyte temperature effect on the current efficiency of brass electrode dissolution polarized alternating current: i_{Ti}=60 A/m^2, i_B=400 A/m^2, [Na_3PO_4]=1.0 M, τ=0.5 h.

Summing up, the electrochemical dissolution laws of the brass electrode polarized with alternating current in a neutral medium - sodium phosphate aqueous solution have been systematically studied for the first time. The study results showed that the electrochemical process was intensified when replacing one of the two brass electrodes into the titanium wire. The basic electrochemical parameters effect on the brass electrode dissolution by forming copper and zinc ions in (Na_3PO_4) sodium phosphate solution were investigated and the effective alloy dissolution conditions were considered: (i_B=400 A/m^2, i_{Ti}=60 kA/m^2, [Na_3PO_4]=1.0 M, ν=50 Hz, t=30°C).

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АЙНЫМАЛЫ ТОКПЕН ПОЛЯРИЗАЦИЯЛАНҒАН ЖЕЗДІҢ НАТРИЙ ФОСФАТЫ СУЛЫ ЕРІТІНДІСІНДЕГІ ЕРУ ЗАҢДЫЛЫҚТАРЫ

Аннотация. Өндірістік жиіліктегі айнымалы токпен поляризацияланған Cu-Zn құймасы - жездің электрохимиялық қасиеті натрий фосфаты сулы ерітіндісінде алғаш рет зерттелді. Құйма еруінің ток бойынша шығымына (ТШ) жез (200-1200 А/м^2) және титан (20-120 кА/м^2) электродтарындағы ток тығыздықтарының, натрий фосфаты ерітіндісі концентрациясының (0,5-2,0 М), айнымалы ток жиілігінің (30-180 Гц), электролиз ұзақтығының (0,25-1,5 сағ.) әсерлері қарастырылды.

Айнымалы ток режиміндегі электролиз кезінде жездің мыс (II) және мырыш (II) иондарын түзе қарқынды еритіндігі алғаш рет көрсетілді. Ал, тұрақты ток электролиз барысында құйманың электрохимиялық еруінің ТШ мәні өте төмен болды. Айнымалы токпен поляризацияланған жез электродындағы ток тығыздығын жоғарылатқан сайын құйма еруінің ток бойынша шығымы алғашында жоғарылап, 400 А/м^2-бастап біркелкі төмендеп, оңтайлы жағдайда (400 А/м^2) ТШ мәні 80% құрады. Титан электродындағы ток тығыздығын арттырғанда құйма еруінің ТШ максимум арқылы өтіп, ток тығыздығы 60 кА/м^2 кезінде Cu (II) және Zn (II) иондары түзілуінің ТШ сәйкесінше 50% және 30% құрады. Жез еруінің ток бойынша шығымы 1,0 М натрий фосфаты ерітіндісінде максималды мәнді көрсетті. Электролиз ұзақтығы мен айнымалы ток жиілігін арттырған сайын жез электродының ток бойынша шығымы төмендейтіндігі анықталды.

Алынған нәтижелердің негізінде мыс және мырыш фосфатын синтездеудің мүмкіншіліктері көрсетілді.

Түйін сөздер: жез, айнымалы ток, электролиз, натрий фосфаты, титан электроды.

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ЗАКОНОМЕРНОСТИ РАСТВОРЕНИЯ ЛАТУНИ В ВОДНОМ РАСТВОРЕ ФОСФАТА НАТРИЯ ПРИ ПОЛЯРИЗАЦИИ ПЕРЕМЕННЫМ ТОКОМ

Аннотация. Впервые исследовано электрохимическое поведение сплава Cu-Zn - латуни при поляризации переменным током промышленной частоты в водном растворе фосфата натрия. Рассмотрено влияние плотности тока на латунном электроде (200-1200 А/м^2) и титановом электроде (20-120 кА/м^2), концентрации раствора фосфата натрия (0,5-2,0 М), частоты переменного тока (30-150 Гц) и продолжительности электролиза (0,25-1,5 час) на выход по току (ВТ) растворения сплава.

Впервые показано, что при переменнотоковом режиме электролиза происходит интенсивное растворение сплава с образованием ионов меди (II) и цинка (II). При электролизе с постоянным током значение ВТ электрохимического растворения сплава было значительно ниже. При повышении плотности тока на латунном электроде, поляризованном переменным током, выход по току растворения сплава плавно снижается и при оптимальных условиях (400 А/м^2) значение ВТ составило 80%. При изменении плотности тока на титановом электроде ВТ растворения сплава проходит через максимум и ВТ образования ионов Cu (II) и Zn (II) составляет, соответственно, 50% и 30% при плотности тока 60 кА/м^2.

Максимальное значение ВТ растворения латуни наблюдалось при 1,0 М концентрации раствора фосфата натрия. Установлено, что при увеличении продолжительности электролиза и частоты переменного тока значение ВТ латуни снижается.

На основе полученных результатов была показана вожможность синтеза фосфатов меди и цинка.

Ключевые слова: латунь, переменный ток, электролиз, фосфат натрия, титановый электрод.

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REFERENCES

[1] Bayeshov A.B., Bayeshova A.K., Bayeshova C.A. **(2014)** Electrochemistry (theory and practice). [Electrokhimiya (teoriyasi men koldaniui)]. Almaty: Kazakh university. - P. 316. ISBN 978-601-04-0671-1. (In Kazakh)

[2] Nurdillayeva R.N., Bayeshov A.B. **(2007)** Electrochemical dissolution kinetics and mechanism in copper sodium chloride solution [Zhezdin natrij hloridi eritindisindegi jelektrohimijalyk eru kinetikasy men mehanizmi]. NEWS of the Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology, Volume 5, №365. – P. 77-80. (In Kazakh)

[3] Bayeshov A.B., Bayeshova A.K. **(2012)** Electrochemical methods for the production of inorganic substances [Elektrohimicheskie sposoby poluchenija neorganicheskih veshhestv]. Germanija, Lambert, Academic Publishing. P. 72. ISBN 978-3-659-26096-4. (In Russian)

[4] James Evans, Lutgard De Jonghe. **(2016)** The Production and Processing of Inorganic Materials. Springer Nature, TMS.– P. 551. ISBN 978-3-319-48163-0. (In Eng)

[5] Sujit K.J., Devibala B., Rajalingam P. **(2015)** Experimental analysis of microstructure and mechanical properties of coper and brass based alloys. International Journal of Automotive and Mechanical Engineering (IJAME). ISSN 2229-8649 (Print); ISSN 2180-1606 (Online); Volume 11, P. 2317-2331. (In Eng)

[6] Bayeshov A.B., Kadirbayeva A.S., Bayeshova A.K., Zhurinov M.Zh. **(2014)** Acquisition of copper (II) sulphate and chloride by the polarization of the production variable current. [Ondiristik ajnymaly tokpen poljarizacijalau arqyly mys (II) sul'fatyn zhane hloridin alu.] ISSN 2224-5227.- Reports of the National Academy of Sciences of the Republic of Kazakhstan. №4, - P.24-28 (In Kazakh)

[7] Kadirbayeva A.S., Nurdillayeva R.N. **(2011)** Acid copper (I) chloride by polarization of AC in hydrochloric acid solution [Tuz qyshqyly eritindisinde ajnymaly tokpen poljarizacijalau arqyly mys (I) hloridin alu.] Bulletin of university Akhmet Yassawi., Series Chemistry and Technology, - P.103-108 (In Kazakh)

[8] Nurdillayeva R.N., Bayeshov A.B., Serik G.S. **(2018)** The elaboration of copper bromide synthesis by electrochemical method. Bulletin of NAS RK. Volume 1, № 371, -P.73-80. ISSN 1991-3494. (In Eng)

[9] Nurdillayeva R.N., Bayeshov A.B., Serik G.S., Bayeshova A.K. **(2018)** Production of copper bromide at polarization by an alternating current. News of the National Academy of Sciences of the RK, Series Chemistry and Technology, Volume 2, №428. P. 36-43. ISSN 2518-1491 (Online), ISSN 2224-5286 (Print). (In Eng)

[10] Bayeshov A., Baiseitova A.A. **(2005)** The study of the processes of electrochemical dissolution of copper in a solution of sodium carbonate with polarization by alternating current [Izuchenie processov jelektrohimicheskogo rastvorenija medi v rastvore karbonate natrija pri poljarizacii peremennym tokom]. Reports of the National Academy of Sciences of the Republic of Kazakhstan. №4. -P.73 (In Russian)

[11] Bayeshov A.B., Kadirbayeva A.S., Jurinov M.J. **(2014)** Dissolution of a copper electrode in sulfuric Acid at polarization by an industrial Alternating current. Int. J. Chem. Sci. Vol. 12, №3. - P. 1009-1014. ISSN 0972-768X. (In Eng)

[12] Bayeshov A.B., Kadirbayeva A.S., Bayeshova A.K., Adaybekova A.A. **(2015)** Investigation of the electrochemical properties of copper electrode in potassium iodide solution by drawing potentiodynamic polarization curves [Kalij iodidi eritindisindegi mys jelektrodynyng jelektrohimijalyq кasietin potenciodinamikalyq poljarizacijalyq qisyqtar tүsiru arqyly zertteu] NEWS of the Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. –№2. - P. 85-90. ISSN 2224-5227. (In Kazakh)

[13] Bayeshova A.K., Kadirbayeva A.S., Bayeshov A.B. Adaybekova A.A. **(2015)** Electrochemical properties of copper in aqueous potassium bromide solution [Mystyng suly kalij bromidi eritindisindegi jelektrohimijalyq qasieti]. Reports of the National Academy of Sciences of the Republic of Kazakhstan. №2. -P. 46-52. ISSN 1991-3494. (In Kazakh)

[14] Bayeshov A.B., Kadirbayeva A.S., Bayeshova A.K. **(2015)** Electrochemical properties of the polarized copper electrode in sodium sulphate solution of industrial variable current [Ondiristik ajnymaly tokpen poljarizacijalangan mys jelektrodynyng natrij sul'faty eritindisindegi elektrohimijalyq qasietteri]. Proceedings of the VII International Scientific and Practical Conference on innovative development of oil and gas industry Almaty, –P. 409-413 (In Kazakh).

[15] Bayeshov A.B., Kadirbayeva A.S., Bayeshova A.K **(2015)** Electrochemical properties of polarized copper electrodes in neutral and acidic environments of industrial variable current [Ondiristik ajnymaly tokpen poljarizacijalangan mys elektrodynyng bejtarap zhane qyshqyldy ortalardagy jelektrohimijalyq qasietteri] ISBN 2224-5227.- Reports of the National Academy of Sciences of the Republic of Kazakhstan. №3. -P. 18-23 (In Kazakh)

[16] Kabasakaloğlu M., Kıyak T., Şendil O., Asan A. **(2002)** Electrochemical behavior of brass in 0.1 M NaCl. Applied Surface Science Volume 193, Issues 1–4, https://doi.org/10.1016/S0169-4332(02)00258-1 P. 167-174 (in Eng)

[17] Rotty C., Mandroyan A., Doche M.-L., Hihn J.Y **(2016)** Electropolishing of Cu-Zn brasses and 316L stainless steels: Influence of alloy composition or preparation process (ALM vs. standart metod). Surface & Coatings Technology. - P.125-135. https://doi.org/10.1016/j.surfcoat.2016.08.076. (in Eng)

[18] Liu, Q., Luo, Hong Dong., Chunfeng Xiao, K li, Xiaogang. **(2012).** The Electrochemical Behaviour of Brass in $NaHSO_3$ Solution Without and With Cl^-. International Journal of Electrochemical Science. 7. 11123-11136.

[19] Arash F. A., Sajad A **(2015)** Electrochemical Behavior and Passivation of Cu–30Zn Alloy in Aqueous NaOH Solutions. Arab J Sci Eng (2015) 40:2993–2999 doi 10.1007/s13369-015-1788-5 Research article-Chemistry. (in Eng)

[20] E. Geler, D.S. Azambuja. The electrochemical behavior of brass in 0.1 M HCl solution. Journal of the Brazilian Chemical Society. **Print version** ISSN 0103-5053. http://dx.doi.org/10.1590/S0103-50531997000200014

[21] C. Berne, E. Andrieu, J. Reby, J-M. Sobrino, C. BlancThe Electrochemical Behavior of α,β′-Brass in Basic $NaNO_3$ Solutions. This was Paper 726 and 758 presented at the Cancun, Mexico, Meeting of the Society, 2014.

[22] A.B. Bayeshov, R.N. Nurdillayeva, Sh.H. Khabibullayeva (2019) Effect of the bromide ions on the titanium electrode dissolution polarized by alternating current in aqueous solutions. News of the Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. №2. (In Eng) https://doi.org/10.32014/2019.2518-1491.21

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SOME REGULARITIES OF THE DISTRIBUTION OF THE CONTENT OF FREE RADICALS AND VANADIUM (IV) IN OIL BY GEOLOGICAL SECTIONS OF THE EMBA REGION DEPOSITS

Abstract. In laboratory practice, is proposed a method for determining vanadium (IV) and free radicals (FR) in crude oils by electron paramagnetic resonance (EPR) at liquid nitrogen temperature. An important scientific and practical result of the proposed method for the determination of vanadium in crude oils, in contrast to the method of American authors is low nitrogen consumption, and an additional advantage of the method lies in the low cost of the process, since it eliminates the use of expensive temperature attachments for mass laboratory determinations of vanadium. In scientific work, this method was applied to determine vanadium and FR from the section of the Emba region's oil fields.

It has been established that with increasing depth and age of oil-bearing rocks, the density of oil decreases, as well as the content of tetravalent vanadium and FR in it. In some fields of the Emba oil-bearing region (North Kotyrtas, Kara-Arna), is noted an inverse pattern - an increase in the density of oil, the concentration of vanadium and FR is observed during the transition from an elevated part of the formation to a lower part.

Key words: electron paramagnetic resonance, vanadium (IV), free radical, depth of oil.

In recent years, students of higher education on the subjects: oil chemistry and oil geology have lectures on EPR-spectroscopy [1,2]. In laboratory practice, a method for determining vanadium (IV) and free radicals (FR) in crude oils at liquid nitrogen temperature is proposed. An important scientific and practical result of the proposed method for determining vanadium in crude oils, in contrast to the method of American authors [3], is the reduction of nitrogen consumption, as well as an additional advantage of the method is to reduce the cost of the process, since the use of an expensive temperature set-top box is excluded in the mass laboratory definitions of vanadium [1]. In this paper, we used this method to determine vanadium and FR from the oil fields of the Emba region.

Table 1 – The relationship between density and oil content of vanadium (IV) and FR section of field Kyrykmyltyk

Well number	Age	Depth of occurrence, m	Density, g/sm^3	Oil content	
				V(IV),g/t	FR·10^{-17}, spin/g
16	К_1a	398…407	0,9273	26,30	9,36
7	К_1a	389…395	0,9275	23,20	9,20
7	К_1в	431…436	0,9163	14,93	8,38
7	К_1в	436…440	0,9127	11,38	8,38
7	К_1в	465…467	0,9269	13,39	8,67
11	J_2	883…891	0,8878	8,43	3,56
11	J_2	937…943	0,8867	5,96	2,86
15	J_2	918…925	0,8897	6,29	2,64
15	J_2	930…932,5	0,8883	5,13	2,46
1	J_1	911.917	0,8880	4,94	2,44
Note. К_1a –apt, К_{1b}-barrem, К_1q-goter, J_2 – middle jur, J_1 – lower jur.					

Some regularities of the distribution of the content of FR and vanadium (IV) by the section of oil fields with different physical and chemical characteristics by the stratigraphic section were revealed for the Kyrykmyltyk field (table 1 and 2) and South Tagan (table 2). As can be seen from the results of data analysis, with increasing depth and age of oil content of FR and vanadium (IV) naturally decreases.

Paramagnetic characteristics of the oil field Kyrykmyltyk were studied by EPR-spectroscopy with the aim of establishing a relationship between density and oil content of vanadium (IV) and FR. The level of paramagnetism of the oil field Kyrykmyltyk is due to the different compounds of vanadium V(IV) and FR. Table 1 shows that the relationship between oil density and vanadium (IV) and FR content is quite clear. From the results of the analysis of the data given in table 1, it is also seen that with the increase in the depth and age of oil, the vanadium (IV) and FR content naturally decreases. The highest content of vanadium (28 g/t) and FR falls on the oil horizon К$_1$a (apt). The content of vanadium is much higher in oils in lower Cretaceous sediments than in the oils of the Jurassic sediments (that was previously installed for the oil between the rivers Ural and Volga) [4]. A similar change is typical for FR. In oils of lower Cretaceous deposits the concentration of FR is higher than in oils of Jurassic deposits.

For the oil fields Kyrykmyltyk and South Tagan also established the relationship between content FR, vanadium (IV) and physico-chemical characteristics. As can be seen from table 2, the content of sulfur, resins, asphaltenes, as well as the density and viscosity of oils increases with the content of FR and vanadium (IV). There is an inversely proportional relationship between the content of FR and vanadium (IV) in oils and the yield of gasoline fractions.

Within one field with increasing geological age and depth of oil vanadium content decreases (table. 1 and table. 2). In the oil fields of the Emba region, the concentration of FR also decreases with the depth of the oil, similar to that observed in the Maikov deposits of the Hadyzhensk and oil and gas fields lying at shallow depths [5].

Table 2 - Interdependence between vanadium (IV), FR content
and physico-chemical characteristics of low vanadium oils of the South-Emba region

Well number	Deep, m	Age	Vanadium Content, g/t	FR·10^{-17}, spin/g	Density, g/sm^3	Viscosity at 20^0C	Content, %			Fraction output up to 300^0C, %
							sulfur	resins	Asphaltenes	
Kyrykmyltyk										
11	389...396	Cret.	23,2	9,2	0,927	1449	0,35	20,0	2,56	24,1
15	930...931	J_2	5,1	2,5	0,888	99	0,25	8,46	0,76	28,8
11	883...891	J_2	8,4	3,6	0,887	105	0,39	9,01	0,29	32,3
16	469...477	Cret.	17,9	5,9	0,914	519	0,38	14,1	1,19	15,2
South Tagan										
1	274...288	J_2	29,2	42,4	0,972	1785*	0,49	29,5	6,89	8,0
1	597...601	Trias	10,7	12,4	0,905	560	0,23	13,8	0,67	14,8
*Note – Viscosity is calculated at 50^0C										

In some fields of the Emba oil-bearing region (North Kotyrtas, Kara-Arna) the reverse pattern is observed – the increase in the content of vanadium and free radicals with depth, which is explained by vertical migration or gravitational differentiation of oil [6]. This process seems to be due to the complex geological structure of the salt dome structures, which are often subject to tectonic processing.

Oil components containing paramagnetic centers are the most chemically active part of oils. Their free radical form determines the increased activity in the processes of both oil genesis and migration. Paramagnetic centers of oil, which are caused by the presence of compounds of tetravalent vanadium and free radicals, are part of the resinous-asphaltene components of oil [7]. In the transition from the increased part of the fields to the reduced one, there is an increase in oil density, vanadium and FR concentration. For illustration, in fig. 1 it is shown about the central parts of the EPR spectra of oils from the well sections of the 23 North Kotyrtas Deposit, taken at – 900C, containing one of the components of the hyperfine structure V4+ and the singlet from the FR. As can be seen, the amplitude of the signal of EPR of V4+ and FR with increasing depth of oil occurrence is growing. The increase in paramagnetism of oils with increasing depth of their occurrence is clearly observed in the section of the Kara-Arna field located in the southern coastal part of the Emba district. The field is tectonically Diptera is a salt dome structure of closed type with deep (up to 1800m) salt core.

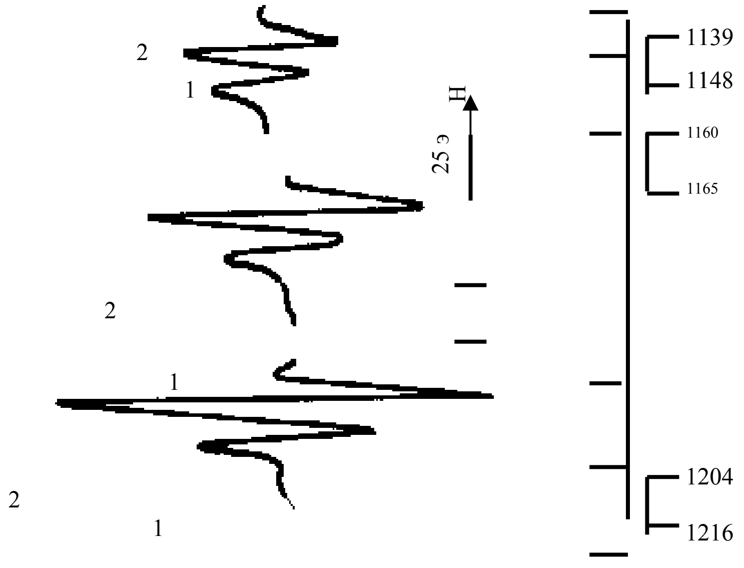

Figure 1- Change of EPR signal of oils in the section of the Kotyrtas North field, well 23.
Deep: a - 1139-1148 m, b-1160-1165 m, c –1204-1216,5 m; EPR signals:1–from V^{4+},2–from FR

Table 3 - Characteristics of oils in the North Kotyrtas field

Well number	Age, horizon	Oil extraction interval,m	Oil density, g/sm^3	V^{4+}, g/t	FR·10^{-17}, spin/g
23	T; III	1139-1145	0,8588	11,50	4,60
	T; III	1160-1165	0,8954	19,97	8,31
	T; IV	1204-1216,5	0,9051	22,51	10,65
22	T; II	1119,5-1128,5	0,8254	2,26	0,69
	T; III	1138,2-1155	0,8315	3,05	1,06
	T; III	1176-1185,7	0,8509	5,05	2,37
38	T; I	1079,5-1085	0,8715	7,80	4,93
	T; II	1133-1139	0,8810	12,10	6,20
5	T; I	1059-1073,5	0,8000	0,37	0,14
	T; II	1100-1104	0,8461	4,59	1,92

Analysis of the results (table.4) shows that there is a fairly clear difference in the distribution of the average vanadium content between the studied productive horizons. It should be noted that the Cenomanian horizon is characterized by the conditioned content of vanadium, and with the increase in the age and depth of oil, the content of vanadium and FR increases, so the industrial importance of the Kara-Arna field as a raw source of vanadium is of practical interest.

Table 4 – Change of paramagnetic properties of Kara-Arna oil field

The number of the studied wells	Oil extraction interval, m	Age	The average content of vanadium, g/t	FR·10^{-17}, spin/g
3	510-555	Senoman	60,08	8,36
4	967-983	Early alb	93,83	10,95
11	1047-1074	Apt	102,44	11,99

Experimental part

EPR spectra were recorded on the E-12 spectrometer of “Varian”. We have found EPR signals from both vanadium and FR ions in the oils of the studied fields. The most intensive hyperfine structure line (HSL) from the complexes of tetravalent vanadium and the single line from FR were used to determine the concentration [8]. The standard concentrations were the oil from Urichtausk field (from well. 8) with known vanadium content (27.6 g/t) and FR ($7{,}8\cdot10^{17}$ spin/sm^3). Oil samples before the analysis were purified from associated water and mechanical impurities by centrifugation (centrifuge T-22) at a speed of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length.

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ЕМБІ АЙМАҒЫНДАҒЫ МҰНАЙ КЕНІШТЕРІНІҢ ГЕОЛОГИЯЛЫҚ ҚИМАЛАРЫ БОЙЫНША ЕРКІН РАДИКАЛДАР МЕН ВАНАДИЙДІҢ (IV) ТАРАЛУ ЗАҢДЫЛЫҚТАРЫ

Аннотация. Шикі мұнайдағы ванадий мен еркін радикалдарды (ЕР) электрондық парамагниттік резонанс (ЭПР) көмегімен сұйық азот температурасында анықтау әдісі ұсынылды.Зертхана жағдайында ванадийді жаппай анықтаудың бұл ұсынылған әдісінің американдық ғалымдардың әдісінен өзгешелігі азот шығынының өте аз болуы және қымбат тұратын температура қондырғысының керексіздігі, прибор резонаторындағы орналасқан ампула көлемінің барлық жағдайда бірдейлігі.

Бұл әдісті Ембі аймағындағы мұнайларға ЕР мен ванадийді анықтау үшін қолдандық. Зерттеу нәтижесі, мұнай үлгілерін алу тереңдігіне және орналасатын жыныстардың геологиялық жасына байланысты, мұнай тығыздығының кемитіні және ондағы төрт валентті ванадий мен ЕР концентрациясының азаятындығын көрсетті. Ал Ембі аймағының кейбір мұнай кеніштері (Солтүстік Қотыртас, Қара-арна) үшін жоғарғы қабаттардан төменгі қабаттарға өту кезінде мұнайдың тығыздығының өсетіндігі және ванадий мен ЕР концентрациясының артатындығы , яғни кері заңдылық тағайындалды.

Түйін сөздер: электрондық парамагниттік резонанс, ванадий (IV), еркін радикал, мұнай орналасу тереңдігі.

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НЕКОТОРЫЕ ЗАКОНОМЕРНОСТИ РАСПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ СР И ВАНАДИЯ (IV) В НЕФТИ ПО РАЗРЕЗАМ МЕСТОРОЖДЕНИЙ ЭМБИНСКОГО РЕГИОНА

Аннотация. В лабораторной практике предлагается способ определения ванадия (IV) и свободных радикалов (СР) в сырых нефтях методом электронного парамагнитного резонанса (ЭПР) при температуре жидкого азота. Важным научно-практическим результатом предлагаемого способа определения ванадия в сырых нефтях, в отличии метода американских авторов является снижение расхода азота, а дополнительное преимущество способа заключается в удешевлении процесса, так как исключается применение дорогостоящей температурной приставки при массовых лабораторных определениях ванадия. В данной работе этот метод применен для определения ванадия и СР по разрезу месторождений нефти Эмбинского региона.

Было установлено, что с увеличением глубины и возраста нефтевмещающих пород происходит уменьшение плотности нефти, содержания в ней четырехвалентного ванадия и СР. На некоторых месторождениях Эмбинского нефтеносного района (Котыртас Северный, Кара-Арна) отмечается обратная закономерность – при переходе от повышенной части пласта к пониженной отмечаются увеличение плотности нефти, концентрации ванадия и СР.

Ключевые слова: Электронный парамагнитный резонанс, ванадий (IV), свободный радикал, глубина залегания нефти.

REFERENCES

[1] Ермолкин В.И., Керимов В.Ю. Геология и геохимия нефти и газа. М.: Недра, 2012. 460 с.

[2] Рябов В.Д. Химия нефти и газа. М.: ИД «Форум», 2009.-336 с.

[3] Saraceno A. T., Fanale D. T., Coggeshal N. D. An electronic paramagnetic resonance investigation of vanadium in petroleum oils // Anal. Chem., 1961. V. 33. P. 500–505.

[4] Насиров Р.Н., Искужиев Б.А.Парамагнитные особенности нефтей месторождения междуречья Урал-Волга. - М.: Миннефтегазпром. 1992. 51 с.

[5] Вдовыкин Г.П., Дубров Ю.Н., Маров И.Н. Свободные радикалы в нефтях Северо-Западного Предкавказья // Геохимия. 1967. №7. С. 861-863.

[6] Насиров Р.Н., Те Л.А., Джакиев К.Т. Существование гравитационной дифференциации нефтей в залежах // Доклады НАН РК. 2003. № 1.С. 84-87.

[7] Nasirov R.N., Shambilova G.K., Zhuldiyev M. Research on the colloid structure of crude oils of the Caspian region by the paramagnetic probe method //J. Magnetic Resonance Imaging. – New York, USA, 2007.- Vol. 25, № 4. P. 574-575.

[8] Nasirov R.N., Nasirov Aizat R. Investigation of Vanadium in Crude Oils of the Caspian Region by Electronic Paramagnetic Resonance (EPR) Method //Abstract of 48th Rocky mountain conference on analytical chemistry. Breckenridge. Colorado. 2006. P. 65.

[9] Volodin, V.N., Trebukhov, S.A., Kenzhaliyev, B.K. et al.Melt–Vapor Phase Diagram of the Te–S System. Russ. J. Phys. Chem. (2018) 92: 407. https://doi.org/10.1134/S0036024418030330

[10] Massalimova B.K., Jetpisbayeva G.D., Altynbekova D.T., Nauruzkulova S.M., Atakozhaeva A.A., Sadykov V.A. LOW-PERCENTAGE Co/CLAY CATALYSTS IN THE PROCESS OF OXIDATIVE CONVERSION OF C3-C4 SATURATED HYDROCARBONSN E W S OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN SERIES CHEMISTRY AND TECHNOLOGY ISSN 2224-5286 Volume 2, Number 434 (2019), 5 – 11 UDC 544.478 https://doi.org/10.32014/2019.2518-1491.11

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