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Д.В.Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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ELECTROLYSIS OF COPPER FORM STRIPPING SOLUTIONS FOR ETCHING PRINTED CIRCUIT BOARDS

Abstract The article reviews the liquid extraction - electrolysis based etching solution regeneration process for printed circuit boards.

It describes process conditions providing the electrolysis of copper from sulphate solutions that are formed at the stage of stripping (re-extraction) of copper ions (II) from organic extractants.

Tests have been carried out in an industrial environment.

It shows that the electrolysis of copper proceeds generating high current efficiency where a stripping solution contains 1.0 mol/l of sulfuric acid and 0.8 - 1.0 mol/l of copper ions (II), the current density is 1.0 - 6.0 A/ dm^2 and electrolyte is mixing. An analysis has been made of the composition of cathode copper obtained as a result of electrolysis from the reference electrolyte and stripping solutions upon contact with organic extractants. It has been found that the purity of cathode copper reaches 95 - 98% of the base substance. It has also been found that stripping solutions progressively accumulates an insoluble precipitate comprising about 40% of lead, which may be attributed to the mechanical destruction of the active anode layer composed of lead oxides (PbO_2). The study shows that it is necessary to look for a anode material to replace lead dioxide anodes having poor stability in this process.

Keywords: printed circuit boards, etching, copper-ammonia solutions, copper-chloride solutions, regeneration, extraction, stripping solutions, electrolysis, anode, cathode copper, current density, current efficiency.

Introduction

The operation of etching the copper layer from the non-conductor surface is the requisite stage in the process of manufacturing printed circuit boards [1, 2]. At present, two types of etching solutions are primarily used, i.e. those of hydrochloric acid or alkaline ammonium. And in both cases, the formulation includes dichloride copper lending a distinct quality to the etching mechanism [3-5].

The dissolution process is driven by the interaction of metallic copper with ions of divalent copper acting as an oxidizing agent for the solution, resulting in a gradual increase in the total content of copper ions in the solution thus progressively slowing down the etching rate necessitating changing the solution. In up-to-date processes it is essential to maintain the etching rate at the same level. It is achievable by the fixed composition of the etching solution [6,7].

This can be done by using regeneration systems. The maximum desired effect has been produced by the regeneration process based on the recovery of copper ions by extraction from an aqueous etching solution [8-10]. Following the extraction stage, copper ions are re-extracting into the sulfate electrolyte depositing metallic copper onto the electrolyzer cathode [11–13]. The reactions describing the entire etching and regeneration process cycle are detailed in Table 1.

Table 1- The etching and regeneration reactions using the method of liquid extraction & electrolysis of copper-ammonia and copper-chloride based etching solutions

Item No.	Operations	Typical reactions for etching and regeneration	
		Copper ammonia solution	Copper chloride solution
1	Etching	a) $Cu^0_{met.} + Cu(NH_3)_4Cl_2 \rightarrow 2Cu(NH_3)_2Cl$; б) $2Cu\ (NH_3)_2Cl + 1/2O_2 + 2NH_4OH + 2NH_4Cl \rightarrow 2Cu(NH_3)_4Cl_2 + 3H_2O$.	a) $Cu^0_{met.} + CuCl_2 \rightarrow 2CuCl$; б) $2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 {}_+ H_2O$.
2	Extraction	$2HR^*_{(org.)} + Cu(NH_3)_4Cl_2 + 2H_2O \rightarrow CuR_2{}^*_{(org.)} + 2NH_4Cl + 2NH_4OH$	$2HR^{**}_{(org.)} + CuCl_2 \rightarrow CuR_2{}^{**}_{(org.)} + 2HCl$
3	Stripping	$CuR_2{}^*_{(org.)} + H_2SO_4 \rightarrow CuSO_4 + 2HR^*_{(org.)}$	$CuR_2{}^{**}_{(org.)} + H_2SO_4 \rightarrow CuSO_4 + 2HR^{**}_{(org.)}$
4	Electrolysis	a) cathode: $CuSO_4 + 2e \rightarrow Cu^0_{cat.} + SO_4^{2-}$; b) anode: $H_2O - 2e \rightarrow 1/2O_2\uparrow + 2H^+$	a) cathode: $CuSO_4 + 2e \rightarrow Cu^0_{cat.} + SO_4^{2-}$; b) anode: $H_2O - 2e \rightarrow 1/2O_2\uparrow + 2H^+$
5	The resultant reaction is as follows:	$Cu^0_{met.} \rightarrow Cu^0_{cat}$	$Cu^0_{met.} \rightarrow Cu^0_{cat}$
Legend: $HR^*_{(org.)}$ and $HR^{**}_{(org.)}$ - extractants, $CuR_2{}^*_{(org.)}$ and $CuR_2{}^{**}_{(org.)}$ - copper organic compounds, $Cu^0_{cath.}$ – non-conductor copper, $Cu^0_{cath.}$ – cathode copper			

It can be seen from the above-referenced reactions that the etching of copper and the regeneration of etching solutions using the liquid extraction & electrolysis method looks balanced making all solutions reusable and electrolytic copper the only by-product. In addition, it is evident that these etching solution regeneration systems have the common stage of electrically depositing copper from sulfate stripping solutions.

The process flow diagram of continuous regeneration of etching solutions for printed circuit boards is shown in Figure 1.

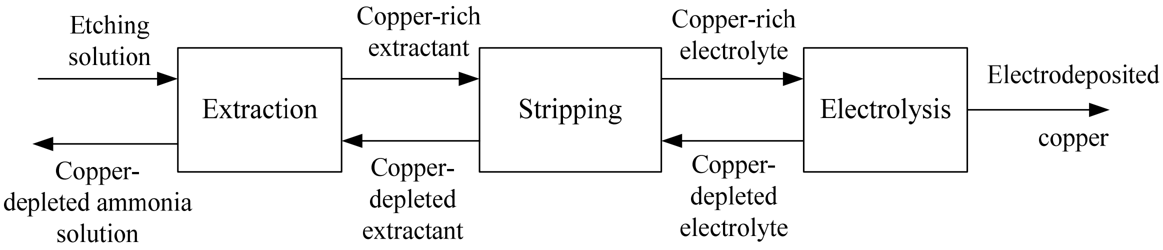


Figure 1 - Process flow diagram of continuous copper extraction and stripping followed by the electrochemical deposition of copper

The stages of extraction and re-extraction (stripping) have covered in sufficient detail earlier [14], while the features of copper electrolysis relating to this process have not been discussed.

Therefore, the purpose of this study was to examine the features of the cathode extraction of copper from stripping solutions.

Test Technique

To simulate the regeneration process and to obtain re-extraction copper-enriched solutions, the plant shown in Figure 2 was used.

The plant operates two ETs33F PTFE centrifugal extractors splitting the aqueous and organic phases under the impact of centrifugal forces at a rotor speed of 2,700 rpm [15]. The extractors enable a maximum of 15 l/h of the solution to be processed in a flow through mode.

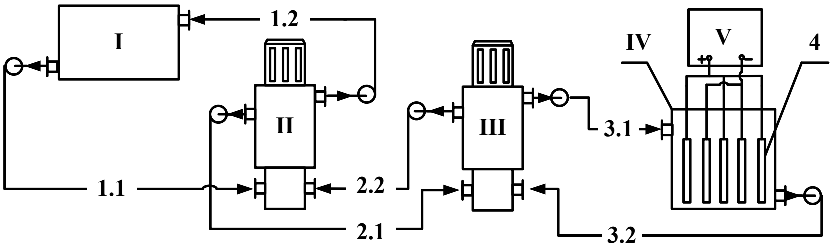
The plant includes a copper etching tank and a solution stripping copper electrolysis bath. During the test the plant was used in an industrial like environment. It was connected to a printed circuit board etching machine, as it is difficult to produce the requisite amount of etching solutions in laboratory conditions.

Polarization measurements were carried out in a three-electrode 50 cm^3 electrochemical cell using an IPC - Pro MF potentiostat/galvanostat. A copper plate with a 1 cm^2 surface was used as a working electrode; a platinum plate – an auxiliary electrode; a saturated silver chloride electrode –a reference electrode.

The obtained potential data were recalculated with respect to the reference hydrogen electrode (RHE). Polarization curves were recorded in a potential & dynamic mode with a potential sweep rate of 10 mV/s.

The assay test of the sediment was carried out using a JEOL JSM-5610 LV scanning electron microscope complete with an Oxford Instruments energy dispersive X-ray attachment. The dispersive parameters of the sediment were determined by laser diffraction using an Analysette NanoTec laser particle sizer.

To determine the concentration of copper (II) ions in the solution the complexometric titration method was applied. A 0.1 N solution of Trilon B (EDTA) was used as the titrant [16].



1.1 – Copper-rich etching solution; 1.2 – Copper-depleted etching solution; 2.1 – Copper-rich extractant;
2.2 – Copper-depleted extractant; 3.1 – Copper-rich electrolyte; 3.2 – Copper-depleted electrolyte; 4 – Electrodeposited copper;
I – Etching bath; II – Extractor 1; III – Extractor 2; IV – Electrolytic bath; V – DS source

Figure 2 - The test plant setup for solution etching and regeneration of solutions is given below

The current efficiency in% (CE) of cathode copper was obtained from polarization measurements using the formula:

$$CE= [(I_{copper)} /(I_{copper+hydrogen})]\cdot t \cdot 100\%, \qquad (1)$$

where:

I_{copper}– current strength (A) applied to extract copper is expressed as the difference between the current strength applied to extract both copper and hydrogen ($I_{copper+hydrogen}$) and extract hydrogen ($I_{hydrogen}$), t – electrolysis time (h).

The current applied to extract hydrogen was obtained from polarization measurements in the background electrolyte, i.e. a sulfuric acid solution. The current strength has been calculated by the formula $I = i\cdot S$, where: i is the current density (A/dm^2); S is the working electrode surface, dm^2.

In preparative electrolysis the specimen mass was determined before and after the electrolysis process while the current efficiency (CE) was measured gravimetrically:

$$CE = (m_{pr}/m_{т})\cdot 100\% \qquad (2)$$

where:

$m_{pr.}$ – the weight of copper deposited on the specimen during electrolysis, r; $m_{т}$ – the calculated mass of copper that is presumed to be deposited during electrolysis r.

$m_{т} = g\cdot I\cdot t$, where: g is the electrochemical copper equivalent, 1.186 g/(A·h).

To extract copper from copper-ammonia solutions, a DH-510A [17] (Deltaplast LLC (Russia)) extractant was used.

To extract copper from copper chloride solutions a MX-90 (firm SIGMA –Engineering AB (Sweden)) extractant was used.

The anodes contain lead-base lead dioxide.

Test Results and Discussion Findings

Since the entire regeneration cycle for etching solutions is a chain in interrelated processes, it was essential to determine the parameters of copper extraction from stripping solutions and to set the process parameters that are to be maintained at this stage.

During the polarization measurements of solutions with different acid content the permissible values of current densities below the limit values at which dense copper deposits are formed were obtained (Figure 3).

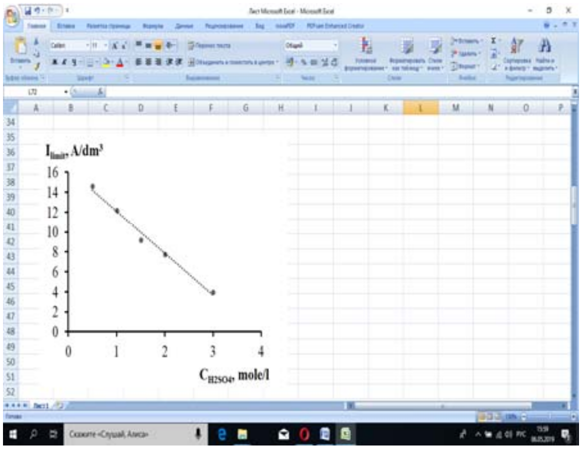


Figure 3 -The function of the limiting current density (i_{limit}) of copper extraction and a H_2SO_4 concentration in electrolyte The cathode potential is E = 220 mV (RHE)

It follows from the referenced data that solutions with a low content of sulfuric acid are more suitable for the electrolysis of copper, as they allow for a more expanded range of current densities at which compact copper deposits precipitate, which is well in accord with the literature data stating that dense copper coatings can be obtained with a sulfuric acid content of about 0.4– 0.7 mol/l [18].

But conversely, it is known that re-extraction runs rapidly with a sulfuric acid concentration of about 2.0 mol/l [19]. To finally settle on the process parameter in question, the value of copper current efficiency was determined as a function of sulfuric acid content in electrolyte. These data are reflected in figure 4.

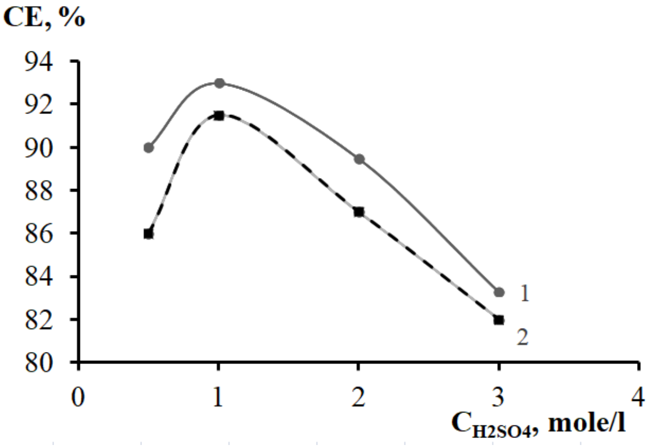
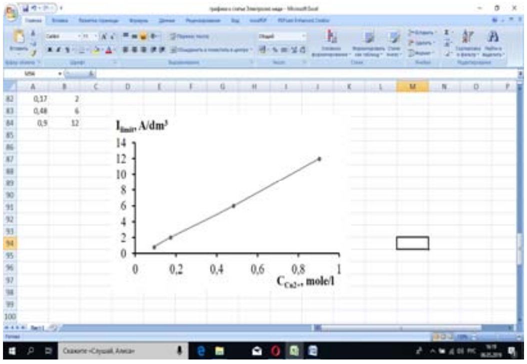


Figure 4 - The function of copper CE and the H_2SO_4 concentration in electrolyte during the electrolysis of the solution containing 0.50 mole/l of Cu^{2+} ions and i_c, A/dm^2 :1 – 1,5; 2 – 2

It was found that the maximum value of CE is observable with a sulfuric acid content of about 1.0 mol/l which is the most suitable for copper re-extraction and electrolysis.

On the other hand, the efficiency of copper electrolysis is much related to the content of copper (II) ions in a stripping solution. Figure 5 shows the relation between limiting current densities and the concentration of copper ions in a solution.



0,17	2
0,48	6
0,9	12

Figure 5 - The function of the limiting $i_к$ and the copper concentration
in a sulphate solution. C(H_2SO_4) 1.0 mol/l, E=0 mV (RHE)

A growing content of copper (II) ions in a stripping solution enables electrolysis in a wide range of current densities, and the linear function indicates that the diffusion of discharging copper ions to the cathode is critical. Stirring in electrolyte makes it possible to increase cathode current density by a factor of 1.5.

The obtained value of the current efficiency showed that copper is efficiently extracted from extraction solutions at the electrolyzer cathode reaching the limits of about 95-98% (Figure 6).

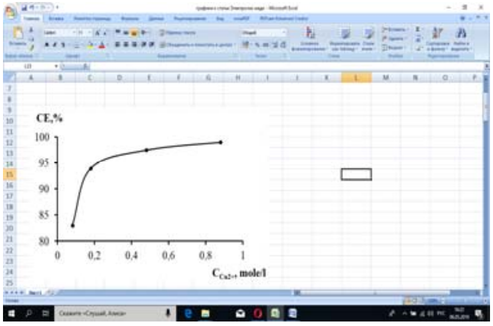


Figure 6 -The function of copper CE and a concentration of Cu^{2+} ions
in a sulfuric acid solution C(H_2SO_4) 1 mole/l, E=220 mV (RHE)

Figure 7 - Shows the relation of copper current efficiency and cathode current density at various concentrations of copper ions in a solution.

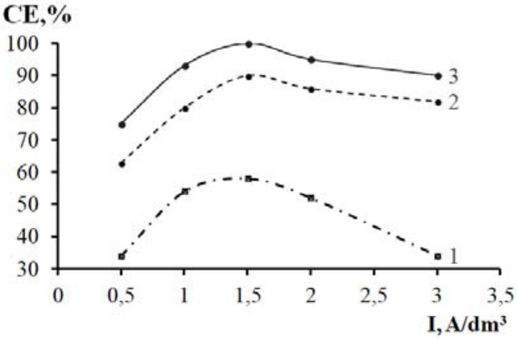


Figure 7 - The function of the copper CE and the cathode current density
at the concentration of copper ions in a solution, mol/l: 1- 0.08; 2- 0.39; 3-0.78

It was shown that while a high concentration of copper ions in a solution is maintained, the process performs well in a wide range of current densities. In the tests where a solution was mixed with air, current densities increased by a factor of a 1.5-2 can be used. The referenced results imply that the efficient electrolysis of copper requires a copper concentration in a stripping solution to be maintained at about 0.8-1.0 mol/l with the content of sulfuric acid being about 1.0 mol/L.

An analysis was mode of the composition of cathode copper obtained as a result of electrolysis from the reference electrolyte and stripping solutions upon contact with the organic extractants DX-510 A and MX-90 (table 2).

Electrically deposited copper comes out to be fairly pure. A small inclusion of oxygen can be attributed to partial deposit oxidation with ambient air oxygen. The inclusion of carbon can be accounted for by carbon dioxide present in electrolyte as well as the stripping solution being contaminated with an organic extractant.

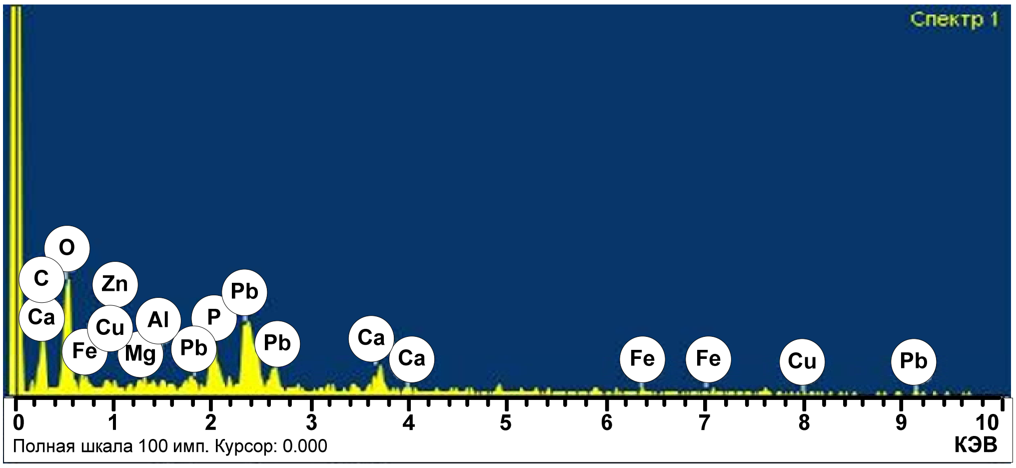
Table 2 - The element composition of copper obtained from solutions containing 0.80 mol/l of copper ions, 1.0 mol/l of sulfuric acid

Solution	Element	wt% in a deposit
Reference solution free of organic impurities	[C] / [O] / [Cu]	[0.11] / [2.67] / [97.22]
Stripping solution (using MX-90)	[C] / [O] / [Cu]	[0.73] / [3.98] / [95.29]
Stripping solution (using DX-510A)	[C] / [O] / [Cu]	[0.51] / [1.67] / [97.82]

When a reference plant is used to regenerate etching solutions, an insoluble precipitate is known to gradually accumulate in a stripping solution. The composition of this substance has been determined to find out what causes this phenomenon.

It was shown that the substance consists of amorphously structured inhomogeneous granules sized between 10 µm and 50 µm. Some impurities in the composition were found and quantified by a scanning electron microscope (Figure 8).

The deposit contains calcium, magnesium, aluminum, iron and zinc ions, which can be attributed to the fact that tap water was used to prepare the etching solution. It was found that the insoluble precipitate contains about 40% of lead. Lead can occur in a solution only as a result of mechanical destruction of the active anode layer comprising lead oxides (PbO_2). It is necessary to make allowance for the super high sensitivity of PbO_2 anodes to cathodic polarization that may take place when the electrolyzer is shut down. When powered off, the electrolyzer starts to function as a battery with the PbO_2 cathode, While PbO_2 gets partially reduced and the electrode gets covered by less stable phase lead oxides of lower valence [20-22].



Item No.	1	2	3	4	5	6	7	8	9	10
Element	C	O	Mg	Al	P	Ca	Fe	Cu	Zn	Pb
wt%	12.4	23.1	0.2	0.1	5.9	6.4	8.4	3.4	1.3	38.6

Figure 8 - The element distribution diagram for the insoluble precipitate in a stripping solution of sulfuric acid

Therefore, it can be stated that it is undesirable to use low-wearing anodes with an active layer containing lead oxides when copper is electrically deposited from stripping solutions in regeneration processes using etching solutions for printed circuit boards where such application requires electrolysis to be frequently stopped.

Conclusion

The tests have shown that the electric deposition of copper from stripping solutions in the regeneration process based on the liquid extraction-electrolysis system should be carried out under the following conditions:

a) the content of sulfuric acid etching solutions order is 1,0 mole/l; b) the content of copper (II) ions is 0.8-1.0 mol/l; c) the working current density is 1.0-6.0 A/dm^2; g) electrolyte mixing under these conditions an electrolytic deposit containing 95-97% of copper is produced.

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БАСПА ПЛАТАЛАРЫН ӨҢДЕУ РЕЭКСТРАГИРЛЕУ ЕРІТІНДІЛЕРІНЕН МЫС ЭЛЕКТРОЛИЗІ ЕРІТІНДІЛЕРДІҢ МЫСТЫҢ ЭЛЕКТРОЛИЗІ

Аннотация. Сулы экстракция –электролиз принципі бойынша жұмыс жасайтын баспа платаларын өңдеу ерітінділерін регенерациялау технологиясы қарастырылды.

Органикалық экстрагенттерден мыс (II) иондарын реэкстракциялау басқышында түзілетін күкіртқышқылды ерітінділерінен мыстың электрохомиялық жолмен бөлінуін қамтамасыз ететін технологиялық режимдер анықталды.

Тәжірибелер өндірістік шарттарда жүргізілді.

Мыстың электролизі реэкстрагирлеу ерітіндісінде 1,0 моль/л күкірт қышқылы, 0,8 - 1,0 моль/л мыс (II) иондары, ток тығыздығы 1,0 – 6,0 А/дм^2 болғанда және электролитті араластыру кезінде жоғары ток бойынша шығыммен жүретіндігі көрсетілді. Органикалық экстрагенттермен әсерлескен реэкстрагирлеу ерітінділерінің жэәне модельді электролит электролизінен кейін алынған катодты мыстың құрамы сарапталды. Негізгі зат бойынша катодты мыстың тазалығы 95-98 %-ды құрайды. Сонымен қатар, реэкстрагирлеу ерітіндісінде шамамен 40% қорғасыннан тұратын ерімейтін тұңбаның жиналатындығы анықталды. Бұл қорғасын оксидінен (PbO_2) тұратын анодтың белсенді қабатының механикалық бұзылуымен байланысты болуы мүмкін. Бұл технология үшін тұрақтылығы төмен болған қорғасын оксидінен жасалынған анодтарды алмастыра алатын материалды іздестіру керектігі көрсетілді.

Түйін сөздер: баспалы платалар, өңдеу, мыс-аммиак ерітінділері, мыс-хлоридті ерітінділер, регенерация, экстракция, реэкстрагирлеу ерітінділері, электролиз, анод, катодты мыс, ток тығыздығы, ток бойынша шығым.

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ЭЛЕКТРОЛИЗ МЕДИ ИЗ РЕЭКСТРАГИРУЮЩИХ РАСТВОРОВ ТРАВЛЕНИЯ ПЕЧАТНЫХ ПЛАТ

Аннотация. Рассмотрена технология регенерации растворов травления печатных плат, работающая по принципу жидкостная экстракция – электролиз.

Определены технологические режимы, обеспечивающие электровыделение меди из сернокислых растворов, образующихся на стадии реэкстракции ионов (II) меди из органических экстрагентов.

Эксперименты проводились в промышленных условиях.

Показано, что электролиз меди протекает с высоким выходом по току при содержании в реэкстрагирующем растворе 1,0 моль/л серной кислоты, 0,8 - 1,0 моль/л ионов (II) меди, плотности тока 1,0 – 6,0 А/дм^2 и перемешивании электролита. Проанализирован состав катодной меди, полученной при электролизе из модельного электролита и реэкстрагирующих растворов, после контакта с органическими экстрагентами. Установлено, что чистота катодной меди достигает 95 – 98 % по основному веществу. Вместе с тем было установлено, что в реэкстрагирующем растворе происходит постепенное накопление нерастворимого осадка, который примерно на 40% состоит из свинца. Это может быть связано с механическим разрушением активного слоя анода, состоящего из оксидов свинца (PbO_2). Показана необходимость поиска материала для анодов, заменяющих аноды из двуокиси свинца, малоустойчивых в данной технологии.

Ключевые слова: печатные платы, травление, медно-аммиачные растворы, медно-хлоридные растворы, регенерация, экстракция, реэкстрагирующие растворы, электролиз, анод, катодная медь, плотность тока, выход по току.

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ELECTROFLOTATION EXTRACTION OF POWDERED CARBON-BASED MATERIALS FROM AQUEOUS SOLUTION WITH USING OF SURFACTANTS

Abstract. Comparative electroflotation studies of powdered carbon materials from an aqueous solution of sodium sulfate electrolyte were carried out.

Kinetic electroflotation dependences of various carbon materials particles (carbon nanoflakes and activated carbons OU-B and BAU-A) are shown. It is established that the particles of carbon nanoflakes are most effectively extracted in the presence of nonionic surfactants. Whereas the extraction degree of activated carbons does not reach 20% in the same conditions.

Electroflotation studies of powdered carbon materials from aqueous solutions with the addition of coagulants Al^{3+} and Fe^{3+} were carried out to improve the efficiency and intensity of particles extraction. We studied aqueous solutions containing different types of surfactants: anionic, cationic and nonionic. Studies have shown that carbon nanoflakes are extracted quite effectively regardless of nature either the coagulants or the surfactants.

The extraction degree of activated carbon particles OU-B reached 90-95% if iron ions were present in an aqueous solution of cationic or nonionic surfactant. But the efficiency of the process was reduced in the presence of Al^{3+} due to the formation of a large amount of insoluble aluminum hydroxide.

We also studied the surface characteristics of powdered carbon materials (electrokinetic potential (ζ-potential) and hydrodynamic radius of the particles) for a better understanding of the electroflotation process.

Keywords: carbon materials, electroflotation, surfactants, coagulant, ζ-potential, hydrodynamic radius.

Introduction. Activated carbon is a highly porous carbon adsorbent, which is obtained from various carbon-containing organic materials [1]. Activated carbon is widely used for treatment, separating and extracting gaseous and liquid substances [2-6]. In the Russian Federation and Kazakhstan, as well as in world practice, the largest share in the consumption of activated carbon is a processing of drinking and technical water.

Activated carbons are unique adsorbents [7-9] due to their hydrophobic properties in comparison with such adsorption materials as silica gels, zeolites, ionites and etc.

Activated carbons with a particle size less than 0.1 mm are considered powdered materials. This type of coal is often used for the liquid phase; it is thoroughly mixed with the liquid to be purified. After adsorption of impurities, the coal is removed from the solution by filtration or precipitation [10, 11].

The particle size distribution, which is carefully controlled by modern grinding processes, greatly influences the rate of adsorption, filtration, and precipitation. In addition, the small particle size makes it difficult to extract the formed dispersed phase "carbon material - adsorbate".

One of the most popular methods of particle extraction is presently flotation [12-16]. Studies of the electroflotation extraction of powdered carbon materials, such as activated carbons [17], and carbon nanomaterials [18-20] have been published before.

This article presents the experimental results of electroflotation extraction of powdered carbon materials, namely, activated carbons BAU-A and OU-B, as well as carbon nanoflakes (CNF), from aqueous solutions of different composition.

Methods and researching objects. Carbon nanoflakes (bulk density 0.27 g/cm^3; ash content 0.5%; specific surface 243 m^2/g), activated carbon OU-B (GOST 4453-74) and BAU-A (GOST 6217-74) were selected as objects of research. Colloid-dispersed systems of carbon materials in aqueous solutions with surfactants (anionic surfactant — NaDDS; cationic surfactant — Katinol; nonionic surfactant – Triton X-100), metals salts $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and electrolytes Na_2SO_4, NaCl were prepared for conducting experiments.

Laboratory studies of the efficiency of the electroflotation extraction were carried out in a non-flowing electroflotation unit with an insoluble anode at a constant pH. The column of electroflotation unit is made of glass with the cross-sectional area 10 cm^2 and the volume of the treated solution 500 ml. The height of the unit is 800 mm, the sampling valve is located at a height of 40 mm above the electrode unit.

The electrode unit includes an insoluble anode made of ORTA (titanium base with a film coating of cobalt and ruthenium oxides caused by thermal decomposition of a mixture of their salts) and a cathode made of stainless steel mesh with a cell size of 0.5 × 0.4 mm (wire thickness 0.3 mm). The cathode is located above the anode in order to allow free passage of the anodic oxygen bubbles into the column of electroflotation unit. A rubber packing separates electrodes. The device is powered by a DC power source B5-48. The range of bulk current densities is 0.1-0.5 A/l. Gas saturation occurs due to hydrogen and oxygen released at the cathode and anode.

In fine of the treatment, sampling is performed through the valve in order to determine the residual concentration of the pollutant in the treated solution. When studying the kinetics of the process, sampling is carried out every 5 min.

Electroflotation efficiency was evaluated by the degree of extraction (α, %), which was calculated as the ratio of the difference between the initial (C_0) and final (C_1) content of pollutants in the solution to their initial content: $\alpha = \frac{C_0 - C_1}{C0} \times 100\%$.

The analysis of the carbon material concentration was carried out using an adapted quantitative analysis method (with calibration graph) on a PROMEKOLAB PE-5300B spectrophotometer. The determination of the hydrodynamic radius of the particles and the electrokinetic potential was carried out by the method of dynamic light scattering with the use of equipment PHOTOCOR Compact-Z.

The experiments were conducted using analytical equipment of the MUCTR resource-sharing center.

Experimental results and discussion. Figure 1 shows the kinetic dependence of the degree of extraction of particles of carbon materials from an aqueous solution of the electrolyte Na_2SO_4 in the presence of a nonionic surfactant.

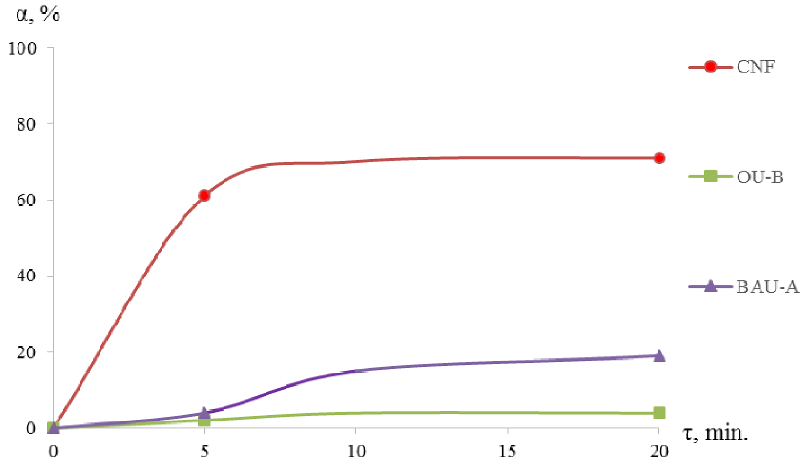

Figure 1 - Kinetic dependence of the degree of extraction of particles of carbon materials from an aqueous solution in the presence of a nonionic surfactant: C (CNF, OU-B) = 100 mg/L; C (BAU-A) = 1000 mg/L; C (TX-100) = 100 mg/L; C (Na_2SO_4) = 500 mg/L; i_v = 0.2 A/l; pH 7.0

The analysis showed that CNF particles are most efficiently extracted from an aqueous solution of a nonionic surfactant — after 10 minutes of electroflotation the recovery rate is 69%. While the degree of extraction of activated carbon reaches 5-20%.

Below are the studies of the electroflotation extraction of carbon materials from aqueous solutions of electrolytes of different composition.

Table 1 shows the results of the study of electroflotation of carbon materials (CN) from an aqueous solution of anionic surfactant in the presence of metal hydroxides Al^{3+} и Fe^{3+}.

Table 1 - Effect of the nature of carbon materials on the degree of extraction of the floatation complex "CN-Me$(OH)_3$" from an aqueous solution in the presence of metal hydroxides and anionic surfactant NaDDS

Me^{3+}	Recovery rate "CN-Me$(OH)_3$" α, %					
	CNF		OU-B		BAU-A	
	5 min	30 min	5 min	30 min	5 min	30 min
*without Me^{3+}	3	5	2	2	5	26
Al(III)	85	94	22	36	27	75
Fe(III)	83	95	15	20	5	15

i_v = 0.2 A/L; pH 7.0; C(CNF, OU-B) = 100 mg/L; C(BAU-A) = 1000 mg/L;
C(NaDDS) = 100 mg/L; C(Na_2SO_4) = 500 mg/L; *C(Na_2SO_4) = 500 mg/L

Analysis of the experimental data showed that after 5 minutes of electroflotation, the degree of extraction of ULF reaches 83-85% regardless of the nature of the added coagulant. After completion of the extraction process, the recovery rate reached 94-95%.

Unlike carbon nanomaterial, OU-B activated carbon was not efficiently removed (20-36%). Whereas the extraction process of BAU-A carbon in the presence of Al^{3+} coagulant did not show effective results in the first minutes, and upon completion of the purification process, the degree of particle recovery reached 75%.

The results of the study of the electroflotation of activated carbons and carbon nanoflakes from an aqueous solution of a cationic surfactant in the presence of metal hydroxides Al^{3+} и Fe^{3+} are presented in Table 2.

Table 2 – Effect of the nature of carbon materials on the degree of extraction of the “CN-Me$(OH)_3$” flotation complex from an aqueous solution in the presence of metal hydroxides and a cationic surfactant Katinol

Me^{3+}	Recovery rate "CN-Me$(OH)_3$" α, %					
	CNF		OU-B		BAU-A	
	5 min	30 min	5 min	30 min	5 min	30 min
*without Me^{3+}	68	73	9	52	3	36
Al(III)	90	95	14	81	3	51
Fe(III)	92	96	71	94	23	81

i_v = 0.2 A/L; pH 7.0; C(CNF, OU-B) = 100 mg/L; C (BAU-A) = 1000 mg/L;
C(Katinol) = 100 mg/L; C(Na_2SO_4) = 500 mg/L; *C(Na_2SO_4) = 500 mg/L

It was established that, regardless of the nature of the particles in the presence of the Fe^{3+} coagulant, the extraction degree reached 81-96%. However, the addition of Al^{3+} coagulant makes it possible to efficiently remove only CNF and OU-B carbon after 30 minutes of the electroflotation.

Similar results were shown by experiments on the extraction of carbon materials from an aqueous solution of nonionic surfactants in the presence of metal hydroxides Al^{3+} и Fe^{3+} (Table 3).

Differences in the extraction of particles of carbon materials are primarily associated with the methods of obtaining these materials, which affect their textural and surface characteristics. In addition, the size of particles and their charge is important in electroflotation.

Table 4 presents the results of the study of the electrokinetic potential and the hydrodynamic radius of the CNF particles.

Table 3 – Effect of the nature of carbon materials on the degree of extraction of the "CN-Me$(OH)_3$" flotation complex from an aqueous solution in the presence of metal hydroxides and nonionic surfactant TX-100

Me^{3+}	Recovery rate "CN-Me$(OH)_3$" α, %					
	CNF		OU-B		BAU-A	
	5 min	30 min	5 min	5 min	30 min	30 мин
*without Me^{3+}	69	71	3	4	4	25
Al(III)	80	93	21	86	3	3
Fe(III)	94	95	58	92	66	91

i_v = 0,2 A/l; pH 7.0; C(CNF, OU-B) = 100 mg/L; C(BAU-A) = 1000 mg/L;
C(TX-100) = 100 mg/L; C(Na_2SO_4) = 500 mg/L; *C(Na_2SO_4) = 500 mg/L

Table 4 – Effect of the nature of surfactants on the electrokinetic potential ζ and the hydrodynamic radius R of CNF particles in an aqueous solution in the presence of metal hydroxides

Type of surfactant	NaDDS			Katinol			TX-100		
Additives	Na_2SO_4	$Fe(OH)_3$	$Al(OH)_3$	Na_2SO_4	$Fe(OH)_3$	$Al(OH)_3$	Na_2SO_4	$Fe(OH)_3$	$Al(OH)_3$
ζ, mV	-24	-3	+7	+1	+7	+12	-18	+10	+12
R, µm	14	28	57	11	67	10	22	39	69

C(CNF) = 100 mg/L; C(surfactant) = 100 mg/L; C(element) = 500 mg/L; i_v = 0.2 A/l; pH 7.0; τ (electroflot.) = 30 min

In the presence of cationic surfactant Katinol, CNF particles recharge (ζ = +1-12 mV) and acquire more hydrophobic properties, which positively affects their electroflotation extraction. In addition, in the presence of iron (III) coagulant, the particles have a maximum size of 69 microns.

The same results and changes in the particle surface properties were observed in the presence of anionic surfactant and Al^{3+} coagulant, as well as in the presence of nonionic surfactant and Fe^{3+}, Al^{3+} coagulants. In the absence of coagulants, the surface of the particles acquired a high negative charge, which could complicate the electroflotation extraction of CNF.

The characteristics of OU-B activated carbon in the presence of various electrolytes were also studied (Table 5).

Table 5 – The effect of the pH of the electrolyte solution on the magnitude of the electrokinetic potential ζ and the hydrodynamic radius R of the particles of OU-B

	OU-B					
	Na_2SO_4			NaCl		
pH Specifications	3	7	11	3	7	11
ζ, mV	-5	-16	-37	-10	-18	-18
R, µm	17	6	8	10	12	11

C(OU-B) = mg/L; C(electrolyte) = 1 mg/L

Analysis of the experimental data made it possible to establish that the maximum particle size of OU-B (10-17 µm) can be achieved in an acidic medium of sulfate background, as well as at any pH of the chloride background. However, the high negative electrokinetic potential of the particles of activated carbon can affect and hinder their extraction.

Conclusions

Consequently, conducted experiments show that electroflotation extraction of carbon materials depends on their nature, method of preparation, as well as on texture and surface specifications (potential and particle size).

In addition, the presence of cationic and nonionic surfactants, Al^{3+}, Fe^{3+} coagulants in solutions contribute to the change of particle properties due to the formation of flotation complexes, which leads to effective electroflotation extraction of carbon materials.

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ҚҰРАМЫНДА БАЗ БАР БОЛҒАН СУЛЫ ЕРІТІНДІЛЕРДЕН ҰНТАҚТӘРІЗДІ КӨМІРТЕКТІ МАТЕРИАЛДАРДЫ ЭЛЕКТРОФЛОТАЦИЯЛЫҚ ЖОЛМЕН АЛУ

Аннотация. Натрий сульфатының сулы электролиттерінен электрофлотация жолымен алынған ұнтақтәрізді көміртекті материалдардың салыстырмалы зерттеулері жүргізілді.

Әртүрлі көміртекті материалдардан тұратын бөлшектерді бөліп алудың, яғни көміртекті наноқабыршақ пен ОУ-Б және БАУ-А белсенді көмірлердің кинетикалық тәуелділігі көрсетілді. Ионогенді емес БАЗ бар кезде көміртекті наноқабыршақ бөлшектері ең тиімді алынатындығы, ал белсенді көмірдің алыну дәрежесі 20 % жетпейтіндігі анықталды.

Электрофлотацияның интенсивтілігін және тиімділігін жоғарылату мақсатында Al^{3+} және Fe^{3+} коагулянттарын қосылған сулы ерітінділерден ұнтақтәрізді көміртекті материалдарды бөліп алу бойынша зерттеулер жүргізілді. Құрамында әртурлі БАЗ болған (анионды, катионды және ионогенді емес) сулы ерітінділер зерттелді. Зерттеулер БАЗ және коагулянттың табиғатына қарамастан көміртекті наноқабыршақтар анағұрлым тиімді бөлініп алынатындығын көрсетті.

Құрамында катионды немесе ионогенді емес БАЗ бар болған сулы ерітіндіде темір иондары болғанда ОУ-Б белсенді көмір бөлшектерінің алыну дәрежесі 90-95 %-ға жетті. Al^{3+} бар болған кезде қиын еритін алюминий гидроксиді түзілу себебті процесс тиімділігі төмендейді.

Электрофлотация процессін жақсы түсіну мақсатында ұнтақтәрізді көміртекті материалдардың беттік сипаттамасы, яғни электрокинетикалық потенциал (ζ-потенциал) және бөлшектердің гидродинамикалық радиусы зерттелді.

Түйін сөздер: көміртекті материалдар, электрофлотация, беттік-активті заттар, коагулянт, ζ-потенциал, гидродинамикалық радиус

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ЭЛЕКТРОФЛОТАЦИОННОЕ ИЗВЛЕЧЕНИЕ ПОРОШКООБРАЗНЫХ УГЛЕРОДНЫХ МАТЕРИАЛОВ ИЗ ВОДНЫХ РАСТВОРОВ В ПРИСУТСТВИИ ПАВ

Аннотация. Проведены сравнительные исследования электрофлотационного извлечения порошкообразных углеродных материалов из водного раствора электролита сульфата натрия.

Показаны кинетические зависимости извлечения частиц различных углеродных материалов: углеродных наночешуек и активированных углей ОУ-Б и БАУ-А. Установлено, что в присутствии неионогенного ПАВ наиболее эффективно извлекаются частицы углеродных наночешуек, тогда как степень извлечения активированных углей не достигала 20%.

Для повышения эффективности и интенсивности электрофлотации были проведены исследования по извлечению порошкообразных углеродных материалов из водных растворов при добавлении коагулянтов Al^{3+} и Fe^{3+}. Были изучены водные растворы, содержащие различные типы ПАВ: анионное, катионное и неионогенное. Исследования показали, что углеродные наночешуйки извлекаются достаточно эффективно, независимо от природы коагулянта и ПАВ.

Степень извлечения частиц активированного угля ОУ-Б достигала 90-95%, если в водном растворе катионного или неионогенного ПАВ присутствовали ионы железа. Тогда как в присутствии Al^{3+} эффективность процесса снижалась за счет образования большого количества осадка труднорастворимого гидроксида алюминия.

Для лучшего понимания процесса электрофлотации были изучены поверхностные характеристики порошкообразных углеродных материалов: электрокинетический потенциал (ζ-потенциал) и гидродинамический радиус частиц.

Ключевые слова: углеродные материалы, электрофлотация, поверхностно-активные вещества, коагулянт, ζ-потенциал, гидродинамический радиус.

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SYNTHESIS AND CATALYTIC PROPERTIES OF COMPOSITES WITH Pd-(2-HYDROXYETHYL CELLULOSE) ON BENTONITE

Abstract. Palladium composites based on 2-hydroxyethylcellulose (HEC) and bentonite (BT) have been synthesized to use them as “green” catalysts for the process of phenylacetylene hydrogenation under mild conditions. The introduced amount of HEC in the composites was 5, 10, and 20%. Viscometer method shows the degree of polymer fixation on the surface of the mineral sorbent. The HEC/BT systems with polymer content of 4.1; 9.0; 18.9% have been obtained. Samples of the obtained HEC-containing composites were characterized by X-ray, scanning and transmission electron microscopy. The data obtained have confirmed the fixing of the polymer on the surface of support.

The sorption capacity of the developed HEC-bentonite composites to Pd^{2+} ions has been studied. The content of palladium in the prepared composites desreased with the increasing of HEC amount in the [Pd(HEC)BT] systems and were : 0.9% Pd-BT/HEC (4%), 0.8% Pd-BT / HEC (9%), 0.6% Pd-BT / HEC (19%). To compare the activity and selectivity of composites with different content of HEC in phenylacetylene hydrogenation, the catalysts with the equal palladium content (0.6%) have were prepared. The developed catalysts showed high activity in the hydrogenation at 40°C and atmospheric pressure of hydrogen. The most effective was 0.6% Pd-BT/HEC composite with a HEC content of 9%, the selectivity to styrene was 92.0% with 96.4% conversion of the phenylacetylene.

Keywords. 2-Hydroxyethylcellulose, polysaccharides, bentonite, catalytic activity, hydrogenation, palladium catalysts.

Introduction

Recently, the design of catalytic systems with the natural plant components is in the focus of scientific interests [1-19] as renewable and environmentally friendly raw materials for chemical syntheses [20]. Polysaccharides, such as cellulose, chitosan, pectin, containing of various functional groups in their structures are able to form complexes with metal ions [21, 22]. Cellulose is one of the most promising polysaccharides for developing catalytic systems [15-17] due to its hydrophilicity, chirality, biodegradability, wide chemical modifying ability, and a large surface area. The disadvantage of cellulose in the synthesis of complex compounds with metal ions is its insolubility in water. Therefore, in this work, hydroxyethylcellulose (HEC), was used as a soluble cellulose modification for catalyst preparation.

Catalytic properties of the developed palladium catalysts supported on HEC-modified bentonite have been tested in hydrogenation of phenylacetylene under mild conditions.

Experimental part

The method of sequential adsorption of polymer and metal salt from water solutions was used for the preparation of palladium catalysts [23].

A natural sorbent - bentonite (BT) was used as a support. A cellulose derivative, 2-hydroxyethylcellulose, was chosen as the nanoparticle stabilizer. The polymer amount was chosen to obtain composites of support with 5%, 10% and 20wt.% of the polysaccharide. Palladium chloride was used to prepare the catalysts with 1 wt. % of Pd. The metal ion concentration in the catalyst after adsorption was determined on an SF-2000 spectrophotometer (Russia, 2015) using calibration curves. Calibration was based on the measure of concentration of series of standard palladium solutions.

IR spectra were obtained on Karl Zeiss Specord-IR-75 spectrometer in the range of 4000-400 cm^{-1}.

The morphology and structure of the initial bentonite and bentonite-based HEC-containing composites as well as sizes of metal nanoparticles were examined by scanning and transition electron microscopy.

The phenylacetylene hydrogenation reaction was carried out in thermostatic reactor in ethanol (25 ml) at 40^{0}C and atmospheric hydrogen pressure. Before the reaction the catalyst was saturated with hydrogen for 30 minutes and the tested substrate was injected to the reactor. Hydrogen uptake was measured and reaction products were detected by chromatographic analysis ("Khromos", Russia). The catalyst selectivity was calculated as the proportion of the target product to the sum of all reaction products at a given conversion.

Results and discussion

Synthesis of polysaccharide-silicate composites (PSC) was carried out at room temperature and included the following stages:

a) adding of a polymer solution to an aqueous suspension of bentonite;
b) stirring the PSC for 2 hours;
c) precipitation of the polymer in suspension of the support for 24 hours;
d) washing and drying the PSC at room temperature.

The scheme of catalysts' preparation is presented on the Figure 1.

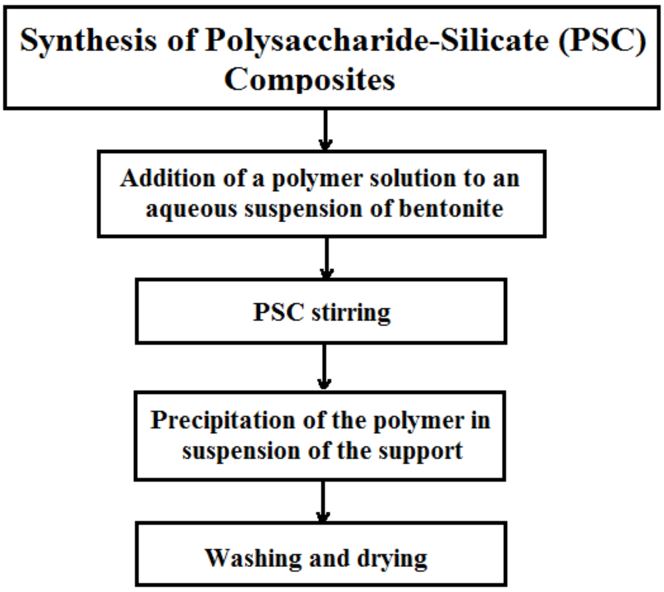


Figure 1 – The scheme for production of polysaccharide-inorganic composites

The concentration of the polymer in the mother liquor of composite was determined using a viscosity calibration curve. The amount of adsorbed polymer was determined by the difference in mass of polymer in the mother liquor before and after sorption. Calculated results of actual content of the polymer in composites are presented in Table 1. It has been shown that the degree of HEC adsorption increases from 81.7 to 94.6% with an increase in the amount of polymer introduced.

Table 1 - Adsorption of HEC on BT

The amount of entered HEC, %	% precipitated HEC from the entered initial amount	The content of HEC in the HEC/BT, %
5.0	81.7	4.1
10.0	90.2	9.0
20.0	94.6	18.9

The presence of polysaccharides in the composites also demonstrated by IR spectroscopic data, according to which the absorption bands of asymmetric and symmetric stretching vibrations of -CH groups of HEC in the range of 2950-2800 cm^{-1} were appeared in the spectra of composites (Table 2). In addition, a shift in the absorption bands of the deformation vibrations of polysaccharide -OH groups in the range of 1450– 1350 cm^{-1} was observed. These changes can be explained by the formation of hydrogen bonds between the oxygen-containing groups of the polymer and OH-centers of bentonite confirming chemisorption of HEC on the surface of the aluminosilicate.

Table 2 – IR spectroscopy data of the studied samples

Sample	νOH	νCH	δOH δC-OH	δOH(BT) νAl-O
BT	3620 3457	-	-	1141 820 525
HEC	3424	2919 2973	1415 1386	
HEC/BT	3620 3416	2925 2876	1422 1381	1042 796 519
Pd-HEC/BT	3619 3432	2938 2872	1462	1046 801 522

The slight shift in bands characteristic to -OH and Al-O groups indicates the participation of BT hydroxy groups in the binding of polymer (Table 2).

According to scanning microscopy testing, an enlargement and aggregating of HEC-bentonite species (Figure 2, a) to compared with initial bentonite (Figure 2, b) were observed due apparently to the coating of the alumosilicate with the polysaccharide.

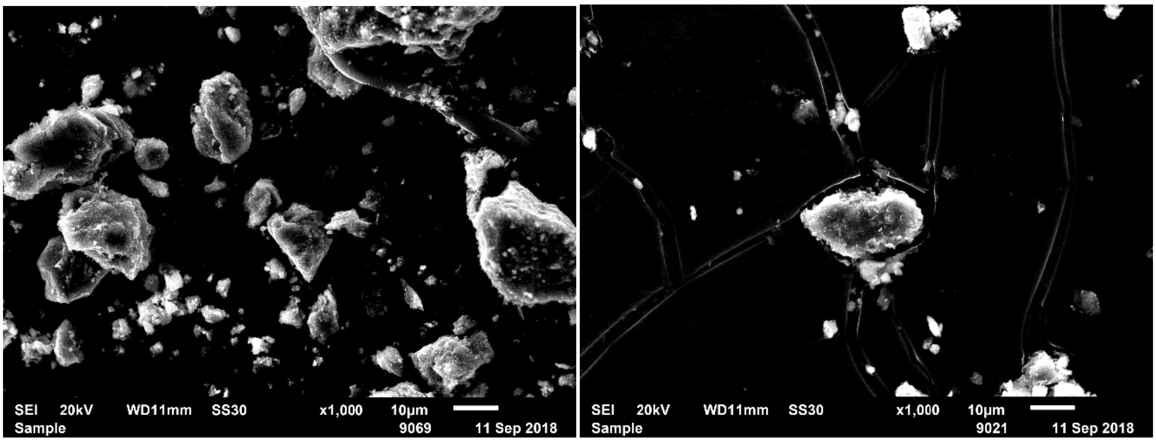


Figure 2 – SEM images of HEC(9%)/BT (a) and Bentonite (b)

In order to obtain catalysts, the solution of palladium (II) salt was dropwise added into the suspension of HEC-bentonite composite in the amount corresponding to the formation of 1%Pd-HEC/bentonite system. Figure 3 provides a general scheme for the preparation of the supported polymer-modified catalysts.

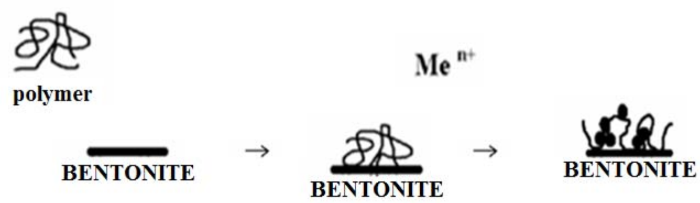


Figure 3 – Scheme of the formation of HEC-based catalysts

The content of metal immobilized on the polymer-modified surface of inorganic material was determined from the change in the concentration of metal ions in the mother liquor before and after sorption. Data on sorption are presented in the Table 4.

It is shown that the degree of deposition of palladium ions on the HEC modified bentonite decreases with an increase in the content of polysaccharide on the composites (Table 4).

Table 4 - Sorption of Palladium Ions on HEC/BT Composites

Composite	$m_{Me}\cdot10^{-3}$ in the initial solution, g	$m_{Me}\cdot10^{-3}$ in solution after sorption, g	The degree of adsorption		The metal content in catalyst, %
			$m_{Me}\cdot10^{-3}$, g	%	
4% HEC/BT	1.91	0.28	1.63	85.30	0.85
9% HEC/BT	1.91	0.30	1.61	84.30	0.84
19% HEC/BT	1.91	0.86	1.05	55.00	0.55

The IR spectroscopy data (Table 2) showed the shifts of the absorption bands of the HEC functional -OH and -C-OH groups in the in the region of 1450-1350 cm^{-1} of the in spectrum of three-component Pd-HEC/BT composites. The shift in the absorption bands of the -CH-group valence vibration indicates change in the conformation of the polysaccharide and interaction of palladium ions with the polymer layers of HEC/BT.

According to TEM images, the obtained Pd-HEC/BT composites are characterized by agglomerates consisting of nanosized (4-10 nm) palladium particles (Figure 4).

Thus, palladium containing composites based on natural materials like modified cellulose and bentonite have been prepared. Interaction of the components was confirmed be IR-spectroscopy and electrom microscopy. The polysaccharide contributes to the formation of uniform palladium nanoparticles, which form clusters on the surface of bentonite coated with a polymer. The amount of Pd in the composites depends on the quontity of the HEC in the composite. The smallest amount of Pd (o.6wt.%) was detected on the HEC/BT with the content of the polymer of 19%.

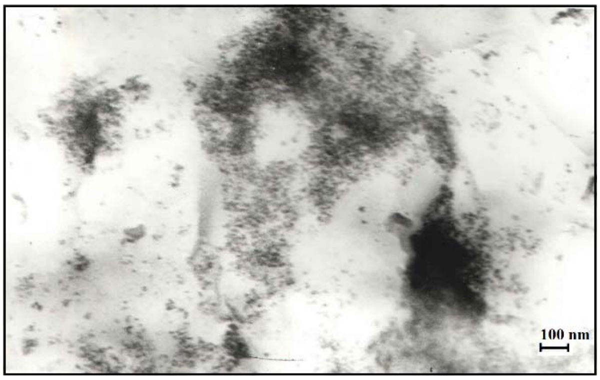
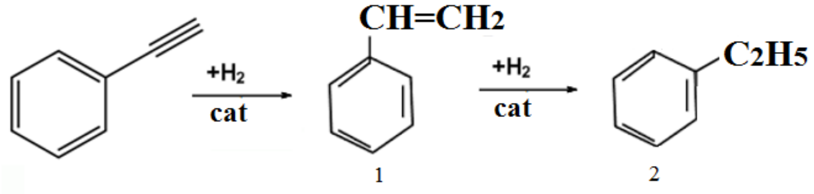


Figure 4 – TEM images of Pd-HEC/BT

To compare catalytic properties of the composites with different HEC content, the catalysts with 0.6 wt.% of palladium was prepared.

The liquid phase hydrogenation of phenylacetylene was chosen as a model reaction.

Phenylacetylene is hydrogenated with formation of styrene (1) which then reduced to ethylbenzene (2):



The hydrogenation rate is increased with the increasing of polymer content in the catalysts from 4% to 9% (Table 5). The further increase of the polysaccaride percentage in the catalyst lead to a desrease in its effectiveness. The optimal palladium catalyst contained 9% HEC and was characterized with the selectivity to styrene of 92% at 96.4% conversion of the substrate (Table 5).

It can be assumed that the reason of low hydrogenation selectivity on the catalyst with a low HEC content (4%) was incomplete coating of the surface of bentonite with a polymer, and part of the palladium was adsorbed directly on the bentonite, and as a result the catalytic centers can be heterogeneous. In the case of an excess amount of polymer in the catalyst (19%), the reason for the low selectivity may be the difficulty of transporting the substrate to the active palladium centers located inside the macromolecular network.

To prove this assumption, it is necessary to conduct additional studies of synthesized catalysts. At the same time, the obtained results confirm the possibility and prospectiveness of using natural materials, such as cellulose and bentonite, to produce complex three-component polymer-inorganic composites with fixed transition metal nanoparticles and to use them as catalysts.

Table 5 – Results of the Hydrogenation of Phenylacetylene on 0.6% Pd/BT-HEC catalysts with different polymer content

Catalyst	Reaction rate, W*10^{-6}, mol/s		Selectivity to styrene, %	Conversion, %
	C≡C	C=C		
Pd/BT-HEC (4%)	3.2	2.7	82.2	70.3
Pd/BT-HEC (9%)	3.2	3.7	92.1	96.4
Pd/BT-HEC (19%)	3.1	3.1	87.2	90.5
Note – Experimental conditions: T=40°C; P=1 atm; m_{cat}=0.05g; solvent – ethanol.				

Conclusions

A HEC-based polysaccharide-silicate composite with varying amounts of polymer (5%, 10%, and 19%) has been obtained by the adsorption method. The preparation method of composites eliminates high-temperature calcination and recovery. By the viscometer method, it was found that the degree of adsorption of HEC varies within 81.7-94.6%. The presence of polysaccharides in the composition of the obtained composites was confirmed by IR spectroscopy, TEM and SEM. It was established that a change in the amount of polymer in the composition of the catalyst affects the selectivity of the hydrogenation process. The prospects of using polysaccharide-silicate composites as components of hydrogenation and oxidation catalysts are shown. Such systems can be attributed to a new generation of "green" catalysts.

The optimal catalyst for the hydrogenation of phenylacetylene is a palladium HEC/BT catalyst with a HEC content of 9%, the selectivity of which for styrene was 92% at 96.4% conversion of the substrate.

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БЕНТОНИТТІҢ БЕТІНДЕ Pd-2-ГИДРОКСИЭТИЛЦЕЛЛЮЛОЗА БАР КОМПОЗИТТЕРДІҢ СИНТЕЗІ МЕН КАТАЛИТИКАЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Жұмсақ жағдайда фенилацетиленді гидрлеу процесінде «жасыл» катализатор ретінде пайдалану үшін 2-гидроксиэтилді целлюлоза (ГЭЦ) және бентонит (БТ) негізінде палладий ГЭЦ-силикатты композиттер синтезделді.

Композиттер құрамындағы ГЭЦ-ның есептік саны 5, 10 және 20% құрады. Вискозиметриялық әдіспен минералды сорбенттің бетіне полимердің бекітілу дәрежесі көрсетілді.

Құрамында 4,1, 9,0, 18,9% полимері бар ГЭЦ/БТ жүйелері алынды. Алынған ГЭЦ-құрамды композиттер ИКС, сканерлейтін және жарық түсіретін электрондық микроскопия әдістерімен сипатталған. Алынған мәліметтер тасымалдаушының бетіне полимердің бекітілгенін растады.

Pd^{2+} иондарына қатысты әзірленген ГЭЦ-силикатты композиттердің сорбциялық белсенділігін зерттеу бойынша жұмыстар жүргізілді. Әзірленген композиттердің құрамында палладийдің құрамы ГЭЦ мөлшерінің ұлғаюымен азайды: 0,9% Pd-П/ ГЭС (4%), 0,8% Pd-БТ/ГЭЦ (9%), 0,6% Pd-БТ/ГЭЦ (19%). Құрамында ГЭЦ бар композиттердің белсенділігі мен селективтілігін салыстыру үшін палладий мөдшері бірдей (0,6%) катализаторлар дайындалды.

Әзірленген палладий катализаторлары 40°С температурада және сутегінің атмосфералық қысымында фенилацетиленді гидрирлеу реакциясында белсенділік көрсетті. Ең жоғары тиімділікке құрамында 9% ГЭЦ бар 0,6% Pd-БТ/ГЭЦ композит ие, оның қатысында субстраттың конверсиясы кезінде 92,0% болған стирол бойынша талғампаздылық 96,4% құрады.

Түйін сөздер: 2-гидроксиэтилді целлюлоза, полисахаридтер, бентонит, каталитикалық белсенділік, гидрлеу, палладий катализаторлары.

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СИНТЕЗ И КАТАЛИТИЧЕСКИЕ СВОЙСТВА КОМПОЗИТОВ С Pd-2-ГИДРОКСИЭТИЛЦЕЛЛЮЛОЗОЙ НА БЕНТОНИТЕ

Аннотация. Синтезированы палладиевые ГЭЦ-силикатные композиты на основе 2-гидроксиэтилцеллюлозы (ГЭЦ) и бентонита (БТ) с целью применения их в качестве «зеленых» катализаторов для процесса гидрирования фенилацетилена в мягких условиях. Расчетное количество ГЭЦ в составе композитов составляло 5, 10 и 20%. Вискозиметрическим методом показана степень закрепления полимера на поверхности минерального сорбента. Были получены ГЭЦ/ БТ системы с содержанием полимера 4,1, 9,0, 18,9%. Образцы полученных ГЭЦ-содержащих композитов были охарактеризованы методами ИКС, сканирующей и просвечивающей электронной микроскопии. Полученные данные подтвердили закрепление полимера на поверхности носителя.

Проведены исследования по изучению сорбционной активности разработанных ГЭЦ-силикатных композитов по отношению к ионам Pd^{2+}. Содержание палладия в составе разработанных композитов уменьшалось с увеличением количества ГЭЦ: 0,9% Pd-БТ/ ГЭЦ (4%), 0,8% Pd-БТ/ГЭЦ (9%), 0,6% Pd-БТ/ГЭЦ (19%). Для сравнения активности и селективности композитов с различным содержанием ГЭЦ были приготовлены катализаторы с одинаковым содержанием палладия (0,6%).

Разработанные палладиевые катализаторы показали активность в реакции гидрирования фенилацетилена при температуре 40°С и атмосферном давлении водорода. Наибольшей эффективностью и активностью обладает 0,6% Pd-БТ/ГЭЦ композит с содержанием ГЭЦ 9%, селективность на котором по стиролу составила 92,0% при 96,4% конверсии субстрата.

Ключевые слова. 2-Гидроксиэтилцеллюлоза, полисахариды, бентонит, каталитическая активность, гидрирование, палладиевые катализаторы.

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EFFECT OF THE TERMAL TREATMENT TEMPERATURE ON THE DURABILITY AND THE CRACKING ACTIVITY OF THE CATALYSTS ON THE BASE OF MODIFIED MONTMORILLONITE

Abstract. Increase of the durability of granules of Al (2.5) NaHMM +HLaY-catalyst at crush with temperature increase of calcination of catalysts from 500 to 650^{0}C is found. It is noticed that the introduction of zeolite Y in the replaced rare-earth form leads to growth of durability of the granulated catalyst.

It is shown that preliminary calcination at 550,600^{0}C of the zeolitecontained catalysts supported on the activated Al-pillared montmorillonite in Na-and CaNa – forms, leads to significant reduction of yields of gasoline on these catalysts that demonstrates that heat treatment of the catalyst increases durability, but does not provide necessary activity of the catalyst in the fuel direction.

Keywords: catalytic cracking, termal treatment, pillared montmorillonite, gasoline, light gasoil, vacuum gasoil.

Introduction. One of the most important operational characteristics of heterogeneous catalysts is their mechanical strength with respect to compression, bump and abrasion, depending on the technology of the catalytic process [1,2]. With the continuous movement of the catalyst in the form of a fluidized bed in catalytic cracking units, the catalyst particles are hit against the equipment walls and against each other with the formation of crumb catalyst and dust, which requires constant replenishment and significantly increases the cost for the production of cracking products. For catalytic processes, an important role is played by the selection of the matrix or carrier, which provides the necessary porous structure, specific surface area, heat resistance, and mechanical strength of the catalyst. It is known that the strength characteristics of catalysts are determined by their composition and textural properties - porosity, specific surface, size of primary particles, etc. However, there are very few works in the literature devoted to the study of the relationship between strength and physicochemical properties of catalytic systems [3]. In connection with the above, the development of new effective ways to increase the mechanical strength of catalysts for oil refining based on natural clays and zeolites seems to be an actual task for modern oil refining.

In this work, Tagansky montmorillonite was used as a matrix of catalysts, on the basis of which new highly efficient cracking catalysts were synthesized by pillaring of clays [4,5]. However, the strength of catalysts based on matrices with pillared montmorillonite does not always corresponded to the requirements of their operation. To increase the strength and durability of the catalysts, pretreatment of natural montmorillonite was varied by adjusting the calcination temperature, which is accompanied by an increase in the bulk density and strength of the catalysts.

The purpose of the work is to determine the crush strength and the activity of catalysts based on Al-pillared montmorillonite and zeolite Y in the cracking of vacuum gas oil, depending on the temperature of the preliminary calcination of the catalyst.

Experimental part

In the synthesis of pillared clays, an aluminum hydroxocomplex of the proposed composition $[Al_{13}O_4 (OH)_{24} (H_2O)_{12}]^{7+}$, abbreviated (Al_{13}^{7+}) with a four-coordinated aluminum atom, was used as a fixing agent. The method of obtaining oligomeric (Al_{13}^{7+}) consists in hydrolysis of an aqueous $AlCl_3$ solution with an aqueous solution of NaOH with a ratio of $OH^- / Al^{3+} = 2.5$ and a final pH = 4.1 under conditions of vigorous stirring. The procedure for the synthesis of aluminum montmorillonite (AlNaHMM) is described in[6]. The catalyst was additionally modified with zeolite Y in the substituted La-form (15%).

Elemental analysis of the catalyst samples was carried out by the method of energy dispersive - X-ray fluorescence spectroscopy on the energy dispersive microanalysis system INCA - Energy 450, installed on a JSM6610LV scanning electron microscope, JOEL, Japan.

The crush strength of the investigated catalysts was determined from the results of three measurements on the device “Prochnomer katalizatorov” PK-21-015, JSC BSKB «Neftekhimavtomatika» (Russian).

The catalytic activity of the samples was determined in a laboratory flow-type installation, corresponding to the standard, with a fixed catalyst bed in an amount of 30 ml. The catalytic activity was determined in the temperature range 480-550^{0}C with a bulk feed rate of 1 hour^{-1}. Vacuum gas oil (VG) of the Pavlodar Petrochemical Plant (PPCP) with the end of boiling point of 510^{0}C was used as a raw material for cracking. During the distillation of catalyzate, the gasoline fractions $T_{b.p.}$-205^{0}C and light gas oil 205-350^{0}C were collected. The analysis of the hydrocarbon composition of gasoline cracking was performed on a chromatograph “Chromos-1000” with a flame ionization detector and a capillary column 100 m long; temperature is 250^{0}C; helium is carrier gas.

Results and discussions

At present, montmorillonite is successfully used in the matrix of Russian industrial cracking catalysts [7,8]. In addition to participation, along with other components of the matrix (aluminosilicate, aluminum oxide) in the formation of the porous structure of the catalyst and the primary cracking of large hydrocarbon molecules, montmorillonite provides the mechanical strength of the catalyst, which is determined by the pretreatment method of montmorillonite, its porous structure and composition. It is known that the pillaring of clays with metal oxides with the formation of columnar structures leads to the formation of new porous materials with a high specific surface, a large volume of micro- and mesopores, and an increased thermal stability [9]. Matrix-based catalysts with Al-pillared montmorillonite were chosen as objects for developing ways to increase crushing strength due to the fact that they had the highest activity on gasoline output, but were distinguished by low strength. To increase the strength and durability of the catalysts, pretreatment of natural montmorillonite was varied by adjusting the temperature of calcination in air and introducing various additives before the intercalation stage. To select the optimum temperature for calcining catalysts, two batches of Al (2.5) NaHMM + HLaY and Al (2.5) CaNaHMM + HLaY catalysts were prepared. A preliminary analysis of the samples was carried out (Table 1), from which it is clear that NaMM activation with sulfuric acid helps remove Na^+ ions from the initial montmorillonite and reduces the sodium content from 1.4% in the original NaMM to 0.2% in activated NaHMM and remove it completely after aluminum pillaring. The elemental compositions of the initial NaMM and CaNaMM are close to each other. The difference was found only in some excess of iron in NaMM compared to CaNaMM. The introduction of HLaY into the catalyst leads to an increase in the sodium content to 0.5%, and the amount of La is 2.0%. The composition of the catalyst varies little after testing in cracking.

Table 1 - The elemental composition of composite catalysts based on Al-pillared montmorillonite before and after the cracking of vacuum gas oil on it

Sample	C	O	Na	Mg	Al	Si	Cl	Ca	Fe	La
NaMM	7.78	51.6	1.4	2.1	11.3	24.7	0.3	0.56	0.39	-
NaHMM	8.09	52.5	0.2	2.0	11.4	25.0	-	0.38	0.37	-
Al(2.5)NaHMM	11.2	54.6	-	1.2	11.9	20.8	-	-	0.25	-
Al(2.5)NaHMM+HLaY	10.5	53.7	0.5	0.8	10.8	21.5	-	-	0.21	2.03
Al(2.5)NaHMM+HLaYafter the experience	10.4	52.4	0.4	0.9	11.3	22.7	-	-	0.20	1.75
CaNaMM	7.8	52.0	0.9	1.9	12.0	24.6	-	0.61	0.25	-

The crush strength of the studied catalysts, as can be seen from the results of Table 2, depends on the composition and temperature of the preliminary calcination.It is noticed that the introduction of zeolite Y in the replaced rare-earth form leads to growth of durability of the granulated catalyst.With an increase in the temperature of calcination of Al (2.5) NaHMM + HLaY- catalyst from 500 to 650^0C, its strength increases sharply and at 600^0C reaches its maximum value and then decreases. On the spent catalyst, the strength at all calcination temperatures is slightly lower than the strength of the initial, and the maximum strength equal to 104.6 N / cm^2 was found at a calcination temperature of 550^0C.

Table 2 - Strength characteristics of Al (2.5) NaHMM + HLaY- catalysts depending on the temperature of calcination by compression method

	Sample	Calcination temperature, ^{0}C	Strength, N / cm^2
	Al(2.5)NaHMM	500	50.1
	Al(2.5)NaHMM+HLaY	500	80.1
		550	100.3
		600	107.2
		650	94.3
	Al(2.5)NaHMM+HLaY (after experience)	500	80.1
		550	104.6
		600	70.3
		650	77.4

Earlier, we showed that Al (2.5) NaHMM + HLaY showed high activity on the yield of gasoline during the cracking of VG PPCP. This vacuum distillate has the end of boiling point (EBP) of 534^0C. Fractional composition: initial boiling point(IBP) - 282^0C; 5% -342; 10% -360; 50% -423; 90% -494; 95% -516^0C. Mass fraction of sulfur is 0.103%, density at 20^0C-885.6 kg / m^3.

The conversion of VG at its cracking increases with increasing temperature, while the yield of gasoline drops from 51.2% at 480^0C to 33.6% at 550^0C, and the yield of light gas oil grows in these conditions by 2.7% (Table 3). The maximum yield of gasoline obtained on this catalyst at 480^0C. The conversion of SH and the total yield of light products under these conditions are also maximum and amount to 93.0 and 69.4%, respectively [10]. The amount of gaseous reaction products increases with increasing cracking temperature from 17.8% at 48 ° C to 26.8% at 550^0 C. The amount of coke deposited on the catalyst during the cracking process also increases with increasing process temperature.

Table 3 - Material balance of VG cracking on Al (2.5) NaHMM + HLaY– catalyst at different temperatures

Raw material	VG		
Experience temperature, ^{0}C	480	500	550
Yield of products,%			
Gas	17.8	20.0	26.8
Gasoline (IBP-205^0C)	51.2	43.5	33.6
Coke	5.8	6.4	7.7
Light gas oil (205 - 350^0C)	18.2	18.0	20.9
Heavy gas oil (>350^0C)	4.2	9.1	8.2
Losses	2.8	3.0	2.8
Conversion	93.0	87.9	89.0
The total content of light products	69.4	61.5	54.5

The main disadvantage of this catalyst is its very low strength, which increases during calcination at high temperatures (Table 2). To determine the effect of calcination temperature on the activity of these catalysts in cracking, a batch of VG PPCP grade A, type 2 was used. The EBP of VG was 510^0C, the density at 20^0C 907.7 kg / m^3, kinematic viscosity at 50 ° C is 22.691 mm^2 / s, sulfur content is 1.43%,the temperature of hardeningis 27^0C, coking ability 0.21wt.%.

Table 4 - The main technical parameters of VG PPCP, obtained in 2018

	Sample	Test method	Norm	Actual values
1	Fractional composition: a) up to 350^{0}C is distilled,% not more than b) 90% distilled at 0C, not higher	TURB-3002206696.004-2001	 18 535	
2	Density at 20^{0}C, kg / m3	GOST 3900	870÷952	907.7
3	Kinematic viscosity at 50° C, mm^2 / s	GOST 33	5÷25	22.691
4	Mass fraction of sulfur,% mass.	ST RK ISO 8754	no more 2	1.7-1.43
5	Flash point in closed crucible, ^{0}C	GOST 6356	not less 61	145
6	Pour point, ^{0}C	GOST 20287 (method A)	not less 10	27
7	Coking ability, % mass.	GOST 19932	no more 3	0.21
8	Fe amount,% mass.	X-ray fluorescence analysis		0.05
9	Ni amount, % mass.	X-ray fluorescence analysis		0.01

The catalyst calcined at temperatures of 500, 550 and 600^{0}C was tested in the cracking of VG at different temperatures (Table 5). Analysis of the data presented in Table 4 shows that with an increase in the temperature of the experiment from 480 to 550^{0}C and calcining to 600^{0}C, the catalyst activity in the fuel direction decreases significantly. Thus, the yield of gasoline decreases from 40.5% to 27.1% with an increase in the temperature of the experiment from 480 to 500^{0}C and calcining from 500 to 550^{0}C. A decrease in the yield of gasoline and an increased (growth of ~ 2 times) the formation of gases is probably due to a change in the porous structure, acidity, and elemental composition of the catalyst with increasing temperature of calcination. This is confirmed by a further decrease in the yield of gasoline with an increase of the calcinationtemperature to 600° C (Table 5). Under these conditions, the yield of gasoline decreases to 21.4%, while the yield of light gas oil increases to 23.1% and gaseous products to 48. 3%.

Table 5 - Material balance of VG cracking on Al (2.5) NaHMM + HLaY-catalyst at different temperatures of the experiment and calcining (up to $T_{calc.} = 600^0$, regeneration at 550^{0}C)

Raw material	VG			
Experience temperature, ^{0}C	480	500	500	550
Calcinat on temperature, ^{0}C	500	550	600	600
Yield of products,%				
Gas	28.6	41.6	48.3	43.6
Gasoline (IBP-205^{0}C)	40.5	27.1	21.4	21.1
Light gas oil (205 - 350^{0}C)	20.8	11.2	23.1	25.0
Heavy gasoil (> 350^{0}C)	4.4	12.1	3.8	5.6
Coke	3.7	3.9	2.2	2.7
Losses	2.0	4.1	1.2	2.0
Amount of products	100	100	100	100

The next series of experiments was carried out using montmorillonite in CaNa-form from the quarry«Zapadny» of 12 horizons containing the following alkaline cations: $Na^+ > 35$ mg / eq, $Ca^{++} \geq 28$ mg / eq, $Mg^{++} = 24$ mg / eq, $K^+ \sim 4.0$ mg / eq. (Table 6). After activating with acid and pillaring ofmontmorillonite by aluminum the composition and textural characteristics approach to the previously used MM in the Ca- and Na-forms. The raw material was VG PPCP grade B type 2 with a density of 907.7 kg / m^3, kinematic viscosity at 50^{0}C equal to 27.05 mm^2/s, the sulfur content is 1.5 wt.%,the temperature of hardeningis 30^{0}C and coking ability is 0.14 wt.%.

Table 6- Material balance of VG cracking on Al (2.5) CaNaHMM + HLaY-catalyst at temperatures of 480, 500, 550^{0}C, calcining at 500, 550, 600^{0}C and the ratio of catalyst : raw = 1:1

Raw material	VG					
Experience temperature, ^{0}C	480	500	500	500	550	*550
Calcination temperature, ^{0}C	600	500	550	600	600	*600
Yield of products, %						
Gas	36.4	5.8	28.9	29.2	42.2	32.6
Gasoline (IBP-205^{0}C)	39.2	58.5	46.8	46.4	30.0	36.2
Light gas oil (205 - 350^{0}C)	16.8	29.1	16.2	17.2	19.2	14.8
Heavy gas oil (>350^{0}C)	3.2	2.0	3.5	2.9	3.8	4.7
Coke	2.4	2.5	2.4	1.8	2.5	8.2
Losses	2.0	2.1	2.2	2.5	2.3	3.2
Amountofproducts	100	100	100	100	100	100

* ratio of catalyst: raw = 2: 1.

A freshly prepared catalyst, calcined at 500^{0} C, cracks VG at 500^{0}C to produce 58.5% of gasoline, the amount of which decreases with an increase in the preliminary calcination temperature to 550°C and 600°C to 46.8% and 46.4%, respectively (Table 6). Heat treatment of the catalyst at 600^{0} C reduces the yield of cracking gasoline regardless of the process temperature itself. The yield of gasoline increases with increasing ratio of catalyst: VG from 1: 1 to 2: 1.

The results indicate that heat treatment of the catalyst increases the strength, but does not provide the necessary catalyst activity in the fuel direction. A decrease in the activity of a catalyst calcined at a high temperature is possible, due to the influence of the temperature of the calcination on the textural and acidic characteristics of the catalyst,hasinfluence on the cracking direction.

The group composition of gasoline formed during the cracking of VG on Al (2.5) NaHMM + HLaY depending on the temperature of calcination is presented in Table 6, from which it can be seen that with increasing temperature of calcination an increase in the number of isoparaffins is observed while the relative content of olefins and aromatic hydrocarbons in gasoline is reduced by 18-20%. The octane number (O.N.) of gasoline cracking by motor method (m.m) decreases with increasing temperature of preliminary calcination of catalysts from 550 to 650^{0}C by 5 units.

Table 7- Group composition of gasoline cracking VG on Al (2.5) NaHMM + HLaY at different temperatures of the calcining of the catalyst

Catalyst	Calcinati-on temp-re, ^{0}C	Hydrocarbon composition				
		Paraffin-naphthenic hydrocarbons,mass.%	Isoparaffins,mass.%	Olefins,mass.%	Aromaticsmass.%	O.N. (m.m)
Al(2.5) NaHMM+ HLaY	550	13.2	16.86	39.88	19.14	65.0
	600	10.87	28.38	24.24	21.49	63.0
	650	9.02	27.58	31.63	15.61	60.0

Conclusion

An increase in the crushstrength of granules Al (2.5) NaHMM + HLaY-catalyst was found with an increase in the temperature of calcination of the catalysts from 500 to 650^{0}C. It is noticed that the introduction of zeolite Y in the substituted rare-earth La-form also leads to an increase in the strength of the granular catalyst.

It was shown that preliminary calcination of zeolite-containing catalysts deposited on pillared Al activated montmorillonite in Na- and CaNa-forms at 550, 600^{0}C leads to a significant decrease in gasoline yield on these catalysts, which indicates that thermal treatment of the catalyst increases the strength, but does not provide the necessary catalyst activity in the fuel direction.

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ТҮРЛЕНДІРІЛГЕН МОНТМОРИЛЛОНИТ НЕГІЗІНДЕГІ КАТАЛИЗАТОРЛАР БЕРІКТІГІ МЕН КРЕКИНГТЕУ БЕЛСЕНДІЛІГІНЕ ТЕРМИЯЛЫҚ ӨҢДЕУ ТЕМПЕРАТУРАСЫНЫҢ ӘСЕРІ

Аннотация. Термиялық өңдеу температурасын 500-ден 650^0C дейін жоғарылатқанда Al(2.5)NaHMM+HLaY-катализаторы түйіршіктерінің үгітілуге қарсы беріктілігі артатыны табылды. Түйіршіктелген катализаторға араластырылған сирек жер La-формасына Y цеолитин енгізу беріктіліктің өсуіне әкелетіні байқалды.

Na- және CaNa-формалы Al-мен пилларирленіп белсендірілген монтмориллонитке енгізілген цеолитқұрамды катализаторларды 550,600^0C кезінде алдын ала термиялық өңдеу осы катализаторларда бензин шығымының төмендеуіне алып келеді, бұл катализаторды термиялық өңдеу беріктілікті арттырғанымен отын бағытында катализатордың қажетті белсенділік таныта алмайтынын көрсетеді.

Түйін сөздер: Катализдік крекинг, термиялық өңдеу, пилларирленген монтмориллонит, жанармай, жеңіл газойль, вакуумдық газойль.

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ ПРОКАЛКИ НА ПРОЧНОСТЬ И КРЕКИРУЮЩУЮ АКТИВНОСТЬ КАТАЛИЗАТОРОВ НА ОСНОВЕ МОДИФИЦИРОВАННОГО МОНТМОРИЛЛОНИТА

Аннотация. Найдено увеличение прочности гранул Al(2.5)NaHMM+HLaY- катализатора на раздавливание с повышением температуры прокалки катализаторов с 500 до 650^0C. Замечено, что введение цеолита Y в замещенной редкоземельной La- форме также приводит к росту прочности гранулированного катализатора.

Показано, что предварительная прокалка при 550, 600 ^{0}C цеолитсодержащих катализаторов, нанесенных на пилларированный Al активированный монтмориллонит в Na- и CaNa –формах, приводит к существенному уменьшению выходов бензина на этих катализаторах, что свидетельствует о том, что термическая обработка катализатора повышает прочность, но не обеспечивает необходимой активности катализатора по топливному направлению.

Ключевые слова: каталитический крекинг, термическая обработка, пилларированный монтмориллонит, бензин, легкий газойль, вакуумный газойль.

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CATALYTIC HYDRODEAROMATIZATION OF MOTOR FUELS AS A METHOD OF PRODUCING ECO-FRIENDLY FUELS

Abstract. The aim of the work was to study the process of hydrodearomatization of gasoline fractions and diesel fuels for the production of environmentally friendly fuels with a low content of aromatic hydrocarbons. Hydrogenation of two gasoline fractions of LLP Atyrau Refinery (AR) and LLP Pavlodar Refinery (PR) and two diesel fuels of PA and LLP PetroKazakhstanOilProducts, Shymkent (PKOP) on Rh-Pt/Al_2O_3 catalyst was studied. The influence of the technological parameters of hydrodearomatization process (pressure 1-5 MPa, temperature 25-200°C) on the content of benzene and aromatic hydrocarbons was studied. At temperatures of 50-200°C and hydrogen pressures of 2-5 MPa, benzene is completely removed from the fractions, and the amount of aromatic hydrocarbons is reduced by 1.5-2 times. Some operational properties (kinematic viscosity at 20°C, pour point and cloud point, flash point, density at 20°C, iodine number, aromatic hydrocarbon content) of the initial diesel fuels of PA and PKOP and after catalytic treatment were determined. In process of hydrodearomatization all operational indicators were improved and approached the standards for diesel fuel, and the cetane index increased by 1-2 units.

Keywords: catalyst, hydrogenation, hydrodearomatization, aromatic hydrocarbon, gasoline fraction, diesel fuel.

Introduction

In the world production of motor fuels, there is a constant tendency to tighten not only their operational but also environmental characteristics. One of the ways to improve the environmental characteristics of motor gasolines is to reduce the content of aromatic hydrocarbons, in particular, benzene. The problem of reducing the benzene content in motor gasolines is particularly acute for domestic oil refining. The content of benzene and aromatics in gasolines, significantly exceeding international standards (Euro 5 < 1% benzene and < 30% aromatics, Euro 6 - 0.1% benzene and 11% aromatics), is due to the predominant production of gasolines by reforming process.

The main reactions of hydrocarbons on the catalyst during the reforming process are the dehydrogenation of naphthenes and the dehydrocyclization of paraffin hydrocarbons, which lead to the accumulation of aromatic compounds with a high octane number in the reforming product. However, these compounds are the most toxic of all hydrocarbon groups and they form poisonous substances during combustion. Particularly dangerous is benzene, which forms benzopyrene during combustion, which, according to the degree of toxicity belongs to the first hazard class with a maximum permissible concentration - 0.000001 mg/m^3. Up to 58% aromatics are formed in reforming plants, and the benzene content can exceed 3% vol. This implies the task of development and implementing additional reformate processing processes in order to reduce the benzene content in it. Benzene reduction in reforming products is possible by the following methods [1-2]:

- hydrogenation of benzene with the formation of cyclohexane, leading to some decrease in the octane number of the component;
- extraction of pure benzene, cost-effective only with its further effective use;
- alkylation with low molecular weight olefins, which allows not only to solve the problem of benzene removal, but also to increase the yield of the target high-octane component;

- hydroisomerization of benzene to cyclohexane followed by isomerization to methylcyclopentane with a slight increase in the octane number and yield of the target component;
- transalkylation of benzene and aromatic hydrocarbons C_{9+}, leading to a decrease in the yield of the target product;
- fractionation of the reformate to obtain a set of fractions, then mixed in various proportions to achieve the desired result,
- reforming + hydroisomerization of benzene - hydrogenation of benzene to cyclohexane, followed by its isomerization to methylcyclopentane (RIGIZ).

The authors of RIGIZ [1] explain the benefits of hydroisomerization of cyclohexane to methylcyclopentane with a higher octane number of the latter 92, while cyclohexane has 88 units.

Diesel fuel in its composition has 15-30% aromatic hydrocarbons, 10-40% paraffin hydrocarbons and 20-60% naphthenic hydrocarbons. The high content of aromatic hydrocarbons reduces the value of the cetane number of diesel fuel and increases the emissions of particulate matter into the environment, adversely affects the ignition time, and increases the height of the non-soaking kerosene flame. For these reasons, reducing the content of aromatic hydrocarbons by hydrogenation is also relevant to improve the environmental friendliness of diesel fuels. In the process of hydrogenation, aromatic hydrocarbons are converted to naphthenic hydrocarbons, and the olefins found in fuels are converted to more stable paraffin or naphthenic hydrocarbons depending on their nature in the feedstock [3-4].

According to the regulation EN590:2010 in force in the European Union, the content of polycyclic aromatic hydrocarbons (PAHs) in diesel fuels should not exceed 8% wt. [3]. In the USA, the total content of aromatic hydrocarbons in diesel fuels is limited to 10% vol., and PAHs - 1.4% vol. [4]. The standards adopted in Sweden are the most stringent in the world: the volume fraction of aromatic hydrocarbons in diesel fuels should not exceed 5%, and PAHs - 0.02% [5].

Tighter requirements for motor fuels are observed in the CIS countries. According to the current Technical Regulations of the Customs Union of Russia, Belarus and Kazakhstan, diesel fuel may contain no more than 11% wt. PAHs.

The use of fuel purified from aromatic hydrocarbons (gasoline and diesel fuel) can significantly reduce its consumption, minimize the load on the engine and have minimal environmental impact.

A significant number of studies have been devoted to the problem of hydrodearomatization of oil products for the production of environmentally friendly fuels [6-16]. The most effective catalysts are metals of group VIII, which, in terms of activity for the hydrogenation of benzene, are arranged in the following order Rh> Ru >> Pt >> Pd >> Ni> Co.

In industry, both catalysts based on metals of group 8 and sulfide are used, but in the latter, hydrogenation of benzene and aromatic hydrocarbons is carried out under more stringent conditions. The most widely used carriers in the industry are active alumina, synthetic amorphous and crystalline aluminosilicates (zeolites). Two-stage of deep hydrodearomatization processes have become common in abroad in which NiW or NiMo sulphide catalysts are used in the first stage and more active acid supported bimetallic platinum-palladium catalysts in the second stage. The developers of two-stage processes are such largest companies as Shell, UOP, Criterion Catalyst.

Thus, in the literature on catalysis in recent years, there has been considerable interest to the process of hydrogenation of aromatics, which is largely explained by the practical application in the production of environmentally friendly fuels.

In previous works [17-20], it has been studied by us the catalytic hydrogenation of aromatic hydrocarbons, developed catalysts and process conditions for the hydrodearomatization process (removal of benzene and decrease in the content of polyaromatic hydrocarbons) of gasoline fractions of "Atyrau Refinery" LLP. The aim of this work is the catalytic hydrogenation of benzene, mono- and polyaromatic hydrocarbons in gasoline fractions of "Atyrau Refinery" LLP and Pavlodar Oil Chemistry Refinery (POCR LLP) , as well as diesel fuels POCR LLP and PKOP LLP (PetroKazakhstan Oil Products, Shymkent)

Experimental part

Bimetallic modified catalysts based on Group 8 metals (Pt and Rh) on aluminum oxide were prepared for hydrodearomatization of gasoline fractions and diesel fuels. At preparation of catalysts $RhCl_3 \cdot 3H_2O$,

$H_2PtCl_6 \cdot 6H_2O$ of "chemically pure" mark were used. Solutions of these compounds were applied by the adsorption method on the prepared carrier Al_2O_3. A mixture of aqueous solutions of two metals was applied at preparation of bimetallic catalysts. The catalyst samples were filtered off and dried at 100-110°C to constant weight. The reduction of supported catalysts was carried out in a quartz tube with electrical heating in a hydrogen stream at 200°C for 4 hours, then the catalysts were cooled in a hydrogen stream until room temperature.

The experiment was carried out on a kinetic installation - the autoclave of "Amar Equipment Ltd" in the isobaric-isothermal regime.

The chromatography method was used to determine content of benzene and aromatic hydrocarbons.

Results and discussion

Hydrodearomatization of the gasoline fractions was carried out on the prepared catalysts. Stable catalyzate of Atyrau Refinery (AR) and gasoline fraction Stable catalyszate of PCOP refinery. Both fractions were obtained as a result of reforming.

Table 1 presents data on the content of benzene 1.0 - 3.23% and aromatic hydrocarbons 55.04-58.68% in both fractions.

Table 1 - The content of benzene and aromatic hydrocarbons in the gasoline fractions of AR and PKOP

Name of fraction	Benzene content, mas. %	Aromatics content, mas. %
Stable catalyzate of AR	3.23	55.04
Stable catalyzate of PKOP	1.0	58.68

We studied the effect of the content of the active catalytic phase on the composition of the components of two gasoline fractions during hydrodearomatization on 0.2% $Rh\text{-}Pt/Al_2O_3$, 0.5% $Rh\text{-}Pt/Al_2O_3$and 1.0% $Rh\text{-}Pt/Al_2O_3$ catalysts.

Figure 1 shows the composition of the catalysis before and after the catalytic treatment of the gasoline fraction. The stable catalyzate AR at 50°C and 0.4 MPa. With an increase in the content of the active phase, the conversion of aromatic hydrocarbons increases, its content decreases from 55.05% to 34.7% for the catalyst 0.2% $Rh\text{-}Pt/Al_2O_3$, 32.5% for the catalyst 0.5% $Rh\text{-}Pt/Al_2O_3$ and 28.4% for the catalyst 1.0% $Rh\text{-}Pt/Al_2O_3$. On all three catalysts, benzene is completely removed from the fraction.

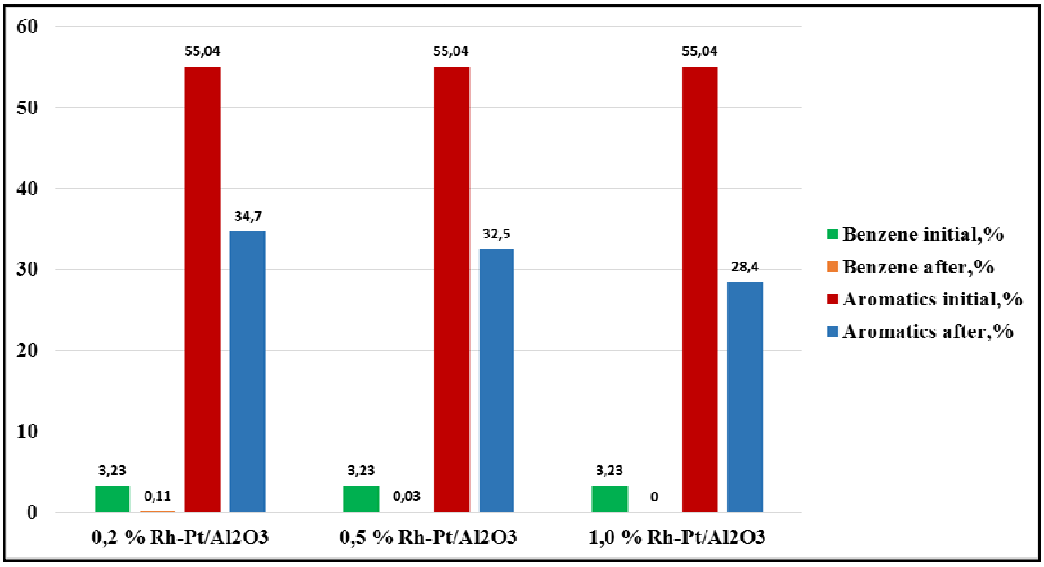

Figure 1 - Hydrogenation of the fraction Stable catalyzate AR on catalysts 0.2% $Rh\text{-}Pt/Al_2O_3$, 0.5% $Rh\text{-}Pt/Al_2O_3$ and 1.0% $Rh\text{-}Pt/Al_2O_3$ at 50°C and 0.4 MPa

Figure 2 shows the composition of the catalyzate before and after the catalytic treatment of the gasoline fraction. Stable catalysis of PKOP at 50°C and 4.0 MPa. On all three catalysts, benzene is completely removed from the fraction. With an increase in the content of the active phase, the conversion of aromatic hydrocarbons increases, its content decreases from 58.7% to 33.8% for the catalyst 0.2% Rh-Pt/Al_2O_3, 29.95% for the catalyst 0.5% Rh-Pt/Al_2O_3 and 29.0% for the catalyst 1.0% Rh-Pt/Al_2O_3.

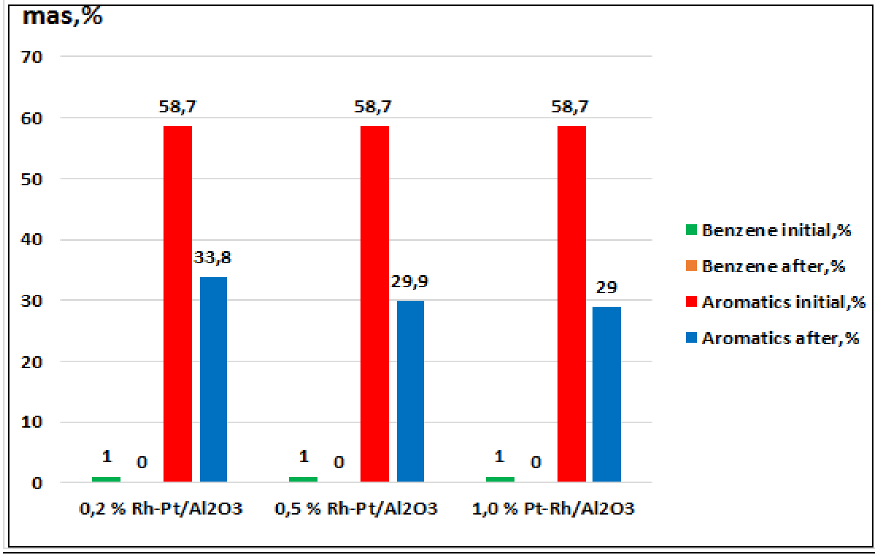

Figure 2 - Hydrogenation of the fraction Stable catalyzate PR on catalysts 0.2% Rh-Pt/Al_2O_3, 0.5% Rh-Pt/Al_2O_3 and 1.0% Rh-Pt/Al_2O_3 at 50°C and 4.0 MPa

The technological parameters (temperature and pressure of hydrogen) of the process of hydrodearomatization of two gasoline fractions were tested. The influence of temperature in the range of 25-200°C and hydrogen pressure of 1.0-5.9 MPa on the content of benzene and aromatic hydrocarbons was studied.

Table 2 presents data on the hydrogenation of a sample of gasoline. Stable catalyzate AR in the temperature range 25-200°C. In the entire temperature range, benzene is absent, i.e. its conversion was 100%. The content of aromatic hydrocarbons decreased from 55.04% to 20.54%. At 1.0-3.0 MPa, the benzene content decreases from 3.23% to 0.12-0.01%, and at 4.0-5.0 MPa, benzene was completely hydrogenated. The content of aromatic hydrocarbons with increasing pressure from 1.0 to 5.0 MPa decreases from 55.04 to 23.79%.

Table 2 - Hydrodearomatization of the fraction Stable Catalyzate AR at 0.5% Rh-Pt/Al_2O_3

Conditions		Benzene content, mas. %		Aromatics content, mas. %	
		Initial	After	Initial	After
P, MPa at 50°C	1.0	3.23	0.12	55.04	40.21
	2.0		0.05		36.92
	3.0		0.01		33.85
	4.0		-		29.73
	5,0		-		23,79
T, °C at 4 MPa	25	3.23	-	55.04	34.73
	50		-		29.73
	100		-		26.54
	150		-		23.91

Table 3 presents data on the hydrogenation of a sample of gasoline Stable catalyzate PR in the temperature range 25-200°C. In the entire temperature range, benzene is absent, i.e. its conversion was 100%. The content of aromatic hydrocarbons decreased from 58.68% to 25.74%. With a change in hydrogen pressure from 1.0 to 3.0 MPa, the benzene content decreases from 1.0% to 0.7-0.01%, and at 4.0-5.0 MPa, benzene was completely hydrogenated. The content of aromatic hydrocarbons decreases with pressure from 1.0 to 5.0 MPa from 58.68 to 29.05%.

Table 3 - Hydrodearomatization of the fraction Stable Catalyzate PR at 0.5% Rh-Pt/Al_2O_3

Conditions		Benzene content, mas. %		Aromatics content, mas. %	
		Initial	After		Initial
P, MPa at 50°C	1.0	1.0	0.7	58.68	50.21
	2.0		0.04		46.95
	3.0		0.01		33.85
	4.0		-		29.93
	5,0		-		29.05
T, °C at 4 MPa	25	1.0	-	58.68	34.93
	50		-		29.93
	100		-		28.76
	150		-		26.91
	200		-		25.74

Figure 3 shows data on the group composition of organic substances in two gasolines of the initial fractions and after hydrogenation over Rh-Pt(90:10)/Al_2O_3, P = 3 MPa, T = 50°C. For the Stable Catalyzate AR the benzene content in the initial state was 3.23 wt.%. After the reaction, benzene is absent, i.e. 100% benzene conversion. The amount of aromatics decreased from 55.04 wt.% to 23.79 wt.%.

It should be noted that the number of olefins decreased almost 2 times from 0.23% to 0.11 wt.%, this is very favorable for gasolines, since the presence of olefins leads to instability (the oligomerization and polymerization reaction proceeds).

The amount of paraffins slightly increased from 12.22 wt.% to 13.99 wt.%. And the content of isoparaffins increased from 27.16 wt.% to 36.81 wt.%. Apparently, the isomerization of paraffins to isoparaffins occurred. The content of naphthenes increased sharply from 2.12 wt.% to 25.3 wt.%.

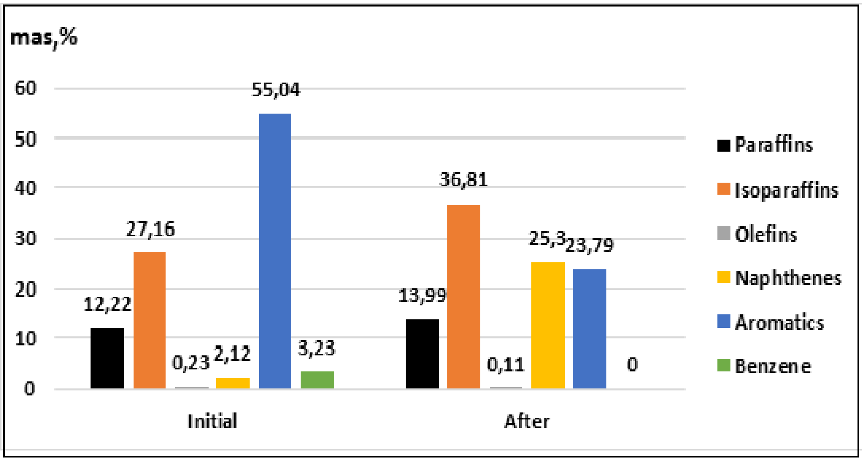

Figure 3 - Group composition of hydrocarbons of the Stable Catalyzate AR before and after catalytic treatment

Figure 4 showed that in the initial Stable Catalyzate PR there was 1.0 wt.% benzene; after hydrogenation benzene was not found in the catalyzate - i.e. it was completely hydrogenated. The aromatic content in the original gasoline was 58.68 wt.%, After hydrogenation it became 29.39 wt.%.

The amount of olefins decreased significantly from 10.2 wt.% to 0.51 wt.%, which leads to the stability of gasoline. In addition, the content of isoparaffins increased from 17.05 wt.% to 28.2 wt.%. This indicates the occurrence of the hydroisomerization reaction on this catalyst, which is favorable for the octane number.

The data on the octane number, density of the initial gasoline fractions before and after the catalytic treatment, shown by chromatographic analysis, are shown in Table 4. The octane number by the research method of the initial Stable Catalyzate AR is 83, after processing it decreased to 81. For the gasoline fraction, Stable Catalyzate PR octane number according to the research method before and after the experiment is 87. In this case also, the octane number has not changed. This indicates that the processing of gasoline practically does not reduce the octane rating. Densities slightly increased after treatment for both fractions, and the saturated vapor pressure decreased, which is understandable from the point of view of changing the hydrocarbon composition to a heavier region - naphthenes have a higher density and lower vapor pressure compared to aromatic hydrocarbons.

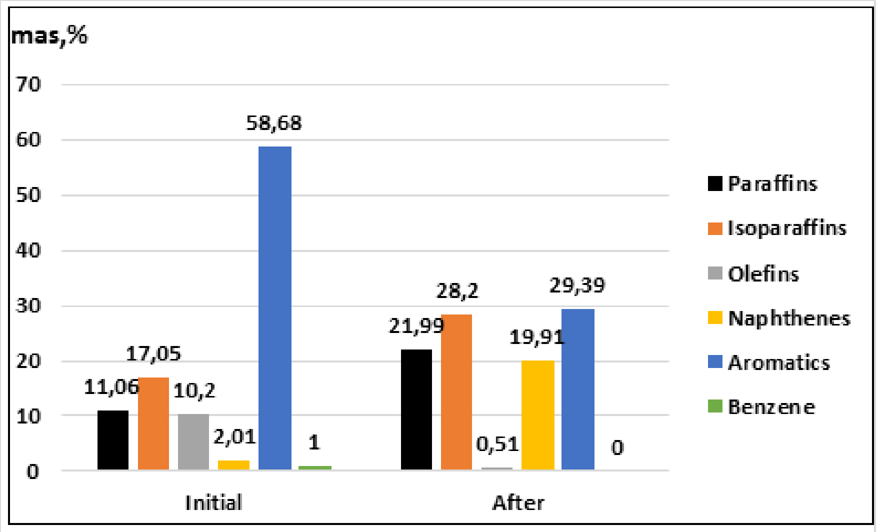

Figure 4 - Group composition of hydrocarbons of the Stable Catalyzate PR before and after catalytic treatment

Table 4 - Indicators of gasoline fractions before and after catalytic treatment

Name of fractions	Octane number		Saturated vapor pressure, kPa		Density at 20°C, g/l	
	initial	after experiment	initial	after experiment	initial	after experiment
Stable catalyzate AR	83	81	23.64	19.86	779.87	785.55
Stable catalyzate PR	87	86	24.65	19.39	789.4	793.50

It should be noted that the studied processes of hydrodearomatization of gasoline fractions were carried out under mild conditions – temperature 50°C compared with 160-330°C used in world industry. Under more stringent conditions, the process of complete hydrogenation of aromatic hydrocarbons can occur with the opening of the benzene ring, which is undesirable, because alkanes have a low octane number.

The same catalyst was tested during the hydrodearomatization of two diesel fuels obtained from PR and PKOP. In diesel fuels, olefins, mono- and poliomatic hydrocarbons can be hydrogenated. Table 5 shows the hydrogenation of PKOP diesel fuel (180-350°C) and PR diesel fuel (169-347°C). The change in the operational characteristics of diesel fuels during hydrogenation to Pt-Rh/Al_2O_3 is presented in table 5.

Table 5 - Physico-chemical indicators of diesel fuels of PR and PKOP in the process of hydrogenation

Condi-tions	Densi-ty at 20°C, g/cm^3	Cloud point, °C	Pour point, °C	Flash point in a closed crucible, °C	Kinematic viscosity at 20°C, mm^2/s	Aroma-tics content, %	Iodine number, gI_2/100g of fuel	Cetane index
Diesel fuel PKOP (180-350^{o}C)								
Before hydrogenation	0.833	5	0	61	4.5	13.80	3.2	52
Pt-Rh/Al_2O_3	0.839	- 2	- 4	57	4,6	0.73	0	53
Diesel fuel PR (169-347^{o}C)								
Before hydroge-nation	0.841	- 15	- 8	64	4.8	12.90	2.9	49
Pt-Rh/ Al_2O_3	0.850	- 18	- 12	58	5.0	0.68	0	51

In the presence of a $Pt\text{-}Rh/Al_2O_3$ catalyst, the density increases for PR fuel from 0.841 to 0.850 g/cm^3, and for PKOP fuel from 0.833 to 0.839 g/cm^3 (the norm for diesel fuel is 0.860 g/cm^3). Clouding and solidification temperatures decrease respectively for PR fuel increased from -15 to -18°C and from -8 to -12°C, and for PKOP fuel - from 5 to -2°C and from 0 to -4°C. The flash point in a closed crucible for PR fuel decreases from 61 to 57°C, and for PKOP fuel from 64 to 58°C, whereas according to the norm 55°C.

The viscosity of AR fuel increases from 4.8 to 5.0 mm^2/s and for PKOP fuel from 4.5 to 4.6 mm^2/s (according to the norm of 3-6 mm^2/s). The aromatics content (including mono- and polyaromatic hydrocarbons) for PR fuel decreases from 12.90 to 0.68%, for PKOP fuel from 13.8 to 0.73%. The iodine number indicates the presence of double bonds, i.e. the presence of olefins. For PR fuel, the iodine number decreased from 3.2 to 0 g I_2/100 g of fuel, for PKOP fuel it decreased from 2.9 to 0 g I_2/100g of fuel, which indicates that olefins were practically hydrogenated on the catalyst.

The cetane index increased by 1-2 units: for PR fuel from 49 to 51, for PKOP fuel from 52 to 53. The cetane index depends on the ratio of naphthenic and aromatic hydrocarbons, and in our case, the aromatics were hydrogenated to form naphthenic hydrocarbons.

Thus, the advantage of catalytic hydrodearomatization is the improvement of performance indicators and approximation to the standards for diesel fuels obtained at Kazakhstan refineries.

The technology of hydrodearomatization of automobile gasolines and diesel fuels is applicable for the production of eco-friendly fuels with a low content of aromatic hydrocarbons, which will reduce the volume of gaseous emissions and extend the service life of cars by 1/3, which will also bring economic benefits.

Conclusions

The process of hydrodearomatization of two gasoline fractions of AR and PR and two diesel fuels of PR and PKOP on the prepared $Rh\text{-}Pt/Al_2O_3$ catalysts was studied. The effect of the process parameters of the hydrodearomatization of gasoline fractions (pressure 1-5 MPa, temperature 25-200°C) on the content of benzene and aromatic hydrocarbons was studied. At of 50-200°C and 2-5 MPa, benzene is completely removed from the fraction, and the amount of aromatic hydrocarbons is reduced by 1.5-2 times. The group composition of gasoline fractions showed a decrease in the number of aromatic hydrocarbons, olefins and an increase in paraffins of the iso-structure, which indicates the occurrence of not only a hydrogenation reaction, but also hydroisomerization. Some operational properties (kinematic viscosity at 20°C, pour point and cloud point, flash point, density at 20°C, iodine number, aromatic hydrocarbon content) of the starting diesel fuel PR and PKOP and after catalytic treatment were determined. In the presence of a $Pt\text{-}Rh/Al_2O_3$ catalyst, all performance indicators improve and approach the standards for diesel fuel, the content of aromatic hydrocarbons decreased to 0, and the cetane index increased by 1-2 units.

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ЭКОЛОГИЯЛЫҚ ТАЗА ОТЫН АЛУ ӘДІСІ РЕТІНДЕ МОТОР ОТЫНЫН КАТАЛИЗДІК ГИДРОДЕАРОМАТИЗАЦИЯЛАУ

Аннотация. Жұмыстың мақсаты құрамында ароматты көмірсутектері төмен экологиялық таза отындарды өндіру үшін бензинді фракциялар мен дизель отындарын гидродеароматизациялау процесін зерттеу болып табылады. Атырау мұнай өңдеу зауыты Жеке Шаруашылық Серіктестігі (АМӨЗ) және Павлодар мұнайхимиялық зауыты Жеке Шаруашылық Серіктестігі (ПМХЗ) екі бензинді фракциясын және АМӨЗ мен ЖШС PetroKazakhstanOilProducts, Шымкент (ПКОП) екі дизельді отынын $Rh\text{-}Pt/Al_2O_3$

катализаторларында гидрлеу зерттелді. Гидродеароматизация процесінің технологиялық параметрлерінің (қысымы 1-5 МПа, температурасы 25-200^{o}С) бензол мен ароматты көмірсутектердің құрамына әсері зерттелді. 50-200^{o}С температурада және 2-5 МПа сутегі қысымдарында бензол фракцияда толығымен жойылады, ал ароматты көмірсутектер саны 1,5-2 есе төмендейді. ПМХЗ және ПКОП бастапқы дизель отындарының және катализдік өндеуден кейінгі кейбір пайдалану қасиеттері анықталды (20^{o}С кезіндегі кинематикалық тұтқырлығы, кату және тұндыру температурасы, тұтану температурасы, 20^{o}С кезіндегі тығыздығы, йод саны, хош иісті көмірсутектердің құрамы). Гидродеароматизация процесі кезінде барлық пайдалану көрсеткіштері жақсарады және дизель отыны үшін нормаларға жақындайды,ал цетандық индекс 1-2 бірлікке ұлғайды.

Түйін сөздер: катализатор, гидрлеу, гидродеароматизация, ароматты көмірсутектер, бензин фракциясы, дизель отыны.

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КАТАЛИТИЧЕСКАЯ ГИДРОДЕАРОМАТИЗАЦИЯ МОТОРНЫХ ТОПЛИВ КАК СПОСОБ ПОЛУЧЕНИЯ ЭКОЛОГИЧЕСКИ ЧИСТЫХ ТОПЛИВ

Аннотация. Целью работы являлось изучение процесса гидродеароматизации бензиновых фракций и дизельных топлив для производства экологически чистых топлив с низким содержанием ароматических углеводородов. Изучено гидрирование двух бензиновых фракций ТОО Атырауский нефтеперерабатывающий завод (АНПЗ) и ТОО Павлодарский нефтехимический завод (ПНХЗ) и двух дизельных топлив ПНХЗ и ТОО PetroKazakhstanOilProducts, Шымкент (ПКОП) на Rh-Pt/Al_2O_3 катализаторе. Исследовалось влияние технологических параметров процесса гидродеароматизации (давление 1-5 МПа, температура 25-200^{o}С) на содержание бензола и ароматических углеводородов. При температурах 50-200^{o}С и давлениях водорода 2-5 МПа бензол полностью удаляется из фракции, а количество ароматических углеводородов снижается в 1,5-2 раза. Определены некоторые эксплуатационные свойства (кинематическая вязкость при 20^{o}С, температуры застывания и помутнения, температура вспышки, плотность при 20^{o}С, йодное число, содержание ароматических углеводородов) исходных дизельных топлив ПНХЗ и ПКОП и после каталитической обработки. В процессе гидродеароматизации все эксплуатационные показатели улучшаются и приближаются к нормам для дизельного топлива, а цетановый индекс увеличился на 1-2 единицы.

Ключевые слова: катализатор, гидрирование, гидродеароматизация, ароматические углеводороды, бензиновая фракция, дизельное топливо.

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STUDY OF ON THE ELECTROCHEMICAL BEHAVIOR OF TITANIUM IN ACIDIC BROMIDE SOLUTION BY RECORDING THE POTENTIODYNAMIC POLARIZATION CURVES

Abstract. The electrochemical dissolution of titanium in a potassium bromide solution acidified with a sulfuric acid solution by recording cyclic and anodic potentiodynamic polarization curves was studied for the first time. The influence of the sulfuric acid and potassium bromide solutions concentration on the titanium electrode oxidation was considered.

A polarization curve was performed in 1.0 M potassium bromide solution in the presence of 0.5 M sulfuric acid and the titanium oxidation anodic maximum was recorded. To explain the titanium dissolution characteristics during the polarization by industrial alternating current, cyclic anodic-cathodic (CAC) and cyclic cathode-anodic (CCA) polarization curves of the titanium electrode in potassium bromide sulfate solution were recorded. At the CAC voltammogram, when the titanium potential is shifted to the anode direction, titanium oxidation current is recorded at potentials from “plus” 1.3 V to “plus” 2.3 V. In the cathode direction of the CCP voltammogram curve between potentials “minus” 0.7–1.0 V, a hydrogen evolution current is observed. The dependence of anodic potentiodynamic polarization curves on the concentration of sulfuric acid and potassium bromide solutions was studied, in both cases an increase in the titanium oxidation maximum current was observed, a mechanism was also established and the reactions sequence proceeding on the electrode was calculated.

Studies have shown that electrode reactions occur by a complex mechanism.

Keywords: titanium, potassium bromide, sulfuric acid, electrode, potentiodynamic polarization curves, oxidation current.

Titanium can be called modern techniques and industry metal since most of its part is used for space, aero- and hydro technologies needs. In its turn, titanium (IV) oxide is the main titanium industry product. The classic methods of its production are a complex process that involves the production of titanium sulfate, tetrachloride and bromide solutions for obtaining titanium minerals called ilmenite, leucoxene and rutile. It is very difficult to extract these salts directly from titanium residues (scrap) since titanium is a highly corrosion-resistant metal with high-melting temperature in many aqua environments [1]. It is important to determine the electrochemical dissolution laws, mechanisms and kinetics of corrosion-resistant metals in various aqueous solutions.

M.S. Amrutha used a four-stage mechanism to determine chemical constants by investigating of Ti in varying concentrations of hydrofluoric acid (0.01 M÷1.0 M) through applying potentiodynamic polarization and electrochemical impedance spectroscopy methods [2]. F. Fasmin presented a kinetic model of titanium electrode anode dissolution in 0.1 M hydrofluoric acid in active and passive regions [3]. A.B. Bayeshov et al. have considered electrochemical dissolution of titanium in the sulfur, hydrochloric acid and phosphoric acid medium in the solution with fluoride ions in the presence of alternating current [4-9]. The study result shows that titanium electrode dissolves with high current efficiency in acidic solutions containing fluoride ions.

U. Tetsuya studied the electrochemical dissolution of titanium electrode in the TMHA-Tf_2N ionic liquid. It was determined that no dissolution of titanium was observed during the anodic potential sweep up to +6.0 V due its oxide film formation. Prior to electrochemical experiments, more mechanical smoothing of titanium surface led to the shift of the titanium potential immersed in the electrolyte to a negative value. In this case, the anode titanium dissolution in the zone with the potential value "minus" 0.95 ÷ "plus" 1.6 V was determined [10].

D. Baehre considered the electrochemical dissolution behavior of pure titanium electrode, TiMaAl6V4 and intermetallic Ti60Al40 (γ-TiAl) in potassium bromide-, sodium chloride-, sodium nitrate aqueous solutions at different pH-values. During the study, the methods of cyclic voltammetry, linear sweep voltammetry polarization and chronoamperometry were performed. As a result, a positive effect of halide compounds on the titanium electrode dissolution and its alloys was determined [11].

Literature data analysis shows that electrochemical properties of titanium in bromide acidic environment have not been studied yet. Having investigated titanium (III) ions oxidation mechanism, A.B. Bayeshov and G.M. Iztileuov show that titanium (III) ions oxidation occurs as a result of the hydrolysis process at high temperatures and can be met either in $[Ti(H_2O)_6]Cl_3$ or $[Ti(H_2O)_6]SO_4$ form in the acidic medium. As a result of the study, at 333 K temperature, an increase of titanium (III) ion oxidation wave in a sulfuric acid concentration of 300 g/l was observed, and the most maximum current negative value was "minus" 0.8 V in the graphite electrode and "minus" 0.02 V in lead electrode [12].

Y. Jiang and Y. Wu investigated the electrochemical reaction mechanism of titanium alloy in neutral (NaCl) aqua environment performed by polarization curves. It was defined the formation of titanium intermediate oxide shell through oxidizing during its anode dissolution in the sodium chloride solution [13].

The advantage of the titanium anode oxidation process as a coating in materials surface covering in the biomaterials production has been shown in a number of studies [14, 15]. E.A. Kornyushova et al. studied electrochemical properties of titanium and platinum electrodes in dicarboxylic amino acids. Due to the implementation of the surface reactions in the titanium electrode, the oxide shell has been grown; thereby the existence of its adsorbing properties has been determined [16]. Young-Taeg Sul et al. discovered the electrochemical properties of titanium biomaterials in acetic acid, phosphoric acid, calcium hydroxide and sodium hydroxide, and showed that the anode voltage stress (dV/dt) in acidic electrolyte was higher than in alkaline electrolyte [17].

In the given work, electrochemical properties of titanium were studied by recording potentiodiodynamic polarization curves in potassium bromide aqueous solution acidified by sulfuric acid solution.

The polarization measurement was performed using potentiostat "Autolab". Voltampereometric studies were conducted in three-electrode thermostated electrolysis cells. A silver-chloride electrode was used as a reference electrode, and platinum cord as an auxiliary electrode. The outer surface of titanium covered by teflon with a diameter of 2 mm and used as a working electrode.

Before each experiment, the titanium electrode was rinsed with distilled water and smoothed in 500 µm and 200 µm sandpaper material, defatted and washed thoroughly with filter paper. Different concentrations of KBr and H_2SO_4 aqueous solutions were used as electrolytes.

When the titanium electrode is polarized by direct current in the Galvanometric case, its surface is passivated by oxidized layers and electrode dissolution by forming titanium ions is accompanied by very low current efficiency. Results of our previous research show, titanium electrode intensively dissolved in the sulfuric acid bromide solution polarized by the industrial alternating current has been observed [18, 19].

The titanium electrode properties in potassium bromide solution were investigated first in potassium bromide and sulfuric acid solution, subsequently by recording anodic and cyclic potentiodynamic polarization curves in mixed solutions of potassium bromide and sulfuric acid.

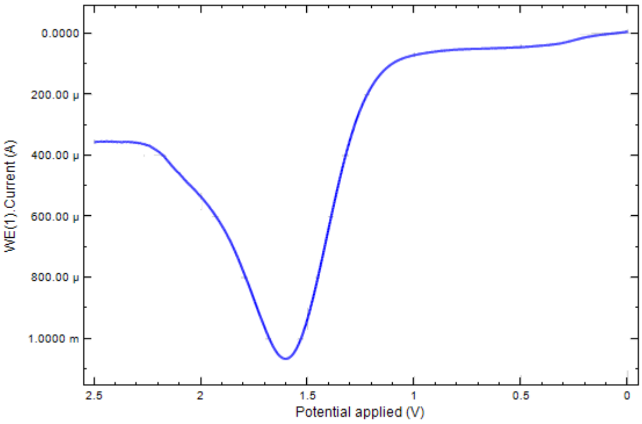
Anodic polarization curves were taken to determine the titanium electrode specificity to dissolve in potassium bromide and sulfuric acid.

In the potentiodynamic polarogram taken in the anode direction the titanium oxidation wave in potassium bromide or sulfuric acid solutions was not recorded.

In subsequent studies, 1.0 M potassium bromide solution was dissolved in 0,5 M sulfuric acid solution and polarization curve "potential-current density" was recorded. In this solution, it is possible to notice that the anodic titanium oxidation current was recorded in the anode potentiodynamic curve.

In the cyclic mode, potassium bromide and sulfuric acid solutions were recorded in cycles between "plus" 2.5 V and "minus" 1.0 V in order to detect the specificity of processes occurring in the titanium electrode polarized by industrial alternating current with the frequency of 50 Hz.

When the CAC potential shifts in the anode direction, the maximum oxidation current between "plus" 1.3 V ÷ "plus" 2.3 V potential is recorded on the polarogram (Figure 1). In the polarogram of cathodic direction there were no significant oxidation waves, the hydrogen evolution was detected at "minus" 0.7 V and at negative potentials.



[KBr]=1M; [H_2SO_4]=0.5M; ν=50мВ/с

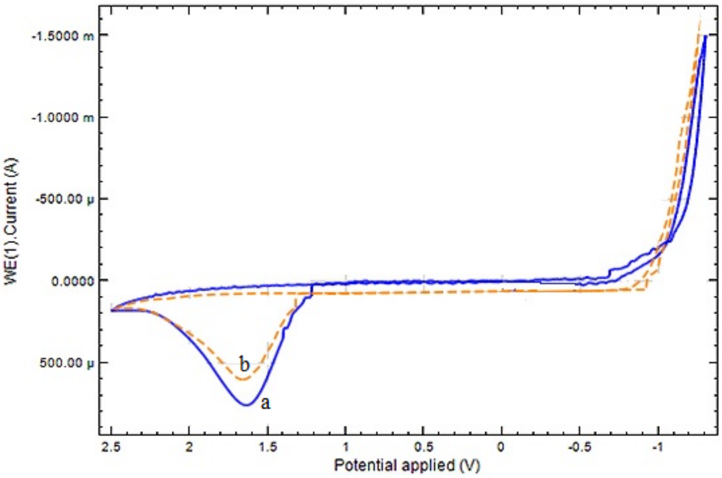
Figure 1 - Anodic potentiodiodynamic polarization curve of titanium electrode in acidic bromide solution

In the acidified potassium bromide solution, titanium oxidation in the anode direction can be described by the reaction. In the cathodic direction, mainly hydrogen ion discharge occurs (reaction 2).

$$Ti - 3e^- \rightarrow Ti^{3+} \qquad E^0 = -1,21V \tag{1}$$

$$2H^+ + 2e^- = H_{2\uparrow} \tag{2}$$

In the polarization curve taken in the CCA direction, the main processes occurring in the electrode are repeated (Figure 2). The CCA polarogram cathode direction shows that beginning from "minus" 0.7-1.0 V potential hydrogen gas division is observed and only the titanium oxidation maximum value decreases (Fig. 1, b-curve).

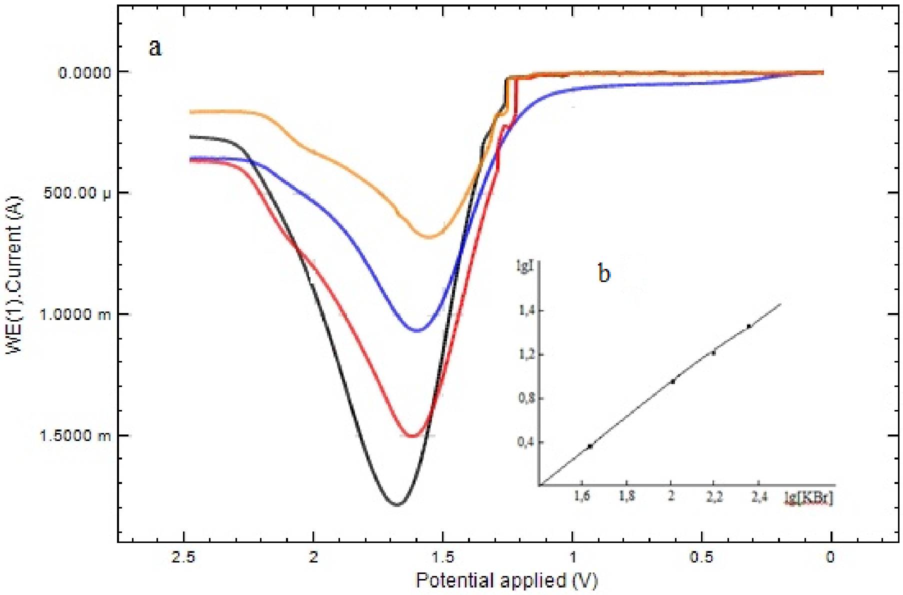


[KBr]=1.0 M; [H_2SO_4]=0.5 M; ν=50мВ/с

Figure 2 - Cathodic-anodic (a) and anodic-cathodic (b) cyclic voltammogram of titanium electrode in the acidic bromide solution

The potassium bromide concentration effect on titanium electrode anodic potentiodiodynamic polarization curves is shown in Figure 3 (a). Increasing the potassium bromide solution concentration can significantly increase the oxidation current height. According to the experiment results, dependence taken on lg[KBr] – lgi coordinate is straight linear (b). Table 1 was completed based on this dependence result and the reaction rate for bromide ions was 0.2.

Logarithmic dependence should be straight linear to determine the reaction sequence. The reaction sequence was mathematically determined [20].



[KBr]=0.5-2.0 M; $[H_2SO_4]$=0.5 M; ν=50мB/c

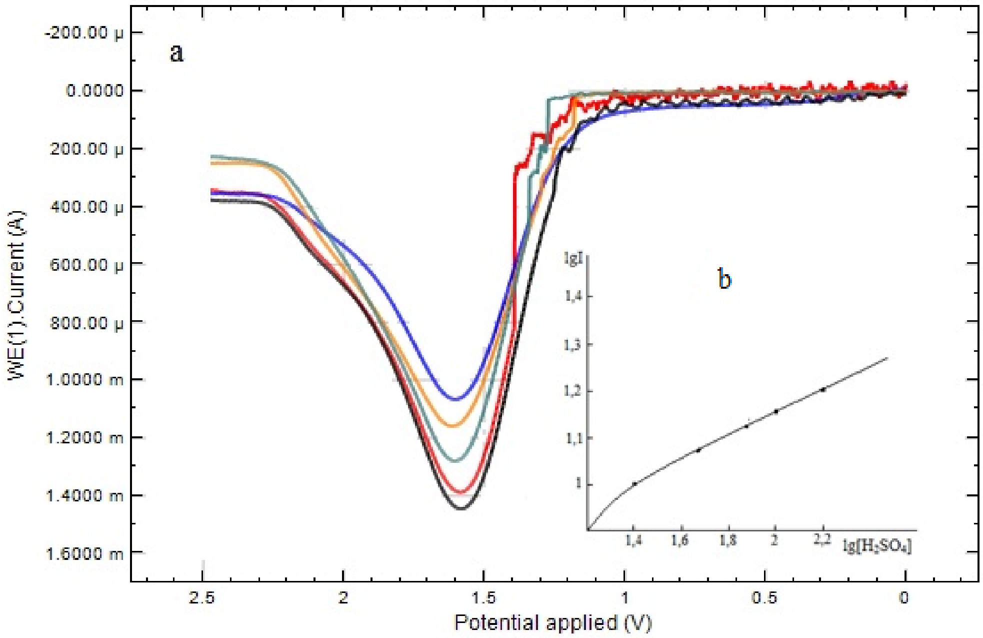
Figure 3 - Dependence of titanium electrode anodic potentiodynamic polarization curves on the anode maximum of potassium bromide concentration (a) and the lg$i$-lgC_{KBr} dependence on potassium bromide concentration (b)

Table 1 - The electrode reaction order of bromide ions occurring during electrolysis

№	C_{el}	lgC=x	i	y=lgi	x·y	x^2
1	0.5	-0.301	65	1.8	-0.5418	0.29
2	1.0	0	105	2.0	0	0
3	1.5	1.76	150	2.2	0.3872	0.1499
4	2.0	0.301	180	2.25	0.6772	0.4586
Σ	-	0.176	-	8.25	0.5226	0.8985

$$b=\frac{n\sum x\cdot y-\sum x\cdot\sum y}{n\sum x^2-\left(\sum x\right)^2}=\frac{4\cdot 0.5226-(0.176\cdot 8.25)}{4\cdot 0.8925-(0.176)^2}=0.17\approx 0.2$$

Figure 4 (a) shows the titanium electrode dependence on the anodic potentiodynamic polarization curves and on the sulfuric acid concentration. Increasing the sulfuric acid concentration can significantly increase the oxidation current height rightfully. According to the experiment results, the dependence taken on the lg$[H_2SO_4]$ – lgi coordinate is straight linear (b). Increasing the sulfuric acid concentration increases the oxidation current height evenly. Based on this dependence result, Table 2 was completed and the fact that the reaction rate for sulfuric acid was 0.04 was detected.



$[KBr]=1.0$ M; $[H_2SO_4]=0.25\text{-}1.50$ M; ν=50мВ/с

Figure 4 - The dependence of sulfuric acid concentration on the anode maximum at titanium electrode anodic potentiodynamic polarization curves (a) and the dependence the logarithms of sulfuric acid concentration and the maximum current height (b)

Table 2 - The sequence of electrode reactions on sulfuric acid during electrolysis

№	C_{el}	lgC=x	I	y=lgi	x·y	x^2
1	0.25	-0.602	105	2.02	-1.216	1.4800
2	0.50	-0.302	115	2.06	-0.620	0.3800
3	0.75	-0.120	130	2.11	-0.250	0.0625
4	1.00	0	140	2.15	0	0
5	1.50	0.176	145	2.16	0.380	0.1400
Σ	-	-0.847	-	10.5	-1.706	2.0600

$$b=\frac{n\sum x\cdot y-\sum x\cdot\sum y}{n\sum x^2-\left(\sum x\right)^2}=\frac{5\cdot(-1.706)-(-0.847\cdot 10.5)}{5\cdot 2.06-(-0.847)^2}=0.04$$

Summing up, the electrochemical properties of titanium in acid bromide solution were first studied by recording potentiodynamic polarization curves. No dissolution of titanium electrode was observed during the anodic polarization in 1.0 M potassium bromide and 0.5 M sulfuric acid solutions separately from each other. With a view to increasing the electrochemical dissolution process, polarization curves were taken in 1.0 M potassium bromide solution in the presence of 0.5 M sulfuric acid and the maximum oxidation rate recording was observed. In this case, the mechanisms and kinetics of electrode reactions were determined. The titanium electrode was studied by recording polarization CAC and CCA in potassium bromide and sulfuric acid solutions. The specificity of titanium electrode dissolution polarized with alternating current of 50 Hz is determined. The dependence of anodic potentiodynamic polarization curves on the sulfuric acid concentration and the potassium bromide concentration was investigated and in both cases the current maximum increase was observed and the reactions sequence was determined.

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ТИТАННЫҢ ҚЫШҚЫЛДЫ БРОМИДТІ ЕРІТІНДІСІНДЕГІ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІН ПОТЕНЦИОДИНАМИКАЛЫҚ ПОЛЯРИЗАЦИЯЛЫ ҚИСЫҚТАР ТҮСІРУ АРҚЫЛЫ ЗЕРТТЕУ

Аннотация. Күкірт қышқылымен қышқылданған калий бромиді ерітіндісінде титанның электрохимиялық еру заңдылықтары циклді және анодты потенциодинамикалық поляризациялық қисықтар түсіру арқылы алғаш рет зерттелді. Титан электродының анодтық тотығу процесіне күкірт қышқылы мен калий бромиді ерітінділерінің концентрация әсері қарастырылды.

Құрамында 1,0 М калий бромиді және 0,5 М күкірт қышқылы бар ерітіндіде поляризациялық қисықтар түсірілді және бұл кезде анодты тотығу максимумының тіркелгендігі көрсетілді.

Өндірістік жиіліктегі айнымалы токпен поляризацияланған титанның еру ерекшелігін түсіндіру үшін титан электродының калий бромиді мен күкірт қышқылы бар ерітінділердегі циклді анод-катод (ЦАК), циклді катод-анод (ЦКА) бағыттарында поляризациялық қисықтар түсірілді. ЦАК полярограммасында титан потенциалын анод бағытына қарай ығыстырғанда «плюс» 1,3 В ÷ «плюс» 2,3 В потенциалы аралығында титанның тотығу тогы тіркелді. ЦКА полярограммасының катод бағытында «минус» 0,7-1,0 В потенциалдарынан бастап, сутек газының бөліну тогы байқалды.

Анодты потенциодинамикалық поляризациялық қисықтарға әртүрлі күкірт қышқылы және калий бромиді концентрацияларының әсері зерттеліп, екі жағдайда да титанның анодты еру ток максимумдарының жоғарылайтындығы анықталды, сонымен қатар, электродта жүретін реакциялардың реті есептеліп, механизмі анықталды.

Зерттеу нәтижесінде титан электродында жүретін реакциялардың өте күрделі механизммен іске асатындығы көрсетілді.

Түйін сөздер: титан, калий бромиді, күкірт қышқылы, электрод, потенциодинамикалық поляризациялық қисықтар, тотығу тогы.

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ИССЛЕДОВАНИЕ ЭЛЕКТРОХИМИЧЕСКОГО ПОВЕДЕНИЯ ТИТАНА В КИСЛЫХ БРОМИДНЫХ РАСТВОРАХ МЕТОДОМ СНЯТИЯ ПОТЕНЦИОДИНАМИЧЕСКИХ ПОЛЯРИЗАЦИОННЫХ КРИВЫХ

Аннотация. Впервые исследовано электрохимическое растворение титана в растворе бромида калия, подкисленном раствором серной кислоты методом снятия циклических и анодных потенциодинамических поляризационных кривых. Рассмотрено влияние концентрации растворов серной кислоты и бромида калия на процесс окисления титанового электрода.

Снята поляризационная кривая в 1,0 М растворе бромида калия в присутствии 0,5 М серной кислоты и зафиксирован анодный максимум окисления титана. Для объяснения особенностей растворения титана при поляризации промышленным переменным током сняты циклические анодно-катодные (ЦАК) и циклические катодно-анодные (ЦКА) поляризационные кривые титанового электрода в сернокислом растворе бромида калия. На ЦАК полярограмме при смещении потенциала титана в анодном направлении регистрируется ток окисления титана при потенциалах от «плюс» 1,3 В до «плюс» 2,3 В. В катодном направлении полярограммы ЦКА кривой между потенциалами «минус» 0,7-1,0 В наблюдается ток выделения водорода. Исследована зависимость анодных потенциодинамических поляризационных кривых от концентрации раствора серной кислоты и бромида калия, в обоих случаях наблюдается увеличение максимума тока окисления титана, также установлен механизм и рассчитан порядок реакций, протекающих на электроде.

Исследования показали, что электродные реакции протекают по сложному механизму.

Ключевые слова: титан, бромид калия, серная кислота, электрод, потенциодинамические поляризационные кривые, ток окисления.

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STUDY ON THE EFFECT OF THE DRUG FS-1 ON ACTIVITY OF BACTERIAL ANTIOXIDANT SYSTEM

Abstract. The effect of iodine-containing complex FS-1 on the antioxidant system in *M. smegmatis* is described. It is shown that FS-1 under *in vitro* experimental conditions at doses of 2 μg/ml and 4 μg/ml inhibits the functional activity of bacterial superoxide dismutase enzyme on the example of atypical mycobacteria *M. smegmatis*, i.e. resistance to oxidative stress.

Keywords: Iodine-containing complex FS-1, antioxidant system, oxidative stress.

Introduction. The widespread introduction of anti-infectious drugs in medical and veterinary practice has resulted in the emergence of various resistance mechanisms in microorganisms that neutralize or reduce their effect [1-3]. Currently, this problem has acquired a global scale and led to a decrease in the drug treatment effectiveness or its complete loss [4-6].

The reason for the spread of infection is not only the resistance of the causative agent to the drugs used, but also the acquisition of resistance and adaptation to the effects of the defense mechanisms of the immune system in the macroorganism [7-9]. It has been established that the course of the disease and nature of the treatment for a number of infectious diseases are influenced by free radical oxidation processes [10, 13]. The protective role of the immune system in the macroorganism and, first of all, phagocytosis with an oxygen-dependent mechanism of action on bacteria is known [11]. In this case, phagocytes kill the absorbed microbes by various superoxide radicals through the action of the antioxidant enzyme system in microorganisms. The antioxidant enzyme system in microorganisms is composed of catalase, peroxidase, antioxidant superoxide dismutase (SOD), etc., involved in the neutralization of free radicals. Catalase and SOD protect microorganisms from exogenous and endogenous oxidative stresses by neutralizing superoxide radicals. The superoxide toxic radical formed in the cells as a result of metabolic processes by means of the SOD and catalase enzymes is converted into hydrogen peroxide, followed by its decomposition into harmless molecular oxygen and water. Microorganisms, in turn, acquire resistance and adaptation to oxidative stress, as a result of which they survive in the nidus of inflammation, frequently inside phagocytes [12-15].

The cells of microorganisms in their structure and functions are a full-fledged unicellular organism responsible for physiological regulation and self-reproduction [16]. The mechanism of action of modern chemotherapeutic drugs on the microbial cell is complex and multiform. It is associated with their effects on the microbial enzyme system, respiratory rate, metabolism, on the processes of reproduction and vital activity of bacteria. Therefore, the need to study the effect of chemotherapeutic drugs on the microbial cells, their morphological features, emerging endogenous and exogenous oxidative stresses during both metabolic and infectious processes, seems relevant.

This paper presents the results of a study on the effect of the new iodine-containing drug FS-1 (Patent of the Republic of Kazakhstan No. 28746, 2014) developed at JSC Scientific Center for Anti-Infectious Drugs on the activity of the bacterial antioxidant system in mycobacteria.

Materials and Methods. As a model microorganism, a fast-growing atypical culture *Mycobacterium smegmatis* ATCC 607, obtained from the American Type Culture Collection, was used. The examined concentrations of the drug FS-1 were chosen based on MBC against this test culture, and amounted to 2 and 4 µg/ml. 0.1% solution of adrenaline hydrochloride (FSUE Moscow Endocrine Plant, Russia), 0.2 M bicarbonate buffer (pH 10.65) were used in this study.

The effect of the substance under study on the antioxidant system in bacteria was determined by *in vitro* autooxidation of adrenaline [17]. During the autooxidation of adrenaline in alkaline medium at room temperature, an adrenaline oxidation product was formed, which absorbed at a wavelength of 347 nm. The formation of this product was inhibited by bacterial superoxide dismutase. It was found that the emergence of the adrenaline oxidation product significantly outpaced the formation of adrenochrome (480 nm). It was therefore proposed to use the determination of this substance to measure the antioxidant activity of various compounds.

To this end, 2 ml of bicarbonate buffer (pH 10.65) were poured into test tubes, 2 ml of a suspension of *M. smegmatis* ATCC 607 at a concentration of 1.5×10^8 CFU/ml prepared in physiological saline (pH 7.2) were added, followed by the introduction of the examined concentrations of FS-1 and 0.1 % solution of adrenaline hydrochloride. The experimental tubes were incubated for 15 min at room temperature and further centrifuged at 5,000 rpm for 5 min. A sample without adding the substance under study, i.e. containing 2 ml of bicarbonate buffer, 2 ml of physiological saline, and 0.2 ml of 0.1% adrenaline hydrochloride solution, served as a control.

The optical density of the supernatant was measured every 30 seconds for 10 min (20 cycles) in the spectral range from 200 to 500 nm using the Perkin – Elmer Lambda 35 double-beam spectrophotometer (USA). The operating principle for this device is based on measuring the ratio of two light fluxes that passed through the comparison channel (blank - 2 ml of bicarbonate buffer, 2 ml of saline solution) and the sample channel in the cuvette compartment, which allows the background values to be cut off.

The degree of impact of the substance under study on the antioxidant system in bacteria was calculated according to the following formula [17]:

Percentage of inhibition (activity units = $[1 - (OD_{control} / OD_{exp})] \times 100\ \%$ (1),

where $OD_{control}$ is the average value (n=20) of the optical density of the control sample ; OD_{exp} is the average value (n=20) of the optical density of the experimental sample.

The values above 30% were considered as a significant suppression of the activity of the bacterial antioxidant system under the effect of the substance under study.

The results of measuring the kinetics of the process for autooxidation of adrenaline in alkaline medium and in the presence of the examined concentrations of the drug FS-1 were presented as mean values from 2 independent experiments. In a statistical analysis of the control and experimental samples with GraphPad Prism version 6.00 for Windows (GraphPad Software, La Jolla California USA), the obtained data were checked for normal distribution using the Shapiro-Wilk test. When confirming the null hypothesis, the further data processing was carried out by the parametric method (One-way ANOVA). The results were considered significant at $p \leq 0.05$.

Results and Discussion

The effect of the drug FS-1 on the antioxidant system in *M. smegmatis* by *in vitro* autooxidation of adrenaline was studied. Spectral studies of the control sample in the range 200 to 500 nm revealed 3 absorption maxima at 242 nm, 292 nm, and 347 nm (Fig. 1). An aqueous solution of adrenaline gives a maximum absorption at 279 nm, while in alkaline medium (bicarbonate buffer, pH 10.65) there is a slight shift in the absorption maximum in the UV region to 292 nm [17]. As shown in Figure 1, by measuring the entire spectrum for 10 min, it was possible to detect the dynamics of spectral changes at 347 nm, which increased in direct proportion to the measurement time. An increment in the optical density of accumulation of the primary adrenaline oxidation product was 0.01-0.02 OU (optical density)/min; when measuring immediately, the optical density at 347 nm was equal to 0.18 A, after 10 minutes it was 0.35 A. Moreover, the optical density in the spectrum characteristic of adrenaline in alkaline medium (292 nm) decreased only by 0.01 A (from 1.41 A to 1.40 A) for 10 min.

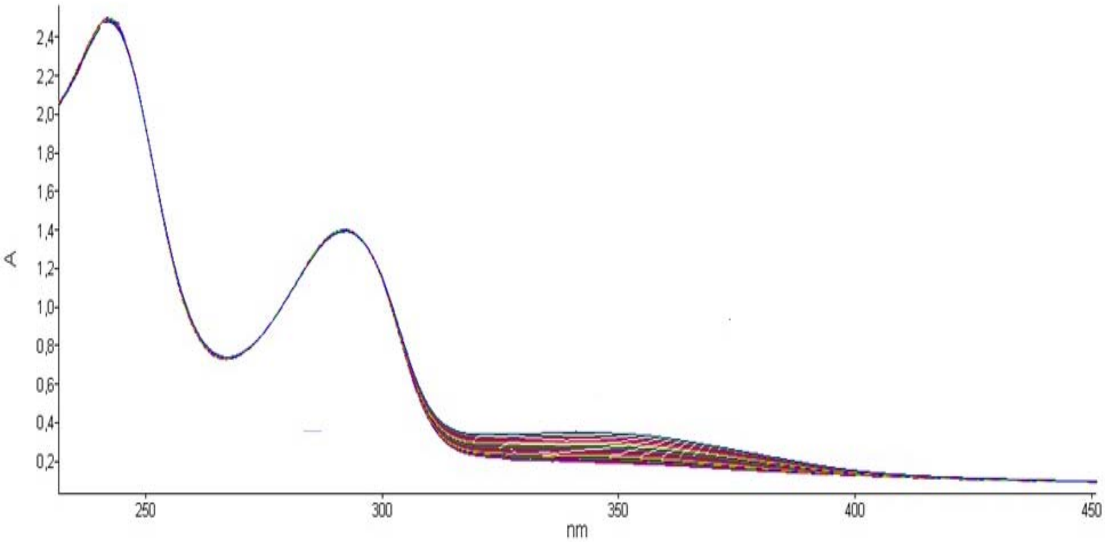

Figure 1 - UV

Spectral studies of the experimental samples in the range of 200 to 500 nm revealed that the introduction of the drug FS-1 in the examined concentrations resulted in a slight shift in the wavelength from 242 nm to 240 nm, 292 nm to 295 nm, and 347 nm to 333 nm (Fig. 2, 3).

Figure 2 shows the results of UV spectroscopy of the experimental sample containing 2 µg/ml of FS-1 where a time-dependent dynamics of spectral changes at 347 nm is clearly visible. An increment in the optical density of accumulation of the primary product of adrenaline autooxidation under the effect of the drug FS-1 at a concentration of 2 µg/ml was on average 0.05 OU/min. The optical density of the experimental sample containing 2 µg/ml of FS-1 with immediate measurement at 347 nm was equal to 0.54 A, after 10 minutes it was 1.05 A.

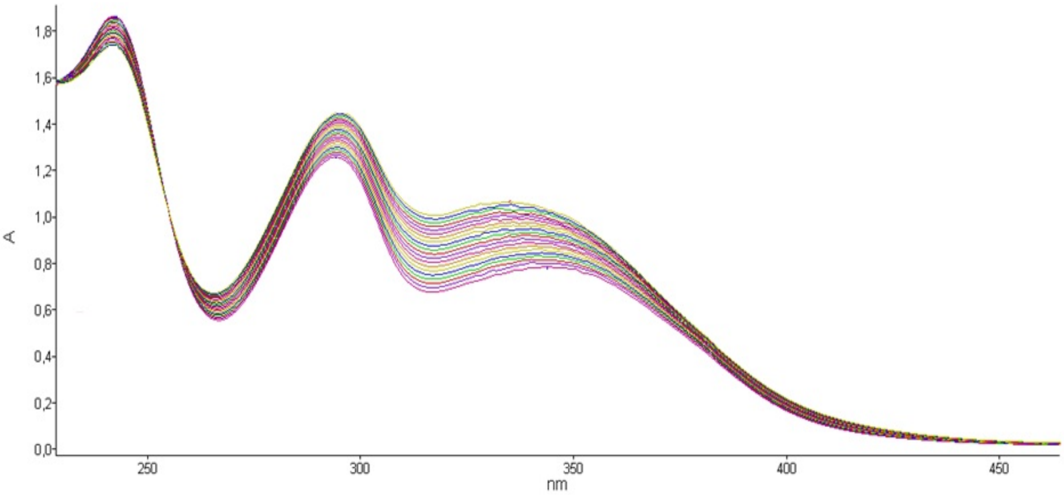

Figure 2 - UV absorption spectrum of the experimental sample containing 2 µg/ml of FS-1

Spectral measurements of the experimental sample containing 4 µg/ml of FS-1 at 347 nm for 10 minutes showed a time-dependent increasing dynamics of spectral changes (Fig. 3). An increment in the optical density of accumulation of the primary adrenaline oxidation product under the effect of the drug FS-1 at a concentration of 4 µg/ml was on average 0.035 OU/min; when measuring immediately, the optical density at 347 nm was equal to 0.83 A, after 10 minutes it was 1.18 A.

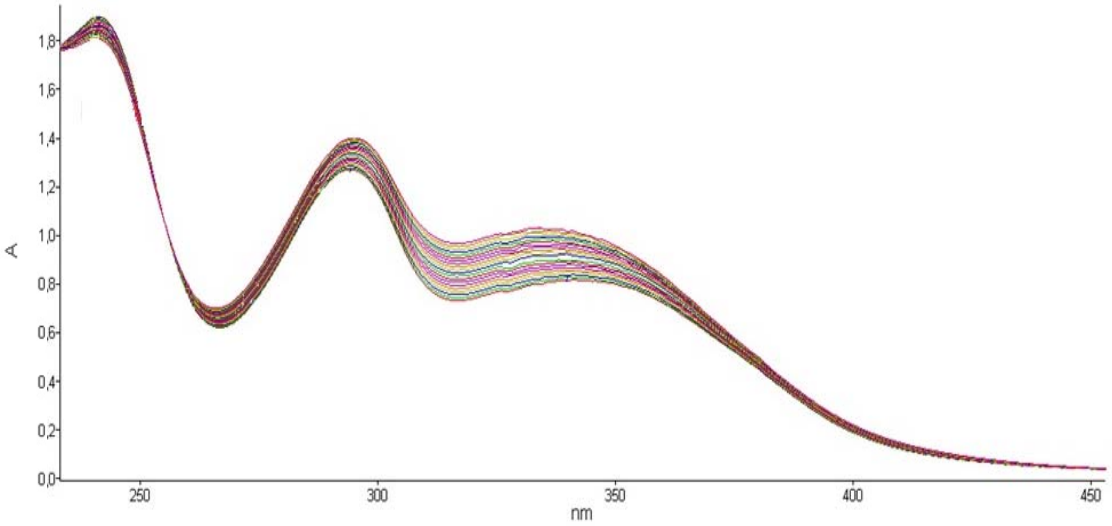

Figure 3 - UV absorption spectrum of the experimental sample containing
4 μg/ml of FS-1

Figure 4 presents summary data showing the dynamics of changes in the optical density of the control and experimental samples at a wavelength of 347 nm for 10 minutes.

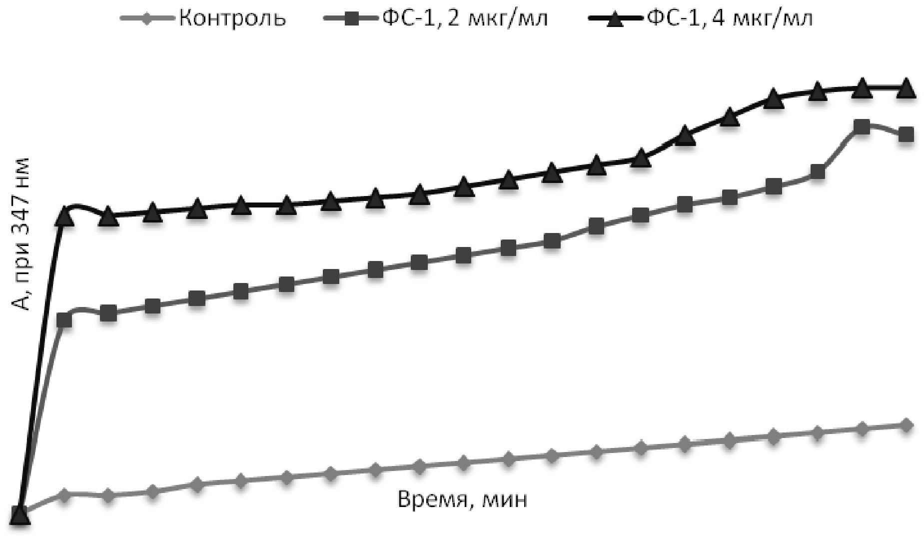

Figure 4 -Dynamics of changes in optical density of the control and
experimental samples at a wavelength of 347 nm

As can be seen in Figure 4, the introduction of the drug FS-1 into the experimental samples at concentrations of 2 and 4 μg/ml compared with the control sample enhanced 2.5 ($p < 0.0001$) and 1.8 ($p < 0.0001$) times, respectively, the accumulation of the adrenaline autooxidation product in the supernatant, which is toxic to *M. smegmatis*.

The degree of impact of the drug FS-1 at a concentration of 2 μg/ml on the antioxidant system in bacteria calculated by the formula (1) was 80%, which indicated a significant inhibition of the functional activity of the bacterial superoxide dismutase enzyme under the effect of the examined substance.

The concentration of the drug FS-1 of 4 μg/ml also inhibited the functional activity of superoxide dismutase in *M. smegmatis* ATCC 607; the degree of impact of the examined substance on the antioxidant system in the test culture was 85%.

Bacteriological control of the supernatant after exposure to FS-1 at doses of 2 and 4 µg/ml on the bacterial antioxidant system showed a lack of growth on the Levenshtein-Jensen egg-based culture medium.

The studies thereby found that the drug FS-1 under *in vitro* experimental conditions at doses of 2 and 4 µg/ml exhibited a pronounced inhibitory activity on the antioxidant enzyme system in atypical mycobacteria *M. smegmatis*. This led to a loss of resistance to oxidative stress in bacterial cells and their death.

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«Инфекцияға қарсы препараттар ғылыми орталығы» АҚ -ы

БАКТЕРИАЛДЫ АНТИОКСИДАНТТЫ ЖҮЙЕСІНІҢ БЕЛСЕНДІЛІГІНЕ ФС-1 ДӘРІЛІК ЗАТЫНЫҢ ӘСЕР ЕТУІН ЗЕРТТЕУ

Аннотация. Бұл жұмыста *M.smegmatis* бактериясының антиоксидантты жүйесіне құрамында иод бар ФС-1 кешенінің әсер ету нәтижелері ұсынылды. Эксперименттік *in vitro* жағдайда ФС-1 дәрілік заты 2 және 4 мкг/мл дозасында әсер еткен кезде *M.smegmatis* – атипті микобактериялар мысалында супероксиддисмутаза бактериялық ферментінің функционалдық белсенділігін, яғни тотығу күйзелісіне тұрақтылығын төмендететіні көрсетілді.

Түйін сөз: құрамында иод бар ФС-1 кешені, антиоксидантты жүйесі, тотығу күйзелісі.

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HYDROPROCESSING OF GASOLINE AND DIESEL FRACTIONS ON MODIFIED ALUMO-NICKEL-MOLYBDENUM CATALYSTS

Abstract. The paper presents the results of the study of hydroprocessing of gasoline and diesel oil fractions on alumina catalysts modified with variable valence metals, additives of phosphorus and lanthanum. The process of hydroprocessing gasoline and diesel fractions was studied in a high-pressure flow installation with a fixed catalyst bed at temperatures of 320-400°C, pressure 2.5-4.0 MPa and flow rate of the feedstock 1-3 h^{-1}.

The results obtained in tests of catalysts in the process of hydroprocessinggasoline and diesel oil fractions show that the greatest hydrodesulfurization activity is observed at a temperature of 380-400°C, a pressure of 4.0 MPa and a flow rate of 1 h^{-1}. Under optimal conditions, during the processing of straight-run gasoline fraction, the highest octane number is characteristic of the KGO-21 catalyst (NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3): 91.8 (RM) and 72.4 (MM). The KGO-23 catalyst (NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3) has a high hydroabsorbing activity. After hydroprocessing of straight-run gasoline and catalytic cracking gasoline, sulfur was not detected on this catalyst. When hydroprocessing the diesel fraction of oil, the lowest pour point and cloud point of diesel fuel are achieved on the KGO-21 catalyst: minus 58.9 ° C and minus 57.7 ° C, respectively. Diesel fuel produced on this catalyst contains the least amount of residual sulfur compared with other catalysts.

By the method of temperature-programmed desorption of ammonia, it was found that the concentration of acid sites on the KGO-21 catalyst is $31.3 \cdot 10^{-4}$mol NH_{3des} / g cat. On the surface of the KGO-23 catalyst, two forms of adsorbed ammonia were found with a T_{des} = 175 and 220 ° C (10.2 and 9.5 molNH_{3des} / g cat, respectively). The total amount of NH_{3des} = $19.7 \cdot 10^{-4}$molNH_{3des} / g cat. The KGO-21 catalyst has the highest concentration of acid sites, which determines its high hydroisomerizing activity in the hydroprocessingof gasoline fractions.

Keywords: straight-run gasoline, diesel oil fraction, zeolite, catalyst, hydropurification.

Introduction

In connection with the involvement in the processing of high-sulfur oil and the deepening of its processing, the requirements for hydroprocessing catalysts for petroleum fractions increased. Currently, there is a tendency to tighten the requirements for the composition of motor fuels, the insufficiently high quality of which is one of the causes of environmental pollution; therefore the focus of many refineries is on increasing the depth of hydrodesulfurization. In this regard, for the production of high-quality motor fuels at the present stage, catalytic processes of deep hydroprocessing of petroleum fractions are of great importance [1–9]. In the world production of motor fuels, there is a constant trend of tightening their environmental performance. According to international standards, a significant limitation of the content of sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is required. The effectiveness of hydroprocessing processes is mainly determined by the properties of the catalysts used. Existing hydroprocessing catalysts do not satisfy the increased quality requirements for motor fuels. For carrying out deep hydroprocessing of various fractions of oil, it is necessary to use new efficient catalysts and technologies.

Global priorities for the development of the oil sector are the creation and introduction of new catalytic technologies based on the use of catalysts that will improve the quality of oil refining. The creation of new catalysts for the directed refining of oil and its fractions will now and in the near future remain a relevant scientific and practical task. Industrial catalysts for hydroprocessing petroleum fractions in Kazakhstan and the CIS countries do not always meet the increased requirements for the quality of motor fuels. To improve the quality of motor fuels (gasoline, diesel fuel), cheaper production for the refineries of the Republic of Kazakhstan, the development of highly efficient multifunctional catalysts for the processing of oil fractions is an urgent and priority task.

The development of new efficient catalysts for the hydroprocessing of motor fuels is necessary for the creation of new technologies in this area. At the same time, much attention is paid to the development of a hydroprocessing catalyst for a certain type of crude oil. In this regard, the creation of new highly efficient catalysts for the hydroprocessing of gasoline and diesel oil fractions is very important [1-21].

This paper presents the results of the study of hydroprocessing of gasoline and diesel oil fractions on new alumonickel, tungsten, molybdenum catalysts modified with additives of ZSM-5, BEA, phosphorus and lanthanum zeolites.

Experimental part

New zeolite-containing alumina catalysts, modified by the introduction of metals with variable valence and phosphorus, were developed and prepared. The catalysts were prepared by impregnating a mixture of aluminum hydroxide with high silica zeolites HZSM-5, BEA, and water-soluble salts of nickel, molybdenum, lanthanum, and phosphoric acid. After impregnation, samples of the catalysts were molded and dried at 150°C for 5 hours, then calcined at 550 ° C for 5 hours.

The activity of the synthesized catalysts was studied in the hydroprocessingof gasoline and diesel oil fractions. The process was carried out in a flow-through installation with a stationary catalyst bed at temperatures of 320-400°C, bulk flow rate of feedstock 1-3 hours^{-1}, pressure 2.5-4.0 MPa.

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

The physicochemical characteristics of the catalysts were studied using BET, electron microscopy [22], and temperature-programmed desorption of ammonia [23].

Results and discussion

With enlarged laboratory tests of hydroprocessing of straight-run gasoline on the $NiO-MoO_3-La_2O_3-P_2O_5-Al_2O_3$-ZSM catalyst (KGO-21) at a temperature of 320°C, the content of isoalkanes increases from 36.8 to 44.3% compared to the initial (table 1). At a temperature of 400°C, the content of isoalkanes decreases and is equal to 30.7%. With an increase in temperature in the range of 320-400°C, the amount of aromatic hydrocarbons increases from 10.4 to 28.3%, the yield of naphthenic hydrocarbons increases from 20.3 to 30.3%. The amount of olefins in the catalyzate depends little on the process temperature and is 4.3–5.8%. The yield of the liquid phase with increasing temperature from 320 to 400°C decreases from 74.8 to 55.4%. The octane number of gasoline refined at 400°C is maximum and equal to 91.8 (RM) and 72.4 (MM). Under these conditions, the sulfur content in the resulting gasoline is reduced from 0.0092% to 0.0028%.

Table 1 - Effect of temperature on the process of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initialgasoline	T,^{o}C			
		320	350	380	400
Paraffins C_5-C_6	27,3	20,7	10,0	8,5	5,0
Iso-alkanes	36,8	44,3	32,4	32,6	30,7
Olefins	4,8	4,3	5,4	5,6	5,8
Aromatic hydrocarbons	9,2	10,4	18,7	24,8	28,3
Naphthenic hydrocarbons	21,9	20,3	33,4	28,5	30,3
The output of the liquid phase		74,8	65,7	59,0	55,4
The octane number by research method	78,9	84,3	89,8	90,0	91,8
The octane number bymotor method	60,9	70,4	69,2	71,8	72,4
Mass fraction of sulfur,%	0,0092	0,0036	0,0033	0,0030	0,0028
Note: V=2 h^{-1}, P=4,0MPa					

Studying the effect of pressure on the process of hydroprocessing straight-run gasoline on the KGO-21 catalyst showed that with an increase in pressure in the range of 2.5-4.0 MPa, the maximum amount of isoalkanes is observed at P = 2.5 MPa and is 34.9% (Table 2). With a further increase in pressure, their amount decreases to 30.7% at 4.0MPa, while the concentration of naphthenic hydrocarbons increases from 22.9% to 30.3%. The concentration of aromatic and olefinic hydrocarbons depends little on pressure and varies between 27.3-29.7% and 4.6-5.8%, respectively. The yield of the liquid phase is 50.4-55.4%. The octane number of gasoline refined at 4.0 MPa is 91.8 (RM) and 72.4 (MM). The sulfur content in catalyzate is reduced from 0.0092% (initial gasoline) to 0.0028% at 4.0 MPa.

Table 2 - Effect of pressure on the process
of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initial gasoline	P, MPa			
		2,5	3,0	3,5	4,0
Paraffins C_5-C_6	27,3	7,9	6,0	4,0	5,0
Iso-alkanes	36,8	34,9	34,3	30,6	30,7
Olefins	4,8	4,6	5,3	5,0	5,8
Aromatic hydrocarbons	9,2	29,7	27,3	28,4	28,3
Naphthenic hydrocarbons	21,9	22,9	27,1	32,0	30,3
The output of the liquid phase		52,0	50,4	53,2	55,4
The octane number by research method	78,9	89,6	88,3	88,9	91,8
The octane number by motor method	60,9	72,9	71,8	70,1	72,4
Mass fraction of sulfur,%	0,0092	0,0047	0,0035	0,0033	0,0028
Note: T=400°C, V=2 h^{-1}					

During the hydroprocessing of straight-run gasoline fraction on the KGO-21 catalyst, the increase in the volumetric feed rate of the feedstock from 1.0 to 2.5 h^{-1} does not change the content of isoalkanes in the catalyst and is equal to 30.1 - 30.7% (Table 3). The amount of aromatic and naphthenic hydrocarbons in the resulting product also varies little with the change in the volumetric feed rate. The yield of olefinic hydrocarbons ranges from 4.9 to 5.8%. The octane number of the gasoline produced is increased compared with the initial (78.9) to 90.9-91.8 (RM), the residual sulfur content is reduced compared with the raw material from 0.0092 to 0.0036.

Table 3 - Effect of volumetric feed rate on the process
of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initial gasoline	V, h^{-1}			
		1,0	1,5	2,0	3,0
Paraffins C_5-C_6	28,0	5,0	4,9	5,0	4,1
Iso-alkanes	35,5	30,6	30,2	30,7	30,1
Olefins	4,8	4,9	5,4	5,8	5,2
Aromatic hydrocarbons	8,1	31,6	30,6	28,3	29,7
Naphthenic hydrocarbons	23,6	27,8	28,9	30,3	30,8
The output of the liquid phase	-	50,1	48,0	55,4	43,0
The octane number by research method	78,9	89,0	90,9	91,8	90,7
The octane number by research method	60,6	71,3	70,7	72,4	72,1
Mass fraction of sulfur,%	0,0092	-	0,0019	0,0028	0,0036
Note: T=400°C, P=4,0MPa					

The study of hydroprocessing of straight-run gasoline fraction on the KGO-21 catalyst showed that the greatest hydrodesulfurizing activity was observed at a temperature of 380-400°C, a pressure of 4.0 MPa and a space velocity of 1 h^{-1}.

In the process of hydroprocessing the diesel fraction of oil on the KGO-21 catalyst, the pour point of the diesel fraction at 320°C decreased from minus 18.3 to minus 35.9°C. As the process temperature rises to 400°C, the pour point decreases to minus 58.9°C. The cloud point under these conditions falls from minus 11.3 to minus 57.7°C. The output of hydrofluorised diesel fuel is 90.0-100.0% (Table 4). The sulfur content is reduced to 0.0536%.

Table 4 - Effect of temperature on the process of hydro processing of the diesel fraction of oil on the catalyst KGO-21

Process temperature, °C	Sulfur content,%	Pour point, °C	Cloud point, °C	Yield, %
Initialdieselfraction	0,560	-18,3	-11.3	-
320	0,367	-35,9	-30,7	100
350	0,251	-51,3	-51,0	92,5
380	0,135	-54,9	-48,1	91,0
400	0,0536	-58,9	-57,7	90,0
Note: V=2 h^{-1}, P=4,0 MPa				

Studying the effect of the volumetric feed rate on the process of hydroprocessing the diesel fraction of oil on the KGO-21 catalyst showed that with a decrease in the volumetric rate from 3.0 to 1.0 h^{-1}, the amount of sulfur in the catalyzate decreases from 0.1942% to 0.0536%. The greatest decrease in the freezing and cloud point temperatures on this catalyst — down to minus 58.9°C and minus 57.7°C, respectively — is observed at an optimal flow rate of the feedstock of 2.0 h^{-1}. A decrease in catalyst activity with an increase in the feed rate of raw materials is due to a decrease in the contact time of reactants with active sites of the catalyst.

When hydroprocessing a straight-run gasoline fraction on the $NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3$ (KGO-23) catalyst at 320°C, the content of isoalkanes increases from 35.8 to 40.8%. With further increase in temperature to 400°C, their number reaches a maximum value of 44.6% (Table 5). The yield of the liquid phase in the range of 320 - 400°C decreases with increasing temperature from 95.0 to 86.4%, which is associated with an increase in hydrocracking. Under these conditions, the share of aromatic hydrocarbons in the obtained catalyzate increases from 9.5 to 11.4%, the content of naphthenic hydrocarbons decreases from 21.3% in the initial gasoline to 16.1% at 400°C. The concentration of olefinic hydrocarbons in the resulting catalyzate ranges from 5.8 to 7.3%. The octane number of gasoline hydroennobled in these conditions remains almost unchanged. The KGO-23 catalyst showed high hydrodesulfurization activity: after hydroprocessingof straight-run gasoline, sulfur was not detected on it.

Table 5 - Effect of temperature on the process of hydroprocessing straight-run gasoline on the catalyst KGO-23

Products,%	Initial gasoline	T,°C			
		320	350	380	400
Paraffins C_5-C_6	27,6	25,3	23,9	21,8	22,3
Iso-alkanes	35,8	40,8	36,1	39,0	44,6
Olefins	5,8	5,8	7,3	6,7	5,6
Aromatic hydrocarbons	9,5	9,5	8,8	12,1	11,4
Naphthenic hydrocarbons	21,3	18,6	23,9	20,4	16,1
The output of the liquid phase		95	93,6	88,6	86,4
Octane number by research method	80,2	80,0	82,9	78,2	80,8
Octane number by motor method	61,1	62,2	66,5	62,5	66,9
Mass fraction of sulfur, %	0,0050	-	-	-	-
Note: V=2 h^{-1}, P=4,0 MPa					

The process of hydroprocessing of catalytic cracking gasoline on the KGO-23 catalyst was studied (Table 6). Studies have shown that at 320-400°C, the amount of isoalkanes and aromatic hydrocarbons increases from 25.8 to 41.8-48.6% compared to the initial and from 29.2 to 33.6-36.9%, respectively. The content of naphthenic hydrocarbons varies between 7.0 and 9.0%. The octane number of the gasoline produced at 400°C is 86.7 (RM) and 80.0 (MM). It should be noted that in catalytic cracking gasoline hydrated on the KGO-23 catalyst, as in the case of straight-run gasoline, sulfur was not detected, indicating a high hydrodesulfurization activity of this catalyst.

Table 6 - Effect of temperature on the process of gasoline hydroprocessing of catalytic cracking on the catalyst KGO-23

Products,%	Initial gasoline	T,°C			
		320	350	380	400
Paraffins C_5-C_6	5,6	9,8	10,1	14,5	8,4
Iso-alkanes	25,8	48,0	47,8	48,6	41,8
Olefins	31,5	4,8	3,9	4,3	4,9
Aromatic hydrocarbons	29,2	29,3	29,1	33,6	36,9
Naphthenic hydrocarbons	7,9	8,0	9,0	7,0	8,0
The output of the liquid phase		95	87,5	85	84,5
Octane number byresearch method	88,3	85,3	85,2	86,1	86,7
Octane number bymotor method	80,1	78,3	78,6	80,0	80,0
Mass fraction of sulfur,%		-	-	-	-
Note: V=2 h^{-1}, P=4,0 MPa					

With the consolidated testing of the KGO-23 catalyst in the process of one-stage hydroprocessing of the diesel fraction of oil with sulfur content of 0.6400%, it was shown that with increasing process temperature from 320 to 400°C, the pour point and cloud point of the diesel fraction after the hydroprocessing on the catalyst change little. The output of hydroennobled diesel fuel is 94.5-98.0%. The sulfur content after hydroprocessing the diesel fraction at 380-400°C on the catalyst KGO-23 is reduced to 0.1100%.

When hydroprocessing straight-run gasoline fraction of oil on the catalyst NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-4) with increasing temperature from 320 to 400°C, the content of isoalkanes increases from 26.3% (initial), reaching a maximum value of 41.9% at 380 ° C, slightly decreasing at 400°C (Table 7). Under these conditions, the yield of aromatic hydrocarbons increases to 20.2% (380°C). The amount of olefins in the catalyzate is 4.4-5.0%. The octane number of refined gasoline obtained at 380°C is maximally 84.3 (RM) and 69.9 (MM).

Table 7 - Effect of temperature on the process of hydroprocessing of straight-run gasoline fraction on the catalyst KGO-4

Products,%	Initial gasoline	T, °C			
		320	350	380	400
ParaffinsC_5-C_6	33,4	23,9	10,9	16,6	19,2
Iso-alkanes	26,3	38,9	40,3	41,9	39,8
Olefins	3,7	4,7	5,2	4,4	5,0
Aromatic hydrocarbons	5,6	8,6	19,1	20,2	11,6
Naphthenic hydrocarbons	31,0	23,9	24,5	16,9	24,4
The output of the liquid phase		63,5	60,0	47,0	50
Octane number by research method	77,7	82,2	81,8	84,3	81,0
Octane number by motor method	53,8	67,1	66,8	69,9	65,9
Sulfur content, %	0,0370	0,0239	0, 0230	0, 0227	0,0220
Note: V=2 h^{-1}, P=4,0 MPa					

The yield of liquid catalyzate is equal to 47.0-63.5%. The sulfur content in the catalyzate after hydroprocessing decreased from 0.037 to 0.0220%.

The catalyst KGO-4 was also tested in the process of hydroprocessing the diesel oil fraction. The pour point of the diesel fraction after its hydroprocessing on the KGO-4 catalyst at 400°C has decreased to minus 38.8°C, whereas in the feedstock the pour point is equal to minus 18.3°C. The cloud point under these conditions varies from minus 11.3 to minus 28.2°C. The output of hydroennobleddiesel fuel is 96.1-100%. At the same time, the sulfur content decreases from 0.560% in the initial fraction to 0.1025% (Table 8).

Table 8 - Effect of temperature on the process of hydroprocessing of the diesel fraction of oil on the catalyst KGO-4

Experience temperature, °C	Sulfur content,%	Pour point, °C	Cloud point, °C	Yield, %
The original diesel fraction	0,560	-18,3	-11,3	-
320	0,3295	-30,2	-21,9	100
350	0,2198	-35,1	-25,0	99,6
380	0,1826	-38,1	-27,2	98,5
400	0,1025	-38,8	-28,2	96,1
Note: V=2 h^{-1}, P=4,0 MPa				

Acid-basic characteristics of catalysts are essential for the processing of hydrocarbons. The acidic characteristics of the catalysts were studied by the method of temperature – programmed desorption of ammonia (Table 9).

Table 9 - Acid-basic characteristics of KGO catalysts

Catalyst	Maximum peak temperature, °C		Amount of desorption ammonia bath, 10^{-4}mol/gcat		ΣNH_{3des} 10^{-4} mol/gcat
	1	2	1	2	
KGO-4	—	195	—	21,0	21,0
KGO-21	—	215	—	31,3	31,3
KGO-23	175	220	10,2	9,5	19,7

From the data presented in Table 9, it can be seen that on the surface of the catalysts NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-4), NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-21), NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3 (KGO-23), there are strong acid sites with T_{des} equal to 195, 215, 220°C, respectively. The amount of ammonia desorbed from the surface of NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3(KGO-4) is 21.0 • 10^{-4}mol NH_{3des}/g cat. The concentration of acid sites on the NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 catalyst is higher - 31.3 • 10^{-4}mol NH_{3des}/g cat. On the surface of the catalyst NiO-MoO_3-La_2O_3-P_2O_5-BEA-ZSM-Al_2O_3(KGO-23), two forms of adsorbed ammonia were found with a Td of 175 and 220°C. Their number is close to 10.2 and 9.5 mol NH_{3des}/g cat, respectively. The total amount of NH_{3des} = 19.7 10^{-4}mol NH_{3des}/g cat.

The analysis of the obtained results shows that under optimal conditions during the processing of straight-run gasoline fraction, the highest octane number is characteristic for the catalyst KGO-21: 91.8 (RM) and 72.4 (MM), respectively. It should be noted that the KGO-21 catalyst has the highest concentration of acid sites (31.3 • 10^{-4}mol NH_{3des}/g cat, T_{des} = 215°C), which determines its high hydroisomerizing activity in the process of hydroprocessing gasoline fractions. The catalyst KGO-23 has a high hydrodesulfurizing activity. After hydroprocessing of straight-run gasoline and catalytic cracking gasoline, sulfur was not detected on this catalyst.

When hydroprocessing the diesel fraction of oil, the lowest pour point and cloud point of diesel fuel are achieved on the KGO-21 catalyst: minus 58.9°C and minus 57.7°C, respectively. Diesel fuel produced on this catalyst contains the least amount of residual sulfur compared with other catalysts.

The new modified zeolite-containing KGO catalysts developed for the gasoline and diesel fractions hydroprocessing processes are hydrotreated, hydroisomerized and hydrocracked in one stage and allow to obtain low-sulfur, high-octane gasoline and low-coagulation diesel fuel. When hydroprocessing on KGO catalysts with dehydrating and hydrogenating abilities, n-alkanes on the metal centers of the catalyst start to dehydrate, the olefin formed on the acid center turns into carbonium ion, which is easily isomerized [24].

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МОДИФИЦИРЛЕНГЕН АЛЮМОНИКЕЛЬМОЛИБДЕН КАТАЛИЗАТОРЛАРДА БЕНЗИН ЖӘНЕ ДИЗЕЛЬ ФРАКЦИЯЛАРЫН ГИДРОӨҢДЕУ

Аннотация. Жұмыста ауыспалы валентті металдармен модифицирленген және фосфор мен лантан қосылған алюмооксидті катализаторларда мұнайдың бензин және дизель фракцияларының гидроөңдеу нәтижелері келтірілген. Бензин және дизель фракцияларын жоғары қысымды ағынды қондырғыда катализатордың стационарлы қабатында температура 320-400°С, қысымы 2,5-4,0 МПа және шикізаттың көлемдік берілу жылдамдығы 1-3 сағ$^{-1}$ болғанда гидроөңдеу процесі жүргізілді.

Мұнайдың бензин және дизельді фракцияларын гидроөңдеу процесінде катализаторларды сынау нәтижесі бойынша ең жоғары гидрокүкіртсіздену 380-400^0 С температурада, қысымы 4,0 МРа және көлемдік берілу жылдамдығы 1 сағ$^{-1}$ болғанда байқалды. Тура айдалған бензин фракциясын тиімді жағдайда өңдегенде октан саны ең жоғары көрсеткіші КГО-21 катализаторына (NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3): 91,8 (ЗӘ) және 72,4 (МӘ) тән. КГО-23 катализаторы (NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3) ең жоғары гидрокүкіртсіздендіру активтілігін көрсетті. Осы катализатормен тура айдалған бензин және каталитикалық крекинг бензинін гидроөңдегеннен кейін күкірт мүлде байқалмады. Мұнайдың дизельдік фракциясын гидроөңдегенде КГО-21 катализаторы ең төмен қату және лайлану температурасына ие болды: сәйкесінше -58,9^{0}С және -57,7^{0}С. Осы катализатордан алынған дизельдік отын құрамындағы қалған күкірт мөлшері басқа катализаторлармен салыстырғанда ең аз мөлшерді құрады.

Аммиактың температуралық-бағдарламалы десорбция әдісі арқылы КГО-21 катализаторында қышқылдық орталықтарының концентрациясы $31{,}3\cdot10^{-4}$ моль $NH_{3дес}$ /г.катализатор құрады. КГО-23 катализаторының бетінде адсорбцияланған аммиактың екі түрі $T_{дес}$ 175 және 220°С тең (10,2 және 9,5 моль $NH_{3дес}$ /г.катализатор сәйкесінше). Десорбцияланған аммиактың жиынтық мөлшері $19{,}7\cdot10^{-4}$ моль$NH_{3дес}$ /г.катализатор тең. Қышқылдық орталықтың ең жоғарғы концентрациясы КГО-21 катализаторында байқалып және бензин фракцияларын гидроөңдеу процестерінде жоғары гидроизомерлеу активтілігін анықтайды.

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

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ГИДРОПЕРЕРАБОТКА БЕНЗИНОВЫХ И ДИЗЕЛЬНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМОНИКЕЛЬМОЛИБДЕНОВЫХ КАТАЛИЗАТОРАХ

Аннотация. В работе приведены результаты исследования гидропереработки бензиновых и дизельных фракций нефти на алюмооксидных катализаторах, модифицированных металлами с переменной валентностью, добавками фосфора и лантана. Процесс гидропереработки бензиновых и дизельных фракций изучали в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400°С, давлении 2,5-4,0 МПа и объемной скорости подачи сырья 1-3 ч$^{-1}$.

Результаты, полученные при испытаниях катализаторов в процессе гидропереработки бензиновых и дизельных фракций нефти, показывают, что наибольшая гидрообессеривающая активность наблюдается при температуре 380-400°С, давлении 4,0 МРа и объемной скорости подачи 1ч$^{-1}$. В оптимальных условиях при переработке прямогонной бензиновой фракции наиболее высокое октановое число характерно для катализатора КГО-21 (NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3): 91,8 (ИМ) и 72,4 (ММ). Катализатор КГО-23 (NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3) обладает высокой гидрообессеривающей активностью. После гидропереработки прямогонного бензина и бензина каталитического крекинга на этом катализаторе сера не обнаружена. При гидропереработке дизельной фракции нефти наиболее низкие температуры застывания и помутнения дизельного топлива достигнуты на катализаторе КГО-21: минус 58,9°С и минус 57,7°С соответственно. Дизельное топливо, получаемое на этом катализаторе, содержит наименьшее количество остаточной серы по сравнению с другими катализаторами.

Методом температурно-программированной десорбции аммиака установлено, что концентрация кислотных центров на катализаторе КГО-21 составляет $31{,}3\cdot10^{-4}$ моль $NH_{3дес}$ /г кат-ра. На поверхности катализатора КГО-23 обнаружены две формы адсорбированного аммиака с $T_{дес}$, равной 175 и 220°С (10,2 и 9,5 моль $NH_{3дес}$ /г кат-ра соответственно). Суммарное количество $NH_{3дес}$ = $19{,}7\cdot10^{-4}$ моль $NH_{3дес}$ /г кат-ра.

Наибольшей концентрацией кислотных центров обладает катализатор КГО-21, что и определяет его высокую гидроизомеризующую активность в процессах гидропереработки бензиновых фракций.

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

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COMPARATIVE ANALYSIS OF BIOLOGICALLY ACTIVE COMPLEXES OBTAINED BY THE SCF COF METHOD - PLANT EXTRACTION OF PLANTS OF DAUCUS CAROTA, SOLANUM LYCOPERSICUM, CRATAEGUS TURKESTANICA A. POJARK SPECIES

Abstract. The article presents the results of a study of the qualitative and quantitative extracts obtained by the method of supercritical fluid extraction by carbon dioxide from the fruits of the plant *Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark.*

Extraction on a Thar SFE-1000 CO_2-extraction unit under the following conditions: temperature range in the reactor is 40-80 ° C, CO_2 pressure is 180-200 bar, with a gas flow of 100 ml / min, ethyl alcohol was used as a co-solvent.

The obtained extract was investigated by gas chromatography on a gas chromatograph with an Agilent Technologies 7890N / 5973N GC / MS mass-selective detector.

The studied extracts identified in *Daucus carota*: carotenoids, limonene (0.2%), o-cymol (0.29%), cariofillen (0.3%), phytol acetate (4.25%), eicosane (1.2 %), falkarinol (4.5%), squalene (0.8%), vitamin E (0.6%), campesterol (0.8%), stigmasterol (2.34%), gamma sitosterol (2.49 %).

Crataegus turkestanica A. Pojark: Limonene (0.42%), o-cymol (0.28), phytol acetate (1.45%), eicosane (3.65%), falkarinol (0.255%), squalene (2, 0%), vitamin E (0.57%), campesterol (0.78%), alpha-tocopherol (1.83%), gamma-sitosterol (4.83%).

Solanum lycopersicum: Carotenoids, fatty acid esters (oleic, linolenic, hexadecanoic, octadecadienoic), eicosane (2.65%), lupeol (2.33%), phytol acetate (1.61%), alpha-amyrin (7.46 %), vitamin E (1.08%), tetracosane (3.81%)

For a more complete study of the chemical composition of supercritical extracts of the extract, gas chromatography with a mass selective (GC-MS) detector was used.

Work on the study of extracts obtained under other conditions of extraction is currently ongoing.

Key words: Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark, SFE, HPLC-MS.

Introduction

One of the most important humanitarian tasks that directly affect the quality of life is a high level of provision of high-quality drugs. In part, this task can be solved by producing a number of drugs from widely used and affordable starting materials by processing them using modern methods. In particular, in the Republic of Kazakhstan, natural, renewable plant resources are the richest source of biologically active substances. Therefore, at present, interest has increased in the search for new drugs based on plant raw materials of the Republic of Kazakhstan, since they, in most cases, are much less toxic, cause allergic reactions much less frequently. Therefore, the search for new technologies for the isolation of safe bioactive complexes is considered an important task at the present time [1].

Supercritical fluid extraction is a technological process consisting in converting one or more components of a solid or liquid mixture into a “supercritical gas-fluid”. Produced by contacting a mixture of components to be separated with a gaseous extractant at a temperature and pressure above the critical point. The most widely used as extractants (solvents) are CO_2, ethane, ethylene, propane, SF_6, etc [2-3].

Features of supercritical carbon dioxide. Supercritical gas has the characteristic of more rapid mass movement compared with traditional liquid organic solvents. Despite a slightly lower density compared to a liquid, the dynamic viscosity of the compressed gases most likely corresponds to the values of the normal gaseous state. The diffusion coefficient of supercritical gas is more than ten times higher than that of a liquid [4].

A gas in a supercritical state, better than a classical solvent penetrates into the extracted material, is able to more effectively absorb and transport soluble components of the substance [5-8].

The use of carbon dioxide allows completely and sparingly separating it from the extract and carrier material as opposed to classical solvents, the elimination of which is not always complete. In other words, the extracts obtained using this technique are completely free of solvent [9-10].

Supercritical fluid extraction is controlled, which allows you to adjust the extraction of a component from plant materials. It is precisely this that allows to obtain not only natural food ingredients, such as natural antioxidants, preservatives, dyes, flavoring substances, but also pharmaceutical ingredients. [11].

The objects of research were Kazakhstani plant species *Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark.*

Material and methods

The supercritical extraction method was carried out on a Thar SFE-1000 CO2-extraction unit under the following conditions: the temperature range in the reactor was 40–80 ° C, the CO_2 pressure was 180–200 bar, with a gas flow of 100 ml / min, as a co-solvent ethanol

The obtained extract was investigated by gas chromatography on an Agilent Technologies 7890N / 5973N GC / MS gas chromatograph with a mass selective detector under the following conditions: a DB-35MS column (30 mx 250 mm x 0.25 mm) was used, the helium carrier gas velocity was 1 ml / min The temperature of chromatography is programmed from 40 ° C (holding 0 min) to 300 ° C with a heating rate of 5 ° C / min (holding 5 min). Detection is carried out in SCAN m / z mode 34-800. The Agilent MSD Chem Station software (version 1701EA) was used to control the gas chromatography system, record and process the obtained results. Data processing includes the determination of retention time, peak areas, as well as the 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 is more than 550 thousand). It was also carried out quantitative determination by UV spectrometry [12-13].

Results and discussion

The purity of the objects under study are determined in the framework of the State Pharmacopoeia of the Republic of Kazakhstan 1 edition. [14].

The results of the study of supercritical extracts obtained from objects of *Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark* species are presented in Tables 1-3 and in Figures 1-3.

The quantitative content of the main BAS groups was determined by the HPLC-MS method. The table contains the substances that have the greatest amount.

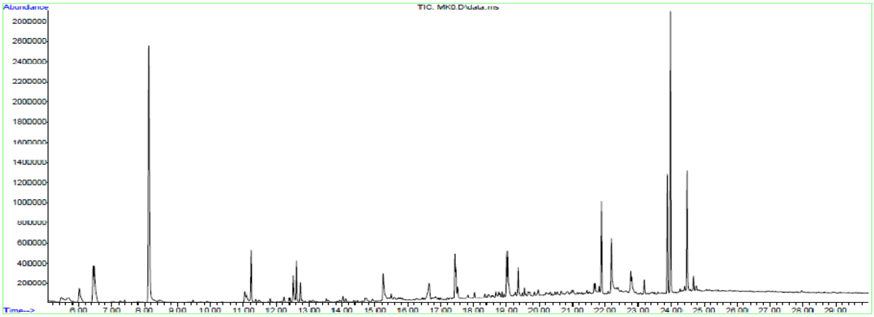

Figure 1- Chromatogram of supercritical extract obtained from the plant *Daucus carota*

From the results of the chromatographic analysis, it can be seen that many substances were identified in the supercritical extract obtained from the fruits of the *Daucus carota* plant;

Table 1 - Characteristics of the supercritical extract obtained from the plant *Daucus carota*

Raw material	*Daucus carota*
Production	Supercritical fluid extraction with carbon dioxide, in the absence of inorganic salts, without solvent residues, reproducible microorganisms.
Type of extract	Liquid from light yellow to yellow salad color.
Composition	PUFA, carotenoids, limonene (0.2%), o-cymol (0.29%), caryophyllen (0.3%), phytol acetate (4.25%), eicosane (1.2%), falkarinol (4 , 5%), squalene (0.8%), vitamin E (0.6%), campesterol (0.8%), stigmasterol (2.34%), gamma sitosterol (2.49%).
Using	It is recommended to use in the care of fading, flaky and problem skin.
Naturalness	The product is 100% natural, does not contain impurities and is not manufactured according to the chemical formula.
Storage	In a sealed package in a cool dark place at least 2 years.

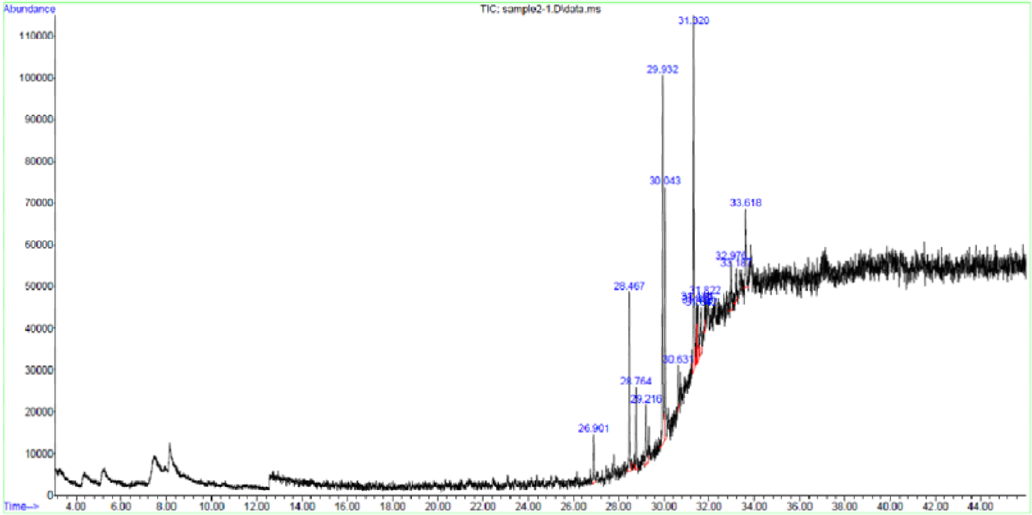

Figure 2- Chromatogram of supercritical extract obtained from plant *Crataegus turkestanica A. Pojark*

From the results of the study of the supercritical extract obtained from the fruit of the plant *Crataegus turkestanica A. Pojark* by HPLC, it was found that the largest number of compounds are identified at 23-34 minutes of the process. A more detailed analysis of the extract is presented in table 2.

Compared with previous samples, the largest number of signals is noted, the total analysis is presented in table 3.

Table 2 - Characteristics of the supercritical extract obtained from the plant *Crataegus turkestanica A. Pojark*

Raw material:	*Crataegus turkestanica A. Pojark*
Production:	Supercritical fluid extraction with natural carbon dioxide, in the absence of inorganic salts, without solvent residues, reproducible microorganisms.
Type of extract:	Liquid from light yellow to yellow.
Composition:	Limonene (0.42%), o-cymol (0.28), phytol acetate (1.45%), eicosane (3.65%), falkarinol (0.255%), squalene (2.0%), vitamin E (0.57%), campesterol (0.78%), alpha-tocopherol (1.83%), gamma-sitosterol (4.83%).
Using:	It is recommended to use in the care of fading, flaky and problem skin.
Naturalness:	The product is 100% natural, does not contain impurities and is not manufactured according to the chemical formula.
Storage:	In a sealed package in a cool dark place at least 2 years.

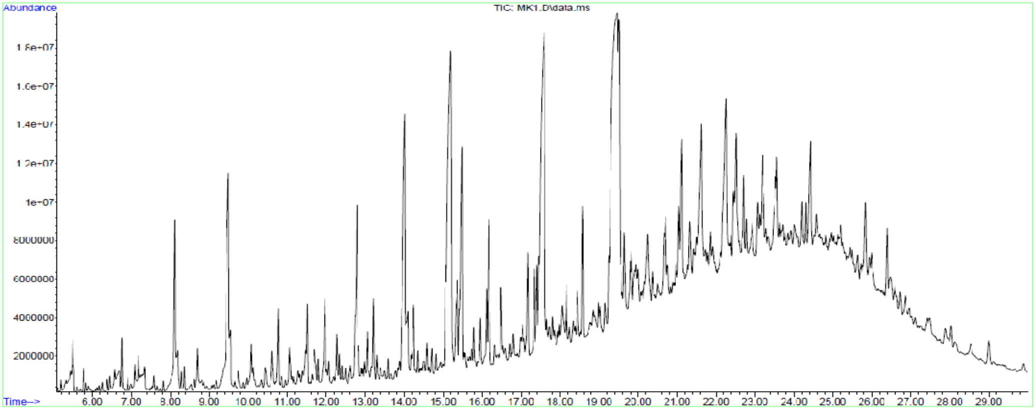

Figure 3 - Chromatogram of supercritical extract obtained from plant *Solanum lycopersicum*

Table 3 - Characteristics of the supercritical extract obtained from the plant *Solanum lycopersicum*

Raw material:	*Solanum lycopersicum*
Production:	Supercritical fluid extraction with natural carbon dioxide, in the absence of inorganic salts, without solvent residues, reproducible microorganisms.
Type of extract:	Oily mass from orange-yellow to orange-red color with a faint characteristic odor.
Composition:	Carotenoids, fatty acid esters (oleic, linolenic, hexadecanoic, octadecadienoic), eicosane (2.65%), lupeol (2.33%), phytol acetate (1.61%), alpha-amyrin (7.46%), vitamin E (1.08%), tetracosane (3.81%).
Using:	Components can have anti-inflammatory, antioxidant, wound healing agent, improves skin elasticity and elasticity ..
Naturalness:	The product is 100% natural, does not contain impurities and is not manufactured according to the chemical formula.
Storage:	In a sealed package in a cool dark place at least 2 years.

From the results presented in Table 3, there is a significant presence of esters of fatty acids, hydrocarbons, as well as plant steroids and biologically active micronutrients.

The results allow us to draw the following conclusions.

Conclusion

Firstly, essential oils are found in the extracts of Daucus carota, as well as in a sufficient amount of falkarinol - 4.5%. According to British scientists, falkarinol is a natural pesticide that kills cancerous tumors. Cariofillen, a bicyclic sesquiterpene, which affects the taste and smell of the product, is found in carrots.

Secondly, in the extracts of Crataegus turkestanica A. Pojark, solanum lycopersicum found: essential oils, carotenoids, squalene, vitamins and sterols. Squalene is the strongest anti-tumor agent. Stervalene triterpene has emollient, bactericidal, wound healing, antioxidant properties.

Sterols have anti-inflammatory, anti-allergic, anti-edematous, analgesic properties. Plant sterols, or phytosterols, are alcohols containing 28-30 carbon atoms. These include β-sitosterol, stigmasterol, campesterol, spinsterol, and others.

Vitamin E (tocopherols) has anti-inflammatory action, antioxidant activity, is involved in the biosynthesis of heme and proteins, cell proliferation, tissue respiration, and other important processes of tissue metabolism.

For the first time, supercritical fluid extraction was used to study Kazakhstani species of three edible products, the obtained extracts were studied by HPLC.

Analysis of supercritical fluid extracts of three edible products by HPLC indicates the presence of interesting compounds.

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DAUCUS CAROTA, SOLANUM LYCOPERSICUM, CRATAEGUS TURKESTANICA A. POJARK ӨСІМДІК ТҮРЛЕРІНЕН ЖКФ CO_2-ЭКСТРАКЦИЯ ӘДІСІМЕН АЛЫНҒАН БИОЛОГИЯЛЫҚ БЕЛСЕНДІ КЕШЕНДІ САЛЫСТЫРМАЛЫ САРАПТАУ

Аннотация. Мақалада жоғарғыкритикалық флюидті әдіс көмегімен көмірқышқыл газы қатысында *Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark* өсімдік жемістері экстракциясының сапалық және сандық құрамын зерттеу нәтижелері келтірілген.

Экстракциялау Thar SFE-1000 қондырғысында келесі жағдайда жүргізілді: реактордағы температура аралығы - 40-80ºC, қысым CO_2 – 180-200 бар, газдың ағыны 100 мл/мин, со-ертінді есебінде пайдаланылған ертінді этил спирті.

Алынған экстракт масс-селективті детектор Agilent Technologies 7890N/5973N GC/MS газды хроматографта газ хроматографиясы әдісімен зерттелді

Daucus carota - дан алынған экстрактіде ең көп мөлшерде келесі заттар анықталды:*:* каротиноидтар, лимонен (0,2%), *о*-цимол (0,29%), кариофиллен (0,3%), фитол ацетаты (4,25%), эйкозан (1,2%), фалькаринол (4,5%), сквален (0,8%), Е дәрумені (0,6%), кампестерин (0,8%), стигмастерин (2,34%), гамма ситостерол (2,49%).

Crataegus turkestanica A. Pojark экстрактісінде ең көп мөлшерде келесі заттар табылған: лимонен (0,42%), о-цимол (0,28), фитол ацетаты (1,45%), эйкозан (3,65%), фалькаринол (0,255%), сквален (2,0%), витамин Е (0,57%), кампестерин (0,78%), альфа-токоферол (1,83%), гамма ситостерол (4,83%).

Ал *Solanum lycopersicum* экстрактісінде анықталған мына заттар*:* каротиноидтар, май қышқылдарының эфирлері (олеин, линолен, гексадекан, октадекадиен), эйкозан (2,65%), лупеол (2,33%), фитол ацетаты (1,61%), альфа-амирин (7,46%), Е дәрумені (1,08%), тетракозана (3,81%)

Басқа жағдайларда алынған экстрактілер құрамын зерттеу жұмыстары жалғасуда.

Түйін сөздер: *Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark, СКФ-экстракция, хромато-масс спектрометр.*

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СРАВНИТЕЛЬНЫЙ АНАЛИЗ БИОЛОГИЧЕСКИ АКТИВНЫХ КОМПЛЕКСОВ, ПОЛУЧЕННЫХ МЕТОДОМ СКФ CO_2 -ЭКСТРАКЦИЕЙ РАСТЕНИЙ ВИДОВ *DAUCUS CAROTA, SOLANUM LYCOPERSICUM, CRATAEGUS TURKESTANICA A. POJARK.*

Аннотация. В статье представлены результаты исследования качественного и количественного экстрактов, полученных методом сверхкритической флюидной экстракции углекислым газом из плодов растении *daucus carota, solanum lycopersicum, crataegus turkestanica A. Pojark.*

Экстракция проведена на установке Thar SFE-1000 при следующих условиях: температурный диапазон в реакторе-40-80ºC, давление CO_2 – 180-200 бар, при потоке газа 100 мл/мин, в качестве со-растворителя был использован этиловый спирт.

Полученный экстракт исследован методом газовой хроматографии, на газовом хроматографе с масс-селективным детектором Agilent Technologies 7890N/5973N GC/MS.

В изучаемых экстрактах идентифицированы в *Daucus carota:* каротиноиды, лимонен (0,2%), о-цимол (0,29%), кариофиллен (0,3%), ацетат фитола (4,25%), эйкозан (1,2%), фалькаринол (4,5%), сквален (0,8%), витамин Е (0,6%), кампестерин (0,8%), стигмастерин (2,34%), гамма ситостерол (2,49%).

Crataegus turkestanica A. Pojark: Лимонен (0,42%), о-цимол (0,28), ацетат фитола (1,45%), эйкозан (3,65%), фалькаринол (0,255%), сквален (2,0%), витамин Е (0,57%), кампестерин (0,78%), альфа-токоферол (1,83%), гамма ситостерол (4,83%).

Solanum lycopersicum: Каротиноиды, эфиры жирных кислот (олеиновая, линоленовая, гексадекановая, октадекадиеновая), эйкозан (2,65%), лупеол (2,33%), ацетат фитола (1,61%), альфа-амирин (7,46%), витамин Е (1,08%), тетракозана (3,81%)

Работы по исследованию экстрактов, полученных при других условиях извлечения, в данный момент продолжаются.

Ключевые слова: Daucus carota, Solanum lycopersicum, Crataegus turkestanica A. Pojark, СКФ-экстракция, хромато-масс спектрометрия.

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PHYSICAL-AND-CHEMICAL FEATURES AND MECHANISM OF COPPER OXIDE (I) FORMATION IN ALKALINE CHLORIDE SOLUTIONS

Abstract. The most promising ways to obtain highly dispersed copper oxides are electrochemical methods. This method of transferring copper into a solution allows finding accurately the formation modes of the required valence ion and obtaining high chemical purity compounds. The methods of producing copper oxide (I) are based on the anodic oxidation of metallic copper in an alkaline chloride-containing solution. The main advantage of the electrochemical method is the possibility of obtaining high quality powder with a smaller particle size not containing metallic copper and bivalent copper oxide. The results of studying anodic corrosion of copper in weakly alkaline and acidic chloride solutions show that, depending on the content of chloride ions in the solution and the specified potential value, there can be formed complex copper chloride compounds that in the process of hydrolysis form copper oxide (I) powder. The region of thermodynamically stable existing of monovalent copper chloride complexes at low potential values and pH increases.

In this work there has been for the first time made the calculation and a diagram has been constructed that allows determining only the most probable pH, pCl^- and the electrode region, in which copper oxide (I) can be obtained.

Key words: copper oxide (I), complex copper chloride, equilibrium potentials, thermodynamics, diagram of equilibrium systems.

Summary. To predict the reactions occurring under specific conditions for producing copper oxide (I), and to establish the regions of preferential existence of a particular phase, we constructed the E –pH diagram for the $Cu - Cu^- - H_2O$ system. The concentration of chloride ions is assumed to be 4.25 $mol.dm^{-3}$, the activity coefficient is 0.78, the pH varies from 0 to 14, the temperature is 298 K. The work presents a diagram of the stable existence of the Cu_2O and CuCl compounds depending on the solution pH and pCl^-. It shows the equilibrium conditions in the $Cu - Cu^- - H_2O$ system at pH equal to 13 depending on pCl^-. The potential range at which Cu_2O is stable is very limited and its width is within 0.2 V under the conditions studied for the synthesis of copper oxide (I).

The diagrams calculated by us allow determining only the most probable region of pH, pCl^- and the electrode potential, in which copper oxide (I) can be obtained.

Introduction. Powdered copper oxide (I) is used to prepare solder paste, copper-containing additives in friction and anti-friction couples and a number of other industries. The most large-scale consumer of copper oxide (I) has recently become the chemical industry, using this reagent to prepare biocidal paints that protect the underwater part of ships and structures from fouling by microorganisms [1].

However, copper oxide (I) currently being produced does not fully meet the requirements of mechanical engineering, electronic and chemical industries in terms of the particle size, chemical composition and scale of production. Thus, in manufacturing raw materials for semiconductors of the electronics industry [2], materials with high anti-wear tribological properties [3-5], antifouling paints, there is required dispersed nano-sized copper oxide (I) with a high content of the main component. Copper oxide (I) of nanoscale is almost impossible to be obtained by traditional pyrometallurgical, autoclave and chemical methods.

Experiment methodology. One of present day methods of obtaining high dispersion oxides of metals is an electrochemical method. The advantage of this method of preparation is formation of nanoscale powder particles in the electrode layer. The lack of knowledge of the electrochemical processes occurring on the electrodes, the mechanism of powder formation, the reasons for the poor performance of the electrolysis process formed by limited anode current densities impede the industrial development of the electrochemical method of producing copper oxide (I) by direct current electrolysis. Experimental data on the destruction of metals in alkaline solutions are given in works [6–9]. In electrolysis using various forms of current other than direct current, it becomes possible to carry out a number of electrochemical processes with the best performance. In works [10-17] it was shown that during the electrolysis of copper under the conditions of non-stationary electrolysis in aqueous electrolytes, its intensive destruction with the formation of copper oxides was observed.

Discussing results. The results of studying anodic corrosion of copper in weakly alkaline and acidic chloride solutions show that depending on the content of chloride ions in the solution and the value of the specified potential, chloride complexes of copper (I) $CuCl_m^{-(m-1)}$ or $CuCl_{\text{тв}}$ ions can be formed. Increase the flow velocity contributes to increasing the limiting anodic current density values. Copper oxide (I) is formed as a result of the hydrolysis reaction of copper (I) chloride complexes.

The electrochemical method of converting metals into a solution allows finding accurately the ion formation modes of the required valence and obtaining a compound of high chemical purity for the main component.

The reactions have the following values of standard potentials (E°):

$$Cu - 2e \leftrightarrow Cu^{+2}\ E^{\circ} = 0.3377 \pm 0.0007B \quad (1)$$

$$Cu - e \leftrightarrow Cu^{+}\ E^{\circ} = 0.5072 \pm 0.0015B \quad (2)$$

Judging by the values of standard potentials in aqueous solutions that do not contain complexing ligands, with anodic polarization there is more likely running reaction (1) [3].

In the presence of chloride ions, the picture changes: so for the reaction

$$Cu + Cl^{-} \leftrightarrow CuCl_{\text{тв}} + e, \quad (3)$$

the E° value is equal to 0.137 B, that is much more negative than the potential of reaction (1) [4].

Besides, in chloride solutions there can be copper oxidation to complex ions in the reaction:

$$Cu + mCl^{-} \leftrightarrow CuCl_m^{-(m-1)} + e \quad (4)$$

It should be noted that at a high concentration of chloride ions in the solution, the composition of copper (1) is as follows: $CuCl_4^{-3}$ and $CuCl_3^{-2}$, at this there is mainly formed $CuCl_4^{-3}$.

Let us calculate the standard potential according to m=4 ($E^{\circ}CuCl_4^{-3}/Cu$). The dissociation constant (Kg)$CuCl_4^{-3}$ makes $2.5 \cdot 10^{-6}$ [3, 4]. The copper electrode equilibrium potential for reaction (2), according to the Nernst equation is equal to: Cu^{+}/Cu

$$E = E^{0}_{Cu^{+}/Cu} + \frac{RT}{nF} lgCl_{Cu^{+}}.$$

In the solution containing chloride ions and copper in the form of $CuCl_4^{-3}$, the standard potential value makes:

$$E_{CuCl_4^{-3}/Cu} = E^{0}_{Cu^{+}/Cu} + 0.05914lgKg + 0.05914lg\frac{[CuCl_4^{-3}]}{[Cl^{-}]^{4}}. \quad (6)$$

Then:

$$E^0_{CuCl_4^{-3}/Cu} = 0.5072 + 0.05914\lg(2{,}5\cdot10^{-6}) = 0.176B\,. \qquad (7)$$

This calculation allows drawing a conclusion that the chloride medium is thermodynamically most favorable for copper oxidation with the formation of Cu (I) ions at the anode, whereas in solutions that do not contain a complexing ligand, copper is more likely to dissolve with forming copper (II) by reaction (1).

The calculation has been performed for the system at 298 K due to the absence of literature and reference data for the dissociation constants of copper (I) chloride complexes at elevated temperatures. Since relative changes in potentials do not change with increasing temperatures, the results obtained are useful in analyzing reactions carried out at temperatures higher than 298 K.

To predict the reactions occurring under specific conditions for the production of copper oxide (I), and to establish the regions of the predominant existence of a particular phase, we have constructed the E –pH diagram for the Cu – Cu^+ – H_2O system (Figure 1). The concentration of chloride ions is assumed to be 4.25 $mol.dm^{-3}$, the activity coefficient is 0.78, the pH value varies from 0 to 14, the temperature is 298 K. Figure 2 shows the diagram of the stable existence of Cu_2O and CuCl compounds depending on the solution pH and pCl^-, and Figure 3 shows the equilibrium conditions in the Cu – Cu^+ – H_2O system at pH equal to 13 depending on pCl^-.

Electrochemical and chemical reactions, as well as such expressions for equilibrium potentials are given in Table 1. The values of standard potentials and constants are taken on the basis of works [18, 21].

Table 1 – Reactions equations and standard potentials values

No. of reactions equation	Equilibrium potentials and pH
Electrochemical reactions	
1. $2Cu + H_2O \leftrightarrow Cu_2O + 2H^+ + 2e$	$E=0.471 - 0.0591pH$
2. $Cu + H_2O \leftrightarrow CuO + 2H^+ + 2e$	$E=0.569 - 0.0591pH$
3. $Cu + 2H_2O \leftrightarrow Cu(OH)_2 + 2H^+ + 2e$	$E=0.609 - 0.0591pH$
4. $Cu_2O + H_2O \leftrightarrow 2CuO + 2H^+ + 2e$	$E=0.669 - 0.0591pH$
5. $Cu_2O + 3H_2O \leftrightarrow 2\,Cu(OH)_2 + 2H^+ + 2e$	$E=0.747 - 0.0591pH$
6. $Cu \leftrightarrow Cu^{+2} + 2e$	$E=0.337 + 0.0295\lg\alpha_{Cu}{}^{+2}$
7. $Cu^+ \leftrightarrow Cu^{+2} + e$	$E=0.153(\alpha_{Cu}{}^{+} = \alpha_{Cu}{}^{+2})$
8. $Cu + Cl^- \leftrightarrow CuCl_{тв} + e$	$E=0.124 - 0.0591\lg\alpha_{Cl}{}^{-}$
9. $Cu + 2Cl^- \leftrightarrow CuCl_2^- + e$	$E= 0.189+0.0591\lg\alpha_{CuCl_2^-} - 0.1182\lg\alpha_{Cl}{}^{-}$
10. $Cu + 3Cl^- \leftrightarrow CuCl_3^{-2} + e$	$E=0.229+0.0591\lg\alpha_{CuCl_3^{-2}} - 0.1773\lg\alpha_{Cl}{}^{-}$
11. $Cu + 4Cl^- \leftrightarrow CuCl_4^{-3} + e$	$E=0.176+0.0591\lg\alpha_{CuCl_4^{-3}} - 0.2364\lg\alpha_{Cl}{}^{-}$
12. $Cu_2O+2H_2O+Cl^- \leftrightarrow Cu_2(OH)_3Cl+H^++2e$	$E=0.451+0.0295pH - 0.00295\lg\alpha_{Cl}{}^{-}$
13. $2CuCl + 3H_2O \leftrightarrow Cu_2(OH)_3Cl + Cl^- + 3H^+ + 2e$	$E=0.785 - 0.0882pH - 0.0295\lg\alpha_{Cl}{}^{-}$
14. $CuCl + 2H_2O \leftrightarrow Cu(OH)_2 + Cl^- + 2H^+ + e$	$E=0.777 - 0.0591pH - 0.0591\lg\alpha_{Cl}{}^{-}$
15. $Cu^+ + H_2O \leftrightarrow HCuO_2^- + 3H^+ + e$	$E=1.733 - 2.232pH$
Chemical reactions	
16. $Cu_2O + 2H^+ + 2Cl^- \leftrightarrow 2CuCl + H_2O$	$pH = 5.66 + \lg\alpha_{Cl}{}^{-}$
17. $2CuO + H^+ + Cl^- + H_2O \leftrightarrow Cu_2(OH)_3Cl$	$pH = 7.4 + \lg\alpha_{Cl}{}^{-}$
18. $2CuCl_2^- + H_2O \leftrightarrow Cu_2O + 4Cl^- + H^+$	$pH = 4.63 + \lg\alpha_{Cl}{}^{-} - \lg\alpha_{CuCl^-}$

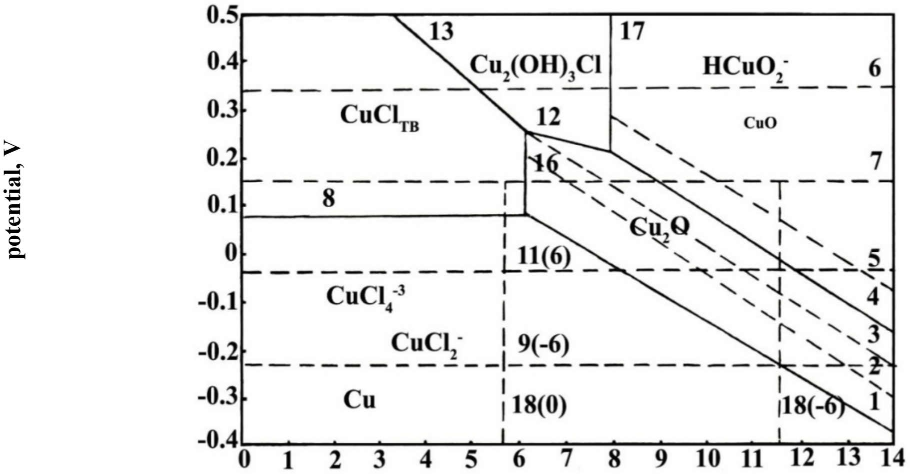

Figure 1 - E—pH diagram for the Cu – Cu^+ – H_2O system
C_{NaCl} = 4.25 mol.dm^{-3}
T = 298 K

According to the diagram (Figure 1), the region of thermodynamically stable existence of CuCl decreases with the values of potential smaller than +0.09 V and with increasing pH. At potentials corresponding to the region above line (13), dicupritrioxychloride may be formed, and at pH exceeding 6.18 copper (I) chloride may hydrolyze to form copper oxide (I).

It should be noted that at high pH the equilibrium potential of reaction (I) is more negative than the potential of the copper oxidation to copper (I) chloride and is comparable with the potential for the formation of complex copper ions: $CuCl_2^-$,$CuCl_3^{-2}$, $CuCl_4^{-3}$ (reactions 9, 10, II). Therefore, during electrochemical oxidation of copper in the test solution with pH =13 and with E lower than 0.09 V, the formation of a solid CuCl phase on the anode is thermodynamically unlikely.

Attention is drawn to the wide range of pH values and at the same time a narrow range of potential values at which the existence of copper oxide (I) is likely. At potentials above lines (1–5), copper oxide (I) is oxidized to copper (II) oxide and copper (II) hydroxide.

Straight line 16 (Figure 2) is the hydrolysis equilibrium line (according to equation (16). Below line (16) copper chloride is stable above, its hydrolysis occurs with the formation of copper oxide (I). [22]

The regions of stable existence of metallic copper, copper (I) chloride and copper oxide (I) at pH 13, depending on pCl^- are presented in Figure 3. Straight lines 1, 8 and 16, corresponding to the above equations, are the lines of the equilibrium state of the systems. In region 1 the metallic phase is stable. In region II chloride copper compounds are stable that can hydrolyze to form Cu_2O at pCl^- that is higher than 6, 18. In region III Cu_2O is stable.

The range of potentials at which Cu_2O is stable is very limited and its width is within 0.2 - x V under the conditions studied for the synthesis of copper oxide (I).

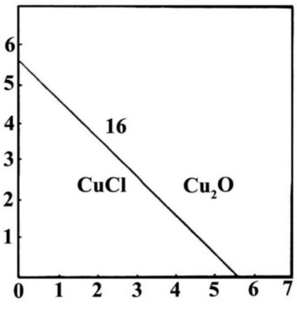

Figure 2 – Diagram of the CuCl– Cu_2O system equilibrium

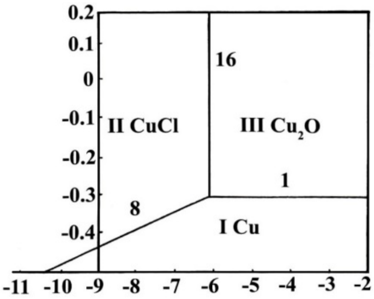

Figure 3 – Diagram of the Cu – CuCl– Cu_2O system equilibrium (pH = 13)

Conclusions. Thus, the diagrams calculated by us allow determining only the most probable region of pH, pCl^- and the electrode potential, in which it is possible to obtain copper oxide (I).

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СІЛТІЛІ ХЛОРИДТІ ЕРІТІНДІЛЕРДЕ МЫС ОКСИДІНІҢ (I) ТҮЗІЛУ МЕХАНИЗМІ МЕН ФИЗИКА-ХИМИЯЛЫҚ ЕРЕКШЕЛІКТЕРІ

Аннотация. Мыстың жоғары дисперсті оксидтерін алудың ең тиімді тәсілдері электрохимиялық әдістер болып табылады. Мыс ерітіндісіне ауыстырудың көрсетілген әдісі талап етілетін валенттілік ионының түзілу режимін дәл табуға және жоғары химиялық тазалықты қосылыстарды алуға мүмкіндік береді. Мыс оксидін(I) алу әдістері сілтілі хлорлы ерітіндіде металл мыстың анодты тотығуына негізделеді. Электрохимиялық әдістің негізгі артықшылығы металл мысы және екі валентті мыс оксиді жоқ бөлшектерінің мөлшері аз, жоғары сапалы ұнтақты алу мүмкіндігі болып табылады. Әлсіз сілтілі және қышқыл хлоридті ерітінділердегі мыстың анодты коррозиясын зерттеу нәтижелері ерітіндідегі хлорид-иондардың құрамына және берілетін әлеуеттің көлеміне байланысты гидролиз процесінде мыс тотығы (I) ұнтағын қалыптастыратын мыстың хлоридті кешендері пайда болуы мүмкін екенін көрсетті. Бір валентті мыстың хлоридті кешендерінің термодинамикалық тұрақты өмір сүру аймағы әлеуеттің аз мәндері және pH өсуі кезінде қысқарады.

Бұл жұмыста бірінші рет есептеу жүргізілді және мыс оксидін (I) алу мүмкін болатын электрод потенциалын **Тірек сөздер:** мыс тотығы (I), мыстың хлоридтік комплекстер, тепе-тендік потенциалдар, термодинамика, тепе-тендік құрылымдар диаграммасы

ың PH, pCl– ықтимал аймағын ғана анықтауға мүмкіндік беретін диаграмма жасалды.

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ФИЗИКО-ХИМИЧЕСКИЕ ОСОБЕННОСТИ И МЕХАНИЗМ ОБРАЗОВАНИЯ ОКСИДА МЕДИ (I) В ЩЕЛОЧНЫХ ХЛОРИДНЫХ РАСТВОРАХ

Аннотация. Наиболее перспективными способами получения высокодисперсных оксидов меди являются электрохимические методы. Указанный метод перевода в раствор меди позволяет достаточно точно найти режимы образования иона требуемой валентности и получить соединения высокой химической чистоты. Методы получения оксида меди(I) базируются на анодном окислении металлической меди в щелочном хлоридсодержащем растворе. Основным преимуществом электрохимического метода является возможность получения порошка высокого качества с меньшим размером частиц, не содержащих металлическую медь и оксид двухвалентной меди. Результаты исследований анодной коррозии меди в слабощелочных и кислых хлоридных растворах показали, что в зависимости от содержания хлорид-ионов в растворе и величины задаваемого потенциала могут образовываться хлоридные комплексы меди, которые в процессе гидролиза формируют порошок оксида меди (I). Область термодинамически устойчивого существования хлоридных комплексов одновалентной меди при малых значениях потенциала и росте pH сокращается.

В данной работе впервые произведен расчет и построена диаграмма, которая позволяет определить только наиболее вероятную область pH, pCl^- и потенциала электрода, в которой возможно получение оксида меди (I).

Ключевые слова: оксид меди (I), хлоридные комплексы меди, равновесные потенциалы, термодинамика. диаграмма равновесных систем**.**

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SELECTING OPTIMAL MODES OF KNOTWEED RAW MATERIALS PRESSING OUT AND DEVELOPING TECHNOLOGY FOR OBTAINING DRY EXTRACT

Abstract. A complex of studies on the choice of optimal conditions for extraction of medicinal plant raw materials of poultry mountain and the development of technology for obtaining dry extract from plant raw materials was concluded. There is a tendency to develop resource-saving technologies in ways of creating new drugs from plant raw materials. This is ensured by the use of various extractants, schemes and extraction modes, using equipment that can significantly increase the release of radioactive and active substances.Several variants of extraction of raw materials by the proposed technology using different temperature regimes and time exposures were studied. We used 40, 50, 60, 70% aqueous solutions of ethyl alcohol as an extractant and determined that 60% aqueous solution of ethyl alcohol has a better ability with respect to the amount of flavonoid grass red tape to select the optimal method of extraction of plant raw materials. Quantitative determination of the amount of flavonoids in the herbs of the red ribbon is made in four Parallels and their metrological characteristics are calculated.According to the experimental data, the optimal number of particles was 2 mm.

Keywords: Flavonoid, avicularin, hyperoside, quercitrin, isoquercitrin, carotene, rutin.

Introduction

Knotweed, Polygonum aviculare L. is a plant that belongs to the families of alpine fleeceflower blooming since June throughout the summer. Most of them ripe in the second half of August and the flowers are small and green. Knotweed has a wide range of biological activities. It is an annual herbaceous plant up to 30 cm in height, rough, up to 100 cm long. Pale scaly tracheas are observed in the nodes. It is most common in all the regions of Kazakhstan. They can be found on the roadsides, in plowed places, in places of walks, in river Sands, in courtyards, in gardens, arrays.

Grass is used for medicinal purposes. The upper part of plants up to 40 cm in length is stocked up when flowering with a sharp knife or wrapper. The storage term is 3 years [1].

The plant of the knotweed contains flavonoids (avicularin, hyperoside, quercitrin and isoquercitrin), tannins (up to 0.4%), vitamins (ascorbic acid, up to 0.9% by dry weight, carotene, vitamin K), silicic acid compounds (up to 4.5%), as well as resins, essential oils, drying, oils, sugar.

It is used for treating colds, bronchitis, pneumonia, pleurisy, cough cracks, bronchial asthma, pulmonary tuberculosis, insomnia, inflammation of the oral mucosa and red chin, gastritis, dysentery, liver, gastrointestinal tract, biliary tract, skin diseases, urinary tract burns, rheumatism, wounds.

One of the urgent tasks of modern pharmacotherapy is the problem of choosing medicines of natural origin for treating the hepatobiliary system. Socio-economic living conditions of the population and environmental pollution, the use of food containing preservatives, medication without a doctor's prescription leads to stress on the liver and contribute to the likelihood of the development of certain diseases.

Currently, the pharmaceutical market is increasing the range of medicines used in treating diseases of liver and biliary tract, of which there are more than a thousand items. The pharmaceutical industry in different countries releases hepatoprotective agents of knotweed for treating the liver pathology.

In recent years the approaches to the development of new products of plant materials have tended to develop resource-saving technologies, which is ensured by the use of various extractants, extraction schemes and modes, the use of equipment that allows significant increasing the yield of extractive and active substances.

The development and introduction into practice of a resource-saving method of extraction (due to the maximum depletion of raw materials), as well as preparing stable preparations based on plant extracts, is an urgent task.

The aim of the work is selecting the optimal modes of extraction of the knotweed plant material and developing a technology for producing a dry extract.

Experimental part

At present there are a large number of various extraction schemes designed to increase the yield of active substances, to ensure maximum depletion of raw materials and enrichment of the extract with target biologically active substances (BAS). Among them there is a scheme of extraction of raw materials with purified water, proposed by Sargin B.V. et al., implemented on examples of raw materials rich in ascorbic acid (fruits of viburnum ordinary, Viburnum opulus), water-soluble phenolic compounds (weeping birch leaves, Betulapendula Roth).

The scheme proposed by Sargin B.V. et al., was taken as the basis of our studies with some modifications. In the variant proposed by Sargin B.V., the general conditions of the primary and subsequent heating of the extracted plant material are indicated in a fairly wide range of temperatures and heating time. The cooling conditions are not specified, only the time interval is given, however, the final temperature of the extracted mixture is not indicated.

Results and discussion

In this regard, several variants of extracting raw materials according to the proposed technology with the use of various temperature regimes and temporary exposures are given in Table 1.

At stage 3 of the extraction process (initial heating of the mixture) there were selected the conditions for gradual increasing the temperature from 20 °C to 40 °C by 1 °C and 5 °C in various time intervals. Further, at stages 4, 6 (infusion of the raw material at a constant temperature), the possibility of extracting the raw material by holding the extractable mixture at a constant temperature, as well as the possibility of reducing the extraction time by eliminating this stage, was evaluated.

Table 1 – Selecting an optimal scheme of the raw material extracting

Stage No.	Mode	Scheme 1 (n=5)	Scheme 2 (n=5)	Scheme 3 (n=5)
1	The plant material was placed in a ceramic vessel.	The vessel is pre-aged in an oven-thermostat at 20 ° C for 1 hour		
2.	Filled with the calculated volume of the extractant, taking into account the coefficient of absorption of raw materials			
3.	The plant material heating	Increasing the temperature of the extracted mixture from 20 °C to 40 °C within 2 hours	Increasing the temperature of the extracted mixture from 20 °C to 40 °C within 2 hours	Increasing the temperature of the extracted mixture from 20 °C to 40 °C for 2 hours
4.	Infusion of raw materials at a constant temperature	Holding at the temperature 40°C within an hour		None
5.	Subsequent heating	With a gradual increase in temperature to 90 °C within 2-6 hours	With a gradual increase in temperature to 90 °C within 8 hours (by 1°C every 10 min)	With a gradual increase in temperature to 90 °C within 8 hours (by 3°C every 30 min)
6.	Infusion of raw materials at a constant temperature	Holding at the temperature 90°C within an hour		Without holding
7.	Cooling	Within 6 hours	Gradualcoolingfrom90 °Cto20 °C within 10.5 hours (by1 °C every 10 min)	At the end of the extraction time, the ceramic vessel was removed from the thermostat and cooled at room temperature.

At stage 5 of the extraction process, the possibility of gradually increasing the temperature of the extracted mixture from 40 °C to 90 °C for 8 hours, by 1 °C every 10 minutes and by 3 °C every 30 minutes, was evaluated. Later, at stage No. 7, the conditions for cooling the mixture were specified.

Thus, three variants of obtaining water extracts are considered: the first one according to the scheme described in the patent, the 2nd and the 3rdby the modified method. In addition, when performing the first option, cooling was performed without removing the extraction tank from the thermostat, but only turning it off.

In all three cases, the raw material of knotweed was used in the dry-air state, previously crushed, mixed and sifted from dust; the first stage for all three extraction schemes was left unchanged.

Table 2 – Comparative assessment of the extractable matters content and the leading BAS groups in the ready extract and the infusion of knotweed, (M ± m)

The studied indicator	Water extract Scheme 1 (n=5)	Water extractScheme2 (n=5)	Water extractScheme3 (n=5)	Infusion (n=5)
The content of extractives, %	26.4±0.3	28.6±0.4*.**.$^{\Delta}$	14.9±0.03	10.2±0.05
The content of polyphenolic compounds in terms of rut in, %	1.81±0.02	2.03±0.02*.$^{\Delta}$	1.4±0.01	0.9±0.02
The content of tannins in terms of gallic acid,%	13.07±0.02	14.01±0.02*.**.Δ	9.86±0.03	6.15±0.03

Note: * - significant difference with infusion ($p < 0.05$); ** - significant difference with the aqueous extract obtained according to scheme 3 ($p < 0.05$); Δ - significant difference with the aqueous extract obtained according to scheme 1 ($p < 0.05$)

Then, to select the optimal method of pressing out the plant raw material of knotweed, we used 40, 50, 60, 70% aqueous solutions of ethyl alcohol as an extractant and found that a 60% aqueous solution of ethyl alcohol has the best extracting ability with respect to the sum of bird's mountaineer (Table 3) [5].

Table 3 –Selecting the extractant concentration

Ethyl alcohol concentration, %	Optical density of the complex with $AlCl_3/HCl$ at 411 nm	Content of the total flavonoids in the extract, %
40	0.446	0.024 ± 0.001
50	0.460	0.025± 0.002
60	0.577	0.031± 0.001
70	0.419	0.022± 0.003
80	0.384	0.020± 0.004

The optimal size of the particles according to experimental data made 2 mm (see Table 4).

Table 4 –Raw material grinding degree

Grass particles size, mm	Optical density of the complex with $AlCl_3/HCl$ at 411 nm	Content of the total flavonoids in the extract, %
1	0.381	0.020± 0.003
2	0.598	0.032± 0.001
3	0.420	0.022± 0.002
4	0.345	0.018± 0.004
5	0.488	0.026± 0.001

From the experimental data it can be seen that as the extraction temperature increases, a proportional increase in product recovery is observed (Table 5) [5,6]. This indicates that the phenolic compounds in the grass of a bird highlander easier go into solution at higher extraction temperatures of 40-80 ºC and at the ratio of raw material-extractant 1:15 (Table 6), the duration of extraction is 90 minutes (Table 7).

Table5 -Determining extraction temperature

Extraction temperature, °C	Optical density of the complex with $AlCl_3$/HCl at 411 nm	Content of the total flavonoids in the extract, %
40	0.339	0.018± 0.0002
50	0.355	0.019± 0.0003
60	0.385	0.020± 0.0004
70	0.391	0.021± 0.0001
80	0.405	0.022± 0.0005

Table 6 –Selecting the extraction multiplicity and the raw material to extractant ratio

Raw material and extractant ratio	Optical density of the complex with $AlCl_3$/HCl at 411 nm	Content of the total flavonoids in the extract, g
1:6	0.389	0.0615 ± 0.00004
1:10	0.236	0.0625 ± 0.00005
1:15	0.161	0.0637 ± 0.00003

Таблица 7 – Selecting the extraction duration

Heating time at the boiling temperature, min	Optical density of the complex with $AlCl_3$/HCl at 411 nm
30	0.233 ± 0.0003
60	0.234 ± 0.0001
90	0.274 ± 0.0002

The quantitative determining of the total flavonoids in the grass of knotweed was carried out in four parallels and their metrological characteristics were calculated. The relative error of determining (ε) is 2-10% at the confidence level of 95[7,8]. The high relative error of a single determination (ε1) is due to the fact that in differential spectrophotometry, aliquots of solutions containing substances absorbing in UV light are taken not only for the tested extract and standard substance, but also for comparison solutions.

Conclusion

Thus, we carried out a set of studies for selecting the optimal conditions for extracting the knotweed medicinal plant raw materials and developing a technology for producing dry extract from plant raw materials. The optimal particle size, according to experimental data, is 2 mm, the ratio of raw materials-extractant is 1:15, the duration of extraction is 90 minutes with 60% ethyl alcohol.

The data presented in Table 2 indicate that the content of extractive substances in the aqueous extract obtained according to scheme 2 is 1.1 times and 1.9 times respectively higher than that in extracts obtained according to scheme 1 and 3 and the content of extractive substances is 2.8 times higher in the infusion. At the same time, the content of polyphenolic compounds in terms of rutin (%) in the extract obtained according to scheme 2 exceeded the content of those in the extracts obtained according to schemes 1 and 3 and in water extraction of the knotweed raw material is 1.1 times, 1.5 times and 2.3 times higher, respectively.

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ҚЫЗЫЛ ТАСПА ӨСІМДІК ШИКІЗАТЫН СЫҒЫНДАУДЫҢ ОҢТАЙЛЫ РЕЖИМДЕРІН ТАҢДАУ ЖӘНЕ ҚҰРҒАҚ СЫҒЫНДЫ АЛУ ТЕХНОЛОГИЯСЫН ӘЗІРЛЕУ

Аннотация. Қызыл таспа дәрілік өсімдік шикізатын сығындаудың оңтайлы шарттарын таңдау бойынша және де өсімдік шикізатынан құрғақ сығынды алу технологиясын әзірлеуге зерттеулер кешені жүргізілді. Өсімдік шикізатынан жаңа препараттар жасау тәсілдерінде ресурс үнемдеуші технологияларды әзірлеу үрдісі байқалады. Бұл әртүрлі экстрагенттерді, экстракцияның схемалары мен режимдерін қолданумен, экстрактивтік және әсер етуші заттардың шығуын едәуір дәрежеде арттыруға мүмкіндік беретін аппаратураны пайдаланумен қамтамасыз етіледі. Әр-түрлі температуралық режимдерді және уақытша экспозицияларды қолдана отырып, ұсынылған технология бойынша шикізатты экстрагирлеудің бірнеше нұсқасы зерделенді.Қызыл таспа өсімдік шикізатын сығындаудың оңтайлы әдісін таңдау үшін бізэкстрагент ретінде 40, 50, 60, 70% этил спиртінің су ерітінділерін пайдаланды және 60% этил спиртінің су ерітіндісі қызыл таспа шөбі флавоноидінің сомасына қатысты ең жақсы алатын қабілеттілікке ие екендігін анықтады.Қызыл таспа шөптеріндегі флавоноидтардың сомасын сандық анықтау төрт параллельде жүргізіледі және олардың метрологиялық сипаттамалары есептелінеді. Тәжірибелік деректер бойынша бөлшектердің оңтайлы мөлшері 2 мм, шикізат – экстрагент арақатынасы 1: 15, экстракция ұзақтығы 90 минут, экстрагент концентрациясы 60% этил спиртін құрады.

Түйін сөздер: Флавоноид,авикулярин, гиперозид, кверцитрин, изокверцитрин, каротин, рутин.

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ВЫБОР ОПТИМАЛЬНЫХ РЕЖИМОВ ОТЖИМА РАСТИТЕЛЬНОГО СЫРЬЯ ПТИЧЬЕГО ГОРЦА И РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ СУХОГО ЭКСТРАКТА

Аннотация. Проведен комплекс исследований по выбору оптимальных условий отжима лекарственного растительного сырья птичьего горца и разработке технологии получения сухого экстракта из растительного сырья. Наблюдается тенденция разработки ресурсосберегающих технологий в способах создания новых препаратов из растительного сырья. Это обеспечивается применением различных экстрагентов, схем и режимов экстракции, использованием аппаратуры, позволяющей в значительной степени повысить выброс радиоактивных и действующих веществ. Изучены несколько вариантов экстрагирования сырья по предложенной технологии с использованием различных температурных режимов и временных экспозиций. Птичий горец для выбора оптимального метода отжима растительного сырья использовали в качестве экстрагента 40, 50, 60, 70% водных растворов этилового спирта и определили, что 60% водный раствор этилового спирта обладает лучшей способностью относительно суммы флавоноида травы красной ленты. Количественное определение суммы флавоноидов в травах красной ленты производится в четырех параллелях и рассчитываются их метрологические характеристики. По опытным данным оптимальное количество частиц составило 2 мм, соотношение сырья – экстрагента 1: 15, продолжительность экстракции 90 минут, концентрация экстрагента 60% этилового спирта.

Ключевые слова: флавоноид,авикулярин, гиперозид, кверцитрин, изокверцитрин, каротин, рутин.

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OPTIMIZATION OF METHODS OF QUANTITATIVE DETERMINING FLAVANOIDS IN KNOTWEED RAW MATERIAL

Abstract. The method of quantitative determination of flavonoids in the grass of the mountaineer avian is developed. Improvement of the existing Pharmacopoeia technique for determining the total content of flavonoids in the grass of the mountain bird is an urgent task, since the long procedure of extraction of raw materials of the bird mountain and the maximum extract of flavonoids. The optimal conditions of the experiment were chosen. Parameter optimization of pharmacopoeial methods is the reduction of time of the extraction of flavonoids (total extraction time 1.5 hours) with the introduction of the calculation formula of the correction factor for the incomplete extraction. The content of flavonoids in the grass of the bird Highlander determined by Pharmacopoeia was 1.62 ± 0.02%. The content of the amount of flavonoids is normalized in the raw material at a level of not less than 0.5%. To determine the metrological characteristics of the developed technique, 10 parallel definitions were carried out The relative error of definition does not exceed 3,13 %.A rapid method for determination of flavonoids in poultry sold in buckets for 5 minutes in a variant of the extraction with 70% ethanol. The definition error does not exceed 3.13 %.

Keywords: flavonoids, quantification, UV-spectrophotometry, Herba Polygonum aviculare.

Introduction

Polygonum aviculare L (knotweed) possesses a wide range of biological activity. The drug from knotweed is used to stop bleeding, inflammation of the urinary tract and stone binding in the kidney. Knotweed is an annual herb of the buckwheat family. The root is rod-like, low- branched. Stems are 10-60 cm long, spread on the soil or ascending, often branched from the base. The leaves are from elliptical to linear-lanceolate form, narrowed at the base in a short petiole, 1-4 cm long and 0.5-2 cm wide. The flowers are located in the leaf axils 2-5. The perianth is deeply dissected, five-membered, green at the bottom, white or pink at the top. The fruit is a triangular, black, occasionally chestnut nutlet. It flows and fruits from May to late autumn, in Western Siberia from mid-June to September.

Flavonoids are a large class of natural compounds, the variety of which is mainly caused by the structure of the aglycone (oxidation state of the three-carbon fragment, the position of the side phenyl radical, the size of the heterocycle and other features), as well as the composition of the glycoside fragment.

Physicalproperties. Flavonoids are crystalline substances with a specific melting point, odorless, having a yellow color (flavones, flavonols), colorless (isoflavones, flavanones).

The group of flavonoids also includes anthocyanins (natural dyes of plants), which are colored differently depending on the pH of the medium: in an acidic medium, they are red (salts of cations), in alkaline blue (salts of anions) [1].

The grass of knotweed is included in the USSR State Pharmacopoeia XI edition and the European Pharmacopoeia, the Pharmacopoeia of Kazakhstan. All the regulatory documents provide for standardization of raw materials by the content of flavonoids. However, there is a difference in the methods of quantifying these compounds in the given raw material. The domestic pharmacopoeia provides for triple extraction of knotweed flavonoids (in the form of glycosides) with 70% alcohol (each extraction lasting 30 minutes), followed by adding aluminum chloride solution to the aliquot of the extract and measuring the optical density of the solution at 410 nm after 20 minutes. For the calculations, the specific absorption index of the avicularin complex with aluminum chloride at 410 nm is equal to 330. The total content of flavonoids is normalized in raw materials at the level of at least 0.5%. The European Pharmacopoeia uses a unified method. The essence of the method lies in the fact that a sample of the raw material is subjected to acid hydrolysis in acetone, the obtained aglycones are extracted with ethyl acetate and the optical density of the complex of aglycones with aluminum chloride in ethyl acetate – methanol – acetic acid is measured. The content of flavonoids is calculated using the specific absorption rate of hyperoside that is 500 under the conditions of determining. The content of flavonoids is normalized in raw materials at the level of at least 0.3% [2].

The opportunities for improving the existing pharmacopoeial methodology of determining the total content of flavonoids in the knotweed grass lie in the area of optimizing a rather long procedure of flavonoid extraction (1.5 hours), when you can abandon the exhaustive extraction mode of the detected substances and enter a correction factor for incomplete extraction into the calculation formula [3].

Experimental part

The parameter of optimization of the pharmacopoeial procedure is reducing the time of extraction of flavonoids (the total extraction time is 1.5 hours) with introducing a correction factor for the incompleteness of extraction into the calculation formula. The content of flavonoids in the knotweed grass determined by the pharmacopoeial method was 1.62 ± 0.02%.

The main parameter of optimization of the pharmacopoeial method for determining the content of flavonoids in the knotweed grass is reducing the extraction time, alongside with such parameters as the concentration of alcohol used for the extraction of flavonoids and the maximum absorption of the complex of flavonoids with aluminum chloride was tested under the experimental conditions. The dependence of the yield of flavonoids on the concentration of alcohol and the time of extraction was tested in experiments with at least 4 repetitions. Since 70% ethyl alcohol is used in the pharmacopoeial procedure for extraction, this concentration and extreme concentrations used for the extraction of flavonoids, i.e. 40% and 95%, were tested. The results are presented in Table 1 [4-5].

Table 1 -Dynamics of extracting flavonoids from the knotweed grass depending on the extraction time a
t different concentrations of alcohol (with the ratio of raw materials/extractant equal to 1:100), %

The yield of flavonoids, (% by weight of dry raw materials)/(% of the total amount in raw materials)	Alcohol concentration, (%)	Extraction time, min.			
		5	10	15	30
	40	1.32±0.03 81	1.33±0.03 82	1.37±0.02 85	1.50±0.05 93
	70	1.51±0.04 93	1.52±0.03 94	1.53±0.03 94	1.55±0.03 96
	95	0.37±0.02 23	0.46±0.02 28	0.56±0.02 35	0.79±0.04 49

The results obtained indicate that 70% of the ethanol concentration is optimal in the studied range. In this case, the bulk of flavonoids are removed by the solvent already within the first minutes of extraction, and subsequently, few residues are extracted [6].

To check the maximum absorption of the products of the knotweed flavonoids reaction with aluminum chloride, we recorded the electronic spectra of the extraction itself, the reaction products of flavonoids with aluminum chloride against the background of 95% alcohol and against the extraction itself (differential spectrum). The long-wavelength maximum of the differential spectrum was at the mark of 407 nm, which fits into the permissible deviation intervals (± 5 nm), so all measurements were carried out at the wavelength specified in the pharmacopoeial method, 410 nm. All of the above makes it possible to offer an express method for determining flavonoids in the knotweed grass, when the bulk of these compounds are extracted from raw materials within a relatively short period of time and instead of a long exhaustive extraction of flavonoids remaining in the pile, a correction factor for extraction incompleteness is entered into the calculation formula [7].

Results and discussion

Express-method of quantitative determining flavonoids in the knotweed grass.The analytical sample of the raw material is crushed to the size of particles passing through the sieve with holes 1 mm in diameter. About 1 g (exact weight) of the crushed raw material is placed in a 250 ml thin flask, 100 ml of 70% alcohol are added, the flask is attached to the reflux condenser and heated in a boiling water bath within 5 minutes after boiling the solvent. Then the flask is cooled to the room temperature under a stream of cold water and filtered through a filter paper into a measuring cylinder with the capacity of 100 ml (solution A). 4 ml of the A solution are placed in a 25 ml volumetric flask, 2 ml of a 2% solution of aluminum chloride in 95% alcohol are added and the volume of the solution is brought to the mark with 95% alcohol; after 20 min. the optical density of the solution is measured on the spectrophotometer at the wavelength of 410 nm in a cell with a layer thickness of 10 mm. The following solution is used as the reference solution: 4 ml of the A solution are placed in a measuring flask with the capacity of 25 ml, 1 drop of diluted hydrochloric acid is added and the volume of the solution is adjusted to the mark with 95% alcohol. The content of the total flavonoids in terms of avicularin and absolutely dry raw materials in percent (X) is calculated by the formula:

$$X = \frac{\mathrm{D} * \mathrm{V} * 25 * 100 * 1.07}{330 * \mathrm{m} * 4 * (100 - \mathrm{W})},$$

where D is the optical density of the test solution; 330 is the specific absorption coefficient of the complex of avicularin with aluminum chloride at 410 nm; V is the volume of the A solution in the measuring cylinder; m is the mass of raw material in grams; 1.07 is the correction factor for incomplete extraction of flavonoids; W is the mass loss during the raw materials drying in percent.

To determine metrological characteristics of the developed methodology, 10 parallel determinations were carried out (Table 2). The method error does not exceed 3.13%.

Table 2 –Metrological characteristics of the express-method of determining flavonoids in the knotweed grass

f	X	S^2	S	P	t	(0.95; 9)	Δx ε. %
9	1.62	0.005055	0.0711	0.95	2.26	0.05	3.13

Thus, the express-method of determining flavonoids in the knotweed grass is implemented in the variant of extraction with 70% ethyl alcohol within 5 minutes. The determination error does not exceed 3.13% [8].

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ҚЫЗЫЛ ТАСПА ШИКІЗАТЫНДА ФЛОВАНОИДТАРДЫ САНДЫҚ АНЫҚТАУ ӘДІСТЕМЕСІН ОҢТАЙЛАНДЫРУ

Аннотация. Қызыл таспа шөмішіндегі флавоноидтардың сандық анықтау әдістемесі әзірленді.Қызыл таспа шөмішіндегі қосынды құрамындағы флавоноидтерді анықтаудың қазіргі фармакопеялық әдістемесін жетілдіру өзекті міндет болып табылады,өйткені қызыл таспа шикізаты ұзақ процедуралы экстракция және флавоноидтермаксимум түрде алынады.Эксперимент жүргізудің оңтайлы шарттары алынды. Фармакопеялық Әдістеменің оңтайландыру параметрі флавоноидтарды экстракциялау уақытын (экстракцияның жалпы уақыты 1,5 сағат) есептеу формуласына экстракцияның толық еместігіне түзету коэффициентін енгізумен қысқарту болып табылады. Фармакопеялық әдіспен анықталған құс қыша шөмішіндегі флавоноидтардың мөлшері 1,62 ± 0,02% құрады.Флавоноидтар сомасының құрамы шикізатта кемінде 0,5% деңгейінде нормаланады. Әзірленген Әдістеменің метрологиялық сипаттамаларын анықтау үшін 10 параллельді анықтау жүргізілді. Анықтаудың салыстырмалы қатесі 3,13 % аспайды. Қызыл таспа шөмішіндегі флавоноидтарды анықтаудың Экспресс-әдісі 70% этил спиртімен экстракция нұсқасында 5 минутта іске асырылады. Анықтау қатесі 3,13 % аспайды.

Түйін сөздер: флавоноидтар, сандық анықтау, УК-спектрофотометрия,қызыл таспашөбі.

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ОПТИМИЗАЦИЯ МЕТОДИКИ КОЛИЧЕСТВЕННОГО ОПРЕДЕЛЕНИЯ ФЛОВАНОИДОВ В СЫРЬЕ ГОРЦА ПТИЧЬЕГО

Аннотация. Разработана методика количественного определения флавоноидов в траве горца птичьего. Усовершенствование существующей фармакопейной методики определения суммарного содержания флавоноидов в траве горца птичьего является актуальной задачей так как продолжительная процедура экстракции сырья птичьего горца и максимум извлечь флавоноиды. Подобраны оптимальные условия проведения эксперимента. Параметром оптимизации фармакопейной методики является сокращение времени экстракции флавоноидов (общее время экстракции 1,5 часа) с введением в расчетную формулу поправочного коэффициента на неполноту экстракции. Содержание флавоноидов в траве горца птичьего, определенное фармакопейным методом, составило 1,62 ± 0,02%. Содержание суммы флавоноидов нормируется в сырье на уровне не менее 0,5%. Для определения метрологических характеристик разработанной методики провели 10 параллельных определений. Относительная ошибка определения не превышает 3,13 %. Экспресс-метод определения флавоноидов в траве горца птичьего реализуется в варианте экстракции 70% этиловым спиртом в течение 5 минут. Ошибка определения не превышает 3,13 %.

Ключевые слова: флавоноиды, количественное определение, УФ – спектрофотометрия, трава горца птичьего.

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STUDYING THE COMPOSITION OF COMPLEXES ON THE BASIS OF PALLADIUM(II), COPPER(II), IRON(III) CHLORIDES AND POLYVINYLPYRROLIDONE

Abstract. The compositions of polymer-metal complexes based on palladium(II), copper(II), iron(III) chlorides and polyvinylpyrrolidone were established by potentiometric and conductometric methods. The values of the Bjerrum formation functions were calculated. According to the experimental data obtained for determination the composition of the complex, titration curves were constructed and the optimal molar ratios of the reacting components were found. The obtained calculated data indicate the formation of polymeric complexes of palladium and copper, in which one complex-metal ion forms into three compound mono-link of polyvinylpyrrolidone. And in the case of the iron polymeric complex, there is one ion of the complexing metal for the four constituent mono-link of polyvinylpyrrolidone. Coordination saturation of metal complexing agents in these complexes is due to solvent molecules or anion of metal salts. The structure and morphology of the synthesized complexes were studied using IR- spectroscopy and scanning electron microscopy. It has been established that the oxygen atoms of polymeric ligands take part in the formation of a coordination bond with the metal ion. The results of electron microscopy indicate the formation of polymer films of a complex with a porous inhomogeneous amorphous structure.

Key words. Polyvinylpyrrolidone, palladium, copper, iron, complexation, Bjerrum method, stability constants, composition, thermodynamics.

Introduction

Coordination compounds are widely used as homogeneous and heterogeneous supported catalysts. Chemical transformations in the presence of coordination compounds underlie many catalytic processes. It is known that they are able to activate molecules of alkenes, alkynes, carbon monoxide, oxygen, which opens up broad opportunities for the development of new catalytic processes [1].

An additional impetus for the development of catalysis by complexes was the general tendency to create milder reaction conditions. Classical processes using heterogeneous metal oxide or metal catalysts are sometimes called “expensive” processes, bearing in mind the high costs per ton of product produced. These costs are determined by high temperatures and pressures at a fairly low, as a consequence, the selectivity of the process. In addition, relatively low degrees of conversion of the starting materials often lead to the need to separate the reaction product from highly diluted mixtures, as well as the recycle of unreacted reagent. Polymer-metal complexes used as homogeneous catalysts, on the contrary, usually operate at low temperatures and pressures with high efficiency and selectivity for the reaction products [2].

The aim of this work is to study the process of complexation of polyvinylpyrrolidone (PVP) with Pd^{2+}, Cu^{2+}, Fe^{3+} ions.

Experimental part

Palladium(II) chloride $PdCl_2$, copper(II) chloride $CuCl_2 \cdot 2H_2O$, iron(III) chloride $FeCl_3 \cdot 6H_2O$, polyvinylpyrrolidone (molecular weight 40,000, AppliChem, Germany), hydrochloric acid, sodium hydroxide, sodium chloride were used without prior purification.

The processes of complexation of palladium(II), copper(II) and iron(III) ions with PVP were investigated by potentiometric and conductometric methods [3]. Potentiometric studies were carried out in thermostated conditions on the pX-150MI ionomer using silver chloride and glass electrodes. The pH measurement accuracy was 0.02 pH units. Conductometric studies were performed on a ConductivityMeter 13701/93 device (PHYWE) under thermostatically controlled conditions.

IR spectra of PVP and Pd(II)-PVP, Cu(II)-PVP and Fe(III)-PVP complexes were recorded on a FT IR-4100 type A JASCO instrument in the range of 4000–450 cm^{-1} at Kaiserslautern Technical University (TUK, Germany). SEM images were taken on a JSM-6490LA Jeol instrument equipped with an X-ray dispersive energy detector (EDX) for elementary analysis (JEOL, Japan). IR spectra and SEM images were obtained in analytical laboratories at the Technical University of Kaiserslautern (TUK, Germany). The stability constants of the PMC are calculated on the basis of the modified Bjerrum method [4].

Results and their discussion

In the works [5-7], the results on the determination of the compositions of polymer-metal complexes (PMC) based on PVP-$PdCl_2$, PVP-$CuCl_2 \cdot 2H_2O$, PVP- $FeCl_3 \cdot 6H_2O$ using potentiometric and conductometric titration were presented.

The reactivity of a chain molecule is largely determined by the chemical composition, configuration and conformation of the macromolecule, and knowledge of which makes it possible to determine the role and mechanism of the catalytic action of various functional groups of macromolecules that are part of the active centers [8]. The correctness of the final calculations depends on the theoretical laws and the accuracy of the source data. The calculations performed give results that should be consistent with the experimental data. In this connection, the modified Bjerrum method [9,10] was used to clarify the composition and determine the strength of the PMC. The polymer ligand solution was titrated with acid (HCl) or base (NaOH), depending on the nature of the complexing metal salt, with a change in the pH of the medium in the absence and presence of ions of the studied metals in the temperature range of 298–343 K (temperature selection due to the use of PMC as catalysts in the oxidation of octene–1 in an oxygen atmosphere [5]), with three values of the ionic strength of a solution of 0.1; 0.5; 1.0 mol/L (constants, determined for a given ionic strength, can be considered almost constant for solutions with ionic strength, which were taken when performing experiments. That is, for most calculations these values can be used without corrections for ionic strength [11] (sodium chloride was used as an indifferent electrolyte).

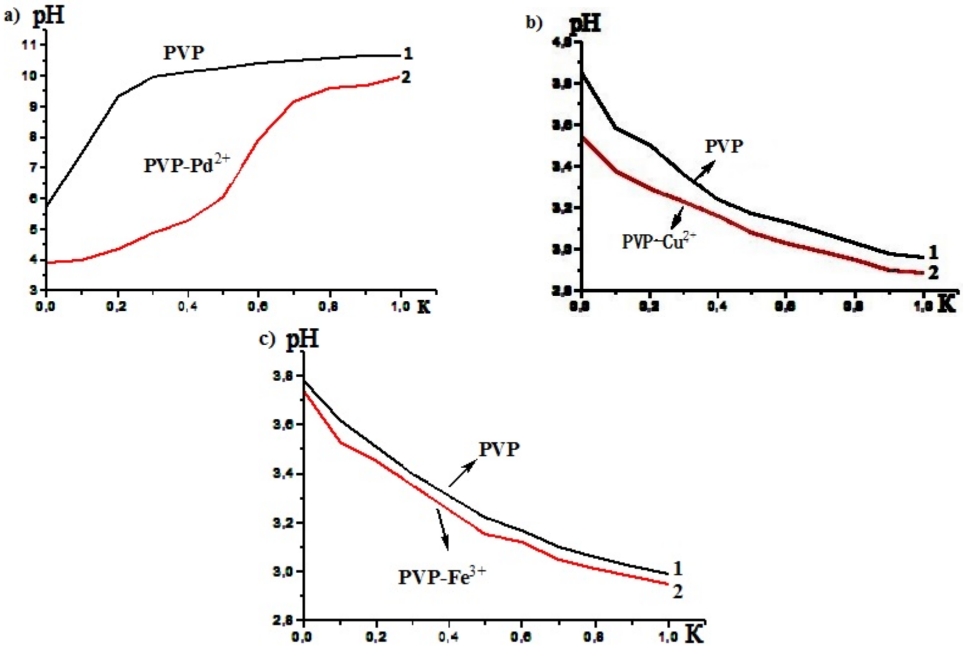

Figure 1 – Potentiometric titration curves of aqueous solutions of polyelectrolyte PVP (1a-c) and polymer–$PdCl_2$ (2a), polymer–$CuCl_2$ (2b) systems, polymer–$FeCl_3$ (2c) sodium hydroxide (curves 1a, 2a) and hydrochloric acid (curves 1b, 2b, 1c, 2c) at T = 298 K, I = 0.10 mol/L (where K is the optimal molar ratio of the reacting components $[Me^{2+/3+}]/[PVP]$)

Figure 1 shows the curves of potentiometric titration of PVP with sodium hydroxide (1a, 2a) and hydrochloric acid (1b, 2b, 1c, 2c) in the absence and presence of Pd^{2+} (1a), Fe^{3+} (2b), Cu^{2+} (3b) ions at T = 298 K, I = 0.10 mol/L (potentiometric titration curves for other values of temperature and ionic strength have a similar appearance).

As can be seen from Figure 1, the titration curves in the presence of complexing metal ions are in a more acidic region than in their absence, indicating the complexation process between the polymer ligand and the metal ion.

A modified Bjerrum method was used to interpret the bias of the titration curves. The obtained data, performed with its use, are presented in Table 1.

Table 1 – The calculated values of the Bjerrum's formation functions of PVP–$PdCl_2$, PVP–$CuCl_2$, PVP–$FeCl_3$ systems (T = 298K, I = 0.10 mol/L)

System	$[LH^+]$, mol/L [a]	[L]. mol/L [b]	$[L_C]$, mol/L [c]	pL [d]	n [e]
PVP – Pd^{2+}	$2,48 \cdot 10^{-4}$	$0,01 \cdot 10^{-5}$	$3,08 \cdot 10^{-3}$	6,89	2,99
	$6,01 \cdot 10^{-4}$	$0,04 \cdot 10^{-5}$	$2,73 \cdot 10^{-3}$	6,39	2,65
	$9,49 \cdot 10^{-4}$	$0,09 \cdot 10^{-5}$	$2,38 \cdot 10^{-3}$	6,09	2,31
	$13,00 \cdot 10^{-4}$	$0,15 \cdot 10^{-5}$	$2,03 \cdot 10^{-3}$	5,83	1,97
	$16,40 \cdot 10^{-4}$	$0,26 \cdot 10^{-5}$	$1,69 \cdot 10^{-3}$	5,59	1,64
	$19,80 \cdot 10^{-4}$	$0,44 \cdot 10^{-5}$	$1,35 \cdot 10^{-3}$	5,36	1,31
	$23,20 \cdot 10^{-4}$	$0,78 \cdot 10^{-5}$	$1,00 \cdot 10^{-3}$	5,11	0,97
	$26,60 \cdot 10^{-4}$	$1,20 \cdot 10^{-5}$	$0,66 \cdot 10^{-3}$	4,92	0,31
PVP - Cu^{2+}	$0,99 \cdot 10^{-4}$	$3,46 \cdot 10^{-1}$	$9,00 \cdot 10^{-4}$	0,46	2,7
	$1,99 \cdot 10^{-4}$	$2,81 \cdot 10^{-1}$	$8,01 \cdot 10^{-4}$	0,55	2,4
	$2,99 \cdot 10^{-4}$	$0,76 \cdot 10^{-1}$	$7,02 \cdot 10^{-4}$	1,12	2,1
	$3,97 \cdot 10^{-4}$	$0,69 \cdot 10^{-1}$	$6,03 \cdot 10^{-4}$	1,16	1,8
	$4,97 \cdot 10^{-4}$	$0,71 \cdot 10^{-1}$	$5,03 \cdot 10^{-4}$	1,15	1,5
	$5,96 \cdot 10^{-4}$	$0,68 \cdot 10^{-1}$	$4,03 \cdot 10^{-4}$	1,17	1,2
PVP – Fe^{3+}	$0,64 \cdot 10^{-3}$	$1,07 \cdot 10^{-3}$	$11,6 \cdot 10^{-3}$	2,97	1,34
	$1,52 \cdot 10^{-3}$	$1,51 \cdot 10^{-3}$	$10,3 \cdot 10^{-3}$	2,82	1,19
	$2,36 \cdot 10^{-3}$	$1,44 \cdot 10^{-3}$	$9,50 \cdot 10^{-3}$	2,84	1,10
	$3,42 \cdot 10^{-3}$	$1,58 \cdot 10^{-3}$	$8,30 \cdot 10^{-3}$	2,80	0,96
	$4,18 \cdot 10^{-3}$	$1,20 \cdot 10^{-3}$	$7,90 \cdot 10^{-3}$	2,92	0,91
	$5,21 \cdot 10^{-3}$	$1,17 \cdot 10^{-3}$	$6,90 \cdot 10^{-3}$	2,93	0,80
	$6,38 \cdot 10^{-3}$	$1,23 \cdot 10^{-3}$	$5,70 \cdot 10^{-3}$	2,91	0,66

Not: [a] $[LH^+]$ – concentration of the protonated ligand groups; [b] [LH+] – concentration of the free ligands which are not involved in a complexing process; [c] $[L_C]$ – concentration of the ligand groups connected in a complex; [d] pL or -lg[L] – concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pKα + mlg[L]/[LH+], where m - the empirical coefficient considering interlink interaction of a polymeric chain; [e] n – Bjerrum's formation functions or average coordination number of a metal ion.

The calculated data confirm the formation of PMC with the composition [Me]:[L] = 1:3 in the PVP–Pd^{2+}, PVP–Cu^{2+} systems, and with the composition [Me]:[L] = 1:4 in the PVP–Fe^{3+} system. It is known that transition metal ions, when interacting with polymers, may not realize their maximum coordination number, since the ions of these metals can be coordinated to saturate with anionic acids or solvent molecules [12]. In turn, steric repulsion between large ligands in volume and electrostatic mutual repulsion of anion ligands when they are replaced by water molecules at a positively charged metal ion can also inhibit the coordination of additional ligands [13].

For a more detailed understanding of the complexation of high-molecular-weight ligands with metal ions, it is necessary to calculate the changes observed in this important thermodynamic parameters, such as Gibbs' energy, enthalpy and entropy of these processes. Since systems involving high-molecular compounds are complex, in this connection, the authors of a number of papers [14,15] suggested that the classical laws of thermodynamics can also be applied to systems with polymeric ligands.

From table 2 it follows that the most stable complex is PMC based on PVP and iron(III) chloride. This fact is due to the following factors: first, the complex formation reaction can be explained using the theory of acids and Lewis bases. According to the Lewis theory, acids are ions or compounds that accept a pair of electrons, i.e. such particles are electron acceptors. Thus, metal ions can be considered as polybasic acids with a deficiency of electronic pairs, corresponding to the maximum coordination number, which form bonds with bases. Secondly, the strength of the acid increases with increasing valence (in the systems under consideration, palladium and copper are in the bivalent state, and iron in the trivalent state). It is also known that metal ions are divided into three large groups: the first group is alkaline and alkaline-earth elements; the second group – transition metals with d^{10}- or d^8-electron configuration (Pd^{2+}, Cu^{2+}), which are more inclined to form stable complexes with ligands through sulfur, arsenic, phosphorus atoms; the third, largest group includes transition metal ions with partially filled d-orbitals.

Ions of metals of this group, first of all, form complexes with nitrogen and oxygen-containing ligands. According to Pearson's theory [16], Pd^{2+}, Cu^{2+} ions are soft acids, while the Fe^{3+} ion is a hard acid, and the oxygen atom is a hard base. The most stable complexes are formed by the interaction of hard acids and bases, on the one hand, and soft acids and bases, on the other one. From this it follows that among the represented metals, iron ions have a high affinity for oxygen [17].

Calculation of thermodynamic parameters showed that the complex formation of PVP with Pd^{2+}, Cu^{2+}, Fe^{3+} ions is characterized by negative values of Gibbs' energy, which indicates a spontaneous process of PMC formation in these systems (Table 2). The following pattern is observed for the Pd^{2+}–PVP complex: a positive value of the change in enthalpy ($\Delta_r H^0$) in the temperature range 298–318 K indicates the endothermic nature of polycomplex formation, therefore, with an increase in temperature in the specified interval, the stability of the latter increases. And in the temperature range 318-343K, the complexation process is accompanied by the release of heat (an exothermic process), as a result of which the strength of the polymer-metal complex decreases with increasing temperature. The obtained fact of the ambiguous effect of temperature on the complexation process is probably due to conformational changes in the structure of the polymer-polyvinylpyrrolidone as shown in [18]. The authors found that the conformational changes of PVP in an aqueous medium are accompanied by exoeffects, the values of which depend on the temperature and molecular weight of the polymer.

The complexation reactions of copper and iron ions with PVP are accompanied by exoeffects, as indicated by negative enthalpy values. With an increase in temperature in the temperature range of 298–318 K, the stability of PMC decreases.

Complexation processes in binary PVP–Pd^{2+} and PVP–Cu^{2+} systems are characterized by positive entropy values, which is caused by the destruction of the hydration shells of PVP ligand groups and the displacement of water molecules from the first coordination sphere of metal ions. The formation of iron complexes with PVP is characterized by negative values of entropy change. Negative entropy change ΔS with a negative enthalpy change ΔH indicates that the reaction under study is possible at sufficiently low temperatures and the linear dependence of Δ on ΔS is described by the equation $\Delta H = -0.36\Delta S + \text{const}$, which indicates donor-acceptor interaction [8].

Table 2 – Thermodynamic characteristics of the complexation of Pd^{2+}, Fe^{3+}, Cu^{2+} ions with PVP

System	T, K	$\lg\beta^0$	- Δr G, kJ/mol	± Δr H, kJ/mol	±Δr S, J/(mol·K)
PVP – Pd^{2+}	298	9,10±0,08	56,94±0,62	1288,4±0,10	4541,7±0,15
	318	14,20±0,20	109,17±0,69		
	343	11,20±0,09	81,10±0,60	898,5±0,12	2335,3±0,12
PVP – Cu^{2+}	298	14,5±0,19	82,719±0,09	175,7±0,30	218,621±0,94
	308	14,4±0,18	84,906±0,11	487,5±0,80	1307,13±0,57
	318	11,50±0,25	71,834±0,08	244,9±0,90	544,255±0,30
PVP – Fe^{3+}	298	31,00 ± 0,01	176,849 ± 0,01	725,653±0,01	1841,620±0,01
	318	23,00 ± 0,03	140,016±0,04	174,334±0,01	5041,910±0,02
	343	10,10± 0,02	64,397±0,05	1134,375±0,01	3213,150±0,06

The nature of the modifying effect of PVP on Pd(II), Cu(II), Fe(III) ions and the possible molecular structure of the PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$ complexes was studied using IR spectroscopy (Figure 2). As can be seen from the IR spectra, the peak characteristic of the C=O bond in PVP becomes asymmetric after the addition of metal chlorides, which indicates a strong interaction between PVP and Pd(II), Cu(II), Fe(III) in the complexes PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$. The IR spectra of the complexes under study contain a band at 3400 cm^{-1}, characteristic of PVP. The carbonyl group in PVP is characterized by a peak at 1651 cm^{-1}, extended due to the C=N bond in the lactam ring. This band shifts to 1510–1645 cm^{-1} in the studied complexes. Differences in the IR spectra of PVP and PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$ complexes are observed as a result of donor-acceptor interaction between the oxygen atom in the polymeric ligand PVP and metal ions – complexing agents [18-20].

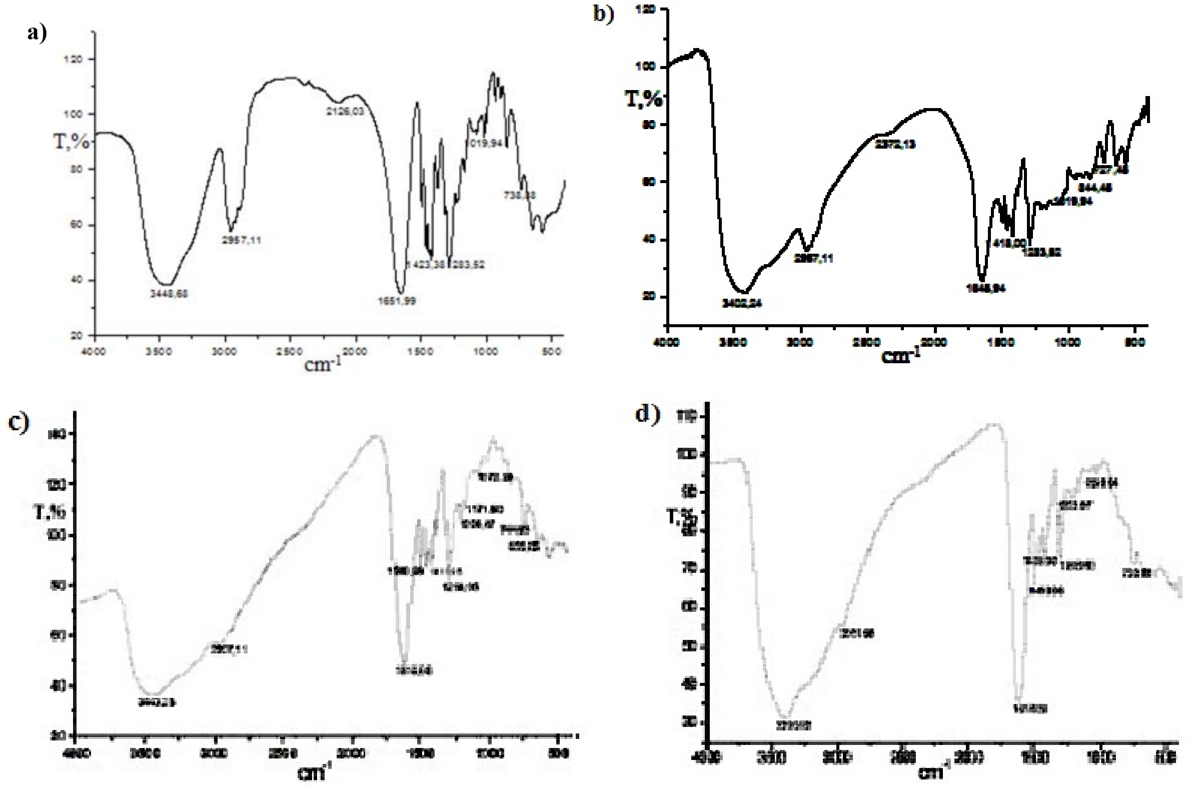

Figure 2 – IR spectra of PVP (**a**) and complexes of $[Pd(PVP)_3Cl_2]$ (**b**), $[Cu(PVP)_3Cl_2]$ (**c**), $[Fe(ПВП)_4(H_2O)_2Cl_3]$ (**d**)

To study the surface of polymer-metal complexes, the method of scanning electron microscopy was used (Figure 3). Analysis of micrographs indicates the formation of polymer films with a porous inhomogeneous amorphous structure.

Conclusion

Thus, the composition of the PMC was defined by modifying method of Bjerrum. The coordination of the polymer ligand of PVP in the complexes was confirmed by IR spectroscopy and scanning electron microscopy. The morphology and peculiarities of their surface were studied. It has been established that the oxygen atoms of polymeric ligands participate in the formation of a coordination bond with metal ions of complexing agents. Electron microscopy results indicate the amorphous structure of the complexes. The thermodynamic parameters of the PMC were calculated, which indicate the process of complexation between metal ions and the polymer ligand.

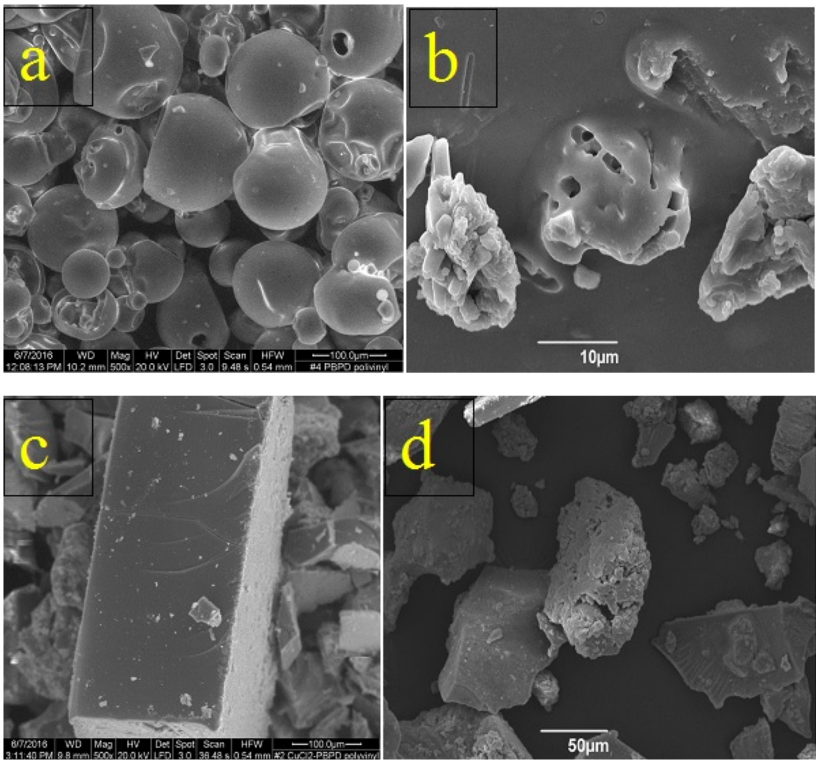

Figure 3 – SEM images of PVP (**a**) and complexes PVP-$PdCl_2$ (**b**),
PVP-$CuCl_2$ (**c**), PVP-$FeCl_3$ (**d**)

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ПАЛЛАДИЙ(II), МЫС(II), ТЕМІР(III) ХЛОРИДТЕРІ ЖӘНЕ ПОЛИВИНИЛПИРРОЛИДОН НЕГІЗІНДЕГІ КЕШЕНДІ ҚОСЫЛЫСТАРДЫҢ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Палладий(II), мыс(II), темір(III) хлоридтері және поливинилпирролидон негізіндегі полиметалдық кешенді қосылыстардың құрамы потенциометрлік және кондуктометрлік әдістермен анықталған. Бьеррумның түзілу функциясы мәндері есептелген. Алынған тәжірибиелік мәліметтерге сүйене отырып, титрлеу қисықтары тұрғызылып, әрекеттесуші құраушылардың оптималды мольдік қатынастары табылған. Есептеу нәтижесінде алынған мәліметтер палладий және мыс кешенді қосылыстарының түзілгендігін дәлелдейді, ондағы поливинилпирролидонның үш буынына бір металл–кешентүзгіш ионы келеді. Ал темірдің полимерлі кешенді қосылысында поливинилпирролидонның төрт буынына бір металл–кешентүзгіш ионы сәйкес келеді. Металл – кешентүзгіш иондарында координациялық қаныгу үдерісі еріткіш молекуласы немесе металл тұздары аниондары есебінен жүзеге асады. ИҚ–спектроскопия және сканирлеуші электрондық микроскопия (СЭМ) әдістері көмегімен синтезделген кешенді қосылыстардың құрылысы және морфологиясы зерттелген. Полимерлі лигандтағы оттегі атомы металл – кешентүзгіш ионымен координациялық байланыс түзуге қатысатындығы дәлелденген. Электрондық микроскопия нәтижесі кеуекті біртекті емес аморфты құрылымға ие кешенді қосылыстың полимерлі қабықшасының түзілетіндігін көрсетеді.

Түйін сөздер. Поливинилпирролидон, палладий, мыс, темір, кешентүзілу, Бьеррум әдісі, тұрақтылық константасы, құрамы, термодинамика.

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ИЗУЧЕНИЕ СОСТАВА КОМПЛЕКСОВ НА ОСНОВЕ ХЛОРИДОВ ПАЛЛАДИЯ(II), МЕДИ(II), ЖЕЛЕЗА(III) И ПОЛИВИНИЛПИРРОЛИДОНА

Аннотация. Составы полимерметаллических комплексов на основе хлоридов палладия(II), меди(II), железа(III) и поливинилпирролидона были установлены потенциометрическим и кондуктометрическим методами. Были рассчитаны функции образования Бьеррума. По полученным экспериментальным данным по определению состава комплекса были построены кривые титрования и найдены оптимальные мольные соотношения реагирующих компонентов. Полученные рассчитанные данные свидетельствуют об образовании полимерных комплексов палладия и меди, в которых на три составных монозвена поливинилпирролидона приходится один ион металла-комплексообразователя. А в случае полимерного комплекса железа на четыре составных монозвена поливинилпирролидона приходится один ион металла-комплексообразователя. Координационная насыщенность металлов-комплексообразователей в этих комплексах осуществляется за счет молекул растворителя или аниона солей металлов. Методами ИК-спектроскопии и сканирующей электронной микроскопии (СЭМ) исследованы строение и морфология синтезированных комплексов. Установлено, что атомы кислорода полимерных лигандов принимают участие в образовании координационной связи с ионом металла-комплексообразователя. Результаты электронной микроскопии указывают на образование полимерных плёнок комплекса с пористой неоднородной аморфной структурой.

Ключевые слова: поливинилпирролидон, палладий, медь, железо, комплексообразование, метод Бьеррума, константы устойчивости, состав, термодинамика.

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NMR SPECTRA OF PHOSPHORYLATED CARBAMIDE-CONTAINING HETEROCYCLES: PECULIARITIES OF CHEMICAL SHIFTS FROM THE VALENCE STATE OF THE PHOSPHORUS AND THE SIZE OF THE CYCLE

Abstract. The article discusses the results of using NMR spectroscopy to study the structure and flexibility of the skeleton of the analyzed molecules of phosphaze compounds and the electronic environment of nitrogen and phosphorus atoms. The authors carried out a cumulative system analysis of chemical shifts in the ^{31}P and ^{13}C NMR spectra of 89 phosphorus derivatives of carbamidecontaining heterocycles, which differ in the valence state of the phosphorus atom, the size of the cycle and the method of cycle junction.

Key words: heterocyclic compounds, NMR spectroscopy, phosphazo compounds, phosphorylated carbamide containing heterocycles (PCCH), 3-coordinated phosphorus atom, 5-coordinated phosphorus atom.

Introduction

Phosphazaheterocycles containing an urea fragment and a phosphoryl group in the cyclic skeleton are attractive because these links of molecules, acting as the key structural elements of these compounds, give them a skeleton of the structure and contribute to the formation of multifunctional reaction centers. The simultaneous combination of urea fragments and phosphoryl groups in a molecule makes it possible to impart specific physicochemical and practically useful properties to the target substance, the investigation of which is the subject of many studies, including and using NMR spectroscopy.

The use of NMR spectroscopy to study the structure of phosphaza compounds allows not only to identify the compounds, but also to judge the flexibility of the skeleton of the analyzed molecules and the electronic environment of nitrogen and phosphorus atoms. In addition, a generalized analysis of chemical shifts of an array of phosphazacycles helps to reveal their characteristics for the considered range of compounds. However, so far no attempts have been made of the cumulative analysis of an array of NMR spectral data of phosphorus-containing urea-containing heterocycles.

In order to fill this gap, we carried out a cumulative system analysis of chemical shifts in the 31P and 13C 89 NMR spectra of phosphorus-containing urea-containing heterocycles, which differ in the valence state of the phosphorus atom, the size of the cycle and the method of junction cycles.

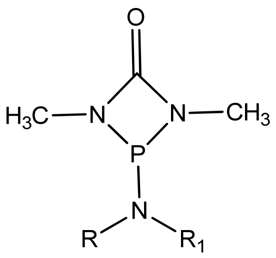
In a number of works [1–14] devoted to the synthesis of the corresponding phosphazacycles, the ^{31}P NMR spectroscopy data was used to identify a larger number of different phosphorylated carbamide containing heterocycles (PCCH). This paper summarizes the intervals of changes in chemical shifts (CS) of PCCH in the ^{31}P NMR spectra, which are illustrated by the data given depending on the valence state of phosphorus, the size of the cycle and the method of junction.

Results and discussion

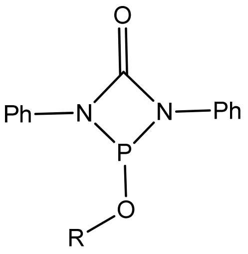
CHEMICAL SHIFTS OF 3-COORDINATED PHOSPHORUS ATOM IN PCCH NMR SPECTRA

Analyzed PCCH containing 3 valence phosphorus atom are represented by 4-membered phosphazacycles (diazaphosphetidinediones 1-6), 5-membered phosphazacycles (diaza-phospholidinediones 7-10) and 6-membered phosphazacycles (triazaphosphorinandiones 11-25).

A comparative analysis of CSphosphetidinediones1-2 [1] and 3-6 [2] shows that, for all other equal structural parameters, the electronegativity of the substituent, directly attached to the phosphorus atom,has a decisive influence on CS. In other words, in the series of phosphetidinediones1-6 alkoxy groups (compounds 3-6) cause pronounced disshielding of the phosphorus atom (10 ppm), rather than amino groups (compounds 1-2)



1-2



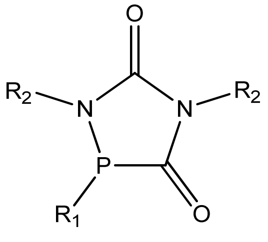
3-6

1 - R_1=Me, R=Ph (83.6);
2 - R_1=Me, R=циклогексил (81.9);
3 - R=Me (95.2);
4 - R=Et (93.1);
5 - R= i-Pr (92.3);
6 - R=n-Bu (93.1)

As one can see from the above data, the formation of N, N-P-N and N, N-P-O units in the 4-membered PCCH cycle of the compounds 1-6 contributes to the appearance ofCSof phosphorus atoms in the positive spectral region in the interval 81.9-95.2 ppm.

The CS values of 5-membered PCCH 7-10 [3] correspond to the interval from 24.2 to 38.3 ppm, which indicate a significant screening of the phosphorus atom in the diazaphospholidinediones 7-10 compared to the 4-membered phosphetidinones1-6. In this case, the strong-field shift of phosphorus atoms in compounds 7–10 compared with phosphazacycles 1–6 is due to the isolation of the second urea nitrogen atom by the carbonyl group at the 5th position of the cycle, which excludes its direct electronegative effect on the phosphorus atom. At the same time, a similar effect of the carbonyl group, as can be seen from the comparison of CS, is not comparable with the influence of the nitrogen atom.

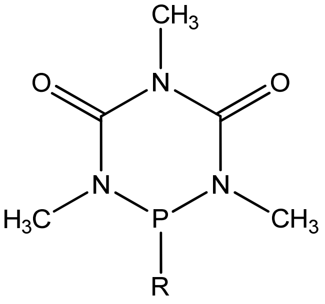
Thus, the formation of the N, C-P-C = O link in PCCH 7-10, compared with FCSG 1-6, causes a significant strong-field shift (by 50 ppm) of phosphorus.



7-10

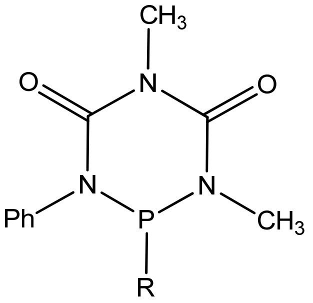
7 - R_1=R_2=Me (30.7);
8 - R_1=Me, R_2= n-Bu (24.2);
9 - R_1=i-Pr, R_2=Me (30.8)
10 - R_1= CH_3, R_2 = C_6H_5 (38.3)

Turning to the 6-membered PCCH 11-25 [4-6], it should be noted that the influence of substituents (R) in the N, N> P-R unit on the CS of the ^{31}P nucleus appears in the interval of 66.7-106.9 ppm.



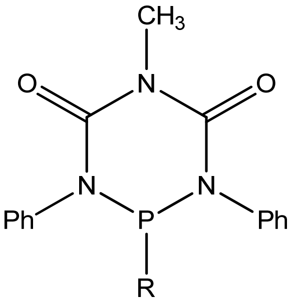
11-18

11 - R=NMe_2 (82.7 ppm);
12 - R=NEt_2 (80.1 ppm);
13 - R=NPh_2 (66.7 ppm);
14 - R=$NHCH_2CH_2Cl$ (70.6 ppm);
15 - R=$N(CH_2CH_2Cl)_2$ (82.3 ppm);
16 - R=OMe (90.6 ppm);
17 - R=$OSi(Me)_2$ (90.6 ppm);
18 - R=$N(CH_3)CH_2CH_2N(CH_3)_2$ (81.0 ppm);



19-21

19 - R=Me (80.5 ppm);
20 - R=Cl (106.9 ppm);
21 - R=Ph (68.4 ppm);



22-25

22 - R=Me (79.9 ppm);
23 - R=Ph (68.7 ppm);
24 - R=Cl (101.6 ppm);
25 - R=NMe_2 (79.3 ppm)

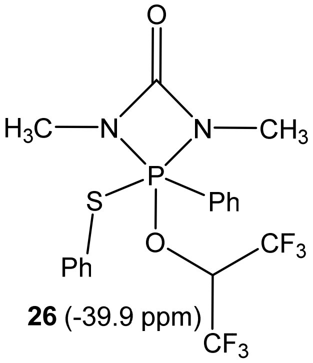
At the same time, in the series of triazaphosphorinandiones of the general formula 11-25 CS of the phosphorus atom bound to the R group, depending on the nature of the substituent in the P-R link, shifts to a weaker field in the series: P-C (compounds 19, 21-23 [6]) <P-N (Compounds 11-15 [6], 18 [4], 25 [6]) <P-O (compounds 16, 17 [5]) - P-Cl (compounds 20, 24 [6]). The established order of CS change in phosphazacycles 11-25 is in accordance with the electronegativity of the substituent R, directly attached to the phosphorus atom. The displacement of electrons by the R substituent from the phosphorus atom in these compounds contributes to the localization of the lone electron pair at the skeletal carbamide nitrogen atoms, thereby causing an additional contribution to the weak-field shift of phosphorus atoms.

From the CS data presented, it is clear that the effect of the distribution of electrons in the carbamide unit of the heterocyclic fragment of molecules 11–25 is worse than the direct displacement of electrons within the P – R sigma bond in the considered phosphazocycles. It is quite well established that CS of the three-coordinated phosphorus atom in PCCH 1-25 locate in the positive spectral region within 24.2-106.9 ppm and in the given corridor, the CS values depend on the chemical environment of the phosphorus atom.

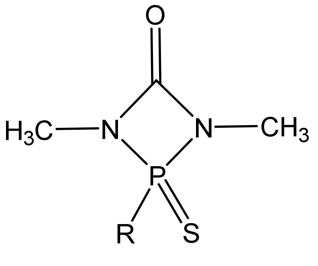
CHEMICAL SHIFTS OF THE 5-COORDINATED PHOSPHORUS ATOM IN PCCH NMR SPECTRA

A general analysis of the changes in ^{31}P CS in PCCH shows that 3-coordinated phosphazacycles 1–25 exhibit CS in the positive spectral region, whereas for 5-coordinated phosphazacycles this property is mixed. In other words, CH for 5-coordinated phosphazacycles 26–49 [7, 8] is characteristic both in the positive spectral region and in the negative region with a clear tendency toward the latter.

The change in cholesterol ^{31}P CS in a series of thiylateddiazaphosphophetidinone derivatives 26-49 is very interesting. So, if thionic phosphetidinones 27-34 [7] exhibit ^{31}P CS in the positive spectral region (58.5–83.1 ppm), regardless of the nature of the R substituent, then thiylatedchlorophosphetidinones 35-46 (-44.0; -49.6 ppm) and alkoxyphosphetidinone 26, (-39.9 ppm) show negative CS values [8].

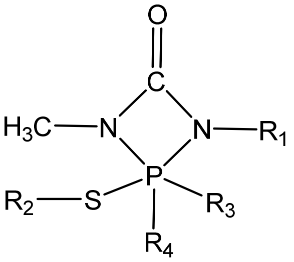


26 (-39.9 ppm)



27-34

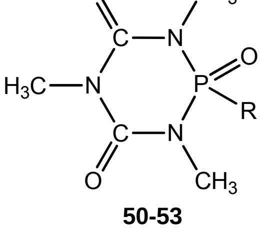
27 - R=Cl (59.20 ppm);
28 - R=NMt$_2$ (64.4 ppm);
29 - R=Net$_2$ (65.2 ppm);
30 - R=(CH$_2$)$_4$ (58.5 ppm);
31 - R=OMe(67.5 ppm);
32 - R=SMe$_2$ (83,1 ppm);
33 - R=NPh$_2$ (58.5 ppm);
34 - R=N-(циклогексил)$_2$ (58.8 ppm)



35 - R_1 = Ph, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-44,3 ppm)
36 - R_1 = Ph, R_2 = Ph, R_3 = Ph; R_4 = Cl (-49,6 ppm)
37 - R_1 = Ph, R_2 = CH_3, R_3 = CH_3; R_4 = Cl (-44,0 ppm)
38 - R_1 = Ph, R_2 = Ph, R_3 = CH_3; R_4 = Cl (-46,2 ppm)
39 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = CH_3; R_4 = Cl (-44,6 ppm)
40 - R_1 = 4-$CH_3C_6H_4$, R_2 = Ph, R_3 = CH_3; R_4 = Cl (-45,6 ppm)
41 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = CH_2Cl; R_4 = Cl (-47,33 ppm)
42 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = t-Bu; R_4 = Cl (-20,6 ppm)
43 - R_1 = 4-$O_2NC_6H_4$, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-48,6 ppm)
44 - R_1 = 4-$O_2NC_6H_4$, R_2 = Ph, R_3 = Ph; R_4 = Cl (-50,9 ppm)
45 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-43,8 ppm)
46 - R_1 = 4-$CH_3C_6H_4$, R_2 = Ph, R_3 = Ph; R_4 = Cl (-48,7 ppm)
47 - R_1 = CH_3, R_2 = Ph, R_3 = Ph; R_4 = 4-$O_2NC_6H_4$ (-54,1 ppm)
48 - R_1 = CH_3, R_2 = 4-$CH_3C_6H_4$, R_3 = t-Bu; R_4 = 4-$O_2NC_6H_4$ (-34,1 ppm)
49 - R_1 = CH_3, R_2 = 4-$CH_3C_6H_4$, R_3 = Ph; R_4 = 4-$O_2NC_6H_4$ (-53,9 ppm)

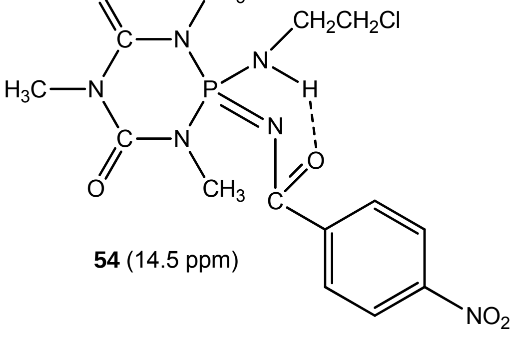
In the series of phosphetidinones 26-49 in the first approximation, the carbamide group of the heterocycle is equivalent in its effect on the phosphorus atom. Consequently, when comparing CS of the phosphorus atoms in these phosphazacycles, their positive shift is provided by the sp^2 hybridized state of the thionic group, and the negative shift of CS, along with other groups, is mainly due to the shielding effect of the thiol group, since chlorine atoms and alkoxy groups are present in all compounds 26–49.

One of the interesting features in the data analysis ^{31}P NMR spectra of phosphazacycles 50-53 [9] and 54-57 [10] is that the location of CS of phosphorus atom significantly depends on the hybridization of the P = X bond. So, for example, a distinct dependence of the CS shift to the negative region in the series P = N <P = O <P = S in compounds 50-57 is revealed.

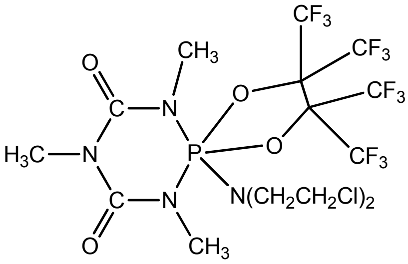


50-53

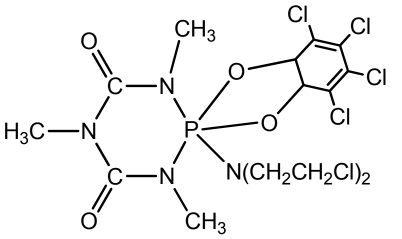
50 - R=NHCH$_2$CH$_2$Cl (3.1 ppm);
51 - R=N(CH$_2$CH$_2$Cl)$_2$ (3.1 ppm)
52 - R=Cl (5.1 ppm);
53 - R=N(CH$_2$CH$_2$)$_2$ (4.2 ppm)



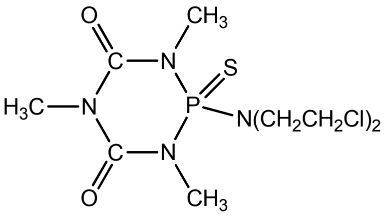
54 (14.5 ppm)



55 (-36.0 ppm)



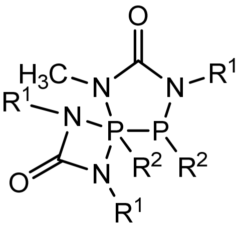
56 (-38.8 ppm)



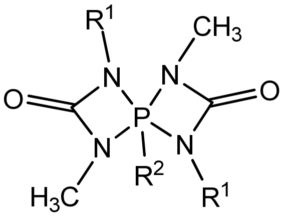
57 (-58.8 ppm)

The effect of other substituents at the phosphorus atom in these compounds on the screening of the P atom is not as obvious as the change of the heteroatom in the P = X fragment of the PCCH examined.

For the series of spiro compounds 58-75 with the nodal phosphorus atom CS ^{31}P become more characteristic. All PCCH with the nodal phosphorus atom in the spiro compounds 58-62 [11] and 63-75 [12] give only negative CS ^{31}P values (from -64.3 ppm to -79.9 ppm). For example, in phosphazacycles 58, 59 there are two CH ^{31}Ps (wherein in different valence states), however, CS of the nodal atom of phosphorus can be clearly recognized due to its strong negative shift (-64.3; -69.0 ppm), while the three-coordinated atom P gives positive CH in the region of 1.9-6.3 ppm.

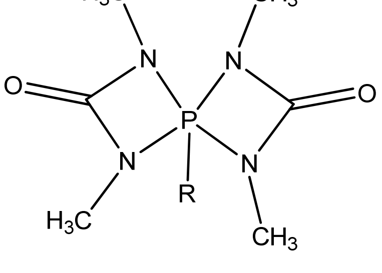


58 - R_2=Me, R_1=Ph (1.9; -69.0 ppm)
59 - R_1=R_2=Ph (6.3; -64.3 ppm)



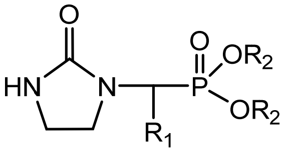
60 - R_1 = C_6H_4-CF_3-3, R_2 = C_6F_5 (-79.9 ppm)
61 - R_1 = Me, R_2 = Ph (-67.8 ppm)
62 - R_1 = Ph, R_2 = Ph (-68,5 ppm)

The intervals of CS ^{31}P changes for spiro compounds 63-75 [12] are largely determined by the direct influence of the substituents R at the phosphorus atom, and their oscillation range varies from -51.4 ppm to -119.1 ppm Attention is drawn to the fact that by varying halogen-containing substituents R for spirocycles 63-66 CS ^{31}P become more negative in the series: F <Cl <Br <I. The observed order of CS change of the nodal atom of phosphorus in compounds 63-66 is in full accordance with the electronegative properties of halogens. The phenyl group in the spirocycle 60-62, 70, 72 sensitively screens the phosphorus atom compared with the methyl derivatives 68, 69, 71, 73-75, which is most likely due to the anisotropic effect of the aromatic core.



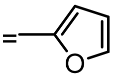
63 - R = Cl (-56.0 ppm);
64 - R = F (-51.4 ppm);
65 - R = Br (-73.3 ppm);
66 - R = I (-119.1 ppm);
67 - R = CN (-89.4 ppm);
68 - R = MeP($SiMe_3$) (-56.1 ppm);
69 - R = OMe (-57.0 ppm);
70 - R = OPh (-61.1 ppm);
71 - R = SMe (-56.0 ppm);
72 - R = SPh (-59.4 ppm);
73 - R = NMe_2 (-57.3 ppm);
74 - R = N_3 (-66.2 ppm);
75 - R = $NPMe_3$ (-71.0 ppm)

One of the factors affecting the location of CS ^{31}P in the PCCH is the possibility of molecular flexibility of a heterocycle that is not directly related to the phosphorus atom. So, in imidazolidone 76-85, this possibility leads to shielding, and for imidazolidones 86-89 – to unshielding of the phosphorus atom compared to phosphoric acid itself or its esters, as indicated by the significantly strong-field shift of cholesterol, observed on going to compounds 76-85 and weak-field shift on going to compounds 86-89.

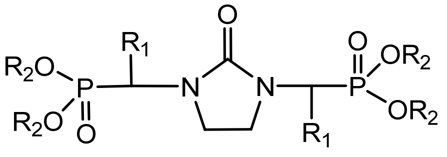


76-80

76 - R_1, R_2= C_6H_5 (-12,4 ppm);

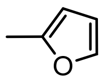
77 - R_1 =  , R_2= C_6H_5 (-9,8 ppm);

78 - R_1 = CH_3, R_2= C_6H_5 (-21,2 ppm);
79 - R_1 = C_6H_5, R_2= $ClCH_2CH_2$ (-12,5 ppm)
80 - R_1 = C_6H_5, R_2= H (-16,4 ppm);

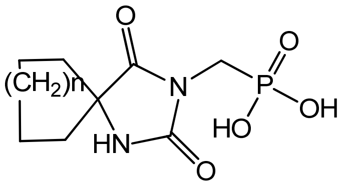


81-85

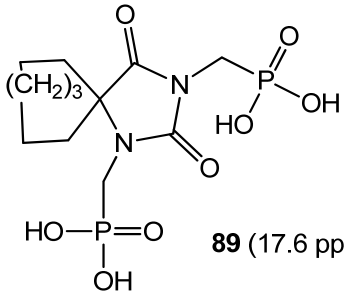
81 - R_1, R_2= C_6H_5 (-11,6 ppm);

82 - R_1 =  , R_2= C_6H_5 (-9,2 ppm);

83 - R_1 = CH_3, R_2= C_6H_5 (-16,2 ppm);
84 - R_1 = C_6H_5, R_2= $ClCH_2CH_2$ (-11,0 ppm)
85 - R_1 = C_6H_5, R_2= H (-15,8 ppm);



86 - n=0 (18.1 ppm, 20,6 ppm)
87 - n=1 (15.5 ppm, 19,4 ppm)
88 - n=2 (17.6 ppm, 20,0 ppm)



89 (17.6 ppm, 21,1 ppm)

Conclusion

Comparative consideration of CS of the phosphorus atom in PCCH with five-coordinated phosphorus shows that they undergo a negative shift, and their location mainly depends on the hybrid state of P atom in the cycle and the junction type of the cycles

An attempt to make a comparative analysis of CS of the carbonyl group (C = O) in PCCH did not reveal significant differences due to their changes in a narrow range of values (151-156 ppm), regardless of the valence state of the phosphorus atom in the cycle and the method of junction of cycles (for example, in the spiro compounds and bicycles 58-75). Only some shielding of C = O-group in PCCH compared with urea itself (159.5 ppm) [15] and the bicyclic bisurea of octane series - glycoluril (161.9 ppm) [15] is of interest. The observed effect appears to be determined by an increase in steric stresses (compression) in PCCH due to the limitations in the flexibility of their skeleton, and, as a consequence, by strengthening the order of the amide bond. The informational content of the NMR spectra analysis of PCCH is somewhat reduced due to the absence of CS data of the NH groups. But this circumstance is due to the fact that almost all synthesized and identified PCCH given in [1-14] contain substituents at the nitrogen atoms.

The dependences of chemical shifts on the structure of bicyclic bimocarbons and spiro compounds obtained can be used to study the properties of macromolecular nitrogen-containing systems, as shown by the example of some nitrogenous alkaloids [16].

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ФОСФОРИЛИРЛЕНГЕН КАРБАМИДҚҰРАМДЫ ГЕТЕРОЦИКЛДАРДЫҢ ЯМР СПЕКТРЛАРЫ: ФОСФОРДЫҢ ВАЛЕНТТІЛІК ҚҰРАМЫ МЕН ЦИКЛДАР ӨЛШЕМІНЕ БАЙЛАНЫСТЫ ХИМИЯЛЫҚ ҚОЗҒАЛЫСТАРДЫҢ ЕРЕКШЕЛІКТЕРІ

Аннотация. Мақалада талданып отырған фосфазақосылыстар молекулаларының құрылымы мен қаңқаларының иілгіштігін және азот пен фосфор атомдарының айналасындағы электрондарды зерттеуде ЯМР-спектроскопияны қолдану нәтижелері талқыланады. Авторлар 89 карбамидқұрамды гетероциклдардың фосфортуындыларын ЯМР ^{31}P и ^{13}C спектрларындағы химиялық қозғалыстарды жүйелі талдау жүргізілген. Бұл қосылыстар бір-бірінен фосфор атомының валенттілік күйімен, циклдар өлшемімен және циклдардың бір-бірімен қосылу әдісі бойынша ерекшеленеді.

Түйін сөздер:гетероциклдықосылыстар, ЯМР-спектроскопия, фосфазоқосылыстар, фосфорилирленген карбамидқұрамды гетероциклдар (ФКҚГ), 3-координирленгенфосфор атом, 5-координирленгенфосфор атом.

УДК 543.429

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СПЕКТРЫ ЯМР ФОСФОРИЛИРОВАННЫХ КАРБАМИДСОДЕРЖАЩИХ ГЕТЕРОЦИКЛОВ: ОСОБЕННОСТИ ХИМИЧЕСКИХ СДВИГОВ ОТ ВАЛЕНТНОГО СОСТОЯНИЯ ФОСФОРА И РАЗМЕРА ЦИКЛА

Аннотация. В статье обсуждаются результаты применения ЯМР-спектроскопии для изучения структуры и гибкости скелета анализируемых молекул фосфазасоединений и электронногоокружения атомов азота и фосфора. Авторами проведен совокупный системный анализ химических сдвигов в спектрах ЯМР ^{31}P и ^{13}C 89 фосфорпроизводных карбамидсодержащих гетероциклов, которые отличаются валентным состоянием атома фосфора, размером цикла и способом сочленения циклов.

Ключевые слова: гетероциклические соединения, ЯМР-спектроскопия, фосфазосоединения, фосфорилированные карбамидсодержащие гетероциклы (ФКСГ), 3-координированный атом фосфора, 5-координированный атом фосфора.

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SEPARATE DETERMINATION OF THE AMOUNT OF OIL EXTRACTED BY ONE WELL FROM TWO LAYERS

Abstract. The authors of this article proposed a different sampling technique for determining reservoir productivity. Relative shares of two in common developed layers in the general output of one production well are determined by vanadium content in oil of several neighboring wells working at each of productive layers separately. Results of experiments on mixture of oil of different layers of the Kalamkas field showed that concentration of vanadium changes in proportion to a volume ratio of oil that confirms competency of such offer.

Proposed method was approved in Martyshi and Southeast Kamyshitov multi-layer deposits. The flow rate of the studied reservoirs according to EPR spectroscopy data is in good agreement with the field data.

Unconditional advantages of the EPR method are its productivity providing a possibility of receiving the express – information, higher precision and reliability in comparison with the listed methods and no need to stop production wells when sampling oil for a research.

Key words: electronic paramagnetic resonance, photocolorimetric method, vanadium paramagnetism, relative flow rate, multilayer deposit.

To solve the problems of development of oil fields of Western Kazakhstan, R. N. Nasirov and others [1] used data from the study of vanadium paramagnetism. It is found that in the Kalamkas field in the context of productive layers there is a clear distinction between two independent deposits by paramagnetic features and vanadium distribution (in the upper – 200g/t, in the lower -140g/t). This gave rise to the authors argue that the vanadium content is a reliable correlation feature that can be used in monitoring the development of oil reservoirs.

In the geological and field analysis of oil field development it is necessary to have information about the operating modes of productive horizons. Basically, the control over the development of deposits is carried out by geophysical and hydrodynamic methods. However, for the most complete study of oil fields, it is desirable to use other, non-traditional methods of research.

In recent years, one of the promising areas of control over the development of the field was the study of changes in the physical, in particular optical and paramagnetic properties of oils.

I. F. Glumov and A. F. Gilmanshin [2] used the photocolorimetric method of separate determination of oil inflow into the well from two layers operated jointly. The relative debits were calculated according to the formulas:

$$q_1 = \frac{(K^{II} - K^*)}{(K^{II} - K^I)}; \tag{1}$$

$$q_{II} = 1 - q_1 , \tag{2}$$

where K ,^{I} K^{II} ,K^* - light absorption coefficients of oil, respectively, of the first, second layers and produced oil.

The main disadvantage of this method is the inability to directly determine the optical properties of oils with a significant content of colored substances (asphaltenes and resins). The method of electronic paramagnetic resonance (EPR) is devoid of this disadvantage and can be used for separate determination of reservoir productivity. Paramagnetism of oils is mainly due to the presence of various complex compounds V^{4+} and free radicals (FR) in them.

V. M. Arbuzov with co-authors [3] proposed to replace the optical density with the concentration of tetravalent vanadium or FR in formula (1) and then to determine the productivity of both layers. In one specially drilled well, first samples are taken from the upper layer, then from the lower and, finally, a mixture of oils from both layers is taken.

The authors of this article propose a different method of sampling to determine the productivity of layers. The relative share of the two jointly developed seams in the overall production rate of one producing well is based on the content of vanadium in the oil for a few nearby wells operating at each of the productive strata separately. The results of experiments on the mixing of oils from different layers of the Kalamkass field showed that the concentration of vanadium varies in proportion to the volume ratio of oils, i.e. confirmed the validity of such a proposal [4].

In the present work, using the EPR method, a new technique was introduced to the fields of Martyshi and Southeast Kamyshitov.

The above-salt oil and gas deposits in the Ural-Volga region are characterized by a complex geological structure, due to the influence of salt tectogenesis, as a result of which they are divided by numerous discharges into individual wings, blocks, fields. Oil and gas resources are dispersed in these blocks and fields.

The EPR method was used to estimate the productivity of the jointly operated I and II layers of the VII middle Jurassic horizon in the North-West wing of the Southeast Kamyshitov field. Well 7 receives oil from these formations. The content of vanadium in the oils of I and II layers is given in table.1. Its average concentration in these layers is 24.7% and 13.3%, respectively. According to the formulas (1) and (2) it is possible to determine the productivity of these layers: as a percentage of the well flow rate 7, it is 11 and 89, respectively. As can be seen from table 1, the productivity of the second layer is much higher compared to the productivity of the I layer, which, in our opinion, is due to their different permeability (table. 2) calculated from well testing data.

Table 1 - Determination of the relative flow rate of two jointly operated oil reservoirs at the Southeast Kamyshitov field

Well number	Horizon age	Oil production rate		Data according to EPR	
		t/day	%	V^{4+}.g/t	Oil production rate, %
The North–West wing					
7	J_2; VII (I+II layers)	29,3	100	23,5	11 (I layer)
					89 (II layer)
19	J_2; VII (I layer)	3,0	100	24,7	-
18	J_2; VII (II layer)	25,0	100	13,6	-
131	J_2; VII (II layer)	23.5	100	13,1	-
South-East wing					
117	J_2; VI	9,2	100	13,2	95(VI)
	J_2;VII				5 (VII)
123	J_2; VI	7,1	100	10,0	-
110	J_2;VII	3,3	100	71,1	-
16	J_2; VII	3,2	100	68,3	-

Table - Permeability of oil-saturated reservoirs in the middle Jurassic horizons, mkm^2

Horizon age	Permeability, 10^{-3} mkm
The North–West wing	
J_2; VII (I layer)	0,338
J_2;VII (II layer)	0,505
South-East wing	
J_2; VI	0,217
J_2;VII	0,070

High productivity of the VI horizon in comparison with the VII within the South-Eastern wing can be associated not only with its permeability (table.2), but also with the physical and chemical properties of the oil lying in it. The flow rate of the studied layers according to EPR spectroscopy is in good agreement with the field data.

To clarify the process of development by EPR, paramagnetic features of the oil field Martyshi (between the Ural - Volga) were studied). The main object of the development here consists of I the Neocomian and the Aptian - Neocomian horizons. According to the results of the development in previous years, it was assumed that the I Neocomian horizon either does not participate at all in this process, or takes a small part in it. To find out the share of the Neocomian horizon I in the total flow rate, the EPR method was used to analyze the vanadium content in the oils selected from the wells of joint operation of the I Neocomian and Apt - Neocomian horizons, as well as only the Apt - Neocomian horizon.

The average value of vanadium content from the oil of jointly operated horizons is 6.72 g/t, from the oil of the Apt - Neocomian horizon is 6.78 g/t. Apparently, the proximity of these values means that the Neocomian horizon I is practically not developed. The main reason for this, in our opinion, is a significant difference in the permeability of the layers, despite the fact that the other reservoir properties of the layers and the physico - chemical properties of oils are close. Permeability of the Apt - Neocomian horizon is 0,414 mkm^2, I Neocomian is 0,143 mkm^2.

Thus, based on the data obtained by the EPR method, it is possible to recommend the I Neocomian horizon of the Martyshi field for the development of an independent well grid.

In conclusion, it should be noted that in the practice of operating multi-layer oil fields in individual production wells, several productive deposits are often combined into one development object. Under these conditions, the possibility of determining the share of each deposit in the total well flow rate is a very complex and extremely important problem.

The undoubted advantages of the EPR method are its performance, which provides the possibility of obtaining express information, higher accuracy and reliability compared to the above methods and the absence of the need to stop producing wells when sampling oil for research [5,6].

EXPERIMENTAL PART

EPR spectra were recorded on the E-12 spectrometer of Varian company. We have found EPR signals from vanadium ions in the oils of the studied fields. For the determination of concentrations used the most intense line hyperfine structure (HFS) of complexes of tetravalent vanadium [5,7]. The standard concentrations were the oil from Urichtau field (from well 8) with known vanadium content (27,6 g/t). Samples of oil before the analysis was subjected to purification from associated water and solids by centrifugation (centrifuge T-22) when the rotation frequency of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length.

Gratitude. The authors express their gratitude to the head of the laboratory of electron paramagnetic resonance (EPR) of Institute of Organoelement compounds from Russian Academy of Sciences - S. P. Solodovnikov for assistance in recording the spectra of oil on the EPR spectrometer.

CONCLUSIONS

We have proposed a different, simpler sampling technique for determining reservoir productivity. The relative flow rates of the two jointly operated formations are determined by the measurements of wells located near the two layers being operated simultaneously. The proposed method is tested in the multi-layer fields of Martyshi and Southeast Kamyshitov. The flow rate of the studied layers according to EPR spectroscopy data is in good agreement with the field data.

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ЕКІ ТҮРЛІ ҚАБАТТАН БІР СКВАЖИНА КӨМЕГІМЕН ӨНДІРІЛЕТІН МҰНАЙДЫҢ ЖЕКЕ ҚАБАТ БОЙЫНША ДЕБИТЫН АНЫҚТАУ

Аннотация. Бұл жұмыс авторлары көп қабатты мұнай кеніштерінен өндірілітен мұнай мөлшерінің, әр қабаттан мұнай дебитын анықтау үшін мұнай үлгісін алудың басқаша әдісін ұсынады. Екі түрлі қабаттан бір скважина көмегімен алынған мұнайдың қоспасындағы ванадий мөлшерін, оның маңында орналасқан жеке қабаттар мен жұмыс жасайтын скважина мұнайындағы ванадий мөлшерімен салыстыру қажет.

Бұл әдіс Мартыши және Оңтүстік Шығыс Камишиті көп қабатты мұнай кеніштерінде сынақтан өтті. Зерттелген қабаттардың ЭПР спектроскопия көмегімен анықталған ванадий мөлшерімен есептелген мәліметтер бұл гаризонттардың өндірістік геологиялық дебиттері мен толық сәйкес келеді. Сонымен қатар тәсілдің іске асуы үшін керекті мұнай үлгілерін алу кезінде мұнай өндірістік ұңғыларды тоқтатудың қажеті жоқ.

Түйін сөздер: электрондық парамагниттік резонанс, фотоколориметрлі әдіс, ванадий парамагнитизмі, салыстырмалы дебит, көпқабатты мұнай кеніші.

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РАЗДЕЛЬНОЕ ОПРЕДЕЛЕНИЕ КОЛИЧЕСТВА НЕФТИ, ДОБЫВАЕМОЙ ОДНОЙ СКВАЖИНОЙ ИЗ ДВУХ ПЛАСТОВ

Аннотация. Относительные доли двух совместно разрабатываемых пластов в общем дебите одной добывающей скважины определяются по содержанию ванадия в нефти нескольких соседних скважин, работающих на каждом из продуктивных пластов раздельно. Результаты экспериментов по смешению нефтей разных пластов Каламкасского месторождения показали, что концентрация ванадия изменяется пропорционально объемному соотношению нефтей, т.е. подтвердили правомочность такого предложения.

Предлагаемый способ апробирован в многопластовых месторождениях Мартыши и Камышитовое Юго – Восточное. Дебит изученных пластов по данным ЭПР спектроскопии хорошо согласуется с промысловыми данными.

Безусловными преимуществами метода ЭПР являются его производительность, обеспечивающая возможность получения экспресс – информации, более высокая точность и надежность по сравнению с перечисленными методами и отсутствие необходимости остановки добывающих скважин при отборе проб нефти для исследования.

Ключевые слова: электронный парамагнитный резонанс, фотоколориметрический метод, парамагнитизм ванадия, относительный дебит, многопластовое месторождение.

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CATALYTIC CRAKING OF A VACUUM GASOLINE ON HLaY - A ZEOLITE CATALYST ON A NONACTIVATED ALUMINUM MILLED

Abstract. A comparison of the phase, elemental composition of CaNa-montmorillonite (MM) with the properties of MM in the Na-form was made, and it was found that the initial CaNaMM and NaMM, as well as the catalysts based on them, are close to each other in elemental and phase compositions. The textural properties of montmorillonites are determined and it is shown that the specific surface area, pore volume and number of micropores of the initial CaNaMM is slightly higher than that of NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times.

Using the TPD NH_3 method it was shown that the catalyst based on CaNaMM exceeds the catalyst based on NaMM in total acidity, the number of medium and strong acid sites (Table 3). It was shown that a zeolite-containing catalyst with a matrix of Al-pillared MM in the CaNa-form exhibits high activity in the cracking of vacuum gas oil (VG) with the production of 60% light gas oil. The high thermal stability of the cracking catalyst on the base of MM in the CaNa-form and its high mechanical strength have been established.

Keywords: catalytic cracking, zeolite, pillar montmorillonite, light gas oil, gasoline, gas, vacuum gas oil.

Introduction. The oil refining and petrochemical industry plays an important, and in some cases the most important role in the economy of any country [1-4]. In this regard, worldwide attention is paid to the deepening of oil refining, expanding the range, improving the quality of commodity fuels, especially environmental properties [5,6]. The tightening of environmental requirements for car engines around the world leads to a gradual transition from gasoline to diesel engines. Thus, in Europe, gasoline consumption decreased by 22%, and diesel fuel consumption increased by 19% [7]. Increased demand leads to the search for new sources of diesel fuel. One of such sources is potentially catalytic cracking, in which, in addition to gasoline and light hydrocarbon gases, a distillate fraction is produced - light catalytic cracking gas oil (LGCC) with a boiling range of 200-350^{0}C. LGCCs are used as a component of diesel fuel when compounding with a straight-run diesel fraction of up to 30%. The share of LGCC in commercial diesel fuel is limited to a high content of aromatic hydrocarbons, sulfur, low cetane number and high density [8]. Due to the growing demand for diesel fuel and the constant improvement of technology and catalysts, the catalytic cracking process can now be considered as a way to produce not only gasoline, but also high-quality diesel fuel [9]. In modern plants using industrial cracking catalysts by cracking vacuum gas oil, it ranges from 10–15% with a rather low cetane number (25–30 points) [9–11]; on advanced ball catalysts, increased yield of light gas oil (37,6-38,2%)was observed [12], and on granulated, for example, a series of "Adamant" light gasoil yield even higher (42,6-45,4%) [13].

Zeolites used in the composition of catalysts should have high activity and selectivity in the cracking of petroleum fractions, stability under high-temperature effects in air and water vapor, and the necessary dimensions of the entrance windows in the structure cavity [14-16]. Zeolites of the X and Y types in the rare-earth exchange form or in the ultra stable form are most relevant to such requirements, and therefore they find their primary use in the synthesis of cracking catalysts [17, 18].

For the preparation of the matrix of cracking catalysts, it was proposed to use a new class of materials based on natural bentonites, modification of which by pillaring allows increasing the specific surface, their thermal stability and significantly increasing the volume of micro- and mesopores [19,20]. In chemical modification of layered aluminosilicates with an expanding lattice, it becomes possible to regulate the acid-base properties of the surface and fix transition metal compounds on it, which was the basis for using these materials as catalysts in hydrocarbon conversion reactions: cracking, isomerization, alkylation, etc. [22, 23].

Based on zeolite Y in a lanthanum-substituted form (HLaY) deposited on an aluminum pillar montmorillonite in the Na-form (AlNaMM), a composite catalyst for cracking heavy vacuum gas oil has been developed to produce light gas oil with a yield of 55-67% depending on the volume of the catalyst. An increase in the yield of light gas oil was found (up to 72%) after steam treatment of the catalyst [24]. The composition of the catalyst for the production of light gas oil during the cracking of VG is protected by the innovative patent of the Republic of Kazakhstan [25]. In connection with the use of zeolite HLaY on Al-pillar MM in Na-form in the composition of the catalyst for producing light gas oil, it was of interest to reveal the dependence of the cracking properties of this catalyst on the composition of MM, its physicochemical properties, as well as on the composition and properties of vacuum gas oil.

The purpose of the work is the synthesis of HLaY zeolite-containing catalysts deposited on Al-pillared montmorillonite in CaNa- form and revealing the influence of the composition of the initial MM, its exchange form and physicochemical characteristics on the yield of light gas oil during cracking of vacuum gas oil of make B with increased sulfur content.

Experimental part

Tagan montmorillonite (Kazakhstan) from the Zapadny open pit, 12 horizons containing the following alkaline cations were used as raw materials for the preparation of the catalyst: $Na^+ > 35$ mg / eq, $Ca^{++} \geq 28$ mg / eq, $Mg^{++} = 24$ mg / eq, $K^+ \sim 4.0$ mg / eq. The aluminum hydroxocomplex of the supposed composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ abbreviated (Al_{13}^{7+}) with a four-coordinated aluminum atom, was used as a fixing agent in pillaring. The method of obtaining oligomeric (Al_{13}^{7+}) consists in hydrolysis of an aqueous $AlCl_3$ solution with an aqueous solution of NaOH with a ratio of $OH^- / Al^{3+} = 2.5$ and a final pH = 4.1 under conditions of vigorous stirring. The procedure for the synthesis of aluminum montmorillonite (AlNaHMM) is described in [19-22]. The catalyst was additionally modified with zeolite Y in the substituted La-form (15%), molded into granules, dried for 24 hours at room temperature, then calcined at 150°C (2 hours) and 500°C (2 hours).

Elemental analysis of the catalyst samples was carried out by the method of energy dispersive - X-ray fluorescence spectroscopy on the energy dispersive microanalysis system INCA - Energy 450, installed on a JSM6610LV scanning electron microscope, JOEL, Japan.

The textural characteristics of the catalysts were determined by the isotherms of low-temperature adsorption and desorption of nitrogen on an Accusorb device (BET method).

XRD samples of catalysts were carried out using a DRON-4 * 0.7 X-ray diffractometer; with CoK_α and CuK_α radiation. The diffractometric reflexes of the catalyst samples were compared with ICPDS powder standards.

The catalytic activity of the samples was determined in a laboratory flow-type installation corresponding to the standard, with a fixed catalyst bed in an amount of 40 ml. The catalytic activity was determined in the temperature range 500-550^{0}C. Vacuum gasoil (VG) of make B, type 2 of Pavlodar Petrochemical Plant (PPCP) was used as a raw material for cracking with the following characteristics: the density 907.7 kg / m^3, kinematic viscosity at 500°C equal to 27.05 mm^2 / s, sulfur content 1.5 mass.%, harden point 30^{0}C and coking ability 0.14 wt.%, with the end of boiling 510^{0}C. During the distillation of catalyzate, the gasoline fractions $T_{b.b.}$-205^{0}C and light gas oil 205-350^{0}C were collected. The analysis of the hydrocarbon composition of gasoline cracking was performed on a chromatograph “Chromos-1000” with a flame ionization detector and a capillary column 100 m long; temperature is 250°C; the carrier gas is helium.

Results and its discussion

The physicochemical characteristics of the Tagan montmorillonite in the Na-form, which was used previously, and in the CaNa-form, as well as HLaY-zeolite catalysts with their use are shown in Table 1-3.

Table 1 shows the data on the elemental composition of calcium-sodium and sodium forms of the Tagan montmorillonite and catalysts based on them. The table includes the average of 3 measurements in weight%.

Table 1 - The elemental composition of composite catalysts based
on Al-pillared montmorillonite in CaNa-and Na-forms

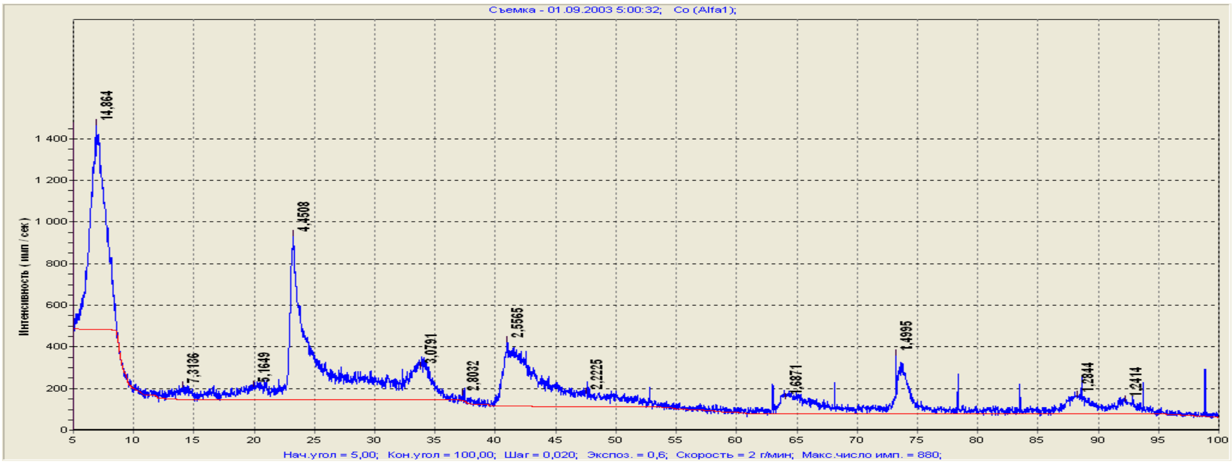
Sample	O	Na	Mg	Al	Si	Ca	Fe	La
CaNaMM	54,6	1,0	2,1	13,4	27,9	0,7	0,3	
Al(2.5)CaNaMM	56,4		1,6	16,7	25,0		0,3	
Al(2.5)CaNaMM+HLaY	53,8	0,2	1,1	19,8	23,2		0,2	1,7
NaMM	51,6	1.4	2,1	11,3	24,7	0.56	0.39	
Al(2.5)NaMM	54,63	-	1,19	11,87	20,83	-	0,25	-
Al(2.5)NaMM+HLaY	53,66	0,48	0,79	10,80	21,53		0,21	2.03

From the analysis of the data in Table 1, it follows that pillaring of Al leads to the complete replacement of sodium and calcium from both types of MM and a decrease in the relative amounts of magnesium and silicon. The aluminum content after pillaring increased, which confirms the formation of aluminum-oxide columns. With the introduction of HLaY, the amount of La in the CaNaMM-based catalyst is 1.7% and 0.2% of Na appears, while the amount of La and Na in Al (2.5) NaMM + HLaY is significantly higher (2.03 and 0.48%). It should be noted a higher content of Fe in the initial NaMM (0.39%) compared to CaNaMM (0.3%). In the process of pillaring and introducing zeolite, a decrease in the amount of Fe is observed, more significant in the case of a catalyst based on NaMM. In the prepared catalysts based on two different MM, the amount of Fe is approximately the same.

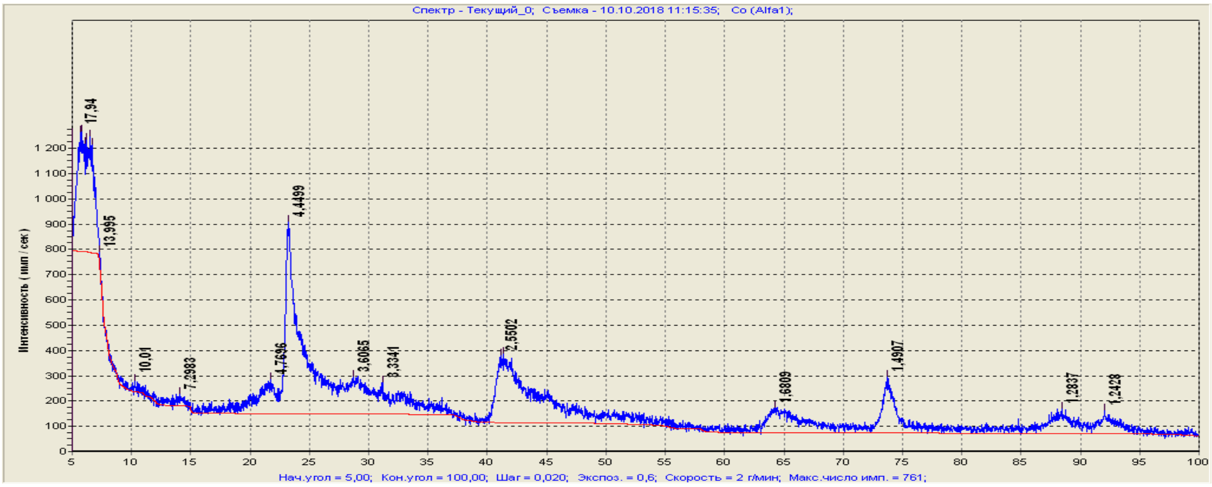
According to the X-ray phase analysis (XRD) in the initial samples of CaNaMM next phases were identified with reflexes: MM-11.0; 4.46; 3.23; 2.50; 1.67; 1.50; 1.28; quartz-4.27; 3.34; 2.45; 2.23; 2.12; 1.98; 1.81; 1.54; HLaY-14,6; kaolinite-7.2.

It can be seen from Figure 1 that when pillary CaNaMM, the first basal reflex increases from d_1 = 14.8Å to 17.9Å. The introduction of zeolite leads to a slight decrease in the first basal reflex to d_1 = 16.3Å and the appearance of reflex 14.6. A comparison with the Al (2.5) NaMM + HLaY- catalyst shows that in this case the separation of the MM layers in the finished catalyst is much less than –11.0 Å, and the reflex 14.6 also appears when HLaY is introduced [23].

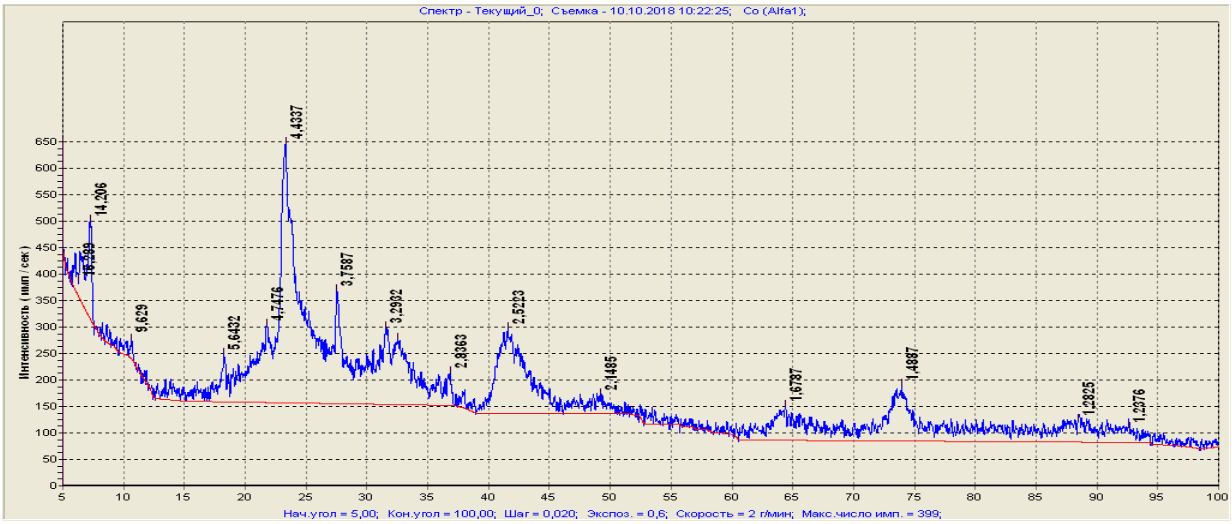
The textural properties of the initial MM in CaNa- and Na-forms and the catalysts based on them are presented in Table 2. The specific surface area of CaNaMM grows when pillaring Al from 86.4 cm^3/g to 190.5 cm^3/g, and with the introduction of HLaY there is a further increase in the specific surface to 308.6 cm^3/g. The total pore volume also increases with pillaring, which is accompanied by an increase in the number of micropores and a decrease in the number of mesopores. It is of interest to compare the textural properties of the original form of CaNaMM with the properties of montmorillonite in the Na-form, which we used earlier to prepare the catalyst. From table 2 it can be seen that the specific surface area, pore volume and number of micropores in the initial CaNaMM are slightly higher than in NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times. For both carriers, an increase in the number of micropores is observed in pillaring: in the case of CaNaMM, by 1.5 times, and for NaMM, by 2.9 times. The introduction of zeolite leads to a further increase in the number of micropores, while in the case of NaMM, modifying with HLaY zeolite reduces the number of micropores in the catalyst. A comparison of the cracking catalysts based on MM in the CaNa- and Na-forms shows that Al(2.5)CaNaMM+HLaY has a much more developed surface and a greater number of micropores than the catalyst based on NaMM.



CaNaMM



Al(2,5)CaNaMM



Al(2.5)CaNaMM+HLaY

Figure 1 - Diffractograms of the original CaNaMM, pillared Al (2.5) CaNaMM and modified with zeolite Al (2.5) CaNaMM + HLaY

Table 2 - Comparative textural characteristics of the original calcium-sodium and sodium forms of the Tagan montmorillonite and catalysts based on them

Sample	S, m^2/g	Total pore volume, sm^3 / g	R, Å	Relative amount,%	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
CaNaMM	86,4	0,083	10,0-73,0	30,0	70,0
Al(2.5)CaNaMM	190,5	0,182	10,0-75,0	44,1	55,9
Al(2.5)CaNaMM+HLaY	308,6	0,167	11,0-72,0	57,4	42,6
NaMM	80,9	0,081	11,5-75,0	26,7	73,3
Al(2.5)NaMM	123,4	0,176	10,0-90,0	78,5	21,5
Al(2.5)NaMM+HLaY	124,2	0,107	10,0-65,0	50,0	50,0

Comparison of acidic properties of cracking catalysts based on MM in various exchange forms showed that the catalyst based on CaNaMM exceeds the catalyst based on NaMM (Table 3) in total acidity, the number of medium and strong acid sites. The distribution of acid sites in strength is almost completely preserved on the catalyst after testing in the cracking reaction. According to the relative amount of acid sites of different strength, the catalysts using MM of different composition are close to each other.

Table 3 - Acidity of zeolite-containing Al (2.5) CaNaMM + HLaY-catalyst before and after the experiment according to TPD ammonia

Sample	Content a.c.	Acid Centers			
		Weak<200^0C	Medium 200-300^0C	Strong >300^0C	Total acidity
Al(2,5)CaNaMM+ HLaY(before)	%	29,67	35,58	34,75	100
	µmol NH_3/g	87,36	104,76	102,31	294,43
Al(2,5)CaNaMM+ HLaY (after)	%	26,31	36,14	37,55	100
	µmol NH_3/g	77,72	106,76	110,92	295,4
Al(2,5)NaMM+ HLaY	%	45,0	30,0	25,0	100
	µmol NH_3/g	112,5	75,0	62,5	250,0

The data on the VG cracking on Al (2.5) CaNaMM + HLaY- catalyst is shown in Figure 2.

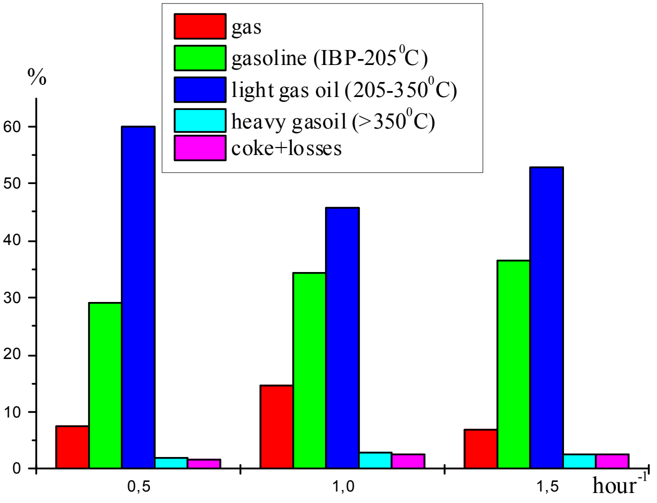


Figure 2 – Data of the VG cracking on Al (2.5) CaNaMM + HLaY-catalyst by varying the space velocity at the T = 500^0C

From the results of the material balance of the cracking of VG, it can be seen that on Al(2.5)CaNaMM+HLaY-catalyst, with the space velocity of 0.5hour $^{-1}$ the maximum yield of light gas oil equal to 60.0% was obtained at a cracking temperature of 500^{0}C. With an increase of the space velocity, the yield of light gas oil decreases, the amount of produced gas and gasoline increases. The tested catalyst is characterized by the formation of a large amount of light gas oil in the process of cracking VG.

An increase of the cracking temperature from 500°C to 550°C leads to a slight decrease in the yield of light gas oil from 60.0% at 500^{o}C to 58.8% at 550° C. Comparative data on the activity of Al(2.5)CaNaMM+HLaY catalysts in the cracking of VG at a temperature of 500-550^{0}C are presented in table 3.

Table 4 – Material balance of VG cracking
on Al (2.5) CaNaMM + HLaY- catalyst at various temperatures

Products	The yield of products, wt.%	
Temperature	500^{0}C	550^{0}C
Gas	7,4	8,4
Gasoline (b.b.-205^{0}C)	29,2	29,6
Light gas oil (205 - 350^{0}C)	60,0	58,8
Heavy gas oil (>350^{0}C)	1,9	1,8
Coke+Losses	1,5	1,4
Amount of products	100	100

Thus, for Al (2.5) CaNaMM + HLaY catalyst, optimal conditions were selected for producing light gas oil by cracking VG with a yield of at least 60%: the cracking temperature is 500^{0}C, the feed space velocity is 0.5 hour^{-1}. Cetan number of gas oil is 63, sulfur content 1.91 wt.%. The crush strength of this catalyst granule is 166.3 N / sm^2. The strength of NaMM based catalyst granules is higher and amounts to 216-230 N / sm^2 [24].

To determine the thermal stability of Al (2.5) CaNaMM + HLaY catalyst, it was subjected to thermovapor treatment at the temperature 750^{0}C during 6 hours with 100% vapor.. Table 4 presents comparative data on the effect of thermovapor treatment of the synthesized catalyst on the activity in the cracking of the VG at the temperature 500^{0}C.

Table 5 - Material balance of VG cracking on Al (2.5) CaNaHMM + HLaY at 500^{0}C before
and after thermovapor treatment (tv/t) at the feed space velocity 0.5 hour $^{-1}$

The yield of products, wt.%	Before (tv/t)	After(tv/t)
Gas	7,4	7,3
Gasoline (b.b.-205^{0}C)	29,2	27,7
Light gas oil (205 - 350^{0}C)	60,0	60,9
Heavy gas oil (>350^{0}C)	1,9	2,5
Coke+Losses	1,4	1,6
Amount of products	100	100

As follows from the data of table 5, the yield of light gas oil after termovapor treatment increases to 60.9%, the yield of gasoline, on the contrary, decreases by 1.5%, and the yield of heavy gas oil increases by 0.6% compared to the results before tv/t. Comparison with the results obtained earlier on the catalyst using NaMM [23,24] showed that before tv/t the catalyst based on CaNaMM shows higher activity and the yield of light gas oil and gasoline-60.0 and 29.2% (see table .4) probably due to higher specific surface area and acidity (see Tables 2 and 3). The yield of light gas oil and gasoline on Al(2.5)NaMM + HLaY at 500^0 C is 55.0 and 17%, respectively (Table 6). However, after tv/t, the yield of light gas oil increases to 72%, and the yield of gasoline decreases to 7.9 %. According to the results on Al (2.5) CaNaMM + HLaY, the yield of light gas oil after tv /t increases only by 1-2%, while the yield of gasoline remains at a fairly high level (27.7%).

Table 6 - Cracking VG PPCP on Al (2.5) NaMM + HLaY before and after tv/t (reactor 50 ml) [23,24]

Cracking products	Yield,% wt.			
	before vapor treatment		after vapor treatment	
	500°C	550°C	500°C	550°C
Gas	2.0	19.3	3.0	5.0
Gasoline	17.0	20.5	7.9	25.5
Coke	7.8	2.3	9.8	10.0
Light gas oil (205 - 350^0C)	55.0	45.3	72.0	52.1
Heavy gas oil (>350^0C)	15.0	10.0	5.5	5.4
Losses	2.2	2.2	2.0	2.0
Conversion	82.8	87.4	92.7	92.6
Amount of products	72.0	75.8	79.9	77.6

Thus, the obtained results showed that the developed highly active and stable catalyst for the cracking of vacuum gas oil with obtaining 60.0% of light gas oil retains its activity when using MM with various exchange cations and exhibits high thermal stability during cracking VG with sulfur content up to 1.5 mass .%. The catalyst can be recommended for practical use.

Conclusion

A comparison of the phase, elemental composition of CaNa-montmorillonite with the properties of montmorillonite in the Na form was made and it was found that the initial CaNaMM and NaMM, as well as the catalysts based on them, are close to each other in elemental and phase compositions. The textural properties of montmorillonites are determined and it is shown that the specific surface area, pore volume and number of micropores of the initial CaNaMM is slightly higher than that of NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times.

Using the method of TPD NH3, it was shown that the catalyst based on CaNaMM exceeds the catalyst based on NaMM in total acidity, the number of medium and strong acid sites (Table 3). It was shown that a zeolite-containing catalyst with a matrix of Al- pillared MM in the CaNa-form exhibits high activity in the cracking of VG with obtaining 60% light gas oil. The high thermal stability of the cracking catalyst on the base CaNaMM and its high mechanical strength have been established.

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БЕЛСЕНДІРІЛМЕЙ АЛЮМИНИЙМЕН ПИЛЛАРИРЛЕНГЕН МОНТМОРИЛЛОНИТТЕГІ HLaY – ЦЕОЛИТТІ КАТАЛИЗАТОРЫНДАҒЫ ВАКУУМДЫҚ ГАЗОЙЛЬДІҢ КАТАЛИТИКАЛЫҚ КРЕКИНГІ

Аннотация. CaNa-монтмориллониттің фазалық, элементтік құрамы Na- формалы монтмориллонит қасиеттерімен салыстырылды және бастапқы CaNaMM және NaMM, сонымен қатар солар негізіндегі катализаторлар элементтік және фазалық құрамы бойынша өзара ұқсас болатыны анықталды. Монтмориллониттердің текстуралық қасиеттері анықталып, бастапқы CaNaMM меншікті беті, кеуектер көлемі, микрокеуектер саны NaMM қарағанда бірнеше артық екені көрсетілді. Меншікті беті алюминиймен пилларирлегенде 2,2 есе өседі, ал NaMM бұндай жағдайда 1,5 есе артады.

NH_3 ТПД әдісімен CaNaMM негізіндегі катализатор жалпы қышқылдық, орта және күшті қышқылды орталықтар саны бойынша NaMM негізіндегі катализатордан асып түсетіні көрсетілді (3-кесте). Al пилларирленген CaNa-формалық монтмориллонит матрицалы цеолитқұрамды катализатор ВГ крекингінде 60% жеңіл газойль түзіп жоғары белсенділік танытады. CaNa-формалы MM негізіндегі крекинг катализаторының жоғары термиялық тұрақтылығы мен оның жоғары механикалық беріктігі анықталды.

Түйін сөздер: каталитикалық крекинг, цеолит, пилларирленген монтмориллонит, жеңіл газойль, жанармай, газ, вакуумдық газойль

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КАТАЛИТИЧЕСКИЙ КРЕКИНГ ВАКУУМНОГО ГАЗОЙЛЯ НА HLaY – ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ НА НЕАКТИВИРОВАННОМ ПИЛЛАРИРОВАННОМ АЛЮМИНИЕМ МОНТМОРИЛЛОНИТЕ

Аннотация. Проведено сопоставление фазового, элементного состава CaNa-монтмориллонита со свойствами монтмориллонита в Na- форме и найдено, что исходные CaNaMM и NaMM, а также катализаторы на их основе близки между собой по элементному и фазовому составам. Определены текстурные свойства монтмориллонитов и показано,что что удельная поверхность, объем пор и количество микропор у исходного CaNaMM несколько выше, чем у NaMM. Удельная поверхность при пилларировании алюминием растет в 2,2 раза, в то время как в случае NaMM рост составляет 1,5 раза.

Методом ТПД NH_3 показано, что по суммарной кислотности, количеству средних и сильных кислотных центров катализатор на основе CaNaMM превосходит катализатор на основе NaMM (табл.3). Показано, что цеолитсодержащий катализатор с матрицей из пилларированного Al монтмориллонита в CaNa-форме проявляет высокую активность в крекинге ВГ с получением 60% легкого газойля. Установлена высокая термическая стабильность катализатора крекинга на основе ММ в CaNa-форме и его высокая механическая прочность.

Ключевые слова: каталитический крекинг, цеолит, пилларированный монтмориллонит, легкий газойль, бензин, газ, вакуумный газойль.

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THE POSSIBILITY OF NEUTRALIZING WHITE PHOSPHORUS USING MICROBIAL CULTURES

Abstract. The growth of microorganisms of various taxonomic groups (fungi, streptomyces and bacteria) was observed for the first time in culture media containing white phosphorus P_4 as the source of phosphorus. This is the first known example of the incorporation of white phosphorus into the biospheric circulation of the phosphorus element. The highest concentration applied in this study exceeds the Threshold Limit Value (TLV) of white phosphorus in wastewater by 5000 times, and in drinking water by up to 100,000,000 times! The growth selection of cultures resistant to P_4 was carried out for the first time. We identified the microorganisms, growing on white phosphorus, as new strains of *Aspergillus niger* and *Streptomyces sampsonii.* The number *A. niger* AM1 and *S. sampsonii* A8 were assigned to them, respectively. Strains of the *A. niger* isolates were shown to better adapt to P_4 than the bacteria.

Keywords: biodegradation, white phosphorus, environmental protection, chemical pollution.

Introduction

White phosphorus P4 is widely used in industry and is a key compound in the production of drugs, phosphate fertilizers, polymers and a number of other important substances and materials. According to the review article [1], Russia's portion amidst global consumption of white phosphorus in 2004 was estimated to be 5.7%, Kazakhstan - 8.1%, China - 71.1%, USA - 8.6%, Western Europe - 5.8% and India - 0.7%. Therefore, the penetration of white phosphorus into the environment is undoubtedly possible. Meanwhile, white phosphorus is one of the most dangerous environmental pollutants [2]. Protocol III of the 1980 Convention on Certain Conventional Weapons officially prohibits the use of P_4 for military purposes. However, the ban is constantly violated, which leads to human casualties and severe environmental pollution. Effective methods of purifying the envirinment from this pollutant have not yet been developed [2]. The only approach to P_4 detoxification currently involves its oxidation into phosphoric acid with the aid of copper sulfate solution; however, the implementation of this method is limited due to its high cost and toxicity. Biodegradation is considered to be one of the most practically significant and frequently used methods of industrial waste disposal [3, 4].

At the same time, phosphorus posseses a unique quality - being in the form of a simple substance, it remains a very strong poison, while in its oxidized state, it acts as a biogenic element that is absolutely necessary for all living organisms (Fig. 1, above). Thus, the primary task lies in finding an efficient and environmentally friendly approach to oxidize white phosphorus into phosphate. We propose to use microorganisms for this purpose.

The lower picture of Figure 1, illustrates the coassimilation of several toxic substances in a single metabolic pathway, demonstrating the perfect nature of the biochemistry of microorganisms, depicted on the basis of literature sources [6-8]. The inclusion of two toxic xenobiotics (formaldehyde and hydrocyanic acid) into the composition of sugars and amino acids is perhaps the most significant example of biodegradation. This is a substantial fundamental argument in favor of the possibility of biodegradation of even such dangerous xenobiotics as white phosphorus.

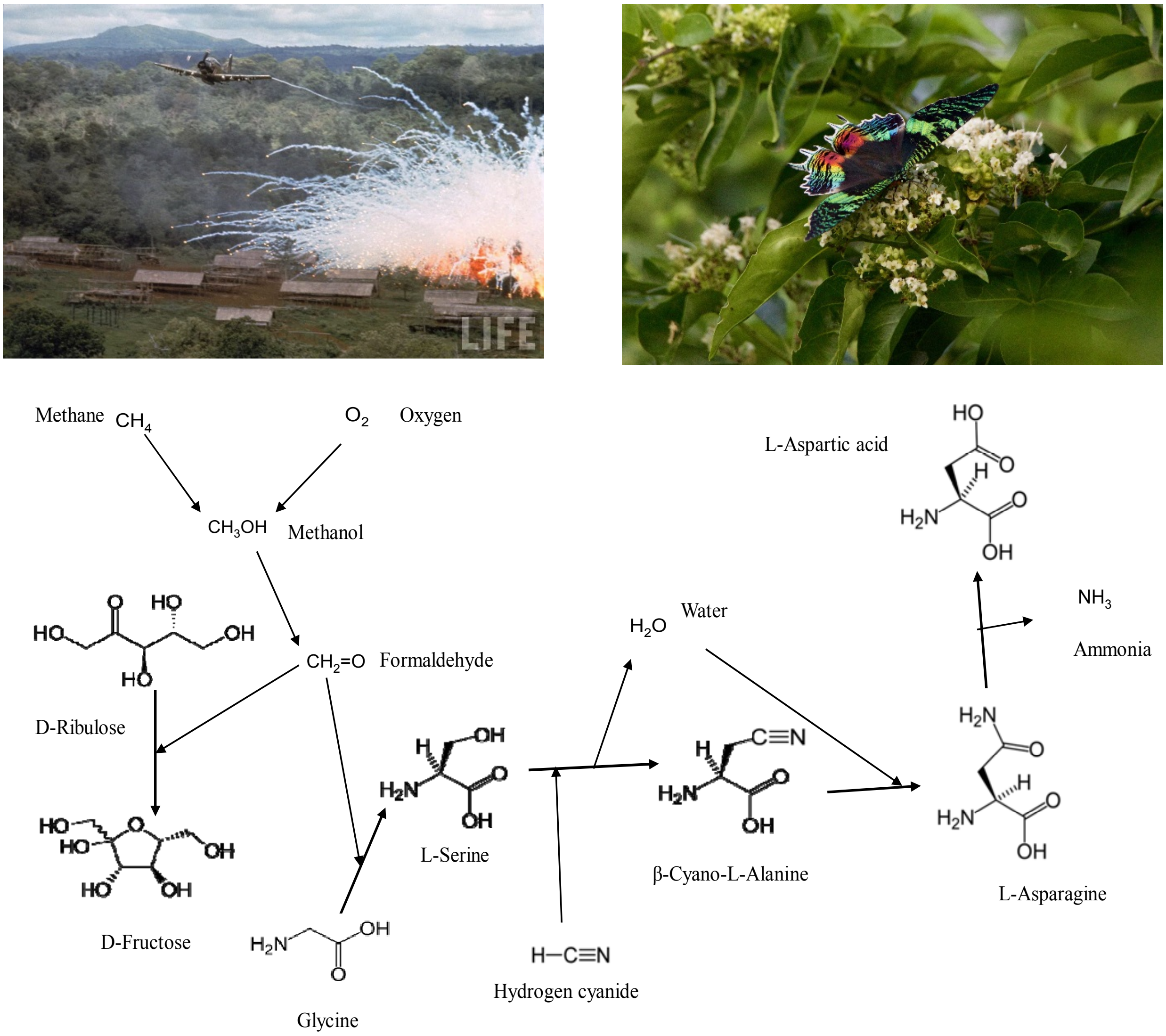

Figure 1 - Phosphorus in its diverse forms. Top left: Explosion of a phosphorus bomb during the Vietnam War (image from https://www.pinterest.ru). Top right: the final oxidized form of phosphorus, phosphate is a food source for plants and plays a crucial role in the existence of all forms of life. Image from https://elementy.ru. Below. The inclusion of formaldehyde and cyanide into the structure of sugars and amino acids is a strong example of biodegradation. Synthesis of methanol from methane (which in itself is a product of microbial metabolism [5]), is carried out by methanotrophic bacteria; serine and fructose from methanol - by some methylotrophic bacteria and yeast; β-cyano-L-alanine from hydrocyanic acid and serine - by the bacteria *Chromobacterium violaceum*; asparagine from cyanoalanine - by a number of plants. A figure of A.Z. Mindubaev

This publication is a continuation of the series of work done by of our team [9, 10], which showed that microorganisms survive upon being in contact with white phosphorus, adapt to its presence in the environment and process it into less dangerous compounds. The purpose of this work is to compare the resistance and ability of microorganisms of different strains and taxonomic groups to the biodegradation of white phosphorus. And also to identify the minimum inhibitory concentration (MIC) of this substance in each case.

Experimental part

For the first time, we have successfully observed growth of a stable microbiota, cultured in an artificial nutrient medium containing white phosphorus as the sole source of phosphorus in concentrations ranging from 0.01 to 1. Culturing was carried out in a modified Pridhem-Gottlieb medium. The classical Pridham-Gottlieb medium does not contain monosaccharides as carbon sources, and petroleum products act as such. Our modification includes glucose as a carbon source. 1 L of the modified medium contained:

glucose – 5 g, $(NH_4)_2SO_4$ – 2,64 g, $MgSO_4$ – 0,49 g, $CuSO_4 \cdot 5H_2O$ – 0,1 g, $FeSO_4 \cdot 7H_2O$ – 0,02 g, $MnCl_2 \cdot 4H_2O$ – 0,15 g, $ZnSO_4 \cdot 7H_2O$ – 0,27 g, and white phosphorus in different concentrations. 7.4 g of $K_2HPO_4 \cdot 3H_2O$ and 2.38 g of KH_2PO_4 were added to the control medium as a source of phosphorus. Semi-fluid modification of the medium was achieved after adding 4.8 g of agar. White phosphorus was emulsified in sterile distilled water. The concentration of white phosphorus prior to inoculation was calculated as follows. An emulsion was prepared from 1 g of white phosphorus in 50 ml of water to achieve a 2% solution. After cultivation, the concentrations of P_4 in the media were not measured. However, the growth of the microorganism itself indicates its decline, since phosphate is essential for growth, and in this case, it could only be formed from white phosphorus.

Aspergillus niger AM1, the spores of which were introduced together with white phosphorus, was initially cultured in a medium with white phosphorus concentrations (w/v) of 0.01 and 0.05%. Phosphate was added to the positive control. No sources of phosphorus were added to the negative control. After 60 days, the fungi were reinoculated into media with concentrations of white phosphorus 0.05; 0.1 and 0.2%. Following another 60 days, the strains were subcultured to higher concentrations of P_4 0.5; and 1%. The cultivation of *Streptomyces sp.* A8 isolated from sewage sludge containing white phosphorus was carried out in a similar manner. The concentration (w/v) of white phosphorus 0.05; 0.1 and 0.2% was used for the culture of fungi and streptomycetes, but not for bacteria, since the latter do not tolerate high concentrations of this substance.

Inoculation of *A. niger* AM1 and *S. sp.* A8 was carried out using spores, while bacteria were cultivated in the form of vegetative cells. Spore suspension contained 10^8 fungal bodies per ml; 0.2 ml was added per 20 ml of medium. Cultures were grown in flasks with 20 ml of culture medium without aeration, as well as Petri dishes. Incubation was carried out in a thermostat, at 25°C.

For genetic analysis, DNA samples from the culture of the fungus A. niger AM1 and streptomycete S. sp. A8 were isolated according to the method described in [11]. Next, the polymerase chain reaction (PCR) of the obtained DNA fragments was carried out using primers to the conservative sites of the 5.8S rDNA gene ITS1 (AAATTTAGGGGAATT) and ITS2 (GGGTTGGTTGGCCCGT).

To compare the resistance of black Aspergillus strains to white phosphorus, our strain Aspergillus niger AM1 was used, as well as three strains from the All-Russian collection of microorganisms in the Skryabin Institute of Biochemistry and Physiology of Microorganisms (IBPM RAS) (Table 1).

Table 1 - *Aspergillus niger* strains from the All-Russian collection of microorganisms (ARCM), with which the study was conducted

Species	Strain	Substrate of isolation	Place of isolation
Aspergillus niger	BKM FW-650	Permafrost deposits, 170 years old, Depth: 20.50-20.55 m deep	Taglu, Canada
Aspergillus niger	BKM FW-2664	Frozen volcanic ash, Depth:1.8-1.85 m	Kamchatka Peninsula, Russia
Aspergillus niger	BKM FW-2731	Permafrost, volcanic ash, Depth: 14.5 m	Kamchatka Peninsula, Russia

The cultures were grown in 96-well Corning microplates, the growth rate was estimated by measuring the optical density (OD) at λ 550 nm using a microplate reader Infinite F200 Pro, Tecan (Austria). This was done to conduct parallel cultivation of different strains, while comparing their growth rate in media with different concentrations of white phosphorus. In our experiments, the maximum concentration of white phosphorus in the wells of the plates reached 1%.

For comparison, cultures of bacteria *Achromobacter xylosoxidans*, *Pseudomonas aeruginosa*, *Bacillus firmus* and *Salmonella typhimurium* were sown. The purpose of these studies was to detect the minimum inhibitory concentration (MIC) of white phosphorus for these microorganisms.

To establish the nature of Aspergillus' resistance to P_4, reseeding was carried out in a medium with phosphate as a source of phosphorus, without P_4. The culture grown in this medium was re-inoculated into a medium with 0.2% white phosphorus. As a control, A. niger AM1, which had previously grown in an environment with white phosphorus, was also cultured.

An Avance 400 (Bruker) high resolution NMR spectrometer was used to monitor the P_4 processing. Sampling was done using insulin syringes. The test medium was purified from fungal hyphae and mycelia using a Millex®-HV filter (Syringe-driven Filter Unit) with pore diameter is 0.45 microns. Parameters for spectrum analysis: Bruker Avance III 400 MHz 31P {1H} - (161.9 MHz, 25 ºC).

Since white phosphorus actively reacts with ions of divalent copper at room temperature, until recently its biodegradation was not confirmed: the transformations could be explained by a chemical reaction. For the first time, we carried out a further modification of the Pridhem-Gottlieb medium, excluding from its composition copper sulfate ($CuSO_4$) and phosphate. The growth of the microbes under similar conditions, but in the absence of $CuSO_4$ and phosphates would provide stronger foundation for the biodegradation of P_4. Statistical data processing was performed using Microsoft Excel 2013.

Results and discussion

In the negative control without sources of phosphorus, a few (11) colonies of Aspergillus niger AM1 were observed. They occupied a relatively large area and grew very slowly (with undeveloped mycelium and weak sporulation). Without doubt, this was due to the lack of phosphorus. Interestingly, in the experimental medium with 0.05% white phosphorus, there were fewer colonies (33 colonies) than in the positive control (49 colonies), but their growth and sporulation was normal in comparison with the phosphorus deficient medium.

Subsequently, it can be concluded that not all fungal spores survive in a medium with white phosphorus. However, the survivors have the ability to utilize either P_4 itself or the products of its chemical transformations as a source of phosphorus. Reseeding was carried out in media with the following concentrations of white phosphorus, 0.05; 0.1; 0.2; 0.5 and 1% P4, in order to facilitate their adaptation to the toxicant. The results suggest that black Aspergillus tolerates the presence of white phosphorus in the medium, even at a concentration of 1%. The highest concentration of white phosphorus studied by us, being 1% P4 corresponds to about 5000 times the Threshold Limit Value (TLV) of white phosphorus in wastewater. Moreover, the TLV of elemental phosphorus in water bodies for household drinking and use is only 0.0001 mg / l, which is lower than 1% by one hundred million ($1 \cdot 10^8$) times [12]. In environments with a lower content of P_4, the growth of fungi is more intense - this was determined visually. After the fourth reseeding, streptomycete also began to grow at a P_4 concentration of 1%, i.e., it developed resistance even faster and more efficiently than the fungus.

For the genetic identification of a fungus, the nucleotide sequence of its regions ITS1 and ITS2 was determined according to morphological characters attributed to the species A. niger. Comparison of the obtained sequence with the sequences of the GenBank database (NCBI) using the BLAST system allowed us to identify this microorganism as a new strain of Aspergillus niger and thus, the number *A. niger* AM1 was assigned to it [9].

For strain A8, the similarity of the 16S rDNA nucleotide sequences (amplification by primers fD1 and rP2) of the compared streptomycete fragments selected from the NCBI database and the isolates tested was 94–99.7%. In particular, the greatest similarity - 99.74% - was found between isolate A8 and *Streptomyces sampsonii*. It is proposed to attribute our strain to this species.

Intriguingly, in the medium with white phosphorus, a spontaneous appearance of an *Aspergillus niger* AM1 culture with altered morphology and color, which grows faster in the medium with the xenobiotic under study was observed. In one of the culture replicates, the colony began to develop faster than in others, although the conditions were completely identical. 55 days after inoculation, the leading culture began to produce pigment and acquired a more saturated yellow color, which stained both the colonies and the medium and thus, hinting on the fact that this pigment is water soluble. Judging by the fact that this fungus efficiently gathered biomass in the medium with white phosphorus, we conclude that it adapts faster in this medium in comparison to the ancestral culture. We labelled this strain *A. niger* AM2.

The NMR analysis revealed the resistance of the AM1 culture to products of partial oxidation of P4. The very fact of the emergence of resistance to this group of substances (phosphites and hypophosphites, which are antimicrobial agents [13]) is very interesting, however, the expected result — complete metabolic conversion of white phosphorus to phosphate is yet to be confirmed.

It turned out that all four *A. niger* FW-650, FW-2664 and FW-2731 and AM1 strains show resistance to white phosphorus at a concentration of 1% and the MIC was not found for them with respect to the chosen range of P_4 concentrations. Since all the studied strains were randomly sampled strains of *A. niger*, it can be assumed that high resistance to white phosphorus is a sign that characterizes all black aspergillus, or at least most of them. In addition, at concentrations of 0.5 and 0.25%, the AM1 strain grew faster, i.e. proved to be more adaptable (Fig. 2). In the case of bacteria, the MIC was identified to be 0.125% for *A. xylosoxidans*, 0.25% for B. firmus, and 0.5% for both *P. aeruginosa* and *S. typhimurium*. From this it follows that black Aspergillus is more resistant to white phosphorus than bacteria.

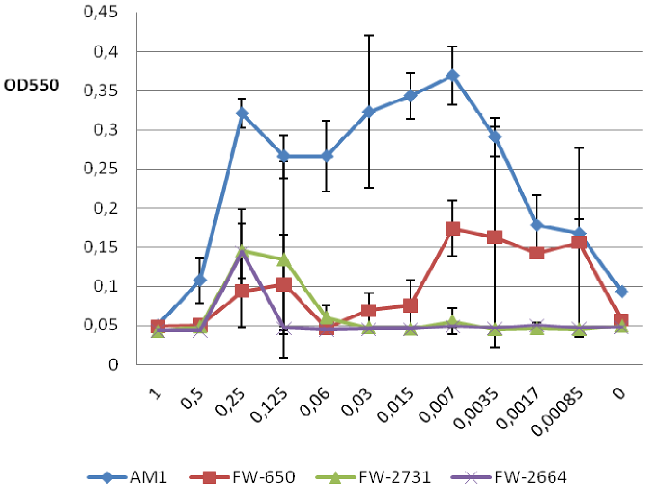

Figure 2 - The growth of *A. niger* strains in a phosphate deficient medium containing white phosphorus, on the third day of cultivation. X- axis: concentration (%) of white phosphorus. Y-axis: optical density at λ=550 nm. The growth rate of strain AM1 is emphasized

It was expected that following growth under favorable conditions, reculturing A. niger AM1 in a medium with P4 could lead to loss in resistance to white phosphorus. In fact, the fungus continued to grow normally in both P4 after being subjected to a medium with phosphate [14]. In line with this, it can be concluded that the resistance to white phosphorus in the studied *A. niger* strain is fixed in the genome, and is an inherited trait transmitted in a number of generations even in the absence of P_4. The vital role of salts of transition metals in the growth and development of microbes is well known [15, 16]. However, excluding copper sulfate from the composition of the nutrient medium revealed that there was no statistical diference between the fungal growth in the presence and absence of $CuSO_4$ (Fig. 3).

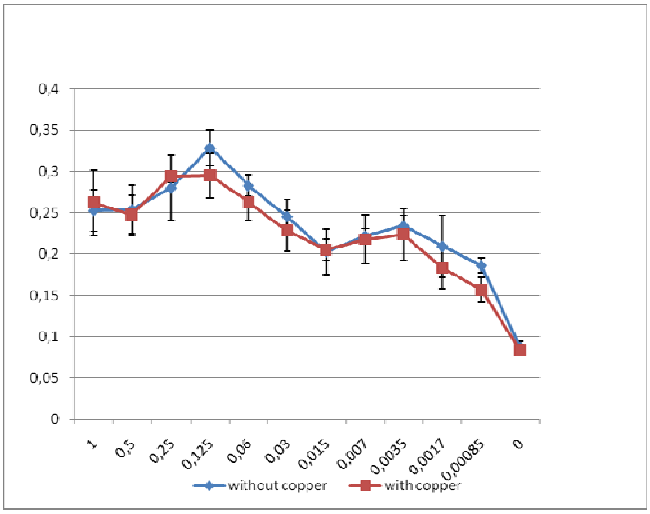

Figure 3 - The growth of *A. niger* AM1 on the fifth day after inoculation. It can be seen that there is no significant differencee between culture growth in the medium variant with copper and without copper. The abscissa axis is the concentration of white phosphorus,%. Y-axis - Optical Density (OD) at λ = 550 nm

It should be noted that when emulsion of white phosphorus was introduced into the copper--dificient medium, no black precipitate (something we noted in earlier studies) was observed. This means that P_4 does not enter into a chemical reaction and remains in the medium for a longer time. This fact is an additional argument in favor of the fact that the biodegradation of white phosphorus takes place, and not the chemical neutralization of copper ions.

Conclusion

The work presented has demonstrated for the first time the inclusion of white phosphorus in the natural cycle of the phosphorus element. The uniqueness of phosphorus is in the fact that this element is absolutely necessary for the vital activity of all life forms. Nonetheless, as a simple substance, white phosphorus is a poison of first class danger, which with great difficulty is subjected to destruction in the environment. Prior to the beginning of our work, the biodegradation of white phosphorus (like its other allotropic modifications) had not been described in the literature.

The significance of the presented work precisely involves the fact that for the first time, it showed the possibility of the growth of microorganisms from different and distant taxonomic groups in culture media containing white phosphorus as the sole source of phosphorus. Thus, oxidation of white phosphorus to phosphate, the harmless component of all living cells has been shown and its further incorporation into the microbial biomass.

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ВОЗМОЖНОСТЬ ОБЕЗВРЕЖИВАНИЯ БЕЛОГО ФОСФОРА МИКРОБНЫМИ КУЛЬТУРАМИ

Аннотация. Впервые наблюдался рост микроорганизмов различных таксономических групп (грибов, стрептомицетов и бактерий) в культуральных средах, содержащих в качестве источника фосфора белый фосфор P_4. Это первый известный пример включения белого фосфора в биосферный круговорот элемента фосфора. Самая высокая концентрация, применённая в данном исследовании, соответствует превышению ПДК белого фосфора в сточных водах в 5000 раз, а в питьевой воде – в 100000000 раз! Впервые проведена селекция на рост устойчивости культур к P_4. Мы идентифицировали микроорганизмы, растущие на белом фосфоре, как новые штаммы *Aspergillus niger* и *Streptomyces sampsonii*, которым были присвоены номера *A. niger* AM1 и *S. sampsonii* A8. Показано, что штаммы грибов *Aspergillus niger* адаптируются к P_4 лучше, чем бактерии.

Ключевые слова: биодеградация, белый фосфор, защита окружающей среды, химическое загрязнение.

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DETERMINATION OF BAS ABOVE-GROUND PART OF PLANTS OF CIRSIUM ARVENSE L.

Abstract: The results of the study of the chemical composition of aerial parts of *Cirsium arvense L.* collected during the fruiting period in the Shamalgan village of Kazakhstan are presented in the article. The quantitative and qualitative composition of biologically active substances was determined. Samples of *Cirsium arvense L.* contain 3.2% of alkaloids, 2.08% of flavonoids, 4.08% of phenolic acids, 4.5% of hydrocarbons, 1.16% of polysaccharides, 3.8% of terpenoids, 1.2% of organic acids, 3.12% of tannins, 0.78% of coumarins, 14.85% of protein and 1.67% of fat. The variety of biologically active compounds have a biological activity according to our results. A comparative analysis of the mineral, amino and fatty acid composition of *Cirsium arvense L.* plant was carried out. The analysis of the mineral composition showed the presence of 11 mineral elements: K, Na, Mg, Ca, Cu, Zn, Cd, Pb, Fe, Ni, Mn, which allows us to recommend the studied plants as raw materials rich in macro- and microelements.

Keywords: biologically active substances; flavonoids; alkaloids; tannins; mineral composition; fatty and amino acid composition.

Introduction

All regions of Kazakhstan are rich in plant resources. These resources play a vital role in dynamic growth of economy of our country. Because of its economic, agricultural and pharmaceutical importance plant resources are still under study. The healing properties of plants are studied in botanical gardens, large research institutes, and special laboratories. However, there are a number of wild-growing plants that have not yet been fully explored. One of the plants with such healing properties is Cirsium arvense. L. (beetle) plant.

Nevertheless, Cirsium arvense. L. is outside the range of vision of the scientists, it is well known from the literature that it is used in traditional medicine in addition to some dishes [1].

Cirsium arvense. L. is not fully discovered. Only the presence of vitamins, carotene, microelements and phytoncides in the plant parts indicates its significance for humanity. Moreover, the roots of this herb contain natural insulin, so it is a real food for people with diabetes. Chemical composition is not fully studied too. The constituent of the plant varies depending on its location. It is known that the leaves contain vitamin C, hydrocarbons, and proteins.

As the research object it was chosen Cirsium arvense. L., which grows in the Chamalgan region of Almaty district. The shoot system of plant was harvested in August, 2016.

The aim of the research is to identify biologically active compounds from Cirsium arvense L.

The practical significance of the work is the phytochemical analysis of the shoot system of Cirsium arvense L. plant. The results obtained Cirsium arvense L. allows to expand the scope of the plant application.

Methods

As the research object it was chosen the shoot system of Cirsium arvense. L., which grows in the Chamalgan region of Almaty district.

General method of research: According to the first edition of the State Pharmacopoeia of the Republic of Kazakhstan it is required to follow the rules for phytochemical examination during the preparation and separation of the sample.

The second strictly followed rule is crushing the raw materials into the same amount. Otherwise it would result in damage of details ratio of raw material. In accordance with GOST 24027. 1-80; 24027. 2-80; 2237-75 the phytochemical analysis of the shoot system of Cirsium arvense L. was done, quantitative and qualitative analysis were carried out [2].

Methods of investigation: The composition on micro- and macro- elements of the shoot system of Cirsium arvense L. was determined by atomic-emission spectral analysis, flavonoids and coumarin by spectrophotometric method, tannins by permanganometric method, amount of oil by Gerber method, amino acids and carbohydrates by paper chromatography, fat and amino acids were determined by gas chromatography [3].

The chemical composition of the butanol extraction of the shoot system of Cirsium arvense L. was investigated by the mass spectrometer detector Clarus-600 (Perkin Elmer) gas chromatography [4].

A certain amount of the shoot system of Cirsium arvense L. was removed and treated with 70% alcohol solutions and distilled water. In the homogeneous chromatography qualitative analysis was carried out and it was found that biologically active substances pass through 70% alcohol solutions. The phytochemical analysis of the shoot system part of Cirsium arvense L. plant was processed. In order to obtain a scheme of the analysis the crushed raw material (shoot system) was treated with 70% alcohol solutions at room temperature for 72 hours. Individual extractions with solvents as chloroform and butanol were done [5].

The investigation on fatty acids constituents of the shoot system of Cirsium arvense L. was done by Italian "Carlo Erba 4200" device for gas chromatography.

Results

Amount of biologically active substances and quality of shoot system of *Cirsium arvense L.* are shown in table 1.

Table 1 - Amount of BAS and quality of shoot system of *Cirsium arvense L.* samples

№	BAS in raw material	Amount in the above-ground part of *Cirsium arvense L.*, %
1	Moisture	11.10
2	Ashiness	7.98
3	Extractive substances 50% alcohol DW Acetone 70% alcohol 90% alcohol Chloroform	 30.32 38.09 2.05 32.3 25.6 3.1
4	Alkaloids	3.2
5	Flavonoids	2.8
6	Phenolic acids	4.8
7	Carbohydrates	4.5
8	Polysaccharose's	1.16
9	Terpenoids	3.8
10	Tannins	3.12
11	Organic Acids	1.2
12	Coumarins	0.78
13	Proteins	14.85
14	Lipids	1.67

In medicinal plants there should not be a lot of moisture, as this reduces their quality during storage. Usually, in the medicinal plant materials the amount of moisture should not exceed 12-15% [6].

The number of micronutrients in the shoot system of an ordinary plant Cirsium arvense. L. were determined using atomic-emisson spectral analysis at a wavelength of 750 nm using an AANALIST-400 instrument and Spekokol 11 spectrophotometer [7].

The results of the study on micro-and macronutrients are shown in Table 2 and Figure 1. As shown in Figure 1, a large amount of potassium from macronutrients and zinc from micronutrients are present in the shoot system of the plant Cirsium arvense L.

Table 2 - Micro and macronutrients found in the shoot system of the plant Cirsium arvense L .

№	Detected Element	Elements per mass of dry substance, %
1	Potassium	67,09
2	Sodium	0,46
3	Calcium	53,39
4	Magnesium	5,47
5	Zinc	0,0875
6	Copper	0,0767
7	Cadmium	0,0012
8	Lead	0,0158
9	Iron	0,4877
10	Manganese	0,0845
11	Nickel	0,0189

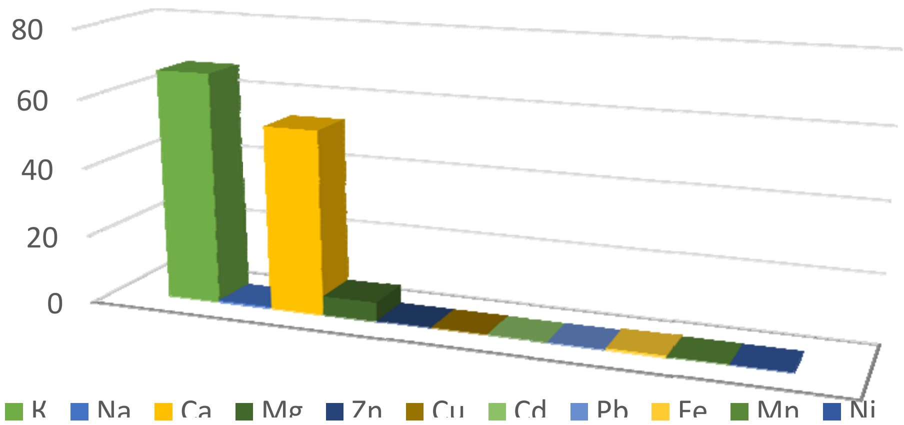

Figure 1 - Micro and macronutrients found in the shoot system of the plant Cirsium arvense L.

During the study, the amounts of vitamins A, C, and E in the shoot system of the plant Cirsium arvense L. were determined. The concentration of vitamin C was determined by the method of titrimetry, using the sodium salt of 2,6-dichlorophenolindophenol. And the concentration of vitamins A and E were determined by the method of fluorometry. As can be seen from table 3, the amount of vitamin C is high.

Table 3 - Numerical values of the amount of vitamins A, C, E in the shoot system of the plant Cirsium arvense L.

Vitamins	Amount, mg/100 g
A	0,406
C	1,9
E	0,886

Gas-liquid chromatography was used to determine the amount of amino acids. Using this method, the amounts of 20 amino acids were determined in the shoot system of the plant Cirsium arvense L. The results are shown in table 4 [8].

Table 4 - The amount of amino acids in the shoot system of the plant Cirsium arvense L.

№	Amino acid	Amount, mg / 100 g
1	Alanine	602
2	Glycine	254
3	Valine	248
4	Leucine	365
5	Isoleucine	280
6	Threonine	228
7	Serine	298
8	Proline	567
9	Methionine	96
10	Asparatat	1080
11	Cystine	42
12	Hydroxyproline	1
13	Phenylalanine	302
14	Glutamate	2116
15	Ornithine	1
16	Tyrosine	325
17	Histidine	268
18	Arginine	406
19	Lysine	194
20	Tryptophan	69

It was determined that in the shoot system of the plant Cirsium arvense L. 20 amino acids are present. Of these, glutomate and aspartate are the most abundant, while ornithine and hydroxyproline contain the least.

Gas-liquid chromatography was also used to determine the amount of fatty acids.

As can be seen from table 5, 23 species of fatty acids are present in the shoot system of the plant Cirsium arvense L. In addition, the amounts of these fatty acids have been determined. Of these, palmitic, myristic and oleic are the most abundant, undecanoic and γ-linolenic acids are the least.

Table 5 - The amount of fatty acids in the shoot system of the plant Cirsium arvense L.

№	Acids	Acid index	Number,%
1	Oil	$C_{4:\ 0}$	1.847
2	Capron	$C_{6:\ 0}$	1.603
3	Caprylic	$C_{8:\ 0}$	1.230
4	Capric	$C_{10:\ 0}$	3.026
5	Undecane	$C_{11:\ 0}$	0.082
6	Lauric	$C_{12:\ 0}$	3.638
7	Tridecane	$C_{13:\ 0}$	0.145
8	Myristic	$C_{14:\ 0}$	12.689
9	Myristolein	$C_{14:\ 1\ (cis\text{-}9)}$	1,011
10	Pentadecane	$C_{15:\ 0}$	1,313
11	Pentadecene	$C_{15:\ 1}$	0.314
12	Palmitic	$C_{16:\ 0}$	34,306
13	Palmitoleic	$C_{16:\ :\ 1}$	1.463
14	Margarine	$C_{17:\ 0}$	0.652
15	Margarine olein	$C_{17:\ 1}$	0.316
16	Stearic	$C_{18:\ 0}$	9.929
17	Oleic	$C_{18:\ 1\ n9C}$	22.483
18	Linoleidine	$C_{18:\ 2\ n6t}$	0.354
19	Lynol	$C_{18:\ 2\ n6c}$	2,506
20	γ -Linolenic	$C_{18:\ 3\ n6}$	0.114
21	Linolenic	$C_{18:\ 3\ n3}$	0.316
22	Arachine	$C_{2\ 0\ 0}$	0.302
23	Eicosenic	$C_{20:\ 1}$	0.162

Conclusion

BAS were analyzed for the first time in the shoot system of the plant Cirsium arvense L. growing in Kazakhstan.

The study resulted in the following conclusions:

1) High-quality and quantitative analyzes were made on biologically active substances in the shoot system of the plant Cirsium arvense L.

2) As a result of a study on biologically active substances in the shoot system of the plant Cirsium arvense L., 20 amino acids and 23 fatty acids were determined using GC / MS.

Evaluation of the implementation of tasks. The tasks were fully completed. In the course of the study, large amounts of biologically active substances were found in the shoot system of the plant Cirsium arvense L. selected as the object of study. It was suggested that this garden weed, which was considered as harmful in CIS countries before that, could be used as a medicinal plant. This means that it is appropriate to continue further research on the composition of the plant, and methods for isolating biologically active substances.

Also, it can be concluded that the isolation and determination of the composition of these biologically active substances can make a huge contribution to the chemistry of natural compounds.

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CIRSIUM ARVENSE L. ӨСІМДІГІНІҢ ЖЕР ҮСТІ БӨЛІГІНДЕГІ ББЗ-ДЫ АНЫҚТАУ

Аннотация. Алғаш рет Қазақстанның Алматы облысы Шамалған аймағында өсетін Cirsium arvense L. өсімдігінің химиялық құрамы нәтижелері келтірілген. Биологиялық белсенді заттардың сапалық және сандық мөлшері көрсетілген, оның ішінде Cirsium arvense L. өсімдігінің құрамынан алкалоидтар 3,2%, флавоноидтар 2,8%, фенол қышқылдар 4,8%, көмірсулар 4,5%, полисахаридтер 1,16%, терпеноидтар 3,8%, органикалық қышқылдар 1,2%, тері илегіш заттар 3,12%, кумариндер 0,78%, ақуыз 14,85%,май 1,67%. Cirsium arvense L. өсімдігінің құрамында биологиялық белсенді заттардың көп болуы олардың биологиялық белсенділік көрсетуіне негізделген. Мақалада Cirsium arvense L. өсімдігінің құрамындағы минералды заттар, май- және аминқышқылдарына салыстырмалы талдау жүргізілген. Минералдық құрамын талдау кезінде 11 минералдық элементтердің бары анықталды: K, Na, Mg, Ca, Cu, Zn, Cd, Pb, Fe, Ni, Mn.

Түйін сөздер: биологиялық белсенді заттар; флавоноидтар; алкалоидтар; тері илегіш заттар; минералдық құрам; май- және амин қышқылды құрамы.

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ОПРЕДЕЛЕНИЕ БАВ НАДЗЕМНОЙ ЧАСТИ РАСТЕНИЙ CIRSIUM ARVENSE L.

Аннотация. В работе приведены результаты исследования химического состава надземной части Cirsium arvense L., собранных в период плодоношения в Шамалган регионе Казахстана. Исследован количественный и качественный состав биологически активных веществ. В растениях Cirsium arvense L. содержат 3,2% алкалоидов, 2,08% флавоноидов, 4,08% фенольных кислот, 4,5% углеводородов, 1,16% полисахаридов, 3,8% терпеноидов, 1,2% органических кислот, 3,12% дубильных веществ, 0,78% кумаринов, 14,85% белка и 1,67% жира. Разнообразие биологически активных соединений обусловливает широкий спектр биологической активности. Проведен сравнительный анализ минерального, жирно- и аминокислотного состава растения Cirsium arvense L. Анализ минерального состава показал наличие в образцах 11 минеральных элементов: K, Na, Mg, Ca, Cu, Zn, Cd, Pb, Fe, Ni, Mn.

Ключевые слова: биологически активные вещества; флавоноиды; алкалоиды; дубильные веществ; минеральный состав; жирно- и аминокислотный состав.

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PHYSICOCHEMICAL INVESTIGATIONS OF VERMICULITE – MICROPOROUS COMPONENT FOR HEAT-RESISTANT MATERIALS

Abstract. The results of investigations of Kulantau field (Turkestan region) vermiculite's physicochemical and physical-technical properties are presented. The vermiculite's chemical and mineralogical composition and its main crystalline phases, which are composed of ferrous magnesium and calcium aluminosilicates of complex composition, are determined by chemical, X-ray diffraction, spectral analysis methods. The complex thermal analysis method established the processes occurring during heating, which allow to judge the physicochemical and structural changes occurring in vermiculite during heat treatment. The electron microscopy method investigated the vermiculite particles' surface morphology. The main physical-technical properties of the expanded vermiculite are determined. It was established that the expanded vermiculite has low bulk density and low thermal conductivity, has high porosity, fire resistance, and refractoriness characteristics. Due to its unique properties, the expanded vermiculite can be effectively used as a microporous component for production of composite heat-resistant materials.

Key words: vermiculite, methods of physicochemical analysis, physical-technical properties, microporous component, composite heat-resistant materials.

Introduction. The Republic of Kazakhstan has huge reserves of natural and technogenic mineral raw materials, which under certain conditions of their processing can become a full-fledged resource for various industries [1-4].

The development of effective types of composite binding materials from natural and technogenic mineral raw materials is one of the most urgent scientific, technical, economic and environmental problems.

Vermiculite is a natural mineral from the group of hydromica, formed in natural conditions as a result of hydration and other secondary changes of various micas. Vermiculites, formed from ferrous magnesium micas – biotite and phlogopite, are of practical importance. The vermiculite's chemical composition corresponds to the approximate formula $(Mg, Fe^{2+}, Fe^{3+})_3\,[(Si, Al)_4\,O_{10}](OH)_2\cdot 4H_2O$. However, vermiculite does not always exactly correspond to the general formula, since it contains various impurities [5].

In Kazakhstan, the most famous deposits of vermiculite are Altyntas, Karatas, Sholak-Kairaktin in Aktobe region; Barchinsk in North Kazakhstan region; Neozhidannoye in Karaganda region; Kulantau in Turkestan region [6].

A special feature of vermiculite is its ability to increase its volume by 10-20 times with a sharp roasting. This expansion phenomenon is due to the fact that during a sharp roasting, the molecular water between the vermiculite flakes quickly turns into steam, which moves the mica flakes always in the direction perpendicular to the mica cleavage. The vermiculite expanded during roasting during cooling retains increased volume with the thinnest air interlayers between the mica flakes, which gives the mineral many valuable properties, in particular fire resistance, refractoriness and low thermal conductivity [7, 8].

Introduction of the expanded vermiculite, as a refractory microporous component, which, being a damper, suppresses the resulting stresses under thermal effects, which contributes to increase in the heat resistance of heat-resistant concrete [9, 10].

In the works [11, 12], proceeding from the theoretical model applied to refractory materials, it was found that the vermiculite use contributes to decrease in the thermal conductivity of heat-resistant vermiculite concrete in comparison with other highly porous materials.

Methods. The *physicochemical investigations* of the vermiculite samples' microstructure were performed using JSM-6490LV scanning electron microscope (JEOL, Japan), with the help of which the elemental chemical composition was also determined by the energy dispersive method.

The *petrographic investigations* of the vermiculite samples were performed using MIN-8 optical polarization microscope by examining immersion preparations in the transmitted light.

The *chemical analysis* of the studied vermiculite samples was performed according to the method adopted for inorganic materials [13, 14].

The vermiculite samples' *microstructure was investigated* using JSM-6490LV scanning electron microscope (JEOL, Japan), which also determined the elemental chemical composition by the energy dispersive method.

The *X-ray diffraction investigation* was performed using Bruker AXS X-ray diffractometer (Germany) on CaK_{α} radiation at a voltage of 40kV and at a current of 40mA, at an angle coverage interval of 2θ 5-80º at a recording step of 0.1° and a recording speed of 2s/step.

The diffraction patterns were decoded automatically using EVA software package of Bruker AXS X-ray diffractometer.

The *thermogravimetric investigations* were performed using TGA/DSC1 Mettler Toledo thermal-analytical system (Switzerland) – a device for combined thermographic analysis and differential scanning calorimetry. The device is designed to measure thermodynamic characteristics (heat and temperature of phase transitions and physicochemical reactions), as well as recording changes in the mass of solid and powdered materials in the temperature range from 25 to 1600ºC.

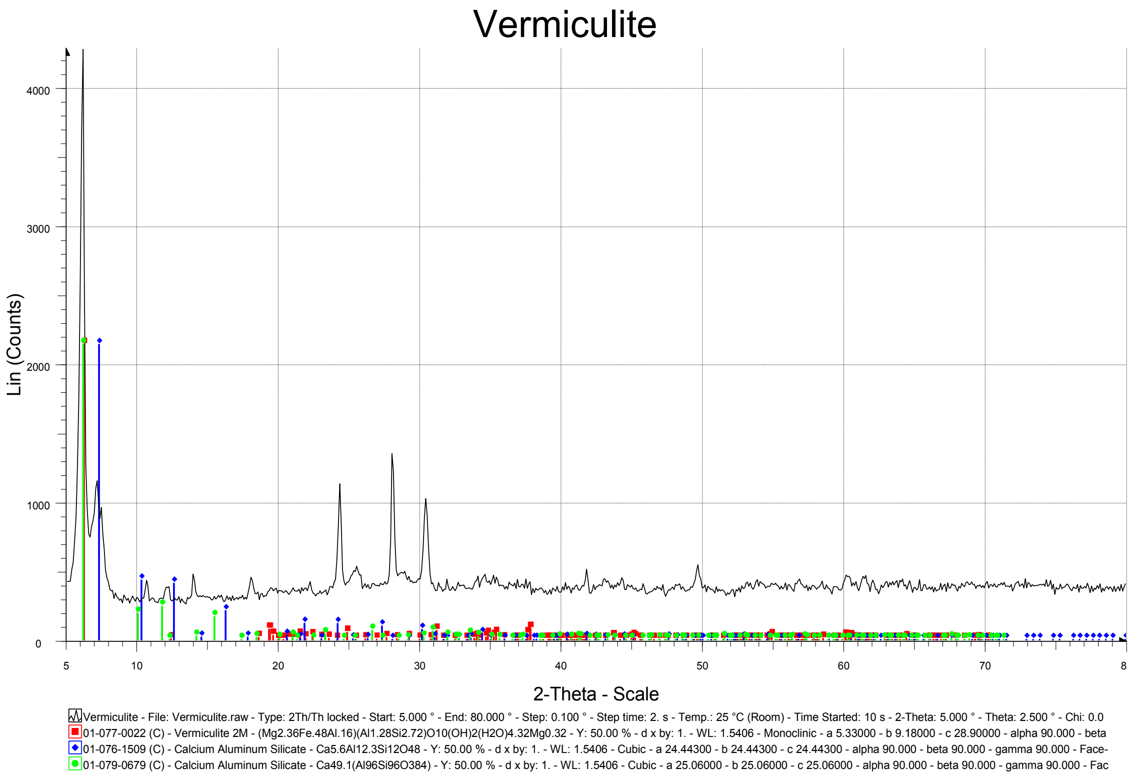

Figure 1 – The diffractogram of the vermiculite sample

Results. The Kulantau field (Turkestan region) vermiculite samples were used for physicochemical investigations.

The chemical composition of the vermiculite is shown in Table 1.

Table 1 – Chemical content of the vermiculite

Content of oxides, mass percent									
SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	FeO	Na_2O	K_2O	MnO	H_2O
32.5	11.4	2.6	16.6	11.5	1.7	5.5	5.6	8.1	4.6

The diffractogram of the vermiculite sample is shown in Figure 1.

As a result of the X-ray investigation of the vermiculite sample, the following main crystalline phases were identified:

- vermiculite $(Mg_{2.36}Fe_{0.48}Al_{0.16})(Al_{1.28}Si_{2.72})O_{10}(OH)_2(H_2O)_{4.32}Mg0_{0.32}$;

- calcium alumosilicates $Ca_{5.6}Al_{2.3}Si_{12}O_{48}$; $Ca_{49.1}(Al_{96}Si_{96}O_{384})$.

Figure 2 shows the derivatogram of the vermiculite sample.

As a result of the complex thermal investigation of the vermiculite sample, the following thermal effects were determined.

When analyzing the vermiculite's TG, DTG and DSC curves, it was found that when the vermiculite is heated, complex thermal transformations were observed: the 1st endo-effect is removal of moisture at a temperature of 90.7ºC with 6% mass loss; the 2nd endo-effect at 176.85°C is removal of moisture with 7.5% mass loss. At a temperature of 653.4°C there is a prolonged release of water (the 3rd effect) with a mass loss of up to 10%, another 0.5% of water is lost at 917°C (the 4th effect). The first two endo-effects are due to the loss of zeolitic water from large and small pores, the 3rd and the 4th effects are due to the loss of water present in the vermiculite in the form of structural OH groups, the removal of which leads to the zeolite structure destruction. The total water mass loss is 11.1%.

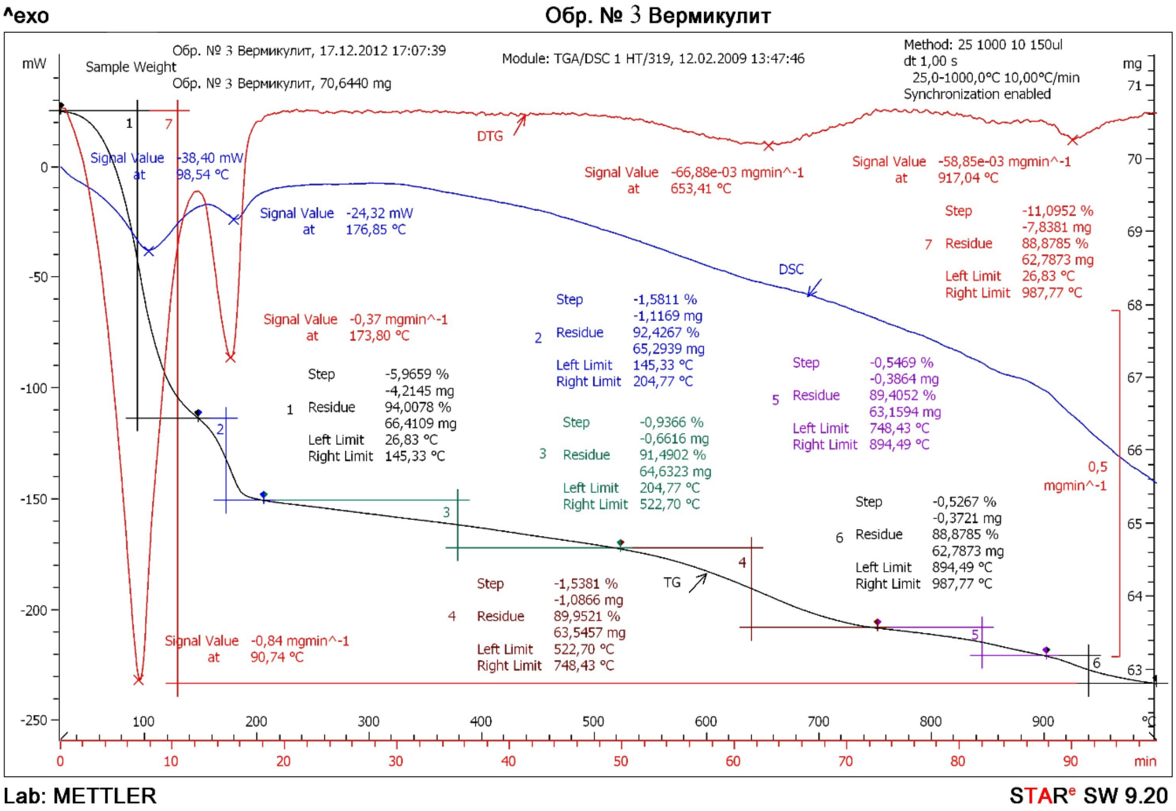

Figure 2 – The derivatogram of the vermiculite

The vermiculite's complex thermal analysis results allow to judge the physicochemical processes occurring in it when heated and associated with various states of water in the vermiculite.

The observed intense endothermic effect in the temperature range of 80-100°C is associated with the adsorption water loss.

The second endo-effect is caused by the release of water (interpacket), bound to exchangeable water ions, which is contained between the mica flakes and is strongly adsorbed on their cleavage planes. In this case, there is a significant samples' mass loss.

The stretched third endo-effect is characteristic of all micaceous materials, including vermiculite, and is associated with the removal of hydroxyl groups.

The results of the surface morphology's electron microscopic investigations and the vermiculite sample's energy dispersive analysis are shown in Figure 3.

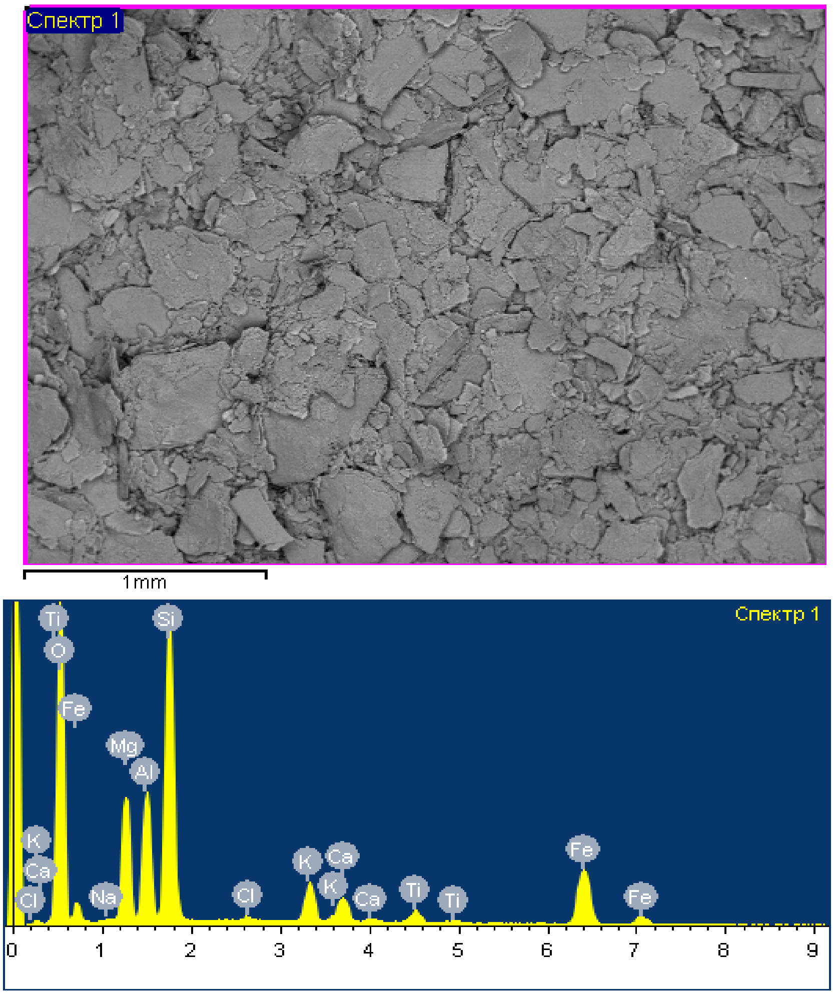

Figure 3 – The surface morphology and the elemental composition when scanning the vermiculite sample

The investigations of the elemental chemical composition (Table 2) showed that the vermiculite composition has a significant content of such elements as Si, Mg, Al, Ca, Fe, K, which characterizes its mineralogical composition.

Table 2 – The elemental chemical composition of the vermiculite

Content of elements, mass percent									
O	Na	Mg	Al	Si	Cl	K	Ca	Ti	Fe
45.89	0.11	8.63	7.82	17.42	0.27	3.04	2.12	1.42	13.28

Table 3 shows the main physical-technical properties of the expanded vermiculite.

Table 3 – The main physical-technical properties of the expanded vermiculite

Main physical-technical properties	Indicators
Loss on ignition, mass percent	1.2 – 11.8
Bulk density, fraction 0.6-5 mm, kg/m^3	100-150 kg/m^3 (Mark 150)
Porosity, including intergranular, %	84 – 95
Operating temperature, ^{o}C	+1350

The expanded vermiculite has a number of valuable properties [15], among them the most important ones include the following:

- low density – 60-200 kg/m^3;
- low thermal conductivity coefficient – 0.048-0.06 W/m · degree (°C);
- high fire resistance, melting point > 1300°C;
- low coefficient of thermal expansion – 0.000014;

Currently, the actual scientific and technical challenge is to create new efficient types of heat-resistant materials, in particular heat-resistant concretes, the production of which saves deficit and expensive raw materials, reduces fuel and energy consumption and reduces labor costs [16].

Heat-resistant materials for thermal units operating at high temperatures should have high strength, low thermal conductivity, high heat resistance, not high cost, and a number of other performance indicators.

Analysis of published works showed that the use of mineral industrial wastes for production of composite binders can be no less effective than the use of specially manufactured technical products [17].

The choice of the expanded vermiculite as a microporous component of heat-resistant materials is due to its high thermal insulation properties and fire resistance, due to which the expanded vermiculite is used in fire-retardant materials.

Conclusion. As a result of the physicochemical investigations, it was established that according to the mineralogical composition, the vermiculite is represented mainly by magnesian aluminosilicates of complex composition.

The expanded vermiculite has such valuable properties as fire resistance, high melting point, low thermal conductivity, low bulk density.

Due to its unique properties, the expanded vermiculite can be effectively used as a microporous component for production of composite heat-resistant materials.

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ЫСТЫҚҚА ТӨЗІМДІ МАТЕРИАЛДАРҒА АРНАЛҒАН МИКРОКЕУЕКТІ КОМПОНЕНТІ – ВЕРМИКУЛИТТІ ФИЗИКА-ХИМИЯЛЫҚ ЗЕРТТЕУ

Аннотация. Түркістан облысы Құлантау кен орнының вермикулитінің физика-химиялық және физика-техникалық қасиеттерін зерттеу нәтижелері келтірілген. Химиялық, рентгенография, спектральды талдау әдістерімен вермикулиттің химиялық және минералогиялық құрамы, және оның негізгі кристалды фазалары күрделі құрамды магнийтемір және кальций алюмосиликаттары анықталады. Кешенді термиялық талдау әдісімен термиялық өңдеу кезінде вермикулиттегі физика-химиялық және құрылымдық өзгерістерді бағалауға мүмкіндік беретін процестері анықтады. Электронды микроскопия әдісімен вермикулиттің бөлшектер бетінің морфологиясы зерттелді. Ісінген вермикулиттың негізгі физика-техникалық қасиеттері анықталды. Ісінген вермикулит төмен тығыздығы мен төмен жылу өткізгіштікке ие, жоғары кеуекті, өртке қарсы және қиын балқу сипаттамалары бар екендігі анықталды. Бірегей қасиеттері арқасында ісінген вермикулит ыстыққа төзімді композитті материалдарды өндіру үшін микрокеуекті компонент ретінде тиімді пайдалануға болады.

Түйінді сөздер: вермикулит, физико-химиялық талдау әдістері, физика-техникалық қасиеттері, микрокеуекті компонент, ыстыққа төзімді композициялық материалдар.

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ФИЗИКО-ХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ ВЕРМИКУЛИТА – МИКРОПОРИСТОГО КОМПОНЕНТА ДЛЯ ЖАРОСТОЙКИХ МАТЕРИАЛОВ

Аннотация. Приведены результаты исследований физико-химических и физико-технических свойств вермикулита Кулантауского месторождения Туркестанской области. Методами химического, рентгенографического, спектрального анализа определены химико-минералогический состав вермикулита и составляющие его основные кристаллические фазы, представленные магнийжелезистыми и кальциевыми алюмосиликатами сложного состава. Методом комплексного термического анализа установлены процессы, протекающие при нагревании, которые позволяют судить о физико-химических и структурных изменениях, происходящих в вермикулите при термической обработке. Методом электронной микроскопии исследована морфология поверхности частиц вермикулита. Определены основные физико-технические свойства вспученного вермикулита. Установлено, что вспученный вермикулит обладает низкой насыпной плотностью и низкой теплопроводностью, имеет высокие характеристики по пористости, огнестойкости, тугоплавкости. Вспученный вермикулит, благодаря своим уникальным свойствам, может эффективно применяться в качестве микропористого компонента для производства композиционных жаростойких материалов.

Ключевые слова: вермикулит, методы физико-химического анализа, физико-технические свойства, микропористый компонент, композиционные жаростойкие материалы.

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POLYSACCHARIDE-STABILIZED PALLADIUM NANOCATALYST FOR SEMI-HYDROGENATION OF COMPLEX ALKYNOLS

Abstract. New Pd-Polysaccharide/ZnO catalysts with palladium content of 0.1%, 0.3%. 0.5% and 1.0% have been developed and tested in the hydrogenation of long-chain acetylenic alcohols used as precursors for syntheses of vitamins and pest-insect pheromones. Pectin and gelan were used as stabilizers of Pd nanoparticles (1-2 nm) fixed on ZnO. TEM study confirmed uniform distribution of the dispersed metal on the surface of zinc oxide. The sizes of palladium nanoparticles in the best catalyst were 1-2 nm. The catalysts with 0.5%wt.Pd demonstrated the highest activity, selectivity to cis-alkenols and stability in multiple runs. TON is varied in the range of 6700-7500 for hexadecinols. TON was 33000 for hydrogenation of 3,7,11,15-tetramethylhexadecin-1-ol-3 (C_{20}). A total hydrogenated amount of this substrate on .05 g of 0.5% Pd-Pec/ZnO catalyst was 48 ml. Deactivation of the catalysts is observed after 64 runs. TEM images showed partial leaching of twisted polymer-metal films from the surface of ZnO.

Keywords. Pectin, gellan, polysaccharides, catalytic properties, hydrogenation, palladium catalysts, alkynols.

Introduction

The principles of green chemistry [1] are targeting to develop energy-saving selective processes for the production of valuable chemicals. Many monomers and plasticizers, aromatic substances, vitamins, pheromones, medicines and other biologically active substances are synthesized catalytically based on a selective hydrogenation of long-chain (C_{10}-C_{20}) acetylene compounds into olefin derivatives [2-9]. These reactions are often carried out at high temperatures and pressures with rather low yields of targeted products. In this case the selection of the proper catalyst is very important. The use of modern nanotechnology approaches for creating new types of nanosized catalysts makes it possible to improve these drawbacks.

Supported catalysts are usually used in the chemical industry, energy, and environmental protection. This is due to the fact that their properties depend on the structure and sizes of the active phase. Reducing its content in the surface of the support leads to a decrease in the particle sizes of the deposited metals and an increase in the number of active centers for catalytic acts and therefore to an increase in the rate and selectivity of the reaction. Polymers with different functional groups are used as one of the nanotechnology approach to synthesize metal nanoparticles and catalysts [10-15]

We have developed a simple method of catalyst preparation based on interaction and stabilization of metal nanoparticles by polymers on the surface of inorganic sorbents (natural and synthetic zeolites, metal oxides) [16, 17]. The developed technique allows to obtain catalysts for selective hydrogenation of wide range of unsaturated compounds [16-22].

The present work demonstrates the possibilities of using an environmentally friendly natural polymers as pectin and gellan to stabilize palladium nanoparticles on the surface of zinc oxide. The developed low-percentage catalysts were studied in the semi-hydrogenation of complex acetylene alcohols. The obtained olefin derivatives are used in the syntheses of vitamins and pest insect pheromones [5].

Experimental part

The method of sequential adsorption of polymer and metal salt from water solutions was used for the preparation of palladium catalysts [22].

The acetylenic alcohols: 3,7,11,15-tetramethylhexadecin-1-ol-3 (C_{20}); 9-hexadecin-1-ol (9-HD-1-ol) and 11-hexadecin-1-ol (11-HD-1-ol) were purchased from Sigma Aldrich and used without additional purification.

Ethanol (reagent grade), palladium chloride ($PdCl_2$, 59-60% Pd, Sigma Aldrich), pectin (Pec, M_w = 15000, the content of uronide components is 90.3%, the degree of esterification is 23.7%, Sigma Aldrich) were also used without additional purification. Zinc oxide (chemically pure) was used as an inorganic support.

Palladium amount in the Pd-Pec/ZnO catalysts was varied from 0.1 to 1.0 wt.% from total composite content. The palladium content in mother liquors before and after metal adsorption was determined from photoelectric colorimetry data, which were obtained on a SF-2000 UV/Vis spectrophotometer (OKB Spectr, Russia) based on calibration curves constructed at the wavelength $\lambda = 425$ nm.

TEM (transmission electron microscopy) of catalyst samples were studied on a JEM-2100 transmission electron microscope (Jeol, Japan) with an accelerating voltage of 100 kV.

The acetylenic alcohol hydrogenation was carried out in thermostatic reactor in ethanol (25 ml) at 40°C and atmospheric hydrogen pressure. Before the reaction the catalyst was saturated with hydrogen for 30 minutes and the tested substrate was injected to the reactor. Hydrogen uptake was measured and reaction products were detected by chromatographic analysis (“Khromos”, Russia). The catalyst selectivity was calculated as the proportion of the target product to the sum of all reaction products at a given conversion.

Results and Discussion

The developed Pd-Pec/ZnO catalysts with 0.1wt.%; 0.3wt.%; 0.5wt.% and 1.0wt.% of Pd have been tested in the hydrogenation of 3,7,11,15-tetramethylhexadecin-1-ol-3 (C_{20}); 9-hexadecin-1-ol (9-HD-1-ol) and 11-hexadecin-1-ol (11-HD-1-ol). The produced olefins of the semi-hydrogenation of these complex acetylene compounds are used in fine chemistry for production of biologically active substances.

The C_{20} acetylene alcohol is hydrogenated with high rate and stability at multiple runs on the same 1% Pd-Pec/ZnO catalyst sample (Table 1). However, the selectivity to the olefin alcohol is quite low (49.9%). Probably, the alkenol is reduced to 3,7,11,15-tetramethylhexadecanol-3 without desorption from the catalyst into the reaction medium.

Table 1 - Hydrogenation of C_{20} acetylene alcohol on Pd-Pec/ZnO catalysts with various content of palladium

Pd content, %	$W*10^{-4}$, mol/l c	S, %	TON
Pd-Pec/ZnO			
1,0	14.8	49.9	10000
0,5	6.6	89.4	33000
0,3	1.7	58.3	550
0,1	0.8	66.1	-
Reaction conditions: 0.05g catalyst; C_{20} = 0.75 ml; 25 ml ethanol; T-40°C; P-1 atm			

A decrease in the metal content in the catalysts from 1.0 to 0.1% leads to a significant decrease in the reaction rate, but the selectivity of the process passes through a maximum attributable to the catalyst with 0.5% metal content (Table 1). It was shown that in 4 minutes the total acetylene alcohol was converted to the olefinic alcohol on this catalyst (Figure 1).

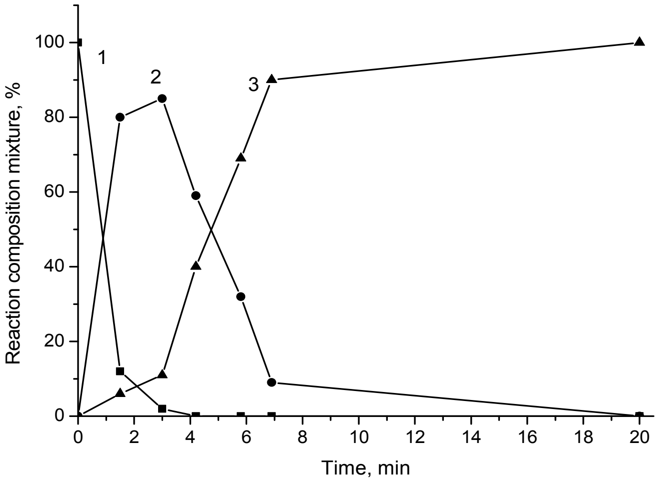

Figure 1 - Hydrogenation of C_{20} acetylene alcohol on 0.5% Pd-Pec/ ZnO. Diagram of the composition of the reaction mixture: (1) C_{20} acetyltnic alcohol, (2) C_{20} olefinic alcohol, (3) C_{20} alcanol. Reaction conditions: catalyst sample weight, 0.05 g; temperature, 40°C; H_2 pressure, 0.1 MPa; solvent, ethanol (25 mL); initial C_{20} acetylene alcohol amount, 0.25 mL

The amount of the saturated alcohol at this time does not exceed 8%. This catalyst also showed the highest stability. TON reaches 33,000 (catalytic acts per 1 palladium atom).

The catalyst was washed with water after 39, 57 and 64 runs of C_{20} alcohol hydrogenation [21]. This treatment lead to a noticeable increase in the reaction rate. A total amount of substrate hydrogenated on .05 g of 0.5% Pd-Pec/ZnO catalyst was 48 ml.

According to the TEM data, the initial catalyst (Figure 2, a) is characterized by the uniformly distributed palladium nanoparticles (1-2 nm) in a bulk polymer matrix fixed on the support. A change in the texture of the surface polymer-metal composite is observed in the catalysts' samples taken after 39, 57 and 64 hydrogenation runs. The polymer matrix swelled in the sample tested after the 64 run (Figure 2, c), a partial peeling of the surface polymer layer is observed on the catalyst. New structures have also been observed. (Figure 2, d). Twisted polymer-metal films in a form of "stars" were appeared separately from support.

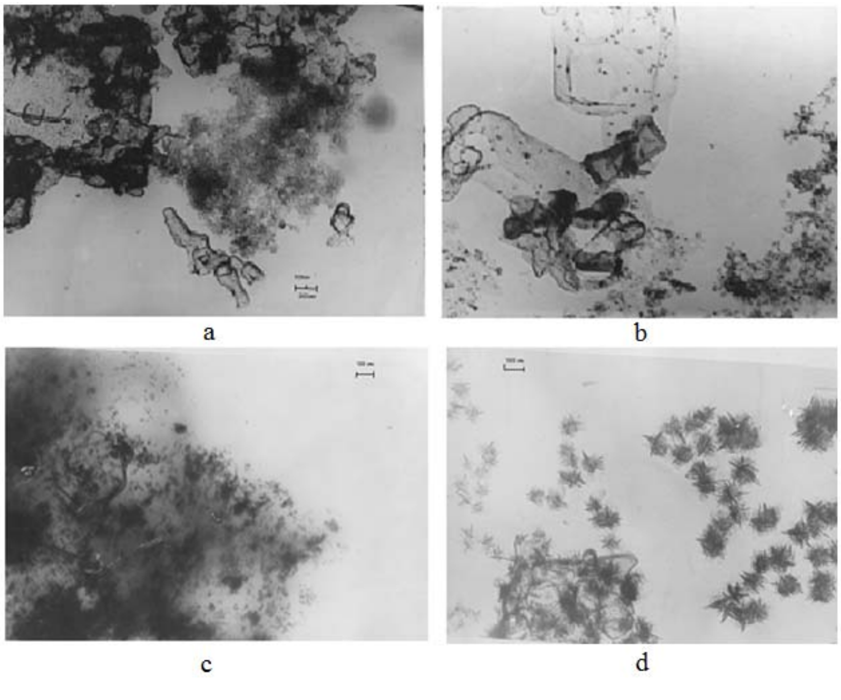

Figure 2 – Microphotographs (TEM) of Pd-Pec/ZnO catalyst. a - initial; b - after 39 runs; c and d - after 64 runs

The introducing gellan instead of Pec leads to the formation of a less active, but more selective catalyst. Such behavior can be explained by differences in the structure of these polysaccharides. Pectin is characterized by one sucrose group in the monomer, as well as a gellan has four such groups . The process slows down sharply after the nearly complete conversion of C_{20} alkynol to alkenol on o.5%Pd-Gel/ZnO catalyst. Selectivity reaches 96% (Figure 3).

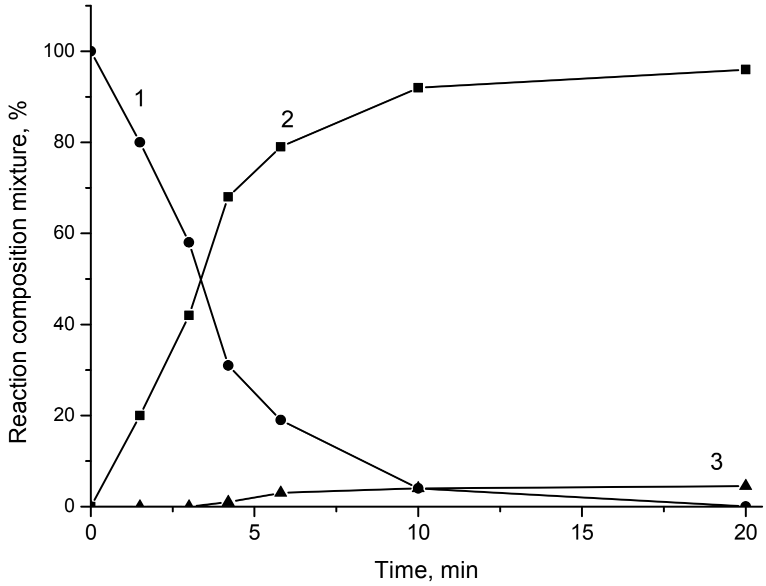

Figure 3 - Hydrogenation of C_{20} acetylene alcohol on 0.5% Pd-Gel/ZnO. Diagram of the composition of the reaction mixture: (1) C_{20} acynol; (2) C_{20} alkenol; (3) C_{20} alkanol. Reaction conditions: $m_{кат}$-0,05g; ethanol-25ml; T-40^{O}C; P-1 atm

Thus, polysaccharide containing catalysts are complex composites including bulk polymer layer with dispersed palladium nanoparticles inside, which is chemosorbed on the surface of ZnO. The catalysts showed high activity and selectivity in semi-hydrogenation of acetylenic alcohols. It is confirmed by hydrogenation of hexadecinols.

Hydrogenation of 9-hexadecin-1-ol (9-HD1-ol) and 11-hexadecin-1-ol (11-HD-1-ol) into cis-alkenols is the most important reaction in synthesis of some pect insect pheromones [6]. The results of the hydrogenation are presented in the Table 2.

It was found that the hydrogenation of 9-HD-1-ol on 0.3 and 0.5% catalysts proceeds at almost the same rates (2.4-2.9 * 10^{-4} mol /l s). In the case of 9-HD-1-ol, the activity of the catalyst increases with increasing palladium content. At the same time, the selectivity of the process on all studied catalysts reaches 100%.

Table 2 – The results of hydrogenation of hexadecins on Pd-Pec/ZnO and Pd-Gel/ZnO catalysts

Pd content in catalysts, wt.%	W*10^{-4}, mol/l s	$S_{cis-C=C}$, %	TON
Pd-Pec/ZnO			
11-hexadecin-1-ol			
0.1	1.9	100	-
0.3	2.4	100	4400
0.5	2.9	100	7200
9-hexadecin-1-ol			
0.1	4.7	100	-
0.3	12.2	100	-
0.5	26.2	100	6700
Pd-Gel/ZnO			
11- hexadecin-1-ol			
0.5	2.7	100	7500
9- hexadecin-1-ol			
0.5	3.3	100	6900
Reaction conditions: 0.05g catalyst; 25 ml ethanol; T-40°C; P-1 atm			

According to chromatographic analysis, in the first 5 minutes, around all of the starting acetylene alcohol is converted to cis-olefin on 0.5% Pd-Pec/ZnO (Figure 4). Only trace amounts of saturated alcohol are detected in the reaction mixture. This catalyst also demonstrates maximum stability during repeated process runs, TON = 6700-7200 (Table 2).

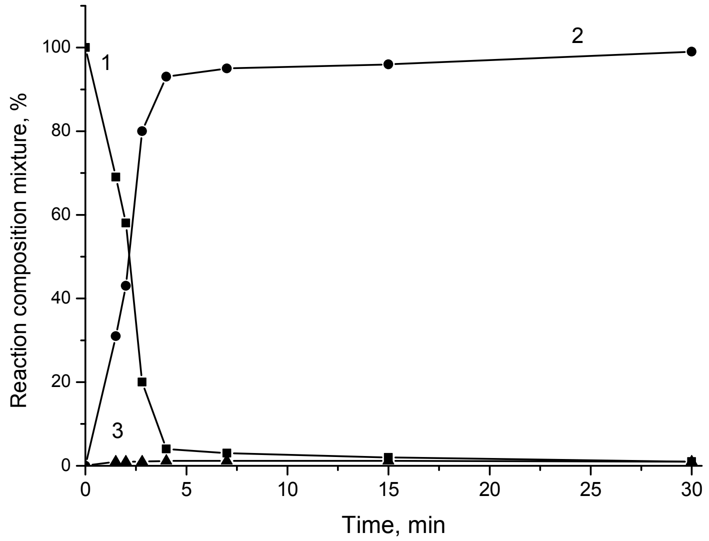

Figure 4 - Hydrogenation of 9-HD-1-ol on 0.5% Pd-Pec/ ZnO. Diagram of the composition of the reaction mixture: (1) C ackynol; (2) C alkenol; (3) C_0 alkanol. Reaction conditions: $m_{кат}$-0,05g; ethanol-25ml; T-40°C; P-1 atm

In contrast to the catalyst modified with Pec, the hydrogenation rate of both of 9-hexadecin-1-ol and 11-hexadecin-1-ol on 0.5% Pd-Gel/ZnO is lower (Table 2) while selectivity to cis-alkenol remains 100% and TON also rather high.

Thus, the developed 0.3-0.5% Pd-Pec/ZnO and 0.5% Pd-Gel/ ZnO catalysts are active, stable and stereoselective hydrogenation catalysts for hydrogenation of complex acetylene alcohols.

Conclusions

Thus, taking into account the principles of green chemistry, the low-percentage palladium catalysts stabilized with polysaccharides have been developed. The process of their synthesis was carried out at ambient conditions from water solutions. These catalysts are characterized with high dispersion of Pd nanoparicles (1-2 nm) evenly distributed on the surface of zinc oxide. The catalyst with 0.5% of Pd demonstrated high activity, stability and selectivity in semi-hydrogenation of complex alkynols. The obtained alkenols are used as biologically active substances, as vitamins and insect pheromones osed in agriculture to predict the development of insect pests and reduce the number of field treatments with toxic pesticides.

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АЛКИНОЛ КОМПЛЕКСТЕРІН ЖАРТЫЛАЙ ГИДРЛЕУГЕ АРНАЛҒАН ПОЛИСАХАРИД-ТҰРАҚТАЛҒАН ПАЛЛАДИЙ НАНОКАТАЛИЗАТОРЛАРЫ

Аннотация. Құрамында 0,1%, 0,3%, 0,5% және 1,0% Pd болатын жаңа Pd-полисахарид/ZnO катализаторлары витаминдер мен пектинді жәндіктердің феромондарын синтездеу үшін прекурсорлар ретінде қолданылатын ұзын тізбекті ацетилен спирттерін гидрлеу үрдісі үшін әзірленді. Пектин мен гелан ZnO бекітілген, Pd (1-2 нм) нанобөлшектерін тұрақтандырғыш ретінде пайдаланылды. ТЕМ зерттеуі дисперсті металдың мырыш оксидінің бетіне біркелкі таралуын растады. Ең жақсы катализатордағы палладий нанобөлшектерінің мөлшері 1-2 нм болды. Құрамында Pd мөлшері 0,5% болатын катализаторлар ең жоғары белсенділікті, цис-алкенолдар үшін селективтілікті және қайталама сынақтарда тұрақтылықты көрсетті. ТОН гексадеколиндер үшін 6700-7500 аралығында болады. ТОН 3,7,11,15-тетраметилгексадекин-1-ол-3 (C_{20}) гидрлеу үрдісі үшін 33000 құрайды. 0,5% Pd-ПЕК/ZnO катализаторының 0,05 г дейін гидрленген субстраттың жалпы мөлшері 48 мл болды. Катализатордың дезактивациясы 64 өтпеден кейін байқалады. ПЭМ көмегімен алынған суреттер ZnO бетінен бұралған полимерлі-металл пленкалардың жартылай сілтісіздігін көрсетті.

Түйін сөздер. Пектин, геллан, полисахаридтер, каталитикалық белсенділік, гидрлеу, палладий катализаторы, алкинолдар.

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ПОЛИСАХАРИД-СТАБИЛИЗОВАННЫЕ НАНОКАТАЛИЗАТОРЫ ПАЛЛАДИЯ ДЛЯ ПОЛУГИДРИРОВАНИЯ КОМПЛЕКСОВ АЛКИНОЛОВ

Аннотация. Новые Pd-полисахарид/ZnO катализаторы с содержанием палладия 0,1%, 0,3%, 0,5% и 1,0% были разработаны и испытаны в гидрировании длинноцепочечных ацетиленовых спиртов, используемых в качестве прекурсоров для синтеза витаминов и феромонов насекомых. Пектин и гелан использовали в качестве стабилизаторов наночастиц Pd (1-2 нм), закрепленных на ZnO. ТЕМ исследование подтвердило равномерное распределение дисперсного металла на поверхности оксида цинка. Размеры наночастиц палладия на лучшем катализаторе составляли 1-2 нм. Катализаторы с содержанием 0,5% Pd продемонстрировали наивысшую активность, селективность по цис-алкенолам и стабильность при многократном использовании. TON варьируется в диапазоне 6700-7500 для гексадецинолов. TON при гидрировании 3,7,11,15-тетраметилгексадецин-1-ол-3 (C_{20}) составляет 33000. Общее количество прогидрированного субстрата на 0,5% Pd-ПЕК/ZnO катализаторе с массой 0,05 г составило 48 мл. Дезактивация катализаторов наблюдается после 64 порции. Данные ПЭМ показали частичное выщелачивание скрученных полимер-металлических пленок с поверхности ZnO.

Ключевые слова. Пектин, геллан, полисахариды, каталитическая активность, гидрирование, палладиевые катализаторы, алкинолы.

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