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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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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

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

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

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LOW-PERCENTAGE Co/CLAY CATALYSTS IN THE PROCESS OF OXIDATIVE CONVERSION OF C3-C4 SATURATED HYDROCARBONS

Abstract. Oxidative conversion of C_3-C_4 hydrocarbons by air to oxygen-containing compounds at T = 400-550°C and space velocity of 7500 h^{-1}, 9000h^{-1} on monoxide catalysts containing 1-, 3-, 5% Co supported on natural red clays was studied. The reaction temperature, contact time, change in the space velocity in the process of partial oxidation of C_3-C_4 hydrocarbons have been studied.

Acid treatment of the sorbents contributed to the development of the surface area and the enlargement of pore radius, which led to an increase of oxygen-containing compounds in the final product. The SiO_2/Al_2O_3 ratio (silica modulus) was increased after acid treatment too.

Key words: catalysts, hydrocarbons, natural clay.

Introduction. The rational use of hydrocarbons and environmental protection are of the most important goals of the fuel and energy complex. Incineration of associated gas is a national problem which leads to environmental and economic damage of our country [1-3]. When burning gas without maintaining the optimal mode of combustion, about 250 harmful chemicals are released into the atmosphere, namely, non-combustible hydrocarbons; oxides of carbon, nitrogen and sulfur; hydrogen sulfide, heavy metals (mercury, chromium), arsenic compounds, aromatic hydrocarbons, including polycyclic compounds [3-5].

These substances pollute the atmosphere, water and soil. Associated gas can be used as a fuel for power generation, as well as hydrocarbons for the production of petrochemical products as a raw material. Efficient use of hydrocarbon resources is one of the most relevant sectors of the oil and gas industry. Associated gas as an unconventional source of hydrocarbons is still not used effectively [5-7].

In recent years, many researchers and manufactures have been interested in the technological processes of converting natural gas into liquid chemicals. Natural gas is a perspective energy source for the needs of mankind in the energy and hydrocarbon raw materials for over hundred years. About 5% of world natural gas is still used as a motor fuel or raw material for petrochemical production. Petrochemical natural gases C_2-C_4 and natural gas are underutilized [1-5].

Methods. Today, about 80-85% of the various processes occurring in the chemical, petrochemical, and oil refining industries are implemented with the participation of the catalysts. The temperature impact on the process of partial oxidation of the propane-butane gas mixture is discussed. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor [7].

To conduct the experiment, the catalysts with different Co content supported on the natural red clay were used. The experiment were carried out at a temperature of 400°C-550°C with a change of space velocity of 7500 h^{-1}, 9000 h^{-1}.

The natural red clay was used as a carrier. Catalysts with 1 -, 3 -, 5% of cobalt supported on the natural red clay (NRC) were produced. The carrier was pretreated with 4 different methods: adjustment of active phase at constant atmospheric pressure in different temperature ranges.

In the case of partial oxidation of C3-C4 hydrocarbons initial and final gaseous products C_2H_4, H_2, CO, CH_4, CO_2 as well as liquid organic substances were detected by the chromatographic method.

Partial oxidation of C3-C4 hydrocarbons was carried out on 1% Co/NRC catalyst, at atmospheric pressure, under the following conditions: C3-C4=33.33%; O_2=7.0%; N_2=26.34%: Ar=33.33%; space velocity of 7500h^{-1}.

When the temperature rises to 300-350°C, liquid organic compound is not formed. In the gas phase, only traces of C_2H_4, H_2, CO, CH_4 and CO_2 are observed.

With gradual increase of temperature to 400°C the following products formed on catalyst are preferably formed: acetaldehyde, 26.6%; acetone - 23.0%; methanol - 20.7%. Aromatic compounds and carboxylic acids are not fully formed. When the reaction temperature reaches 500°C, the reaction selectivity for acetaldehyde and acetone gradually decreases and the selectivity for methanol reaches 41.8%. The conversion of propane is 9.8%, the conversion of butane is 25.4%.

At this temperature, it can be seen that the selectivity for acetaldehyde and methanol gradually increases, and the selectivity for ketone decreases. Conversion of gases contained in compressed petroleum gas at 450°C was equal to: C_3H_8=7.4%; C_4H_{10}=25.4%. Table 1 demonstrates the conversion increase of the propane-butane gas mixture in the following sequence: C_3H_8=4.6-10.2%; C_4H_{10}=17.3-30.0%. With the gradual increase of temperature in the gas-phase product the number of components C_2H_4, H_2, CO, CH_4 and CO_2 increases (table 1).

Table 1 - The effect of temperature on the yield of products
in the liquid phase resulting from the partial oxidation
of C3-C4 hydrocarbons. State of the reaction: C3-C_4:O_2:N_2=7:1:4; W=7500h^{-1}. Catalyst 1Co/ NRC

T, °C	V, % C_3H_8/ C_4H_{10}	**Selectivity, %**												
		Acetaldehyde	acetone	methanol	MEK	ethanol	benzene	propanol	crotonaldehyde	butanol	H- butanol	Acetic acid	Acrylic acid	Propionic acid
400	4,6	26,6	23,0	20,7	21,0	6,4	0	0	1,1	0	0	0,7	0	0
	17,3													
450	7,4	26,0	22,6	25,8	18,7	5,0	0	0	1,0	0	0	0,7	0	0
	21,5													
500	9,8	18,0	16,0	41,8	21,0	3,2	0	0	0	0	0	0	0	0
	25,4													
550	10,2	11,2	27,8	22,8	27,1	4,3	1,7	0	3,6	0	0	0,8	0	0
	30,0													

The NRC carrier used in the experiment was analyzed by physical and chemical methods: BET, elemental analysis.

The main factor determining the catalytic properties is the chemical composition. However, even while maintaining the chemical composition, the catalytic characteristics of the catalysts, depending on the state and method of preparation, undergo changes in surface area as a result of dispersion, porous structure, nature of the interaction of the constituent parts of the catalyst and crystal chemical changes, which ultimately significantly affects the passage of catalytic reactions [7].

The catalytic system 1, 3-, 5% Co/NRC for the reaction of partial oxidation of C3-C4 hydrocarbons was studied. The content of the products formed as a result of partial oxidation reaction carried out in stable state in the temperature diapason of 400°C-550°C on the NRC and other catalytic systems is given in table 2.

According to table 2, the oxidation product obtained on 3% Co/NRC contains acetaldehyde, acetone, methanol, MEK, benzene, crotonaldehyde, propanol, and acetic acid, which were determined by chromatography.

Table 2 - The influence of the contact time of hydrocarbons C3-C4 on the flow of products formed in the process of partial oxidation. State of the reaction: C_3-C_4=33,3%; O_2=7,0%; N_2=26.4%; Ar=33.3%7. 3%Co/ NRC; V=2cm^3

W, h^{-1}	τ, c	T, °C	V, % C_3H_8/ C_4H_{10}	yield , %				
				aldehyde	ketone	alcohols	Carboxylic acid	Gas phase
9000	0,4	500	26,6	29,2	5,4	9,0	0	12,0
			48,3					
		550	40,0	21,4	8,0	6,6	0	19,6
			58,7					
7500	0,5	500	32,3	32,0	19,8	14,1	1,3	20,8
			55,7					
		550	41,8	34,4	20,3	14,2	3,1	35,6
			82,5					

The experiment on 3% Co/NRC catalyst, was conducted at atmospheric pressure, at temperatures of 500-550 °C, at a space velocity of 7500 h^{-1}, 9000 h^{-1}. As it is shown in table 2, 29.2% of aldehyde, 5.4% of ketone and 9.0% of alcohols are formed in the process of liquid catalysis at a temperature of 500 °C on 3% Co/NRC catalyst. The conversion of propane is 26.6%, and the conversion of butane - 48.3%. When the temperature exceeds 550°C, the content of acetaldehyde in the catalyst decreases to 21.4%. In the ranges of these temperatures, the yield of ketone increase to 8.0%. The formation of ketone is increased by 34.4% at a temperature of 600^0C at space velocity of 7500 h^{-1}. Carboxylic acids are not formed at temperatures of 500°C-550°C at space velocity of 9000 h^{-1}, but at space velocity of 7500 h^{-1} at this temperature interval 1.3-3.1% of Carboxylic acids are formed. In the gas phase, ethylene and hydrogen yield is 10-19% (table 2).

Results and discussion. During partial oxidation of C3-C4 the hydrocarbons were processed with cobalt catalysts. The catalysts were investigated by physicochemical methods: X-ray diffraction, BET, elemental analysis.

The phase composition of the catalyst was determined on X-ray diffractometer DROH-4 -07. Comparison of refractometric reflexes was performed using powder paper (standard JCPDS). Natural red clay is X-ray morphic mineral (4.20°) consisting of -α-quartz / 3.33; 2.28 / (JCPDS 5-490) - and kaolinite (JCPDS 29-1488). The diffractogram of the initial catalysts 1,3-, 5% Co/NRC correspond to the clay. Since it is dispersed, due to different doses of metal, the structural elements are not detected.

The determination of the specific surface area and porosity of solids is based on the determination of isothermal adsorption of gas phase molecules on the surface. The adsorption isotherm takes shape on the dependance of the number of adsorbed molecules on pressure at moderate temperatures.

The textural and adsorption characteristics of the catalyst were measured by the American "micrometritics Accusorb" using the BET method for low-temperature nitrogen adsorption.

Table 3 - The surface area of the catalyst, the volume of porosity and changes in the main volume

№	Catalyst composition	results		
		Surface, m^2/g	Pore volume V_{ADSmax},ml/g	Vист, (ml)= $V_{ADSmax}\cdot K(0,001558)$
1	NRC	15,39	221,69	0,345
2	1%Co/ NRC	29,90	221,74	0,345
3	3%Co/ NRC	51,35	467,63	0,729
4	5%Co/ NRC	58,12	328,19	0,511

The catalysts shown in table 3 also have different porosity volumes. The porous volume of NRC is 221.69 ml/g; 1% Co/NRC - 221.74 ml/g; 3% Co/NRC - 467.63 ml/g; 5% Co/NRC- 328.19 ml/g. The main volume of catalysts is as follows: the pore volume of the NRC is 0.345 ml; 1% Co/ NRC - 0.345 ml; 5% Co/ NRC - 0.729 ml; 5% Co/NRC - 0.511 ml.

It has been shown that the surface area of the catalyst and the porosity affect the selectivity of hydrocarbons in the liquid and gas phase resulting from the partial oxidation of hydrocarbons. Natural red clay was treated in four different ways. Elemental analysis of 1-, 3-, 5% catalysts which were used as catalysts for the oxidation process was performed using an Agilent 4200 atomic emission spectrometer. The catalysts were investigated on the Australian apparatus Agilent 4200 MP-AES which is located in Taraz State University named after M.Kh. Dulati at the Department of Chemistry and Chemical Technology. In the new spectrometer, the electromagnetic microwave field excites plasma in nitrogen, which is generated from the air. The concentration of the analyte was determined by the AES method. All measurements were performed using an Agilent 4200 MP-AES equipped with an Agilent 4107 nitrogen generator. The sample introduction system consisted of a two-pass cyclone spray chamber, OneNeb sprayer, Solvaflex pump tube (orange / green) and an Easy-fit burner for sample introduction. Used multi-element calibration standards containing elements with a concentration of 50 mg L^{-1}. The standard was prepared in an environment of 5% HNO_3 / 0.2% HF (v / v).

Table 4 - Results of elemental carrier analysis

elements	NRC	1Co/ NRC	3%Co/ NRC	5%Co/ NRC
	%	%	%	%
Sr	0.0005	0.0005	0.0005	0.0004
Ce		0.003	0.002	0.003
Zn	0.002	0.002	0.002	0.0015
Cu	0.001	0.004	0.002	0.002
Sn	0.0003	0.0003	0.0003	0.0003
Mo	0.00015	0.00015	0.00015	0.00015
Ba	0.003	0.0033	0.0025	0.0025
Ni	0.008	0.005	0.01	0.01
Mn	0.015	0.015	0.015	0.015
V	06	>1	06	06
Tl	0.0015	0.0025	0.0025	0.0025
Pb	0.006	0.01	0.008	0.01
Cr	0.000005	0.000008	0.000005	0.000005
Ag	0.03	0.03	0.02	0.03
Nb	0.0015	0.0015	0.0010	0.001
Be	0.00015	0.00015	0.00015	0.00015
Ge	3	6	9	12
Bi	0.0001	0.0001	0.0001	0.0001
Ga	0.00008	0.0008	0.0008	0.0008
P	-	-	0.003	-
CaO	<01	<01	<01	<01
MgO	01	015	<01	<01
Fe_2O_3	21	15	20	19
Al_2O_3	45	47	48	42
Na_2O	015	<01	015	02
K_2O	-	-	-	-
SiO_2	25	30	25	30

According to elemental analysis, all the elements in table 4 are common in the catalyst used, but the difference lies in the amount of these elements. Also, the main distinguishing feature is the change in the content of oxides in the composition of the carrier. For example, oxide of 3 valence iron is up to 21% of NRC, 1% Co/NRC - 15%, 3% Co/NRC - 20% and 5% Co/NRC - 19%. Al_2O_3 ranges from 42 to 48% in all catalysts. And in the composition of all catalysts 25-30% of SiO_2 was found.

Conclusion. For the development of the petrochemical industry, Kazakhstan has large reserves of hydrocarbon raw materials - natural and associated gases, oil and products of its processing, as well as oil bituminous rocks. The main deposits are developed in the western regions of Kazakhstan. According to the forecast geological exploration data, hydrocarbon reserves in the northern, central and eastern regions are insignificant [6-7].

To ensure the processing of natural resources of hydrocarbon raw materials in the republic, an important issue is the creation of petrochemical complex for the final stages of processing hydrocarbon raw materials to marketable products via the modernization of the existing capacities of oil refining industries to obtain basic products for the oil and gas industry.

The process of partial oxidation of hydrocarbons C_3-C_4 was carried out on catalytic systems 1-, 3-, 5% Co/NRC supported on the NRC.

The influence of temperature, space velocity (750 and 7500 h^{-1}), the effect of the active phase dose were tested, the optimal ways to conduct the C_3-C_4 hydrocarbon partial oxidation process (300^{o}C-600^{o}C) and to obtain the reaction products were determined for the catalytic systems studied.

In the process of oxidation of hydrocarbons C_3-C_4, the following results were obtained:

1) The oxidation process of C_3-C_4 hydrocarbons occurs in a mild state at atmospheric pressure.

2) At 1% Co/NRC catalyst at a ratio of 500°C, C_3-C_4 HC: O_2: N_2: Ar = 5: 1: 4: 5 at a space velocity of 7500 h^{-1}, 41.8% methanol is formed.

It is necessary to conduct a study of catalysts for partial oxidation of C_3-C_4 hydrocarbons on an electronic scanning microscope.

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C_3-C_4 ҚАНЫҚҚАН КӨМІРСУТЕКТЕРДІҢ ТОТЫҒА АЙНАЛУ ПРОЦЕСІНДЕГІ ТӨМЕНГІ ПАЙЫЗДЫҚ Co/САЗБАЛШЫҚ КАТАЛИЗАТОРЫ

Аннотация. С3-С4 көмірсутектерін оттек құрамды композиттерге дейін ауамен тотықтыру кезінде Т = 400-550°С-та және табиғи қызыл сазбалшыққа қондырылған 1-, 3-, 5% Со бар моноксидті катализаторлардағы 7500 сағ$^{-1}$, 9000сағ$^{-1}$ көлемдік жылдамдығы зерттелді. С3-С4 көмірсутектердің жартылай тотығу процесіне реакция температурасы, жанасу уақыты, көлемдік жылдамдықтың өзгерісі зерттелді.

Сорбенттерді қышқылдық өңдеуде бетінің пайда болуына және кеуек радиусының ұлғаюына ықпал етті, бұл катализатта оттегі бар қосылыстардың көбеюіне әкелді. SiO_2/Al_2O_3 қатынасы (силикатты модуль) қышқылдық өңдеуден кейін де артады.

Түйін сөздер: катализатор, көмірсутектер, табиғи сазбалшық.

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НИЗКОПРОЦЕНТНЫЕ Co/ГЛИНОВЫЕ КАТАЛИЗАТОРЫ В ПРОЦЕССЕ ОКИСЕНИЯ НАСЫЩЕННЫХ С3-С4 УГЛЕВОДОРОДОВ

Аннотация. Исследовано окислительное превращение С3-С4 углеводородов воздухом в кислородсодержащие композиции при Т=400-550^{o}С и объемной скорости 7500ч$^{-1}$, 9000ч$^{-1}$ на монооксидных катализаторах, содержащих 1-, 3-, 5% Со, нанесенных на природные красные глины. В процессе полуокисления С3-С4 углеводородов исследовались температура реакции, время контакта, изменение объемной скорости. Кислотная обработка сорбентов способствовала разработке поверхности и увеличению радиуса пор, что приводило к увеличению кислородсодержащих соединений в катализате. SiO_2/Al_2O_3 соотношение (силикатный модуль) также увеличивался после кислотной обработки.

Ключевые слова: катализатор, углеводороды, природная глина.

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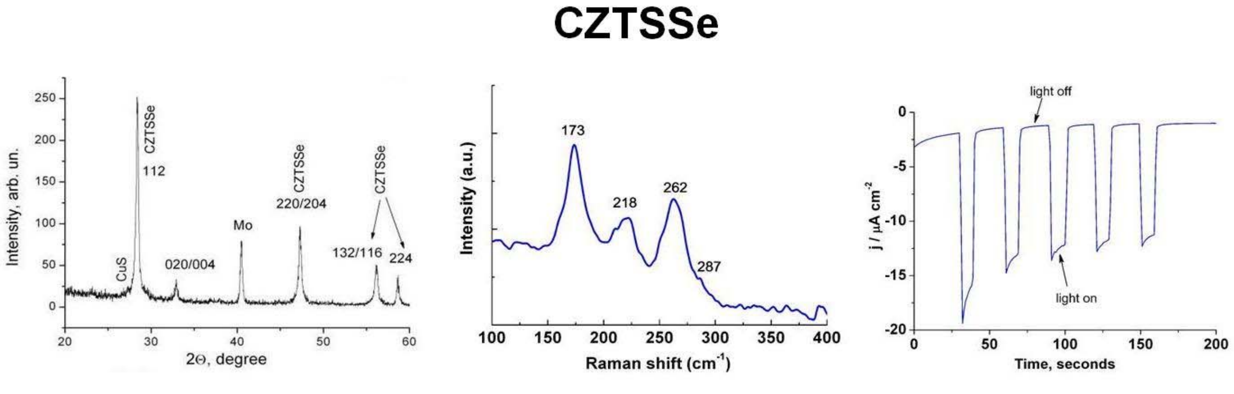
STRUCTURE AND PHOTOELECTROCHEMICAL PROPERTIES OF ELECTRODEPOSITED $Cu_2ZnSn(S,Se)_4$ FILMS

Abstract. A one-step electrochemical synthesis of $Cu_2ZnSnSe_4$ (CZTSe) and Cu_2ZnSnS_4 (CZTS) films on Mo-coated glass from aqueous electrolytes containing both Cu^{+2}, Zn^{+2}, Sn^{+2} and Se^{+4} or S^{+4} ions has been developed. Electrodeposition was performed at a constant potential with subsequent annealing at a temperature of 450 °C in air for 60 minutes. $Cu_2ZnSn(S_{0.96},Se_{0.04})_4$ films were obtained by sulfurizing electrodeposited $Cu_2ZnSnSe_4$ layers in a sulfur atmosphere at 500 °C for 60 minutes. The structure and phase composition of the films was confirmed by XRD and Raman spectroscopy. It was confirmed by the PEC method that all films had p-conductivity. It was established that a change in the chemical composition of the films affects the electrophysical properties, and for $Cu_2ZnSn(S,Se)_4$ layers the photoresponse was 5-6 times higher than for four component compounds.

Key words: electrodeposition, CZTSSe, kesterite, thin film, photoelectrochemistry.

Graphical Abstract



Introduction

Recent progress in creating solar photovoltaic cells based on four-component semiconductors $Cu(In,Ga)Se_2$ (CIGS), Cu_2ZnSnS_4 (CZTS) stimulates researchers to further develop the technology of growing more advanced and efficient thin-film structures [1, 2]. It is known that polycrystalline thin films of the compounds Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and $Cu_2ZnSn(S_xSe_{1-x})_4$ with the structure of kesterite are promising materials for the production of cheap solar cells. These compounds consist of components that are widespread in nature and can be considered as an inexpensive, affordable material, the use of which does not violate environmental standards, in contrast to frequently used cadmium sulfide, copper-indium selenides, etc. The band gap of these kesterites, depending on the content of sulfur and selenium, can vary from 0.98 to -1.8 eV, [3, 4], and a high adsorption coefficient ($\alpha = 10^4$ cm^{-1}) for photons with energies greater than width the band gap allows efficient radiation absorption in the chalcogenide layer to be thinner than a few microns. This reduces the amount of material used. Global studies show that the effectiveness of thin-film elements with a material based on multicomponent chalcogenides with a structure of kesterite is continuously increasing [2-5]. An effective solar radiation conversion of 12.6% was reported, which was achieved for the Cu_2ZnSn $(S_xSe_{1-x})_4$ solid solution [5].

The deposition of thin-film absorption layers is often performed using various vacuum techniques at high temperatures. However, single-stage methods of electrodeposition of four and five-component film semiconductors from aqueous electrolytes at low temperatures are attracting more and more attention [6–9].

One of the important applications of multicomponent chalcogenide semiconductors CZTSSe is their use as photocathodes in photoelectrochemical (PEC) decomposition of water. This process attracts attention due to its environmental friendliness and low cost [10, 11]. Methods for the decomposition of water using CZTS photocathodes were developed when they started using compositions of this material with thin layers of sulphides of other metals, for example, cadmium and indium [12]. The CZTS method of electroplating and the subsequent deposition of metal sulfide layers and their activation with platinum are also being successfully used. For example, modification of CZTS by applying a double layer of In_2S_3 / CdS followed by precipitation of a dispersed Pt catalyst made it possible to obtain in the two-electrode PEC process the efficiency of water decomposition equal to 1.63% without any noticeable degradation of the photocathode due to photocorrosion. In_2S_3 films act as mediators for efficient electron transfer on Pt blotches as well as a protective layer to avoid contact between the CdS layer and the external electrolyte solution [13].

In order to develop the technology of using materials based on kesterite to create thin-film photocells or film photocathodes, information on the correspondence of the composition, structure, and optical, in particular, photoelectrochemical properties of these materials, which significantly depend on the production method, is needed [14].

The work of a number of authors [15–21] is devoted to this question. An XRD microstructural analysis for films prepared by magnetron sputtering of metal precursors followed by sulfurization / selenization showed a strong dependence of domain sizes and microstresses on the composition. Domain sizes increased with increasing sulfur content, and selenium-rich films tended to have a more homogeneous domain size distribution. This phenomenon is associated with a lower energy of formation of binary phases with sulfur, which leads to the formation of kesterites, whereas the increase in microstrains is explained by the replacement of large selenium atoms by smaller sulfur atoms in the lattice and the presence of secondary phases. [18].

The method of single-stage electrodeposition of all components at a constant potential from aqueous solutions allows one to reduce the content of double phases in the structure and their influence on the photoelectrochemical properties [5–8].

In this work, the method of potentiostatic deposition of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ from electrolytes containing simultaneously all components is used. The goal of this work is to compare the structural characteristics of CZT(S,Se) films obtained using a single-stage electrodeposition method with subsequent annealing, and their photoelectrochemical properties.

Experimental part

Electrochemical deposition of thin films of compounds Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ was carried out on Mo/glass substrates (working electrode), from aqueous solutions at a constant potential. The potential was maintained using the Gill AC potentiostat-galvanostat from ACM Instruments relative to the Ag/AgCl electrode (KCl sat). A three-electrode thermostatted cell was used. The counter electrode was a platinum coil (or platinum mesh).

Cu_2ZnSnS_4 (CZTS) films were electrochemically precipitated from an electrolyte based on 0.2 M sodium citrate with the addition of 0.1 M tartaric acid and 0.01 M CuSO4 • 5H2O, 0.005 M SnSO4, 0.01 M ZnSO4 • 7H2O, and 0.05 M Na2S2O3 • 5H2O at pH 4.6. The electrolysis was carried out at a constant potential E = -1.0 V with stirring the electrolyte with a magnetic stirrer at room temperature.

Electrodeposition of $Cu_2ZnSnSe_4$ (CZTSe) films was carried out from an electrolyte with a pH of 1.5 based on a solution of 0.1 M tartaric acid, which contained 0.002 M $CuSO_4 \cdot 5H_2O$, 0.01 M $ZnSO_4 \cdot 7H_2O$, 0.01 M $SnCl_4 \cdot 5H_2O$ and 0.005 M $NaHSeO_3$. The electrolysis was carried out at a constant potential E = -0.6 V with stirring the electrolyte with a magnetic stirrer at room temperature.

The obtained samples were washed with distilled water and dried in air. The obtained CZTS and CZTSe films were annealed at a temperature of 450 °C in an atmosphere of air for 30 minutes.

To form the five-component compound $Cu_2ZnSn\ (Se_x,\ S_{1-x})\ _4$, the process of sulfurization of freshly precipitated thin films $Cu_2ZnSnSe_4$ was carried out. The process was carried out in a quartz tube, where the sample $Cu_2ZnSnSe_4$ and colloidal sulfur were located. Argon was used as the carrier gas. The temperature in the furnace was raised at a rate of 13 °C / min and, after reaching a temperature of 500 ° C, annealing was performed for 60 minutes, then the samples were cooled with the oven to room temperature. After that, the films were not chemically treated. This stage is performed at the State Research Institute for Physical Sciences and Technology, Vilnius.

The study of the structure of the obtained films was performed by the XRD method. XRD spectra were obtained using a SmartLab X-ray diffractometer (Rigaku) at a constant voltage of 9 kW using a rotating Cu anode to study the structure of the samples obtained.

A combined Solver Spectrum system (NT-MDT, Russia) was used to study the Raman spectroscopy method and record the Raman spectra (using a 600/600 grating; 532 nm laser; signal accumulation time 60 seconds). The EDAX method (JSM 6610 LV JOEL, Japan) was used to determine the elemental composition of the electrodeposited CZTS, CZTSe and CZT(S,Se) films after they were annealed.

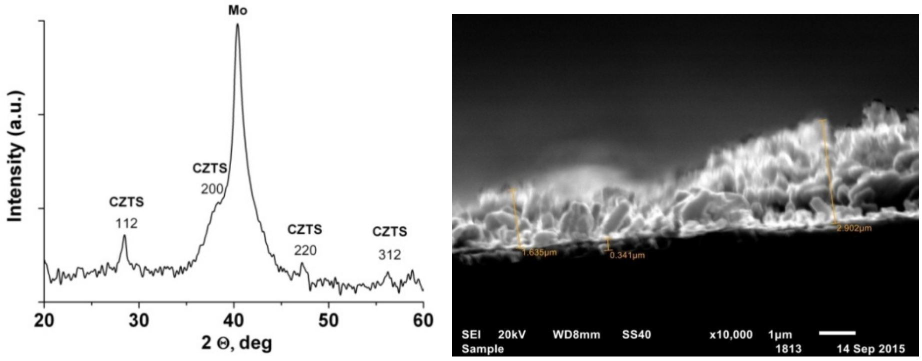
The method of photoelectrochemical (PEC) analysis was performed using a Gill AC potentiostat-galvanostat in a three electrode quartz cell, where the working electrode was made with thin film samples, the platinum coil was used as a counter electrode, and a silver chloride electrode was used as a reference electrode. Photocurrents were recorded in the dark / light mode in a solution of 0.1 M sodium sulfate. A halogen lamp was used as the light source, and the lighting power was 80 mW/cm2.

Results and discussion

Structure analysis

A structural analysis of electrodeposited CZTS films on a Mo/glass substrate and annealed in air at 450 °C was performed using XRD (Fig. 1 (a)). Observed reflexes CZTS kesterite phase and Mo substrate. From the analysis of the diffraction data, it becomes obvious that there are no pronounced reflexes of the double sulfide phases in the electrodeposited films. Estimation of the main peaks corresponds to the provisions 112 and 220 of the kesterite. Peaks are also noted that correspond to the ester levels of 200 and 312. The polycrystalline nature of the precipitates obtained corresponds to the crystal structure of the kesterite [JCPDS card: 26-0575]. Similar results were obtained in [8, 10].

SEM images of deposited CZTS films are shown in Figure 1(b). This picture shows an image in cross-section mode, from which it can be seen that the CZTS film has good adhesion to the glass substrate. CZTS film thickness varies from 0.35 to 2.9 µ.



a b

Figure 1 - (a) XRD spectre and (b) cross-sectional SEM image of CZTS film after annealing

Electrodeposited CZTSe films after annealing were investigated using x-ray diffraction analysis. Figure 2 shows the diffraction patterns before and after annealing. On as-deposited films (Fig. 2, spectrum 1), weak reflections of CZTSe and Mo phases appear (cubic lattice, parameter a = 3.149-3.150 Å). The XRD spectrum of the film after annealing showed three main reflexes at 27.49 °, 45.25 ° and 53.53 °, which correspond well to CZTSe values (ICDD 96-153-1984) with crystalline orientations (112), (220) and (312).

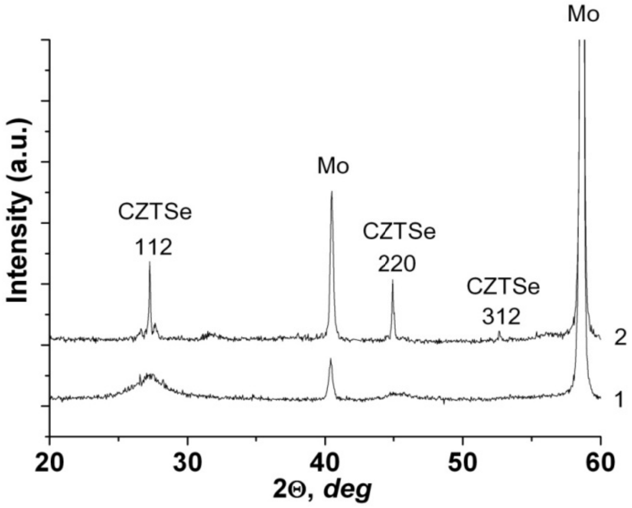
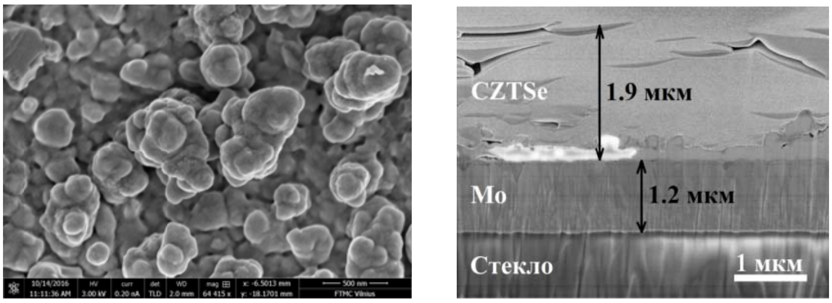


Figure 2 - XRD spectrum of CZTSe films: 1 - before annealing; 2 - after annealing

As can be seen from Fig. 3(a), the grain size and morphology of the film surface is similar to the images obtained in [8] for CZTSe films deposited by an electrochemical method in one stage. The study by the cross-section method showed that the films deposited in our experiments have a maximum thickness of 1.9μ (Fig. 3 (b)).



a b

Figure 3 - SEM images of (a) surface and (b) cross-section of CZTSe/Mo/glass

Immediately after deposition, CZTSe samples were subjected to sulphurization to obtain thin films of the five-component compound CZTSSe. The study of the phase composition of thin films obtained after sulfurizing CZTSe showed the presence of a polycrystalline kesterite phase CZTSSe (Fig. 4). All the dominant diffraction peaks of this film can be attributed to the peaks of the tetragonal structure for CZTSSe: (112), (020/004), (132/116) at 28.4º, 33.05º, 47.39º and 56.15º (ICDD 96- 900-4751). Metal phases other than Mo, as well as intermetallic compounds or oxides were not detected. Detailed analysis of the samples showed that the peak (112) of the CZTSe phase is shifted from 27.49 ° to 28.4 ° due to the partial replacement of Se by S and the formation of the five-component compound CZTSSe. Logarithmic intensity was used to better show low intensity peaks. As can be seen from the fragments of the XRD spectrum, low-intensity peaks can be attributed to the CuS (ICDD 00-085-39280) and ZnS (ICDD 00-002-0564) phases. As well as the presence of double peaks 220/204 and 132/116 at 47.29 º and 56.03 º, confirm the formation of the CZTSSe phase.

All the CZTSSe phase peaks are shifted to large angles, which indicates a decrease in the lattice parameters due to the replacement of Se with S. Given these data, we can conclude that the film was single phase and crystallized in a partially disordered structure of the kesterite.

In addition to the XRD analysis, a combination scattering study (Raman spectroscopy) was performed, which is useful for studying the phase purity and composition of the materials of the kesterite. A simple XRD analysis does not always allow us to determine that a film has a single phase, because many double and triple intermediates have a similar structure and exhibit reflections similar to CZTS (for example, Zn(S)x, Cu2Sn(S)3) [22]. Fig. 5 compares the Raman specters for the three studied compounds CZTS, CZTSe and CZTSSe, obtained using the method of electrodeposition with subsequent annealing.

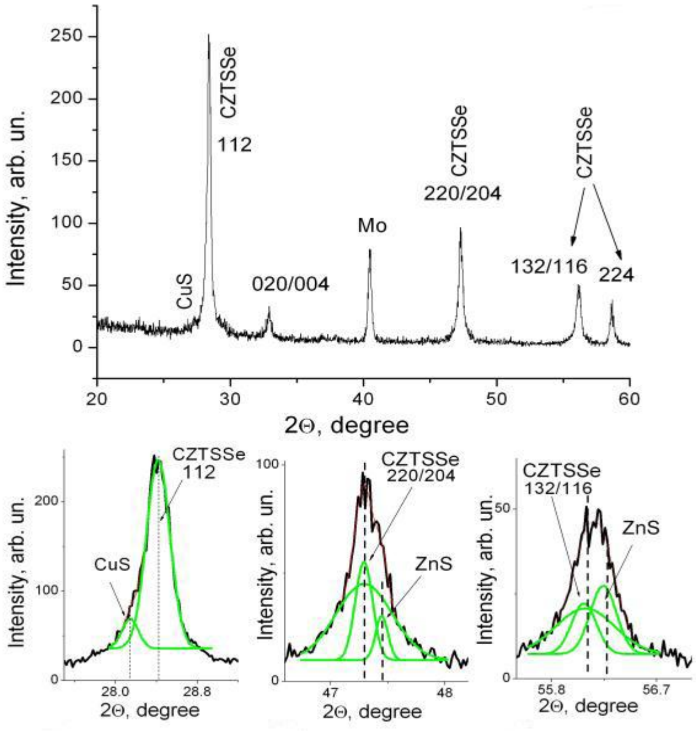
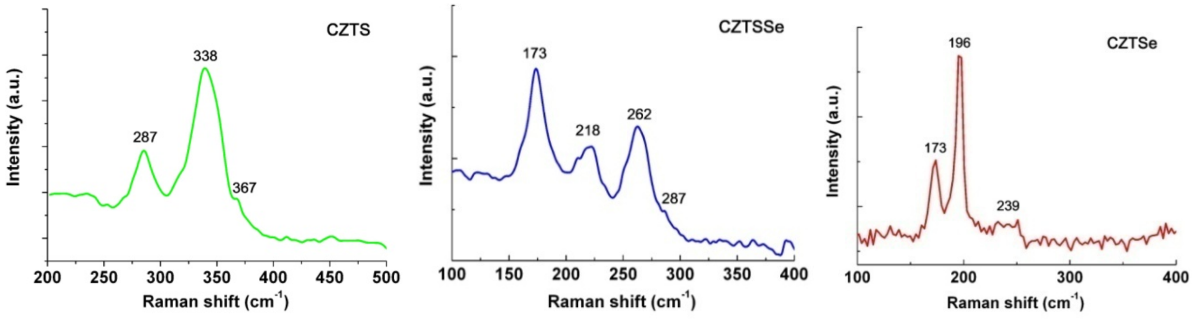


Figure 4 - XRD specter of CZTSSe films

In Fig. 5 (a), the main peaks of the Raman spectrum for CZTS are located around the vibrational mode of the A1 lattice, which reflects the vibrations of the sulfur atom, while the remaining atoms remain fixed. The main peak appears at 338 cm^{-1}, which is consistent with a previously published work for CZTS (338 cm^{-1} main peak with additional peaks at 287, 368 cm^{-1}) [23]. This suggests that under selected conditions of single-stage potentiostatic deposition with subsequent annealing, the compound Cu_2ZnSnS_4 (CZTS) was obtained. Figures 5(b,c) show the Raman specters for the CZT(S,Se) and CZTSe films.



a) b) c)

Figure 5 - Raman specters of kesterite thin films: (a) Cu_2ZnSnS_4 (CZTS); (b) CZTSSe; (c) CZTSe

For the CZTSe compound, the appearance of three peaks was noted (Fig. 5 (c)), where the main vibration mode (196 cm^{-1}) reflects the vibrations of the selenium atom bound to the CZTSe compound. The two main peaks 196 (197) and 173 (170) are most often discussed as the main attributes of the $Cu_2ZnSnSe_4$ structure [19].

For CZT(S,Se) (Fig. 5 (b)), four peaks were found, of which one at 173 cm-1 corresponds to the CZTSe phase and another peak at 287 cm^{-1} corresponds to CZTS, the other two peaks can be attributed to the CZT(S,Se) phase. The strong shifts of the fundamental vibrational modes can be associated with the replacement of Se atoms with a large diameter by small sulfur atoms. The method of Raman scattering refers to the methods of studying the surface with a penetration depth of 100-150 nm with laser energy higher than 2.2 eV [24]. Therefore, the obtained Raman spectra reflect the state of the surface atoms and the structure of the formed films.

To determine the elemental composition of the films obtained, the EDAX method was used (table 1).

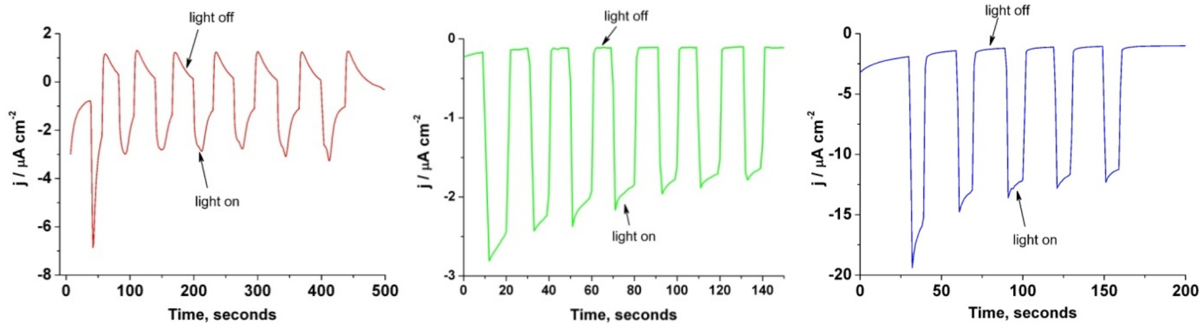
Table 1 - Chemical composition (at.%) of CZTS, CZTSe and CZT(S,Se) thin films

Material	Cu	Zn	Sn	Se	S
CZTS	25.7	11.4	12.4	–	50.3
CZTSe	19.6	10.6	14.6	55.2	–
CZTSSe	13.7	25.98	7.30	1.6	47.5

According to the results of EDX analysis, as a result of sulfurization, a high S/(S+Se) ratio is achieved in films subjected to sulfurization at 500 °C. This ratio remains approximately constant and varies within 0.94 ± 0.02.

Photo electrochemical properties

The photoelectric properties of the obtained materials (CZTSe, CZTS, CZTSSe) were studied using the photoelectrochemical analysis (PEC) method with the Gill AC potentiostat-galvanostat in a three electrode quartz cell, where the working electrode was samples obtained on Mo/glass substrates, the platinum coil served as a counter electrode, a silver chloride electrode (Ag/AgCl, saturated KCl) was used as a reference electrode. Photocurrents were recorded in a solution of 0.1 M sodium sulfate. A halogen lamp (80 mW/cm^2) was used as the light source. The results of the study of photovoltaic properties are presented in Figure 6.



a) CZTSe b) CZTS c) CZTSSe

Figure 6 - Chronoamperometric dependence of the photocurrent of electrodeposited films

The dependence of photocurrent density on time was obtained in the dark / light mode (light off / light on) at a constant potential of -10 mV, which is defined as the stationary potential established between the semiconductor and the electrolyte. The photocurrents of CZTSe films remain constant, while for CZTS they slightly decrease in time and amount to 3 µA/cm^2 and 2-2.5 µA/cm^2, respectively. For the CZT(S,Se)/Mo/glass sample, the photocurrent obtained after sulfurization is higher and amounts to ~ 20 µA/cm^2. Photo corrosion and chemical corrosion are the main problems of semiconductors at PEC, where there is a likelihood of chemical corrosion of the semiconductor surface in the electrolyte. It can be seen from Fig. 6 (b, c) that the photocurrent gradually decreases, and this is probably due to photo-corrosion S^{2-} from the surface of a thin chalcogenide film, since it is more strongly observed on unprotected CZTS photoelectrodes, similar to observations [17]. Whereas for a sample with a CZTSe film (Fig. 6(a)), the photocurrent remains constant for 500 seconds and longer.

For a five component compound, the decrease in photocurrent over time is less noticeable.

The results obtained indicate that a change in the surface and bulk structure of multicomponent chalcogenide films plays a significant role in changing their photoelectrochemical characteristics.

Conclusion

A comparison of the structural and photoelectrochemical characteristics of multicomponent thin-film chalcogenides CZTS, CZTSe, CZT(S,Se) was made. CZTS, CZTSe thin films were obtained by the method of one-step electrodeposition from aqueous electrolytes on Mo/glass substrates with subsequent annealing in air. Freshly precipitated CZTSe films were subjected to sulphurization in sulfur vapor at 550 ° C. It is shown that all obtained films correspond to polycrystalline kesterite. The formation of the corresponding phases of the quaternary and five-component compounds was confirmed. From the fragments of the X-ray fluorescence analysis of the CZT(S,Se) spectrum, it was established that low-intensity peaks can be attributed to the CuS and ZnS phases. Raman spectra confirm the formation of the CZTS, CZTSe, CZT(S,Se) phases and indicate a significant shift of the Raman spectra for CZT(S,Se), which is associated with the partial replacement of selenium atoms with smaller sulfur atoms. The elemental composition of electrodeposited films corresponds to the phases of the compounds. The ratio S/(S+Se) in films subjected to sulphurization at 500 °C varies within 0.94 ± 0.02. The PEC method determined that the photocurrent for the five-component compound CZT(S,Se) is about 5-6 times higher than for the four-component compounds. A directional change in the microstructural parameters and morphology of the CZT(S,Se) films during their manufacture will be necessary to achieve high efficiency in photoelectrochemical application.

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ЭЛКТРОТҰНДЫРЫЛҒАН $Cu_2ZnSn(S,Se)_4$ ҚАБЫҚШАЛАРЫНЫҢ ҚҰРЛЫМЫ МЕН ФОТОЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Cu^{+2}, Zn^{+2}, Sn^{+2}, Se^{+4} немесе S^{+4} иондары бар сулы электролиттерден Мо- қапталған шыныда $Cu_2ZnSnSe_4$ (CZTSe) және Cu_2ZnSnS_4 (CZTS) қабықшаларының бір сатылы электрохимиялық синтезі әзірленді. Электротұндыру үрдісі тұрақты потенциалда орындалды және кейінен 60 минут ішінде 450^{o}C температурасында күйдіру орындалды. Электротұндырылған $Cu_2ZnSnSe_4$ қабаттарын күкірт атмосферасында 60 минут ішінде 500^{o}C -та сульфуризациялау арқылы $Cu_2ZnSn(S_{0,96,}Se_{0,04})_4$ қабықшалары алынды. Алынған қабықшалардың құрлымы мен фазалық құрамы РФА мен Раман спектроскопия әдістерімен расталған. Барлық қабықшалар р-өткізгіштікке ие болғаны PEC әдісімен расталды. Қабықшалардың химиялық құрамының өзгеруі электрофизикалық қасиеттеріне әсер ететіндігі анықталды, ал $Cu_2ZnSn(S,Se)_4$ қабаттарында фотосезімталдығы төрт компонентті қосылыстарға қарағанда 5-6 есе жоғары болды.

Түйін сөздер: электротұндыру, CZTSSe, кестерит, жұқа қабық, фотоэлектрохимия.

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СТРУКТУРА И ФОТОЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА ЭЛЕКТРООСАЖДЕННЫХ ПЛЕНОК $Cu_2ZnSn(S,Se)_4$

Аннотация. Разработан одностадийный электрохимический синтез пленок $Cu_2ZnSnSe_4$ (CZTSe) и Cu_2ZnSnS_4 (CZTS) на стекле, покрытом Mo, из водных электролитов, содержащих одновременно ионы Cu^{+2}, Zn^{+2}, $Sn^{+2,}$, Se^{+4} или $S^{+4.}$ Электроосаждение выполняли при постоянном потенциале с последующим отжигом при температуре 450°C в атмосфере воздуха в течение 60 минут. Пленки $Cu_2ZnSn(S_{0,96,}Se_{0,04})_4$ были получены путем сульфуризации электроосажденных слоев $Cu_2ZnSnSe_4$ в атмосфере серы при 500°C в течение 60 минут. Структура и фазовый состав пленок подтвержден методом РФА и спектроскопии комбинационного рассеяния. Методом PEC подтверждено, что все пленки имели р-проводимость. Установлено, что изменение химического состава пленок влияет на электрофизические свойства, и для слоев $Cu_2ZnSn(S,Se)_4$ фотоотклик оказался в 5-6 раз выше, чем для четрехкомпонентных соединений.

Ключевые слова: Электроосаждение, CZTSSe, кестерит, тонкая пленка, фотоэлектрохимия.

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THE CATALYTICAL OXIDATION OF PROPAN-BUTANE MIXTURE ON THE HYDROGEN AND HYDROGEN CONTENT COMPOUNDS

Abstract. Oxidative conversion of the propane-butane mixture by air into oxygen-containing compositions was studied. It were determined the optimum reaction temperature, contact time, change in the space velocity in the process of partial oxidation of C3-C4 hydrocarbons. The physicochemical studies of the initial and treated catalysts were carried out under experimental conditions. When changing the content of the active component from 1 to 10% on the carrier, it was found that the most optimal is 1% MoCrGa/TC catalyst, on which up to 89.92% of hydrogen is obtained. As a result of varying the composition of the catalyst, the content of the active phase, the ratio of reactants, up to 70% of ethylene was obtained. In addition, in some cases, CH_3OH was obtained, the maximum yield of which is 22%, and also up to 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 is formed on the catalyst surface (corresponding to the Cr^{2+} and Cr^{3+} transition to Cr^{5+}), as well as joint Mo phases with Cr in different valence states, the physical meaning and role of which are to be determined.

Key words: catalysts, propan-butane mixture, natural clay.

Introduction. It requires the creation of large chemical industries on the basis of gas and oil resources to strengthen its economic status concerned to the strategic program of the Republic of Kazakhstan [1-3]. Today Kazakhstan has large reserves of raw materials, which have not been put into production [4-7]. Recently, environmental attention has been focused on reducing their harmful effects by incorporating hydrogen and hydrogen-based additives into fuels used in heat centers as well as for gasoline and diesel fuels. It is known that the use of catalysts for the production of hydrogen and hydrogen-based additives from the alkanes is a progressive and scientifically developed course of research [8-12].

Methods. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. Analysis of the reactants and products was carried out chromatographically with an “Agilent Technologies 6890N” instrument. The catalysts were investigated by X-ray diffraction (XRD), electronic microscopy (EM), infra-red spectroscopy, and their surface area, porosity, and elemental composition were determined [1,5].

Figure 1 shows the effect of temperature on the hydrogen emissions generated by partial oxidation of the propane-butane mixture with the catalysts. It was determined that the yield of H_2 gradually increased as the temperature increased from 623K to 873K.

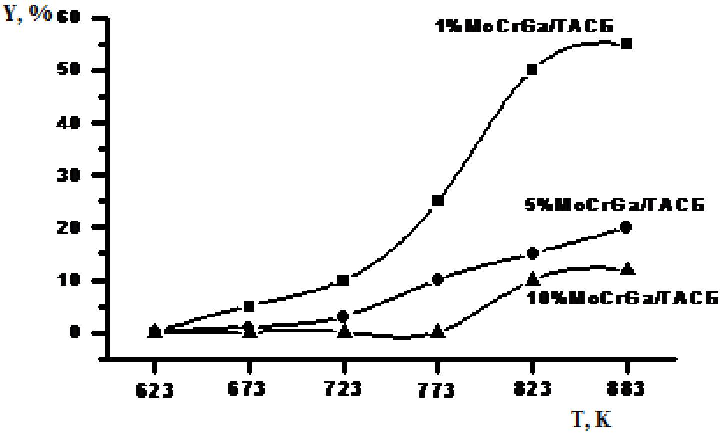

Figure 1 - The effect of temperature on the hydrogen product generated in partial oxidation of propane-butane mixture. Reaction: C_3-C_4:O_2:N_2:Ar=1:1:4:1

As seen from the Figure 2, the change of the active phase between 1 and 10% has a direct impact on the yield of product. It was obtained 89,92% hydrogen from the 1%MoCrGa/NWC three-component catalyst by changing the active phase composition into the supporter.

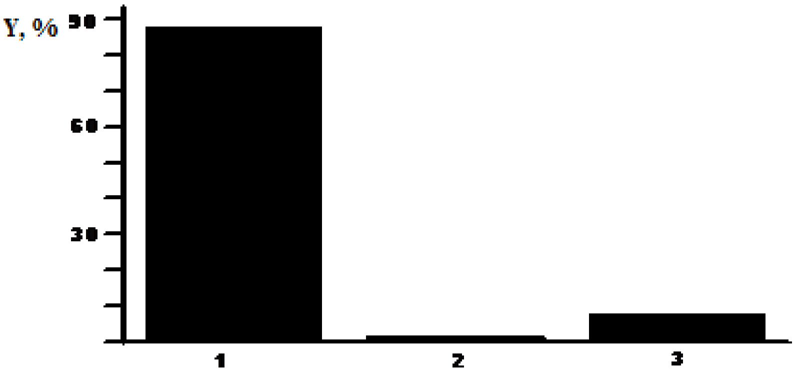

Figure 2 - Influence of active phase composition on hydrogen output. Reaction: C_3-C_4 KC:O_2:N_2:Ar=0,95:1:3,76:0,95; Tp=873K; W=3150 h^{-1};
1–1%MoCrGa/NWC; 2–10% MoCrGa/ NWC; 3-5% MoCrGa/ NWC +ZSM-5+$Al_n(OH)_{3n-1}NO_3$.

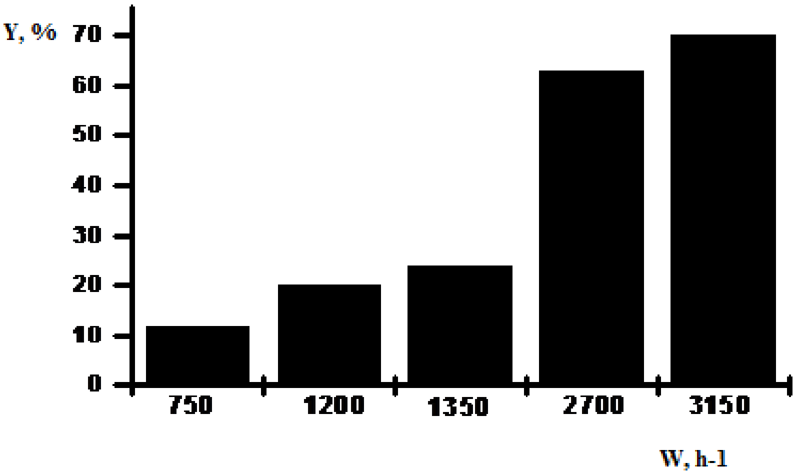

Figure 3 - Influence of volume velocity on the yield of hydrogen in 1%MoCrGa/ NWC catalyst. Reaction: C_3-C_4 KC:O_2:N_2:Ar=0,95:1:3,76:0,95; Tp=823K

The change in 1%MoCrGa/(NWC) of catalyst at 330-15000 h^{-1} speed directly influence the reaction product. The most suitable volume velocity is 3150 hr^{-1} for 1% MoCrGa/NWC catalyst for hydrogen removal 70,0% (Figure 3).

A favorable composition of the process was studied by modifying the starting reactions. It has been determined that by changing O_2 concentration in mixture 89,92 of % hydrogen is formed in 1%MoCrGa/NWC catalyst at a temperature of 873K at a range of 3,8-18,0 %; 71,4% of ethylene is formed in 1% MoCrGa/NWC catalyst at 723K and 450 hr^{-1} of volume velocity, when the reaction mixture is C_3-C_4:O_2:N_2:Ar=5:1:4:5.

Results and discussion. According to the results of the above study, it was found out that the product of the oxidation of propane-butane mixture in the molybdenum, chromium, gallium catalyst placed on the natural white clay has a direct effect on the temperature, reaction mixture, contact time, catalyst composition.

The phase composition and surface area of 1%MoCrGa/NWC catalyst were studied by x-ray amorphous and Brunagoer Emmet-Taylor methods. It has been found that natural white clay is composed of α-quartz, kaolinite and roentgenomorphic composition. In the reaction, the content of raw and processed catalysts corresponds to the natural white clay diffractogram. Due to the dispersion of catalysts, no structural elements corresponding to metals were found. The whole sample consists of α-quartz SiO_2 x-ray amorphous. Cr_2O_3, Cr_3O_{12} structures were observed only during 723K processing. However, the structures corresponding to Ga, Mo are not found in all models. Also, if the surface area of 1% MoCrGa/NWC catalyst is 14,51 m_2/g, hollow volume is 155,53 ml/g then the surface area of 1%MoCrGa/NWC catalyst is 16,80 m_2/g, hollow volume is 303,61 ml/g grows.

According to the results of the electron microscope, the ring-shaped phases Mo_3O_5 and $Mo_{0,42}C_{0,58}$ consist of ring-shaped phases Cr_3O_4, α-Ga_2O_3, Mo_5O_8, γ-MoC in size of 10-20 nm containing the large composition of accumulated thick particles, Ga and MoC mixture in the form of symmetrical reflexes in size of 20 nm of individual particles, CrO, Ga_2O_3, MoO_3 and Mo_2C of thick particle composition of a small aggregate of 10-12nm, particle groups in size of 5-20 nm during the reaction processed at a temperature of 723K on the surface of 1% MoCrGa/NWC catalyst.

In addition to the phase shrinkage, it was determined that the formation of Mo_2C, γ-MoC phases, as well as the change of Mo^{3+} to Mo^{5+} have a positive effect on the growth of hydrogen and ethylene outputs generated during the dehydration of the propane-butane mixture.

Thus, it have been determined the favorable conditions to obtain the appropriate product: 71,4% of ethylene is formed in 1% MoCrGa/NWC catalyst at 723K and 450 hr^{-1} of volume velocity, when the reaction mixture is C_3-C_4:O_2:N_2:Ar=5:1:4:5; 89,92 of % hydrogen is formed in 1%MoCrGa/NWC catalyst at a temperature of 873K and 1350 h^{-1} of volume velocity, when the reaction mixture is C_3-C_4:O_2:N_2:Ar=1:1:4:1. It was studied that oxidation, dehydration and cracking processes are carried out during the research of polyoxide catalysts, which are supported in natural white clay.

Conclusion. Suggested in this research work catalytic reactions can be base for creation of industrial C_3-C_4 mixture utilization process and for production of valuable oxygen-containing compounds.

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ПРОПАН-БУТАН ҚОСПАСЫНЫҢ СУТЕГІ ЖӘНЕ СУТЕКҚҰРАМДАС ҚОСЫЛЫСТАРҒА КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ

Аннотация. Пропан-бутан қоспасын оттек құрамды композициттерге дейін тотықтыру бойынша зерттеулер жүргізілді. Тотығу процесінің оңтайлы температурасы, реакциялық қоспаның бастапқы компоненттерінің коэффициенттері, тасымалдағыштағы белсенді фаза және көлемдік жылдамдық анықталды. Эксперименттік жағдайларда бастапқы және өңделген катализаторлардың физика-химиялық зерттеулері жүргізілді. Белсенді компоненттің құрамын 1%-дан 10%-ға өзгерткен кезде ең оңтайлы катализатор 1% MoCrGa/ТСБ, нәтижесінде сутегінің 89,92%-алынды. Катализатордың құрамын, белсенді фазаның мөлшерін, реагенттердің қатынасын өзгерту нәтижесінде этилен 70%-ға дейін алынған. Сонымен қатар, кейбір жағдайларда CH_3OH алынды, оның максималды шығыны 22%, сондай-ақ 35% метилэтилкетон алынды. Реакция жағдайында катализатордың бетінде жаңа Cr_2O_5 фазасы (Cr^{2+} және Cr^{3+} -ға Cr^{5+} -ке көшу), сондай-ақ әртүрлі валентті Cr-мен бірге Mo-фазалары пайда болатынын ЭМ және РФА зерттеулерінің нәтижесі көрсетті, келешекте физикалық мағынасы мен рөлін анықтау керек.

Түйін сөздер: катализатор, пропан-бутанды қоспа, табиғи сазбалшық

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КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ПРОПАН-БУТАНОВОЙ СМЕСИ НА ВОДОРОД И ВОДОРОДСОДЕРЖАЩИХ СОЕДИНЕНИЙ

Аннотация. Проведены исследования по окислительному превращению пропан-бутановой смеси воздухом в кислородсодержащие композиции. Определены оптимальные температуры процесса, соотношения исходных компонентов реакционной смеси, содержания активной фазы на носителе и объемные скорости. Проведены физико-химические исследования катализаторов исходных и обработанных в условиях эксперимента. При изменении содержания активного компонента от 1 до 10% на носителе установлено, что наиболее оптимальным является 1%MoCrGa/ТГ катализатор, на котором получено до 89,92% водорода. В результате варьирования состава катализатора, содержания активной фазы, соотношения реагирующих компонентов было получено до 70% этилена. Кроме того, в ряде случаев получен CH_3OH, максимальный выход которого составляет 22%, а также до 35% метилэтилкетона. В результате ЭМ и РФА исследований показано, что в реакционных условиях на поверхности катализаторов образуется новая фаза Cr_2O_5 (соответствует переходу Cr^{2+} и Cr^{3+} в Cr^{5+}), а также совместные фазы Mo с Cr в различных валентных состояниях, физический смысл и роль которых предстоит определить.

Ключевые слова: катализатор, пропан-бутановая смесь, природная глина

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SYNTHESIS AND ANTI-MICROBIAL ACTIVITY OF N'-(2-HYDROXY-5-NITROBENZYLIDENE) ISONICOTINOHYDRAZIDE

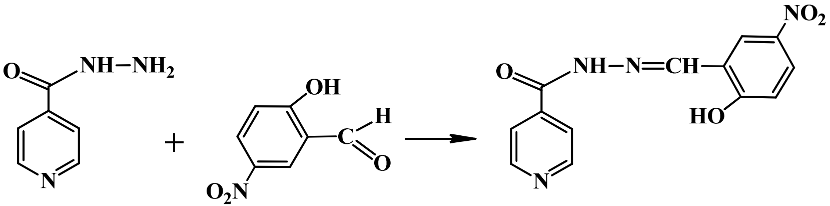
Abstract. The paper presents data on the synthesis, structure and bioactivity of N '- (2-hydroxy-5-nitrobenzylidene) isonicotinohydrazide based on isonicotinic acid hydrazide. The structure of the new hydrazone was studied by ^{1}H and ^{13}C NMR spectroscopy, as well as two-dimensional COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C) spectra. The values of chemical shifts, multiplicity and integral intensity of ^{1}H and ^{13}C signals in one-dimensional NMR spectra are determined. Using spectra in COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C) formats, homo- and heteronuclear interactions have been established, confirming the structure of new isonicotinic acid derivatives. Studies of the synthesized compound for antimicrobial activity against drug-sensitive museum strains of bacteria and fungi have been carried out. According to the results of bioassays, it was shown that a new hydrazone derivative of isonicotinic acid in a dose of 1 μg has a weak potential for antimicrobial activity, and the diameters of growth inhibition zones for *in vitro* test cultures averaged 12 ± 1.0 mm.

Key words: isonicotinic acid, hydrazones, chemical modification, antimicrobial activity.

Isonicotinic acid hydrazide (INH) is today one of the main widely used and fairly inexpensive tuberculostatics, however, it still does not meet the requirements for modern drugs in many clinical settings. On the basis of INH, a large number of various derivatives have been synthesized with a wide variation of the antituberculosis activity and toxicity of the compounds [1-3]. Thus, in 1951, in the Soviet Union, a method was developed for the synthesis of the drug ftivazid by the interaction of isonicotinic acid hydrazide with vanillin [4]. Ftivazide, due to its low toxicity and good individual tolerance, and currently occupies a leading place in the treatment of various forms of tuberculosis [4]. In clinical practice, other isonicotinic acid hydrazones, such as methazide, saluzid, and larusan, are widely used today. However, difficulties in the treatment of tuberculosis are associated with the development of drug resistance of Mycobacterium tuberculosis and, as a result, the drug loses its therapeutic effect. In this regard, the synthesis of new derivatives of isonicotinic acid hydrazones continues, and the search for new highly effective anti-TB drugs is still an urgent task [5].

In addition, it is known that hydrazones are generally widely used in synthetic chemistry due to the simple method of their production [6] and various biological activities besides anti-tuberculosis action (plant growth regulators, herbicides, fungicides, antioxidants) [7, 8]. Continuing research on the modification of isonicotinic hydrazide, it seemed interesting to obtain new hydrazones based on INH, containing additional pharmacophoric groups.

The purpose of this work was to study the reaction of the interaction of isonicotinic acid hydrazide **(1)** with 2-hydroxy-5-nitrobenzaldehyde **(2)**. The synthesis of the new N'-(2-hydroxy-5-nitrobenzylidene)isonicotinohydrazide **(3)** was carried out in ethyl alcohol at 50-60 °C for 4 hours.



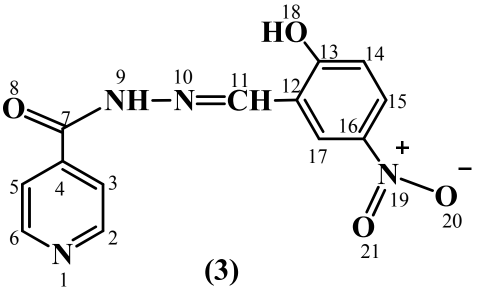
(1) **(2)** **(3)**

The reaction product **(3)** is a well-crystallized substance, soluble in many organic solvents, the yield of the compound is 92.0%.

The composition and structure of N'-(2-hydroxy-5-nitrobenzylidene)-isonicotinohydrazide **(3)** are confirmed by the data of IR-, ^{1}H- and ^{13}C- NMR spectroscopy, as well as two-dimensional spectra of COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C).

In the IR spectrum of compound **(3)** there is an intense absorption band in the region of 3028–3094 cm^{-1}, corresponding to valence N–H vibrations, in the region of 3016–3049 cm^{-1} - to valence C–H vibrations of the pyridine ring, 1870–1955 cm^{-1} - the overtones of the pyridine ring, 1642-1651 cm^{-1} - the vibrations of the C=O bond, the vibrations of the C=N bond are recorded in the region of 1543 cm^{-1}.

The ^{1}H NMR spectrum of the compound **(3)** is characterized by the presence in the aromatic region at 7.05 ppm doublet with an intensity of 1H with ^{3}J 9.2 Hz of the atom H^{14} of the benzene nucleus. The H^{15} proton, adjacent to H^{14}, as a result of spin-spins splitting by a neighbor, also manifests itself as a doublet signal at 8.11 ppm with an integrated intensity of 1H with ^{3}J 8.6, characteristic of aromatic compounds. H^{17} proton of the benzene nucleus, not having proton containing neighbors, is manifested by a singlet at 8.69 ppm with an intensity of 1H. Equivalent protons of the pyridine ring H$^{2.6}$ and H$^{3.5}$ resonated with doublet signals with an intensity of two protons at 8.75 (^{3}J 5.5 Hz) and 7.80 (^{3}J 5.5 Hz) ppm respectively. The proton H^{11}, which is unable to interact with other protons through three bonds, respectively, manifested itself in the form of a singlet signal at 8.54 ppm with an integrated intensity of 1H. The protons of the hydroxyl group and the amide bond manifested themselves in the form of broadened singlets with an integral 1H each in the weakest field of the spectrum at 12.55 and 12.37 ppm respectively.



(3)

In the ^{13}C NMR spectrum of N'-(2-hydroxy-5-nitrobenzylidene)-isonicotinohydrazide **(3)**, signals of the aromatic ring are observed at 117.60 (C^{14}), 120.51 (C^{12}), 127.35 (C^{15}), 140.34 (C^{16}), 145.48 (C^{17}) и 162.12 (C^{13}) ppm. The carbon atoms of the pyridine fragment resonated at 122.05 (C^{3,5}), 150.89 (C^{2,6}) и 140.45 (C^{4}) ppm. Chemical shift signal at 123.91 ppm corresponds to the carbon atom bound by a double bond with the nitrogen atom. In the field of a weak field at 163.09 ppm marked signal carbonyl atom C^{7}. The structure of compound **(3)** was also confirmed by the methods of two-dimensional NMR spectroscopy COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature. The observed correlations in the molecule **(3)** are shown in Figures 1 and 2. In the COSY (^{1}H-^{1}H) spectra of the compound **(3)** spin-spin correlations are observed through three proton bonds of the neighboring methylene groups H^{2}-H^{3} and H^{5}-H^{6} of the pyridine ring cross-peaks with coordinates at 8.73, 7.80 and 7.78, 8.75. Coordinates 8.10, 7.05 and 7.04, 8.11 correspond to the homolytic interaction through three bonds of the neighboring aromatic protons H^{14,15}. Heteronuclear interactions of protons with carbon atoms through one bond were established using HMQC (^{1}H-^{13}C) spectroscopy for all pairs present in the compounds: H^{14}-C^{14} (7.03, 117.61), H^{3,5}-C^{3,5} (7.78, 122.07), H^{15}-C^{15} (8.09, 127.25), H^{11}-C^{11} (8.52, 123.89), H^{17}-C^{17} (8.68, 145.45), H^{2,6}-C^{2,6} (8.73, 150.85).

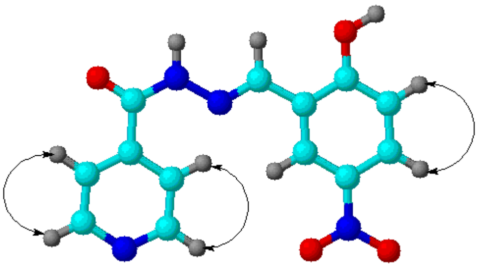


Figure 1 - Scheme of COSY (^{1}H-^{1}H) correlations compounds **(3)**

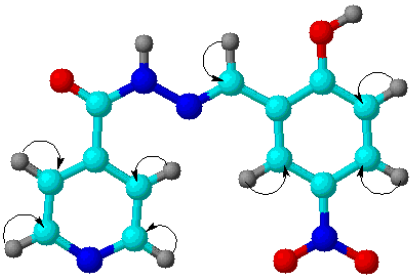


Figure 2 - Scheme of HMQC (^{1}H-^{13}C) correlations of compound **(3)**

In order to study the biological activity of the synthesized new derivative of isonicotinic acid hydrazide, a bioscreening was conducted for the presence of antimicrobial activity against drug-sensitive museum strains of bacteria and fungi. Antimicrobial activity was assessed by the minimum inhibitory concentration (1 µg), and the concentration of reference drugs was 1 mg.

The sensitivity of bacteria *S. aureus, Bacillus subtilis 6633, E. Coli, Ps was determined. Aerugiosa ATCC 9027* and the yeast fungus *Candida albicans* to the test sample **(3)** by the diffusion method using discs, solvent 96% ethyl alcohol. The antibiotic benzylpenicillin sodium, gentamicin and the third-generation cephalosporin antibiotic, ceftriaxone, and nystatin, antifungal activity, have been selected as standards for evaluating antibacterial activity. Test cultures were sown using the lawn method on nutrient media: JSA, Endo medium, nutrient agar and Saburo medium. Then the Petri dishes were incubated for 24 hours at 28-37 °C.

Antimicrobial activity of the samples was assessed by the diameter of the zones of growth inhibition of test strains (mm). The diameters of the zones are less than 10 mm and continuous growth in the cup was evaluated as the absence of antimicrobial activity, 10-15 mm – weak activity, 15-20 mm – moderately pronounced activity, more than 20 mm – pronounced. The main sample was tested in three parallel experiments. Statistical processing was performed by parametric statistics with the calculation of the arithmetic mean and standard error. The results of the identified growth delays on the media are shown in the table.

Table – Antimicrobial activity of N'-(2-hydroxy-5-nitrobenzylidene)-isonicotinohydrazide. Diameters of growth inhibition of test strains, mm

Test substances	S.aureus	B.subtilis 6633	E.coli	Ps.aerugiosa ATCC 9027	C.albicans
N'-(2-hydroxy-5-nitrobenzylidene)-isonicotinohydrazide (3)	12±1.0	13±1.0	13±1.0	11±1.0	12±1.0
Ethyl alcohol 96%	9±1.0	9±1.0	9±1.0	9±1.0	9±1.0
Benzylpenicillin sodium salt	15±1.0	-	16±1.0	12±1.0	-
Gentamicin	22±1.0	30±1.0	31±1.0	30±1.0	-
Ceftriaxone	30±1.0	30±1.0	29±1.0	22±1.0	-
Nystatin	-	-	-	-	25±1.0

These pharmacological studies have shown that N'-(2-hydroxy-5-nitrobenzylidene) isonicotinhydrazide **(3)** at a dose of 1 µg has a weak antimicrobial activity potential, since the diameters of the in vitro growth inhibition zones for test cultures averaged 12 ± 1.0 mm. Chemical modification of derivatives of isonicotinic acid hydrazide can ensure the production of new biologically active substances with antimicrobial activity.

Experimental part

The ^{1}H and ^{13}C NMR spectra of the compounds **(3)** were recorded on a JNN-ECA 400 spectrometer from Jeol (Japan) in a DMSO-d_6 solution relative to the internal TMS standard with a frequency of 400 and 100 MHz on the ^{1}H and ^{13}C cores, respectively. IR spectra were taken on a Cary 600 Series FTIR spectrometer manufactured by Agilent Technologies (USA) using a single reflection attachment on a

Gladiatr diamond manufactured by PIKE (USA). All measurements were carried out at a resolution of 4.0 cm^{-1}, the number of scans was 40. Melting points were determined on an OptiMelt instrument. TLC analysis was performed on Silufol UV-254 plates, the manifestation of iodine vapor. Biological tests of samples of the synthesized compounds for antibacterial and antifungal activity were carried out at the base of the Department of Microbiology of Karaganda State Medical University.

N'-(2-hydroxy-5-nitrobenzylidene) isonicotinohydrazide (3). To a mix-ture of 0.7 g (0.004 mol) of isonicotinic acid hydrazide in 10 ml of ethanol, 0.8 g (0.004 mol) of 2-hydroxy-5-nitrobenzaldehyde dissolved in 10 ml of ethanol was added with stirring at room temperature. Then the reaction mixture was stirred for 4 hours at a temperature of 50-60 °C under reflux. The completion of the reaction was monitored by TLC. The solution was cooled, the precipitated precipitate was filtered. Received 1.3 g (92,0%) of the product (**3**) yellow with a melting point of 285-287 °C. Found, %: C 54.65; H 3.31; N 19.63. Calculated, %: 54.54; H 3.49; N 19.58. $C_{13}H_{10}N_4O_4$. NMR ^{1}H (DMSO-d_6), δ, ppm: 7.05 d (1H, H^{14}, $^{3}J_{HH}$ 9.2 Hz), 8.11 d (1H, H^{15}, $^{3}J_{HH}$ 8.6 Hz), 8.69 c (1H, H^{17}), 8.75 d (2H, $H^{2.6}$, $^{3}J_{HH}$ 5.5 Hz), 7.80 d (2H, $H^{3,5}$, $^{3}J_{HH}$ 5.5 Hz), 8.54 c (1H, H^{11}), 12.15 br. with (1H, OH), 12.37 br. with (1H). NMR ^{13}C (DMSO-d_6), δ, ppm: 117.60 (C^{14}), 120.51 (C^{12}), 127.35 (C^{15}), 140.34 (C^{16}), 145.48 (C^{17}), 162.12 (C^{13}), 122.05 ($C^{3,5}$), 150.89 ($C^{2,6}$), 140.45 (C^{4}), 123.91 (N=CH), 163.09 (C=O).

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N'-(2-ГИДРОКСИ-5-НИТРОБЕНЗИЛИДЕН)ИЗОНИКОТИНО-ГИДРАЗИДІНІҢ СИНТЕЗІ МЕН МИКРОБҚА ҚАРСЫ БЕЛСЕНДІЛІГІ

Аннотация. Жұмыста изоникотин қышқылы гидразидінің негізінде алынған N'-(2-гидрокси-5-нитробензилден) изоникотиногидразидінің синтезі, құрылысы және био-белсенділігі бойынша деректер келтірілген. Жаңа гидразонның құрылысы ЯМР ^{1}H- және ^{13}C-спектроскопия әдістерімен, сондай-ақ COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) екіөлшемді спектрлерінің деректерімен зерттелген. Бірөлшемді ЯМР спектрлерінде ^{1}H және ^{13}C сигналдардың интегралдық қарқындылығы, мультиплеттілігі және химиялық ығысу мәндері анықталды. COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) форматтарындағы спектрлер көмегімен изоникотин қышқылының жаңа туындысының құрылымын растайтын гомо- және гетероядролық өзара әрекеттесулері орнатылды. Бактериялар мен зеңдердің дәрілік-сезімтал музей штаммдарына қатысты микробқа қарсы белсенділікке синтезделген қосылыстарға зерттеулер жүргізілді. Биосынау нәтижелері бойынша 1 мкг дозадағы изоникотин қышқылының жаңа гидразондық туындысы микробқа қарсы белсенділіктің әлсіз шамасына ие, *in vitro* тестілік дақылдардың өсуін кідірту аймағының диаметрлерінің орташа есеппен 12±1,0 мм құрайтыны көрсетілген.

Түйін сөздер: изоникотин қышқылының гидразиді, гидразондар, химиялық түрлендіру, микробқа қарсы белсенділік.

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СИНТЕЗ И ПРОТИВОМИКРОБНАЯ АКТИВНОСТЬ N'-(2-ГИДРОКСИ-5-НИТРОБЕНЗИЛИДЕН) ИЗОНИКОТИНОГИДРАЗИДА

Аннотация. В работе приведены данные по синтезу, строению и биоактивности N'-(2-гидрокси-5-нитробензилиден)изоникотиногидразида, полученного на основе гидразида изоникотиновой кислоты. Строение нового гидразона исследовано методами ЯМР ^{1}H- и ^{13}C-спектроскопии, а также данными двумерных спектров COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C). Определены значения химических сдвигов, мультиплетность и интегральная интенсивность сигналов ^{1}H и ^{13}C в одномерных спектрах ЯМР. С помощью спектров в форматах COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C) установлены гомо- и гетероядерные взаимодействия, подтверждающие структуру нового производного изоникотиновой кислоты. Проведены исследования синтезированного соединения на антимикробную активность в отношении лекарственно-чувствительных музейных штаммов бактерий и грибов. По результатам биоиспытаний показано, что новое гидразоновое производное изоникотиновой кислоты в дозе 1 мкг обладает слабым потенциалом противомикробной активности, диаметры зон задержки роста тестовых культур *in vitro* в среднем составляют 12±1,0 мм.

Ключевые слова: гидразиды изоникотиновой кислоты, гидразоны, химическая модификация, антимикробная активность.

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POLYVINYLPYRROLIDONE-FERROCYANIDE CATALYSTS FOR CYCLOHEXANE OXIDATION

Abstract. Catalysts for cyclohexane oxidation are developed. Polymer-ferrocyanide catalysts fixed on various mineral supports are prepared by the adsorption method. Properties of synthesized catalysts are studied in cyclohexane oxidation with hydrogen peroxide. Reaction is carried out under mild conditions: at 40 °C and atmospheric pressure. All prepared polymer-metal catalysts supported on inorganic substrates are active in the process of cyclohexane oxidation.

Polymer-metal complex fixed on alumosilicate Siral-20 shows 14% more activity than the system fixed on Siral-40. However selectivity of catalyst 5% $K_4[Fe(CN)_6]$ -PVP/Siral-40 is much higher. Under equal conditions, its selectivity for cyclohexanone is 83.4%, whereas selectivity for cyclohexanone of 5% $K_4[Fe(CN)_6]$-PVP/Siral-20 is only 61.7%. Catalyst fixed on γ-Al_2O_3 demonstrates less activity (25.5%) and selectivity than aluminum silicates (cyclohexanone : cyclohexanol ratio is 1.2 : 1). At the same time, with a sufficiently high selectivity for cyclohexanone (70.4%), 5% $K_4[Fe(CN)_6]$-PVP/SiO_2 shows the conversion which is only 17.2%.

The effect of acidic properties of carrier surface on selectivity is studied. It is established that the nature of support (acidic properties of surface) has a significant effect on activity and selectivity of synthesized catalysts.

Polyvinylpyrrolidone-ferrocyanide complex 5%$K_4[Fe(CN)_6]$-PVP/Siral-40 exhibits the best catalytic properties. The conversion of cyclohexane is 42.9%, selectivity for cyclohexanone is 83.4% and cyclohexanone : cyclohexanol ratio is 5: 1.

Key words: polyvinylpyrrolidone, ferrocyanide catalyst, cyclohexane, oxidation, cyclohexanol, cyclohexanone, selectivity.

Introduction

Liquid phase cyclohexane oxidation is an industrially significant process [1,2]. Partial cyclohexane oxidation products - cyclohexanol and cyclohexanone - are used to produce caprolactam, adipic acid, polyamide fibers, nylon-6 and nylon-66 [3,4].

In industry cyclohexane is oxidized by atmospheric oxygen over homogeneous catalytic systems at high temperatures and pressures using toxic solvents. Cobalt, copper, and manganese salts are used as catalysts [5]. At temperatures above 423 K and oxygen pressure up to 3.0 MPa conversion of cyclohexane is 4-15%, selectivity for the sum of cyclohexanone and cyclohexanol is 80–85% [6]. It is quite difficult to carry out reaction of cyclohexane oxidation selectively to cyclohexanol and cyclohexanone which are intermediate products [7-9] of the process.

Selectivity of cyclohexanol and cyclohexanone formation decreases as the degree of initial substance conversion into products rises, therefore in industrial processes in order to increase selectivity it is required to strictly control conversion. In this regard, increasing selectivity of cyclohexanol and cyclohexanone formation with increase in conversion of cyclohexane is a very important challenges of catalysis [10,11].

The problem of saturated hydrocarbons oxidation is associated with high energy consumption for C – H and C – C bonds breaking. In nature reactions of various hydrocarbons oxidation easily proceed with participation of enzymes capable to oxidize with high activity and selectivity non-activated C – H bonds of hydrocarbons [12–15]. In natural oxygenates hem-iron complex of protoporphyrin plays the role of active center. The iron-porphyrin complex is similar to the complex found in oxygen carriers, hemoglobin and myoglobin, as well as in catalase and peroxidase enzymes.

The increased catalytic activity and selectivity of enzymes initiated research aimed on the development of highly efficient catalysts that act like biocatalysts [16-18].

Polymer-metal complexes exhibit high activity and selectivity in oxidation processes. A very promising is use of synthetic nitrogen-containing polymers, which easily form complexes with metal ions, to create catalytic systems [19]. To increase stability with repeated use of catalytic systems, polymer-metal complexes are applied on organic or inorganic supports [20, 21]. Such systems in many cases combine the advantages of both homogeneous and heterogeneous catalysts [22].

Despite the good catalytic properties of polymer-metal complexes on inorganic supports in various processes of organic synthesis, there are very few studies on their characteristics and use in cycloalkane oxidation reactions. Therefore development of new heterogeneous catalysts based on soluble polymer-metal complexes is of great interest for the processes of cyclohexane oxidation.

To create catalytic systems it is preferable to use nitrogen-containing polymers that easily form complexes with metal ions. One of them is water and ethanol soluble polymer of N-vinylpyrrolidone - polyvinylpyrrolidone (PVP). PVP is highly hydrophilic, has a clear tendency to form complexes and good adhesive properties [23, 24]. Among the important properties of this polymer is its non-toxicity.

Catalytic activity of polyvinylpyrrolidone-ferrocyanide complexes fixed on inorganic supports is investigated in the present work. The effect of acidic properties of carrier surface on selectivity of cyclohexane oxidation is studied.

Methods

Polymer-ferrocyanide catalysts were prepared by adsorption method based by deposition of 5% of the active phase on substrate mass. Alumosilicates (Siral-40 with content of SiO_2 40% and Siral-20 with SiO_2 content 20%), SiO_2 and γ-Al_2O_3 were used as carriers. Polyvinylpyrrolidone with a molecular weight of 15,000 was used as a macromolecular modifier.

To assess the effectiveness of poly-N-vinylpyrrolidone-ferrocyanide catalyst in oxidation reaction twice distilled chemically pure cyclohexane was used. Purity of substrate was checked by method of chromatography and according to the refraction index. Concentration of substrate in the experiments was $2.7 \cdot 10^{-3}$ mole/l. 40% solution of hydrogen peroxide was used as oxidizing agent. As a solvent it was used twice distilled chemically pure acetonitrile.

An aqueous solution of polyvinylpyrrolidone containing 0.0522 g of polymer in 5 ml of water was added to the aqueous suspension of carrier (0.5 g of oxide or aluminosilicate in 5 ml of water) at room temperature with constant stirring. Mixture was stirred by magnetic stirrer for 2 hours, after that water solution of potassium ferrocyanide (0.1728 g of salt in 5 ml of water) was added. The resulting system was vigorously stirred for 3 hours, and then left in the mother liquor for 10 hours. The precipitate was washed with a 10-fold volume of water, dried and stored in air at room temperature.

Cyclohexane oxidation was carried out in a laboratory unit (Fig. 1) under mild conditions: at 40 °C and atmospheric pressure.

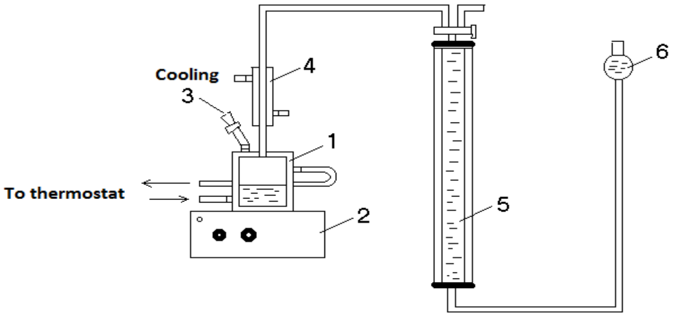


Figure 1 - Volumetric oxidation unit: 1 – thermostatic reactor, 2 – magnetic stirrer, 3 – oxidizer dosing device, 4 – cooler, 5 – measuring burette, 6 – equalizer

A portion of catalyst (0.03 g) was introduced into the reaction vessel with 1.2 ml of acetonitrile. Next, cyclohexane (0.3 ml) and hydrogen peroxide were introduced in the form of 30% aqueous solution, taken in threefold excess with respect to substrate. The reaction mixture was stirred with magnetic stirrer. Oxidation was carried out at 313 K and atmospheric pressure. Reaction mixture was analyzed chromatography after certain periods of time. The amount of released oxygen was determined by volumetric method.

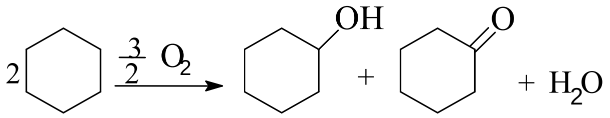
Cyclohexane and products of its oxidation were analyzed by LHM-80M chromatograph with flame ionization detector in isothermal mode. Stainless steel column with length of 3 m and internal diameter of 3 mm was filled with N/W-DMCS chromaton with active phases of 15% Apiezon-L and 3% Carbowax-20M.

Results and discussion

Synthesized catalysts were studied in reaction of cyclohexane oxidation with hydrogen peroxide. Cyclohexane oxidation is carried out according to the scheme below. Oxygen, which is formed during decomposition of H_2O_2, is emitted as a gas, and a part of it is consumed for oxidation of cyclohexane:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \xrightarrow{Cyclohexane} Oxidation\ products$$

Formation of oxygen-containing compounds – cyclohexanol (-ol) and cyclohexanone (-one) takes place according to reaction:



Calculated amount of oxygen required for oxidation of 1 mole of cyclohexane is 0.75 mole.

The results of cyclohexane oxidation on synthesized systems are presented in Table 1.

Table 1 - Yield of cyclohexane oxidation* with H_2O_2 products on catalysts 5% $K_4[Fe(CN)_6]$ -PVP/support

Catalysts	Reaction products, %		Conversion, %	Selectivity,%	
	-ol	-one		-ol	-one
5% K_4 $[Fe(CN)_6]$-PVP/Siral-40	35,8	7,1	42,9	83,4	16,6
5% K_4 $[Fe(CN)_6]$- PVP /Siral-20	30,9	19,2	50,1	61,7	38,3
5% K_4 $[Fe(CN)_6]$- PVP /γ-Al_2O_3	13,7	11,8	25,5	54,9	45,1
5% K_4 $[Fe(CN)_6]$- PVP /SiO_2	12,1	5,1	17,2	70,4	29,6

* Reaction conditions: solvent – acetonitrile, T = 313K, P = 1 atm.

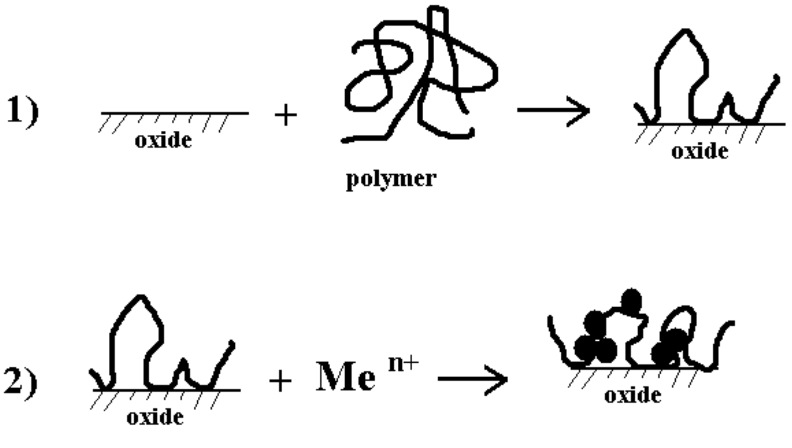


Figure 2 - Scheme of supported polymer-metal complex formation

As can be seen from the data in table, despite the fact that the polymer-metal complex fixed on Siral-20 shows 14% more activity than the system fixed on Siral-40, selectivity of the latter is much higher. Thus, on 5% $K_4[Fe(CN)_6]$ -PVP/Siral-40 catalyst, selectivity for cyclohexanone is 83.4%, whereas for polymer-metal complex fixed on Siral-20 it is only 61.7%. Catalyst supported by γ-Al_2O_3 shows less activity (25.5%) and selectivity than aluminum silicates (cyclohexanone : cyclohexanol ratio is 1.2 : 1). At the same time, with a sufficiently high selectivity for cyclohexanone (70.4%) on 5% $K_4[Fe(CN)_6]$ -PVP/SiO_2, conversion is only 17.2%.

Apparently, high selectivity for aldehyde of the process on catalyst supported on Siral-40 is associated with formation of active centers with participation of polymer ligands that contribute to the specific orientation of substrate (Fig. 2), possibly due to the hydrophobic interaction of cyclohexane with macromolecular chains of PVP (“hydrophobic pocket” in metal-enzymes).

It can be stated that the strength of polymer-carrier bond is determined by high donor capacity of nitrogen atom in polymer structure and by cooperative nature of polymer chain segments interaction with the carrier. Degree of acidity of the surface of carrier plays an important role in adsorption of PVP, since this polymer has a nitrogen-containing functional group capable of interacting with acid sites. According to traditional concepts, aluminosilicate has the greatest degree of acidity, and, therefore, a stronger bond PVP - adsorbent forms on this support. As is known, the concept of acid-base bond on the surface of mineral carriers is due to existence of Lewis and Brønsted acid-base centers. These centers serve to adsorb the molecules of various adsorbates. Irreversible adsorption of polymers takes place in the phase of inorganic carrier, which is very important for formation of strongly bonded polymer-metal complexes. In addition, Siral-40 has higher specific surface area (420 m^2/g) in comparison with other carriers.

Conclusions

New catalysts based on polymer-ferrocyanide complexes fixed on mineral supports have been developed for the process of cyclohexane oxidation with hydrogen peroxide. It was established that all prepared polymer-metal catalysts supported on inorganic substrates are active in cyclohexane oxidation.

Like biomimetic systems, these catalysts exhibit high activity and selectivity in cyclohexane oxidation under mild conditions. The nature of support affects activity and selectivity of synthesized catalysts. It was established that the acidic properties of the carriers’ surface significantly affect selectivity of oxidation process.

The most selective for cyclohexanone is polyvinylpyrrolidone-ferrocyanide complex fixed on aluminosilicate with 40% of SiO_2 (conversion is 42.9%, cyclohexanone : cyclohexanol ratio is 5: 1).

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ФЕРРОЦИАНИДТІ ПОЛИВИНИЛПИРРОЛИДОН-КАТАЛИЗАТОРЛАРЫНЫҢ ЦИКЛОГЕКСАНДА ТОТЫҒУЫ

Аннотация. Циклогександы тотықтыруға арналған катализаторлар дайындалды. Әртүрлі минералды полимерферроцианидті тасымалдағыштарға бекітілген катализаторлар адсорбциялық әдіспен дайындалды. Синтезделген катализаторлар циклогексанның сутегі қос тотығымен тотықтыру реакцияларында зерттелді. Тотықтыру жұмсақ жағдайда (шарттарда), яғни 40^0С-та және атмосферлік қысымда жүргізілді. Нәтижесінде барлық дайындалған полимерметалды катализаторлардың (бейорганикалық тасымалдағыштарда) циклогексанның тотығу процесінде белсенділігі артатыны анықталды.

Siral-40 тасымалдағышында дайындалған катализаторға қарағанда Siral-20 алюмосиликатында дайындалған полимерметалдық кешендердің белсенділігі 14%-ға жоғары 5% $K_4[Fe(CN)_6]$-ПВПД/Siral-40

катализаторының циклогексан бойынша селективтілігі айтарлықтай жоғары. Себебі 5% $K_4[Fe(CN)_6]$-ПВПД/Siral-20-да циклогексан бойынша селективтілік 61,7% тең болғанда сәйкесінше осы жағдайларда (Siral-40 катализаторында) селективтілік 83,4% құрайды. γ- Al_2O_3-та дайындалған катализаторлардың белсенділігі алюмосиликаттарға (25,5%) қарағанда төмен (ОН:ОЛ=1,2:1). Осы уақытта 5% $K_4[Fe(CN)_6]$-ПВПД/SiO_2

Катализаторында циклогексанның селективтілігі (70,4%) жоғары, конверсия 17,2% құрайды. Тасымалдағыш бетінің қышқылдық қасиетінің процесс селективтілігіне әсері зерттелді. Нәтижесінде тасымалдағыш табиғатының (бетінің қышқылдық қасиеті) синтезделген катализаторлар белсенділігі мен селективтілігіне айтарлықтай әсер ететіндігі анықталды. $K_4[Fe(CN)_6]$-ПВПД/Siral-40 поливинилпирролидон – ферроцианидті кешен өте жоғары каталитикалық қасиет көрсетеді. Циклогексанның конверсиясы 42,9%, ОН:ОЛ=5:1 арақатынасында циклогексанның селективтілігі 83,4% тең.

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IMPROVEMENT OF PERFORMANCE PROPERTIES OF DIESEL FUELS WITH MULTIFUNCTIONAL ADDITIVE

Abstract. The article presents research materials on the evaluation of coagulants properties for growth of resins and oxidation products dissolved in diesel fuel. Micrographs of fuel samples after sulfuric acid attack are given. The evaluation and the research results of alkali attack on the fuel are presented. As a result of aqueous carbamide solution attack on the fuel, the ability of aggregation of resins practically dissolved in diesel fuel was established. The research results of combined compositions of reagents are given. The author notes that combination of sulfuric acid and aqueous carbamide solution when added to diesel fuel allows reduce the content of existent resins by half, while the fuel acidity is reduced by 13%. The article also reveals the patterns of changes in the content of existent resins in the fuel from the duration of sedimentation at different combinations of coagulant compositions. According to the research results, it was established that among the considered agents, the greatest effect of the coagulation process of dissolved impurities in the fuel is achieved by its interaction with the aqueous carbamide solution and sulfuric acid.

Key words: diesel fuel, resins, coagulation, physicochemical parameters, sulfuric acid, alkali, carbamide, sedimentation, removal.

Introduction. Diesel fuels are one of the most popular petroleum products used in agricultural machinery. Composition, properties and quality of diesel fuels used in engines of tractors and automobiles largely determine the resource and reliability of components and parts of fuel equipment and cylinder-piston group.

The reliability of work of tractors, combines and automobiles largely depends on the quality of the used diesel fuel, its performance properties.

Main part. Analysis of fuels stored in oil stores and used in agricultural enterprises showed [1] that fuels purchased from commercial structures from “wheels” in 40-60% of cases had a deviation from the standard values for fractional composition, low-temperature, anti-wear, lubricating properties, content of sulfur and existent resins [2].

One of the problems of poor quality and unsatisfactory condition of diesel fuel used in tractors, automobiles and combines are their storage and transportation conditions.

As is well known, among contaminants present in diesel fuel, besides mechanical impurities and free water, easily removed by physical cleaning methods, it contains dissolved resins, asphaltenes, oxidation products, sulfur, which are practically impossible to remove [1-3].

The main difficulty of removal consists in the absence of means of cleaning the fuel from inclusions of dispersed composition less than 0.1-0.5 microns.

Resins present in fuels and sulfur do not always negatively characterize the quality of the fuel, as they are to a certain extent “lubricating components” [2, 4-7].

On the other hand, increased content of resins, sulfur, and heavy fractions in diesel fuel when it is burned in a cylinder-piston group can cause formation of lacquer and increase in wear of parts of the cylinder-piston group. In addition, the above components of the diesel fuel adversely affect the economic performance of the engine and exhaust pollution[8-13].

It is possible to remove dissolved impurities from the fuel by filters, centrifuges, separators only by enlarging their dispersion composition, while it is necessary to use physical and chemical methods of cleaning [6-7].

To select and evaluate the possibility of removal of dissolved impurities, several pretreatment methods of the fuel with coagulants were considered, in particular sulfuric acid, alkali and carbamide attack on the fuel [3, 14-21].

Analysis of the fuel under a microscope with magnification K_{gr} = 110 times shows that there are no inclusions in the fuel with existent resin content of 60 mg/100 cm^3 and mass fraction of sulfur of 0.5% or more.

The following reagents were used to enlarge the dissolved impurities:

1. Sulfuric acid percentagewise to the fuel 0.1-0.5%.
2. Calcined soda solution in water in the ratio 1:5, 1:3, 1:1.
3. Aqueous carbamide solution in the ratio 1:1.

And also their different combinations:

- acid attack, followed by the aqueous carbamide solution attack;
- acid attack, followed by the alkali and aqueous carbamide solution attack;
- alkali attack, followed by the aqueous carbamide solution attack.

In accordance with the research methods, sulfuric acid was alternately added percentagewise 0.1; 0.2; 0.3; 0.4; 0.5% to the diesel fuel with the content of the existent resins 60 mg/100 cm^3 and sulfur content, 0.5 mass %.

The fuel temperature was 20ºC. The mixture was mixed for 0.5 hours. The coagulation process was examined under a microscope and micrographs were taken. The results of the examination are presented in Figure 1 (a, b, c, d).

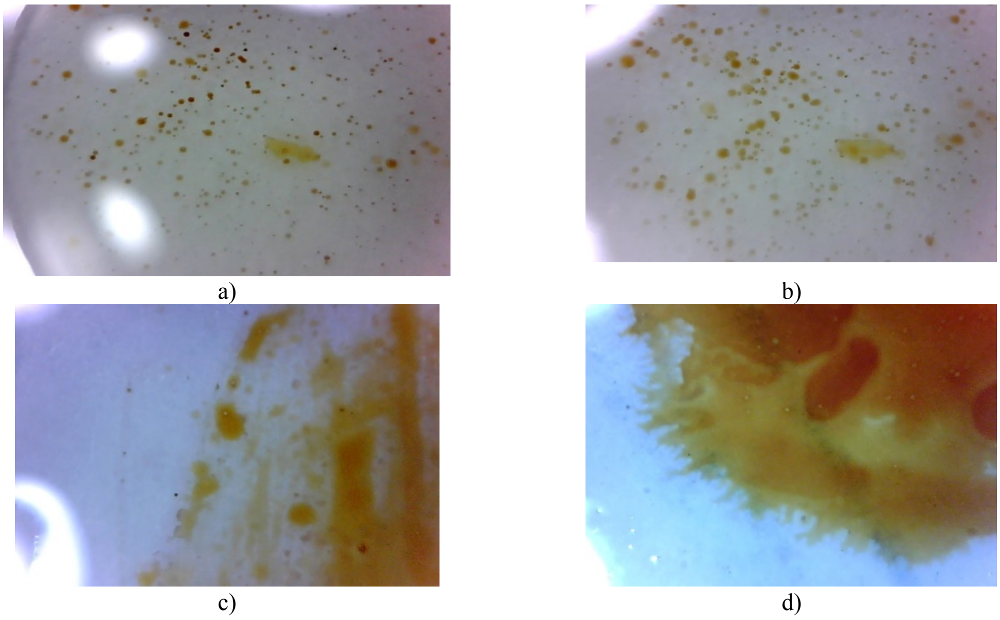


Figure – 1. Micrographs of the diesel fuel samples when adding in it: a) 0.1% of sulfuric acid; b) 0.2% c) 0.3%; d) 0.5%

Figure 1 shows that even a small amount of acid (0.1%) causes the coagulation process and appearance of conglomerates.

With increase in the concentration of acid to 0.3%, increase in the carbon formation is observed. Since the acid can cause increase in the fuel acidity, the acid was evaluated in accordance with GOST, and the content of existent resins in the upper part of the fuel that settled for 30 minutes was measured.

Figure 2 shows the dependence of the change in the fuel characteristics at different concentrations of the added acid.

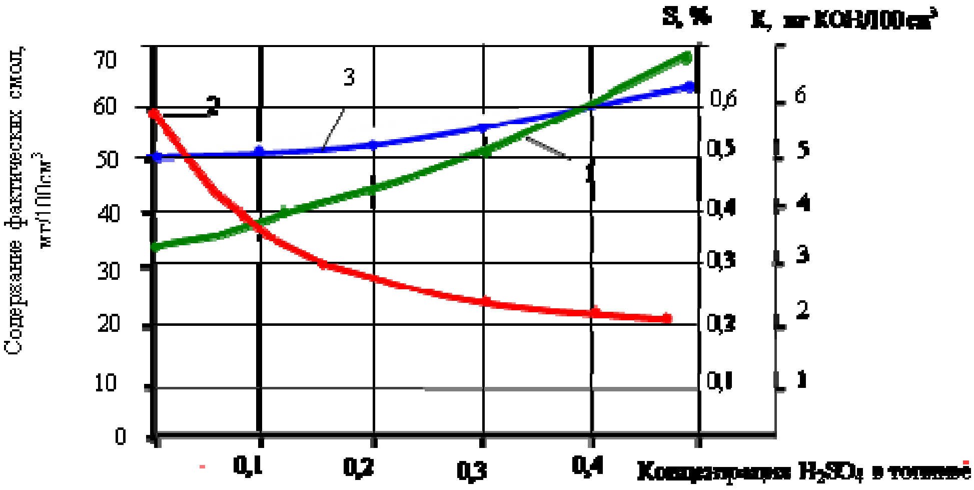


Figure 2 – Change in the fuel characteristics under the sulfuric acid attack

It was established that sulfuric acid allows remove resins from the fuel (Curve 2, Figure 2), however, the value (S) of the sulfur content increases and the acidity (K) of the fuel increases, which is a negative fact.

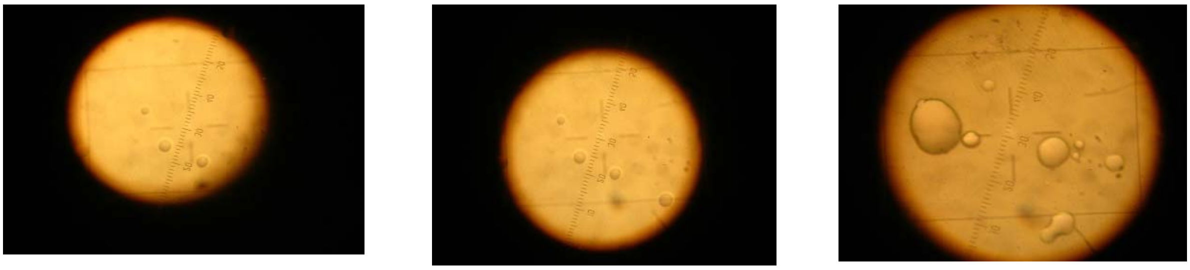
The content of existent resins (Curve 2, Figure 2) is most actively reduced when the acid concentration in the fuel is 0.1-0.2%, increase in the percentage concentration to 0.5 does not lead to significant resin reduction in the fuel.

Water-miscible calcined soda was used for consideration as alkali coagulants. The mixing concentration was 5:1, 3:1, and 1:1. It is noted that when mixing 5 and 3 parts of soda with 1 part of water, 100% dissolution of soda in water is not achieved. When mixing soda with water in proportions 1:1, a good solubility was noted (more than 80%), in accordance with which further research was carried out with the aqueous solution of 1:1, and the percentage of the aqueous alkali solution to the fuel was taken 0.5:1; 1.5 mass %.

The fuel mixed with the aqueous alkali solution was heated to a temperature of 100°C and then the temperature was kept for 0.5-1 hours with constant mixing.

The evaluation of coagulating ability was carried out under a microscope.

Figure 3 shows micrographs of the fuel samples with different concentrations of alkali water.



a) 0.5% b) 1% c) 1.5%

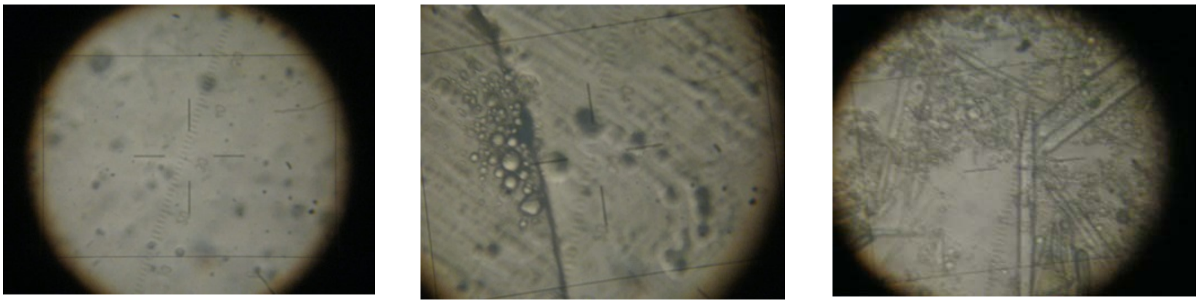
Figure 3 - Micrographs of the diesel fuel samples after the alkali water addition

Analysis of the research results presented in Figure 3 shows that the alkali water at the concentration of its addition into the fuel a) 0.5%; b) 1%; c) 1.5% practically does not have a coagulative effect on the impurities dissolved in the fuel.

If consider the fuel as an ultra-dispersed system with dissolved in it heavy hydrocarbon fractions, sulfur compounds of oil, etc., then the stability of this system can be greatly changed by adding small amounts of electrolytes into it. In lyophobic systems, the addition of electrolytes greatly increases the rate of coagulation. Based on the well-known theoretical laws of coagulation processes, as well as the research results on destabilization of dispersed systems of lubricating oils, the well-known substance – carbamide, which is a mineral fertilizer used in agricultural production, was used to study the coagulating ability of the impurities dissolved in the fuel.

The practical research on the evaluation of the coagulating ability of the dissolved impurities in the diesel fuel under the aqueous carbamide solution attack was carried out on a fuel with the existent resin content of 60 mg/100 cm^3 selected on the oil store of one of the agricultural enterprises of West Kazakhstan region and a fuel stored in one of the commercial oil stores in the city of Uralsk of the Republic of Kazakhstan with the content of existent resins of more than 70 mg/100 cm^3.

Analyzing the research results, let's note that carbamide is able to aggregate the impurities dissolved in the fuel. With increase in the concentration of the added solution with respect to the fuel, the coagulation of particles increases, and in the process of sedimentation as the concentration of the separating agent increases, a layer of recrystallized carbamide is formed. Figure 4 shows fragments of micrographs of the fuel samples when the aqueous carbamide solutions are added into it.



a) at the concentration of 0.1% b) at the concentration of 0.5% c) at the concentration of2%

Figure 4 - Micrographs of the fuel samples (the city of Uralsk, Kazakhstan) when the aqueous carbamide solutions are added into it.T_{fuel} = 90ºC, the time of sedimentation t = 90 min

The research found that the optimal concentration of the added 50% carbamide solution is 0.1-0.5% at the temperature t = 90-100°C. The optimal time of sedimentation is 60-90 min.

The research evaluated the change in the content of the existent resins in the fuel during the aqueous carbamide solution attack on it (Figure 5).

It should be noted that the content of the existent resins (Figure 5) in the fuel, depending on the concentration of the added aqueous carbamide solution, reduces. However, when it is increased by more than 0.5%, the change in the resin content occurs slightly.

In addition, the content of the existent resins in the fuel after the acid attack on it changed to the value of 25-30 mg/100 cm^3. However, the acid increases the fuel acidity, and the carbamide reduces it by 40-45%.

In this regard, the research was carried out on the combined reagent compositions. In particular, the possibility of adding the combinations was considered:

1. 0.1% acid + (50%) 0.5% carbamide solution.
2. 0.1% acid + 0.5% alkali water.

The change in the fuel acidity and the content of the existent resins depending on the duration of sedimentation of different agent combinations is presented in Figure 5.

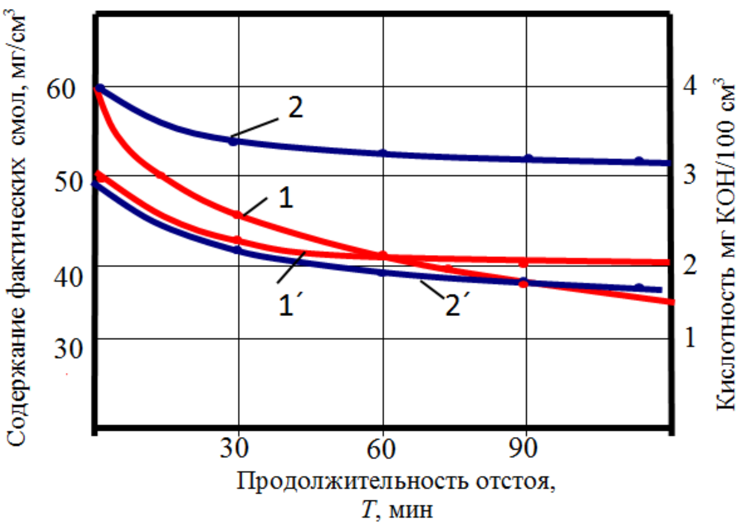


Figure 5 - Pattern of the change in the acidity and the content of the existent resins
in the fuel depending on the duration of sedimentation ($T_{addition}$ = 90°C) at different combinations
of coagulant compositions: 1, 1´- acid + carbamide solution; 2, 2´- acid + alkali

As is seen from Figure 6, the combination of the sulfuric acid and the aqueous carbamide solution when added to the diesel fuel allows reduce the content of the existent resins in it from 60 mg/100 cm^3 to 35 mg/100 cm^3, while the fuel acidity 1´, 2´ reduces from 3 mg KOH/100 cm^3 to 2 mg KOH/100 cm^3. Compared with the attack on the fuel only with the acid, the content of the existent resins in the fuel with the addition of the combined composition reduced almost the same, but the acidity did not increase, but vice versa – decreased.

Conclusions. Considering the combination “sulfuric acid – alkali”, let’s note that adding 0.1% acid and 0.5% alkali water to the fuel does not allow so much, compared to the first combination, reduce the content of the existent resins, but it helps significantly reduce the fuel acidity. This fact is most likely due to the effect of neutralizing the acid with the alkali.

Analyzing the research results, it can be concluded that among the considered agents, the greatest coagulation effect of the dissolved impurities in the fuel is achieved when it interacts with the aqueous carbamide solution, and the addition of the small amount of sulfuric acid activates the process.

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ДИЗЕЛЬДІ ОТЫНДАРДЫҢ ПАЙДАЛАНУШЫЛЫҚ ҚАСИЕТТЕРІН КӨПФУНКЦИОНАЛДЫ ҚОСПАЛАРДЫ ҚОСА ОТЫРЫП ЖОҒАРЫЛАТУ

Аннотация: Мақалада дизельді отында еріген шайыр мен тотығу өнімдерін ірілендіру үшін каогулянттардың қасиетін бағалау бойынша зерттеу материалдары келтірілген. Күкірт қышқылына ұшырағаннан кейін отын үлгілерінің микросуреттері келтірілген. Сілтілік отынға әсерін бағалау бойынша баға берілді және зерттеу нәтижелері келтірілді. Отынға карбамид су ерітіндісімен отынға әсер етуі нәтижесінде дизель отынында іс жүзінде еріген шайырлардың агрегагирлеу мүмкіндігі анықталды. Реагенттердің қосарланған құрамдарына жасалынған зерттеу нәтижелері келтірілді. су ерітіндісі карбонаты мен күкірт қышқылы комбинациясын дизельдік отынға қосқан кезде нақты шайыр құрамын екі есе төмендетуге мүмкіндік береді, оның үстіне отынның қышқылдығы 13 %-ға төмендейтінін автор атап өтеді.

Сондай-ақ, мақалада коагулянттық композициялардың түрлі комбинацияларында шөгінділердің ұзақтығынан отындағы нақты шайырлар құрамының өзгеру заңдылықтары көрсетілген. Жүргізілген зерттеулердің нәтижелеріне сәйкес, қарастырылған агенттердің ішінде ерітілген қоспалардың күйдіру кезінде қышқылдану үдерісінің ең үлкен әсері оның каогуляция мен күкірт қышқылының су ерітіндісімен өзара әрекеттесуімен жүзеге асырылатыны орнатылды.

Түйін сөздер: дизельдік отын, шайырлар, коагуляция, физика-химилық көрсеткіштер, күкірт қышқылы, сілті, карбамид, тұндыру, жойылу.

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ПОВЫШЕНИЕ ЭКСПЛУАТАЦИОННЫХ СВОЙСТВ ДИЗЕЛЬНЫХ ТОПЛИВ С ДОБАВЛЕНИЕМ МНОГОФУНКЦИОНАЛЬНОЙ ПРИСАДКИ

Аннотация. В статье представлены материалы исследований по оценке свойства коагулянтов для укрупнения растворенных в дизельном топливе смол и продуктов окисления. Приведены микрофотографии проб топлив после воздействия на них серной кислотой. Дана оценка и представлены результаты исследований по воздействию на топливо щелочью. В результате воздействия на топливо водным раствором карбамида установлена способность агрегатирования практически растворенных в дизельном топливе смол. Приведены результаты исследований комбинированных составов реагентов. Автор отмечает, что комбинация серной кислоты и водного раствора карбамида при добавлении их к дизельному топливу позволяет в два раза снизить содержание фактических смол, при этом кислотность топлива снижается на 13%. Также в статье выявляются закономерности изменений содержания фактических смол в топливе от продолжительности отстаивания при различных комбинациях составов коагулянтов. По результатам анализа проведенных исследований установлено, что среди рассмотренных агентов наибольший эффект процесса коагуляции растворённых примесей в топливе достигается при взаимодействии его с водным раствором карбамида и серной кислоты.

Ключевые слова: дизельное топливо, смолы, коагуляция, физико-химические показатели, серная кислота, щелочь, карбамид, отстаивание, удаление.

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PHYSICAL-CHEMICAL AND COLLOID-MECHANICAL METHODS OF RESEARCH OF MODIFIED POLYMER REAGENTS OF THE M-PAA SERIES AND THEIR APPLICATION FOR OBTAINING OF OINTMENT

Abstract. This article discusses the surface, bulk and structural properties of polymers. It was determined that the limit value σ for M-PAA (MEA) and M-PAA (PV) is established faster than for individual solutions. It has been established that in polymers viscosity and electrical conductivity increase with increasing concentration, i.e. M-PAA (MEA) and M-PAA (PV) are polyfunctional polyelectrolytes, polymers M-PAA (MEA) and M-PAA (PV) are thermostable. For the study a complex of physicochemical methods were used: potentiometry, spectroturbidimetry, conductometry, viscometry, IR spectroscopy, elemental analysis, thermogravimetry, measurement of surface tension by the Wilhelm method.

Key words: modified polymers, M-PAA (MEA), M-PAA (PV), IR spectra, thermal stability.

Introduction

The preparation of new polymer reagents from their synthesis in the laboratory to their industrial production as an ointment is relatively long and expensive process. Therefore, the most promising and justified way is to expand the range of polymer reagents by modifying the already known base samples [1]. In the [2] work authors synthesized a serial of amino-modified PAN fibers by the reaction of PAN fiber with TETA in the presence of water. The weight and alkali content, namely, amino grafting degree, would be improved by prolonging reaction time and increasing reaction temperature.

2 Experimental part

2.1 Preparation of solutions

For deposition, a 1% polymer solution and a 0.15% hydrochloric acid solution were prepared. With constant stirring, a solution of hydrochloric acid was added to a 1% polymer solution; as a result, the pH dropped to 4 and a gel-like polymer precipitated out, which was washed 3 times with water. Dioxane was precipitated. In this case, the remnants of the starting products were dissolved in dioxane, and the polymer precipitated in the form of a gel. The precipitated, washed samples were dried in a vacuum desiccator. Dialysis of a 1% polymer solution was carried out in a celluloid packet, periodically changing the water (within 1-2 days). Next, the precipitated dialyzed samples were dried in a vacuum oven T = 40-450 ^{0}C for 8-10 hours. To determine the composition of the polymers, thermal analyzes were performed.

2.2 Research Methods

IR spectroscopy and electron microscopy analyzes.

The IR spectra of polymers were interpreted according to the guidelines [3]. The analysis was carried out on an IR-20 spectrometer (in vaseline oil in the range of 700-4000 m^{-1}).

Device: FTIR-spectrometer Shimadzu IR Prestige-21 with prefixed disturbed total internal reflection (ATR) Miracle from Pike Technologies.

Thermogravimetric studies of the polymers were carried out on a derivatogaf in an atmosphere of air at a rate of temperature rise up to 450 °C per minute, and a sample weight of 150 mg.

For a quantitative comparison of the thermal stability of the polymers under study, the activation energies of destruction were calculated [4].

The viscosity of solutions of polyelectrolytes was measured in a viscometer of the Ubbelohde type [5], with a hanging level. For viscometric studies, re-precipitated and thoroughly dried polymers were used.

The viscometer was placed in a thermostat, the temperature was maintained with an accuracy of ± 0.01 ° C.

The concentration of the solution after dilution was calculated by the formula:

$$C = \frac{gVi - 100}{V(Vi + Vj)} Pi / P_2 = \frac{ciVi}{Vi + Vj}, \tag{1}$$

where g is the polymer weight, g;

V is the volume of the volumetric flask, ml;

V_i is the volume of the solution filled in viscometers, ml;

V_J is the volume of the added solvent, ml;

P_i / P_J is the solvent density ratio.

The calculation of the relative η_ (rel.) Specific η (spec), The reduced η_ (red.) Viscosities was carried out according to the following formulas:

$$\eta_{rel.} = \frac{\tau_i}{\tau_0}; \tag{2}$$

$$\eta_{spec} = \eta_{rel.}{}^{-1;} \tag{3}$$

$$\eta_{red.} = \frac{\eta_{spec.}}{c} \tag{4}$$

The characteristic viscosity (η) was found from the graphical dependence η_{red} (C) by extrapolating the straight lines to zero polymer concentration [6].

Measurement of the surface tension was carried out according to the method of Wilhelmy.

When determining the surface tension of the solutions by the method of Wilhelmi, the immersion force of the plates in the liquid was continuously measured. The magnitude of this force depends on the wetting of the measuring plate with liquid.

In the present work, a polished glass plate was used as a measuring plate, as well as made from a plate.

The calculation was carried out as follows:

$$\sigma = \frac{p+shd}{2(1+b)}, \tag{5}$$

p-weight plate, g; s- cross-sectional area, cm; 1 is the width of the plate, cm; -b is plate thickness (-), cm; h-immersion depth, cm; d-density of the measured liquid, g / cm; g-acceleration of gravity.

The surface tension was measured with a thermostatically controlled glass cell with a lid at a temperature of 25 °C; the temperature was kept constant using an I-2 ultra thermostat with an accuracy of +/- 0.02. The reading of the values of P_x was carried out using toroidal weights of the type VT-500 with an accuracy of +/-1 mg.

The pH of polymer solutions was measured on a pH-340 potentiometer with an accuracy of +/- 0.05. The pH in a thermostatically controlled cell, in which the temperature was maintained with an accuracy of 25 +/- 0.01. Further, the formula determined the conductivity (χ):

$$\chi = \frac{\alpha}{Rx}; \tag{6}$$

where - α is the cell constant: α = 0.000147m-1cm-1, at T = 250

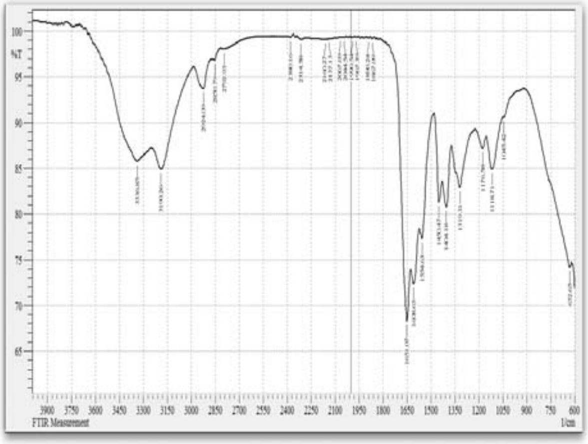
Turbidity was determined on a calorimeter of the type FEK-56 with α = 434Nm. Solutions of the corresponding fractions of polymers were used as reference solutions.

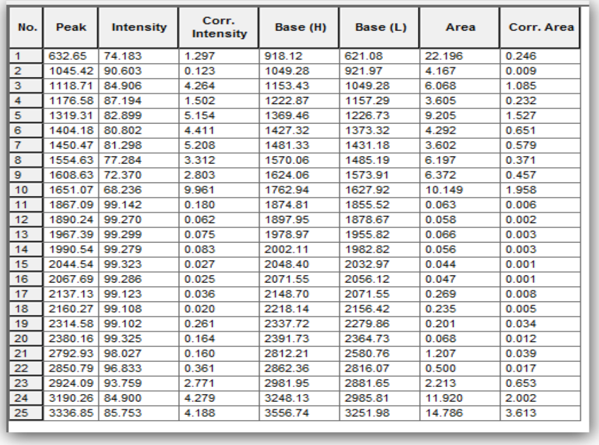
3 Results and discussions

The study of the structural properties of the polymers M-PAA (MEA), M-PAA (PV).

The IR spectra of polymers, whose interpretation was carried out according to the guidelines [7], contain absorption bands in the range of 3200-3500 cm^{-1}, which can be attributed to hydroxyl groups of an alcoholic nature, both free and hydrogen bonded. Bands with frequencies of 1405-1410 and also 1610-1630 cm^{-1} characterize the presence of $-NO_2$, $-COO^-$ groups. According to some authors [8], the pictogroup included in the core contributes to the stability of the first to destruction.

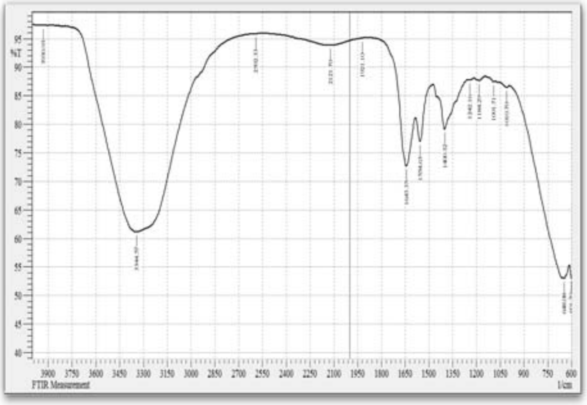
Absorption bands in the range of 1600–1630 cm^{-1} can be attributed to skeletal vibrations of –C = C – bonds, rather distinct bands of stretching vibrations — CH^{2-} groups are observed in the short-wave part of the spectra (2940-2970) cm^{-1}. Characteristic for –CH groups are peaks at frequencies of 780–790 cm^{-1}, and a maximum at a frequency of 1370 cm^{-1} can be attributed to deformational vibrations of –CH groups. In the spectrum of the studied samples, new bands are noted at frequencies of 1480 and 1690 cm^{-1}, which can be identified as $-COONH_2$ and $-(CO)_2NH$ (Figure 1-5) [9].

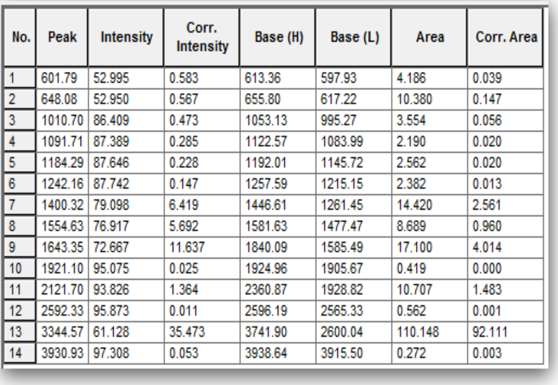




No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	632.65	74.183	1.297	918.12	621.08	22.196	0.246
2	1045.42	90.603	0.123	1049.28	921.97	4.167	0.009
3	1118.71	84.906	4.264	1153.43	1049.28	6.068	1.085
4	1176.58	87.194	1.502	1222.87	1157.29	3.605	0.232
5	1319.31	82.899	5.154	1369.46	1226.73	9.205	1.527
6	1404.18	80.802	4.411	1427.32	1373.32	4.292	0.651
7	1450.47	81.298	5.208	1481.33	1431.18	3.602	0.579
8	1554.63	77.284	3.312	1570.06	1485.19	6.197	0.371
9	1608.63	72.370	2.803	1624.06	1573.91	6.372	0.457
10	1651.07	68.236	9.961	1762.94	1627.92	10.149	1.958
11	1867.09	99.142	0.180	1874.81	1855.52	0.063	0.006
12	1890.24	99.270	0.062	1897.95	1878.67	0.058	0.002
13	1967.39	99.299	0.075	1978.97	1955.82	0.066	0.003
14	1990.54	99.279	0.083	2002.11	1982.82	0.056	0.003
15	2044.54	99.323	0.027	2048.40	2032.97	0.044	0.001
16	2067.69	99.286	0.025	2071.55	2056.12	0.047	0.001
17	2137.13	99.123	0.036	2148.70	2071.55	0.269	0.008
18	2160.27	99.108	0.020	2218.14	2156.42	0.235	0.005
19	2314.58	99.102	0.261	2337.72	2279.86	0.201	0.034
20	2380.16	99.325	0.164	2391.73	2364.73	0.068	0.012
21	2792.93	98.027	0.160	2812.21	2580.76	1.207	0.039
22	2850.79	96.833	0.361	2862.36	2816.07	0.500	0.017
23	2924.09	93.759	2.771	2981.95	2881.65	2.213	0.653
24	3190.26	84.900	4.279	3248.13	2985.81	11.920	2.002
25	3336.85	85.753	4.188	3556.74	3251.98	14.786	3.613

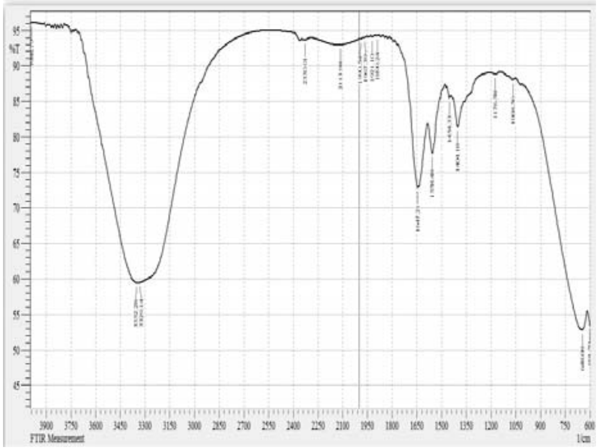
Figure 1 - The main polymer PAA (Polyacrylamide) powder

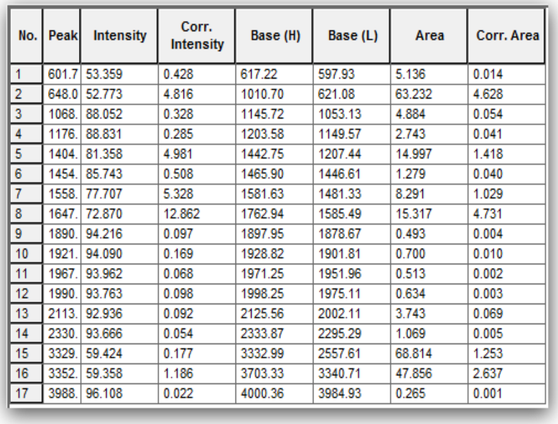




No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	601.79	52.995	0.583	613.36	597.93	4.186	0.039
2	648.08	52.950	0.567	655.80	617.22	10.380	0.147
3	1010.70	86.409	0.473	1053.13	995.27	3.554	0.056
4	1091.71	87.389	0.285	1122.57	1083.99	2.190	0.020
5	1184.29	87.646	0.228	1192.01	1145.72	2.562	0.020
6	1242.16	87.742	0.147	1257.59	1215.15	2.382	0.013
7	1400.32	79.098	6.419	1446.61	1261.45	14.420	2.561
8	1554.63	76.917	5.692	1581.63	1477.47	8.689	0.960
9	1643.35	72.667	11.637	1840.09	1585.49	17.100	4.014
10	1921.10	95.075	0.025	1924.96	1905.67	0.419	0.000
11	2121.70	93.826	1.364	2360.87	1928.82	10.707	1.483
12	2592.33	95.873	0.011	2596.19	2565.33	0.562	0.001
13	3344.57	61.128	35.473	3741.90	2600.04	110.148	92.111
14	3930.93	97.308	0.053	3938.64	3915.50	0.272	0.003

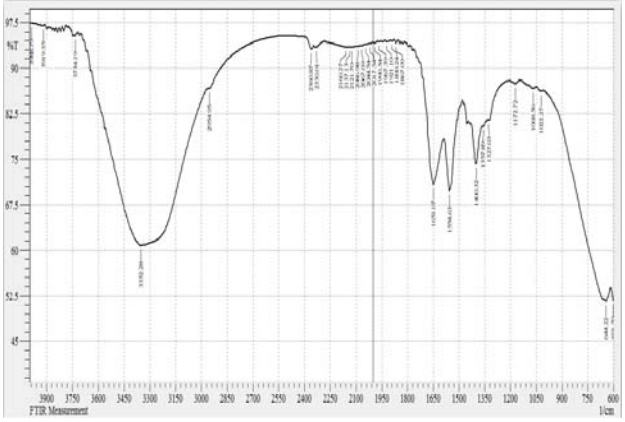
Figure 2 - MEA-PAA 1, colorless, viscous, non-flowing solution

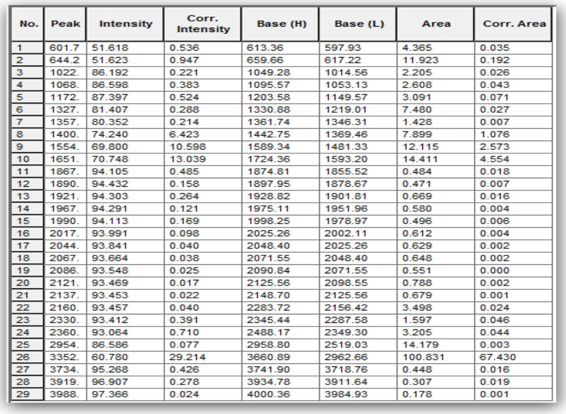




No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	601.7	53.359	0.428	617.22	597.93	5.136	0.014
2	648.0	52.773	4.816	1010.70	621.08	63.232	4.628
3	1068.	88.052	0.328	1145.72	1053.13	4.884	0.054
4	1176.	88.831	0.285	1203.58	1149.57	2.743	0.041
5	1404.	81.358	4.981	1442.75	1207.44	14.997	1.418
6	1454.	85.743	0.508	1465.90	1446.61	1.279	0.040
7	1558.	77.707	5.328	1581.63	1481.33	8.291	1.029
8	1647.	72.870	12.862	1762.94	1585.49	15.317	4.731
9	1890.	94.216	0.097	1897.95	1878.67	0.493	0.004
10	1921.	94.090	0.169	1928.82	1901.81	0.700	0.010
11	1967.	93.962	0.068	1971.25	1951.96	0.513	0.002
12	1990.	93.763	0.098	1998.25	1975.11	0.634	0.003
13	2113.	92.936	0.092	2125.56	2002.11	3.743	0.069
14	2330.	93.666	0.054	2333.87	2295.29	1.069	0.005
15	3329.	59.424	0.177	3332.99	2557.61	68.814	1.253
16	3352.	59.358	1.186	3703.33	3340.71	47.856	2.637
17	3988.	96.108	0.022	4000.36	3984.93	0.265	0.001

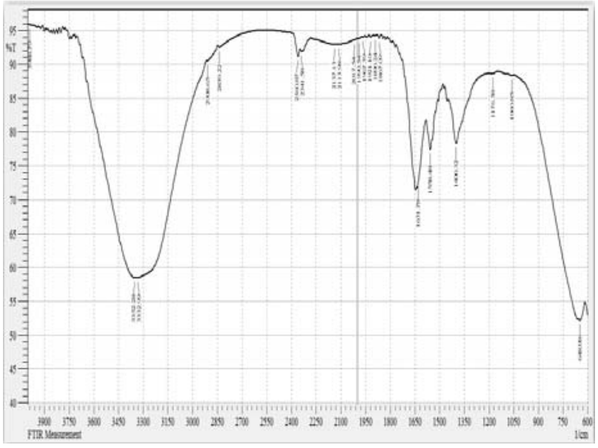
Figure 3 - MEA-PAA 2, yellowish, viscous, non-flowing solution

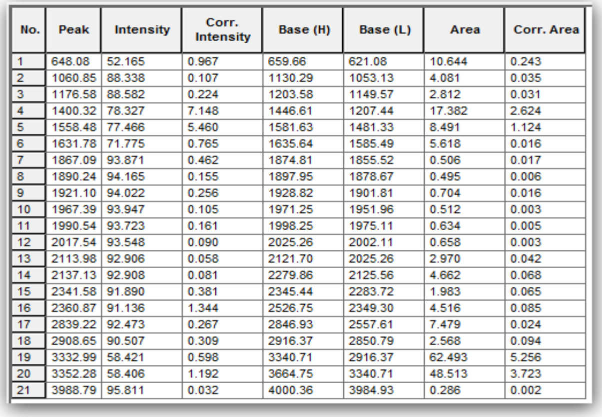




No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	601.7	51.618	0.536	613.36	597.93	4.365	0.035
2	644.2	51.623	0.947	659.66	617.22	11.923	0.192
3	1022.	86.192	0.221	1049.28	1014.56	2.205	0.026
4	1068.	86.598	0.383	1095.57	1053.13	2.608	0.043
5	1172.	87.397	0.524	1203.58	1149.57	3.091	0.071
6	1327.	81.407	0.288	1330.88	1219.01	7.480	0.027
7	1357.	80.352	0.214	1361.74	1346.31	1.428	0.007
8	1400.	74.240	6.423	1442.75	1369.46	7.899	1.076
9	1554.	69.800	10.598	1589.34	1481.33	12.115	2.573
10	1651.	70.748	13.039	1724.36	1593.20	14.411	4.554
11	1867.	94.105	0.485	1874.81	1855.52	0.484	0.018
12	1890.	94.432	0.158	1897.95	1878.67	0.471	0.007
13	1921.	94.303	0.264	1928.82	1901.81	0.669	0.016
14	1967.	94.291	0.121	1975.11	1951.96	0.580	0.004
15	1990.	94.113	0.169	1998.25	1978.97	0.496	0.006
16	2017.	93.991	0.098	2025.26	2002.11	0.612	0.004
17	2044.	93.841	0.040	2048.40	2025.26	0.629	0.002
18	2067.	93.664	0.038	2071.55	2048.40	0.648	0.002
19	2086.	93.548	0.025	2090.84	2071.55	0.551	0.000
20	2121.	93.469	0.017	2125.56	2098.55	0.788	0.002
21	2137.	93.453	0.022	2148.70	2125.56	0.679	0.001
22	2160.	93.457	0.040	2283.72	2156.42	3.498	0.024
23	2330.	93.412	0.391	2345.44	2287.58	1.597	0.046
24	2360.	93.064	0.710	2488.17	2349.30	3.205	0.044
25	2954.	86.586	0.077	2958.80	2519.03	14.179	0.003
26	3352.	60.780	29.214	3660.89	2962.66	100.831	67.430
27	3734.	95.268	0.426	3741.90	3718.76	0.448	0.016
28	3919.	96.907	0.278	3934.78	3911.64	0.307	0.019
29	3988.	97.366	0.024	4000.36	3984.93	0.178	0.001

Figure 4 - PAA-H_2O_2, colorless, viscous, weakly flowing solution





No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	648.08	52.165	0.967	659.66	621.08	10.644	0.243
2	1060.85	88.338	0.107	1130.29	1053.13	4.081	0.035
3	1176.58	88.582	0.224	1203.58	1149.57	2.812	0.031
4	1400.32	78.327	7.148	1446.61	1207.44	17.382	2.624
5	1558.48	77.466	5.460	1581.63	1481.33	8.491	1.124
6	1631.78	71.775	0.765	1635.64	1585.49	5.618	0.016
7	1867.09	93.871	0.462	1874.81	1855.52	0.506	0.017
8	1890.24	94.165	0.155	1897.95	1878.67	0.495	0.006
9	1921.10	94.022	0.256	1928.82	1901.81	0.704	0.016
10	1967.39	93.947	0.105	1971.25	1951.96	0.512	0.003
11	1990.54	93.723	0.161	1998.25	1975.11	0.634	0.005
12	2017.54	93.548	0.090	2025.26	2002.11	0.658	0.003
13	2113.98	92.906	0.058	2121.70	2025.26	2.970	0.042
14	2137.13	92.908	0.081	2279.86	2125.56	4.662	0.068
15	2341.58	91.890	0.381	2345.44	2283.72	1.983	0.065
16	2360.87	91.136	1.344	2526.75	2349.30	4.516	0.085
17	2839.22	92.473	0.267	2846.93	2557.61	7.479	0.024
18	2908.65	90.507	0.309	2916.37	2850.79	2.568	0.094
19	3332.99	58.421	0.598	3340.71	2916.37	62.493	5.256
20	3352.28	58.406	1.192	3664.75	3340.71	48.513	3.723
21	3988.79	95.811	0.032	4000.36	3984.93	0.286	0.002

Figure 5 - PAA-H_2O_2, yellowish, viscous, non-flowing solution

Thus, the IR spectra of the studied samples contain: -NO_2, -$COOH$, $-(CO)_2NH$, -$CONH_2$, -OH groups.

The stability of the obtained polymer to thermo-oxidative degradation was studied on a derivatograph of the Paulik-Paulik-Erdey system using the method of “dynamical thermogravimetry”. The heating rate is 6 deg/min., The interval is 293-870 K. (Table 1).

Table 1 - Characteristics of thermal stability of polymers M-PAA (MEA), M-PAA (PV), K-9

Polymer	T	E, кj/ mol	Weight loss	Initial weight, kg-10^{-1}
M-PAA (MEA)	698,4	96,2	31,5	552,6
K-9	670,7	78,7	49,8	552,3
M-PAA (PV)	703,4	94,3	39,4	550,8

From the data in the table it can be seen that the weight loss in thermogravimetry K-9 is 48.3%, and the polymer M-PAA (MEA) obtained on its basis is 30%, which is 1.5 times less. The weight loss of the polymer M-PAA compared with K-9 is also lower. In addition, the temperature of the onset of active decomposition in new samples increases markedly compared with the baseline ones. Thus, a qualitative assessment of the thermal stability of the process is obtained.

A quantitative comparison of the thermal stability of the samples under study will allow the calculation of the activation energy of destruction [3].

So, for thermo-oxidative destruction of K-9, 78.5 kJ / mol is required, while for the destruction of the polymer M-PAA (PV) - 85.3 kJ / mol, polymer M-PAA (MEA) - 84.1 kJ / mole. This gives grounds to attribute them to thermostable polymers [7].

Conclusion. Summarizing the above, we can draw the following conclusions:

a) Surface properties:

- The limiting value of σ for M-PAA (MEA) and M-PAA (PV) is established faster than for individual solutions;

- adsorption in these polymers is mainly determined by the diffusion of the macromolecule;

c) Bulk properties:

- in the polymers, with increasing concentration, viscosity and electrical conductivity increases, i.e. M-PAA (MEA) and M-PAA (PV) are polyfunctional polyelectrolytes.

c) Structural properties:

- polymers M-PAA (MEA) and M-PAA (PV) are thermostable;

- IR spectra of samples contain -NO_2, -$COOH$, -CN, $-SO_3Na, -OH$,
-$CONH_2$ groups.

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М-РАА СЕРИЯЛЫ МОДИФИЦИРЛЕНГЕН ПОЛИМЕРЛІ РЕАГЕНТТЕРДІҢ ФИЗИКА-ХИМИЯЛЫҚ ЖӘНЕ КОЛЛОИДТЫ-МЕХАНИКАЛЫҚ ӘДІСТЕРМЕН ЗЕРТТЕУ ЖӘНЕ ОЛАРДЫ МАЗЬДЕРДІ АЛУДА ҚОЛДАНУ

Аннотация. Бұл мақалада полимерлердің беттік, көлемдік және құрылымдық қасиеттері қарастырылады. М-РАА (МЕА) және М-РАА (PV) шекті мәні жеке ерітінділерге қарағанда тезірек орнығатыны анықталды. Концентрацияларының артуына байланысты полимерлердің тұтқырлығы мен электрөткізгіштігі артатыны анықталды, яғни М-РАА (МЕА) и М-РАА (PV) полифункциналды полиэлектролиттер болып табылады, М-РАА (МЕА) и М-РАА (PV) полимерлері термостабильді болып табылады. Зерттеу үшін физика-химиялық әдістер жиынтығы пайдаланылды: потенциометрия, спектротурбидиметрия, кондуктометрия, вискозиметрия, ИК-спектроскопия, элементтік анализ, термогравиметрия, Вильгельми әдісімен беттік керілуді өлшеу.

Түйін сөздер: модифицирленген полимерлер, М-РАА (МЕА), М-РАА (PV), ИҚ спектрлері, жылу тұрақтылығы

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ФИЗИКО-ХИМИЧЕСКИЕ И КОЛЛОИДНО-МЕХАНИЧЕСКИЕ МЕТОДЫ ИССЛЕДОВАНИЯ МОДИФИЦИРОВАННЫХ ПОЛИМЕРНЫХ РЕАГЕНТОВ СЕРИИ М-РАА И ИХ ПРИМЕНЕНИЕ ДЛЯ ПОЛУЧЕНИЯ МАЗЕЙ

Аннотация. В данной статье рассматриваются поверхностные, объемные и структурные свойства полимеров. Было определено, что предельное значение σ для М-РАА (МЕА) и М-РАА (PV) устанавливается быстрее, чем для отдельных растворов. Установлено, что в полимерах вязкость и электропроводность увеличиваются с увеличением концентрации, то есть М-РАА (МЕА) и М-РАА (PV) являются полифункциональными полиэлектролитами, полимеры М-РАА (МЕА) и М-РАА (PV) являются термостабильными. Для исследования использовали комплекс физико-химических методов: потенциометрия, спектротурбидиметрия, кондуктометрия, вискозиметрия, ИК-спектроскопия, элементный анализ, термогравиметрия, измерение поверхностного натяжения методом Вильгельми.

Ключевые слова: модифицированные полимеры, М-ПАА (МЭА), М-ПАА (ПВ), ИК-спектры, термостабильность.

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DETERMINATION OF CHEMICAL STRUCTURE OF CYCLOLEHMANOSIDE A FROM ASTRAGALUS LEHMANNIANUS

Abstract. In the present work, the determination of chemical structure of the novel cycloartane glycoside, cyclolehmanoside A is given. Determination of chemical structure was carried out by using of chemical reaction (acidic hydrolysis) and spectral methods (1D and 2D NMR spectroscopy). Novel cycloartane glycoside, cyclolehmanoside A was isolated from aerial parts of *Astragalus Lehmannianus* Bunge (*Leguminosae*) by column chromatography on silica, and its chemical structure was established as 3-O-β-D-xylopyranoside, 6,16-di-O-β-D-glucopyranoside-24S-cycloartane-3β,6α,16β,24,25-pentaol.

Keywords: *Astragalus Lehmannianus* Bunge, *Leguminosae*, cycloartane triterpenoids, cyclolehmanoside A, cyclocanthogenin, ^{1}H, ^{13}C, DEPT NMR spectra, HMBC.

Introduction. Investigation of isolation methods and structural determination of biological active substances from different medicinal plants has great importance for creation of modern high effective natural medicines [1].

Cycloartane line triterpenoidal compounds, cycloartanes are wide spread in plants. At present it is known, that cycloartanes have perspective biological activities. Therefore, investigation of cycloartanes has theoretical and practical value. Cycloartanes were first discovered in astragalus plants. Astragalus plants are good sources of these biological active substances. More 200 cycloartanes have been isolated from the plants of this genus [2]. About 239 astragalus species grow in Uzbekistan [3]. There are 307 species in Kazakhstan [4,5]. Twelve species of astragalus – *Astragalus alopecias*, *A. contortuplicatus, A. filicaulis, A. flexus, A. floccosifolius, A. frigidus, A. glycyphyllus, A. onobrychis, A. sieversianus, A. tribuloides, A. ugamicus, A. u1iginosus* growing in Kazakhstan are used in folk medicine [6]. Roots of *Astragalus membranaceus* are used as diuretic, as gastric and intestinal means, for treating of spleen diseases, during metabolic derangements in Chinese, Korean and Tibetan medicines. It has been determined, that cycloartane glycoside, askendoside D isolated from *Astragalus taschkendicus* has positive action to regulation of heart function and myocardium. Cyclosiversioside F from *Astragalus sieversianus* has hypotensive, anti-inflammatory actions, sedative, analgesic and antitumor activities [2,4,7,8].

The aim of our investigation is determination of chemical structure of the cycloartane glycoside, cyclolehmanoside A isolated from the aerial parts of *Astragalus Lehmannianus* Bunge, growing in Karakalpakstan.

Astragalus Lehmannianus Bunge grows in the Middle Asia (Kyzylkum, Karakum), Kyzyl-Orda region, Near Aral sea regions. The plant is good eaten by cattle.

Materials and methods. *Astragalus Lehmannianus* Bunge was collected from Karakalpakstan (Sultanuzdag) in May 2007.

Plates with silica (0.005-0.043 mm) containing 10% of plaster and plates Silufol UV-254 (Czechia) were used. Column chromatography was carried out on silica 0.1-0.08 and 0.16-0.1 mm. Cycloartanes were detected by spraying of 20% methanol solution of phosphotungstic acid following heating at 120ºC during 5-10 min. Paper chromatography was conducted on «FN-11» using solvent system *n*-BuOH-C_5H_5N-H_2O (6:4:3). Monosaccharides were detected by spraying of aniline phthalate following heating at 110ºC.

Next solvent systems were used for elution of the column and for thin layer chromatography (TLC):

1) chloroform-MeOH (9:1);
2) chloroform-MeOH (6:1);
3) **chloroform-MeOH-H_2O (70:12:1);**
4) chloroform-MeOH-H_2O (70:28:3);
5) chloroform-MeOH-H_2O (60:35:5).

NMR spectrum were obtained on UNITYplus 400 (Varian) in CD_3OD. ^{13}C NMR spectrum were obtained at full suppression of C-H interaction and at the DEPT conditions.

Air dried aerial parts of the plant (1.2 kg) were exhaustive extracted with methanol (MeOH). The obtained MeOH extract was evaporated until thick condition and added twice volume of water. The obtained water solution was treated at first with chloroform, after with *n*-BuOH. *n*-BuOH extract was evaporated and obtained dry residue (68 g) was chromatographed on silica column using solvent systems 4 and 5 for elution. Compound **1** (75 mg) was isolated from *n*-BuOH extract**.**

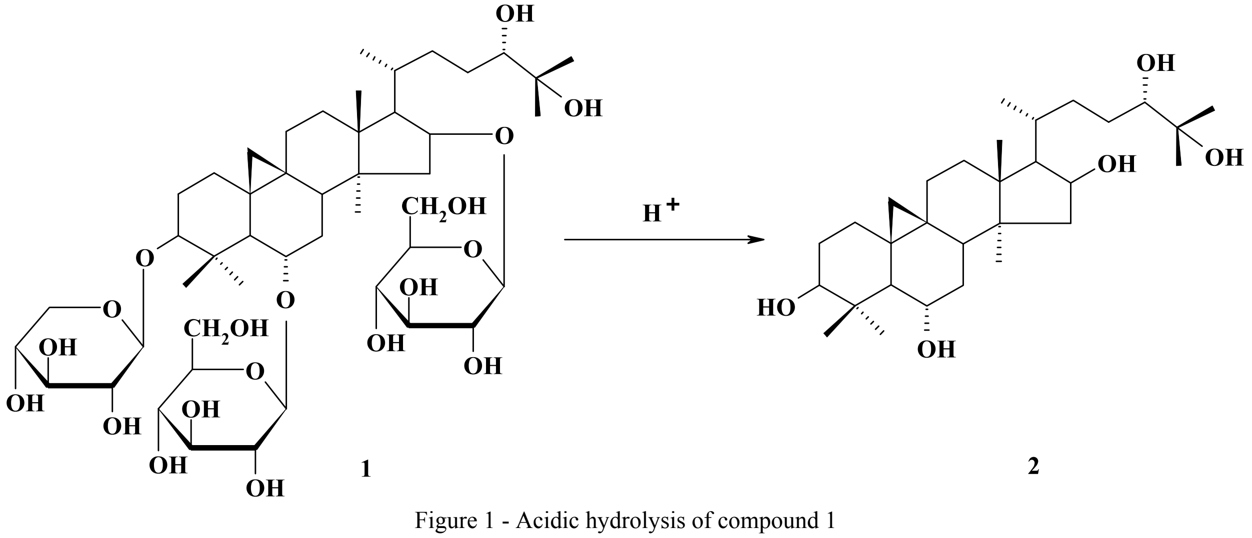
Acidic hydrolysis of compound 1 (Fig.1). Compound 1 (35 mg) was dissolved in 10 ml of MeOH containing 0.5% sulfuric acid and boiled in water bath during 1 hour. Then the reaction mixture was diluted with 20 ml of water and MeOH was evaporated. Laid down precipitate was filtered, washed with water and dried. Filtrate was neutralized with barium carbonate. After neutralization in the filtrate D-xylose and D-glucose were detected by using of paper chromatography method in comparison with standard substances. The obtained precipitate was set to the chromatographic column and eluated with system 1. Genin 2 was isolated in the result of the column chromatography. Genin 2 was identified as cyclocanthogenin by comparing with standard substance on TLC and on basis of ^1H NMR data.

^1H NMR data of cyclocanthogenin (400 MHz, C_5D_5N): 0.34 and 0.62 (2H-19, d, $^2J=4$), 1.05 (CH_3, s), 1.11 (CH_3-21, d), 1.38, 1.44, 1.49, 1.90, 1.90 (5xCH_3, s), 3.67 (H-3, dd), 3.94 (H-24, dd), 4.74 (H-6, td), 4.76 (H-16, td) (Table 1).

Results and discussion.

The ^1H NMR spectrum of the compound 1 showed signals due to cyclopropane methylene at δ0.58 and 0.35 (each 1H, d, J=4Hz) and signals of methyl groups at δ 0.99-1.29. These data indicate that the compound 1 is triterpenoid of cycloartane line (Table 1) [8,9].

Acidic hydrolysis of the compound 1 gives genin 2 identified with cyclocanthogenin [1,7,8]. D-xylose and D-glucose were detected in carbohydrate part of the hydrolysate by using of paper chromatography method in comparison with standard substances (Fig.1).



1

2

Figure 1 - Acidic hydrolysis of compound 1

Table 1 – ^{1}H, ^{13}C NMR and DEPT data of cyclolehmanoside A (1) (CD_3OD, δ, J/Hz, 0-TMS)
and cyclocanthogenin (2) (C_5D_5N, δ, J/Гц, 0-TMS)

Атом С	DEPT	1		2
		δ_C	δ_H	δ_C
1	CH_2	31.36	1.29, 1.60	32.54
2	CH_2	30.42	1.72, 1.98	31.17
3	CH	90.22	3.24	78.10
4	C	42.13	-	42.18
5	CH	53.10	1.68	53.73
6	CH	78.21	3.59	68.04
7	CH_2	34.40	1.65, 1.95	38.33
8	CH	46.11	1.90	46.94
9	C	21.13	-	21.02
10	C	30.11	-	29.71
11	CH_2	26.29	1.37, 1.94	26.17
12	CH_2	33.27		32.95
13	C	46.66	-	45.47
14	C	47.49	-	46.67
15	CH_2	47.94	1.40, 2.13	48.16
16	CH	82.23		71.75
17	CH	58.23		57.11
18	CH_3	18.59	1.15	18.03
19	CH_2	27.55	0.35 и 0.58	29.09
20	CH	30.03		28.44
21	CH_3	17.85	1.0	18.77
22	CH_2	36.82		32.81
23	CH_2	29.90		27.67
24	CH	78.59		76.99
25	C	72.59	-	72.88
26	CH_3	25.55	1.18	25.48
27	CH_3	26.20	1.21	26.07
28	CH_3	19.66	0.99	19.93
29	CH_3	28.41	1.29	29.34
30	CH_3	16.80	1.05	15.87
β-D-Xyl*p*				
1	CH	106.51	4.42	
2	CH	75.12	3.24	
3	CH	77.55	3.33	
4	CH	71.83	3.50	
5	CH_2	67.33	3.21, 3.85	
β-D-Glc*p*				
1	CH	104.78	4.48	
2	CH	76.43	3.26	
3	CH	78.04	3.37	
4	CH	71.32	3.31	
5	CH	77.55	3.27	
6	CH_2	62.80	3.69, 3.85	
β-D-Glc*p*				
1	CH	105.05	4.65	
2	CH	76.43	3.29	
3	CH	77.90	3.43	
4	CH	71.83	3.35	
5	CH	77.05	3.36	
6	CH_2	62.80	3.69, 3.85	

In ^1H NMR spectrum anomeric protons of monosaccharide residues of the compound 1 are observed at δ 4.42 (H-1 of β-D-xylopyranose), δ 4.48 and δ 4.65 (H-1 of β-D-glucopyranoses) $^3J=7.4$, $^3J=7.8$ and $^3J=7.9$ Hz accordingly. So, monosaccharide residues in the glycoside 1 have pyranose form, $^4C_1$-conformation and β-configuration. This conclusion is confirmed by values of chemical shifts of carbohydrate residue carbon atoms in ^{13}C NMR spectrum of 1 (Table 1).

Comparative analysis of ^{13}C NMR spectra of compound 1 and genin 2 showed that carbon atoms C-3, C-6 and C-16 have glycosidation shifts resonating at δ 90.22., δ 78.21 and 82.23 accordingly.

Anomeric carbon atoms of monosaccharide residues resonate at δ 106.51 (C-1 of β-D-xylopyranose), δ 104.78 and δ 105.05 (C-1 of β-D-glucopyranose) in the ^{13}C NMR spectrum of the compound 1. Value of chemical shifts of anomeric carbon atoms indicate, that D-xylose residue linked at C-3, and two D-glucose residues linked at C-6 and C-16 of genin.

In HMBC spectrum of 1 correlation peaks between H-1' of D-xylose (δ 4.42) and C-3 of aglycon (δ 90.22), H-1' of D-glucose (δ 4.48) and C-6 aglycon (δ 78.21), H-1'' of D-glucose (δ 4.65) and C-16 aglycon (δ 82.23) are observed.

Thereby, fully analysis of the spectral data allow us to make conclusion, that isolated compound 1 is cycloartane glycoside having novel chemical structure 3-O-β-D-xylopyranoside,6,16-di-O-β-D-glucopyranoside-24S-cycloartane-3β,6α,16β,24,25-pentaol.

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ASTRAGALUS LEHMANNIANUS ӨСІМДІГІНЕН БӨЛІП АЛЫНҒАН ЦИКЛОЛЕХМАНОЗИД А ХИМИЯЛЫҚ ҚҰРЫЛЫМЫН АНЫҚТАУ

Аннотация. Осы жұмыста жаңа циклоартан гликозиді, циклолехманозид А –ның химиялық құрылымын анықтау берілген. Химиялық құрылым химиялық реакция (қышқылдық гидролиз) және спектральді әдістер (бірөлшемді және екіөлшемді ЯМР спектроскопия) көмегімен анықталды. Жаңа циклоартан гликозиді, циклолехманозид А *Astragalus Lehmannianus* Bunge (*Leguminosae*) өсімдігінің жер үсті бөлігінен силикагельде бағаналы хроматография әдісімен бөліп алынды және оның химиялық құрылымы 3-O-β-D-ксилопиранозид, 6,16-ди-O-β-D-глюкопиранозид-24S-циклоартан-3β,6α,16β,24,25-пентаол екендігі анықталды.

Түйін сөздер: *Astragalus Lehmannianus* Bunge, *Leguminosae*, циклоартан тритерпеноиды, циклолехманозид А, циклокантогенин, ^1H, ^{13}C, DEPT ЯМР спектр, HMBC.

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ОПРЕДЕЛЕНИЕ ХИМИЧЕСКОГО СТРОЕНИЯ ЦИКЛОЛЕХМАНОЗИДА А ИЗ ASTRAGALUS LEHMANNIANUS

Аннотация. В настоящей работе приводится определение химического строения нового циклоартанового гликозида, циклолехманозида А. Определение химического строения проводился при помощи химической реакции (кислотный гидролиз) и спектральными методами (одномерная и двумерная ЯМР спектроскопия). Новый циклоартановый гликозид, циклолехманозид А был выделен из надземной части *Astragalus Lehmannianus* Bunge (*Leguminosae*) колоночной хроматографией на силикагеле, а его химическое строение установлен как 3-O-β-D-ксилопиранозид, 6,16-ди-O-β-D-глюкопиранозид-24S-циклоартан-3β,6α,16β,24,25-пентаол.

Ключевые слова: *Astragalus Lehmannianus* Bunge, *Leguminosae*, циклоартановые тритерпеноиды, циклолехманозид А, циклокантогенин, ^1H, ^{13}C, DEPT ЯМР спектр, HMBC.

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COMPARATIVE ANALYSIS OF THE NONPOLAR FRACTION OF THE AERIAL AND UNDERGROUND PARTS OF THE *LIMONIUM GMELINII* PLANTS BY THE GC-MS METHOD

Abstract. This article discusses the chemical composition of the non-polar fraction obtained from the aerial and underground parts of *Limonium gmelini*i (Willd.) harvested in the Almaty region in 2018. Extracts were obtained by the method of solvent extraction with hexane and studied by means of chromato-mass spectrometry on a gas chromatograph with a mass-selective detector.

As a result, 22 compounds were isolated from the aerial part of *Limonium gmelinii* plant, out of which dominating both quantitatively and qualitatively are hydrocarbons, such as genicosane and eicosane and tricosane; quinoline and phytol derivatives were isolated as well. High content of phytol acetate related to derivatives of acyclic diterpene alcohols has been revealed. In addition, the higher alcohol 3,7,11,15-tetramethyl-2-hexadecan-1-ol has been identified.

Analysis of the non-polar extract obtained from the roots of *Limonium gmelinii* allowed us to isolate 14 compounds, out of which the major share in the amount belongs to the esters of higher carboxylic acids and hydrocarbons. Esters are represented as ethyl esters of hexadecanoic, oleic and linoleic acids with prevalence of polyene acids in them. Among the hydrocarbons, tridecane, tetradecane, heptadecane, octadecane and tetracosane are the most abundant.

Keywords: *Limonium gmelinii*, non-polar fraction, GC-MS, chemical composition.

Introduction

Limonium is a widespread plant genus with about 300 species present on the territory of Central and Western Asia. On the territory of CIS, 35 *Limonium* species have been identified. Usually it is accommodated on coniferous soils and dry mountain ranges, mainly in the south-eastern part of Europe, Caucasus, and Central Asia. In Kazakhstan, out of 18 species the most significant and productive is *Limonium gmelinii* (Willd.). The area of its distribution includes major part of Kazakhstan, Western and Eastern Siberia, European part of Russia, Central Asia, Southeastern Europe, Western China and Mongolia. Currently, the roots and the aerial parts of *L.gmelinii* plants have been introduced into the medicine and State Pharmacopoeia of the Republic of Kazakhstan, harmonized with the European Pharmacopoeia [1-8]; with effective drugs obtained and standardized on the basis of its roots [9-12].

The purpose of this work is a comparative analysis of the chemical composition of hexane extracts obtained from the aerial and underground parts of *L.gmelinii* plants, in order to establish their effect on the biological activity of the studied extracts.

Methods

Extracts from the aerial and underground parts of *L.gmelinii* plants were obtained by the method presented below:

A weighed amount of pre-treated, dried and crushed vegetable raw materials, according to their quality indicators, corresponding to the requirements of the State Pharmacopoeia of the Republic of Kazakhstan, weighing 10 g, was extracted with hexane at a ratio of 1:5 for 48 hours. The extract obtained was filtered and concentrated to 10 ml. The resulting total non-polar extract was studied on a gas chromatograph with a mass selective detector model Agilent 7890N/ 5973N (Agilent Technologies, USA). At the same time, the volume of the gas phase to be taken equals 1.00 μl; the sample introduction temperature is 250°C without division of the flow. Separation was performed using a DB-35 MS chromatographic capillary column with a length of 30 m, an inner diameter of 0.25 mm and a film thickness of 0.25 μm at a constant carrier gas (helium) rate of 1 ml/min. The temperature of chromatography was programmed from 40°C to 200°C with a heating rate of 10°C/min.

The software Agilent MSD ChemStation, version 1701EA) was used to control the gas chromatography system, record and process the obtained results and data. Data processing included determination of retention times, peak areas, as well as processing of spectral information obtained using a mass spectrometric detector. The Wiley 7th edition and NIST'02 libraries were used to decipher the mass spectra obtained (the total number of spectra in the libraries exceeds 550,000 items).

Results and discussion

As a result of studying the hexane fraction obtained from the aerial part of plants of the *Limonium gmelinii* species, 22 compounds were identified, most of which belong to the class of hydrocarbons (Table 1 and Figure 1).

Table 1 – Research data by GC-MS of the aerial part of *Limonium gmelinii* plant species

No.	Retention time, min	Name of compound	Content %
1	8.05	Dodecane	0.20
2	9.52	Tridecane	0.50
3	10.91	Tetradecane	1.21
4	11.54	Dodecane, 2,6,10-trimethyl-	0.60
5	12.23	Pentadecane	2.44
6	12.91	Dichloroacetic acid tridecyl ester	0.57
7	13.49	Hexadecane	3.50
8	13.88	1,2-dihydro-2,2,4-trimethyl Quinoline	0.72
9	14.48	2,6,10,14-tetramethyl-Pentadecane	1.16
10	14.68	Heptadecane	3.14
11	15.35	1-Decanol, 2-hexyl	0.36
12	15.,69	Tetracontan	1.29
13	15.81	Octadecane	2.71
14	16.45	Phytol acetate	12.88
15	16.99	Nonadecan	2.80
16	17.07	3,7,11,15-Tetramethyl-2-hexadecan-1-ol	5.17
17	17.20	2-Pentadecanone 6,10,14-trimethyl	2.46
18	18.48	Eicosane	1.93
19	20.47	Genicosan	7.82
20	22.53	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	0.35
21	22.87	Phytol	0.75
22	27.16	Tricosane	47.44
Total			100.00

As can be seen from the data presented in Table 1, the tricosane hydrocarbon (47.44%) dominates in the obtained hexane extract from the aerial part of the plants *Limonium gmelinii*. A high content of phytol acetate (12.88%) related to derivatives of acyclic diterpene alcohols has been established, in addition, the highest alcohol 3,7,11,15-tetramethyl-2-hexadecan-1-ol, detected in the amount of 5.17%, has been identified.

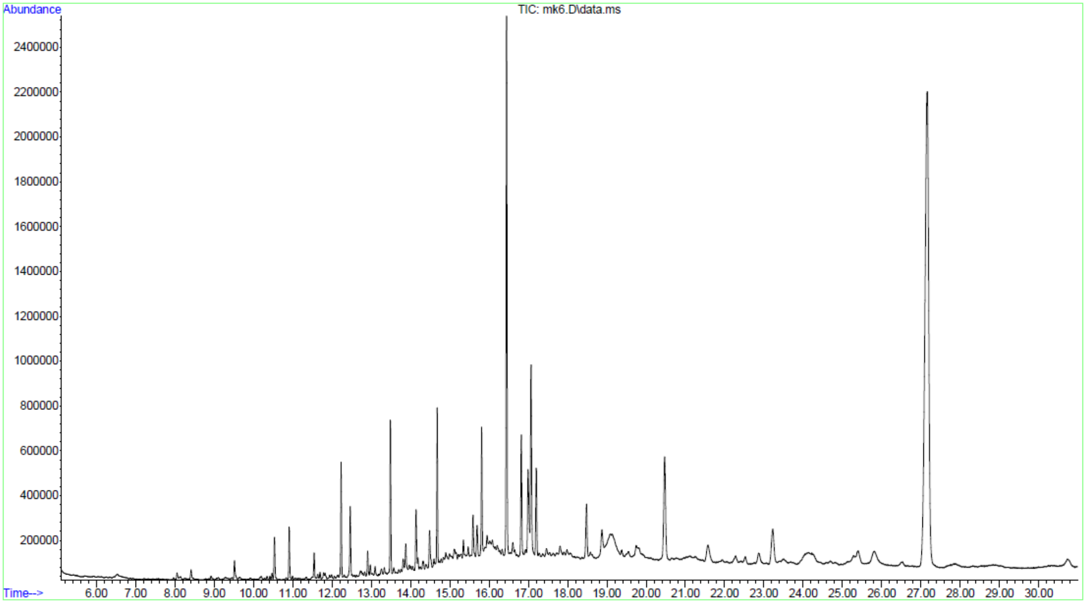

Figure 1 – GC-MS chromatogram of the aerial part of the plant species *Limonium gmelinii*

As can be seen from the data presented in Figure 1, the largest peaks are observed at 16.45 minutes and 27.16 minutes, which advises the extracts that are dominant in the extract, phytol acetate and tricosane, the other compounds are found in significant concentrations such as 3,7,11,15-tetramethyl-2-hexadecan-1-ol, genicosan, hexadecane are also clearly marked on the chart.

From the literature sources it is known that the underground parts of plants, as a rule, contain a relatively small amount of non-polar compounds, since the latter, phytol, in particular, are involved in the process of biosynthesis at the stage of photosynthesis and predominate in chloroplasts. The accumulation of other non-polar and weakly polar compounds, such as hydrocarbons, is more characteristic of the aerial parts of plants, while in the underground parts of plants, respectively, water-soluble carbohydrates and polyphenols dominate [13-23].

In the underground part of the studied plants, 14 compounds were identified (Table 2 and Figure 2).

Table 2 – Research data by GC-MS of the roots of plants of the *Limonium gmelinii* species

No.	Retention time, min	Name of compound	Content, %
1	6.53	Undecane	0.94
2	8.05	Dodecane	2.66
3	9.52	Tridecan	4.07
4	10.91	Tetradecane	4.15
5	10.99	7-Tetradecene, (Z)	0.89
6	12.23	9-methylheptadecane	3.22
7	13.49	Heptadecane	7.62
8	13.83	Phenol, 2,4-bis (1,1-dimethylethyl) -	1.72
9	13.88	Quinoline, 1,2-dihydro-2,2,4-trimethyl-	4.18
10	15.69	Tetracosan	3.43
11	15.81	Octadecane	5.26
12	19.78	Hexadecanoic acid ethyl ester	24.51
13	25.40	Oleic acid ethyl ester	11.16
14	25.78	Ethyl linoleic ester	26.19
Total			100.00

It was established on table 2 that the distinctive feature of the hexane extract of the roots of the studied plants is the predominance of esters of higher carboxylic acids in the amount of 61.86% and hydrocarbons – 32.24%.

The esters are represented as ethyl esters of hexadecanoic, oleic and linoleic acids, with the predominance of polyene acids (60.38%) in them, of which hexadecanoic acid ethyl ester and linoleic acid ethyl ester are the most abundant.

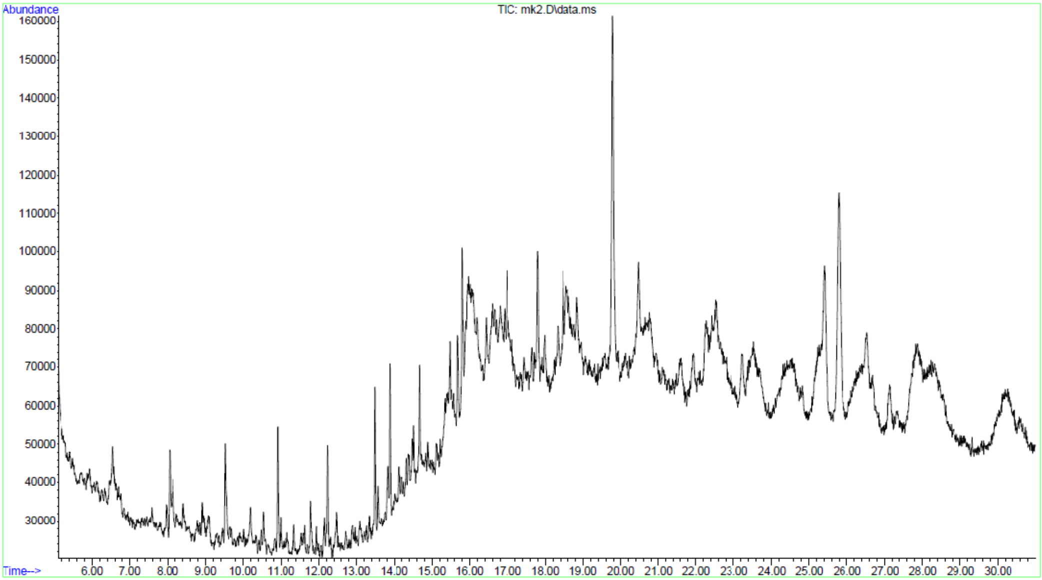

Figure 2 – GC-MS chromatogram of the roots of the plant species *Limonium gmelinii*

From the data presented in Figure 2, it can be seen that most of the dominant in the non-polar fraction of the roots of the plant *Limonium gmelinii* substances, namely Hexadecanoic acid ethyl ester, Oleic acid ethyl ester and Ethyl linoleic ester, belong to the class of organic esters is allocated at the final stages of analysis. The quinoline and phenol derivatives stand out between 1 and 5 minutes of the process. Most of the analysis recorded various compounds belonging to the class of hydrocarbons.

Conclusion

As a result, it was established that in the hexane extract obtained from the aerial part of the plant *Limonium gmelinii*, the dominant groups of substances are hydrocarbons among which the tridecane, tetradecane, heptadecane, octadecane and tetracosane dominate, 76.09%. Also in hexane extract obtained from the aerial part of the plant *Limonium gmelinii* was identified derivatives of phytol and quinoline.

The hexane extract obtained from the roots of the plant *Limonium gmelinii* is dominated by fatty acid esters whose total content is 61.86% in contrast to the aerial part of the plant. In addition, a significant amount of quinoline derivatives was found in the hexane extract from the roots of the plant *Limonium gmelinii*, while in the aerial part of the plant it is represented in trace amounts.

The obtained data can be used to improve the processing of the roots and the aerial parts of the plant *Limonium gmelinii* with the aim of obtaining drugs on its basis.

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LIMONIUM GMELINII ӨСІМДІГІНІҢ ЖЕРҮСТІ ЖӘНЕ ЖЕРАСТЫ БӨЛІКТЕРІНІҢ ПОЛЯРСЫЗ ФРАКЦИЯЛАРЫНЫҢ GC-MS ӘДІСІМЕН САЛЫСТЫРМАЛЫ АНАЛИЗІ

Аннотация. Бұл мақалада 2018 ж. Алматы облысында өңделген *Limonium gmelinii* (*Willd.)* (кермек Гмелина) өсімдігінің жерасты және жерүсті бөліктерінен алынған полярсыз фракциялардың химиялық құрамы қарастырылады. Экстракттар гексанмен сұйық экстракциялау әдісімен алынып, масс-селективті детекторлы газ хроматографта хромато-масс спектрометрия арқылы зерттелді.

Нәтижесінде *Limonium gmelinii* өсімдігінің жерүсті бөлігінен 22 қосылыс, оның ішінде сапалық және сандық тұрғыдан көмірсутектер геникозан, эйкозан және трикозан басым, сонымен қатар хинолин мен фитол туындылары бөлінді. Ациклді дитерпен спирттер туындыларының құрамы жоғары екендігі анықталды, одан бөлек 3,7,11,15-тетраметил-2-гексадекан1-ол жоғарғы спирті идентификацияланды.

Limonium gmelinii тамырынан алынған полярсыз экстракттар анализі 14 қосылыс бөліп алуға мүмкіндік берді, олардың негізгі сандық бөлігін жоғарғы карбон қышқылдарының эфилері мен көмірсутектер құрайды. Күрделі эфирлер полиен қышқылының басымдығымен линоль, олеин гексадекан қышқылдарының этил эфирлері күйінде ұсынылған. Көмірсутектер ішінде көп кездесетіні тридекан, тетрадекан, гептадекан, октадекан мен тетракозан.

Түйін сөздер: Limonium gmelinii, полярсыз фракция, хромато-масс спектрометирия, химиялық құрам.

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СРАВНИТЕЛЬНЫЙ АНАЛИЗ НЕПОЛЯРНОЙ ФРАКЦИИ НАДЗЕМНОЙ И ПОДЗЕМНОЙ ЧАСТЕЙ РАСТЕНИЙ *LIMONIUM GMELINII* МЕТОДОМ GC-MS

Аннотация. В данной статье рассматривается химический состав неполярной фракции, полученной из надземной и подземной частей растения *Limonium gmelinii* (*Willd.*) (кермек Гмелина), заготовленного в Алматинской области в 2018 году. Экстракты были получены методом жидкостной экстракции гексаном и изучены посредством хромато-масс спектрометрии на газовом хроматографе с масс-селективным детектором.

В результате исследования из надземной части растения *Limonium gmelinii* было выделено 22 соединения, доминирующими из которых, как в количественном, так и в качественном плане, являются углеводороды, такие как геникозан и эйкозан и трикозан; также были выделены производные хинолина и фитола. Установлено высокое содержание производных ациклических дитерпеновых спиртов, помимо этого идентифицирован высший спирт 3,7,11,15-тетраметил-2-гексадекан1-ол.

Анализ неполярного экстракта, полученного из корней *Limonium gmelinii* позволил выделить 14 соединений; из них основную долю в количестве составляют эфиры высших карбоновых кислот и углеводороды. Сложные эфиры представлены в форме этиловых эфиров гексадекановой, олеиновой и линолевой кислот с преобладанием в них эфиров полиеновых кислот. Среди углеводородов в наибольшем количестве присутствуют тридекан, тетрадекан, гептадекан, октадекан и тетракозан.

Ключевые слова: Limonium gmelinii, неполярная фракция, хромато-масс спектрометрия, химический состав.

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STUDY OF THE CATALYTIC REACTION OF HYDRAZINOLYSIS OF ALIPHATIC CARBOXYLIC ACIDS

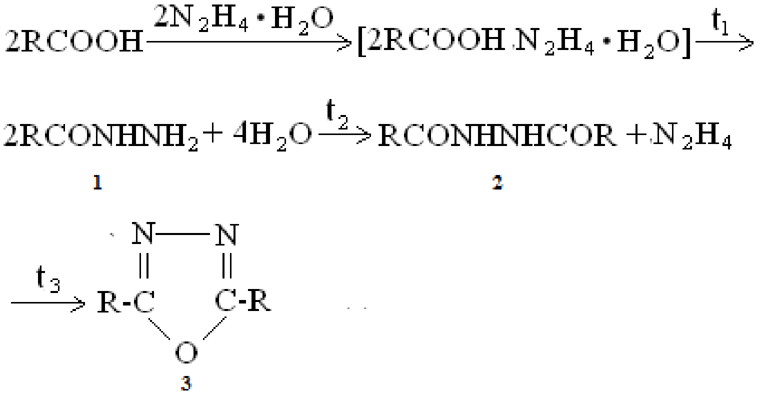
Abstract. In this work, the reaction of hydrazinolysis of aliphatic carboxylic acid in the presence of an ionite catalyst is considered for the first time. The experiments were made in the static conditions. Previously, the corresponding butyl ether was obtained from the butyric acid, which in interaction with hydrazine formed a hydrazide. The influence of various factors (quantity of hydrazine hydrate, catalyst, butyl alcohol, temperature, reaction duration) on the formation of butyric acid hydrazide was studied. It reveals optimum conditions of synthesis under which the most hydrazide yield made 68%. As a result, the IR spectroscopic researches of the mechanism of hydrazinolysis reaction of the butyl ester of butyric acid with active centers of sulphonic cation-exchange. It is shown that the reaction proceeds with the formation of transition complexes on the surface of the cation exchange resin. The practical value of this work is to develop an effective method of butyric acid hydrazide preparation.

Keywords: butyric acid, hydrazinolysis, hydrazine, hydrazide, catalyst.

Aliphatic carboxylic acid hydrazides and their derivatives are widely used in medical practice, in various sectors of the national economy [1]. For example, 3- hydroxyl- 4,4,4-trichloro butyric acid hydrazide has been proposed for use as a biologically active compound.

There are various methods of obtaining hydrazides of aliphatic acids. For example, the most promising way to produce hydrazides is the hydrazinolysis of esters, mainly methyl or ethyl esters of the corresponding carboxylic acids, when heated in a solvent medium. For example, 3 - hydroxy-4,4,4-trichlorobutyric acid hydrazide is obtained in an alcohol medium by the reaction of β- trichloromethyl - β-propiolactone with hydrazine hydrate [2].

In addition, methods are known based on the thermal decomposition of carboxylic acid salts with hydrazine [3]. The main patterns that appear when aliphatic carboxylic acids are heated with hydrazine hydrate are generally known and are depicted by the scheme:



$$2RCOOH \xrightarrow{2N_2H_4 \cdot H_2O} [2RCOOH\,N_2H_4 \cdot H_2O] \xrightarrow{t_1}$$

$$\underset{1}{2RCONHNH_2} + 4H_2O \xrightarrow{t_2} \underset{2}{RCONHNHCOR} + N_2H_4$$

The disadvantage of these methods is that, especially when using acids with radicals R> C_3H_7, along with the main product (**1**), are obtained incommensurate amounts of impurities - 1,2-diacylhydrazines (**2**) and cyclic compounds (**3**). The yield of the main product is increased, in particular, by azeotropic distillation of water. There is also known a method for producing hydrazides by thermal decomposition of $RCONHNH_2 \cdot N_2H_4$ salts (where R = pyrid-4-yl, Ph or lower alkyl) by reacting carboxylic acid (CA) and hydrazine hydrate (HH) with a ratio CA: HH = 1: (1.2 -1.4), in the presence of a catalyst (Al_2O_3, sulfonic cation exchanger) with azeotropic distillation of water [4]. The method is suitable only for lower carboxylic and aromatic acids. Also known is a method of producing hydrazides by thermal decomposition of salts of carboxylic acids with hydrazine hydrate, including mixing carboxylic acid and hydrazine hydrate in a molar ratio of CA: HH = 1: 1.2, heating under reflux in the presence of butanol, active aluminum oxide and benzene, distilling water as an azeotrope at a temperature of 95 °C for 2-8 hours, filtering the melt of the reaction mixture, crystallization, washing and drying the product in vacuum [5]. The yield of hydrazides is 80-95%.

The disadvantage of this method is that it is suitable for obtaining only hydrazides of lower carboxylic aliphatic acids with the radicals R = CH_3, i-C_3H_7. In addition, this method uses solvents that deteriorate the organoleptic properties of the product, which requires additional purification of the target product.

At present, the synthesis of carboxylic acids and their derivatives using heterogeneous catalysts - ionites is the most promising method. In this regard, the synthesis of practically important aliphatic hydrazides in the presence of heterogeneous catalysts is an important task.

The purpose of this study is to investigate the hydrazinolysis of butyl ester in the presence of the sulfonic acid cation exchanger KU-2-8 in the H-form.

Experimental part

Experiments are carried out in static conditions. In a three-neck round-bottom flask with a capacity of 250 ml, equipped with a reflux condenser, 1 g (0.011 mol) of butyric acid, 0.5 g (0.005 mol) of sulfuric acid, 0.9 g (0.012 mol) of butyl alcohol are introduced. The reaction mixture is heated at 90 ° C for 3 hours. Upon completion of the reaction, the mixture is cooled and neutralized with 50 ml of 5% sodium hydrogen carbonate solution. The ether layer is separated and distilled. The butyric acid butyl ester obtained, with a boiling point of 165-166 ° C, is used to further obtaining the corresponding hydrazide.

In a three-neck round-bottom flask with a capacity of 250 ml, equipped with a mechanical stirrer, a thermometer and a reflux condenser, 1 g (0.007 mol) of butyl butyric ester, 0.6 g (0.012 mol) of hydrazine hydrate, 0.67 g of cation exchanger KU-2-8 in H -form, 0.6 g (0.008 mol) of butyl alcohol are introduced. The reaction mixture is heated on a water bath, stirring for 3 hours at a temperature of 80°C. After this time, the mixture is cooled and the cation exchanger is filtered off from the liquid part, washed with 1 ml of butyl alcohol. The alcohol is distilled off from the solution, the remaining solid residue is dried at 30°C. The analysis of butyric acid hydrazide is carried out by the photocolorimetric method. The melting point of hydrazide is 46-49°C. The IR spectra of the starting materials and reaction products are taken on "Impact 410" spectrometer (USA).

Results and their discussion

Butyric acid butyl ester is synthesized by reacting butyric acid and butyl alcohol in the presence of concentrated sulfuric acid.

$$CH_3CH_2CH_2COOH+C_4H_9OH \rightarrow CH_3CH_2CH_2COOC_4H_9+H_2O$$

The optimal reaction conditions for the esterification of butyric acid are the mass ratio of butyric acid: butyl alcohol: sulfuric acid 1: 0.9: 0.5, temperature of 90°C, 3 hours of reaction time. The yield of butyric ester was 70% of the theoretical.

The IR spectrum, boiling point, and the refractive index of butyl acid butyl ester correspond to those of a standard substance. The resulting ester was used to synthesize butyric acid hydrazide.

Butyric acid butyl ester hydrazinolysis was investigated in the presence of cation exchanger KU-2-8 in the H-form.

$$CH_3CH_2CH_2COOC_4H_9 + N_2H_4 \xrightarrow{KU\text{-}2\text{-}8(H)} CH_3CH_2CH_2CONHNH_2 + C_4H_9OH$$

Under the conditions studied, the main product of the interaction of butyric acid butyl ester with hydrazine hydrate is butyric acid hydrazide. The influence of various factors (the amount of hydrazine hydrate and cation exchanger, temperature and duration of the reaction) on the formation of hydrazide are given in the table. During hydrazinolysis of butyl acid butyl ester, the optimum process conditions are the mass ratio ester: hydrazine hydrate : butyl alcohol: cation exchanger = 1: 0.6: 0.6: 0.67, temperature of 80°C, 3 hours of reaction time, while the hydrazide yield amounted to 68%.

Table - Butyric acid butyl ester hydrazinolysis (ester mass is 1 g).

hydrazine hydrate, g	cation exchanger, g	butyl alcohol, g	reaction time, hours	temperature, °C	the hydrazide yield, %
0,6	0,67	0,6	3	80	68
0,6	0,67	0,6	3	40	15
0,4	0,67	0,6	3	80	30
0,5	0,67	0,6	3	80	25
0,8	0,67	0,6	3	80	18
0,6	1,00	0,6	3	80	47
0,6	0,67	0,6	2	80	36
0,6	0,67	1,0	3	80	53

In the infrared spectrum of butyric hydrazide, absorption bands of valence vibrations are observed in the region of 1689 cm $^{-1}$ (C = O), 2946– 2863 cm $^{-1}$ (CH, CH_2, CH_3), 1470-1351 cm $^{-1}$ (C – C), 3440 cm^{-1} (NH) groups, as well as deformation vibrations in the region of 1559 cm^{-1} (NH) groups (figure).

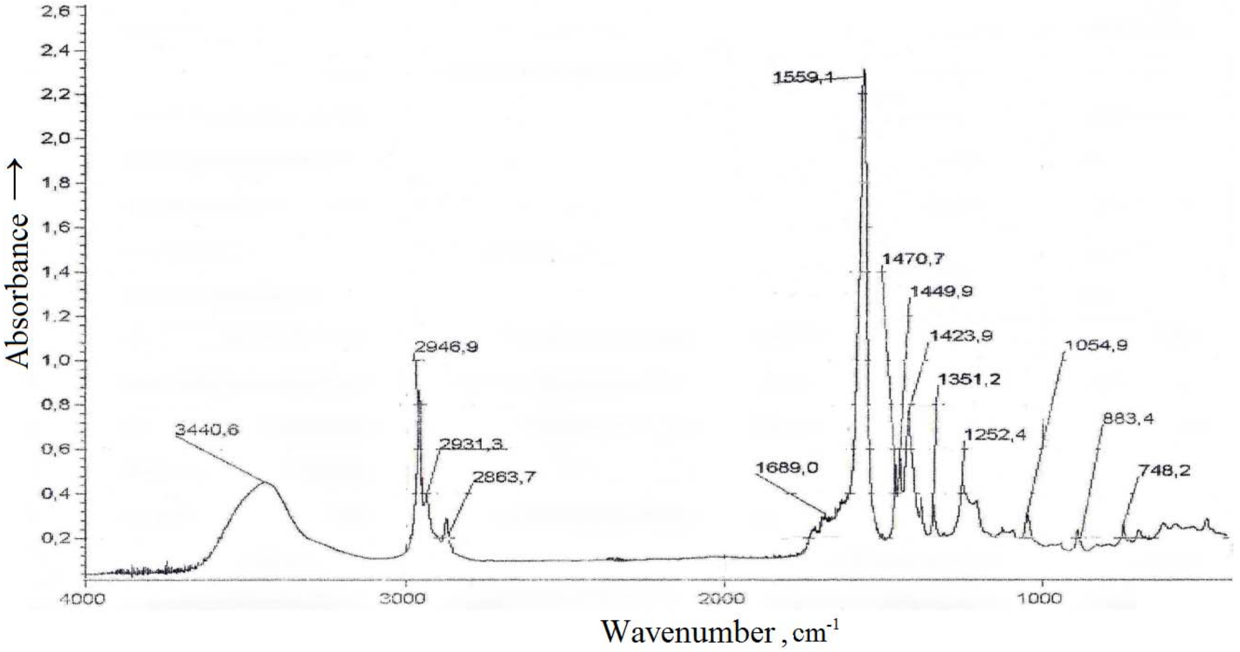
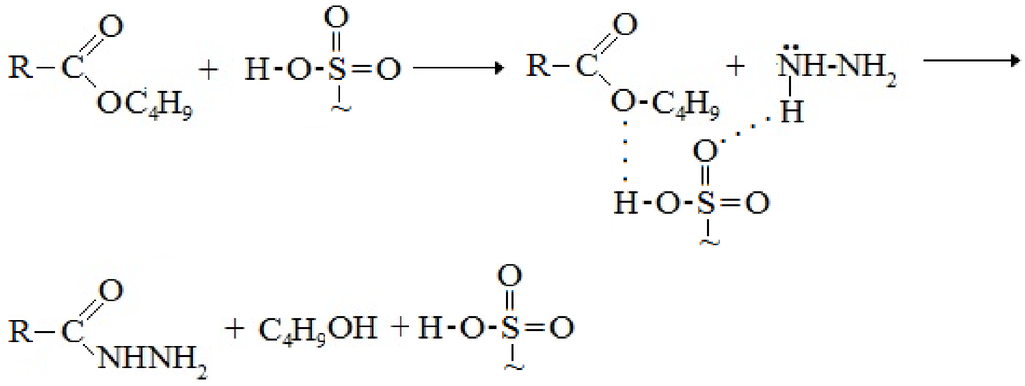


Figure - IR spectrum of butyric acid hydrazide

The mechanism of hydrazinolysis of esters of aliphatic carboxylic acids is still not well understood. According to [7], it can be assumed that hydrazinolysis of butyric acid butyl ester in the presence of an ion exchange resin KU-2-8 (H) is carried out by heterogeneous catalysis and the active centers of the cation exchanger are polymer-bound sulfogroup and hydrogen ions. During the adsorption of butyl ester of butyric acid on sulfonic cation, an intermediate complex is formed, which then interacts with hydrazine to form hydrazide and regenerate the active centers of the ion exchanger.



$R = CH_3CH_2CH_2-$

Thus, we first studied the hydrazinolysis of aliphatic acid esters using the example of butyl acid butyl ester in the presence of KU-2-8 (H) sulfonic cation exchanger, found the optimal process conditions and made conclusions regarding the reaction mechanism.

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АЛИФАТТЫ КАРБОН ҚЫШҚЫЛДАРЫНЫҢ КАТАЛИТТІК ГИДРАЗИНОЛИЗ РЕАКЦИЯСЫН ЗЕРТТЕУ

Аннотация. Бұл жұмыста алғаш рет алифатты карбон қышқылының гидразинолиз реакциясы ионитті катализатор қатысында қарастырылды. Тәжірибелер статикалық жағдайда жүргізілді. Май қышқылынан алдымен оған сәйкес бутилді эфир алынды, ары қарай оны гидразинмен әрекеттестіргенде гидразид түзілді. Май қышқылы гидразидінің түзілуіне әртүрлі факторлардың (гидразингидраттың, катализатордың, бутил спиртінің мөлшері, температура, реакция ұзақтығы) әсері зерттелді. Синтездің оңтайлы жағдайларында май қышқылы гидразидінің шығымы 68 % болды. ИҚ-спектроскопиялық зерттеулер нәтижесінде май қышқылы бутил эфирінің гидразинолиз реакциясы сульфокатиониттің активті орталықтарының қатысуымен жүзеге асатын механизмі ұсынылды. Реакцияның катионит бетінде ауыспалы комплекстердің түзілуімен жүретіндігі көрсетілді. Бұл жұмыстың практикалық маңыздылығы май қышқылының гидразидін алудың тиімді әдісін ойластыру болып табылады.

Түйін сөздер: май қышқылы, гидразинолиз, гидразин, гидразид, катализатор.

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ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОЙ РЕАКЦИИ ГИДРАЗИНОЛИЗА АЛИФАТИЧЕСКИХ КАРБОНОВЫХ КИСЛОТ

Аннотация. В этой работе впервые рассмотрена реакция гидразинолиза алифатической карбоновой кислоты в присутствии ионитного катализатора. Опыты проводили в статических условиях. Предварительно из масляной кислоты был получен соответствующий ему бутиловый эфир, который при взаимодействии с гидразином образовал гидразид. Изучено влияние различных факторов (количества гидразингидрата, катализатора, бутилового спирта, температуры, продолжительности реакции) на образование гидразида масляной кислоты. В оптимальных условиях синтеза выход гидразида масляной кислоты составил 68 %. В результате ИК- спектроскопических исследований предложен механизм реакции гидразинолиза бутилового эфира масляной кислоты с участием активных центров сульфокатионита. Показано, что реакция протекает с образованием переходных комплексов на поверхности катионита. Практическая значимость работы состоит в разработке наиболее эффективного способа получения гидразида масляной кислоты.

Ключевые слова: масляная кислота, гидразинолиз, гидразин, гидразид, катализатор.

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EFFECT OF THE BROMIDE IONS ON THE TITANIUM ELECTRODE DISSOLUTION POLARIZED BY ALTERNATING CURRENT IN AQUEOUS SOLUTIONS

Abstract. The titanium electrode dissolution possibility polarized by industrial alternating current (AC) with 50 Hz frequency in potassium bromide aqueous solution acidified by sulfuric acid was shown for the first time and the process dissolving titanium were determined. The influence of alternating current density (200-1200 A/m^2), potassium bromide solution concentration (1.0-5.0 M) and sulfuric acid concentration (0.5-4.0 M), AC frequency (25-150 Hz), electrolyte temperature (25-80°C) and electrolysis duration (0.5-2 hours) on the current efficiency (CE) of the titanium dissolution were considered. It was observed extremely low CE (1.8%) of the titanium dissolution by polarization anodic direct current. When titanium was polarized by alternating current, the CE reached 60% at a current density of 200 A/m^2 in the titanium electrode, and as the current density was increased the CE of titanium dissolution was decreased. The titanium dissolution CE showed the maximum value in 0.5 M sulfuric acid and 1.0 M potassium bromide solution. The decrease of titanium electrode CE due to the increase of the electrolysis duration and the AC frequency effect was determined.

Keywords: titanium, alternating current, electrolysis, potassium bromide, sulfuric acid.

Today the application of industrial alternating current frequency of 50 Hz to the electrolysis processes in the field of applied electrochemistry contributes to the new scientific trends development. This method allows conducting electrochemical reactions in solutions, dissolving insoluble metals and activating these processes [1-4].

Titanium and its compounds are light, biologically harmless and resistant to corrosion and environmental impacts. Though this metal is one and a half times heavier than aluminum, two times lighter than iron, it is widely used for the production of aircraft engines, orthopedic implants, construction materials, submarines, electrode and pyrotechnics due to its six times stronger solidity [5-7]. Titanium dioxide has a great deal to contribute to the food industry as an additive labeled E171. Titanium (III) nitride is a unique compound in covering metal surfaces, also known as fake gold, which is resistant to the decays king's water and is much cheaper than gold [8].

Titanium is an element with high melting point that is not soluble in acids by chemical methods. Due to its wide use today, obtaining various compounds through its dissolution is of great importance [9].

Titanium dissolution in hydrochloric acid with fluoride ions and in phosphoric acid solution in the presence of industrial alternating current has been shown in scientific works [10-15]. However, the works do not specify the electrochemical properties of titanium electrode in the bromide aqueous media [16-20]. In this regard, the present work considered the electrochemical dissolution behavior of titanium electrode in bromide aqueous media. In addition, the influence of the main parameters (current density, electrolyte temperature and solution concentration, alternating current frequency, etc.) on electrochemical dissolution process of titanium electrode was investigated.

Results and discussion

The preliminary experiments results showed the insolubility of the two titanium plates in bromide aqueous solutions in the presence of direct current as their surface was covered by a layer of oxide film. However, when the two titanium electrodes were polarized with industrial alternating current, intensive dissolution of the metal was observed.

The current density effect on the titanium electrode dissolution in bromide aqueous solution was investigated (Table 1). The research results showed that the current efficiency reached 60% at a current density of 200 A/m^2 in the titanium electrode, but while the current density was increased the CE of titanium dissolution was decreased. This phenomenon can be explained with the oxide film formation on the titanium surface in the anodic half period of the alternating current at high current densities and these inherent oxide films could lead to passivation of electrode surface.

Table 1 - The influence of Current density on titanium electrodes polarized
by alternating current on the CE of their dissolution

[KBr]=1,0 M, [H_2SO_4]=0,5 M, τ=0,5 h

i, A/m^2	200	400	600	800	1000	1200
CE, %	60	41.6	28.2	22.4	18.3	14.7

The potassium bromide concentration effect in the absence of acid in the neutral medium was investigated to determine the titanium dissolution specificity in bromide aqueous solutions (see Table 2). The results showed the current efficiency decrease of the titanium electrode dissolution from 25% to 8% due to the increase of the potassium bromide concentration in the range of 1.0-5.0 M.

Table 2 - The effect of Potassium bromide concentration on the CE
of titanium electrodes dissolution rate polarized by alternating current

i = 200 A/m^2, τ = 0.5 h

[KBr], M	1	2	3	4	5
CE, %	25	17.2	13.4	10	8

Due to the low current efficiency of titanium dissolution in bromide aqueous solutions, it was investigated the titanium dissolution specificity in the presence of sulfuric acid (Table 3). With the increasing sulfuric acid concentration from 0.5M to 2.0 M there was observed dynamically increase of titanium dissolution current efficiency value from 12% to 44%. Further increase of sulfuric acid concentration leads to the current efficiency decrease up to 16%. This phenomenon can be assumed that sulfate ions first interact with the film on the titanium surface and create a favourable condition for the titanium dissolution. Further, the increase of oxygen-containing sulfate ions concentration simplifies the oxide film formation on the titanium surface and allows its passivation.

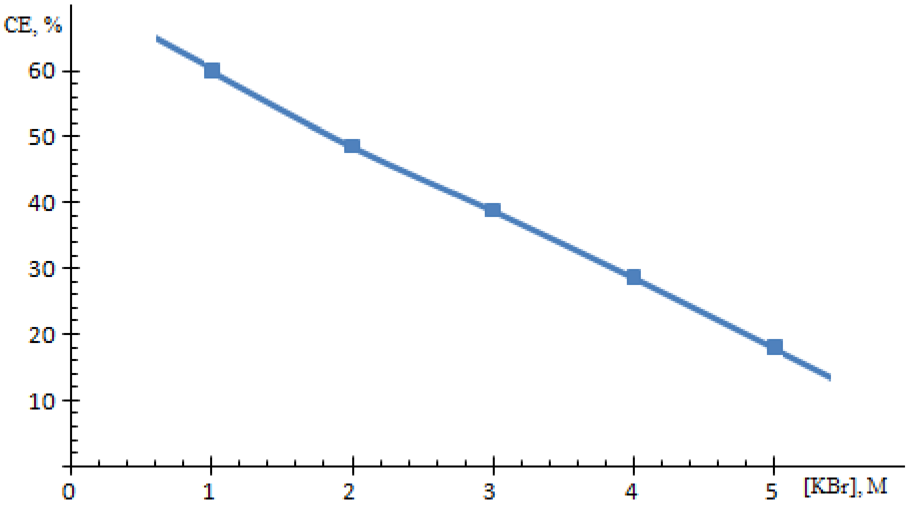
Table 3 - The effect of Sulfuric acid concentration on the CE
of titanium electrodes dissolution rate polarized by alternating current

i = 200 A/m^2, τ = 0.5 h

[KBr], M	0.5	1	2	3	4
CE, %	12	24.5	44	29.6	16

As the current efficiency of alternating current polarized titanium electrode did not exceed 44% in sulfuric acid, the potassium bromide solution was acidified with sulfuric acid 0.5 M and the potassium bromide concentration effect on the solution was investigated (Figure 1). The more the potassium bromide concentration was increased, the less the current efficiency decreased. This phenomenon can be explained by the fact that initially when 1.0 M potassium bromide solution acidified with 0.5 M sulfuric acid, these acidified bromide ions created conditon for titanium dissolving, but futher increasing the potassium bromide concentration leads to the increase of bromide ions amount as a result of which the titanium passivation takes place. In this case, as the potassium bromide concentration effect (Table 2) is considered, a straight line decrease of the current efficiency value was observed. However, it should be noted that current efficiency increased by 2.5 times.

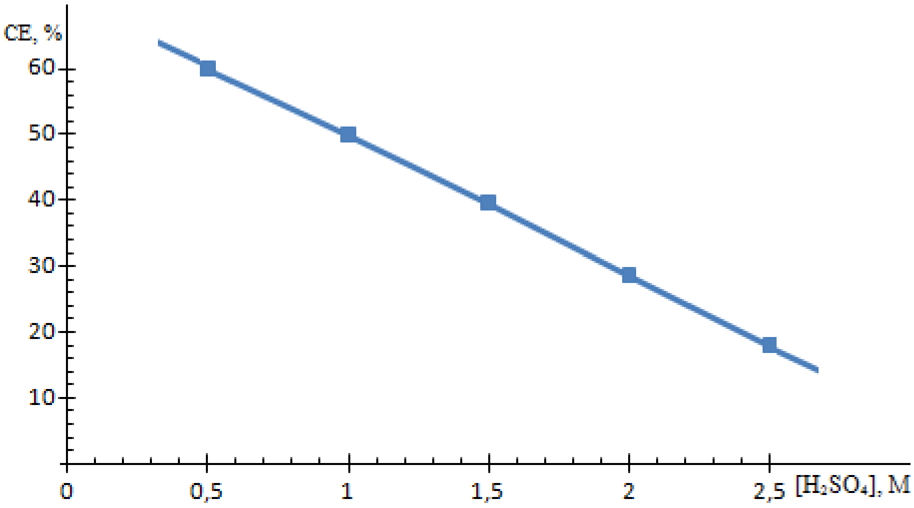
With a view to further increasing the titanium electrode current efficiency, the potassium bromide was acidified with sulfuric acid and the change in its concentration was investigated (Figure 2).



i = 200 A/m^2, [H_2SO_4] = 0.5 M, τ = 0.5 h

Figure 1 - The influence of Potassium bromide concentration on the CE
of titanium electrodes dissolution polarized by alternating current

However, if an sharply fluctuate in a peak was observed in the sulfuric acid concentration, a straight line decrease in the titanium current efficiency took place when the potassium bromide solution was acidified with sulfuric acid solution and the sulfuric acid concentration was increased. The titanium electrode current efficiency decreased from 60% up to 18%.



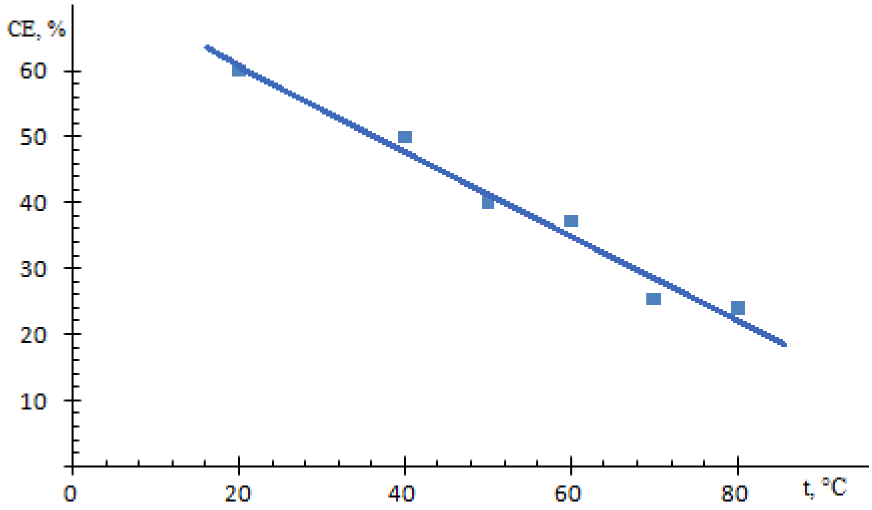
i = 200 A/m^2, [KBr] = 1.0 M, τ = 0.5 h

Figure 2 - The effect of Sulfuric acid concentration on the CE
of titanium electrodes dissolution polarized by alternating current

The temperature effect on titanium electrode dissolution in bromide-acid aqueous solutions was considered (Figure 3). Studies have shown the current efficiency decrease of titanium electrode dissolution due to the temperature increase. According to the fundamental principles, the increase of solution temperature should cause the increase of chemical reactions rate. Explaining the abnormal decrease in the titanium electrode dissolution rate due to the temperature increase requires additional studies. It is possible to assume that as the solution temperature increases, the oxide film stability on the titanium surface increases.

The temperature effect on the current efficiency of alternating current polarized titanium electrode was investigated from 25˚C up to 80˚C. It should be noted that temperature increase lead to downward trend and the titanium current efficiency decreased from 60 to 24%.

Following figure 4 shows the electrolysis duration effect on the current efficiency of alternating current polarized titanium electrode. The current efficiency of titanium electrode decreased from 60% to 20% between 0.5-2.0 hours. As we have seen, as the electrolysis time was increased, the current efficiency firstly increased and then decreased. The bromide ions reacted with the oxide film on the titanium surface and created a complete titanium dissolution. As the time passed, the dissolved titanium slowed down by forming oxide film again on the electrode surface.

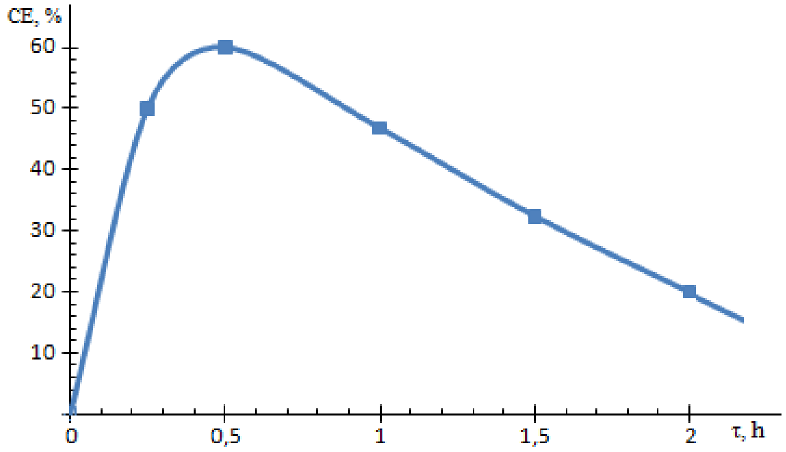


$i = 200\ A/m^2$, $[KBr] = 1.0\ M$, $[H_2SO_4] = 0.5\ M$, $\tau = 0.5\ h$

Figure 3 - The influence of temperature in the CE of titanium electrodes dissolution polarized by alternating current

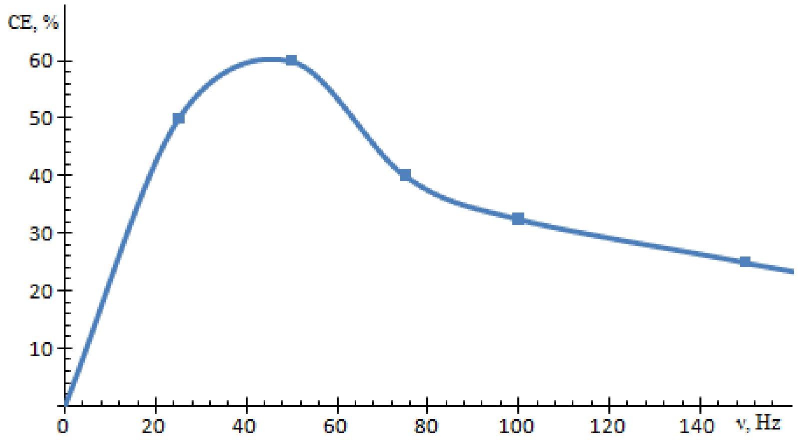
The current frequency effect on the titanium electrode dissolution in bromide-acid aqueous solutions is given in Figure 5. Experimental data have shown that as the current efficiency rate is increased from 25 to 150 Hz, the titanium dissolution current efficiency increases up to 50 Hz and then gradually decreases. This change can be assumed that the more the current frequency increases, the better rational condition is created for the oxygen shell formation on the surface of the alternating current polarized titanium electrode.

The titanium electrode dissolution in bromide-acid aqueous solutions showed a decrease in the current efficiency from 60% to 25% between 50 - 150 Hz.



i = 200 A/m^2, [KBr] = 1.0 M, [H_2SO_4] = 0.5 M

Figure 4 - The effect of electrolysis duration on the CE of titanium electrodes dissolution polarized by alternating current



i = 200 A/m^2, [KBr] = 1.0 M, [H_2SO_4] = 0.5 M, τ = 0.5 h

Figure 5 - The influence of current frequency on current efficiency
of titanium electrodes dissolution polarized by alternating current

In conclusion, titanium electrode dissolution polarized by alternating current in bromide aqueous solutions was shown for the first time. The various parameters influence on the titanium dissolution rate was investigated. It has been found that titanium dissolution current efficiency reached 60% in effective conditions of electrolysis. The results of this study allow dissolving the insoluble titanium electrode in bromide acid solutions and producing technologies for obtaining its various compounds.

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АЙНЫМАЛЫ ТОКПЕН ПОЛЯРИЗАЦИЯЛАНҒАН ТИТАН ЭЛЕКТРОДЫНЫҢ СУЛЫ ЕРІТІНДІЛЕРДЕ ЕРУІНЕ БРОМИД ИОНДАРЫНЫҢ ӘСЕРІ

Аннотация. Ұсынылып отырған жұмыста күкірт қышқылымен қышқылданған калий бромиді ерітіндісінде жиілігі 50 Гц өндірістік айнымалы токпен поляризацияланған титан электродының еритіндігі алғаш рет көрсетілді және еру заңдылықтары анықталды. Титанның еруінің ток бойынша шығымына айнымалы ток тығыздығының (200-1200 А/м^2), калий бромиді ерітіндісі концентрациясының (1,0-5,0 М), күкірт қышқылы концентрациясының (0,5-4,0 М), айнымалы ток жиілігінің (25-150 Гц), ерітінді температурасының (25-80°С), электролиз ұзақтығының (0,5-2 сағат) әсерлері қарастырылды. Тұрақты токпен поляризацияланғанда титанның өте төмен ток бойынша шығыммен еритіндігі байқалды (1,8%). Айнымалы токпен поляризацияланғанда титан электродындағы ток тығыздығы 200 А/м^2 кезінде ток бойынша шығым 60% тең болды да, ток тығыздығын жоғарылатқан сайын оның еруінің ТШ төмендегендігі анықталды. Титан еруінің ток бойынша шығымы 0,5 М күкірт қышқылы және 1,0 М калий бромиді ерітіндісінде максималды мәнді көрсетті. Электролиз ұзақтығының және айнымалы ток жиілігінің әсерін арттырған сайын титан электродының ток бойынша шығымы төмендейтіндігі анықталды.

Түйін сөздер: титан, айнымалы ток, электролиз, калий бромиді, күкірт қышқылы.

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ВЛИЯНИЕ БРОМИД-ИОНОВ НА РАСТВОРЕНИЕ ТИТАНОВЫХ ЭЛЕКТРОДОВ В ВОДНОМ РАСТВОРЕ ПРИ ПОЛЯРИЗАЦИИ ПЕРЕМЕННЫМ ТОКОМ

Аннотация. В данной работе впервые показана возможность растворения титана в сернокислых бромидных растворах при поляризации промышленным переменным током частотой 50 Гц и установлены протекания процесса закономерности растворения титана. Изучено влияние – плотности переменного тока (200-1200 А/м^2), концентрации раствора бромида калия (1,0-5,0 М), концентрации серной кислоты (0,5-4,0 М), частоты переменного тока (25-150 Гц), температуры раствора (25-80 °С) и продолжительности электролиза (0,5-2 часа) на выход по току (ВТ) растворения титана. При поляризации анодным постоянным током наблюдалась низкий ВТ растворения титана (1,8%). А при поляризации титана переменным током, при плотности тока 200 А/м^2 ВТ составил 60 %, а с увеличением плотности тока ВТ растворения титанового электрода уменьшается. Устанавлено, что в растворе, содержащем 1,0 М бромистого калия и 0,5 М серной кислоты наблюдается максимальное значение ВТ растворения титанового электрода. При увеличении продолжительности электролиза и частоты переменного тока ВТ растворения титана уменьшается.

Ключевые слова: титан, переменный ток, электролиз, бромид калия, серная кислота.

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