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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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NEW METHOD FOR DISPOSAL OF GRANULATED PHOSPHORIC SLAG FROM HAZARDOUS GASES

Abstract. New wet method of decontamination of GPS from hazardous gases (PH_3, H_2S, HF, etc.) and their sources (Ca_3P_2, CaF_2 and CaS) is proposed, since dry methods for decontamination turn out to be inviable due to their difficulty and non-efficiency; thus, GPS in construction (and not only) is used without cleaning pursuant to the existing regulatory documents.

The wet method of decontamination of GPS from hazardous gases and their sources is developed based on the following comparative methods:

First – 2 kg GPS were dried at temperature of about 600°C at the drying furnace within 5 hours; then the air mixture was measured from the special hole for presence of gases.

Second – Dried slag after cooling was ground at the vibration mill to the specific surface of 500 m^2/kg with Na_2CO_3 additive or cement (5 % by weight) and FeO (3 %) and without such activating and neutralizing additives; then the qualitative content of gases was measured at the mill and in slag.

Third –2-kg composited sample of GPS was placed in the laboratory vibration mill and was added with water in ratio 1:6 (slag : water by weight). This mixture was ground with Na_2CO_3 additive or cement (5 % by weight) and FeO (3 %) and without them to the specific surface of 500 m^2/kg; then, the qualitative content of gases was measured at the mill and in slag.

It was determined that:

- maximum quantity of gas emission from GPS is observed during drying without decontaminating additives;
- in presence of decontaminating additives, gas emission from GPS is reduced by one step – due to neutralizing properties of additives;
- grinding of dried GPS assists in additional gas emission therefrom – with additive to a lesser extent, without additive – to a greater extent;
- in case of GPS grinding in water environment, gas emission is maximally reduced, and with additive – gases are fully neutralized.

It follows from what has been said that irrespective of the GPS treatment method, introduced additives are capable to neutralize gases; however, the wet method is more efficient in comparison with the dry one, since:

- the wet method does not require drying of GPS; particles are more easily broken to the necessary specific surface with less time;
- in the closed space like the vibration mill, in water environment, gases may not volatilize by any reasons and are fully neutralized with additives and activating agents;
- products of interaction of gases with neutralizing and activating additives become the activating components of ground GPS.

It is shown that during GPS grinding in water environment, the neutralizing and activating additives provide the chemical, physical-chemical and catalytic reactions in the system (totally they are about 20).

Studies of the phase composition, hydration degree of ground GPS and strength of consolidated slag stone produced from ecophosphoslag binding agent show the following:

- Na_2CO_3 has higher activating properties than cement-additive; thus, strength and hydration degree of consolidated ecophosphoslag binding agent with Na_2CO_3 additive are much higher – achieve correspondingly 79.3…83.5 MPa and 21.7…23.3 %, and with cement-additive – only 28.7…37.9 MPa and 16.8…20.4 %;

- Higher activating capability of Na_2CO_3 in comparison with cement-additive is explained by the fact that:

- sodium carbonate in the consolidating system creates the increased alkaline medium (pH>12); therefore, glass-slag is much dissolved; in its turn, assisting in increase in content of hydrate phases in slag stone;

- strengthening of slag stone is positively impacted also by ions Na^+ included into hydrated calcium silicates – C-S-H and CSH (I), resulting in generation of new expanded coordination centers, like MeO_6, assisting in increase and stability of the crystal latitude and hydrate phase, and this is also the positive factor impacting on increase in strength of slag stone.

It is defined that FeO does not only neutralizes hazardous gases and their sources, but activates ground GPS. Neutralizing and activating capability of FeO may be related to presence of electron-free orbitals at the 3d-sublevel of Fe^{2+} (Fe^{3+}), assisting to iron ions as acceptor with neutralizing and activating properties. It may be supposed that such properties shall be common for the compounds, including the elements of transition metals having electron-free orbitals at the 3d-sublevel.

It is detected that consolidated ecophosphoslag binding agent contains mainly two types of hydrated calcium silicates – amorphous tobermorite gel (C-S-H) and submicrocrystalline CSH (I).

Keywords. Granular phosphorus slag, hazardous gases and their sources, iron oxide, soda, cement, strength, degree of hydration.

Introduction. Among technogenic mineral formations (and there are more than 25 billion tons of them in Kazakhstan), granular phosphoric slag in terms of importance and technical and economic efficiency as a raw material in the construction industry and construction is ranked second after granulated blast-furnace slag, and they are interchangeable.

The field of production of building and silicate materials, products and structures based on these technogenic materials is very wide, since they are used in all sectors of the construction industry [1-9].

Unlike the blast-furnace slags the granular slags are ecologically clean mineral raw materials, granular phosphorus slag (hereinafter GFSH) contain hazardous gases (PH_3H_2S, HF, SiF_4 and others.) and minerals (Ca_3P_2 – highly poisonous, CaF_2 and CaS). Gases occur during production of phosphorus and its compounds from a mixture of phosphorite, quartz and coal, and minerals are initially present in the composition of $Ca_3(PO_4)_2$ in the form of impurities, which are constant sources of hazardous gases in slags according to the equation [10]:

$$Ca_3P_2 + 3H_2O + 3SiO_2 = 2PH_3 + 3\,(CaO \cdot SiO_2),$$

$$CaF_2 + H_2O + SiO_2 = 2HF + CaO \cdot SiO_2,$$

$$CaS + H_2O + SiO_2 = H_2S + CaO \cdot SiO_2$$

The presence of these hazardous ingredients in GFS was known from the very beginning (since 1965), but this was not given much importance. Therefore, until 1990 GFS without neutralization was used as independent binders, mineral additives in the production of Portland cement and components in the composition of slag Portland cement [1-9]. As a result of this, GOST 3476-74 [11] which is valid at the present time, was issued. A new standard GOST 31108-2016 [12] allowing the use of GFS without neutralization which has a major socio-ecological and economic danger to biogeocenosis was added.

With an acute cement deficit in Kazakhstan at the end of the 1980s, a decision at the level of the Government of the USSR and KazSSR was made to organize the production of cementless binders based on GFS [13,14]. That time the danger of using them without neutralizing gases was mentioned.

In this regard, Almaty NIIstromproekt, together with the IOCE of the Academy of Sciences of the Kazakh SSR and the NIIKP of the Ministry of Healthcare began to neutralize GFS from PH_3 and H_2S, offering their own formulation [15-17], as a result of which ST RK 2301-2013 was developed [18], where it is clearly stated that GFS should be neutralized from phosphorous and fluoride compounds by the introduction of neutralizing additives.

However, in practice, this regulatory document was not viable, because: the * PH_3 and H_2S neutralizing methods were very complicated and some processes were questionable. For example, GFS is simultaneously used for neutralization (since some additives neutralize some gases, others – the rest gases): calcium hypochlorite [Ca $(OCl)_2$] in an amount of 0.4% by weight, steelmaking slag (5%), caprolactam waste (2 %) and ferro-slag of chromium compounds (6%) [19], which should be used for drying (> 600°C) and grinding the phosphoric slag binders by dry mechanochemical method [20].

The disadvantages of the mechanochemical GFS neutralizing method include the multicomponentness of neutralizing additives, the dependence of the degree of purification on their chemical and mineralogical composition which is not always constant, the negative effect of some of them (for example, calcium hypochlorite, Cr^{6+} , etc.), partial removal harmful impurities with exhaust gases during GFS drying process.

There is also a patent [21] for a method for phosphorus slag purification from harmful gases using vanadium-containing converter slag.

Research methods.

Option 1. A certain amount (2 kg) of GFS was dried at a temperature of about 600°C in a drying oven. Five hours after drying from an opening, the air mixture was measured for the presence of gases.

Option 2. After cooling, the dried slag was ground in a vibratory mill to a specific surface of 500 m^2/ kg with and without Na_2CO_3or cement (5%) and FeO (3%), after which the qualitative gas content in the mill and slag was measured.

Option 3. We took 2 kg of GFS of the averaged sample and placed in a laboratory vibratory mill, and poured water in a ratio 1: 6 (slag: water by weight). This mixture was ground with the addition of Na_2CO_3 or cement (5%) and FeO (3%) and without them to a specific surface of 500 m^2/ kg, after which the qualitative content of gases in the mill and slag was measured.

Note: the quantitative gas content in the studied systems must be checked in two more independent accredited laboratories in order to minimize errors in these studies. The presence of gases in the slag was measured using an ALTAIR gas analyzer.

To define the effect of the type of activators on the strength and degree of hydration of the hardened ecophosphoslag binder, samples were prepared with a composition of 1: 0 (slag dough) 2x2x2 cm in size, solidified under steaming conditions at 90 ° C based on the 3 + 10 + 34 mode (rise + isotherm + descent) .

The phase composition of neoplasms – cementing agents was established using the X-ray and derivatographic units DRON-3M and MOM-1500.

. **Results and discussion.** The results are shown in table 1, from which it can be seen that:

- maximum amount of gas evolution from GFS is observed when it is dried without neutralizing additives;
- in the presence of neutralizing additives, the output of gases from GFS decreases by one step - due to the neutralizing properties of the additives;
- grinding the dried GFS promotes an additional emission of gases from it - with addition to a lesser extent and without - to a greater extent;

Table 1 − Qualitative gas content in GFS depending on the method of its processing

Methods and numbers of treatment		GFS condition	Presence of neutralizing substances	Gas content*
Dry	1	Source in the form of granules	without additive	++++
			with additive	+++
	2	Ground	without additive	+++
			with additive	++
Wet	3	Combined with water	without additive	+
			with additive	-
*4 pluses - maximum gas content, 3 - below maximum, 2 - medium, 1 – small, minus - the absence of gases				

- during the GFS grinding in an aqueous medium without additives, the gas yield decreases as much as possible, and with the additive - the gases are completely neutralized.

It follows from what has been said that, regardless of the processing method of GFS, additives are able to neutralize gases, however, the wet method is significantly more effective than the dry one, because:

- with the wet method, the GFS drying is not required, the particles are easier to grind to the required specific surface with less time;
- in a confined space in the aquatic environment, gases cannot escape for any reason but are completely neutralized by additives and activators;
- the products of the interaction of gases with neutralizing and activating additives themselves become activating components of ground GFS.

GFS-based conglomerate initially consists of the following active components: slag, including harmful gases, phosphide, fluoride, sulfide: water, activator and detoxifying agents. Because of this, during the GFS grinding by wet method, the chemical, physico-chemical and catalytic reactions occur in the system. For example (some of them):

$$Na_2CO_3 + H_2S \rightarrow Na_2S + H_2CO_3$$

$$Ca\,(OH)_2 + 2(HF) \rightarrow CaF_2 + 2(H_2O)$$

$$3[Fe(OH)_3^2] + 3(PH_3) \rightarrow 3(FeO) + 9H_2O$$

$$8[F_2O_3] + Ca_3P_2 \rightarrow Ca_3(PO_4)_2 + 16FeO$$

$$Glass + Na_2CO_3 + H_2O \rightarrow xCaO\,(2Na) \cdot ySiO_2 \cdot zH_2O$$

$$Glass + Ca(OH)_2 \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O$$

Table 2 shows the strength and degree of hydration of slag (cement) stone, which shows that:

- Na_2CO_3 has a higher activating property than cement and thus the strength and degree of hydration of hardened binder with Na_2CO_3 are considerably higher - they reach respectively 79.3 ... 83.5 MPa and 21.7 ... 23.3% and cement - only 28.7 ... 37.9 MPa and 16.8 ... 20.4%.

The increased activating ability of Na_2CO_3 compared with cement is due to the fact that:

- sodium carbonate in the hardening system creates an increased alkaline environment (pH>12), due to which glass slag dissolves in large quantities; this in turn contributes to an increase in the content of hydrated phases in the slag stone;
- slag stone hardening is positively affect also by the ions Na^+ included in the calcium hydrosilicate, resulting in the formation of new extended focal type MeO_6 conducive ascending and lattice stability of the hydrate phase, and this is also a positive effect on increasing slag rock strength in general.

Table 2 − Change in the strength and degree of hydration of hardened ecophosphate slag stone depending on the type of activator and the presence of a neutralizer

Activator,%	Neutralizer,%	Compressive strength, MPa	Hydration degree,%
Cement, 5	-	28,7	16,8
	FeO, 3	37,9	20,4
Na_2CO_3, 5	-	79,3	21,7
	FeO, 3	83,5	23,3

The reduced activating ability of cement compared with sodium carbonate is due to the lower reactivity of $Ca\,(OH)_2$ than Na_2CO_3.

An interesting fact: FeO − not only neutralizes hazardous gases and their sources, but also activates slag. This is probably due to the presence on the 3d sublevel $Fe^{2+}(Fe^{3+})$ of electron-free orbitals) which favors iron ions, like an acceptor with neutralizing and activating properties. If this proposition is correct, then we must assume that these properties should have transition metal ions from manganese to copper with electron-free orbitals in them.

Figure 1 shows the X-ray and thermograms of the original slag and hardened slag stone with the addition of soda and cement.

The GFS structure in the X-ray diffraction pattern (1) is not fixed due to its X-ray amorphous state, however:

- its vitreousness is clearly indicated on the thermogram (6), where two peaks appear: the end effect at 800°C, showing softening of the glass and exoeffect at 920°C, characteristic of crystallization of wollastonite;
- a halo is fixed on it, a characteristic attribute of glass.

On X-ray diffraction patterns of slag stone, regardless of the type of activator, the peaks typical for CSH (I) are recorded (d/n = 3,03; 2,28 and 1,83 Å). On the thermograms of slag stone with soda addition, endo effects appear at 160°C and at 140°C with the addition of cement, belonging to the tobermorite gel. In this case, the tobermorite gel which appeared in the slag stone with the addition of soda, is more stable as a result of the introduction of sodium ions in its structure - because of which the endoeffect is shifted towards an elevated temperature (160°C).

The formation of wollastonite during thermal reactions occurring in samples with activators occurs at low temperatures (800°C and 850°C) in comparison with its occurrence from the initial slag only. This is due to the additional appearance of wollastonite from calcium hydrosilicates, which have low resistance at high temperatures.

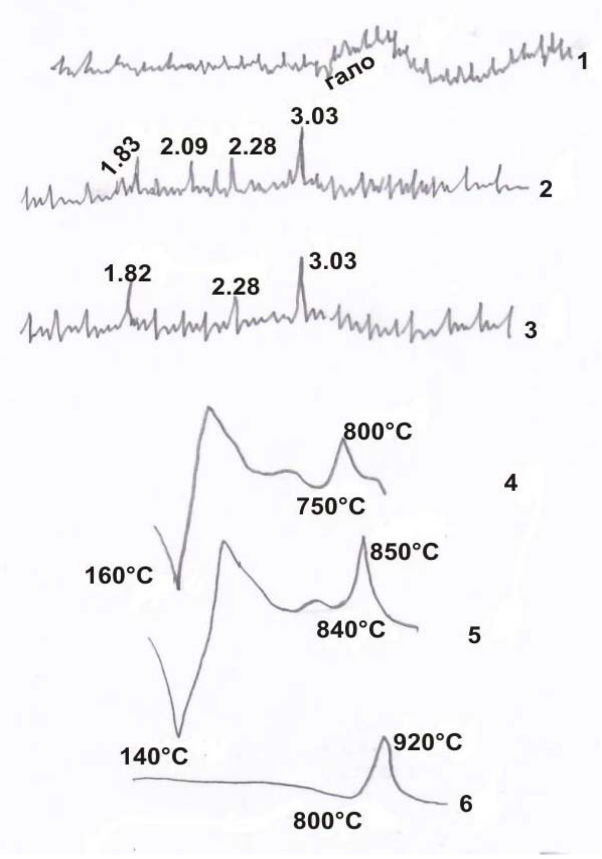

Figure 1 - X-ray diffraction patterns (1-3) and thermograms (4-6) of the initial GFS (1 and 6) and hardened binder with the addition of Na_2CO_3 (2 and 4) and cement (3 and 5)

Finally, it should be noted that both activators and neutralizers do not create independent compounds and do not remain in a free state (doses taken by us), but are included in the structure of calcium hydrosilicates.

Conclusions. It is known that dangerous gases (PH_3, H_2S, HF, etc.) are present in the shells of porous GFS and their sources (Ca_3P_2, CaF_2 and CaS), which makes it undesirable to use it in construction, including road, and in agriculture.

1. However, GFS, according to GOST 3476-74 and 31108-2016, is actively used without neutralization in the production of Portland cement and slag Portland cement, respectively, as a mineral additive and component, which is not acceptable.
2. Meanwhile, there is another regulatory document - ST RK 2301-2013, which clearly states that GFS should be neutralized from phosphorous and fluoride compounds by introducing neutralizing additives by the dry method in the production of cements.

However, this standard is not used in practice by cement producers and not only by them, since methods GFS neutralizing are very complex and some processes are doubtful.

3. In this regard, we proposed (started) a new GFS neutralization trend - the wet method, where hazardous gases and their sources are not only completely neutralized but also become activators, turning into new compounds.

4. It is shown that the hydrated phase of the slag stone consists of calcium hydrosilicates - tobermorite gel and CSH (I), the structure of which includes the components of activators and a neutralizer.

5. It has been suggested that the compound of transition metals of the manganese series to copper, where on the 3d sublevel there are electron-free orbitals capable of neutralizing the dangerous ingredients of GFS.

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ТҮЙІРШІКТЕЛГЕН ФОСФОР ҚОЖДАРЫН ҚАУІПТІ ГАЗДАРДАН ЗАЛАЛСЫЗДАНДЫРУДЫҢ ЖАҢА ТӘСІЛІ

Аннотация. ТФҚ-ны қауіпті газдардан (PH_3, H_2S, HF және т.б.) және олардың көздерінен (Ca_3P_2, CaF_2 және CaS) залалсыздандырудың жаңа дымқыл тәсілі ұсынылады, өйткені залалсыздандыру бойынша құрғақ тәсілдер олардың күрделілігіне және тиімсіздігіне байланысты өміршең емес болып шықты, осыған байланысты ТФҚ құрылыста (және тек онда ғана емес) қолданыстағы нормативтік құжаттарға сәйкес тазартусыз қолданылады.

Зиянды газдардан және олардың көздерінен ТФҚ-ны залалсыздандырудың дымқыл тәсілін әзірлеу кезінде келесі салыстырмалы әдістемелерді қолданамыз:

Біріншісі - 2 кг ТФҚ кептіру пешінде шамамен 600°C температурада 5 сағат бойы кептірілді, содан кейін арнайы тесіктен ауа қоспасын газдың болуына өлшеді.

Екіншісі - кептірілген қож суғаннан кейін дірілдиірменде Na_2CO_3 немесе цемент (салмағы бойынша 5%) және FeO (3 %) қоспасын қосып және осы белсендіретін және бейтараптандыратын қоспаларды қоспай 500 $м^2$/кг меншікті бетке дейін ұсақталды, содан кейін диірмен мен қождағы газдардың сапалық құрамын өлшеді.

Үшіншісі - 2 кг ТФҚ орташаланған сынамасын алып, зертханалық дірілдиірменге салды, содан кейін оған 1:6 ара қатынасында (қож:су салмағы бойынша) су құйылды. Бұл қоспаны Na_2CO_3 немесе цемент (салмағы бойынша 5%) және FeO (3 %) қоспасын қосып және оларды қоспай 500 $м^2$/кг меншікті бетіне дейін ұсақтады, содан кейін диірмен мен қождағы газдардың сапалық құрамын өлшенді.

Анықталғаны:

- ТФҚ-дан бөлінген газдардың ең көп мөлшері залалсыздандыратын қоспаларсыз кептіру кезінде байқалады;
- залалсыздандыратын қоспалар болған кезде ТФҚ-дан газдардың шығуы қоспалардың бейтараптандыратын қасиеттеріне байланысты бір сатыға азаяды;
- кептірілген ТФҚ-ны ұнтақтау газдардың одан қосымша шығуына ықпал етеді – қоспалармен аз дәрежеде, қоспаларсыз - көп дәрежеде;
- ТФҚ су ортасында ұнтақтаған кезде газдардың шығуы барынша азаяды, ал қоспамен – газдар толығымен бейтараптандырылады.

Жоғарыда айтылғаннан ТФҚ өңдеу тәсіліне қарамастан, енгізілетін қоспалар газды бейтараптандыруға қабілетті болғаны байқалады, алайда құрғақ әдіспен салыстырғанда дымқыл тәсіл тиімдірек көрінеді, өйткені:

- дымқыл тәсілді қолданған кезде ТФҚ кептіру талап етілмейді, бөлшектер аз уақытпен қажетті меншікті бетке дейін оңай ұнтақталады;
- дірілдиірмен болып табылатын жабық кеңістікте, су ортасында газдар қандай да бір себептер бойынша ұшып кете алмайды, және қоспалар мен белсендіргіштер арқылы толық бейтараптандырылады;
- газдардың бейтараптандырушы және белсендіруші қоспалармен өзара әрекеттесу өнімдері өздері ұнтақталған ТФҚ-ның белсендіруші компоненттеріне айналады.

ТФҚ-ны бейтараптандыратын және белсендіретін қоспалары бар су ортасында ұсақтау барысында жүйеде химиялық, физикалық-химиялық және каталитикалық реакциялар (жалпы алғанда олардың саны шамамен 20) орын алатыны көрсетілген.

Фазалық құрамды зерттеу, ұнтақталған ТФҚ гидратация дәрежесі және экофосфошлак тұтқышынан алынған қатайған қож тасының беріктігі төмендегілерді көрсетті:

– Na_2CO_3 цементтің-қоспаның неғұрлым жоғары белсендіргіш қасиеттеріне ие, сондықтан Na_2CO_3 қоспасы бар қатайған экофосфошлак тұтқырғыштың беріктігі мен гидратация дәрежесі айтарлықтай жоғары – тиісінше 79,3 ... 83,5 МПа және 21,7 ... 23,3% жетеді, ал цементпен-қоспамен - тек 28,7...37,9 МПа және 16,8...20,4 % жетеді;

– Цемент-қоспамен салыстырғанда Na_2CO_3 жоғары белсендіргіш қабілеті мыналарға негізделген:

- натрий карбонаты қатаятын жүйеде жоғары сілтілі ортаны (pH>12) құрады, соның арқасында шыны қож көп мөлшерде ериді; бұл өз кезегінде қожды тастағы гидраттық фазалардың мөлшерін арттыруға ықпал етеді;

- қож тасының нығыздалуына кристалды тор мен гидратты фазалардың өсуі мен орнықтылығына ықпал ететін MeO_6 типті жаңа кеңейтілген үйлестіру орталықтарының пайда болуы нәтижесінде кальций гидросиликаттарының – C-S-H және CSH (I) құрамына кіретін Na^+ иондары да оң әсер етеді, бұл да қож тасының беріктігінің жоғарылауына оң әсер етеді.

FeO қауіпті газдар мен олардың көздерін бейтараптандырып қана қоймай, сонымен қатар ұнтақталған ТФҚ-ны белсендіретіні анықталды. FeO бейтараптандыратын және белсендіретін қабілеті Fe^{2+} (Fe^{3+}) 3D-төменгі деңгейінде электрондардан бос орбитальдардың болуымен байланысты болуы мүмкін, бұл, акцептор ретінде, бейтараптандыратын және белсендіретін қасиеттері бар темір иондарына ықпал етеді. Мұндай қасиеттерге қосылыстар, соның ішінде 3D-төменгі деңгейде электрондардан бос орбитальдері бар ауыспалы металдар элементтерінің өздері де ие болуы тиіс деп болжауға болады.

Қатайған экофосфоқожды тұтқырда негізінен кальций гидросиликаттарының екі түрі – аморфты тоберморитті гель (C-S-H) және субмикрокристалды CSH (I) пайда болатыны анықталған.

Түйін сөздер: түйіршіктелген фосфор қожы, қауіпті газдар және олардың көздері, темірдің шала тотығы, сода, цемент, беріктік, гидратация дәрежесі.

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НОВЫЙ СПОСОБ ОБЕЗВРЕЖИВАНИЯ ГРАНУЛИРОВАННОГО ФОСФОРНОГО ШЛАКА ОТ ОПАСНЫХ ГАЗОВ

Аннотация. Предлагается новый мокрый способ обезвреживания ГФШ от опасных газов (PH_3, H_2S, HF и др.) и их источников (Ca_3P_2, CaF_2 и CaS), поскольку сухие способы по обезвреживанию оказались нежизнеспособными в виду их сложности и неэффективности, из-за чего ГФШ в строительстве (и не только) применяют без очистки согласно существующим нормативным документам.

При разработке мокрого способа обезвреживания ГФШ от вредных газов и их источников применяем следующие сравнительные методики:

Первая – 2 кг ГФШ подвергли сушке при температуре около 600°C в сушильной печи в течение 5 часов, после чего из специального отверстия измеряли воздушную смесь на предмет присутствия газов.

Вторая – высушенный шлак после остывания измельчали в вибромельнице до удельной поверхности 500 $м^2$/кг с добавкой Na_2CO_3 или цемента (5 % по массе) и FeO (3 %) и без этих активизирующих и нейтрализующих добавок, после чего измеряли качественное содержание газов в мельнице и шлаке.

Третья – взяли 2 кг ГФШ усредненной пробы и поместили в лабораторную вибромельницу, а затем туда же налили воду в соотношении 1:6 (шлак: вода по весу). Измельчали эту смесь с добавкой Na_2CO_3 или цемента (5 % по массе) и FeO (3 %) и без них до удельной поверхности 500 $м^2$/кг, после чего измерили качественное содержание газов в мельнице и шлаке.

Установлено, что:

- максимальное количество выделения газов из ГФШ наблюдается при сушке без обезвреживающих добавок;

- в присутствии обезвреживающих добавок выход газов из ГФШ уменьшается на одну ступеньку – из-за нейтрализующих свойств добавок;
- размол высушенного ГФШ способствует дополниельному выходу газов из него – с добавкой в меньшей степени, без – в большей степени;
- при размалывании ГФШ в водной среде выход газов максимально уменьшается, а с добавкой – газы полностью нейтрализуются.

Из сказанного следует, что независимо от способа обработки ГФШ вводимые добавки способны нейтрализовать газы, однако мокрый способ эффективнее по сравнению с сухим, поскольку:

- при мокром способе сушка ГФШ не требуется, частицы легче размалываются до необходимой удельной поверхности с меньшим временем;
- в замкнутом пространстве, каким является вибромельница, в водной среде газы не могут улетучиваться по тем или иным причинам, а полностью нейтрализуются добавками и активизаторами;
- продукты взаимодействия газов с нейтрализующими и активизирующими добавками сами становятся активизирующими компонентами молотого ГФШ.

Показано, что в ходе измельчения ГФШ в водной среде с нейтрализующими и активизирующими добавками в системе происходят химические, физико-химические и каталитические реакции (в общей сложности их около 20).

Исследования фазового состава, степень гидратации молотого ГФШ и прочность затвердевшего шлакового камня, полученного из экофосфошлакового вяжущего, показали следующее:

- Na_2CO_3 обладает более повышенными активизирующими свойствами цемент-добавка, поэтому прочность и степень гидратации затвердевшего экофосфошлакового вяжущего с добавкой Na_2CO_3 существенно выше – достигают соответственно 79,3…83,5 МПа и 21,7…23,3 %, а с цементом-добавкой – только 28,7…37,9 МПа и 16,8…20,4 %;
- Повышенная активизирующая способность Na_2CO_3 по сравнению с цементом-добавкой обусловлена тем, что:
- карбонат натрия в твердеющей системе создает повышенную щелочную среду (pH>12), благодаря чему стеклошлак растворяется в большом количестве; это в свою очередь способствует увеличению содержания гидратных фаз в шлаковом камне;
- на упрочнение шлакового камня позитивно влияют также ионы Na^+, входящие в состав гидросиликатов кальция – C-S-H и CSH (I), в результате образования новых расширенных координационных центров, типа MeO_6, способствующих возрастанию и устойчивости кристаллической решетки и гидратных фаз, а это тоже положительно влияет на повышение прочности шлакового камня.

Определено, что FeO не только нейтрализует опасные газы и их источники, но и активизирует молотый ГФШ. Нейтрализующая и активизирующая способность FeO, возможно, связана с наличием на 3d-подуровне Fe^{2+} (Fe^{3+}) свободных от электронов орбиталей, что способствует ионам железа, как акцептор, с нейтрализующими и активизирующими свойствами. Можно предполагать, что такими свойствами должны обладать соединения, и в том числе, сами элементы переходных металлов, имеющих в 3d-подуровне пустующие от электронов орбитали.

Установлено, что в затвердевшем экофосфошлаковом вяжущем возникают в основном два вида гидросиликатов кальция – аморфный тоберморитовый гель (C-S-H) и субмикрокристаллический CSH (I).

Ключевые слова: гранулированный фосфорный шлак, опасные газы и их источники, закись железа, сода, цемент, прочность, степень гидратации.

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CATALYTIC WET PEROXIDE OXIDATION PROCESS WITH NEW Fe/Cu/Zr-PILLARED CLAYS DEVELOPED FROM NATURAL CLAY DEPOSITS OF KAZAKHSTAN

Abstaract. This work deals with the development of materials based on natural clays and on pillared clays. The modification of natural clays with zirconium, zinc and iron ions allows to increase their performance as adsorbents or catalysts in the treatment of environmentally hazardous compounds found in wastewater. Clay-based materials were obtained from natural clays and assessed in the treatment of wastewater using model pollutants in aqueous solutions. The natural clays were collected from 3 different deposits of Kazakhstan and tested in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP) at mild conditions (50 ºC, initial pH of 3.0, $C_{4\text{-NP}}$ = 5 g/L and C_{clay} = 2.5 g/L). Fe/Cu/Zr-pillared clays were developed from natural clays and also assessed in the CWPO of 4-NP. Complete removal of 4-NP was achieved after 2 h of reaction time with all pillared clays, and TOC removals up to 78 % after 8 h were reached at those conditions.

Keywords: natural clays; pillared clays; catalytic wet peroxide oxidation; 4-nitrophenol; wastewater.

1. Introduction.

The treatment of wastewater containing hazardous organic compounds is one of the pressing problems facing society nowadays. Catalytic wet peroxide oxidation (CWPO) is one attractive solution to treat these waste streams, which are typically not economically viable to be incinerated or too concentrated for biological treatment (or containing non-biodegradable pollutants) [1-3]. Compared with other oxidants, hydrogen peroxide is most preferred due to its high oxidation potential and its decomposition yielding non-toxic final products (oxygen and water). CWPO allows almost complete removals of organic pollutants from wastewater, including 4-nitrophenol (4-NP), used as model compound in this work [4]. Kazakhstan is one of the richest countries by volumes of natural resources and by the diversity of types and stocks of mineral raw materials, taking a leading place in the world. Clay deposits find wide applications in building ceramics, drilling muds, paper covering and filling, and pharmaceuticals [5]. However, natural and modified clays also have a large surface area and high ion-exchange capacity, allowing them to be used for the removal of heavy metals by adsorption and for the oxidation of organic compounds from water [6-7]. In Kazakhstan, known deposits have not been studied to be used as useful materials for wastewater treatment.

The model compound used in this work, 4-NP is a toxic and bio-refractory compound that can damage the central nervous system, liver, kidney and blood of humans. It has been shown that 4-NP can develop a blood disorder that reduces the ability of blood to carry oxygen to tissues and organs [8]. Since 4-NP is extensively used in the chemical industry for the manufacture of insecticides, herbicides, synthetic dyes and pharmaceuticals [9], it is often observed in effluents of industrial wastewater treatment plants. Some reports dealing with the CWPO of 4-NP using reduced graphene [10], magnetic carbon xerogels

[11], carbon nanotubes [12] and carbon blacks [13] reveal that the main reaction intermediates resulting from the oxidation of 4-NP are 4-nitrocatechol, benzoquinone, hydroquinone, malonic acid, maleic acid and catechol.

In this work, catalytic materials based on pillared clays (PILCs) have been prepared from natural clays of Kazakhstan, collected from the deposits of Zhambyl region of Karatau, Akzhar and from the North part of Kazakhstan, in the deposits of Kokshetau, and tested in the catalytic oxidation of 4-nitrophenol, used as model pollutant present in wastewater.

2. Experimental

2.1 Materials and Synthesis Procedures

Two natural clays with different characteristics, collected from locations in the South of Kazakhstan, regions of Akzhar and Karatau deposits, were used, as well as other natural clay from the North part of Kazakhstan, in the deposits of Kokshetau. The clays were washed with water several times at 50 ºC. The washing with HCl (37 wt.%) was also assessed at 50 ºC in order to eliminate residual content inside the clays.

The Fe/Cu/Zr-PILCs were prepared from the acid washed natural clays, according to the procedure described in the following. $FeSO_4$ (99.5%), $CuSO_4.5H_2O$ (99.9%) and $Zr(SO_4)_2$ were used as precursors of iron, copper and zirconium polycation PILCs. To prepare this material 3.333 mmol of Fe^{2+}, Cu^{2+} and Zr^{4+} polycations from $FeSO_4$ (0.5 g), $CuSO_4.5H_2O$ (0.8 g) and $Zr(SO_4)_2$ (0.94 g) were measured and dissolved in 20 mL of water. To prepare the pillaring solution, NaOH (0.2 M) was added, a solution being obtained containing the polycation precursors at pH = 2.8 at room temperature.

The resultant solution was aged for 24 h at room temperature and after this period, the intercalating solution was slowly added to a 2% (1 g in 50 mL) solution of clay, followed by stirring for 24 h at room temperature. The suspended solids were then separated by filtration and washed with distilled water at 50 ºC to remove dissolved impurities. The final materials were dried at 80 ºC in air atmosphere for 24 h and heat treated during 2 h at 823 K considering a heating rate of 275 K min^{-1} under an inert atmosphere (nitrogen).

To determine the physico-chemical characteristics of the natural clays, X-ray spectral analysis was used. An electron probe microprobe of the brand Superprobe 733 (Super Probe 733) from JEOL (Jael), Japan, was used to determine the angular position and the intensity of reflexes. The elemental composition of the samples and images in various types of radiation were performed using an Inca Energy dispersive spectrometer from Oxford Instruments, England. UV-Vis absorption spectra of the materials were obtained using a T70 Spectrophotometer (PG Instruments, Ltd.) in the wavelength range of 200 to 660 nm, with a scan interval of 1 nm. SEM was performed on a FEIQuanta 400FEG ESEM/EDAX Genesis X4M equipment coupled with an Energy Dispersive Spectrometer (EDS). Transmission electron microscopy (TEM) was performed in a LEO 906E equipment operating at 120 kV, coupled with a 4Mpixel 28 × 28 mm CCD camera from TRS.

3. Results and discussion

The elemental composition of the natural clays is given in table 1. As observed, the natural clays used in this work are rich in iron (3.60-10.66%), an important feature, since iron can play a catalytic active role in the decomposition of hydrogen peroxide to produce hydroxyl radicals and, in consequence, can enhance the catalytic activity of the developed materials in the oxidation of the pollutants by CWPO.

Table 1 - Elemental analysis of the natural clays used in the synthesis of Fe/Cu/Zr-PILCs

Natural clay	mass %									
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Akzhar	54.53	0.80	2.22	6.02	21.99	2.19	8.34	0.31	n.i.*	3.60
Karatau	52.86	0.81	2.26	6.55	21.14	2.26	7.66	1.60	0.22	4.65
Kokshetau	54.71	n.i.*	0.15	13.4	19.17	0.28	0.21	1.43	n.i.*	10.66

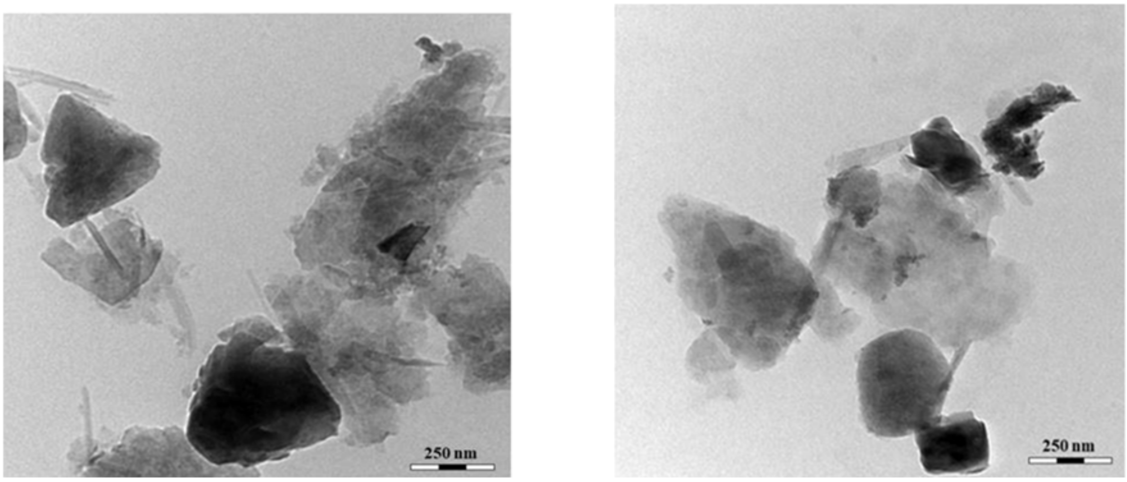
*n.i. = non identified

The results in table 2 show the elemental analysis of the trimetallic Fe/Cu/Zr-PILCs. It can be observed that, generally, the content of Fe increases in the modified clays in comparison with the content in the natural clays, suggesting an exchange and fixation of this intercalating metal in the interlayer space. In the Fe/Cu/Zr-Akzhar PILC 3.60% of Fe, against 1.3% in the corresponding natural clay. It can also be observed that the solids modified with Fe/Cu/Zr have lower Si/Al ratios than those in the natural clays, meaning that the oxides got preferentially stabilized at the interlayer space of the clays, following the targeted cationic exchange mechanism.

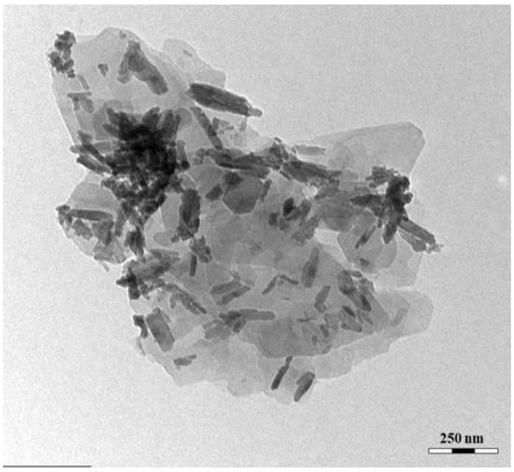
Table 2 - Elemental chemical composition of the Fe/Cu/Zr-PILCs

Pillared clay	mass %											
	O	Na	Mg	Al	Si	S	K	Ca	Ti	Zr	Fe	Cu
Fe/Cu/Zr-Aкzhar	46	1	1.4	6.4	25	0.7	3	0.6	0.3	n.i.	1.3	3.3
Fe/Cu/Zr-Karatau	46.1	1.1	1.8	7.2	25.6	0.5	2.1	0.7	0.4	n.i.	6.2	5.2
Fe/Cu/Zr-Koкshetau	49.8	n.i.	0.3	13.1	22.9	0.2	0.3	n.i.	1.3	0.3	11.7	0.1
*n.i. = non identified												

The surface morphologies of the natural clays and of the synthesized PILCs were observed by transmission electron microscopy (TEM). The micrographs obtained with the natural clays are shown in figure 1. The TEM images of the pillared clays obtained in dark field mode (not shown) put in evidence the defects of the structure, as well as fine particles present in the material, as dark-colored spots.



a) Akzhar b) Karatau



c) Kokshetau

Figure 1 - TEM micrographs obtained for the natural clays

Since the objective of this work was to obtain a method to prodcuce catalysts based on natural clays modified with Fe/Cu/Zr for application in the treatment of wastewaters containing organic pollutants by catalytic wet peroxide oxidation, the trimetallic pillared clays were assessed in the CWPO of 4-NP, following simultaneously the removal of TOC. From the results obtained in figures 2 and 3, it has been placed in evidence that the trimetallic Fe/Cu/Zr pillared clays have high catalytic activity for the oxidation of organic pollutants.

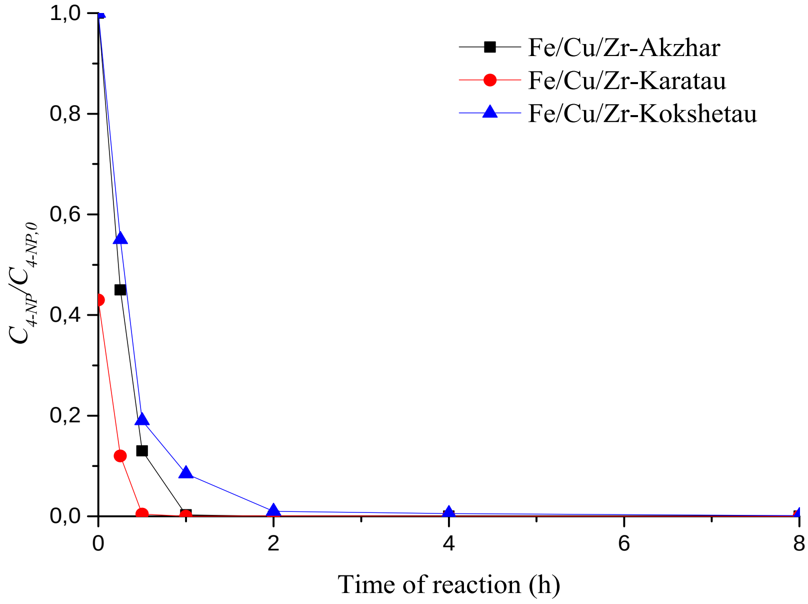


Figure 2 - Catalytic wet peroxide oxidation of 4-NP using the trimetallic PILCs.
Operating conditions: $C_{4\text{-}NP,0}$ = 5 g/L, $C_{H_2O_2,0}$ = 17.8 g/L, catalyst load = 2.5 g/L, initial pH 3.0 and T = 50 °C

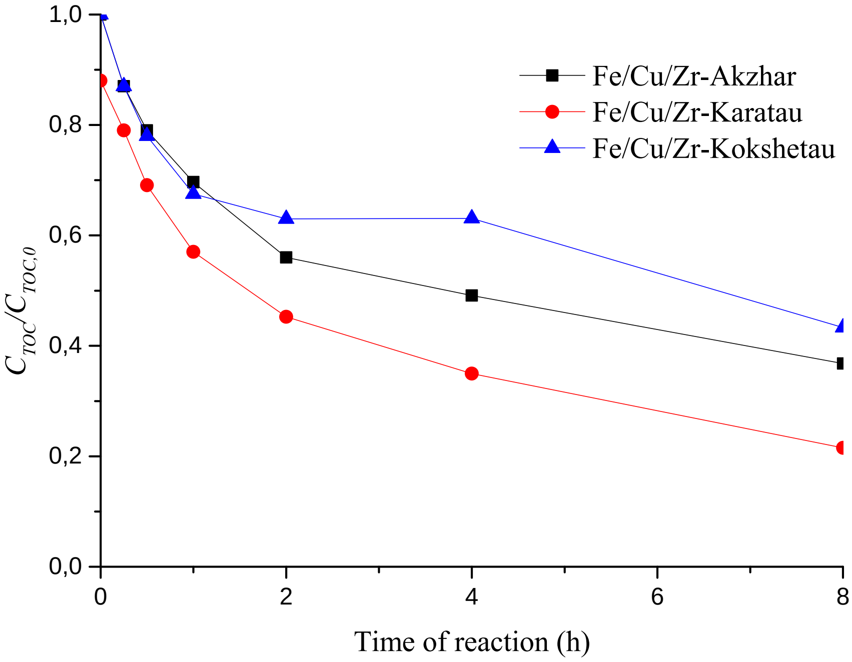


Figure 3 - Removal of TOC during the catalytic wet peroxide oxidation
of 4-NP using the trimetallic PILCs

Operating conditions: $C_{4\text{-NP},0}$ = 5 g/L, $C_{H_2O_2,0}$ = 17.8 g/L, catalysts load = 2.5 g/L, initial pH 3.0 and T = 50 °C.

Comparing the results obtained in the experiments performed with the 3 different Fe/Cu/Zr-PILCs, it is observed that the catalysts Fe/Cu/Zr-Karatau performs better than Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Kokshetau materials. Regarding the removal of 4-NP, Fe/Cu/Zr-Karatau was able to remove completely 4-NP in just 30 min of reaction, while with Fe/Cu/Zr-Akzhar and with Fe/Cu/Zr-Kokshetau, 1 h an 2 h were needed, respectively, to achieve the same complete conversion.

The oxidation of 4-NP with Fe/Cu/Zr-Karatau increased rather rapidly with the increase of contact time. When the TOC removal results (figure 3) are compared with the 4-NP conversions (figure 2), it is concluded that the conversion of 4-NP results in various intermediate products, since the initial 4-NP molecules is not completely mineralized until the final oxidation products $CO_2 + H_2O$. The maximum TOC removal reaches 78% after 24 h in the case of Fe/Cu/Zr-Karatau, 74% with Fe/Cu/Zr-Akzhar, while with Fe/Cu/Zr-Kokshetau, 72% of TOC removal was obtained.

4. Conclusions

A method to produce catalysts based on pillared clays with Fe/Cu/Zr polyoxocations with high catalytic activity for the CWPO of 4-NP was developed with success A distinctive feature of the method is the preliminary acid washing of the original natural clays to remove unbounded impurities. High conversion of TOC (78%) and complete conversion of 4-NP (100%) was obtained with the pillared clay Fe/Cu/Zr-Karatau. Trimetallic pillared clays revealed higher catalytic activity in the catalytic wet peroxide oxidation of 4-NP than that in natural clays.

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ҚАЗАҚСТАННЫҢ ЕЛДІ МЕКЕНДЕРІНІҢ ТАБИҒИ САЗБАЛШЫҚТАРЫНАН АЛЫНҒАН ЖАҢА Fe/Cu/Zr БАҒАНАЛЫ САЗБАЛШЫҚТАРДЫҢ НЕГІЗІНДЕ ЫЛҒАЛДЫ КАТАЛИТИКАЛЫҚ СУТЕГІ АСҚЫНТОТЫҒЫМЕН ТОТЫҚТЫРУ

Аннотация. Мақала табиғи және бағаналы сазбалшықтардың негізінде алынған материалдарды өңдеуге арналған. Ағынды сулардың құрамында кездесетін қауіпті экологиялық қосылыстарды өңдеу кезінде қолданылатын катализаторлар мен адсорбенттердің сапасын арттыру мақсатында, табиғи сазбалшықтарды цирконий, мырыш, темір иондарымен модификациялау арқылы олардың құрылымдық қасиеттерін жақсартуға мүмкіндік береді. Табиғи сазбалшықтар негізінде алынған материалдар әр түрлі процестерде, соның ішінде сулы ортада модельдік ластағышты қолдана отырып, ағынды суларды тазартуға қолданылады. Табиғи сазбалшықтар 4-нитрофенолды қолайлы жағдайда каталитикалық сутегі асқын тотығымен тотықтыру арқылы тексерілген. Кейбір саздардың маңызды қасиеттерінің бірі олардың жоғары адсорбциялық қабілеттері болып табылады, олар майды тазартуда, маталарды ағартуда, сонымен қатар қоршаған ортаның техногендік ластануына қарсы табиғи экологиялық қорғаныш ретінде қолданылады. Балшықтардың жоғары адсорбциялық қасиеттері олардың кристалды құрылымының ерекшелігіне байланысты болып келеді. Монтмориллонит сияқты саз балшықтар кеңейтілетін кристалды құрылымға ие. Осындай минералдардың гидратациясы кезінде су молекулалары мен алмасу катиондары саз балшықтардың арасындағы кеңістікке еніп, адсорбция потенциалының едәуір артуына себеп болады.

Fe/Cu/Zr үшметалды бағаналы сазбалшықтар Қазақстанның елді мекендернің табиғи сазбалшықтарынан өңделді және катализатор ретінде каталитикалық ылғалды сутегі асқын тотығымен тотықтыруға қолданып, 398 К температурада 4-нитрофенолдың, H_2O_2 және жалпы органикалық көміртектің мөлшері анықталды.

1 сағат уақыт ішінде 50 ° С температурада және 5 г / л концентрацияда Fe/Cu/Zr-Каратау бағаналы сазбалшығын қолдану арқылы 4-нитрофенолдың конверсиясы 100% және жалпы органикалық көміртекті жою 78% көрсетті.

Түйін сөздер: табиғи сазбалшық, бағаналы сазбалшық, каталитикалық тотығу, 4-нитрофенол, ағынды су, катализатор.

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КАТАЛИТИЧЕСКОЕ МОКРОЕ ПЕРОКСИДНОЕ ОКИСЛЕНИЕ С НОВЫМИ Fe/Cu/Zr СТОЛБЧАТЫМИ ГЛИНАМИ, РАЗРАБОТАННЫМИ ИЗ ПРИРОДНЫХ ГЛИН МЕСТОРОЖДЕНИЙ КАЗАХСТАНА

Аннотация. Статья посвящена разработке материалов на основе природных и столбчатых глин. Модификация природных глин ионами металлов циркония, цинка, железа позволяет развивать более подходящие текстурные свойства, повышая их эффективность в качестве адсорбента или катализатора при обработке экологически опасных соединений, содержащихся в сточных водах. Материалы на основе глины разрабатываются из природных глин и проверяются в различных процессах, направленных на очистку сточных вод с использованием модельных загрязнителей в водных растворах. Природные глины были испытаны в каталитическом окислении 4-нитрофенола с пероксидом водорода в мягких условиях. Одним из уникальных свойств некоторых глин является их высокая адсорбционная способность, что успешно используется для очистки масел, отбеливания тканей, а также как естественный экологический барьер для борьбы с техногенным загрязнением окружающей среды. Высокая адсорбционная способность глин обусловлена особенностью их кристаллического строения. Такие глинистые минералы, как монтмориллонит имеют раздвижную кристаллическую структуру. При гидратации таких минералов молекулы воды и обменные катионы могут проникать в межслоевое пространство и существенно увеличивать межслоевое расстояние, обусловливая этим существенное увеличение адсорбционного потенциала. Триметаллические глины Fe/Cu/Zr были получены из природных глин казахстанских месторождений и использовались как катализаторы каталитического мокрого пероксидного окисления с последующим измерением 4-НФ, H_2O_2 и общего органического углерода при 398 К. Конверсия 4-НФ составила 100% и удаление общего органического углерода 78% при концентрации 5 г / л и температуре 50 ° С с Fe / Cu / Zr-Каратау при длительности процесса 1 час.

Ключевые слова: природные глины, столбчатые глины, каталитическое окисление, 4-нитрофенол, сточные воды, катализатор.

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GETTING HUMATE IN A COAL OXIDATION PROCESS

Abstract. During last decades the problems of increasing the soil fertility, usage of organic additives to increase the crops yield is becoming more and more relevant. One kind of such additives are humates - sodium and potassium salts of humic acids. Humates and humic acids – chemical basis of soil humus, it's concentrate. And humus – is a basis of activity and stability of the most biochemical soil processes. Raw materials for the production of sodium humates are easily obtainable - these are brown coals, peat, oxidized hard coal, a production technology is complex with low production costs. Especially relevant for the production of humates is the use of oxidized coal. Oxidized coals have a wide range of macro- and microelements, a large number of humic acids, which are similar in composition to soil. The coal oxidized in the seams is practically not used in the national economy and goes to dumps together with overburden. The proposed method allows to improve the cost of the finished product. A method of producing humate by oxidation of coal is known. To study the costs of humic acids, as well as to study the qualitative and quantitative composition of humic acids, alkaline solutions of various concentrations were used. Tasks set during the study: a review of the scientific literature on the properties of HA, their composition and method of production; a technique was developed for conducting an experiment on the effect of alkali concentration, temperature and extraction time on the degree of extraction of HA from the coals of Central Kazakhstan; the regression equations were obtained during mathematical processing of the experimental results, which made it possible to establish the influence of each of these factors on the output of HA; Qualitative and quantitative composition of HA obtained by extraction with alkali of various concentrations was carried out.

Key words: humates, coal oxidation, alkali solutions, brown coal, NaOH, qualitative and quantitative composition.

Introduction. The relevance of this work is associated with the growing tendency to use coal not only as a fuel, but also as a valuable chemical raw material. Specifically, one of the products of the chemical processing of coal is humic compounds, which are widely used in various sectors of national economy.

Humic acids are capable of ion exchange reactions, form soluble and insoluble humates. Humic acids are a powerful geochemical agent that contributes to the decomposition of rocks and minerals, the concentration, dispersion and redeposition of elements in the earth's crust. Humic acids is the main part of the organic matter of the soil (humus), which determines its fertility [1].

All humic acids are soluble in alkalis, humates (salts of humic acids) of alkali metals are soluble in water, humates of other metals are insoluble. Humic acids are thermally unstable, in the temperature range of 100-200° C they are decarboxylated and lose their solubility. With an increase in the degree of coalification (the conversion of peat sequentially to brown, hard coal and anthracite) in the composition of humic acids, the proportion of carbon bound in aromatic cycles increases, which form condensed structures including a large number of rings.

Humic acids are completely cleaved by metallic sodium in liquid ammonia to form ether-soluble products, which, according to T. A. Kukharenko, is evidence of the presence of simple ether bonds in the humic acid molecule, which are the main type of bonds.

The chemical composition of humic acids depends mainly on the acidity of the aquatic environment and the degree of decomposition of plant material.

Of the physical properties of humic acids, we should mention their developed surface, which determines a number of their qualities as biologically active substances and collectors of heavy metals. The specific surface area is estimated to be approximately 900 m^2 / g, which is comparable to the specific surface area, for example, of activated carbon. These properties of humic acids are enhanced by the presence in their molecules of functional groups characteristic of effective complexing agents. The structure of humic acids suggests that their presence in the composition of coals and peats leads to the concentration of heavy metal ions by the latter, which is caused by complexation, sorption and ion exchange.

Humic acids are used in the production of lead-acid accumulators, to stabilize clay slurries during well drilling, as plant growth stimulants and components of organomineral (humic) fertilizers [2].

In recent years, humic acids and humates are increasingly used in various sectors of national economy. They are used as peptizing additives (viscosity reducers) to clay solutions used in well drilling, antiscale to soften water in steam columns, in the ceramic and cement industries, as a means to reduce the permeability of soils.

Due to the presence of active functional groups and a highly developed surface, humic acids are good sorbents (absorbers) and surface active agents. Carbon-alkali extraction of brown coals is used as a pickling material for wood finishing. In known doses, humic acids are antiseptics and can be used, in particular, for the healing of damaged skin of animals. Humic acids also have tanning and coloring properties and are used for the preparation of adhesive and oil paints, as skin tanning agents, for emulsification of bitumen and asphalts, as binders [3-4].

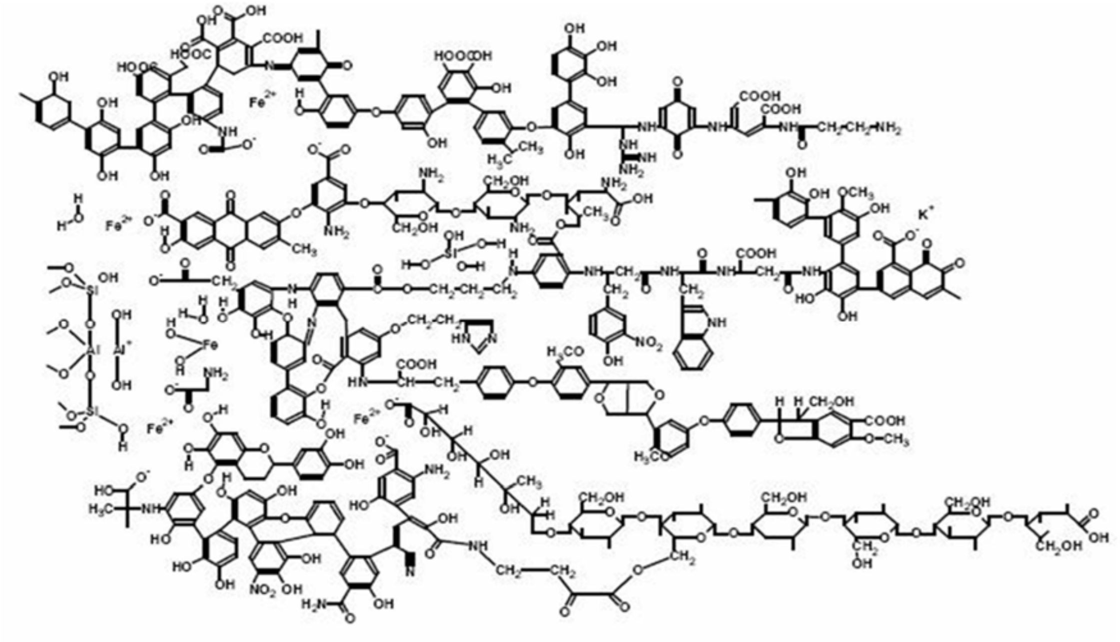

Figure 1 - Hypothetical model of soil humic acid structure

Experimental part. The brown coal from the “Kumyskuduk” open pit mine of the Verkhne-Sokurskoye deposit and the commercial preparation of sodium humate from “Asia COMPOGUM” LLP were used as HA sources according to the following procedure.

When conducting studies on the release of HA, brown coal was chosen as the object of research. For the experiment, a fraction no larger than 50 mm was used. Then, the initial brown coal was crushed on a jaw crusher to a size of 0.5 mm. After that, the crushed brown coal was abraded on VKMD 6 with a size of not more than 0.2 mm. Next, brown coal is placed in a plastic bucket and closed with a lid so that it does not oxidize. Then, for each experiment, the required mass of ground brown coal was taken and experiments were carried out [5].

A portion of crushed brown coal weighing 10 g was embathed with 100 ml of a NaOH solution of a given concentration (2%, 4%, 6%) and thoroughly mixed for a certain time (10 minutes, 25 minutes, 30 minutes). In this case, humic compounds pass into a soluble form in the form of sodium humate. After this, the undissolved brown coal precipitate was filtered off. The filtrate was neutralized with a hydrochloric acid solution until acidic (pH = 2 ... 3), while humic acids insoluble in water and acidic solutions precipitated. The precipitate HA is separated by centrifugation, then washed with distilled water and dried at a temperature of 105° C to constant weight.

The yield of humic acids is determined by next formula:

$$\eta = (m_2/m_1)\times 100\%, \tag{1}$$

where m_1 – mass of brown coal; m_2 - mass of humic acids.

Table 1- Calculated data for building a dependency Y= f(C)

C,%	X_2=-1	X_2=0	X_2=+1
2,0	4,680	7,034	4,712
2,5	4,044	6,461	4,201
3,0	3,546	6,025	3,828
3,5	3,188	5,729	3,595
4,0	2,968	5,572	3,500
4,5	2,887	5,554	3,544
5,0	2,946	5,675	3,728
5,5	3,143	5,934	4,050
6,0	3,480	6,334	4,512

Graphical dependences Y = f (C) of the HA output at fixed concentration values (X_2) are presented in figure 1.

From Figure 1 it follows that the dependence of the HA yield on alkali concentration has a nonlinear dependence. So for an average extraction time of 20 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 7% to 5.6%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 6.5%. With an increase in extraction time of 30 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 4.7% to 3.5%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 4.5%. With a decrease in extraction time of 10 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 4% to 2.9%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 3,5% [6].

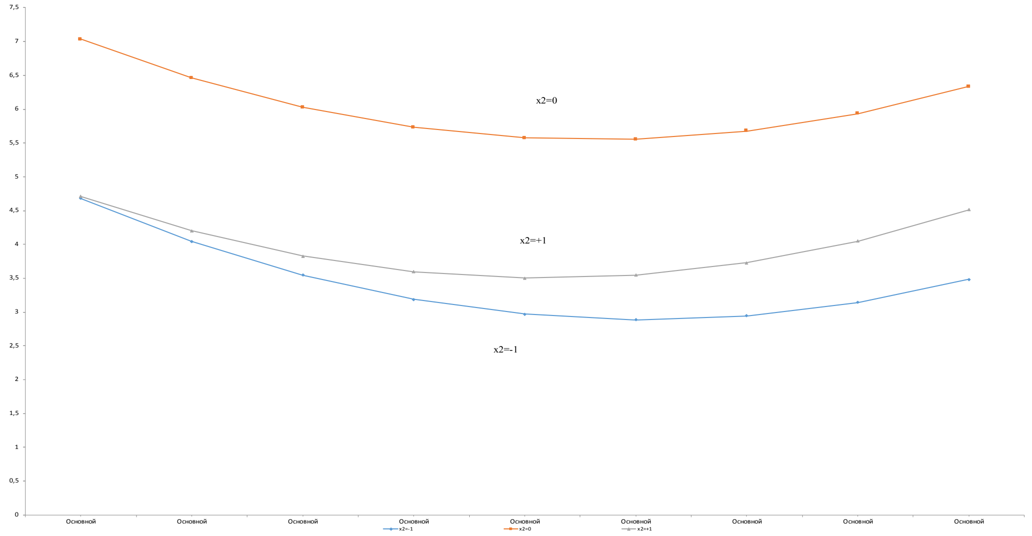

Figure 2 – Dependency diagram of the yield of humic acids
on alkali concentration (-1 = 10 min, 0 = 20 min, + 1 = 30 min).

Similarly, to construct the graphical dependencies Y = f (T), equations (2.39-2.41) were used, with the help of which the HA output was calculated for fixed time values. The calculated data are presented in table 2.

Table 2 - The calculated data for constructing the dependence Y = f (τ)

T	X_1=-1	X_1=0	X_1=+1
10	4.72	3.008	3.52
12.5	5.769	4.119	4.694
15	6.53	4.943	5.58
17.5	7.004	5.479	6.179
20	7.19	5.728	6.49
22.5	7.089	5.689	6.514
25	6.7	5.363	6.25
27.5	6.024	4.749	5.699
30	5.06	3.848	4.86

The graphical dependences Y = f (τ) of the HA output at fixed concentration values (X_2) are presented in figure 3.

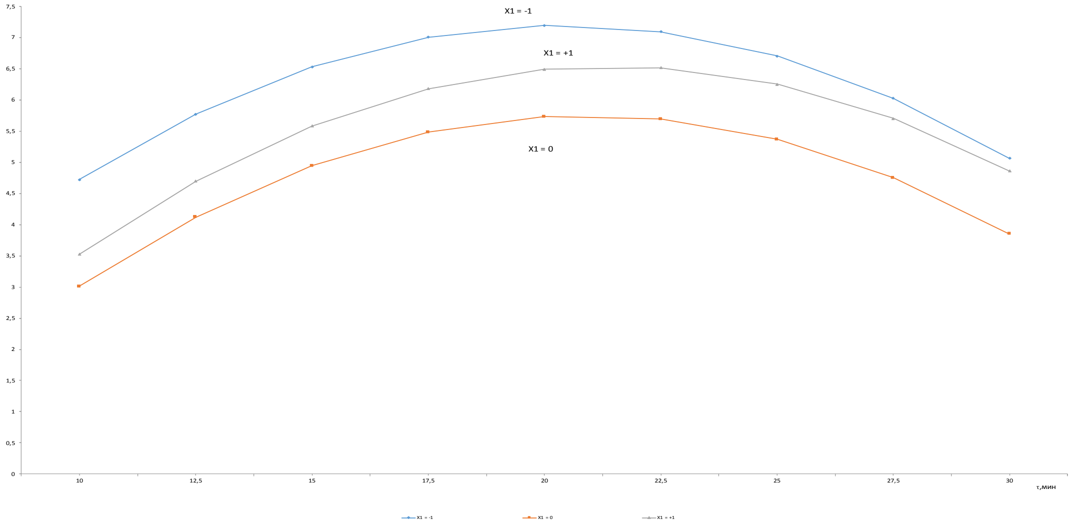

Figure 3 - Dependency diagram of the yield of humic acids on the processing time (-1= 2%, 0= 4%, +1= 6%)

The graphical dependences of the HA yield on the time of processing the coal with NaOH solutions show the presence of a maximum. The maximum value, that is, the time at which the maximum yield of HA can be determined by analyzing equations. The maximum point corresponds to the derivative dy/dτ = 0.

Qualitative and quantitative composition of humic compounds extracted from coal.

The qualitative and quantitative composition of the organic matter extracted from coal by extraction with alkali solutions was determined using an Agilent 7890A gas chromatograph with an Agilent 5975C mass selective detector. Results are processed automatically using the GS-MSDDataAnalysis program.

From the presented data it follows that the qualitative and quantitative composition of the obtained humic acids depends on the concentration of the alkali extractant. This is evidenced by different peak heights corresponding to individual organic compounds. Differences in the number of peaks corresponding to individual chemical compounds can also be noted. Identification of individual organic compounds showed that the composition of the obtained humic compounds is complex and multicomponent. Thus, the qualitative and quantitative composition of HA obtained by extraction of coal with alkali solutions depends on many factors, primarily on the concentration of alkalis. It is likely that in this case various chemical compounds with different degrees of solubility in water and alkalis are formed. This explains the dependence of the HA yield on alkali concentration [7].

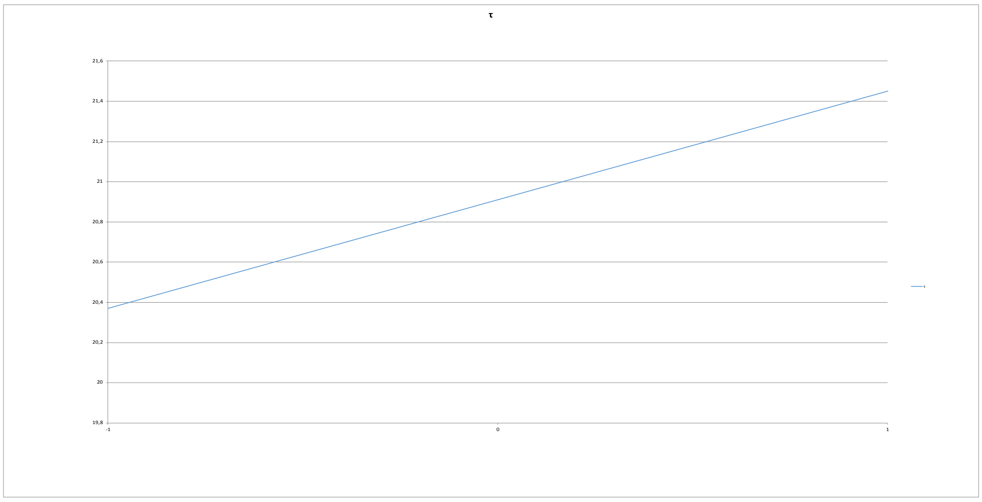

Figure 4 – Dependency diagram of the yield of humic acids in the presence of a maximum

The goal is a financial justification for the extraction of humic acid from brown coal.

The implementation of the process of obtaining the product involves extraction of humic acid by acidifying an aqueous solution of the preparation of sodium humate with hydrochloric acid to pH = 2 and preliminary preparation of humic acid for reactions (centrifugation, washing, drying). During the experiment, Kumyskuduksky coal was selected. The work was carried out in classical conditions.

The methodology of the experiment: 10 grams of brown coal are placed in a beaker (flask), the required volume of extractant is added and the resulting system is mixed for a given time (the volume of extractant and mixing time are selected in accordance with the experimental design matrix for a specific experiment). After mixing, the mixture is settled; filtered; dried. The calculations performed on the experiment planning matrix made it possible to reduce the total number of experiments to 9. Based on the dependence of the yield of the substance on time and the ratio of solvents, optimal synthesis conditions were calculated [8].

The experimental part consisted of 9 experiments. Each experiment was conducted separately. Thus, the total number of experiments was 18.

Qualitative and quantitative composition of the civil code. The alkalis obtained by extraction of coals with solutions of alkalis depend on many factors, primarily on the concentration of alkalis. It is likely that various chemical compounds are formed that have different degrees of solubility in water and alkalis. This explains the dependence of the GC yield on the alkali concentration.

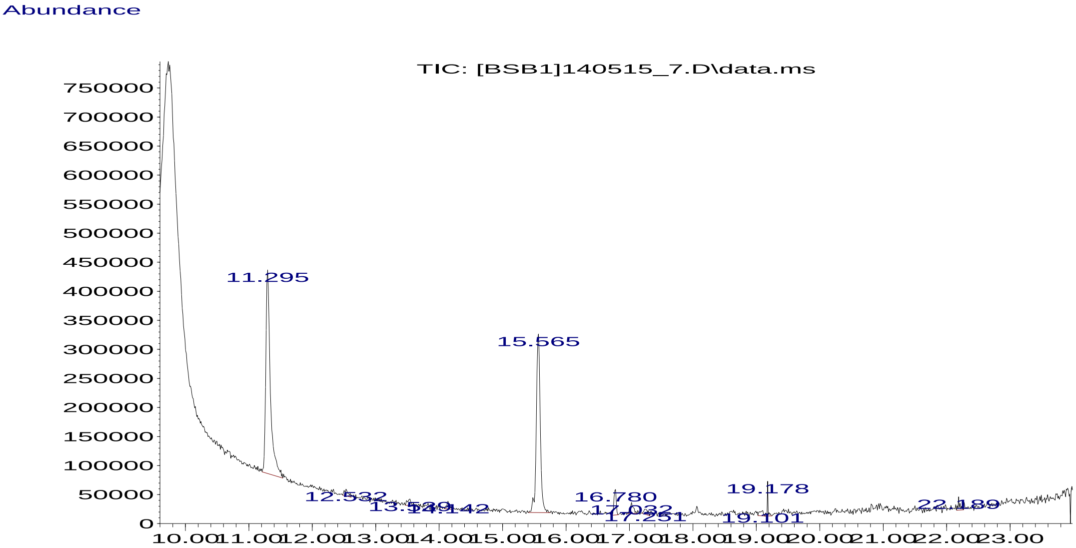

Figure 5 – Chromatogram of humic compounds after coal extraction with 2% alkali solution

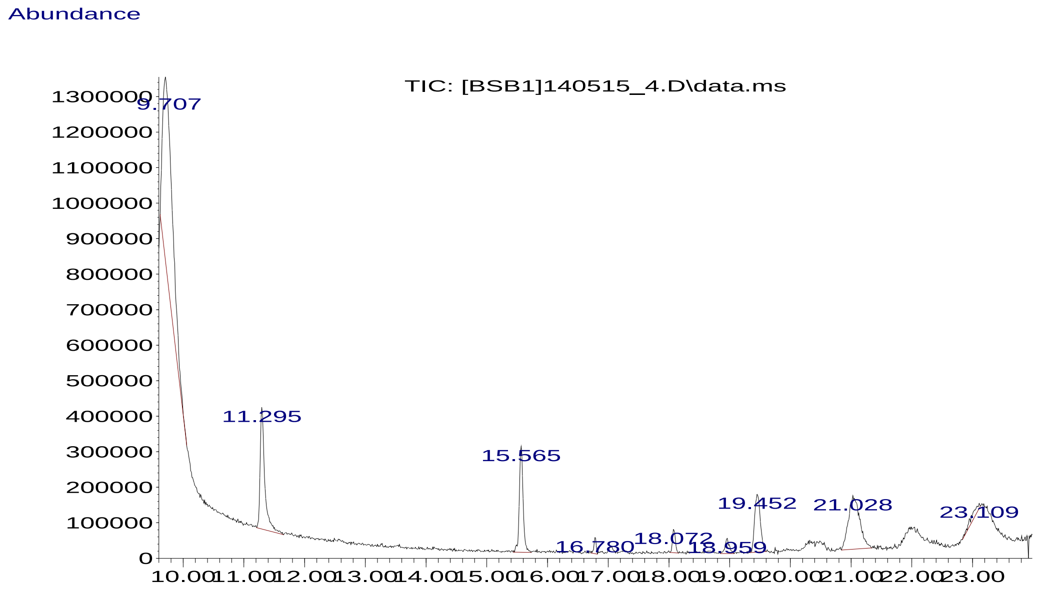

Figure 6 - Chromatogram of humic compounds after coal extraction with 4% alkali solution
Composition of humic compounds obtained during coal extraction with 4% alkali solutions

№	Chemical compounds	Chemical compound content in the sample, %
1	Trichloromethane	45.24
2	O-xylene	14.26
3	Naphthalene	10.27
4	Tetracosane	0.93
5	Dodecane, 2-methyl-6-propyl-eicosan	1.72
6	Sulphurous acid	1.65
7	Pentadecan	8.45
8	Tridecane	15.34
9	Dodecane, 2,6,11-trimethyl-Heptadecane	2.13

Conclusion. The essence of the method involves a single extraction of humic acids from an analytical coal sample with a dilute sodium hydroxide solution when heated, followed by their precipitation with an excess of hydrochloric acid. After processing the initial coal with water vapor in the reactor, the yield of humic acids from them increased. The obtained data shows the possibility of efficient production of humates from oxidized coal. The yield of humic acids depends on alkali concentration, extraction time and process temperature.

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КӨМІРДІ ТОТЫҚТЫРУ ПРОЦЕССІНДЕ ГУМАТ АЛУ

Аннотация. Соңғы онжылдықта топырақтың құнарлылығын арттыру, ауыл шаруашылығы дақылдарының өнімділігін арттыру үшін органикалық қоспаларды қолдану проблемасы өзекті болып отыр. Мұндай қоспалардың бірі-гуматтар-натрий және гумин қышқылдарының калий тұздары. Гуматтар мен гумин қышқылдары-топырақ гумусының химиялық негізі, оның концентраты. Гумус-көптеген биохимиялық топырақ процестерінің белсенділігі мен тұрақтылығының негізі. Натрий гуматтарын алуға арналған шикізат оңай қол жетімді-бұл қоңыр көмір, шымтезек, тотыққан тас көмір, өндіріске төмен шығынмен кешенді алу технологиясы. Тотыққан тас көмір гуматтарын өндіру үшін пайдалану ерекше өзекті. Тотыққан бұрыштардың макро - және микроэлементтердің кең жиынтығы, құрамы бойынша топыраққа жақын гумин қышқылдарының көп мөлшері бар. Қабаттардағы тотыққан көмір халық шаруашылығында іс жүзінде пайдаланылмайды және аршу жыныстарымен бірге үйінділерге түседі. Ұсынылған әдіс дайын өнімнің өзіндік құнын жақсартуға мүмкіндік береді. Көмірді тотықтыру арқылы гуматты алу әдісі белгілі. Гумин қышқылдарының шығындарын зерттеу үшін, сондай-ақ гумин қышқылдарының сапалық және сандық құрамын зерттеу үшін әртүрлі концентрациядағы сілтілі ерітінділер қолданылды. Гумин қышқылын өндіру бойынша тәжірибе жүргізу кезінде зерттеу нысаны ретінде қоңыр көмір алынды. Тәжірибе үшін 50 мм-ден аспайтын фракция қолданылды. Ары қарай қоңыр көмір 0,5 мм болатын жақтаулы уатқышта ұсақталды. Одан кейін ұсақталған қоңыр көмірді көлемі 0,2 мм УКПТД 6-да ысқыладық. Содан соң қоңыр көмір тотығып кетпес үшін оны пластикалық шелекке салып, бетін жауып қоямыз. Әрбір эксперимент үшін қоңыр көмірді тек керекті мөлшерде ғана қолданып, тәжірибелер жүргіздік. Ал егер пайдалану уақытын 30 минутқа артырсақ, гумин қышқылының бөлінуі 4,6%-ды құрайды. Экстракция температурасын 65С°-қа жоғарылатып, экстракция уақытын 10 минуттан 20 минутқа арттырсақ, гумин қышқылының бөлінуі 3,9%-дан 4,7%-ға өседі. Экстракция уақытын 30 минутқа дейін арттырсақ, гумин қышқылының бөлінуі 4,7%-ды құрайды. Экстракция температурасын 20С°-қа төмендеткенде гумин қышқылының бөлінуі 4,1%-дан 5%-ға артады. Экстракция уақытын 30 минутқа дейін арттырсақ, гумин қышқылының бөлінуі 5,3%-ға дейін артады. Эксперимент нәтижелерін математикалық өңдеу кезінде регрессия теңдеулері алынды, бұл көрсетілген факторлардың әрқайсысының ГК шығуына әсерін анықтауға мүмкіндік берді; әртүрлі концентрациядағы сілтілермен экстракциялау алынған ГК сапалық және сандық құрамы жүргізілді. Көмірден алынған органикалық массаның сапалық және сандық құрамын Agilent 5975С масс-селективті детекторы бар Agilent 7890А газ хроматографының көмегімен анықталды. Гумин қышқылдарының сапалық және сандық құрамы сілтінің концентрациясына байланысты, ол туралы алынған хроматограммды дәленделінеді. Математикалық өңдеу зерттелетін факторлардың гумин қышқылдарын алудың тиімділігіне әсерін анықтауға мүмкіндік берді.

Түйін сөздер: гуматтар, көмірдің тотығуы, сілтілі ерітінділер, қоңыр көмір, NaOH, сапалық және сандық құрамы.

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ПОЛУЧЕНИЕ ГУМАТА В ПРОЦЕССЕ ОКИСЛЕНИЯ УГЛЯ

Аннотация. В последние десятилетия все большую актуальность приобретает проблема повышения плодородия почв, применения органических добавок для повышения урожайности сельхозкультур. Одними из таких добавок являются гуматы – натриевые и калийные соли гуминовых кислот. Гуматы и гуминовые кислоты – химическая основа гумуса почв, его концентрат. А гумус – основа активности и стабильности большинства биохимических почвенных процессов. Сырье для получения гуматов натрия легкодоступно – это бурые угли, торфы, окисленные каменные угли, технология получения – комплексная с низкими затратами на производство. Окисленные угли имеют широкий набор макро- и микроэлементов, большое количество гуминовых кислот, которые по своему составу близки к почвенным. Окисленные в пластах угли практически не используются в народном хозяйстве и поступают в отвалы вместе со вскрышными породами. Предлагаемый способ позволяет улучшить себестоимость готового продукта. Известен способ получения гумата путем окисления угля. Для исследования затрат гуминовых кислот, а также для исследования качественного и количественного состава гуминовых кислот были использованы щелочные растворы различной концентрации. При проведении исследований по выходу ГК объектом исследований был выбран бурый уголь. Для эксперимента использовалась фракция не крупнее 50 мм. Далее исходный бурый уголь подвергался дроблению на щековой дробилке до размера 0,5 мм. После чего измельченный бурый уголь истирали на ВКМД 6 размером не более 0,2 мм. Далее бурый уголь помещаем в пластиковое ведро и закрываем крышкой, для того чтобы он не окислился. После чего для каждого эксперимента брали нужную массу измельченного бурого угля и проводили опыты. А если время использования превышает 30 минут, то выделение гуминовой кислоты составляет 4,6%. Если повысить температуру экстракции на 65С, увеличив время экстракции с 10 минут на 20 минут, выделение гуминовой кислоты возрастет с 3,9% до 4,7%. Если увеличить время экстракции до 30 минут, то выделение гуминовой кислоты составляет 4,7%. При снижении температуры экстракции на величину 20С выделение гуминовой кислоты увеличивается с 4,1% до 5%. Если увеличить время экстракции до 30 минут, то выделение гуминовой кислоты увеличится до 5,3%. Задачи, поставленные в ходе исследования: проведен обзор научной литературы по вопросу свойств ГК, их состава и способа получения; разработана методика проведения эксперимента по влиянию концентрации щелочи, температуры и времени экстракции на степень извлечения ГК из углей Центрального Казахстана; получены уравнения регрессии при математической обработке результатов эксперимента, что позволило установить влияние каждого из указанных факторов на выход ГК; проведен качественный и количественный состав ГК, полученных экстракции щелочами различной концентрации. Качественный и количественный состав органической массы, извлеченной из углей путем экстракции растворами щелочей определялся с помощью газового хроматографа Agilent 7890A с масс-селективным детектором Agilent 5975C. Качественный и количественный состав гуминовых кислот зависит от концентрации щелочи, о чем свидетельствуют полученные хроматограммы. Математическая обработка результатов эксперимента позволила определить влияние исследуемых факторов на эффективность извлечения гуминовых кислот.

Ключевые слова: гуматы, окисление угля, щелочные растворы, бурый уголь, NaOH, качественный и количественный состав.

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PRODUCTION OF NITROCELLULOSE FROM CELLULOSE CULTIVATED IN SOUTH KAZAKHSTAN UNDER SUPERCRITICAL CONDITIONS

Abstract. This article presents the results of a study of the process of producing nitrocellulose from Kazakhstani cellulose raw materials using supercritical technology.

Nitration can be carried out both directly and indirectly. Direct nitration processes include the reactions of replacing a hydrogen atom by a nitro group or the addition of nitrating agents via a multiple bond, and indirect nitration involves replacing other atoms or groups of atoms with a nitro group (for example, halogens, sulfo groups). Indirect nitration methods include oxidation reactions of nitrogen-containing substances to nitro compounds, as well as condensation reactions leading to nitro compounds.

At the same time, the traditional method of nitration of cellulose is quite “dirty” from an environmental point of view, since it spends a huge (several thousand times more than the volume of nitrocellulose obtained) amount of water for the subsequent stage of washing nitrocellulose from nitration mixture residues after nitration.

This factor significantly increases the cost of water decontamination and links production to large reservoirs, which is not always possible, especially in arid regions.

In addition, due to the relatively small conversion of the nitration process using a nitrating mixture, the production of nitrocellulose requires the construction of large-scale production workshops. Which is also not always justified.

Associations with the above are of great interest to alternative nitration technologies, in particular nitration under supercritical conditions.

The aim of this work is to study the processes of nitration of cellulose in a supercritical static reactor.

For the experiment, the nitration method was chosen in a static supercritical reactor in a carbon dioxide medium using nitric oxide V as a nitrating agent.

As a raw material, cotton pulp of the 1st grade was used.

The initial reagent for producing nitric oxide V was nitric acid with a concentration of 65%

The process was carried out in a static reactor.

As a result, a white fibrous mass was obtained, similar in appearance to cellulose, readily soluble in acetone and insoluble in water, the density was 1.63 g / cm^3, based on the density, analysis of the melting temperature and the nature of the combustion, we can conclude pyroxylin with a nitrogen content of 12.05 - 12.4%.

Keywords: cellulose, nitration, supercritical conditions, nitrocellulose.

Introduction. Nitration is one of the most important reactions of organic synthesis and is widely used in laboratory practice and production [1-3].

Nitration can be carried out both directly and indirectly. Direct nitration processes include the reactions of replacing a hydrogen atom by a nitro group or the addition of nitrating agents via a multiple bond, and indirect nitration involves replacing other atoms or groups of atoms with a nitro group (for example, halogens, sulfo groups). Indirect nitration methods include oxidation reactions of nitrogen-containing substances to nitro compounds, as well as condensation reactions leading to nitro compounds.

The nitration processes are well studied and mastered by industry, and with their help a large number of highly demanded products are obtained, in particular cellulose nitrates, which are one of the most widely used cellulose ethers, the industrial production of which began back in the 19th century. Different applications of cellulose nitrates are determined by their specific properties. High mechanical strength and the ability to transfer to a plasticized state, good solubility and compatibility with available plasticizers - all this provided high volumes of production of cellulose nitrates for the manufacture of gunpowder, rocket fuel, varnishes, paints [4-9].

At the same time, the traditional method of nitration of cellulose is quite “dirty” from an environmental point of view, since it spends a huge (several thousand times more than the volume of nitrocellulose obtained) amount of water for the subsequent stage of washing nitrocellulose from nitration mixture residues after nitration [10-14].

This factor significantly increases the cost of water decontamination and links production to large reservoirs, which is not always possible, especially in arid regions.

In addition, due to the relatively small conversion of the nitration process using a nitrating mixture, the production of nitrocellulose requires the construction of large-scale production workshops. Which is also not always justified [15-17].

Associations with the above are of great interest to alternative nitration technologies, in particular nitration under supercritical conditions.

The current environmental and social environment urgently requires new approaches to the synthesis of organic substances. In particular, there is a shortage of energy and water resources, which puts the issue of rational use in the forefront. One of the solutions to this problem is the use of carbon dioxide in the supercritical state as a reaction medium [18].

At a pressure of more than 74 atmospheres and a temperature of more than 30 ° C, carbon dioxide passes into a supercritical state, in which its density is like that of a liquid, and its viscosity and surface tension are like that of a gas. Such properties make supercritical carbon dioxide an effective non-polar solvent [19-25].

Carbon dioxide, used in a supercritical state as a reaction medium, has a number of properties inherent in gases. Moreover, it has a number of attractive properties that provide additional benefits when using this gas as an aid in extraction.

- universal dissolving ability with respect to organic compounds, physiologically does not cause concern, because is the final product of the metabolism of a number of living organisms, including humans.

- In relation to the conditions of supercritical fluid extraction, carbon dioxide is chemically inert and does not enter into chemical interactions with reagents.

- CO_2 is relatively safe for the environment, which suggests the possibility of creating an environmentally friendly type of production.

- Carbon dioxide is one of the most accessible and widely used gases in the food industry.

The aim of this work is to study the processes of nitration of cellulose in a supercritical static reactor.

Materials and Methods. For the experiment, the nitration method was chosen in a static supercritical reactor in a carbon dioxide medium using nitric oxide V as a nitrating agent.

The raw materials used were cotton pulp of the 1st grade according to GOST 3818.0 produced by Khlopkoprom-Cellulose LLP in 2019.

The initial reagent for producing nitric oxide V was nitric acid GOST 4461-77 with a concentration of 65% (requires additional strengthening by distillation with oleum).

Results and discussion. The synthesis of pyroxylin under supercritical conditions involves several stages

1 Preparation of nitric acid and bring it, but a sufficient concentration.

Since nitric acid is manufactured industrially and delivered to the market, it has a concentration of not more than 62%, which is insufficient for the nitration reaction and the production of nitrogen pentoxide, it is necessary to strengthen it.

The strengthening process consists in the distillation of nitric acid in a mixture with oleum in a ratio of 1: 3 at atmospheric pressure without access to atmospheric water. As a result, nitric acid with a strength of more than 80% was obtained.

2 getting nitric oxide.

Since the nitration process was selected under supercritical conditions, nitric pentoxide (Nitric Oxide V, N_2O_5) was used instead of the traditional nitrating mixture.

To obtain it, it is necessary to add phosphorus V (P_2O_5, phosphorus pentoxide, phosphoric anhydride, phosphorus pentoxide) to frozen concentrated nitric acid (melting point −41.59 °C, recommended process temperature -78.5 °C).

The reaction must be carried out in the environment of ozone O_3 for which an ozonizer is introduced into the installation.

After addition of phosphorus oxide V, the reaction proceeds at a temperature of 28.0 °C. Under these conditions, nitrogen pentoxide is sublimated and transferred to a collection tank, which is also recommended to be cooled to sub-zero temperatures (from -20 to -40 °C). At the same time, ozone must circulate in the system throughout the process.

The reaction proceeds according to the formula:

$$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$$

And in parallel with the reaction:

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

Figure with the image of the installation for laboratory synthesis of nitrogen pentoxide is shown in figure 1.

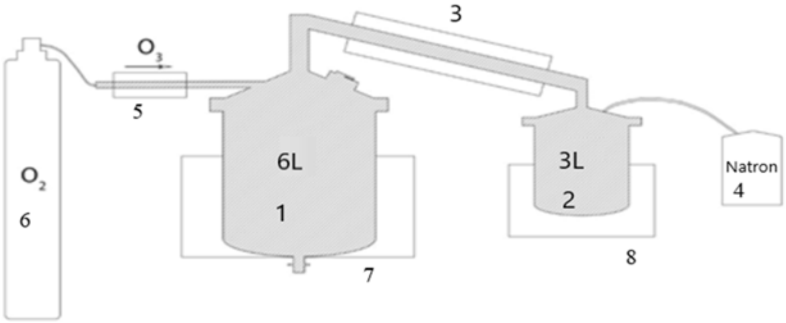


Figure 1 - apparatus for the synthesis of nitrogen pentoxide

Concentrated nitric acid (concentration of more than 75%) is loaded into the reactor 1 and cooled to the freezing point using a refrigerator 2, then phosphorus oxide V is introduced into the reactor 1 in a ratio of 1/1, after which ozone is obtained by passing oxygen from the cylinder 6 through the ozonizer 5, during the reaction, the resulting nitrogen pentoxide is sublimated and condensed in the receiver 2 through the refrigerator 3, while the receiver 2 is also cooled by the refrigerator 8 to stabilize the nitric oxide V, the released and unreacted oxide nitrogen IV is neutralized in tank 4.

As a result, white nitric pentoxide crystals (figure 2) and nitric oxide IV vapors as a by-product will be obtained in the collection.

The reaction yield is 53% based on 100% nitric acid.

Figure 2 - Nitrogen Pentoxide Crystals

It should be noted that the crystals of nitrogen pentoxide are extremely unstable and their long-term storage is impractical; for this reason, the obtained pentoxide should immediately go to the 3-stage cellulose nitration.

3 Cellulose nitration

Cellulose nitration is carried out using nitrogen pentoxide in a ratio of cellulose / pentoxide, 1/6

The process takes 15 minutes

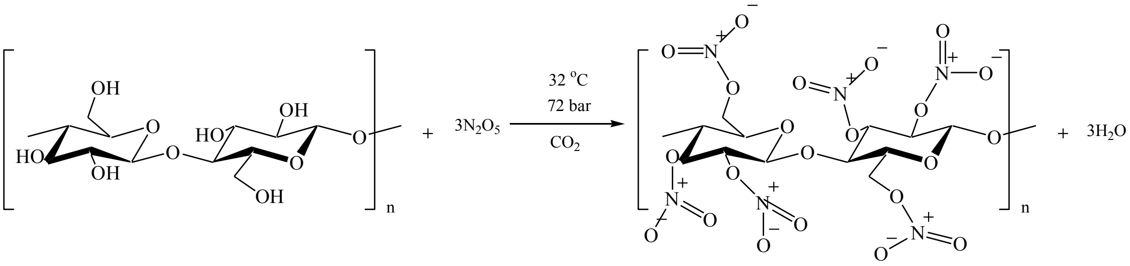
Temperature - 32 ° C

Pressure - not less than 72 atm.

The process was carried out in a static reactor (a reactor with an intensification mixer or a circulation pump for process intensification is recommended)

The reaction yield is almost 100% for cellulose.

The reaction was carried out according to the formula:



As a result, a white loose fibrous mass was obtained, similar in appearance to cellulose, readily soluble in acetone and insoluble in water, the density was 1.63 g / cm³, based on the density, analysis of the melting temperature and the nature of the combustion, we can conclude that pyroxylin with a nitrogen content of 12.05 - 12.4%.

Conclusion. As a result, the first synthesis of pyroxylin from Kazakhstani cellulosic raw materials using supercritical technology was carried out.

The advantages of the process are

-Small water consumption

-Fast reaction

High process selectivity

-High conversion process

-Lack of sulfur compounds in contrast to the traditional nitration method

We continue to work on this process in order to optimize and scale it.

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ОҢТҮСТІК ҚАЗАҚСТАНДА ҚИЫН ЖАҒДАЙДА ӨСІРІЛЕТІН ЦЕЛЛЮЛОЗАДАН НИТРОЦЕЛЛЮЛОЗА ӨНДІРУ

Аннотация. Бұл мақалада суперкритикалық технологияны қолдана отырып, қазақстандық целлюлоза шикізатынан нитроцеллюлоза алу процесін зерттеу нәтижелері келтірілген.

Нитризация тікелей де, жанама түрде де жүргізілуі мүмкін. Тікелей нитраттау процестеріне сутегі атомын нитро тобына ауыстыру немесе бірнеше байланыс арқылы нитраттау агенттерін қосу реакциясы кіреді, ал жанама нитрация басқа атомдарды немесе атомдар тобын нитро тобымен алмастыруды қамтиды (мысалы, галогендер, сульфо топтары). Жанама нитрлеу әдістеріне азот қосылыстарының азотты қосылыстарға тотығу реакциялары, сондай-ақ нитроқосылыстарға апаратын конденсация реакциялары жатады.

Сонымен қатар, целлюлозаны нитраттаудың дәстүрлі әдісі экологиялық тұрғыдан «лас» болып табылады, өйткені ол нитроцеллюлозаның нитратталған қоспадан кейінгі қалдықтарынан кейінгі жуу кезеңі үшін судың үлкен мөлшерін алады (алынған нитроцеллюлозадан бірнеше мың есе көп).

Бұл фактор суды зарарсыздандыру құнын едәуір арттырады және өндірісті ірі су қоймаларымен байланыстырады, бұл әрдайым мүмкін емес, әсіресе құрғақ аймақтарда.

Сонымен қатар, нитрлеу қоспасын қолданып нитраттау процесінің салыстырмалы түрде аз өзгеруіне байланысты нитроцеллюлоза өндірісі ірі өндіріс цехтарын салуды қажет етеді, бұл әрдайым ақталмайды.

Жоғарыда аталған қауымдастықтар альтернативті нитритациялық технологияларға, әсіресе критикалық жағдайларда нитризацияға үлкен қызығушылық тудырады.

Бұл жұмыстың мақсаты - өте критикалық статикалық реактордағы целлюлозаны нитрлеу процестерін зерттеу.

Эксперимент үшін нитрлеу әдісі ретінде азот оксидін V қолдана отырып, көміртегі диоксиді ортадағы статикалық сынғыш реакторда нитрлеу әдісі таңдалды.

Шикізат ретінде 1-ші класстағы мақта целлюлоза пайдаланылды.

Азот оксиді V алу үшін алғашқы реагент концентрациясы 65% азот қышқылы болды

Процесс статикалық реакторда жүргізілді.

Нәтижесінде целлюлозаға ұқсас ақ борпылдақ талшықты масса алынды, ацетонда оңай ериді және суда ерімейді, тығыздығы, балқу температурасы мен жану сипатын талдау негізінде, 1,63 г/см³ болды, қорытынды жасауға болады. пироксилин құрамында азот мөлшері 12,05 - 12,4%.

Түйін сөздер:. целлюлоза, нитрлеу, сыни жағдайлар, нитроцеллюлоза.

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ПОЛУЧЕНИЕ НИТРОЦЕЛЛЮЛОЗЫ ИЗ ЦЕЛЛЮЛОЗЫ, КУЛЬТИВИРУЕМОЙ В ЮЖНОМ КАЗАХСТАНЕ В СВЕРХКРИТИЧЕСКИХ УСЛОВИЯХ

Аннотация. В данной статье представлены результаты изучения процесса получения нитроцеллозы из казахстанского целлюлозного сырья с использованием сверхкритических технологий.

Нитрование может осуществляться как прямым, так и непрямым путем. К процессам прямого нитрования относят реакции замещения атома водорода на нитрогруппу или присоединение нитрующих агентов по кратной связи, к непрямому нитрованию – замену других атомов или групп атомов на нитрогруппу (например, галогенов, сульфогруппы). К методам непрямого нитрования можно отнести реакции окисления азотсодержащих веществ до нитросоединений, а также реакции конденсации, приводящие к нитросоединениям.

В то же время традиционный метод нитрования целлюлозы является достаточно “грязным” с экологической точки зрения, так как затрачивает огромное (в несколько тысяч раз больше объема получаемой нитроцеллюлозы) количество воды на последующую после нитрования стадию промывки нитроцеллюлозы от остатков нитрующей смеси.

Данный фактор значительно повышает затраты на дезактивацию воды и привязывает производство к крупным водоёмам, что не всегда возможно, особенно в засушливых регионах.

Кроме того, по причине относительно небольшой конверсии процесса нитрования с использованием нитрующей смеси, производство нитроцеллюлозы требует строительства масштабных производственных цехов, что тоже не всегда оправдано.

Связи с вышеперечисленным, высокий интерес вызывают альтернативные технологии нитрования, в частности нитрование в сверхкритических условиях.

Целью данной работы является изучение процессов нитрования целлюлозы в сверхкритическом статичном реакторе.

Для проведения опыта был выбран метод нитрования в статическом сверхкритическом реакторе в среде диоксида углерода с применение оксида азота V в качестве нитрующего агента.

В качестве сырья использовалась хлопковая целлюлоза 1 сорта.

Исходным реагентом для получения оксида азота V была азотная кислота концентрацией 65%.

Процесс проводился в статичном реакторе.

В результате получена волокнистая рыхлая масса белого цвета, по внешнему виду похожая на целлюлозу, хорошо растворимая в ацетоне и нерастворимая в воде, плотность составила 1,63 г/см³, на основании плотности, анализа температуры плавления и характера горения можно сделать вывод, что получен пироксилин с содержанием азота 12,05-12,4 %.

Ключевые слова: целлюлоза, нитрование, сверхкритические условия, нитроцеллюлоза.

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STUDY OF THE EFFECT OF AIR CONSUMPTION, LIQUID LAYER HEIGHT AND TEMPERATURE ON THE PROCESS OF FLOTATION SEPARATION OF GROUND PLASTICS

Abstract. For separation of plastic wastes (polyamide (PA), acrylonitrile butadiene styrene (ABS) and polystyrene (PS)), a flotation method is proposed. Using this method, the effect of air consumption, liquid layer height and temperature were studied. As surface-active substances (surfactants), polidocanol, sulphanole and a mixture of surfactants containing sodium laureth sulfate and diethanolamide were used.

To analyze the research results of flotation separation of a mixture of ground plastic wastes, the extraction of the floating component ε and the purity of the concentrate β were calculated.

The research results on the extraction of polystyrene from the air consumption at various concentrations of a mixture of surfactants show that the extraction has a maximum at a certain air consumption. At low air consumption, the process is inefficient, since the working volume of the liquid is not saturated enough with gas bubbles. If the optimum value of air consumption is exceeded, many gas bubbles are formed that are not involved in the flotation process. Such bubbles, moving through a liquid, can create turbulent flows that impede flotation of particles. When moving in a turbulent liquid flow, the bubble-particle complex is prone to destruction, as particles and bubbles have different inertia (mass). In addition, it may be concluded that the air consumption value at which the maximum extraction of the floating component is achieved depends on the type of polymer and surfactant. The air consumption effect nature at different concentrations of surfactants is not changed – only the floating component extraction changes.

The research results on the extraction of polystyrene from the aerated liquid layer height at various concentrations of a mixture of surfactants indicate that at a low height of the aerated liquid layer the probability of collision of a plastic particle with an air bubble is low and some potentially floating particles sink to the bottom of the device, without having time to collide with an air bubble. The optimum height of the processed liquid layer corresponds to a certain air consumption. When the liquid layer height is less than optimal, the achievement of the required extraction degree of the dispersed phase is possible, for example, with an increase in air consumption.

When assessing the effect of liquid temperature on the flotation process, it was found that increasing the liquid temperature above 20°C leads to a sharp decrease in the ABS and PS extraction. This is possibly due to the fact that the dependence of the foaming capacity of surfactants on temperature is characterized by solubility curves and for most surfactants they have an extremum. Probably, an increase in the solution temperature leads to the dehydration of the dissolved surfactant molecules. Moreover, they separate as an independent macrophase, which leads to a decrease in the number of surfactant molecules involved in the flotation process.

Key words: flotation, plastic wastes, surfactants, concentration, air consumption, liquid layer height, temperature.

Introduction. In the world there is a constant increase in the consumption of polymer materials (PM) [1, 2], which occupy a leading position in terms of production of raw materials.

The accelerated growth in the production of polymer materials and the expansion of their applications in various industries is explained by their manufacturability, ease, convenience, cost-effectiveness, safety, a set of valuable operational properties and high aesthetics. Plastics are serious competitors to glass, ceramics and metal [3].

At the same time, the use of products from polymer materials certainly causes waste formation. The increase in PM production and consumption inevitably entails an increase in the amount of their wastes.

In recent years, the problem of processing plastic wastes has become to take an important place in the world, since the bulk of wastes is destroyed by inefficient methods [4-8].

Promising processes for the PM separation are flotation based on different wettability, since they are quite simple in hardware and reliable. The flotation process is close to the sedimentation process in flotation baths, which is widely used in the world. The flotation process may allow to separate plastics with fairly similar or equal densities. This requires the presence of surfactants and gas bubbles in the working volume of the device [9, 11].

Research methods. The methodology for experimental research of the flotation process of separation of plastics is as follows. It is necessary to prepare in advance a charge of the investigated ground plastics with a mass $m_{\text{исх}}$. Due to the complexity of further manual sorting of the concentrate in a multilateral research of the flotation process, it is recommended to feed a charge of a mixture of ground plastics weighing about 10 g. In a laboratory setup, it is possible to study the dependences of the extraction of certain types of plastics on physical and operational factors, while the charge with a mass $m_{\text{исх}}$ containing one type of ground plastic is fed to the flotation. It is also possible to study the separation of a mixture of several types of ground plastics. In the second case, the charge with a mass $m_{\text{исх}}$ should contain particles of ground hydrophobic plastic with a mass $m_{\text{исх}}^{\text{фл}}$ and particles of ground hydrophilic plastic with a mass $m_{\text{исх}}^{\text{ос}}$. When studying the separation of plastics, it is recommended to feed a mixture of plastics to the flotation in a 1:1 ratio.

Research results. In [12], the authors presented the research results of the effect of the concentration of surface-active substances (surfactants) on the process of separation of plastic wastes. The tables with experimental data presented in this work contain the results obtained by changing the air consumption, the liquid layer height and its temperature. When conducting the research, the plastic wastes were polyamide, acrylonitrile butadiene styrene and polystyrene. As surface-active substances, polidocanol, sulphanole and a mixture of surfactants containing sodium laureth sulfate and diethanolamide were used [13-15].

To analyze the research results of the flotation separation of a mixture of ground plastic wastes, the extraction of the floating component ε and the purity of the concentrate β were calculated by the formulas [16]:

$$\varepsilon = \frac{m_{\text{конц}}^{\text{фл}}}{m_{\text{исх}}^{\text{фл}}} \cdot 100\%, \tag{4.1}$$

$$\beta = \frac{m_{\text{конц}}^{\text{фл}}}{m_{\text{конц}}} \cdot 100\%, \tag{4.2}$$

where $m_{\text{конц}}^{\text{фл}}$ – a mass of the floating component (the particles of the ground hydrophilic plastic in the concentrate, kg; $m_{\text{исх}}^{\text{фл}}$ – a mass of the floating component (the particles of the ground hydrophilic plastic in the initial charge, kg; $m_{\text{конц}}$ – a mass of the concentrate, kg.

According to the calculation results of the extraction of the floating component ε and the purity of the concentrate β from the air consumption during the flotation separation of the mixture of the ground polyamide and acrylonitrile butadiene styrene using various surfactants, the dependences were obtained which are shown in figures 1-3.

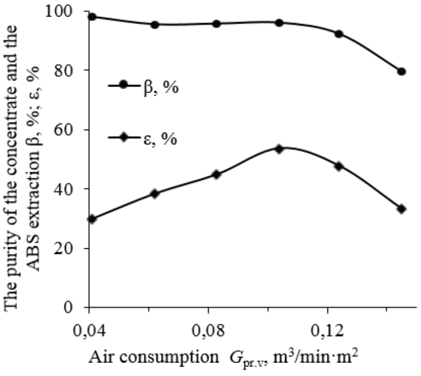

Figure 1 - Dependences of the purity of the concentrate and the ABS extraction from the air consumption at the concentration of sulphanole $11.56 \cdot 10^{-3}$ kg/m^3

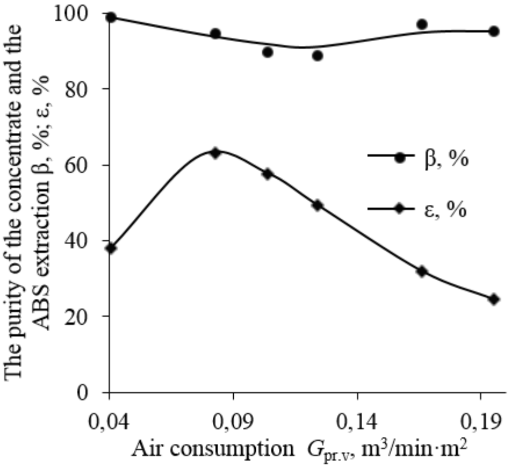

Figure 2 - Dependences of the purity of the concentrate and the ABS extraction from the air consumption at the concentration of polidocanol $8.89 \cdot 10^{-3}$ kg/m^3

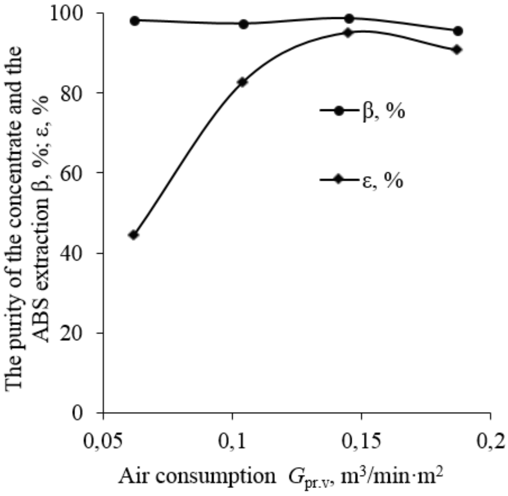

Figure 3 – Dependences of the purity of the concentrate and the ABS extraction from the air consumption at the concentration of the mixture of surfactants $2.7 \cdot 10^{-3}$ kg/m^3

Further, according to the results given in [12], the dependences of the PS extraction on the air consumption are presented, obtained at the concentration of the mixture of surfactants of $5.41 \cdot 10^{-3}$ and $16.22 \cdot 10^{-3}$ kg/m^3 (figure 4.).

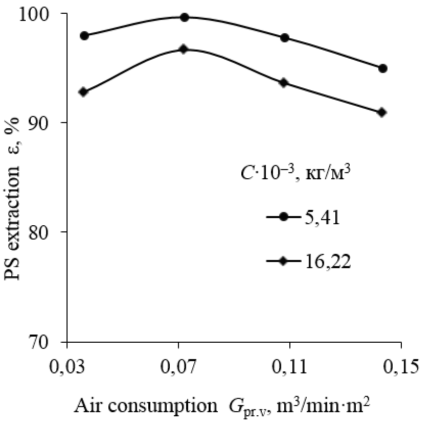

Figure 4 - Dependences of the PS extraction on the air consumption at various concentrations of the mixture of surfactants

As is seen from figures 1-4, the extraction has a maximum at a certain air consumption. The presence of the maximum extraction of the floating component in these figures suggests a characteristic effect of the air consumption on the flotation process of polymers. At low air consumptions, the process is inefficient, since the working volume of the liquid is not saturated enough with gas bubbles. If the optimum value of the air consumption is exceeded, many gas bubbles are formed that are not involved in the flotation process. Such bubbles, moving through a liquid, can create turbulent flows that impede the flotation of particles. When moving in the turbulent liquid flow, the bubble-particle complex is prone to destruction, as particles and bubbles have different inertia (mass) [17].

Also, from the above dependences, it may be concluded that the air consumption value at which the maximum extraction of the floating component is achieved depends on the type of polymer and surfactant. The air consumption effect nature at different concentrations of surfactants is not changed – only the floating component extraction changes.

When using polidocanol, the maximum extraction of ABS is 17% higher than when using sulphanole, and reaches 70.5%. However, the purity of the concentrate in this case is reduced by 2.5%, namely, to 93.5% [18]. When using the mixture of surfactants containing sodium laureth sulfate and diethanolamide, the ABS extraction reaches 95%, and the purity of the concentrate is 98.7%. And when using the same mixture of surfactants during the PS flotation, its extraction reaches 99%.

To determine the optimal height of the aerated working liquid layer from the experimental data presented in [12], the dependences of the PS extraction on the concentration of surfactants were determined at different heights of the aerated liquid layer, which are shown in figure 5.

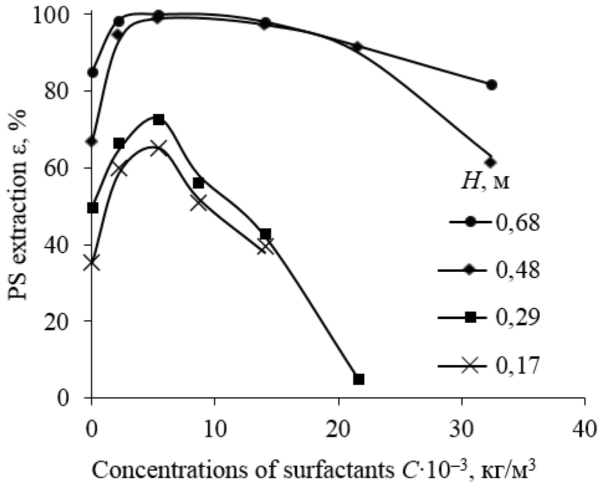

Figure 5 - Dependences of the PS extraction on the concentrations of surfactants at various heights of the aerated liquid layer

As is seen from figure 5, the PS extraction has a maximum at a low concentration of surfactants, namely $5.41 \cdot 10^{-3}$ kg/m^3, and reaches 99% with a sufficient height of the aerated liquid layer.

At a low height of the aerated liquid layer, the probability of collision of a plastic particle with an air bubble is low and some potentially floating particles sink to the bottom of the device, without having time to collide with an air bubble. The optimum height of the processed liquid layer $H_о$ corresponds to a certain air consumption. When the liquid layer height is less than optimal ($H_ж < H_о$) the achievement of the required extraction degree of the dispersed phase is possible, for example, with an increase in the air consumption [19].

In order to more clearly display the effect of the aerated liquid layer height on the PS extraction, the corresponding dependences were obtained at the concentration of surfactants of $2.16 \cdot 10^{-3}$ and $5.41 \cdot 10^{-3}$ kg/m^3, shown in figure 6.

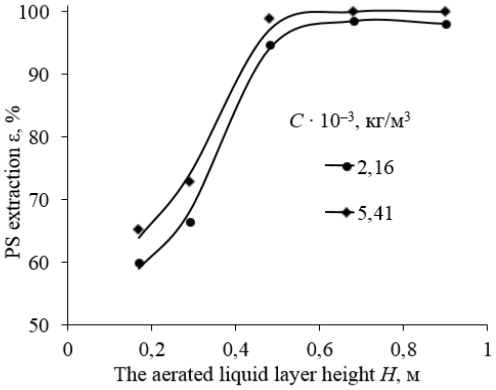

Figure 6 - Dependences of the PS extraction on the aerated liquid layer height
at various concentrations of surfactants

As is seen from figure 6, a sufficient height of the aerated liquid layer is 0.5-0.6 m, its further increase does not have a strong effect on the PS extraction. Exceeding the optimum height of the aerated liquid layer leads to an increase in the material consumption of the device and an increased consumption of the working liquid and surfactant, as well as to an increase in the length of the movement of the bubble-particle complexes, which can increase the probability of their destruction [19].

The graphical dependences given above, as well as in [12], were obtained without additional heating of the working liquid (about 10-15°C). In assessing the effect of the liquid temperature on the flotation process, the experimental research was conducted, the results of which are reflected in [12]. After processing the results of this experimental research, the dependences of the ABS and PS flotation indices on the liquid temperature *t* were plotted, shown in figure 7, 8.

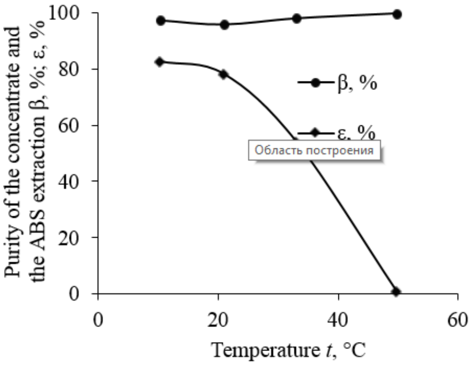

Figure 7 - Dependences of the purity of the concentrate and the ABS extraction on the liquid temperature at the concentration of the mixture of surfactants, containing sodium laureth sulfate and diethanolamide, $2.7 \cdot 10^{-3}$ kg/m^3 and at the air consumption of 0.104 m^3/min·m^2

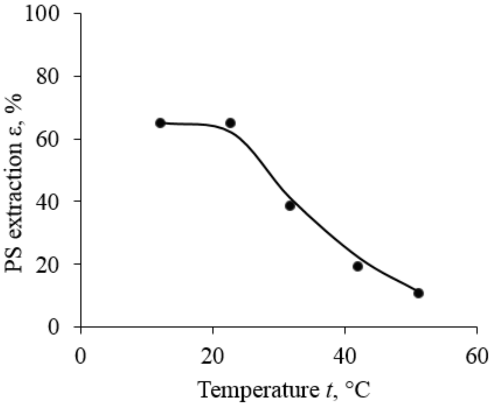

Figure 8 – Dependence of the PS extraction on the liquid temperature at the aerated liquid layer height of 0.17 m, the concentration of the mixture of surfactants of $5.41 \cdot 10^{-3}$ kg/m^3 and the air consumption of 0.072 m^3/h·m^2

As is seen from figures 7 and 8, an increase in the liquid temperature above 20°C leads to a sharp decrease in the ABS and PS extraction. It should be noted that in Figures 7 and 8 there is a pattern of the liquid temperature effect on the extraction of floating components. This is possibly due to the fact that the dependence of the foaming capacity of surfactants on the temperature is characterized by the solubility curves and for most surfactants they have an extremum [20, 21]. Probably, an increase in the solution temperature leads to the dehydration of the dissolved surfactant molecules. Moreover, they separate as an independent macrophase, which leads to a decrease in the number of surfactant molecules involved in the flotation process.

Conclusions. For separation of plastic wastes (polyamide, acrylonitrile butadiene styrene and polystyrene), the flotation method is proposed using surfactants (polidocanol, sulphanole and the mixture of surfactants containing sodium laureth sulfate and diethanolamide). When conducting this method, the effect of the air consumption, the liquid layer height and the temperature were studied.

The research results on the extraction of the floating component from the air consumption show that its maximum extraction depends on the type of polymer and surfactant. The air consumption effect nature at different concentrations of surfactants is not changed – only the floating component extraction changes.

The research results on the extraction of the floating component from the aerated liquid layer height show that the optimum height of the processed liquid layer corresponds to a certain air consumption, and when the liquid layer height is less than optimal, the achievement of the required extraction degree of the dispersed phase is possible, for example, with an increase in the air consumption.

When assessing the effect of the liquid temperature on the flotation process, it was found that increasing the liquid temperature above 20°C leads to the sharp decrease in the ABS and PS extraction. This is due to the fact that the dependence of the foaming capacity of surfactants on the temperature is characterized by the solubility curves and for most surfactants they have an extremum.

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Ұсақталған пластмассаларды флотациялық бөлу үдерісінің ауа шығыны, сұйықтық қабатының биіктігі және температура әсерін зерттеу

Аннотация. Пластмасса қалдықтарын бөлу үшін (полиамид (ПА), акрилонитрилбутадиенстирол (АБС) және полистирол (ПС) флотациялық әдіс ұсынылды. Аталған әдісті қолдану арқылы ауа шығыны, сұйықтық қабатының биіктігі және температураның әсері зерттелді. Беттік-белсенді заттар (ПБЗ) ретінде синтанол, сульфанол және құрамында натрий лаууретсульфаты және диэтаноламид бар ПБЗ қоспасы қолданылды.

Пластмассаның ұсақталған қалдықтары қоспасының флотациялық бөлінуін зерттеу нәтижелерін талдау үшін флотацияланатын компонентті бөлу және β концентратының тазалығы есептелді.

ПБЗ қоспасының әр түрлі концентрациясы кезінде полистиролды ауа шығынынан бөліп алу зерттеулерінің нәтижелері ауаның кейбір шығынында ең көп шығарылу бар екенін көрсетеді. Ауаның аз шығынында процесс тиімсіз өтеді, өйткені сұйықтықтың жұмыс көлемі газ көпіршіктерімен жеткіліксіз қаныққады. Ауа шығысының оңтайлы мәнінен асқан кезде флотация процесіне қатыспайтын көп газ көпіршіктері пайда болады. Мұндай көпіршіктер сұйықтық арқылы қозғала отырып, бөлшектердің флотациясына кедергі келтіретін турбулентті ағындарды жасай алады. Сұйықтықтың турбуленттік ағынында қозғалғанда "көпіршік – бөлшектер" кешені қирауға бейім, себебі бөлшектер мен көпіршіктер әртүрлі инерционды (масса) болады. Сонымен қатар, флотацияланатын компонентті барынша алуға қол жеткізетін ауа шығынының мәні полимер мен ПБЗ түріне байланысты екендігі туралы қорытынды жасауға болады. ПБЗ әртүрлі шоғырлануы кезінде ауа шығынының әсер ету сипаты өзгермейді-флотацияланатын компонентті алу ғана өзгереді.

Полистиролды ПБЗ қоспасының әр түрлі концентрациясы кезінде сұйықтықтың аэрирленетін қабатының биіктігінен бөліп алуды зерттеу нәтижелері сұйықтықтың аэрирленетін қабатының аз биіктігі кезінде пластмасса бөлшектің ауа көпіршігімен соқтығысу ықтималдығы төмен және кейбір әлеуетті флотацияланатын бөлшектер аппараттың түбіне түсіріледі, сонымен қатар ауа көпіршігімен соқтығыспай-ақ. Өңделетін сұйықтық қабатының оңтайлы биіктігіне ауаның белгілі бір шығыны сәйкес келеді. Ал сұйық қабатының биіктігі дисперсиялық фазаны алудың қажетті деңгейіне оңтайлы жетуден азырақ, мысалы, ауа шығыны жоғарылаған кезде мүмкін.

Флотация процессіне сұйықтық температурасының әсерін бағалау кезінде сұйықтық температурасының 20 ° С-тан жоғары көтерілуі АБС және КС шығуының күрт төмендеуіне әкеледі. Бұл ПБЗ-ның көбіктеу қабілетінің температураға тәуелділігі ерігіштің қисығымен сипатталады және ПБЗ-ның көпшілігі үшін экстремуммен түсіндіріледі. Ерітіндінің температурасының жоғарылауы баз ерітілген молекулаларының дегидратациясына әкеп соқтыруы мүмкін. Бұл ретте олар жеке макрофаз түрінде бөлінеді, бұл флотация процесіне қатысатын ПБЗ молекулаларының санының төмендеуіне әкеледі.

Түйін сөздер: флотация, пластмасса қалдықтары, беттік белсенді заттар, концентрация, ауа шығыны, сұйықтық қабатының биіктігі, температура.

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ИЗУЧЕНИЕ ВЛИЯНИЯ РАСХОДА ВОЗДУХА, ВЫСОТЫ СЛОЯ ЖИДКОСТИ И ТЕМПЕРАТУРЫ НА ПРОЦЕСС ФЛОТАЦИОННОГО РАЗДЕЛЕНИЯ ИЗМЕЛЬЧЕННЫХ ПЛАСТМАСС

Аннотация. Для разделения отходов пластмасс (полиамида (ПА), акрилонитрилбутадиенстирола (АБС) и полистирола (ПС)) предложен флотационный способ. С использованием указанного способа изучено влияние расхода воздуха, высоты слоя жидкости и температуры. В качестве поверхностно-активных веществ (ПАВ) использовались синтанол, сульфанол и смесь ПАВ, содержащая лауретсульфат натрия и диэтаноламид.

Для анализа результатов исследований флотационного разделения смеси измельченных отходов пластмасс были рассчитаны извлечение флотируемого компонента ε и чистота концентрата β.

Результаты исследований извлечения полистирола от расхода воздуха при различной концентрации смеси ПАВ показывают, что извлечение имеет максимум при некотором расходе воздуха. При малых расходах воздуха процесс протекает неэффективно, так как рабочий объем жидкости недостаточно насыщается пузырьками газа. При превышении оптимального значения расхода воздуха образуется много газовых пузырьков, не участвующих в процессе флотации. Такие пузырьки, двигаясь через жидкость, могут создавать турбулентные потоки, препятствующие флотации частиц. При движении в турбулентном потоке жидкости комплекс «пузырек – частица» склонен к разрушению, поскольку частицы и пузырьки имеют различную инерционность (массу). Кроме того, можно сделать вывод о том, что значение расхода воздуха, при котором достигается максимальное извлечение флотируемого компонента, зависит от типа полимера и ПАВ. Характер влияния расхода воздуха при различной концентрации ПАВ не изменяется – изменяется лишь извлечение флотируемого компонента.

Результаты исследований извлечения полистирола от высоты аэрируемого слоя жидкости при различной концентрации смеси ПАВ свидетельствуют о том, что при малой высоте аэрируемого слоя жидкости вероятность столкновения пластмассовой частицы с пузырьком воздуха низкая и некоторые потенциально флотируемые частицы опускаются на дно аппарата, так и не успев столкнуться с пузырьком воздуха. Оптимальной высоте слоя обрабатываемой жидкости соответствует определенный расход воздуха. А при высоте слоя жидкости меньше оптимальной достижение необходимой степени извлечения дисперсной фазы возможно, например, при повышении расхода воздуха.

При оценке влияния температуры жидкости на процесс флотации установлено, что повышение температуры жидкости выше 20°С приводит к резкому снижению извлечения АБС и ПС. Это, возможно, объясняется тем, что зависимость пенообразующей способности ПАВ от температуры характеризуется кривыми растворимости и для большинства ПАВ они имеют экстремум. Вероятно, повышение температуры раствора приводит к дегидратации растворенных молекул ПАВ. При этом они выделяются в виде отдельной макрофазы, что приводит к снижению количества молекул ПАВ, участвующих в процессе флотации.

Ключевые слова: флотация, отходы пластмасс, поверхностно-активные вещества, концентрация, расход воздуха, высота слоя жидкости, температура.

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BIOLOGICALLY ACTIVE SUBSTANCES OF COMPOSITIONS BASED ON PLANTS OF THE GENUS HAPLOPHYLLUM

Abstract. The article presents the results of research of biologically active substances of compositions based on the plant of the genus *Haplophyllum* (*Tuberculatum*), which grows in the Bakanas district of Almaty region, Bidens (*Frondosa*), collected in the Enbekshikazakh district and Polygonum (*Aviculare*) from the territory of Tashtykara district of Almaty region. The mineral composition was studied, and the article also provides data on vitamin, amino and fatty acid compositions.

Medicinal raw materials contain many compounds that are potentially harmful to the human body, these can be both mineral components, for example, salts of heavy metals, and various organic substances, both being natural metabolites of the plant and trapped in raw materials from the environment (pesticides used in agriculture or industrial emissions).

The study of mineral composition was carried out using atomic absorption analysis on the basis of the center of physico-chemical methods of research and analysis (cfhma). As a result, information was obtained about the micro- and macronutrient composition of compositions based on a plant of the genus *Haplophyllum* (*Tuberculatum*).

The content of fatty acids was determined by the GVC method and using the following chromatography conditions: carrier gas-helium, flame ionization detector, carrier gas speed 30ml / min, detector temperature 188ºC, furnace temperature 230^{0}C, analysis time 1 hour, steel column 0.4×3mm filled with polyethylene glycoladipinate (20%) on cellulite-545.

Studies of amino acids were carried out on the amino acid analyzer "Carlo Erba", using the gzhx method, chromatography conditions: carrier gas-helium, flame ionization detector 300ºC, evaporator temperature 250ºC, on the WAW chromosome.

The content of vitamins a (retinol) and (tocopherol) was determined by the fluorimetric method on the spectrofluorimeter device. Vitamin C in biological samples was determined by titrimetric method.

Keywords: Haplophyllum (Tuberculatum), Bidens (Frondosa),Polygonum (aviculare), mineral composition, amino acids, fatty acids.

Introduction. Minerals are of great importance for the normal existence of organisms. They are classified as macro-and microelements. Macronutrients include potassium, sodium, calcium, magnesium, phosphorus, chlorine, and sulfur. Comparatively, they come in large quantities.

Trace elements are a group of chemical elements that are contained in the human body and animals in very small amounts, within the range of 10-3-10-12 mg %, these include Nickel, cadmium, lead, chromium, mercury and other d - elements [1].

In ecologically unfavorable areas, a very large number of heavy metals, such as lead, Nickel, chromium, mercury, and any changes in the optimal ratios of trace elements in their composition can lead to unforeseen consequences [2].

In an acidic environment, the movement of molybdenum decreases, but the movement of copper, manganese, zinc, and cobalt increases. Trace elements such as chalk, fluorine, and iodine also move in acidic and alkaline environments. Some trace elements, for example, form compounds that are soluble with organic matter, while others (iodine and copper) are fixed and become inaccessible to plants. The lack or excess of trace elements in the soil leads to their deficiency or excess in the plant and animal body. At the same time, changes in the nature of accumulation (deposition), weakening or strengthening the synthesis of biologically active substances, repeated violation of the processes of interline exchange, creating a new adaptation or violations that lead to endemic diseases of humans and animals develop [3].

Thus, the mineral composition of plants is directly affected by natural and anthropogenic factors. All this should be taken into account when preparing vegetable raw materials.

Currently, there are 14 trace elements necessary for life: iron, copper, manganese, zinc, cobalt, iodine, fluorine, molybdenum, vanadium, Nickel, strontium, silicon and selenium. They increase the activity of enzymes, catalyze biochemical procedures, and promote the synthesis of carbohydrates, proteins, and vitamins. It also participates in metabolism. Trace elements are part of plant preparations and influence their activity[4].

Most studies of *Haplophyllum tuberculatum* evaluated medicinal and phytochemical properties, analysis of some of which produced two alkaloids called alkaloids, lignans, glycosides and flavonoids, etc. in the phytochemical study of *Haplophyllum tuberculatum*, alkaloids such as acutifolium, halilofitin were obtained [5]. The chemical composition of *Polygonum aviculare* is rich and varied. It is a natural storehouse of vegetable protein (17 %), biologically active substances (44%), vegetable fiber (27%), ash compounds (8.9%), simple and complex sugars (2.5%), resin, wax, and tannins. Useful trace elements such as calcium, phosphorus, zinc, and silicon were also found in it [6]. *Bidens frondosa* contains organic acids, essential oil, tannins, polysaccharides, coumarins (umbelliferon, skoletin), triterpenoids, vitamin C (up to 0.9%), carotenoids (0.05 %), carotenes, a large amount of vitamin C (up to 1000 mg%), manganese salts, polyacetylenes, and aromatic acids containing derivatives and thiophenes, flavonoids - (glycosides luteolin, Butin, sulfuretin, Auron) [7-12].

Fatty acids are the basis of metabolic processes in the body, an integral part of the biological synthesis of the body's processes along with the components of lipids. Several fatty acids that have essential properties have vitamin-like effectiveness: olein, arachidone, linol, linolene. Essential fatty acids have cardioprotective properties, improving blood circulation and the cardiovascular system.

Amino acids are organic compounds whose molecules simultaneously contain carboxyl and amine groups. These are substances of primary synthesis, they are present in all organs of all plants. Amino acids are divided into α, β, γ, σ, and others. amino acids, depending on the location of the amino and carboxyl groups. Of these, the most common are α, β and γ. α - l-configuration amino acids are the most important components of peptides and proteins. Also, plants may contain monobasic diamino-and dibasic monoaminoacids.

Vitamin A and E occur in pairs. They improve the condition of the skin, vision, and bones, helping to assimilate each other, increase resistance to infections, and protect the mucous membrane. Retinol is one of the vital vitamins necessary and vital for our body, which belong to the fat-soluble group. The usefulness of vitamin A for health is invaluable: it participates in redox processes, affects protein synthesis, and cell membranes. Retinol interacts well with another fat-soluble vitamin-tocopherol (vitamin E). if the body lacks vitamin E, the absorption of retinol is absorbed, so it is optimal to take these vitamins together.

Ascorbic acid is an organic compound similar to glucose, the sour taste is found in the form of a white crystalline powder. It performs the biological functions of a coenzyme and a reducing agent of certain metabolic processes, and is an antioxidant. Vitamin C strengthens the immune system and protects it from viruses and bacteria, accelerates the healing process, promotes the synthesis of several hormones, regulates the processes of the circulatory system and normalizes capillary permeability, participates in the synthesis of collagen protein. This is necessary for the growth of tissue cells, bones and cartilage of the body, regulates metabolism, improves bile secretion, and restores the external function of the pancreas and thyroid gland.

Materials and methods. *Determination of mineral composition.* The objects of the study were plants of the genus *Haplophyllum (Tuberculatum)* growing in the Bakanas district of Almaty region, Bidens (Frondosa) collected in the Enbekshikazakh district and *Polygonum (aviculare)* from the territory of Tashtykara district of Almaty region, harvesting was carried out in compliance with sanitary requirements and the requirements Of the state Pharmacopoeia of the Republic of Kazakhstan. The quantitative content of micro-and macronutrients was determined from ash residues obtained by the following method.

About 1 g of the drug or 3-5 g of crushed medicinal plant raw materials (exact weight) is placed in a pre-calcined and precisely weighted porcelain, quartz or platinum crucible, evenly distributing the substance along the bottom of the crucible.

Then the crucible is carefully heated, allowing the substance to burn or evaporate at the lowest possible temperature. The burning of the remaining coal particles must also be carried out at a lower temperature as possible; after the coal has burned almost completely, the flame is increased. In case of incomplete combustion of coal particles, the residue is cooled, moistened with water or a saturated solution of ammonium nitrate, evaporated in a water bath and the residue is calcined. If necessary, repeat this operation several times.

Calcination is carried out at low red heat (about 500°C) to a constant mass, avoiding fusing the ash and sintering with the walls of the crucible. At the end of calcination, the crucible is cooled in a desiccator and then the resulting ash is burned again at 600°C until a uniform gray color is obtained.

If the result is not achieved, the remainder is dissolved in concentrated nitric acid, after which it is heated on a tile removing the nitric acid and then in a muffle at 400°C for 30 minutes.

Finally, the precipitate is dissolved in 5 ml of HNO_3 (1:1) when heated. The resulting solution must be heated on the tile to wet salts. The result is dissolved in 10-15 ml of 1H HCl or 1H HNO_3 (the Second option is preferable) and transferred to a 25ml volumetric flask, bringing the volume to the label.

In parallel, a single experiment is carried out, which consists in preparing a solution of the same concentration from the same acid using the same utensils.

Then the finished samples were transferred to the center for physical and chemical methods of research and analysis to determine the mineral composition by atomic adsorption spectroscopy on the ASSIN device of the Karl Zeiss company.

The results obtained are presented below [13,14].

It was revealed that the amount of heavy metals does not exceed the permissible norms of their presence in medicinal raw materials.

Study of the fatty acid composition of the obtained extracts by the GLC method. The content of fatty acids was determined using the GLC method using the following chromatography conditions: carrier gas-helium; flame ionization detector; carrier gas speed 30ml / min; detector temperature 188ºC; furnace temperature 230ºC; analysis time 1H; steel column 0.4 m × 3mm filled with polyethylene glycoladipinate (20%) on cellulite-545.

Sample preparation: 10ml of methanol, 2-3 drops of acetyl chloride are added To the chloroform extracts of the test samples, and then methylation is performed at 60-70^{0}C in a special system for 30 minutes. Methanol is removed using a rotary evaporator, and samples are extracted with 5ml of hexane and analyzed in a Carlo-Erbo-4200 gas chromatograph[15].

Study of the amino acid composition of the obtained extracts by the GLC method. 1 g of the analyte is hydrolyzed in 5ml of 6h hydrochloric acid at 105ºC for 24 hours, in ampoules sealed under a jet of argon. The resulting hydrolysate is evaporated three times to dry on a rotary evaporator at a temperature of 40-50ºC. The resulting precipitate is dissolved in 5ml of sulfosalicylic acid. After centrifugation for 5 minutes, the supernatant is passed through a column with an ion-exchange resin Daux 50, with a speed of 1 drop per second. After that, the resin is washed to a neutral pH.

For elution of amino acids from the column, 3ml of 6h NH_4OH co solution is passed through it at a rate of 2 drops per second. The eluate is collected in a round-bottomed flask with distilled water, which is used to wash the column to a neutral pH. Then the contents of the flask are evaporated dry on a rotary evaporator at a pressure of 1 atm. and a temperature of 40-50ºC.

After adding to this flask, 1 drop of freshly prepared 1.5 % $SnCl_2$ solution, 1 drop of 2.2-dimethoxypropane and 1-2ml of hydrochloric acid-saturated propanol, ee is heated to 110 ºC, maintaining this temperature, for 20 minutes, and then the contents are again evaporated from the flask on a rotary evaporator.

In the next step, 1 ml of freshly prepared acelizing reagent (1 volume of acetic anhydride, 2 volumes of triethylamine, 5 volumes of acetone) is injected into the flask and heated at a temperature of 60 ^{0}C for 1.5-2min. Then the sample is again evaporated on a rotary evaporator to dry and 2ml of ethyl acetate and 1ml of saturated NaCl solution is added to the flask. The contents of the flask are thoroughly mixed and, as 2 layers of liquids are clearly formed, the upper one (etiacetate) is taken for gas chromatographic analysis, which was performed on the gas-liquid chromatograph "Carlo-Erba-4200" (Italy-USA) [16].

Study of vitamins A, E, and C. 0.2 ml of the sample, 1ml of alcohol and 1ml of distilled water are placed in centrifuge tubes, tightly closed with lids and mixed with careful shaking. Add 5ml of hexane and shake again. The contents are centrifuged for 10 minutes at 1500rpm. the Separated hexane layer (3 ml) is used for measurements at wavelengths of 292-310 nm (for tocopherol) and 335-430 nm (for retinol), respectively [17-22].

The content of vitamin C in biological samples was determined by titrimetric method. A sample of at least 0.3 ml is taken in a centrifuge tube, the walls of which are covered with sodium citrate powder. After centrifuging the sample for 30 minutes at 3000 rpm, it is transferred to another test tube and an equal amount of bidistilled water and double the amount of freshly prepared 5% metaphosphoric acid solution is added. The protein precipitate is stirred with a stick and centrifuged for 10 minutes at 3000 rpm. The nadosadochnuyu liquid in an amount (0.1-0.5 ml) is introduced into porcelain titration cuvettes (2 parallel samples) and titrated 0.001 n-0.0005 n with a solution of the sodium salt of 2.6 dichlorophenolindophenol from a special micropipette with a capacity of 0.1 ml.

Results and discussion. To create complexes, first of all, the composite correspondence of plant raw materials to each other was studied and the ratio was chosen. Depending on which ones show up, they were obtained in three types. The percentage of components in the complexes is theoretically justified by taking into account the contribution of each component to the last therapeutic effect and evaluating the activity of plant components. This takes into account the phenomenon of interaction of plant components (interference), since some types of plant raw materials show the greatest activity in an individual or a mixture, and when it changes, there is a decrease in the influence of the participating components. The plant complex was obtained in different ratios. The results are presented in table 1.

Table 1 - plant ratio

№	complex
1	1:1:3
2	2:1:1
3	2:3:1

Based on the data from table 1, the mineral composition of plant complexes was studied in 3 different ratios.

Data on the mineral composition were obtained by atomic absorption analysis conducted at the material and technical base of the center for physical and chemical analysis methods. The results are presented in tables 2 and 3.

Table 2 - Quantitative content of trace elements

Element	Zn	Cu	Pb	Cd	Fe	Ni	Mn
1:1:3							
Content in the sample, %	0.0004892	0.0002358	0.00009821	0.00001683	0.01304	0.00006447	0.001113
2:1:1							
Content in the sample, %	0.0006301	0.0002323	0.00006677	0.00001795	0.01558	0.00006005	0.001059
2:3:1							
Content in the sample, %	0.0007055	0.0004068	0.0001103	0.00002102	0.01162	0.00008746	0.001415

Table 3 - Quantitative content of macronutrients

Element	K	Na	Ca	Mg
1:1:3				
Content in the sample, %	0.6040	0.01851	0.4576	0.07897
2:1:1				
Content in the sample, %	0.5823	0.02051	0.3448	0.08191
2:3:1				
Content in the sample, %	0.6166	0.02578	0.3786	0.06799

Comparing the data given in table 2, we can conclude that the quantitative content of iron dominates all samples of plant complexes in 3 different ratios. Iron is a part of herbal preparations and affects their activity. It is also known that iron increases the activity of enzymes and catalyzes biochemical processes. Promotes the synthesis of carbohydrates, proteins and vitamins.

Among the macro elements presented in table 3 and figure 2, the largest number of elements are K, Ca. They are part of the cell nucleus. Calcium plays an important role in the growth and action of cells. It has a significant impact on the exchange process and contributes to the full digestion of food substances. By strengthening the body's protective function, it increases resistance to external adverse conditions, especially infections.

The content of fatty acids was determined by the GZHC method. The results are presented in table 4.

Table 4 - Quantitative analysis of fatty acids

№	Fatty acids		%
1	$C_{14:0}$	Miristin ($C_{14}H_{28}O_2$)	0,8
2	$C_{15:0}$	Pentadecan ($C_{16}H_{30}O_2$)	1,2
3	$C_{16:0}$	Palmitin ($C_{16}H_{32}O_2$)	4,6
4	$C_{16:1}$	Palmitalein ($C_{16}H_{30}O_2$)	0,4
5	$C_{18:0}$	Stearin ($C_{18}H_{36}O_2$)	2,3
6	$C_{18:1}$	Olein ($C_{18}H_{34}O_2$)	36,5
7	$C_{18:2}$	Linol ($C_{18}H_{32}O_2$)	53,9
8	$C_{18:3}$	Linolene ($C_{18}H_{30}O_2$)	0,3

From the data obtained, it follows that 8 fatty acids were detected. In terms of quantitative content, the dominant fatty acids were oleic and linoleic acids, relatively palmitic and stearic acids. Linolenic acid, which showed the lowest index, plays a large role in the body. Fatty acid, most necessary for the functioning of cell and subcellular membranes.

Amino acids were identified from the plant complex. Studies of amino acids were carried out on the amino acid analyzer "Carlo Erba", using the gzhx method. The data is presented in table 5.

Table 5 - Quantitative analysis of the amino acid composition of aqueous extracts of compositions

	Name of amino acids		Amino acids, mg / 100 g
1	Ala	Alanine	612
2	Gly	Glycine	234
3	Val	Valine.	195
4	Leu	Leucine.	370
5	Ile	Isoleucine	334
6	Thr	Threonine	177
7	Ser	Serine	317
8	Pro	Proline	415
9	Met	Methionine	51
10	Asp	Asparate	1360
11	Cys	Cystine	22
12	O-Prp	Oxyproline	1
13	Phe	Phenylalanine	264
14	Glu	Glutamate	2546
15	Orn	Ornithine	1
16	Tyr	Tyrosine	288
17	His	Arginine	370
18	Arg	Lysine	318
19	Lys	Histidine	189
20	Trp	Tryptophan	72

The analysis revealed their qualitative identity and insignificant quantitative relationships, and also found that the dominant amino acids are asparate, glutamate, alanine: 1360 mg / 100g, 2546 mg/100g, 612 mg / 100g.

The content of vitamins a (retinol) and (tocopherol) was determined by the fluorimetric method on the spectrofluorimeter device . Vitamin C in biological samples was determined by titrimetric method. The data is presented in table 6.

Table 6 - Quantitative content of vitamins A, E and C

Vitamins	mg/100g
A	0,09
E	2,8
C	22

Comparing the data shown in table 6 and figure 2, we can conclude that the quantitative content of vitamin C dominates.

Conclusion

1. For the first time, biologically active substances were studied, including mineral composition, vitamins, amino and fatty acids of compositions based on a plant of the genus Haplophyllum (Tuberculatum) growing in the Bakanas district of Almaty region, Bidens (Frondosa) collected in the Enbekshikazakh district and Polygonum (aviculare) from the territory of the Tashtykara district of Almaty region.

2. It was found that the level of heavy metal content in the studied samples does not exceed the maximum permissible norm.

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HAPLOPHYLLUM ТЕКТЕС ӨСІМДІКТЕР НЕГІЗІНДЕГІ КОМПОЗИЦИЯЛАРДЫҢ БИОЛОГИЯЛЫҚ БЕЛСЕНДІ ЗАТТАРЫ

Аннотация. Мақалада Алматы облысының Бақанас ауданында өсетін Haplophyllum (Tuberculatum) туысының өсімдігі және Еңбекшіқазақ ауданында жиналған Bidens (Frondosa) және Алматы облысының Таштықара ауданының аумағынан Polygonum (aviculare) өсімдітер негізінде композициялардың биологиялық белсенді заттарын зерттеу нәтижелері келтіріледі. Минералды құрам зерттелді, мақалада витаминдік, амин және майлы қышқылдық құрам туралы мәліметтер келтірілген.

Дәрілік шикізат құрамында адам ағзасына зиян келтіретін көптеген қосылыстар бар, олар минералды компоненттер болуы мүмкін, мысалы, ауыр металдардың тұздары, сондай-ақ әр түрлі органикалық заттар, олар өсімдіктердің табиғи метаболиттері болып табылады және қоршаған ортадан шикізатқа түседі (қолданылатын пестицидтер) ауыл шаруашылығында немесе өнеркәсіптік шығарындыларда).

Минералдық құрамды зерттеу физика - химиялық зерттеу және талдау әдістері орталығы (ЦФХМА) базасында атомдық - абсорбциялық талдау әдісімен жүргізілді. Нәтижесінде haplophyllum (Tuberculatum) тұқымының негізіндегі композициялардың микро - және макроэлементтік құрамы туралы мәліметтер алынды.

Май қышқылдарының құрамын ГЖХ әдісімен және хроматографиялаудың келесі шарттарын қолдану арқылы анықтадық: газ-тасығыш – гелий, жалынды-иондаушы детектор, газ тасығыштың жылдамдығы 30мл/мин, детектордың температурасы 188˚С, пештің температурасы 230˚С, талдау уақыты 1с, Болат бағанасы 0.4×3мм, целлит-545 полиэтиленгликольадипинатпен толтырылған (20%).

Аминқышқылдарын зерттеу "Карло Эрба" аминқышқылды талдағышта ГЖХ әдісімен жүргізілді, хроматографиялау шарттары: газ-тасығыш – гелий, 3000с жалынды-иондау детекторы, булау температурасы 250˚С, WAW хромосорбасында жүргізілді.

А (ретинол) және Е (токоферол) витаминдері спектрофлуориметр аспабында флуориметрлік әдіспен анықталған. С витамині биологиялық үлгілерде титриметриялық әдіспен анықталды.

Түйін сөздер: Haplophyllum (Tuberculatum), Bidens (Frondosa), Polygonum (aviculare), минералды құрамы, амин қышқылдары, майлы қышқылдар.

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БИОЛОГИЧЕСКИ АКТИВНЫЕ ВЕЩЕСТВА КОМПОЗИЦИЙ НА ОСНОВЕ РАСТЕНИЯ РОДА HAPLOPHYLLUM

Аннотация. В статье приводятся результаты исследования биологически активных веществ композиций на основе растения рода Haplophyllum (Tuberculatum), произрастающего в Баканасском районе Алматинской области, Bidens (Frondosa), собранный в Енбекшиказахском районе и Polygonum (aviculare) из территории Таштыкараского района Алматинской области. Были исследованы минеральный состав, в статье также приведены данные по витаминному, амино- и жирнокислотному составам.

В лекарственном сырье содержится множество соединений, потенциально способных нанести вред организму человека, это могут быть как минеральные компоненты, например, соли тяжёлых металлов, так и различные органические вещества, как являющиеся естественными метаболитами растения, так и попавшие в сырьё из окружающей среды (пестициды, применяемые в сельском хозяйстве, или выбросы промышленных предприятий).

Исследования минерального состава проводились методом атомно- абсорбционного анализа на базе центра физико- химических методов исследования и анализа (ЦФХМА). В результате получены сведения о микро- и макроэлементном составе композиций на основе растения рода Haplophyllum (Tuberculatum).

Содержание жирных кислот определяли методом ГЖХ и использованием следующих условий хроматографирования: газ-носитель – гелий, пламенно-ионизационный детектор, скорость газо-носителя 30мл/мин, температура детектора 188^{0}С, температура печи 230^{0}С, время анализа 1ч, стальная колонка 0.4×3мм, заполненная полиэтиленгликольадипинатом (20%) на целлите-545.

Исследования аминокислот проводили на аминокислотном анализаторе «Карло Эрба» методом ГЖХ, условия хроматографирования: газ-носитель – гелий, пламенно-ионизационный детектор 300^{0}С, температура испарителя 250^{0}С, на хромосорбе WAW.

Содержание витаминов А (ретинол) и (токоферол) опредилили флуориметрическим методом на приборе спектрофлуориметр. Витамин С в биологических образцах определили титрометрическим методом.

Ключевые слова: *Haplophyllum (Tuberculatum), Bidens (Frondosa), Polygonum (aviculare),*минеральный состав, аминокислоты, жирные кислоты.

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EXPERIMENTAL RESEARCH OF A MULTISTAGE GRAVITATIONAL CLASSIFIER

Abstract. The classification of polydisperse materials is widely used in many industries. Of the wide range of classification equipment, the most promising are multistage gravitational classifiers. The classification process in multistage gravitational classifiers is quite complicated and requires the necessary experimental research to ensure the given efficiency. To receive reliable information allowing to obtain the most effective recommendations for their structure and use, a set of experimental research was carried out. The research results showed that multistage classifiers of small sizes provide a consistently high quality of separation, however their performance, for an apparatus with a cross section of 80x80 mm no more than 100 kg/h, is insignificant, as a result of which they cannot be used for most production processes. Classifiers with higher performance must have significant sizes. It is advisable to use multistage shelf classifiers with boundary separation sizes of 0.5-2 mm. With a boundary size of less than 0.5 mm, a steady decrease in the separation efficiency is observed, and with a boundary size of the order of 0.05-0.1 mm, the classification efficiency decreases sharply. With an increase in the boundary separation grain of more than 2 mm, a decrease in the classification efficiency is also observed (figure 1). The experiments to determine the separation efficiency in the modernized and conventional structures of classifiers in the separation of quartz sand with particle sizes of 0-2 mm relative to the boundary separation size of $\delta_{ср} = 1$ mm showed the following. The mutual arrangement of the efficiency curves shows that an increase in the separation efficiency for the modernized classifier is up to 10% when the optimum, providing the highest quality separation, air velocity per section of the apparatus is achieved. Similar results were obtained for other materials (sylvinite, meal, gypsum) for various boundary separation sizes (from 0.5 to 2 mm). In general, the separation efficiency in the modernized structure of the shelf classifier for various materials was 5-10% higher than in a conventional one. The experimental research of the modernized classifier structure showed that the proposed structural additions, ceteris paribus, contribute to a more uniform distribution of material over the working volume of the apparatus, which, of course, leads to an increase in the quality of separation.

Key words: experimental research, gravitational classifier, multistage, separation efficiency, boundary sizes, section, holes.

Introduction. The grinding and fractionation processes are widely used in many industries. Currently, there are major trends in the development of milling equipment combining grinding and fractionation [1-11]. It should be noted in advance that many researchers [12-18] were involved in the development and research of multistage gravitational classifiers, monographs were written on this subject, and several dissertations were performed. The available data describe in detail the effect of technological and structural factors on the separation process. Thus, it was established that multistage classifiers work quite efficiently with boundary separation sizes from 0.2 to 2-3 mm, while the concentration of the solid phase should not exceed 2-2.5 kg/m^3 of the carrier medium (air). There are empirical dependencies for calculating the air consumption for classification depending on the size of the apparatus and the boundary separation grain. The number of overflow shelves is usually taken 6-10, while the shelves are located at an angle of 45° to the horizon, overlap the classifier section to its middle and the height step between the shelves is taken equal to the width of the apparatus section. Compliance with these recommendations allows achieving separation efficiency in laboratory models up to 90% [12-17]. At the same time, as already noted above, in industrial tests, the separation efficiency of multistage classifiers is significantly decreased, which shows a significant influence on the separation process of the scale factor during the transition from laboratory to industrial plants. In well-known and previously noted works, this factor is practically not paid attention to, only some of them [12, 13] indicate that with an increase in the size of the classifier, its efficiency decreases, however there is no quantitative assessment of this phenomenon.

Research methods. When determining the hydrodynamic parameters and the distribution of dispersed particles of classification substances, standard methods of physicochemical research were used.

The experimental research of a gas-centrifugal classifier was carried out with the aim of:

a) testing the obtained mathematical model of the motion of a single particle in a swirling gas medium;

b) determination of excess pressure on the inner wall of the perforated element;

c) determining the boundary size of the particles passing through the perforation holes.

To study the scale factor influence on the separation of polydisperse materials in a gravitational multistage classifier, several geometrically similar apparatuses with cross-section sizes of 80x80 mm, 140x140 mm, 200x200 mm, 300x300 mm were designed and manufactured. The results of these experimental research on quartz sand with a particle size of 0-5 mm are presented in figure 1.

Research results. The obtained experimental data are presented in figure 1, 3.

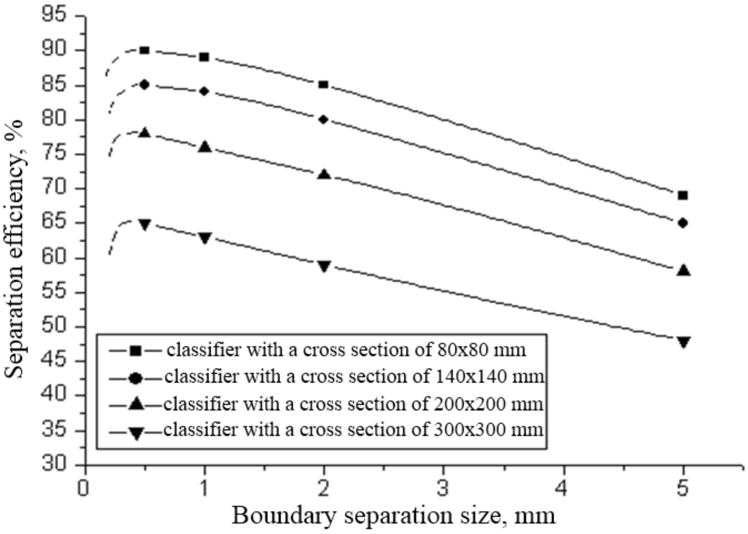


Figure 1 – Separation efficiency depending on the cross-sectional size of the classifier

Visual observations of the separation process carried out during the experiments showed the following. When a coarse fraction was unloaded from the classifier, the material from the last inclined shelf did not flow uniformly over the entire width of the shelf, however it was largely concentrated at its edges, i.e. at the side walls of the apparatus. And the larger the cross-sectional sizes of the classifier, the more this phenomenon manifested itself. This indicates that the material in the classifier’s working volume is distributed unevenly, and as it moves down it may be pushed aside by the air flow to the apparatus walls. In addition, the pulsating nature of the descent of the material flow from the last shelf was observed. The material was unloaded into the tank not by a uniform flow, but by pulsating, with sharp discharge fluctuations. Naturally, with these phenomena, part of the starting material does not have time to contact with the air, but simply falls down, as a result of which the large product is contaminated with fines and the separation efficiency decreases.

Thus, it can be seen from the series of experiments that multistage classifiers of small sizes provide a consistently high separation quality, however their performance, for an apparatus with a cross section of 80x80 mm no more than 100 kg/h, is insignificant, as a result of which they cannot be used for most production processes. Classifiers with higher performance must have significant sizes, and, therefore, as the above research has shown, the separation efficiency will be low, which again complicates their implementation in production.

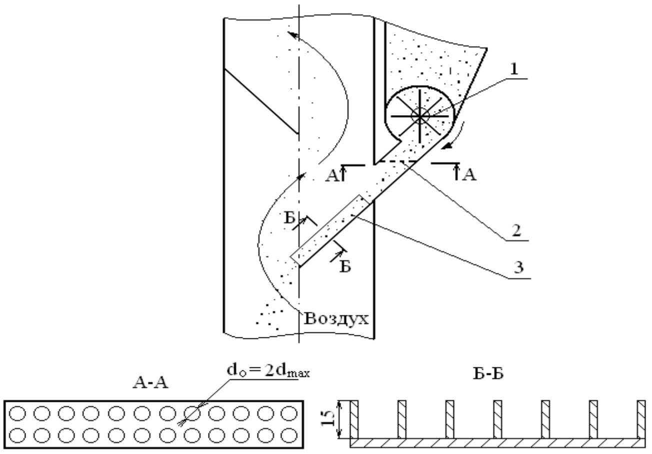
To solve this problem, in order to more evenly distribute the material over the cross section of the apparatus, which should increase the quality of separation, some structural additions were made to the existing classifier structure (figure 2).

The essence of these structural additions is as follows. After the rotary feeder, the perforated sheet (item 2, figure 2) with the hole of d_o size 2 times larger than the maximum particle size in the material to be separated was installed in the feeding tube of the classifier, which follows from the condition to prevent clogging of the holes. Such a structural feature will allow to smooth out the pulsating nature of the movement of the starting material supplied from the feeder. In addition, in order to more evenly distribute the material already in the classifier's working volume and prevent the material accumulation at the apparatus walls, the inclined shelves located below the feeder were made with longitudinal slides (item 3, figure 2). These slides prevent the material from moving in the cross direction of the inclined shelves.

To study the efficiency of structural changes introduced into the classifier apparatus, a series of experiments was carried out to determine the separation efficiency of the polydisperse material into fractions in the modernized structure, the results of which were compared with the separation efficiency in the conventional classifier structure. Classifiers with cross-sectional sizes of 200x200 mm were used as model classifiers, providing a feed capacity of 300 kg/h.

Figure 3 shows the results of experiments to determine the separation efficiency in the modernized and conventional structures of classifiers in the separation of quartz sand with particle sizes of 0-2 mm relative to the boundary separation size of $\delta_{гр} = 1$ mm.

The mutual arrangement of the efficiency curves (figure 3) shows that an increase in the separation efficiency for the modernized classifier is up to 10% when the optimum, providing the highest quality separation, air velocity per section of the apparatus is achieved. Similar results were obtained for other materials (sylvinite, meal, gypsum) for various boundary separation sizes (from 0.5 to 2 mm). In general, the separation efficiency in the modernized structure of the shelf classifier for various materials was 5-10% higher than in the conventional one.



1 – feeder; 2 – perforated sheet; 3 – slides of the inclined shelves

Figure 2 – Structural additions made to the classifier apparatus

Thus, these facts confirm the opinion of many researchers that the separation quality in gravitational classifiers largely depends on the uniform distribution of the starting material over the entire working volume of the apparatus. Naturally, the larger the classifier, the more difficult it is to ensure uniform flow of the medium and material, which, as shown by the above experimental data (figure 3), to a decrease in the separation efficiency. Therefore, at high performance it is more expedient not to increase the size of the classifier, but to partition several relatively small apparatuses into spacer blocks. This will allow to achieve the required performance by setting the required number of sections, and the separation efficiency will be as high as for single classifiers of small sizes.

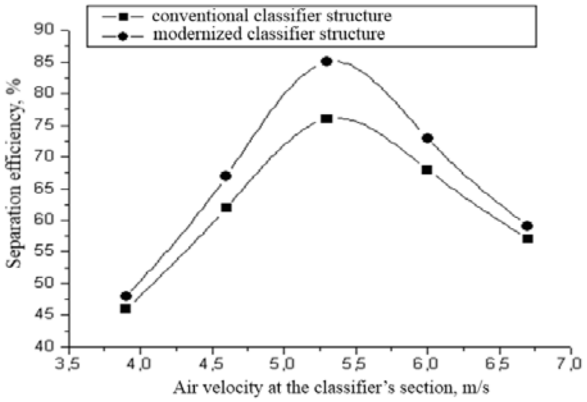


Figure 3 – Separation efficiency of classifiers

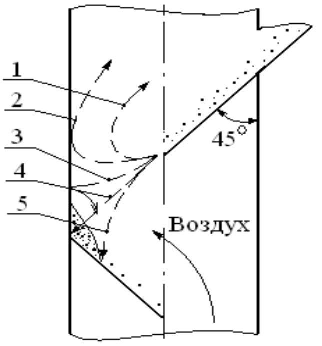
At the same time, visual observations of the separation process in the modernized classifier structure showed that although it was possible to achieve a more uniform distribution of the material across the width of the apparatus, however, there was still a pulsating character of the large fraction descent from the last shelf, as in the case with the conventional classifier structure. The material from the feeder was supplied in a uniform flow, due to the installation of the perforated sheet behind the feeder (item 2, figure 2), and already at the exit from the classifier the material consumption was uneven, pulsating.

To study the causes of this phenomenon, windows were made in the side walls of the apparatus. During the experimental installation operation, these windows were hermetically sealed with organic glass plates, which allowed to visually observe the material movement during the classification process.

The observation of the classification process allowed to establish the following mechanism for the distribution of the material to be separated in the working volume of the classifier, shown in figure 4. Quartz sand with a particle size of 0-2 mm was used as a model material, the separation was carried out relative to the boundary size of $\delta_{гр} = 1$ mm.

When the classifier is working, the starting material, falling down from the inclined shelf, experiences the effect of an ascending air flow. Small particles, with a size smaller than the boundary, are picked up by the air flow and carried upward (items 1, 2, figure 4). Large particles, with a size larger than the boundary, overcome the resistance of the air flow and fall down (items 3-5, figure 4). Boundary-sized particles with the same probability can be carried up into a small product, and fall down into a large one, depending on the influence of many unaccounted or random factors (items 2, 3, figure 4).

Therefore, as can be seen from figure 4, there is a kind of “bombing” by large particles of the shelf attachment area to the classifier wall. Moreover, the velocity vector of large particles is often directed almost perpendicular to the surface of the next shelf (item 4). As a result of this, as the visual observations have shown, a large fraction accumulates here, which was further confirmed by analysis of samples from the material residues in the corners between the shelves and the classifier case taken when the experimental setup was stopped. Upon reaching a certain amount of the material, this accumulation abruptly breaks down, which explains the pulsating nature of the movement of a large fraction at the classifier exit.



(1 – 5) – various size particle movement trajectories
Figure 4 – Various size particle movement in the working volume of the classifier

It would seem that the inclination angle of the shelves is large enough (45°) so that the material slides down, in fact the friction coefficient of various materials on steel is lower than unity for most materials (from the condition that the body is at rest on an inclined surface, it follows that the friction coefficient should be equal to the tangent of the inclination angle of the surface). However, it should be appreciated that the fact that particles falling into the angle between the shelf and the classifier wall are pressed to some extent by the ascending air flow and, in addition, are pressed to the shelf by the following layers of material. All this complicates the movement of the material down, therefore, its accumulation occurs despite the structural conditions of unhindered sliding down the inclined shelf.

The processing of the experimental data for the group of materials studied allowed to obtain a dependence for determining the air velocity over the classifier cross section, which provides the most high quality separation

$$W = 0{,}53 \cdot v_{вит} \cdot \rho_{ч}^{0{,}06} \tag{1}$$

where $v_{вит}$ – particle staying velocity, m/s; $\rho_{ч}$ – density of the material to be separated, kg/m^3.

The dependence (1) is in good agreement with the methods for calculating the air velocity proposed by other researchers [2, 6], which are based on the choice of gas velocity *W* in the apparatus within

$$W_{кр1} < W < W_{кр2}, \tag{2}$$

where $W_{кр1}$ – velocity of the required fraction pneumatic transport start, m/s; $W_{кр2}$ – velocity, the excess of which leads to a sharp increase in the intensity of the removal of a large fraction into a small product, m/s.

Conclusions. The obtained experimental data (figure 1) allow to draw some conclusions:

1. It is advisable to use the multistage shelf classifiers with the boundary separation sizes of 0.5-2 mm. With the boundary size of less than 0.5 mm, a steady decrease in the separation efficiency is observed, and with the boundary size of the order of 0.05-0.1 mm, the classification efficiency decreases sharply. With the increase in the boundary separation grain of more than 2 mm, the decrease in the classification efficiency is also observed. The reason for this is that in order to rise sufficiently large particles into a small product, significant air velocities in the classifier are required (in order to rise into a small product particles of quartz sand with a size of 2 mm and a density of 2000 kg/m^3, the air velocity per section of the apparatus is 7.8 m/s). At high air velocities, the hydrodynamics of the flow of medium and material are disturbed, random turbulent pulsations and turbulences occur, which negatively affect the separation performance. In addition, large particles moving down into a large product can entrain smaller particles, which also reduces the separation efficiency.

2. With the increase in the size of the classifier's cross section, ceteris paribus, the separation efficiency decreases. If a laboratory classifier with the cross section size of 80x80 mm provides the separation efficiency of up to 90-92%, then for an industrial sample with the cross section size of 300x300 mm, it does not exceed 65%. The reasons for this, according to many researchers [12, 13, 20, 21, 22], is that in multistage classifiers (as, indeed, in any other gravitational apparatuses) with significant geometric sizes it is very difficult to uniformly distribute the material over the entire volume of the apparatus and also organize a stable air flow velocity field, avoiding various random pulsations, vortices, circulations, and other similar phenomena that occur during the movement of gases or liquids.

Thus, the experimental research of the modernized classifier structure showed that the proposed structural additions (figure 2), ceteris paribus, contribute to a more uniform distribution of the material over the working volume of the apparatus, which, of course, leads to the increase in the quality of separation.

The material accumulations falling down from the inclined shelves violate the classifier's hydrodynamics, limit the contact of particles with the air flow, as a result of which the quality of separation in industrial installations is reduced in comparison with laboratory models, where the above phenomenon manifests itself to a lesser extent.

In order to improve the quality of separation, theoretical research of particle movement in the working volume of the classifier were carried out, aimed at studying the mechanism of accumulation of material particles on the inclined shelf and eliminating the causes of this phenomenon.

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КӨП КАСКАДТЫ ГРАВИТАЦИЯЛЫҚ КЛАССИФИКАТОРДЫ ЭКСПЕРИМЕНТАЛДЫҚ ЗЕРТТЕУ

Аннотация. Полидисперсті материалдардың жіктелуі өнеркәсіптің көптеген салаларында кеңінен қолданылады. Классификациялық жабдықтың үлкен шеңберінен көп каскадты гравитациялық классификаторлар неғұрлым перспективалы болып табылады. Көп каскадты гравитациялық классификаторлардағы жіктеу процесі өте күрделі болып табылады және берілген тиімділікті қамтамасыз ету үшін қажетті Тәжірибелік зерттеулер жүргізуді талап етеді. Оларды құрастыру және пайдалану бойынша неғұрлым тиімді ұсыныстар алуға мүмкіндік беретін шынайы ақпарат алу мақсатында эксперименттік зерттеулер кешені өткізілді. Зерттеу нәтижелері шағын өлшемді көпкаскадты жіктегіштер бөлінудің тұрақты жоғары сапасын қамтамасыз ететінін көрсетті, алайда олардың өнімділігі 80х80 мм қимасы аппарат үшін 100 кг/сағ артық емес, болмашы, осының салдарынан көптеген өндірістік үдерістер үшін оларды пайдалануға болмайды. Өнімділігі анағұрлым жоғары жіктегіштердің едәуір мөлшерлері болуы тиіс. Көпкаскадты сөрелік жіктегіштерді бөлудің шекаралық өлшемі 0,5–2 мм болған кезде пайдалану орынды. шекара мөлшері 0,5 мм-ден кем болған кезде бөлу тиімділігінің бұлжытпай төмендеуі байқалады, ал шекті мөлшері 0,05–0,1 мм болған кезде жіктеу тиімділігі күрт төмендейді. Бөлінудің шекаралық астығы 2 мм-ден артық ұлғайған кезде жіктеу тиімділігінің төмендеуі байқалады (1-сурет). $\delta_{гр}$ = 1 мм бөлудің шекаралық өлшеміне қатысты 0–2 мм бөлшектері бар кварц құмын бөлу кезінде классификаторлардың жаңғыртылған және кәдімгі конструкцияларындағы бөлу тиімділігін анықтау бойынша эксперименттер мынаны көрсетті. Тиімділік қисығының өзара орналасуы жаңғыртылған жіктеуіштер үшін бөлу тиімділігінің өсімі оңтайлы, неғұрлым сапалы бөлуді қамтамасыз ететін аппараттың қимасына ауа жылдамдығына жеткен кезде 10 %-ға дейін құрайтынын көрсетеді. Ұқсас нәтижелер басқа материалдар үшін алынды (сильвинит, ірі тартылған ұн, гипс) әр түрлі шектік бөлу мөлшері кезінде (0,5-тен 2 мм-ге дейін). Тұтастай алғанда, әр түрлі материалдар үшін сөрелік жіктегіштің жаңғыртылған конструкциясына бөлу тиімділігі әдеттегі материалдарға қарағанда 5-10 % – ға жоғары болды. Жіктеуіштің жаңғыртылған конструкциясының эксперименттік зерттеулері ұсынылған конструктивтік толықтырулар өзге де тең жағдайларда аппараттың жұмыс көлемі бойынша материалды біркелкі бөлуге ықпал ететінін көрсетті, бұл, әрине, бөліну сапасының артуына алып келеді.

Түйін сөздер: эксперименталды зерттеулер, гравитациялық классификатор, көпкаскадты, бөлу тиімділігі, шекаралық өлшемдер, қима, тесіктер.

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ЭКСПЕРИМЕНТАЛЬНЫЕ ИССЛЕДОВАНИЯ МНОГОКАСКАДНОГО ГРАВИТАЦИОННОГО КЛАССИФИКАТОРА

Аннотация. Классификация полидисперсных материалов широко используется во многих отраслях промышленности. Из большого круга классификационного оборудования к наиболее перспективным относятся многокаскадные гравитационные классификаторы. Процесс классификации в многокаскадных гравитационных классификаторах является достаточно сложным и требует проведения необходимых экспериментальных исследований, чтобы обеспечить заданную эффективность. С целью получения достоверной информации, позволяющей получить наиболее эффективные рекомендации по их конструированию и использованию был проведен комплекс экспериментальных исследований. Результаты исследований показали, что многокаскадные классификаторы небольших размеров обеспечивают стабильно высокое качество разделения, однако их производительность для аппарата сечением 80×80 мм не более 100 кг/ч незначительна, вследствие чего для большинства производственных процессов они не могут быть использованы. Классификаторы с более высокой производительностью должны иметь значительные размеры. Многокаскадные полочные классификаторы целесообразно использовать при граничных размерах разделения 0,5 – 2 мм. При граничном размере менее 0,5 мм наблюдается неуклонное снижение эффективности разделения, а при граничном размере порядка 0,05 – 0,1 мм эффективность классификации резко падает. При увеличении граничного зерна разделения более 2 мм также наблюдается (рисунок 1) снижение эффективности классификации. Эксперименты по определению эффективности разделения в модернизированной и обычной конструкциях классификаторов при разделении кварцевого песка с размерами частиц 0 – 2 мм относительно граничного размера разделения $\delta_{гр}$ = 1 мм показали следующее. Взаимное расположение кривых эффективности показывает, что прирост эффективности разделения для модернизированного классификатора составляет до 10 % при достижении оптимальной, обеспечивающей наиболее качественное разделение, скорости воздуха на сечение аппарата. Аналогичные результаты были получены для других материалов (сильвинит, мука грубого помола, гипс) при различных граничных размерах разделения (от 0,5 до 2 мм). В целом, эффективность разделения в модернизированной конструкции полочного классификатора для различных материалов была на 5 – 10 % выше, чем в обычной. Экспериментальные исследования модернизированной конструкции классификатора показали, что предложенные конструктивные дополнения при прочих равных условиях способствуют более равномерному распределению материала по рабочему объему аппарата, что, естественно, приводит к повышению качества разделения.

Ключевые слова: экспериментальные исследования, гравитационный классификатор, многокаскадный, эффективность разделения, граничные размеры, сечение, отверстия.

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COMPARATIVE ANALYSIS OF THE NICOTINE EXTRACTION PROCESS FROM *NICOTIANA TABACUM* L. IN SUPERCRITICAL CONDITIONS UNDER VARIOUS EXTRACTANT FLOWS

Abstract. In this paper, we present a comparative analysis of various methods and conditions for extraction from the plant *Nicotiana tabacum* L., harvested in the Almaty region of the Republic of Kazakhstan in 2019. Extraction was carried out at various temperatures at during the extraction process while maintaining pressure in the system 120 bar and a flow of 100 ml/min and 4000 ml/min with the subsequent development of the technology for producing nicotinic acid by oxidation in an aqueous medium.

The supercritical extraction method was carried out on a CO_2 extraction unit under the following conditions: the temperature range in the reactor 40-80 °C, the pressure 120 bar, a gas flow of 100 ml / min. Extraction was also carried out on the installation which was developed jointly with LLC «Superhydrophobic Coatings» (Nizhny Tagil, Russia) at similar temperatures and pressure but with a 40-fold increase in flow (4000 ml/min).

The obtained extracts were studied on a gas chromatograph with a mass selective detector Agilent Technologies 7890N / 5973N GC / MS. Data processing included determining retention times, peak areas and processing of spectral information obtained by using a mass spectrometric detector. The libraries Wiley 7th edition and NIST’02 were used for evaluation of mass spectra.

As a result, an almost two-fold increase in the efficiency of the extraction process was achieved while maintaining the previous parameters.

In addition, the maximum selectivity of the process is achieved at 120 bar and a temperature 70 ºC. The nicotine content in the final extract increased significantly with reducing the quantitative and qualitative content of impurities which are represented in most higher hydrocarbons and alcohols, which do not have special biological activity and, as a consequence, do not affect the quality of the final product.

Our comparative analysis with previously published data shows that a temperature change significantly increases the selectivity of the extraction process, while the highest nicotine content was noted in the extract obtained at 70 ºC. Also under these conditions the smallest impurity content was noted. In addition, only 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (11.31%) and Tetratetracontane (4.70%) were identified in the extract with nicotine.

Natural nicotine is in demand in the production of alternative methods of tobacco consumption, such as e-cigarette. Nicotine can also be potentially used in medicine as an anesthetic and in the treatment of Alzheimer's disease. In addition, nicotine is used as an insecticide to protect plants. For these purposes, nicotine was used in the form of a pure substance, its sulfate, tobacco dust, and the pure substance was the most active.

Keywords: Nicotiana tabacum L, SFE extraction, nicotine, high flows.

Introduction. Extraction is the main technological process that allows extracting biologically active substances from plant materials

Classical extraction of plant materials is a process of extraction plant raw material with a solvent (extractant).

Moreover, the solvent used often cannot be completely removed from the obtained extract, in addition, the feedstock undergoes a number of changes due to the use of chemical solvents, which casts doubt on the “nativeness” of such extracts. In addition, solvents are not able to provide extraction of a full range of biologically active substances [1].

The prevailing actual environmental and social conditions in the world urgently require new approaches to the extraction of biological components.

The use of a number of extractants with a toxic or mutagenic effect in the pharmaceutical industry is prohibited. One of the solutions to this problem is the use of supercritical carbon dioxide as an extractant. And the technology itself is called supercritical fluid carbon dioxide extraction of plant raw material [2].

Most organic solvents are highly toxic compounds and exhibit an accumulation effect which requires the introduction of additional purification stages for the drug substance and additional quality control methods for such preparations. These measures lead to the inevitable rise in price of the final product. In addition, a significant portion of organic solvents are one way or another petrochemical products and their price will inevitably increase in the future [4].

In this regard, in recent decades, new methods for the extraction of biologically active substances complexes from plant materials have been actively studied and developed.

Supercritical extraction methods have several effective advantages.

Supercritical fluids have been investigated since the last century and at first the greatest commercial interest was the use of supercritical toluene in the processes of shale oil processing in the 1970s. Supercritical water is also being investigated as a means of destroying toxic waste and as an exotic synthesis medium [5].

Supercritical carbon dioxide, the critical temperature 31 °C. and a pressure of 71 bar has great interest in the field of chemistry of natural compounds. Biological materials can be processed at 35 ° C which contributes to their preservation from thermal degradation. The density of supercritical CO2 at a pressure of about 200 bar is close in efficiency to hexane and the solvation characteristics during extraction are also similar to hexane [6].

The main advantages of supercritical carbon dioxide are:

- universal dissolving ability of organic compounds. It does not cause concern physiologically because is the final product of the metabolism of a number of living organisms, including humans;
- carbon dioxide is chemically inert and does not with with recoverable substances;
- CO_2 is relatively safe for the environment which suggests the possibility of creating an environmentally friendly type of production;
- carbon dioxide is one of the most accessible and widely used gases in the food industry.

A large number of industrial products are obtained using supercritical technologies (decaffeinated coffee, cholesterol-free oil, lean meat, rose oil, etc.).

The solvation characteristics of supercritical CO_2 can be modified by the addition of a co-solvent such as ethanol which can significantly increase the extraction efficiency. However, the solvent residue in the product somewhat eliminates the main advantage of the process which consists in the complete absence of impurities in the final extract [7, 8].

In connection with the foregoing, the development of the scientific foundations and the development of extraction processes and techniques that will allow the operation of extraction plants using carbon dioxide in the liquefied and compressed state to be switched on to a high-performance and energy-saving mode are necessary, while it is necessary to reduce the pressure level in the apparatuses, create conditions of steady and safe work.

The improvement of the technique and technology for the extraction of plant materials with carbon dioxide is possible on the basis of deepening research on both the extraction process itself and the operation of the entire complex of apparatuses of the extraction plant.

In earlier articles, we determined the optimal pressure for the process of extraction of nicotine from the plant *Nicotiana tabacum* L. [9-17].

In this article we show transfer factor and its effect on the efficiency of the extraction process in more detail the mass.

Materials and methods. Plant raw material (*Nicotiana tabacum* L.) for the extraction was harvested in the Almaty region in 2019. The tobacco was dried and crushed in a cutting mill to an average particle size 3 mm for increasing the specific area and the efficiency of the extraction process accordingly.

Prepared plant raw material was divided into 6 samples weighing 500 g to determine the completeness of extraction based on the loss in mass [18-20].

Then, samples numbered 1–3 were extracted on a extraction unit Thar SFE-1000 under the following conditions: temperature 40–70 ° C; CO_2 pressure 120 bar; a gas flow of 100 ml/min.

Samples 4-6 were extracted with the installation developed jointly with LLC "Superhydrophobic Coatings" (Nizhny Tagil, Russia) under the Target Financing Program BR05236420 "Angry Technologies Based on Supercritical Media" at similar temperatures (40-80ºC) and a CO_2 pressure 120 bar but with a flow of carbon dioxide of 4000 ml / min) [21-22].

The obtained extracts were studied by gas chromatography with a mass selective detector. The analysis was performed on a gas chromatograph with a mass spectrometric detector 6890N/5973C (Agilent, USA) equipped with a autosampler Combi-PAL (CTC Analytics, Switzerland). 1.00 µl of the sample was injected into the gas chromatograph injector using an autosampler at an injector temperature 250 °C for GC-MS analysis. Chromatography was performed using an HP-5ms capillary column (Agilent, USA): a length 30 m, an inner diameter 0.25 mm, a film thickness 0.25 µm at a constant carrier gas velocity 1.0 ml/min (helium> 99.995%, Orenburg-Tekhgaz, Russia). The program for heating the chromatographic column: holding 5 min at 40 ° C, heating at a speed 10 °C / min to 280 ° C, holding for 5 min. The total chromatographic time was 34 minutes. The temperatures of the quadrupole and the detector ion source were 150 and 230 °C, respectively.

Mass spectrometric detection was carried out in the ion scanning mode in the m/*z* range 40 to 550 with a solvent delay of 5 min. The peaks found in the chromatograms were identified using the NIST'11 and Wiley 10 mass spectral libraries [23–25].

Results and discussion. We found that increasing the flow almost 2 times increases the efficiency of the extraction process, in addition, the duration of the process is significantly reduced from 2 hours to 15 minutes, with a relatively small increase in energy consumption.

The results are presented in table 1.

Table 1 – Results of the effectiveness of the process
of extraction of nicotine from the plant *Nicotiana tabacum* L.

№	Flow ml/min	T, ºC	Duration extraction, min	Mass, g	Loss in mass relative to plant raw material, %	P, bar
1	100	40	120	500	0,43	120
2	100	50	120	500	0,5	120
3	100	70	120	500	1,05	120
4	4000	40	15	500	1,54	120
5	4000	50	15	500	1,8	120
6	4000	70	15	500	2,1	120

It is possible to achieve an extremely high yield of nicotine, which is 46.40% at a flow of 100 ml/ min and 83.9% at a flow of 4000 ml/min, and this is a very high rate for alkaloids under the conditions of supercritical fluid CO_2 extraction at a pressure 120 bar and the temperature 70 °C. At lower temperatures, and specifically 40 ºC, the yield is 18.2% with a smaller and 68.2% with a larger flow, and at 50 ºC 25.9% with a lower and 71.1%, respectively.

The data on the nicotine content in the extracts are presented in figure 1.

The indicated changes in the composition are explained by the fact that during supercritical processes, pressure and temperature are crucial not only for the completeness of extraction but also for the properties of the extractant [26–35].

Comparative analysis of the chemical composition with previously published data shows that a change in temperature significantly increases the selectivity of the extraction process while the highest nicotine content was observed in the extract obtained at 70 °C and under these conditions the smallest quantity of impurities was noted, in addition, 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (11.31%) and Tetratetracontane (4.70%) were identified.

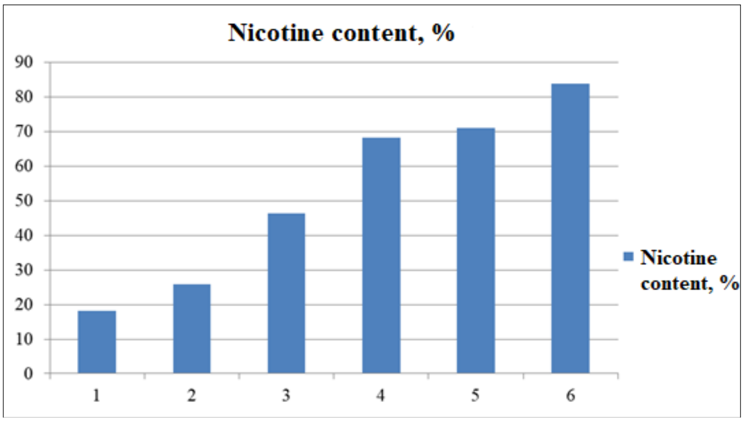

Figure 1 – Nicotine content in supercritical extracts obtained from spreading *Nicotiana tabacum* L. at different flows

Conclusion. As a result, an almost two-fold increase in the efficiency of the extraction process was achieved with maintaining the previous parameters.

That can significantly improve the environmental friendliness and energy efficiency of the extraction process.

In addition, the maximum selectivity of the process was achieved at 120 bar and a temperature 70 ºC. The nicotine content in the final extract increased significantly with reducing the quantitative and qualitative content of impurities. These impurities are represented in most higher hydrocarbons and alcohols which do not have special biological activity and, as a result, do not affect the quality of the final product.

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ЭКСТРАГЕНТТІҢ ТҮРЛІ АҒЫМДАРЫ КЕЗІНДЕ АСА СЫНИ ЖАҒДАЙЛАРДА NICOTIANA TABACUM L ӨСІМДІГІНЕН НИКОТИНДІ ЭКСТРАКЦИЯЛАУ ПРОЦЕСІН САЛЫСТЫРМАЛЫ ТАЛДАУ

Аннотация. Бұл мақалада біз 2019 жылы Қазақстан Республикасының Алматы облысында жиналған *Nicotiana tabacum L.* өсімдігінен алудың әртүрлі әдістері мен шарттарына салыстырмалы талдау ұсынамыз. Экстракция кезінде әр түрлі температурада жүйеде қысымды ұстап тұру кезінде 100 бар / мин және 4000 мл/мин. Сулы ортада тотығу арқылы никотин қышқылын алу технологиясын одан әрі дамыта отырып.

Экстракционды экстракция әдісі CO_2 алу қондырғысында келесі жағдайларда жүргізілді: реактордағы температура диапазоны - 40-80ºC, CO2 қысымы - 120 бар, газ шығыны 100 мл / мин. Superhydrophobic Coatings LLC-мен (Нижний Тагил, Ресей) бірлескен қондырғыда ұқсас температурада (40-80ºC) және CO_2 қысымы - 120 бар, бірақ ағынның 40 есе ұлғаюымен (4000 мл / мин).

Алынған сығындылар Agilent Technologies 7890N / 5973N GC / MS массалық іріктеу детекторымен газды хроматографта зерттелді. Мәліметтерді өңдеудің құрамына ұстап тұру мерзімдерін, шың аудандарын және масс-спектрометриялық детектордың көмегімен алынған спектрлік ақпаратты өңдеу кіреді. Алынған масс-спектрлердің шифрын ашу үшін Wiley 7 басылымы мен NIST'02 кітапханалары пайдаланылды.

Нәтижесінде, алдыңғы параметрлерді сақтай отырып, өндіру процесінің тиімділігі екі есеге артты.

Сонымен қатар, 120 барда және 70 ºC температурада процестің максималды селективтілігіне қол жеткізіледі. Соңғы сығындыда никотиннің мөлшері айтарлықтай жоғарылады, бұл көмірсутектер мен спирттердің көпшілігінде кездеседі, олар арнайы биологиялық белсенділікке ие емес және нәтижесінде өнімнің сапасына әсер етпейді.

Бұрын жарияланған мәліметтермен салыстырмалы талдау көрсеткендей, температураның өзгеруі экстракция процесінің селективтілігін едәуір арттырады, ал 70 никельден алынған сығындыда никотиннің ең жоғары мөлшері байқалды, сонымен қатар бұл жағдайда никотиннен басқа экстракцияда тек 3 анықталды. 7,11,15-тетраметил-2-он алтазид-1-ол (11,31%) және тетра-тетраконтан (4,70%).

Табиғи шикізаттан алынған никотин темекіні тұтынудың балама әдістерін, мысалы, электронды темекі өнімдерін өндіруде сұранысқа ие, никотин сонымен қатар медицинада анестезия ретінде және Альцгеймер ауруын емдеуде қолдануға болады. Сонымен қатар, никотин инсектицид ретінде өсімдіктерді қорғау үшін қолданылады. Бұл мақсаттарда никотин таза зат түрінде қолданылды, оның сульфаты, темекі шаңы, ал таза зат ең белсенді болды.

Түйін сөздер:. *Nicotiana tabacum* L, СКФ-экстракция, никотин, жоғары ағындар.

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СРАВНИТЕЛЬНЫЙ АНАЛИЗ ПРОЦЕССА ЭКСТРАКЦИИ НИКОТИНА ИЗ РАСТЕНИЯ *NICOTIANA TABACUM* L В СВЕРХКРИТИЧЕСКИХ УСЛОВИЯХ ПРИ РАЗЛИЧНЫХ ПОТОКАХ ЭКСТРАГЕНТА

Аннотация. В данной статье нами представлен сравнительный анализ различных методов и условий экстракции из растения *Nicotiana tabacum* L., заготовленного в Алматинской области Республики Казахстан в 2019 году. При различных температурах проведения процесса экстракции с сохранением давления в системе 120бар и потока 100 мл/мин и 4000 мл/мин, с последующей отработкой технологии получения никотиновой кислоты путём окисления в водной среде.

Метод сверхкритической экстракции был проведён на установке CO_2-экстракции при следующих условиях: температурный диапазон в реакторе – 40-80ºС, давление CO_2 – 120 бар, при потоке газа 100 мл/мин. И на установке, разработанной совместно с ООО “Супергидрофобные покрытия” (Нижний Тагил, Россия), при аналогичных температурах (40-80ºС) и давления CO_2 – 120 бар, но с увеличенным в 40 раз потоком (4000 мл/мин).

Полученные экстракты исследовали методом газовой хроматографии на газовом хроматографе с масс-селективным детектором Agilent Technologies 7890N/5973N GC/MS. Обработка данных включала в себя определение времен удерживания, площадей пиков, а также обработку, спектральной информации, полученной с помощью масс-спектрометрического детектора. Для расшифровки полученных масс-спектров использовали библиотеки Wiley 7th edition и NIST’02.

В результате достигнуто практически двукратное повышение эффективности процесса экстракций при сохранении прежних параметров.

Кроме того, при 120 бар и температуре 70 ºС достигается максимальная селективность процесса. Содержание никотина в конечном экстракте значительно возросло, одновременно с уменьшение количественного и качественного содержания примесей, которые представлены в большинстве высшими углеводородами и спиртами, не имеющими особой биологической активности и, как следствие, не влияющими на качество конечного продукта.

Проведённый нами сравнительный анализ с ранее опубликованными данными показывает, что изменение температуры значительно повышает селективность процесса экстракции, при этом наибольшее содержание никотина отмечено в экстракте, полученном при 70 ºС, также при данных условиях отмечено наименьшее содержание примесей, в экстракте помимо никотина идентифицированы только 3,7,11,15-тетраметил-2-гексадецен-1-ол (11,31%) и тетратетраконтан (4,70%).

Никотин, полученный из натурального сырья, востребован в производстве альтернативных способов потребления табака, таких как e-cigarette, также никотин потенциально может быть использован в медицине в качестве анестетика и в терапии болезни Альцгеймера. Кроме того, никотин применяется в качестве инсектицида для защиты растений. Для этих целей использовали никотин в виде чистого вещества, его сульфат, табачную пыль, причём наибольшей активностью обладало чистое вещество.

Ключевые слова: *Nicotiana tabacum* L, СКФ-экстракция, никотин, высокие потоки.

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JUSTIFYING THE OPTIMALITY OF ESTABLISHED REGIMES FOR SWISS CHEESE DOUBLE- SIDED PRESSING

Abstract. The article discusses conditions when, under the established regime of double-sided pressing, which results in a more equally dimensioned distribution of moisture in Swiss cheese, the prerequisites for microbiological processes flowing are improved, as evidenced by the results of biochemical investigations. A new constructive solution is also proposed for double-sided cheese pressing molds with the possibility of fully automating the processes of molding and pressing, using mechanisms of step pressing of the cheese mass with a reduction in the number of pneumatic cylinders, with the automatic controlling valve of cheese grain filling and cheese removal by a telescopic pneumatic cylinder.

Keywords. Anisotropy, soluble and non-protein nitrogen, valve, ruler, tooth, shell, telescopic, perforated, corrugated, clamps.

Introduction. One of the most important problems of the dairy industry is to increase the efficiency of production and the quality of products, by using perfect high-productivity equipment and technology. In cheese making, the least perfect and rather labor - intensive technological processes are molding, wrapping the cheese mass in tissues, pressing and removing cheese from the mold. At the same time, the processes of cheese mass molding and pressing are the most important in cheese making, since they provide the cheese type features and the necessary quality of cheese. The imperfection of these technological processes leads to unequally dimensioned distribution of moisture and hardness in the cheese mass, and consequently to unequally dimensioned distribution and development of microflora, as well as the non-intensive flow of biochemical processes in the cheese mass, as a result of which the quality of the cheese reduces. The sources of flavoring and aromatic substances of cheese are all macronutrients: fats, proteins, carbohydrates. The hydrolysis of these macronutrients is carried out by microorganisms, which means that without microorganisms it is impossible to produce cheese [1], [2], [3]. Thus, it is extremely necessary to create conditions (moisture, temperature and PH) in order to produce cheese of the required quality. It is more important to distribute moisture in the cheese mass, which depends on the wrapping of the tissue, the repressing, the optimal regimes (pressure and duration), the pressing method and non- combining of technological processes (assembly of molds, filling of cheese, cheese shaping, pressing and removal of cheese from the mold), which lead to increased anisotropy of the cheese mass. In this area, a technological analysis of the review literature has been carried out to determine the influence of each of these technological processes, anisotropy change (unequally dimensioned distribution of moisture) in the cheese mass. Technological analysis shows that abroad, as well in CIS, two methods of cheese making have been used: self-pressing and single-sided pressing of cheese mass.

In case of self-pressing, the upper layers of the cheese mass press the lower ones. During single-sided pressing from top to bottom, in the direction of the being pressed side, the pressure, of course, drops. In both methods, repressing of the cheese mass is required for the equation of moisture distribution and density in the upper and lower layers of cheese mass. If the pressure on the cheese mass in the technological regime is higher than the norm, then draining of tissue is more than pressing which leads to quick drying and hence to the closing of the capillaries holes and finally to the settling of whey in the capillaries. In addition, pressed cheese pieces can be cut off from pressed cheese during the removal from the mold. Unwanted microorganisms can enter these places, which later degrade the quality of the cheese. If the pressure is less, then the cheese is non-pressed up, i.e. again leads to settling of whey in the capillaries. These operations increase the cheese cost, reduce the productivity, interfere with the implementation of linear production, make difficult the integrated mechanization and automation of cheese making production [4].

Theory of anisotropy formation. When cheese grains are displaced by suppressing of the pressing force, capillaries are formed in the inter-granular space, through which whey leaks in different directions to the surface of the cheese mass. Wherein, the repressing and the tissue result in the correspondence of the holes of cheese press cloth with the pressing, as a result of which, the sizes of the pressed cheese are increased and the holes are quickly dried and closed, leading to the settling of the whey in the capillaries. Whey can exit through other capillaries if the pressure is higher than in neighboring capillaries, but the pressing duration is prolonged. And, if the whey remains in the capillaries, the humidity will be greater than in those capillaries which holes have not been closed. As a result, anisotropy, which is so undesirable in cheese making, is increased. In addition, with single-sided pressing, the pressure from the side being pressed towards the lower layers decreases, hence the density in the upper and lower canvas is not the same, for which they are exposed to repressing [4].

The above-mentioned factors negatively affect the intensity of the biochemical and microbiological processes. In this regard, the most important problem of cheese making production is the development and widespread industrial implementation of new progressive technologies and technical means, that is the non-tissue pressing of cheese.

Thus, the above-mentioned technological processes increase the anisotropy of the cheese mass, reducing the quality of the cheese.

Technical analysis. In the last decade, many processes of natural cheese making production are mechanized and automated. Several semi-industrial and industrial methods of continuous cheese mass making, its molding and pressing and various periodical and continuous operating apparatus are used. Molding - dosing devices, presses (lever, screw and pneumatic, horizontal, tunnel) are used to make high-quality cheese mass. Until now, ways, constructions of molds and devices, which are applied in cheese-making production, are mainly used for single-sided pressing of cheese. Among them, tunnel presses occupy a special place, in which two types of devices are used as power elements that develop the pressing force: [5], [6].

1. Pneumatic cylinders - a separate pneumatic cylinder presses on each cheese block. Wherein, the difference in height of each of the cheese block is not important, presses with pneumatic cylinders have a large working space height, which simplify loading. In addition, their construction provides parallelism of the upper and lower planes at any loading and any way of molding. This positive property makes such presses attractive to many cheese manufacturers. This press construction is very expensive and material-intensive, but it is considered the best and is used in the production of large mass cheese.

2. Flexible inflatable force elements. The disadvantage of such elements is the small size of the working stroke (with large differences in the height of the cheese blocks, the quality of the cheese can deteriorate), advantage - in high specific pressure, provided by the specificity of the press construction using of flexible power elements. At the same time, the main way to create a pressuring is the energy of compressed air and in most often a separate pneumatic cylinder presses on each cheese block in them. Wherein, the consolidation of the cheese mass in the direction from the pressed side to down anyway drops, and in order to get the same density of the upper and lower sides, the cheese is repressed. This is a very labor-intensive process, leading to unequally dimensioned distribution of moisture and hardness in the cheese mass, therefore, to unequally dimensioned distribution and development of microflora and to non-intensive flow of biochemical processes in the cheese mass, as a result of which the quality of the cheese decreases. Therefore, the current way of single-sided pressing of cheese with repressing and using tissues leads to anisotropy of cheese [5], [6].

Highly automated presses manufactured by the Press Pallet company are distinguished from existing types of tunnel presses. Press pallets are combined into blocks, having a common compressed air supply system, as well as a system of lifting and transporting devices for loading and unloading presses (press section equipped with Shalon Megar press pallets [7]).

Analysis of existing pressing systems allows us to conclude that they are constantly being improved, but the main way to create pressure is to use the energy of compressed air. Improvements relate to the automation of loading and unloading systems but not the constructions of molds, pressing molds and equipment [5], [6].

Thus, to produce high-quality cheese, it is necessary to get a cheese mass with a more equally dimensioned distribution of moisture and hardness during pressing. Consequently, the improvement and development of high-productive continuously operating technical means, techniques and technology for natural cheese production, especially the processes of getting the cheese mass, its molding and pressing, was and is an urgent task of science and practice.

Thus, until now, the ways and constructions of molds and devices used for the establishing of single-sided pressing are distinguished by a number of disadvantages (turning, wrapping the cheese mass in molding tissues, pressing, removing of pressed cheese, assembling and disassembling the molds, non-combining of these processes, manual labor, the large area occupied by the equipment), and the cheese produced by these ways are characterized by anisotropy [4]. The above-mentioned disadvantages interfere with the establishment of linear production, complicate the complex mechanization and automation of cheese making production. Therefore, in order to produce high-quality cheese, it is necessary to get cheese mass with increased homogeneity during pressing. To achieve this, it is necessary to develop new ways and technical means for cheese pressing and combining processes of cheese grain filling, molding and pressing of cheese mass and the removal of the pressed cheese from molds, which is still very actual and significant. The aim of the work is to develop a technology that combines the technological processes of cheese making (filling cheese grain, molding and pressing of cheese mass and removing pressed cheese from the molds), their automation with a reduction in the number pneumatic cylinders and replacing the energy of compressed air with electromagnetic forces, as well as the development of technical means for the implementation of pressing cheese without repressing and the use of tissues.

We offer three ways of double-sided pressing: double-sided, non-tissue pressing; double-sided, non-tissue step pressing (with less number of pneumatic cylinders) and double-sided, non-tissue pressing using electromagnetic forces (without pneumatic cylinders).

To solve this goal, we have formulated the following tasks:

1. To develop technological foundations and technical means for double-sided, non-tissue pressing of natural branded cheese and to improve the developed technical means.

a) to reconstruct the pressing mold of the French line of the company Pierre Cuerin for double-sided pressing of Swiss cheese.

b) to develop a device for determining the hardness of cheese.

2. To set the optimal regime (pressure and duration) of double-sided pressing for Swiss cheese depending on the height and mass [8].

3. To study the effect of double-sided pressing (the first method) on the quality of the Swiss cheese.

Materials and Methods. Based on the above, we offer 2 ways of double-sided pressing: double-sided non-tissue pressing; double-sided, step non-tissue pressing(with a less number of pneumatic cylinders).

The method of doing the research. Experimental studies were carried out according to standard and generally accepted methods based on the GOST. Determination of nitrogenous substances in Swiss cheese by Kjeldahl method GOST 23327 -1978 was made at the Gorelovsky cheese factory of the Bogdanovsky district in Georgian SSR. The moisture content in the cheese was made by express method (GOST 3625-75). The hardness of the cheese was determined by using the constructed and made device. The essence of the work is the fact that the necessary cone inclination of 20 degrees is achieved by penetrating the device into the cheese mass in a matter of seconds. (Fig. 1). In the control experiment, Swiss cheeses were exerted to double-sided pressing in reconstructed mold of the French line by Pierre Cuerin, which is intended for single-sided pressing of large cheese [9] [10].

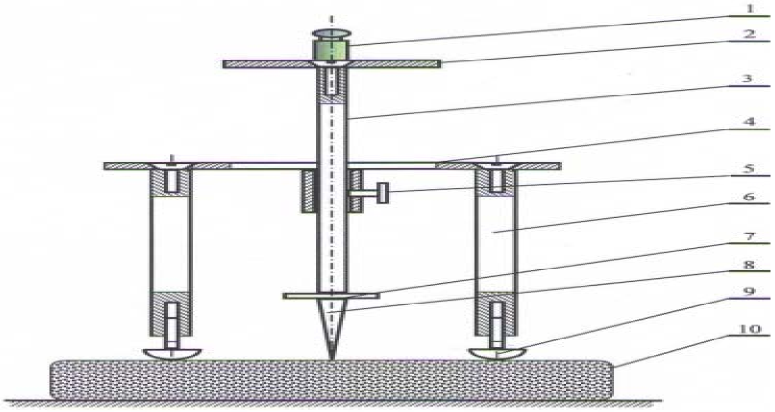

Figure 1 - Device for determining the cheese hardness:
1- weight, 2,4 –discs, 3 –rod, 5 – local screw, 6 –legs, 7 – ledge, 8 – cone, 9 – supports, 10 – cheese

The aim of the work was to study a new method of double-sided, non-tissue pressing to reduce the anisotropy of cheese by excluding its repressing and shortening the pressing duration, which should lead to an increase in the cheese quality, as well as the design of molds for its implementation. The study of the effect of double-sided pressing on the quality of Swiss cheese is determined by the establishment of the technological regime (pressure duration). To justify the optimality of the established regime, rheological and biochemical investigations were carried out.

Research Results. The results of rheological investigations have shown that cheese exerted to double-sided pressing differ in a more constant distribution of hardness and moisture, however according to the average data, the moisture content in both pressing methods slightly differs from each other (experimental 39.82% and control 39.47%), but in samples of control cheese taken from 5 different points, the fluctuation in moisture content in the cheese mass is slightly greater (1.9% versus 0.5% in experimental). The hardness of the cheese mass in the upper and lower canvases of the experimental fresh Swiss cheese is 12.7 and 11.5 sec, already then, as in the control cheese, it is correspondingly 61 and 60.6 sec, which is 5 times more than in the experimental cheese, due to the crust forming, which occurs due to repressing and the usage of tissue. In the latter, the layer becomes less consolidated, consequently, the edible portion of the cheese increases. The hardness fluctuation is more for control cheese. They are more constant in the cheese which is made by double-sided pressing. The hardness of the surface layer (30 mm deep) of fresh and mature cheese is determined by using a special device that we have constructed.

The effect of double-sided pressing on the content of nitrogenous substance in fresh and 5.5 months aged Swiss cheese. Nitrogen forms were determined in samples of the same cheese. The research results are presented on table.

From the data on Table 1, it can be seen that the soluble forms of nitrogenous substances in fresh Swiss experimental cheese during double-sided pressing, account to 11.604-12.319% of the total nitrogen, and non-protein - 9.544-9.802%, or correspondingly 0.572% (11,604-11,032) -1,03 (12,319-11,289) and 0,377% (9,802-9,425) -1,252 (9,544-8,292) more than in control cheese with repressing, and according to average data, the content of soluble forms of nitrogenous substances is more than 0.835% (12.018-11.183%), and the content of non-protein nitrogenous substances is more than 0.732% (9.666-8.934%).

Thus, the content of total and soluble nitrogen in experimental and control 5.5months aged cheese is almost at the same level, and from the aspect of non-protein nitrogen content, types of cheese differ from each other in favor of experimental cheese. So, the content of soluble nitrogen in 5.5 months aged experimental cheese was on average 22.42% of the total nitrogen, i.e. 0.68% more than in control cheese (21.74%). The content of non-protein nitrogen in experimental cheeses was on average of 14.21% of the total nitrogen, which is more, compared to control cheese with repressing (3.40%) by 0.81% (table 1).

With double-sided pressing, as a result of a more equally dimensioned distribution of moisture in the cheese, the conditions for microbiological processes are also improved. This is evidenced by data from biochemical studies, i.e. the established regime of double-sided pressing is optimal (rational).

The content of nitrogenous substance in fresh and 5.5 months aged Swiss cheese

Cheese		Total nitrogen, %	Nitrogen Type, %		In relation to the total nitrogen,%	
			soluble	non-protein	soluble	non-protein
Fresh cheese						
Experimental	I	4,432	0,546	0,423	12,319	9,544
	II	4,438	0,515	0,435	11,604	9,802
	III	4,435	0,538	0,428	12,131	9,651
Average		4,435	0,533	0,429	12,018	9,666
Control	I	4,061	0,448	0,369	11,032	9,086
	II	4,004	0,452	0,332	11,289	8,292
	III	4,106	0,461	0,387	11,227	9,425
Average		4,057	0,454	0,363	11,183	8,934
5,5months aged cheese						
Experimental	I	4,49	1,011	0,648	22,52	14,43
	II	4,48	1,010	0,650	22,54	14,51
	III	4,46	0,990	0,610	22,20	13,68
Average		4,48	1,004	0,636	22,42	14,21
Control	I	4,30	0,912	0,580	22,21	13,49
	II	4,52	0,980	0,610	21,68	13,50
	III	4,53	0,966	0,598	21,32	13,20
Average		4,45	0,9531	0,596	21,74	13,40

Discussions. For the first time, double-sided, non-tissue pressing was proposed which excludes the repressing, with a decrease in the anisotropy of Swiss cheese and a reduction of pressing duration.

1. A pressing mold of the French company Pierre Cuerin was reconstructed for the experiment.
2. A device for measuring the density of cheese mass was designed and made.
3. The technological regime of double-sided, non- tissue pressing was determined, which excludes repressing and reduces the duration Swiss cheese pressing.
4. The optimality of proposed new regime for double-sided pressing of Swiss cheese was investigated.
5. Rheological and biochemical investigations were also carried out in order to justify the optimality of the proposed regime of double-sided pressing of Swiss cheese.
6. Schemes of mold for double-sided pressing of Swiss cheese, which have to be automated, were developed.

Conclusion. The results of the experiments and research fully justify the optimality of the proposed above regime for double-sided pressing of Swiss cheese.

According to the research results, we can conclude that the proposed technological regime of double-sided pressing of Swiss cheese is optimal.

Conclusion. Based on the above-mentioned research results, we can conclude that it is appropriate to continue further research of the effect of double-sided pressing on the quality of Swiss cheese with a justified technological regime.

According to the above-mentioned research results, it can be seen that this technological solution of the first method of double-sided pressing, positively affects the quality of Swiss cheese. It is appropriate to give a further technical solution for the implementation of the proposed double-sided pressing.

The purpose of the technical solution is to develop a technology that combines the technological processes of cheese making (mold assembly, cheese grain filling, molding and pressing of the cheese mass, disassembling the molds and removal of the pressed cheese from the molds, their automation with a reduction in the number of pneumatic cylinders, as well as the development of technical means for implementing cheese pressing without repressing and without using tissues.

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ШВЕЙЦАРИЯ ІРІМШІГІН ЕКІЖАҚТЫ ПРЕСТЕУ ҮШІН БЕЛГІЛЕНГЕН РЕЖИМДЕРДІҢ ОҢТАЙЛЫЛЫҒЫН НЕГІЗДЕУ

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ОБОСНОВАНИЕ ОПТИМАЛЬНОСТИ УСТАНОВЛЕННЫХ РЕЖИМОВ ДЛЯ ДВУХСТОРОННЕГО ПРЕССОВАНИЯ ШВЕЙЦАРСКОГО СЫРА

Аннотация. В статье рассматривается впервые предложенный новый способ двухстороннего бессалфеточного, без перепрессовок прессования сыров. Его испытание проведено на швейцарских сырах, реконструрированием нами прессформы фирмы Pierre-Gurie (Франция), предназначенной для одностороннего бессалфеточного, без перепрессовок на прессформу двухстороннего прессования. Ожидаемые результаты – значительное сокращение продолжительности прессования с уменьшением анизотропии и с исключением перепрессовки применением салфетки.

При испытании также впервые определен технологический оптимальный режим (давление продолжительности) двухстороннего прессования швейцарского сыра, который длился 8 часов 20 минут, отвесом головки 50-65 кг, высотой 12-15 см, диаметром 70 см, что позволит значительно сократить продолжительность почти в 2 раза по сравнению с существующим односторонним прессованием чехской линии (16-18 ч), не влияя на качество.

Прессующее усилие постепенно увеличивалось (4 этапа), от 0784-2,744 н/см2 или 7980-31920 Пас.

После созревания эти сыры прошли дегустацию (высший сорт). Оказалось, что по данным органолептическим показателям, они ни чем не отличались от качества и анализов стандартных требований (оценка в баллах – опытные – 89, контрольные - 88 почти одинаковые) .

Для обоснования оптимальности технологического режима двухстороннего прессования были проведены реологические биохимические исследования.

Результаты этих исследований показали, что пробы, взятые с 5 разных точек по содержанию влаги, по средним данным, составило в свежих опытных и контрольных швейцарских сырах 39.82% и 39,4%, т.е. почти одинаковые, а колебание содержания влаги составляют, соответственно, 0,5% и 1,9%. Низкое колебание (0,5%) у сыров выработанным двухсторонним прессованием является равномерное распределение влаги в сырной массе.

Твердость сырной массы свежих опытных швейцарских сыров составляет 12,7 верхних и 11,5 нижних полотнах, а у контрольных с применением салфеток с перепрессованием, из-за образующейся корки, соответственно, 60 и 60,6 сек, что в 5 раз больше опытных сыров. Колебание твердости намного выше контрольных сыров, в опытных – более постоянна. Твердость сыра определялось нами сконтрурированного и изготовленного устройства. Растворимый азот в свежих опытных швейцарских сырах, по средним данным, больше на 0,835%, а небелковых на 0, 732%.

В 5,5 месячных опытных сырах содержание растворимого азота, по средним данным, 22,42% от общего азота, что на 0,68% больше, чем в контрольных сырах – 21,74%. Содержание небелкового азота в опытных, по средним данным, 14,21% от общего азота, что больше по сравнению с контрольными сырами 13,40% на 0,81%.

Исходя из вышеуказанных результатов исследований можно заключить, что предлагаемый способ технологического режима двухсторонним прессованием (давления продолжительности) швейцарского сыра является оптимальным. Вывод двухстороннего бессалфеточного без перепрессовок прессования обеспечивает более равномерный и стабильный сдвиг сырных зерен под давлением прессующего усилия с одновременным уплотнением с обеих сторон сырной массы. Вследствие этого влага распределяется по всем слоям сырной массы более равномерно. В результате этого уплотняющий слой получается более тонким, а это приводит к неотстаиванию сыворотки в капяллярах, образующих межзерновое пространство. Течка сыворотки осуществляется через капилляры по всему направлению наружной сырной массы, а также уменьшению онизотропии, т.е. к повышению однородности сырной массы. На основании этого равномерно развиваются и распределяются микроорганизмы и биохимические процессы протекают интенсивно. А это, т.е. оптимальность, обоснуют результаты исследования.

Совмещая вышеуказанные результаты можно заключить, что двухстороннее бессалфеточное без перепресовок прессование положительно влияет на качество швейцарского сыра и дает возможность проводить дальнейшие исследования.

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ACTIVATION METHOD OF CLEANING PROCESS GAS

Abstract. This article presents the results of joint research of "ABsalut Ecology" LLP with Karstu of industrial electrochemical aeroion plants B30-500 and AP-21, capable of cleaning technological gas emissions from toxic impurities SO_2 (at least 90%), NO_x (at least 80%), CO_2 (at least 90%) and dust particles (99.9%); with the return to production of part of the burned carbon (in the form of fine soot).

It was found that in the discharge zone of the V30-500 and AP-21 installations, the active factors affecting the chemical process are: high voltage of the electric field ; secondary ionization of substances; polarization of molecules; high temperature; photoionization; microwave radiation; shock wave. Two processes take place simultaneously in the reaction zone of the plants: activation and reduction of CO_2, CO, NO_x, and SO_2 oxides to elementary substances in the core of the electronic injector.

Reduction of CO_2, CO, NO_x, and SO_2 oxides in the reaction zone proceeds simultaneously by various mechanisms: catalytic reduction and dissociation. It is established that the catalytic system in the installation is an electronic injector, which serves as a source of active particles that determine the rate of chemical reactions. Reducing agents CO, NH_3 are present in the gas to be treated , and are also formed in the reaction zone of the plant.

As a result of the reactions, elementary substances are formed. The speed constants of elementary processes in a discharge strongly depend on the electric field strength, and the speed of individual processes may depend in a non-linear way on the current density, so by changing these parameters, you can change the selectivity and speed of recovery processes in the installation.

It is shown that ionization and dissociative processes with the formation of various radicals and ions are feasible in non-equilibrium weakly ionized plasma. The degree of capture of aerosols and dust increases with a decrease in the size of dust-like particles, and in dry electric filters, on the contrary, falls to zero.

The ways of increasing the efficiency of technological gas treatment plants (geometric parameters of new plants, increasing their productivity, using new high-voltage power sources, flotation and filtration devices, and dispatching control systems) were determined.

The efficiency of the gas treatment plant does not decrease when the particle size of the captured aerosols decreases, starting from the size of about 5 microns and lower, the cleaning efficiency approaches 100%.

The research results are shown as graphs that show the concentration of gas before and after treatment. The degree of air purification from dust particles and aerosol impurities ranges from 60% to 99%.

Keywords: soot, activation, electrochemical installations, air ionization, atmospheric pollution, ecology, initiation, carbon conversion, aeroionizers, cyclones, scrubbers, electrofilters.

Introduction. Nowadays the issue of solving environmental problems is acute throughout the world. The scientific and technological revolution, the intensive growth of production are the basis of negative changes in the environment, these include: air pollution; destruction of the fertile layer of the earth; poisoning and pollution of the rivers, lakes, oceans, etc. As a result of human and industrial activities of the people more than 200 million tons of carbon monoxide, 151 million tons of sulfur (IV) oxide, and over 50 million tons of oxides nitrogen, more than 50 million tons of various hydrocarbons, more than 250 million tons of fine aerosols are annually emitted into the Earth’s atmosphere [1].

The relevance of this article is caused by the alarming situation in the ecology of the Republic of Kazakhstan. The highest level of air pollution is observed in the cities of Ust-Kamenogorsk, Shymkent, Aktobe, Balkhash, Temirtau.

This problem makes the young generation think about how to return the human environment, our Earth, to that perfect natural balance that existed earlier. By lowering the air pollution levels, countries can reduce the burden of diseases such as stroke, heart disease, and lung cancer, as well as chronic and acute respiratory diseases, including asthma. In 2012, an estimated 3.7 million premature deaths occurred in urban and rural areas worldwide due to the air pollution. According to the recent WHO estimates of the total global burden of disease, approximately 7 million cases of premature death are caused by the air pollution and the indoor air [2].

The main causes of the high level of air pollution in the cities of Kazakhstan are as follows:

- outdated production technologies,
- inefficient gas cleaning equipment,
- mismatch of coal fuel to boiler units,
- a huge amount of accumulated and new dumped waste (billions of tons).

From the above-said it follows that the enterprises of Kazakhstan need comprehensive purification, which will not only clean up gas emissions, but also make it possible to obtain carbon black products in the form of environmentally friendly compounds.

A scientific-engineering group of the ABsalut Ecology LLP headed by A. Borissenko, Doctor of Chemistry, Professor, Academician, developed and introduced into production new electrochemical plants of the B30-500 and AP-21 models that not only clean technological gas emissions from toxic impurities (CO_x, NO_x, SO_2, H_2S, etc.), return to production a part of the burned carbon (in the form of fine soot), but also purify the air in residential premises saturating it with negative air ions and enriching it with oxygen.

In the discharge zone of the B 30-500 and AP-21 plants, the active factors affecting the chemical process are as follows:

- high voltage of the electric field;
- secondary ionization of substances;
- polarization of molecules, excitation of molecules and atoms;
- high temperature;
- photoionization;
- microwave radiation (electromagnetic waves);
- shock wave.

Process gases entering the B 30-500 and AP-21 units have the following component composition: CO_2, CO, SO_2, CH_4, N_2, O_2, H_2O.

Experimental part. In the reaction (discharge) zone, in the presence of the active factors described above, there can take place the reactions of all components with the formation of elementary substances and various compounds, i.e. taking into account the experimental data obtained in the laboratory of the ABsalut Ecology LLP, it follows that in the near-cathode unipolar charged region of the B 30-500 and AP-21 plants, in the conditions of a non-equilibrium weakly ionized plasma, ionization and dissociative processes can occur with the formation of various radicals and ions [3].

In the aggregate, all these processes can lead to the reduction of carbon oxides (CO_2), sulfur dioxide (SO_2) and nitrogen oxides (II, IV).

- CO_2

a) occurrence of complete or partial dissociation of carbon oxides:

$$CO_2 \rightarrow C + O_2$$

$$CO_2 \rightarrow CO + \tfrac{1}{2} O_2$$

$$CO \rightarrow C + \tfrac{1}{2} O_2$$

$$CO^* + CO^* \leftrightarrow C + CO_2$$

$$CO_2{}^*{}_{(г)} + C_{(т)} \rightarrow C_{(о)} + CO_{(г)}$$

b) processes of reducing by atomic hydrogen:

$$CO_2 + H \rightarrow C + HO_2$$
$$CO + 2H \rightarrow C + H_2O$$

c) carbon oxides interaction with atomic oxygen:

$$CO_2^* + O \leftrightarrow CO + O_2$$

d) carbon oxides interaction with forming methane, other hydrocarbons and elemental carbon:

$$8H + CO_2 \rightarrow CH_4 + 2H_2O$$
$$CO + 3H_2 \leftrightarrow CH_4 + H_2O$$

$CH_4 \rightarrow C_2H_2$, C_2H_4, C_2H_3 and others → solid products.

Thus, in the unipolar (negative) charged zone, carbon dioxide dissociation and reduction reactions are possible.

- **SO_2** - the mechanism of electrochemical transformations is also possible, leading to the reduction of sulfur dioxide molecules to elemental sulfur in the dark discharge zone in the solid needle electrode – gas – liquid anode system [4].

a) complete or partial dissociation of sulfur dioxide molecules

$$SO_2 \rightarrow S\downarrow + O_2$$

b) reducing sulfur dioxide by atomic hydrogen

$$SO_2 + 4H^* = S\downarrow + 2H_2O$$

c) reducing by hydrogen sulfide with forming elemental sulfur (hydrogen sulfide is one of the intermediate products that are formed when reducing sulfur dioxide):

$$6H^* + SO_2 = H_2S + 2H_2O$$
$$SO_2 + H_2S = 3S\downarrow + 2H_2O$$

d) in the reducing gas discharge medium there is also possible the reaction of hydrogen sulfide H_2S dissociation to free sulfur:

$$H_2S \rightarrow S + H_2 \text{ [5]}$$

- **N_xO_y** – here there are also possible electrochemical transformations of nitrogen oxides to the elemental composition (nitrogen).

$$N + NO \rightarrow N_2 + O$$
$$N + NO_2 \rightarrow 2NO$$
$$N + NO_2 \rightarrow N_2 + 2O$$
$$O + NO_2 - O_2 + NO$$
$$N_2O \rightarrow 2N_2 + O_2$$
$$2NO_2 \rightarrow N_2 + 2O_2 \text{ [6]}$$

Today, as a result of tremendous work, the industrial unit B 30-500 provides the degree of purification of process gases of at least: an integrated one 99.7%; from carbon monoxide (CO) 97%; from sulfur dioxide (SO_2) 95%; from nitric oxide (NO_2) 80%; from dust and aerosol particles 99.5%. The data has been repeatedly confirmed:

1) by specialists of the ABsalut Ecology LLP company on German Testo 350 instruments. Using this device, there can be monitored the operation of an industrial gas treatment plant and recorded the cleaning changes in real time.

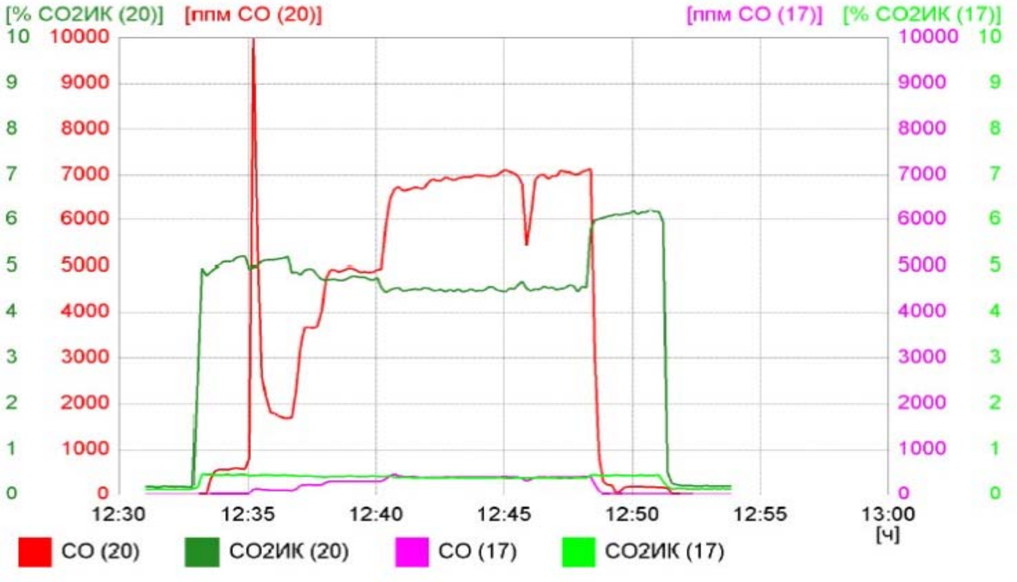


Figure 1 - Gas measurements in the reaction zone of the industrial gas cleaning plant

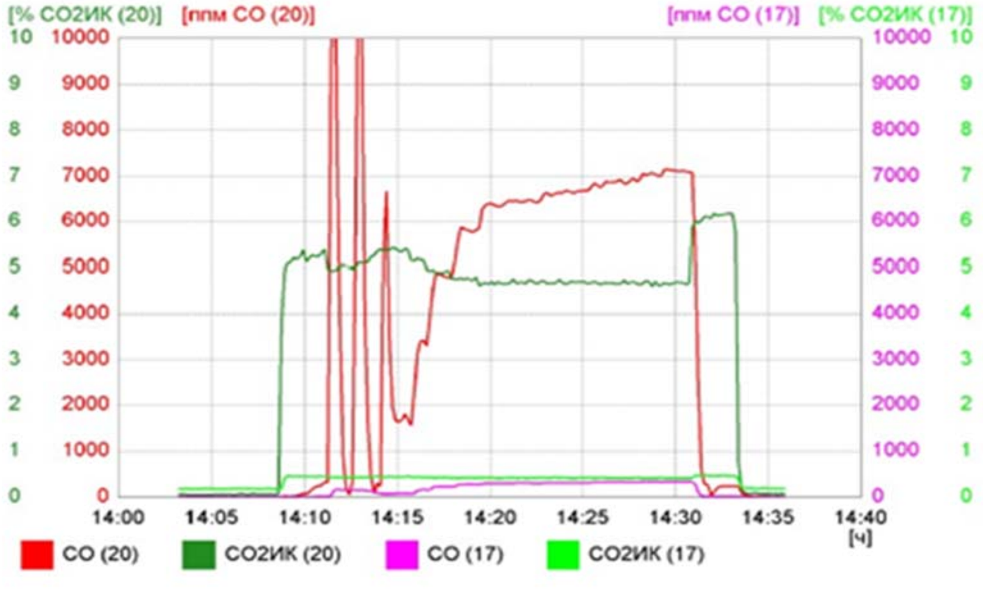


Figure 2 - Gas measurements in the reaction zone of the industrial gas cleaning plant

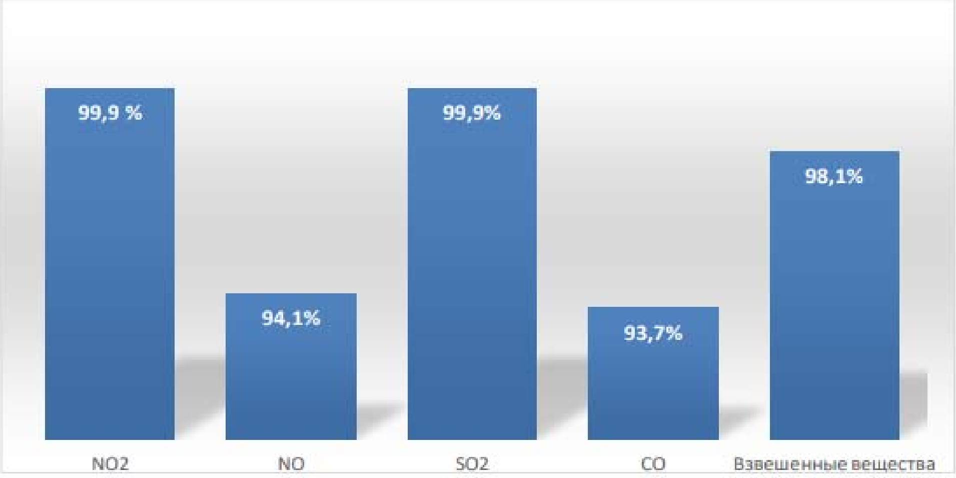
The graphs are plotted using two Testo 350 instruments: one instrument measures gas at the inlet to the gas treatment plant, the other one at the outlet. The graphs show 4 lines of different colors:

- CO (20) - red line, CO2IK (20) - dark green line show the amount of gas at the inlet to the gas treatment plant, i.e. gas concentration before cleaning;
- CO (17) - pink line, COIK (17) - light green line show the amount of gas at the outlet of the gas treatment plant, i.e. gas concentration after cleaning.

To the left and right of the graphs there are scales of the CO_2 range in percent and CO in ppm.

1) Results obtained by the independent laboratory of the Tsentrgeolanalit LLP.

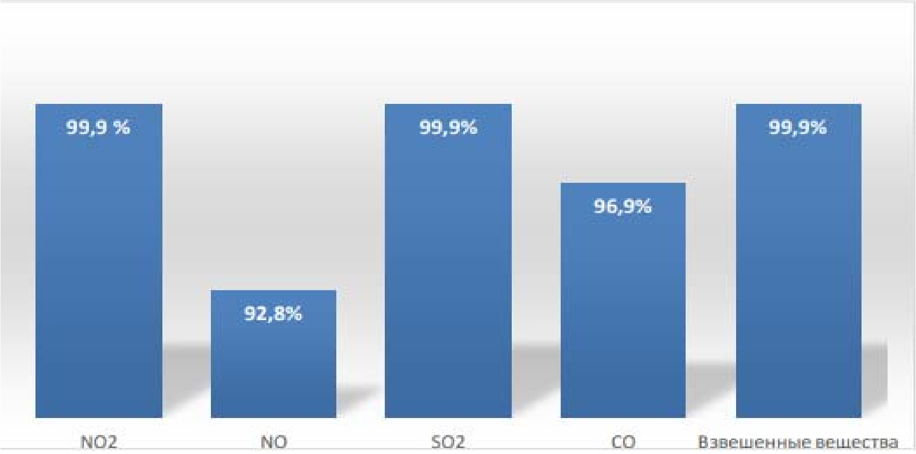
Minutes No. EC050517/1. Meteorological conditions: T +3°C, pressure 718 mm Hg, humidity 70%. Sampling equipment: Aspirator ABA-180, Gas analyzer DAG-500.



Suspended matters

Figure 3 - Gas measurements in the process of operation of the industrial gas cleaning plant. Minutes No. EC050517/1

Minutes No. EC061117/1. Meteorological conditions: T +24°C, pressure 707 mm Hg, humidity 20%. Sampling equipment: Aspirator ABA-180, Gas analyzer DAG-500.



Suspended matters

Figure 4 - Gas measurements in the process of operation of the industrial gas cleaning plant. Minutes No. EC061117/1

The introduction and use of the results of these studies allows preparing for the implementation of an integrated quality and environmental management system (ISO 9001: 2015, ISO 14001: 2015) at the ABsalut Ecology LLP, increasing the efficiency of process gas purification processes, as well as preparing a draft program for the use of the materials, obtained as related materials (fullerenes, carbon black, etc.) during the operation of the plants. Based on the results of these studies, measures were prepared to further improving the plant for cleaning process gases and atmospheric air, and the technology of cleaning and reducing the purification products.

The plant by A.V. Borissenko is intended not only for purifying nature, but also for obtaining useful substances from harmful wastes.

From all the above-said it follows that the scientific and engineering group of the ABsalut Ecology LLP headed by Dr. of Chemistry, Professor, Academician A.V. Borissenko, has developed and introduced the technology that uses a new activation method of cleaning industrial and utility gases in the unipolar ionized region when exposed to a strong electric field. This technology is patented and has no analogues in the world. With its help there can be solved one of the vital problems of the mankind: atmospheric air pollution.

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ТЕХНОЛОГИЯЛЫҚ ГАЗДЫ ТАЗАЛАУДЫҢ АКТИВАЦИЯЛЫҚ ӘДІСІ

Аннотация. Бұл мақалада технологиялық газ шығарындыларын SO2 (кемінде 90%), NOx (кемінде 80%), CO2 (кемінде 90%) және шаң тәріздес бөлшектерден (99,9%) тазартуға қабілетті В30-500 және АП-21 өнеркәсіптік электрохимиялық аэроиондық қондырғылардың ҚарМТУ-мен "ABsalut Ecology" ЖШС бірлескен зерттеулерінің нәтижелері келтірілген.

В30-500 және АП-21 қондырғыларының разрядтық аймағында химиялық процеске әсер ететін белсенді факторлар мыналар болып табылады: электр өрісінің жоғары кернеуі; заттардың қайталама иондалуы; молекулалардың поляризациясы; жоғары температура; фотоионизация; СВЧ-сәулелену; соққы толқыны.

Қондырғының реакциялық аймағында бір уақытта екі процесс өтеді- CO_2, CO, NOx, SO_2 оксидтерін активтендіру және электрондық инжектордың белсенді аймағындағы Элементарлық заттарға дейін қалпына келтіру. Реакциялық аймақта CO_2, CO, NOx, SO_2 оксидтерін қалпына келтіру әр түрлі тетіктер бойынша бір мезгілде өтеді: каталитикалық қалпына келтіру және диссоциация. Каталитикалық жүйе қондырғысында химиялық реакциялардың жылдамдығын анықтайтын белсенді бөлшектердің көзі болып табылатын электрондық инжектор болып табылады. CO, NH_3 қалпына келтіргіштер тазартылатын газда болады, сондай-ақ қондырғының реакциялық аймағында құрылады.

Реакциялардың өтуі нәтижесінде қарапайым заттар пайда болады. Электр өрісінің кернеулігіне, сондай-ақ жекелеген процестердің жылдамдығына электр өрісінің кернеулігіне қатты байланысты, токтың тығыздығына байланысты болуы мүмкін, сондықтан осы параметрлерді өзгерте отырып, селективтілікті, қондырғыдағы қалпына келтіру процестерінің жылдамдығын өзгертуге болады.

Әр түрлі радикалдар мен иондардың пайда болуымен ионизациялық және диссоциативтік процестердің өтуі жүзеге асырыла отырып, әлсіз ионизирленген плазма жағдайында көрсетілген. Аэрозольдар мен шаңды ұстау дәрежесі шаң тәріздес бөлшектер мөлшерінің азаюымен артады, ал құрғақ электр сүзгілерінде керісінше нөлге дейін төмендейді.

Технологиялық газдарды тазарту бойынша қондырғылардың тиімділігін арттыру жолдары анықталды (жаңа қондырғылардың геометриялық параметрлері, олардың өнімділігін арттыру, жаңа жоғары вольтты қоректену көздерін, флотациялық-сүзу құрылғыларын, диспетчерлік бақылау жүйелерін пайдалану және т.б.).

Газ тазарту қондырғысының тиімділігі 5 микрон және одан төмен мөлшерден бастап ауланатын аэрозольдер бөлшектерінің мөлшерін азайтқан кезде төмендетілмейді, тазарту тиімділігі 100%- ға жақындап келеді.

Зерттеу нәтижелері тазартқанға дейін және кейін газ концентрациясын көрсететін графиктер түрінде келтірілген. Ауаны шаң тәріздес бөлшектерден және аэрозоль қоспаларынан тазарту дәрежесі 60%-дан 99%-ға дейін ауытқиды.

Түйін сөздер: электрохимиялық қондырғылар, ауаны иондау, атмосфераның ластануы, экология, бастамашылық жасау, көміртекті конверсиялау, аэроионизаторлар, циклондар, скрубберлер, электр сүзгілері.

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АКТИВАЦИОННЫЙ МЕТОД ОЧИСТКИ ТЕХНОЛОГИЧЕСКОГО ГАЗА

Аннотация. В данной статье приведены результаты совместных исследований ТОО «ABsalut Ecology» с КарГТУ промышленных электрохимических аэроионных установок В30-500 и АП-21, способных очищать технологические газовые выбросы от токсичных примесей SO_2 (не менее 90%), NOx (не менее 80%), CO_2 (не менее 90%) и пылевидных частиц (99,9%) с возвращением в производство часть сожжённого углерода (в виде мелкодисперсной сажи).

Установлено, что в разрядной зоне установок В30-500 и АП-21 активными факторами, воздействующими на химический процесс, являются: высокое напряжение электрического поля; вторичная ионизация веществ; поляризация молекул; высокая температура; фотоионизация; СВЧ-излучение; ударная волна.

В реакционной зоне установок протекают одновременно два процесса – активация и восстановление оксидов CO_2, CO, NOx, SO_2 до элементарных веществ активной зоне электронного инжектора. Восстановление оксидов CO_2, CO, NOx, SO_2 в реакционной зоне протекают одновременно по различным механизмам: каталитическое восстановление и диссоциация. Установлено, в установке каталитической системой является электронный инжектор, который служит источником активных частиц, определяющих скорость химических реакций. Восстановители CO, NH_3 присутствуют в очищаемом газе, а также образуются в реакционной зоне установки.

В результате протекания реакций образуются элементарные вещества. Константы скоростей элементарных процессов в разряде резко зависят от напряженности электрического поля, а также скорости отдельных процессов, могут нелинейным образом зависеть от плотности тока, поэтому изменяя эти параметры можно изменять селективность, скорость восстановительных процессов в установке.

Показаны в условиях неравновесной слабоионизированной плазмы, осуществимо протекание ионизационных и диссоциативных процессов с образованием различных радикалов и ионов. Степень улавливания аэрозолей и пыли увеличивается с уменьшением размеров пылевидных частиц, а в сухих электрофильтрах, наоборот, падает до нуля.

Определены пути повышения эффективности установок по очистке технологических газов (геометрические параметры новых установок, увеличение их производительности, использование новых высоковольтных источников питания, флотационно-фильтрационных устройств, систем диспетчерского контроля и пр.).

Эффективность газоочистной установки не снижается при уменьшении размера частиц улавливаемых аэрозолей, начиная с размера около 5 микрон и ниже, эффективность очистки приближается к 100%.

Результаты исследований приведены в виде графиков, которые показывают концентрация газа до и после очистки. Степень очистки воздуха от пылевидных частиц и аэрозольных примесей колеблется от 60% до 99%.

Ключевые слова: сажа, активация, электрохимические установки, ионизация воздуха, загрязнение атмосферы, экология, инициирование, конверсия углерода, аэроионизаторы, циклоны, скрубберы, электрофильтры.

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HYDROGENATION OF AROMATIC HYDROCARBONS ON MODIFIED METAL CATALYSTS SUPPORTED ON CARBON CARRIER

Abstract. The catalyst of the selection hydrogenation of benzene in engine fuels is developed. Methods of drawing low-percentage rhodium catalysts on the basis of natural and synthetic carriers are developed for hydrogenation of benzene in main products. It is established the optimum modes of carrying out hydrogenation of benzene on rhodium catalysts applied on zeolite and clay with the given structural characteristics. It is defined that 1 % the rhodium catalysts supported on zeolite increases selectivity on cyclohexane. Results showed that carrying out reaction of hydrogenation of benzene on the developed rhodium catalyst allows to receive pollution-free motor fuel with the low maintenance of aromatics.

Keywords: hydrogenation, aromatic hydrocarbons, benzene, catalysts, clay, zeolite.

Introduction. The rapid growth of road transport in the developed countries where car density has reached 10-20 km^2 resulted in severe contamination of the environment and especially emissions of harmful air basin exhaust gases [1]. A huge amount of pollutants produced during the combustion of motor gasoline, results in the fact that environmentally requirements are deduced in first place among all the requirements for gasoline. Ecological Problems of associated with environmental pollution at the expense exhaust emissions requires improving the quality of motor fuels. Aromatic hydrocarbons are subjected to catalytic hydrogenation to transfer them to naphthene for reduce the amount of them. The study of the process of catalytic hydrogenation of aromatic hydrocarbons and suitable catalysts improvement are an important task. The structure of aromatic hydrocarbons has a significant effect on carbon formation in combustion chambers and valves on engines, which impairs their performance indicators such as power, economic and environmental characteristics. Under the influence of high temperatures, aromatic hydrocarbons undergo oxidative conversion and are the main source of fouling [2]. Among the aromatic hydrocarbons the most low-boiling aromatic compound is benzene. Benzene damages many organs and vital systems, but, in general considering he is a poison blood [3]. Petrol fraction has to have several properties for using them as a component of engine fuel. So, for example, there is the extreme content of aromatic hydrocarbons and sulfur compounds above which the fraction cannot be used. This extreme content is caused by the fact that the considered fraction in termination products contains in particular quantity, and the compounding will not allow to receive the marketable products answering on aromatic and sulfur content are gray to requirements of standards [4].

Mainly, various hydrogenation processes are applied to decrease in content of sulfur and aromatic compounds in petrol fractions. Hydrotreating, hydroupgrading, hydro-dearomatization are considered to them. The specified processes are carried out with use of sulfidic Ni-W and Co-Mo. Processes are carried out in flowing system at temperatures 350-450 ℃ at feed rate of raw materials 1-3 of the 1/hour and pressure of hydrogen, as a rule, to 50 atm. (sometimes even to 70-100 atm.) Reactions of catalytic hydrogenation of benzene and dehydrogenation of cyclohexane can go only on the transitional metals having face-centered cubic structure or hexagonal structure and besides atomic radiuses of strictly particular sizes [5-6]. Palladium, platinum, iridium, rhodium, osmium are active catalysts of hydrogenation of benzene and a dehydrogenation to cyclohexane and meets the above requirements [7]. At the beginning of our century, Sabatye and Sanderan found that benzene is easily hydrogenated into cyclohexane in the presence of nickel catalysts. Hydrogenation carried out at T= 120-250 ℃ and P=2-6 MPas and rate of volume flow on benzene 0.5-2 p^{-1}. Conversion level reaches 95 %. On platinum catalysts hydrogenation of benzene proceeds under the same conditions, as on nickel, and the almost complete conversion at selectivity is reached, by the close to 100 % [8-9]. The advantages of platinum catalysts are necessary to carry them a little smaller sensitivity to sulfur compounds and a possibility of reactivation of the catalyst, than at nickel. The disadvantages are sensitivity to presence of moisture at raw materials that causes the necessity carefully to drain benzene [10].

Selective hydrogenation of benzene to cyclohexane (SHBC) has attracted many attentions during the past decades [11-12], due to its simplicity, high yields and costs compared with other cyclohexane production methods. Hydrogenation of benzene in cyclohexane is the main method of receiving cyclohexane. Cyclohexane is used for production of caprolactam in the industry of synfils, for receiving hexane diacid and cyclohexanol. Clear benzene, free of sulfur compounds, hydrogenate in a liquid phase over the nickel or platinum catalyst at 4 MPas, 200 ℃ and rate of volume flow of supply of raw materials 1-3p^{-1}. The benzene containing sulfur and nitrogen compounds is hydrogenated over the nickel tungsten sulphide catalyst at 24 MPs, 300 °C and rate of volume flow 0.5 p^{-1}. At hydrogenation of benzene in cyclohexane light-end and other by-products are practically not formed [13-14]. Nickel catalysts on carriers are most often used: alumina, chromium oxide, etc. The nickel-chrome catalyst, as well as other nickel contacts, easily gets poisoned with sulfur compounds. Poisoning is bound to strong, irreversible adsorption of the last, i.e. to blocking of the fissile surface, and at elevated temperatures and to formation of chemical combinations [15].

Catalysis using nanoscale materials has been one of the most active research areas in recent years because of its relevance to chemical and energy related applications. Recently, several excellent review articles have shown that nanocatalysts with high dispersion and narrow size distributions stabilized by appropriate supports or capping materials can work under milder conditions with higher activity and selectivity as compared to conventional heterogeneous catalysts [16-17]. It is known that transition metal nanoparticles are effective catalysts, and the catalytic activity depends on their shape, size, and surface structure of the solid supports [18-20]. Modifying of natural zeolites becomes particularly important in connection with a possibility of creation of catalysts on their basis for process of thermocatalytic transfomation of low-quality hydrocarbon raw materials in alicyclic rings. It is established that the greatest positive effect gives modifying of zeolites platinum, palladium and rhodium.

In the real work optimum conditions of a dearomatization on the basis of benzene hydrogenation reaction, for receiving cyclohexane are picked up. Rhodium catalysts operate in more weak conditions and have more selectivity than the traditional systems based on other metals. Kazakhstan possesses huge reserves of natural zeolite and clay which can be used as catalysts of hydrogenation of aromatic hydrocarbons for receiving an ecological straight product – cyclohexane. The aims of the work were synthesis of new rhodium nanosized catalysts on the carbon carrier with the increased efficiency and having high selectivity at hydrogenation of aromatic hydrocarbons for receiving pollution-free engine fuel.

Experimental. Red clay, Tonkeris clay, zeolite are used, as a basis for body height and formation of nanocarbon composites. The choice of Tonkeris clay is caused by the fact that as a part of this clay oxides Fe_3O_4, TiO_2, MgO, Cr_2O_3 which have to promote education in the course of a carbonization of fibrous carbon and nanostructures were found. This catalytic carbon causes increase in a specific surface area and porosity that leads to formation of a transport time of system [21].

Rhodium catalysts on the basis of zeolite are prepared by an impregnation method with the subsequent calcination. The impregnated zeolite is exposed to process of a carbonization during 3-5 clocks. The received catalyst containing 0.5-2 % of rhodium is used for hydrogenation.

Carbon materials were prepared by a carbonization and activation at a temperature 400 °C for the carrier. Argon current is passed for increase in a specific surface area to exemplars during a carbonization. Carbonization was carried out at temperatures of 650-750 °C at an interval of 25°C. Propane is used as a source of carbon.

The research of activity of the synthesized catalysts was conducted in laboratory flowing installation of high pressure in the range of temperatures of 50-300 °C, pressure of 0.1-3.0 MPs, rate of volume flow 1.0-4.0 hour^{-1}. Feed rate of hydrogen made 30-60 ml/min.

Hydrocarbon part was analyzed on a chromatograph «Chromatec Cristall 5000». The detector is flame and ionization. Gas carrier is nitrogen, temperature from 90°C to 180°C, a stainless steel column (long 3m, diameter 3mm).

Electronic and microscopic studying of exemplars was carried out on the JEM-100CX device at the accelerating voltage of 100 kV. The device allows study objects at high-res (3.0E).

Results and discussion. The rhodium and cobalt carbon catalysts supported on various carriers were prepared and tested. Also low-percentage rhodium carbon catalysts on the carbonized apricot stones were synthesized. Different concentration of rhodium supported on a series of carriers: Al_2O_3, zeolite, clay. Cobalt contained carbon catalysts were prepared for comparison of catalytic activities.

At researches of clay breeds from various regions of Kazakhstan for production of catalysts, us it is established what the kaolinit of clays is inexpedient to use additives for carriers of carbon catalysts. Carbonization of clays in the range of temperatures 700-750 °C well develops a specific surface area. Chemical composition of clays is presented in table 1.

Studying chemical composition of clays and a research of process of a carbonization it is possible to tell all clays can be used as carriers of rhodium carbon catalysts. As a part of clays as appears from table 8, there are ion-exchange cations: Na^+, K^+, Ca^{2+}, Mg^{2+} which decrease almost twice at processing. Also the increased content of iron in TC is observed.

Table 1 – Chemical composition of clays

Clay	Mass %										
	SiO_2	Al_2O_3	Fe_3O_4	TiO_2	Na_2O	K_2O	CaO	MgO	Cr_2O_3	H_2O	others
TC	52.4	15.6	8.2	1.7	1.3	3.22	1.2	4.4	0.08	8.3	3.6
RC	65.3	21.7	0.8	1.7	0.21	0.83	0.7	0.3	-	4.9	5.8
WC	56.8	15.6	8.9	0.9	0.7	2.9	0.5	3.2	0.1	7.5	2.9

Physical and chemical characteristics of the synthesized catalysts are shown in table 2. Rhodium salts apllied on zeolites for creation of bifunctional catalysts of hydrogenation. The metal centers allow to maintain low equilibrium concentration of olefins in a reaction mixture and prevent coking up of a surface of the catalyst.

Table 2 – Main physical and chemical characteristics
of the synthesized rhodium carbon catalysts on different carriers

Indicatores	Zeolite	Zeolite	Clay	Zeolite+Clay	Al_2O_3
Content of Rh, mass, %	-	0.5	0.5	0.5	0.5
Content of C. mass. %	-	5.0	15.0	12.0	9.0
Surface area. m^2/g	112.0	122.0	106.0	156.0	96.0
Carbonization. Hour	1.0	3.0	1.0	3.0	2.0

Results of hydrogenation of benzene on cobalt and rhodium catalysts at a temperature of 450 °C and 25 atm are shown in table 3. The composition of hydrogenates of benzene depends not only on a catalytic activity and also from conditions of supply of hydrogen and benzene. Follows from the received experimental results that with increase in supply of benzene in an original stock. a cyclohexane exit gradually decreases because of shortage of hydrogen. On cobalt catalysts conversion of benzene contains 51 % at temperature of 430 °C.

Table 3 – Conversion of benzene on different catalysts (CAS)

T.^{0}C	Conversion of benzene %		
	0.5 % Rh	5 % Co	7 % Co
350	47	24	27
380	49	29	32
400	59	33	35
430	64	41	42
450	65	42	45
480	65	45	48

From all tested exemplars, the rhodium catalyst on zeolite differed in the highest activity. It is considered that for efficient operation of bifunctional catalysts the metal centers have to be as it is possible closer to the acid centers therefore most often the metal component is applied immediately on the surface of zeolite.

Further synthesized rhodium catalysts applied on clay. Their catalytic activity in benzene hydrogenation reaction was checked. It is by practical consideration defined that at a research of activity of 0.5-2 % of the rhodium put catalyst formation of methylcyclopentane, methylcyclopentane, cyclohexane is observed.

Figure 1 shows the graphical dependence of benzene conversion on temperature. It can be seen from the figure that among all the modified catalysts, the catalyst based on clay containing 0.5 % rhodium exhibits the least catalytic activity.

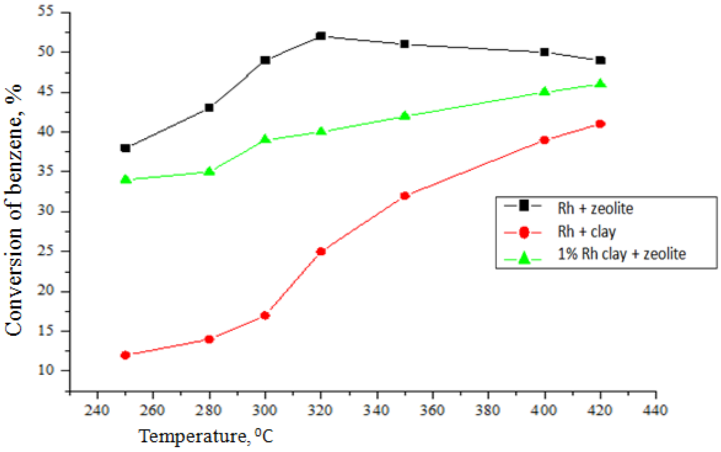


Figure 1 – Dependence of benzene conversion on temperature on different catalyst

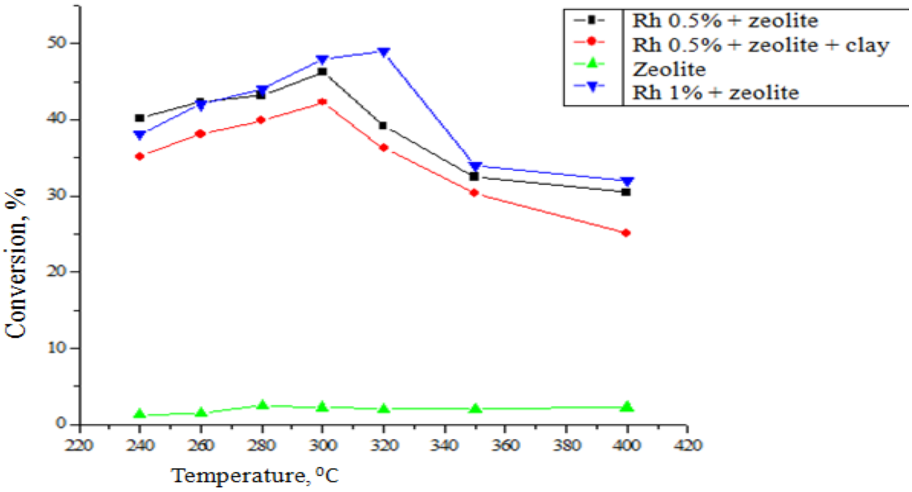


Figure 2 – Dependence of the yield of cyclohexane on various catalysts

Dependence of yield of cyclohexane on amount rhodium in catalysts are shown in Figure 2. The catalytic activity increases in the benzene hydrogenation reactions, when the zeolite is modified with 1 % rhodium. According to data figure 2, Rh 1% catalyst supported on zeolite is the most active catalysts. As noted above, the zeolite modified with 0.5 rhodium allows one to obtain dimethylbutane (2,2-DMB), methylcyclopentane and cyclohexane in the mixture of isomers. A comparative physicochemical analysis of the carbonized modified rhodium zeolite showed that catalytic hydrogenation of benzene catalyzed in the reactions for obtaining valuable by-products.

The obtained results showed that in the study of the catalytic activity of rhodium catalysts, active and selective catalyst was 1% rhodium supported on zeolite, the maximum amount of the desired products was observed in the reaction mixture.

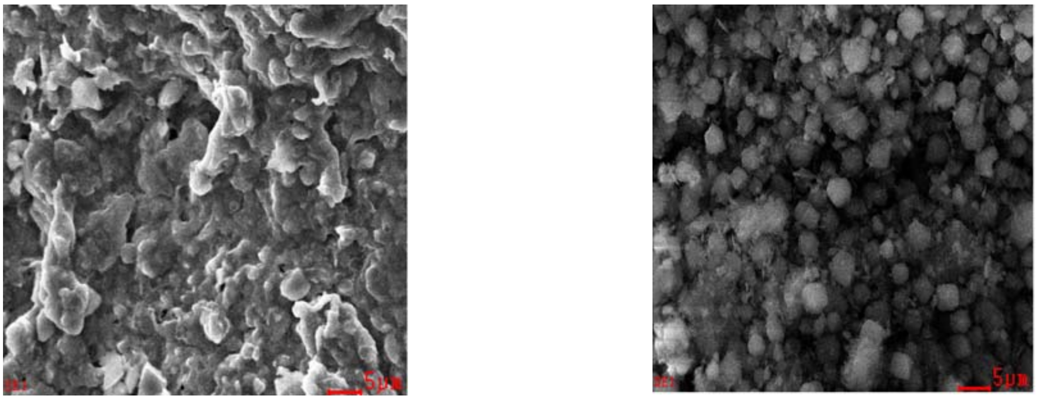
Catalysts with a different ratio of components of the fissile phase were prepared and investigated in the course of benzene hydrogenation. The catalyst synthesized rhodium 0.5 % worked within 20 hours in an interval of temperatures 400-420 °C under pressure hydrogen of 18 atm. before activity loss.

Catalysts with a different ratio of components of the fissile phase were prepared and investigated in the course of benzene hydrogenation. The catalyst synthesized rhodium 0.5 % worked within 20 clocks in an interval of temperatures 400-420 °C under pressure hydrogen of 18 atm. before activity loss. The deactivated catalyst was investigated by physical and chemical methods of the analysis. Comparisons of specific surface areas and activity of prepared, the deactivated and regenirated exemplars shows, that at thermal regenerations in the atmosphere of hydrogen catalytic activity is restored (table 4).

After regeneration in argon current at temperatures of 650 °C on rhodium catalysts activity for 50 % allowed to restore catalytic carbon. And regeneration of rhodium catalysts in the atmosphere of hydrogen restored catalytic activity for 80 %.

Table 4 – Characteristics of synthesized Rh catalysts

Catalysts	Surface area. m^2/g
0.5 % Rh on carbon	535
0.5 % Rh on deactivated carbon	180
0.5 % Rh on deactivated carbon (in argon flow)	322
0.5 % Rh on regenerated carbon (in hydrogen flow)	480



a

b

a) – 1% of Rh/zeolite

b) – 0.5% of Rh/zeolite

Figure 3 – SEM pictures of catalysts

The synthesized rhodium catalysts were investigated by method by an electronic and microscopic method. It is shown in Figure 3, that exemplars of the rhodium catalyst put zeolite are in an amorphous crystalline state, and amorphous is understood as an amorphous state, i.e. in this state there can be also crystal ultra-dispersible particles with sizes less than 500 nanometers. Rhodium the applied zeolite with clay raises dispersion of a surface. Apparently from the figure 3 (b), rhodium catalysts nanoparticles of 50 nanometers in size, and were formed less.

Conclusion. The catalyst of the selection hydrogenation of benzene in engine fuels is developed. Methods of drawing low-percentage rhodium catalysts on the basis of natural and synthetic carriers are developed for hydrogenation of benzene in main products.

It is established the optimum modes of carrying out hydrogenation of benzene on rhodium catalysts applied on zeolite and clay with the given structural characteristics. It is defined that 1% the rhodium catalysts supported on zeolite increases selectivity on cyclohexane.

Influence of the rhodium catalyst on effectiveness in reactions of hydrogenation of benzene in cyclohexane and main products is defined. Conversion of 1 % the rhodium catalyst makes 75-80 %, with ultimate yield of isomers of 65 % (methyl cyclohexane, methylcyclopentane).

Results showed that carrying out reaction of hydrogenation of benzene on the developed rhodium catalyst allows to receive pollution-free motor fuel with the low maintenance of aromatics.

As a result it is possible to improve significantly ecological characteristics of engine fuel for achievement of parameters, conditioned Euros-4.

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АРОМАТТЫ КӨМІРСУТЕКТІ КӨМІРТЕК ТАСЫМАЛДАҒЫШТАҒЫ МОДИФИЦИРЛЕНГЕН МЕТАЛЛ КАТАЛИЗАТОРЫНДА ГИДРЛЕУ

Аннотация. Соңғы жылдары көп ел мотор отының сапасына қатысты қатаң талап қоюда. Мотор отынына қойылған талаптар автомобильді бензин құрамындағы күкірт мөлшері, буланғыштығы мен бензиннің көміртекті қоспасы: ароматты және олефинді көмірсутектер мөлшерін азайтуға негізделеді. Көмірқышқыл газы, күкірт диоксиді, күйе сынды зиянды заттар олардың жануы барысында қозғалтқышқа көп мөлшерде түседі. Сонымен қатар, көптеген ароматты көмірсутектер аса улы зат болып саналады.

Осыған байланысты мотор отыны құрамындағы ароматты көмірсутектің, әсіресе, бензолдың мөлшерін азайту мәселесі өзекті болып есептеледі. Бензол және оның шала жану өнімі бензопирен-канцерогенді зат, адам және жануар өміріне қауіп тудырады. Ароматты көмірсутекті каталитикалық гидрлеуді зерттеу және қазіргі таңда нарықтағы катализаторлардың сапасын арттыру да маңызды. Бензолды каталитикалық гидрлеу реакциясы тек қана атомдық радиусы нақты бір өлшемдерге ие, түйіршіктелген кубтік немесе гексагоналды құрылымға ие ауыспалы металдарда жүреді. Палладий, платина, иридий, родий, осмий бензолды гидрлеу үдерісінің активті катализаторы және жоғарыдағы аталған талаптарға толықтай сай келеді.

Циклогександы бензолды гидрлеу реакциясы арқылы алуға негізделген деароматтау үрдісінің тиімді шарттары осы жұмыста таңдалынды. Өзге металдарға негізделген дәстүрлі жүйелерден гөрі, родий катализаторлары жоғары селективті және жеңіл жағдайда қызмет атқарады. Экологиялық таза өнім циклогександы алуға арналған ароматты көмірсутектерді гидрлеу үрдісі катализаторларының тасымалдағышы ретінде қолданыла алатын саз бен цеолиттің үлкен қоры Қазақстанда бар. Экологиялық таза мотор жанармайын алу үшін ароматты көмірсутектерді гидрлеуге арналған жоғары селективті көміртекті тасымалдағышта өнімі жоғары отандық родийлі катализаторды алудың жаңа әдістері жұмыстың мақсаты болып саналады.

Карбондау үдерісі кезінде талшықталған көміртегі мен наноқұрылымның пайда болуына себеп болатын Fe_3O_4, TiO_2, MgO Cr_2O_3, оксидтері болғандықтан Төңкер глинасы таңдалды. Цеолит негізіндегі родий катализаторларын отырғызу әдісі арқылы алады. Синтезделген катализаторлардың белсенділігі жоғары қысымдағы зертханалық қондырғыда, 50-300° С температура және 0,1-3,0 МПа қысым диапазонында зерттелді, көлемдік ағым жылдамдығы 1,0-4,0 сағ$^{-1}$.

Мотор отын құрамындағы бензолді селективті гидрлеуге қолданылатын катализатор дайындалды. Бензолды мақсатты өнімге гидрлеу үшін табиғи және синтетикалық тасымалдағыштар негізінде төменгі мөлшердегі родий отырғызу әдісі қолданылды. Құрылымдық сипаттамалары белгілі цеолит пен глинаға отырғызылған родий катализаторларында бензолды гидрлеудің тиімді режимі анықталды. Цеолитке отырғызылған 1% родий катализаторы циклогексан бойынша селективтілікті арттыратыны анықталды. Бензолды циклогексанға дейін гидрлеу реакциясының эффективтілігіне родий катализаторларының әсері анықталды. 1% родий катализатор қатысында, үдеріс нәтижесінде 65% (метилциклогексан, метилциклопентан) изомерлер шығымы болған жағдайда конверсия 75-80% көрсетті.

Нәтижелерге сәйкес, жасалынған родий катализаторында бензолды гидрлеуді жүргізу құрамында ароматты көмірсутектің мөлшері төмен экологиялық таза мотор отынын алуға мүмкіндік беретіндігін көрсетті. Нәтижесінде Еуро-4 стандарттарына сай параметрлерге жететін дәрежеде мотор отындарының экологиялық сипаттамаларын арттыруға болады.

Түйін сөздер: гидрлеу, ароматты көмірсутектер, бензол, катализаторлар, саз, цеолит

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ГИДРИРОВАНИЕ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ НА МОДИФИЦИРОВАННЫХ МЕТАЛЛ–КАТАЛИЗАТОРАХ НА УГЛЕРОДНОМ НОСИТЕЛЕ

Аннотация. В последние годы все более ужесточаются требования к качеству моторного топлива во всех странах. Строгие условия на автомобильный бензин ограничивают содержание серы, испаряемость и углеводородный состав бензина: ароматических и олефиновых углеводородов. Вредные вещества, такие как окись углерода, двуокись серы, сажа попадают в двигатели в больших количествах при их сгорании. Кроме того, многие ароматические углеводороды также являются высокотоксичными веществами.

В связи с этим, уменьшение количества ароматических углеводородов, особенно бензола, в моторных топливах является актуальной и неотложной задачей. Бензол и продукт неполного окисления бензопирен – канцерогенное вещество, накапливающееся в окружающей среде, оказывает негативное влияние на безопасность жизни людей и животных. Важной задачей является изучение процесса каталитического гидрирования ароматических углеводородов и улучшение соответствующих катализаторов. Реакции каталитического гидрирования бензола могут протекать только на переходных металлах, имеющих гранецентрированную кубическую или гексагональную структуру и, кроме того, атомные радиусы строго определенных размеров. Палладий, платина, иридий, родий, осмий являются активными катализаторами гидрирования бензола циклогексана и отвечают вышеуказанным требованиям.

В данной работе подобраны оптимальные условия деароматизации на основе реакции гидрирования бензола для получения циклогексана. Родиевые катализаторы работают в более мягких условиях и обладают большей селективностью, чем традиционные системы, основанные на других металлах. Казахстан обладает огромными запасами природного цеолита и глины, которые могут быть использованы в качестве носителя катализаторов гидрирования ароматических углеводородов для получения экологического чистого продукта – циклогексана. Целью работы являются новые методы получения родиевых наноразмерных катализаторов с повышенной продуктивностью на углеродном носителе, обладающем высокой селективностью при гидрировании ароматических углеводородов для получения экологически чистого моторного топлива.

Выбор тонкерской глины вызван тем, что в составе определены оксиды Fe_3O_4, TiO_2, MgO Cr_2O_3, которые способствуют образованию волокнистого углерода и наноструктур в процессе карбонизации. Родиевые катализаторы на основе цеолита получают методом пропитки с последующим прокаливанием. Исследование активности синтезируемых катализаторов проводилось в лабораторной установке высокого давления в диапазоне температур 50-300° С, давления 0,1-3,0 МПа, скорости объемного потока 1,0-4,0 час$^{-1}$.

Разработан катализатор селективного гидрирования бензола в моторных топливах. Разработаны способы нанесения низкопроцентных родиевых катализаторов на основе природных и синтетических носителей для гидрирования бензола в целевые продукты. Установлены оптимальные режимы проведения гидрирования бензола на родиевых катализаторах, нанесенных на цеолит и глину с заданными структурными характеристиками. Определено, что 1% родиевых катализаторов, нанесенных на цеолит, увеличивает селективность по циклогексану. Влияние родиевого катализатора на эффективность реакции гидрирования бензола в циклогексан и в основные продукты были определены. Конверсия 1% родиевого катализатора составляет 75-80% при конечном выходе изомеров 65% (метилциклогексан, метилциклопентан).

Результаты показали, что проведение реакции гидрирования бензола на разработанном родиевом катализаторе позволяет получать экологически чистое моторное топливо с низким содержанием ароматических углеводородов. В результате можно значительно улучшить экологические характеристики моторного топлива для достижения параметров, соответствующих стандартам Евро-4.

Ключевые слова: гидрирование, ароматические углеводороды, бензол, катализаторы, глина, цеолит.

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SYNTHESIS AND STRUCTURE OF HYDRAZONE DERIVATIVES OF HARMINE

Abstract. The present paper deals with chemical synthesis based on 8-acetylharmine. It was established that interaction of 8-acetylharmine with hydrazine hydrate produces (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole in a yield of 69%. It was shown, that reaction of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole with functionally substituted aromatic aldehydes (anisaldehyde, 2-fluorobenzaldehyde, 2,4- dimethoxybenzaldehyde) by boiling in methanol leads to the formation of the corresponding *N*-arylidenehydrazones with 56-82% yields. The structure of the synthesized compounds was characterized on the basis of one-dimensional ^{1}H, ^{13}C and DEPT NMR methods, as well as data from two-dimensional COSY, HMQC, and HMBC spectra, elemental analysis and mass spectra. Correlation spectroscopic methods provided information for identification of three bond protons-protons and one bond protons-carbons correlations COSY (^{1}H -^{1}H) and HMQC (^{1}H-^{13}C, ^{1}H-^{15}N). Homo- and heteronuclear interactions, confirming the structures of new derivatives of harmine, are determined. The use of modern physicochemical and spectroscopic research methods in the present work allowed reliable and unambiguous characterization of the structure and properties of the obtained compounds.

Key words: harmine, hydrazone derivative of 8-acetylharmine, N-arylidenehydrazones, ^{1}H-, ^{13}C-NMR spectra, two-dimensional NMR spectra.

Introduction. It is well known that modification of alkaloids gives a wide opportunity to obtain compounds whose biological activity spectrum is significantly expanded and modified in comparison with the starting substance.

In order to search for new synthons and biologically active compounds and to find effective drugs of a given spectrum of activity, a chemical modification of the alkaloid harmine was carried out [1]. Alkaloid of β-carboline type harmine **1** is contained in the plant *Peganum harmala* L., widely distributed on the territory of Republic of Kazakhstan.

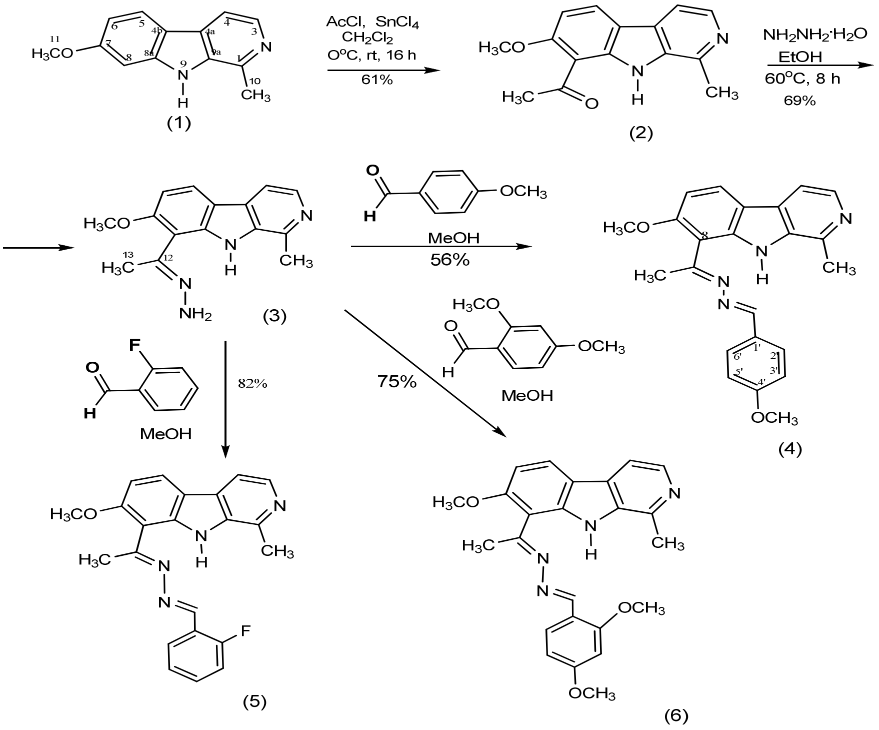
According to the literature data, the indole alkaloid harmine **1** has a wide spectrum of pharmacological activity. Harmine affects the central nervous system, showing neuroprotective activity in neurological diseases. Derivatives of harmine have neurotropic activity, and its water-soluble form, harmine hydrochloride, has antidepressant, antihypoxic (hypobaric hypoxia) and anti-Parkinson effects [1-6].

Moreover, it should be noted that in recent years, the synthesis of hydrazones has attracted great attention not only because of the significant biological activity of the target compounds, but also because the possible synthesis of various heterocycles based on them, including energy-intensive materials.

In this regard, our aim was to continue research on the transformation of the available alkaloid harmine in order to obtain new biologically active compounds.

Experimental part. Earlier, we published effective methods for the synthesis of derivatives of β-carboline alkaloids 8-formylharmine and 8-acetylharmine. By the condensation of 8-acetylharmine **2** with aromatic aldehydes the corresponding chalcones were synthesized, the reaction of which with hydrazine hydrate in acetic acid resulted in 3-substituted 1-acetylpyrazolines [7-11].

In continuation of our work, new derivatives of the alkaloid harmine **1** were synthesized; on the basis of 8-acetylharmine **2**, 8-acetylhydrazone harmine **3** was synthesized and a number of *N*-arylidenehydrazones harmine **4-6** were obtained with a yield of 56-82% (scheme 1).



The structure of the synthesized compounds was characterized by the complex of physicochemical methods: IR, UV, one-dimensional NMR ^{1}H, ^{13}C and DEPT and two-dimensional COSY spectroscopy (^{1}H -^{1}H), HMQC, HMBC (^{1}H-^{13}C, and ^{1}H-^{15}N), mass spectrometry and elemental analysis data.

Materials and research methods. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZR 500 MHz spectrometer (500 MHz ^{1}H and 125 MHz ^{13}C). The ^{19}F NMR spectrum of compound **5** was recorded on a JEOL JNM-ECZR 500 MHz spectrometer (282 MHz) in $CDCl_3$. The ^{15}N NMR spectra were obtained on a JEOL JNM-ECZR 500 MHz (60.84 MHz) in CD_3OD using CH_3NO, as monitor sample δ_N 167,6 ppm.

Different types of proton-proton and carbon-proton correlation spectroscopy were used to assign signals in the NMR spectra (COSY, DEPT, HMBC, HMQC). High-resolution mass spectra were recorded on a DFS Thermo Scientific mass spectrometer, evaporator's temperature 150-240 °C, EI ionization (70 eV). Melting points were determined on Opti Melt apparatus. The reaction progress was monitored by TLC method on Silufol UV-254 plates. For the detection of alkaloids derivatives the Dragendorff's reagent was used. The reaction products were isolated by column chromatography on Al_2O_3 (stage II act.).

Results of the study. We have established that the interaction of 8-acetylharmine **2** with an excessive amount of hydrazine hydrate in ethanol leads to the formation of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole **3**, yield 69%, composition $C_{15}H_{16}N_4O$, melting point 207-209 °C, $[\alpha]^{24}_D$ -187.5 (*c* 0.16; $CHCl_3$).

N-arylidenehydrazones of harmine **4-6** were prepared (yield 65-83%) starting from (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole **3** which easily reacted with functionally substituted aromatic aldehydes (anisaldehyde, 2-fluorobenzaldehyde, 2,4-dimethoxybenzaldehyde).

The IR-spectrum of compounds **3–6** contain intense stretching bands at 3327–3220 cm^{-1}, which belong to the (–NH) group, and at 3178–2827 cm^{-1} (C–H aromatic and methoxy groups). In the spectra of all compounds, a set of absorption bands was observed in the region of 1617–1606, and 1569–1418 cm^{-1}, corresponding to the presence of aromatic groups in the structure (C=N) and (C=C). The bending vibrations of the C=N-N groups correspond to bands 1293–1202 and 1113 cm^{-1}.

In the ^{1}H NMR spectrum of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole **3**, singlet signals were observed in the region of δ 2.71 and 2.12 ppm, corresponding to proton signals of the methyl groups at C-1 and C-12. Signals of protons of the methoxy group at C-7 were observed in the region of δ 3.86 ppm in a form of singlet. The proton signals H-3, H-4, H-5, H-6 of the β-carboline core appear at δ 8.15, 7.81, 8.12 and 7.04 ppm, with coupling of 5.8; 5.8; 8.2; 8.2 Hz, respectively. The characteristic signal of NH_2 groups was observed in the low field in the region of δ 8.03 and 8.05 ppm. The proton signal of the N-H group of the pyrrole ring was observed in the low magnetic field at δ 10.51 ppm.

The ^{13}C NMR spectrum of compound **3** contained 6 singlet signals at 116.47, 123.36, 135.64, 138.67, 141.58, 156.81 ppm, characteristic for carbon atoms C-4a and C-4b, C-9a, C-8a, C- 1, C-7, as well as 5 doublet signals at δ 105.00, 105.82, 129.02, 137.24 ppm related to carbon atoms C-6, C-8, C-4, C-5, C-3, respectively. The signals of carbon atoms related to CH_3CN, $-CH_3$, $-OCH_3$, were observed at δ 18.51, 21.94, 55.55 ppm, in the form of quartets. The carbon atom C=N appears as a singlet at δ 145.95 ppm.

For assignment of all ^{1}H and ^{13}C NMR signals, a number of two-dimensional spectroscopic methods were used: ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N HMBC.

The ^{1}H and ^{13}C NMR spectra of synthesized derivatives of harmine **4-6** contained a set of characteristic signals of protons and carbon atoms of the β-carboline core and the corresponding substituent. The proton CH= of side chain in the ^{1}H NMR spectrum of compounds **4-6** resonated as a broadened singlet in the region of δ 8.73-8.32 ppm. Signals, characteristic for the protons of the aromatic ring H-3'-5' appeared at δ 6.18-8.69 ppm, respectively. The characteristic signals of carbon atoms in the ^{13}C NMR spectra belonging to $-CH_3C=N$, $-CH_3$, $(-OCH_3)$, $(-OCH_3)_2$ groups occurred in the regions of δ 19.84-19.94, 20.21-20.42, 55.56-56.43 ppm, respectively, as quartets. Doublet (d) signal related to the CH=N substituent was observed at δ 150.43-157.20 ppm. The singlet signal of the -C=N group in the C-8 substituent shifted to the low magnetic field relative to the location in the spectrum of hydrazone **3** and were detected at δ 163.59-167.68 ppm.

The correct assignment of signals in the ^{1}H NMR spectrum of compound **3** confirm the two-dimensional ^{1}H–^{1}H COSY correlation spectra (Fig. 1).

For compound **3**, the ^{1}H–^{1}H COSY spectrum shows the spin-spin correlation between the protons of methine groups: H-3 and H-4 of the pyridine ring with a cross peak of 8.15, 7.81 ppm (doublets with J = 5.8 Hz) and between H-5 and H-6 of the aromatic ring with the correlation of signals at δ 8.12, 7.04 ppm (J coupling of 8.2 Hz).

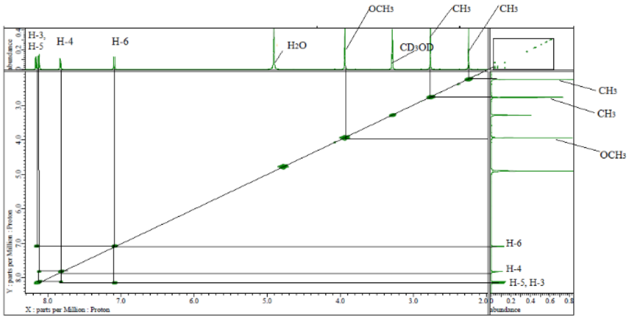


Figure 1 - Two-dimensional ^{1}H-^{1}H COSY spectrum of compound **3**

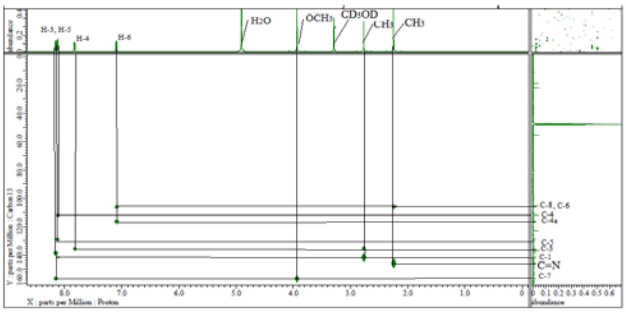


Figure 2 - Two-dimensional spectrum HMBC (^{1}H-^{13}C) of compound **3**

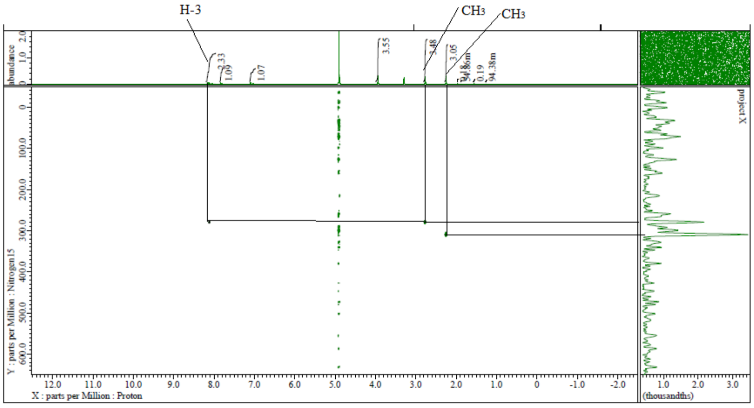


Figure 3 - Two-dimensional spectrum HMBC (^{1}H-^{15}N) of compound **3**

The assignment of signals in the ^{15}N NMR spectra was carried out according to the two-dimensional spectrum of the inverse correlation of ^{1}H–^{15}N on the long-range interactions (HMBC). To assign the chemical shifts of carbon atoms that are not related to hydrogen atoms, heteronuclear correlation methods for long-range bonds were applied: ^{1}H–^{13}C HMBC (Fig. 2) and ^{1}H–^{15}N HMBC (Fig. 3) [19]. With the help of the correlation spectra for long-range bonds all carbon atoms that are not connected with hydrogen atoms in the molecule were uniquely determined, thereby completely confirming the structure of the obtained compounds **3-6**.

The ^{1}H–^{13}C HMBC showed correlation peaks of the CH_3 protons (C-13) with C-8 and C=N atoms. CH_3 protons (C-10) interacted with atoms C-1 and C-3. Protons of OCH_3 (C-11) correlated with the C-7 atom. This experiment confirmed the assignment of the methyl groups.

An analysis of the ^{1}H–^{15}N HMBC spectra showed that the CH_3 proton (C-13) (δ 2.12 ppm), showed correlation with the nitrogen atom of the group C=N at 310 ppm. Proton H-3 (doublet, δ 8.15 ppm), and the CH_3 protons (C-10) (δ 2.71 ppm), showed interaction with a nitrogen atom in position 2 of the pyridine ring (δ_N 280 ppm).

All of these data suggest that the synthesized compound has the following structure (figure 4).

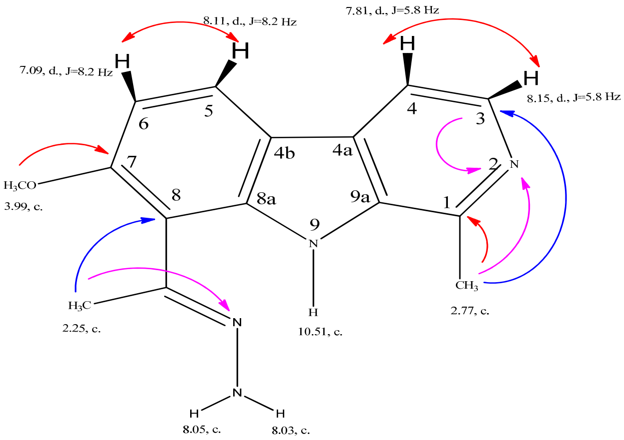


Figure 4 - The main correlations in the ^{1}H-^{13}C and ^{1}H-^{15}N HMBC spectra of compound **3**

Experimental part. (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole (3). Solution of 0.5 g (1.96 mol) 8-acetylharmine **2** in 25 ml of ethanol was stirred, and meanwhile 2.94 g (0.06 mol) of hydrazine hydrate was added dropwise in excess. The reaction mixture was stirred for 7-8 hours at a temperature of 60 °C. The precipitate formed was filtered and recrystallized from EtOH. Yield 69%, yellow paurocrystalline powder, melting point 207-209 °C, $[\alpha]^{24}_D$ -187.5 (*c* 0.16; $CHCl_3$). UV-spectrum (EtOH), λ_{max}/nm (log ε): 213 (2.85), 243 (2.99), 302 (2.66), 328 (2.22), 341 (2.17). IR-spectrum (KBr, ν, cm^{-1}): 3327, 3220, (-NH), 3170, 3096, 2890, 2827 (-C-H), 2983, 2927, 2915, (-OCH_3 of phenyl fragment), 1617 (-C=N), 1569, 1446, 1418 (-C-C), 1293, 1222, 1202 (-C=N-N), 1113 (-N-N).

^{1}H NMR spectrum (500 MHz, DMSO, δ, ppm, *J*/Hz): 2.12 (3H, s, CH_3CN), 2.71 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 7.04 (1H, d, *J*=8.2, H-6), 7.81 (1H, d, J=5.8, H-4), 8.03, 8.05 (2H, s, NH_2), 8.12 (1H, d, *J*=8.2, H-5), 8.15 (1H, d, *J*=5.8, H-3), 10.51 (1H, br. s, NH). ^{13}C NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): s. 141.58 (C-1); d. 137.24 (C-3); d. 112.1 (C-4); s. 116.47 (C-4a); s. 129.02 (C-4b); d. 123.31 (C-5); d. 105.0 (C-6); s. 156.81 (C-7); s. 105.82 (C-8); s. 138.67 (C-8a); s. 135.64 (C-9a); q. 18.51 ($CH_3C{=}N$); q. 55.55 (-OCH_3); q. 21.94 (-CH_3); s. 145.95 (C=N). Mass-spectrum, *m/z* (I_{rel}, %): 277 (100), 308 (37), 237 (22), 278 (18), 236 (15). Found, *m/z*: 268.1319 $[M]^+$. $C_{15}H_{16}N_4O$. Calculated, *m/z*: 268.1298. Elemental analysis: found, %: C 69.10; H 7.17; N 17.8. $C_{15}H_{16}N_4O$. Calculated, %: C 67.16; H 7.00; N 17.87.

7-Methoxy-8-((*E*)-1-((*E*)-(4-methoxybenzylidene)hydrazono)ethyl)-1-methyl-9*H*-pyrido[3,4 *b*]indole (4). To a solution of 0.1 g (0.37 mol) of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole **3** in 10 ml of methanol, while stirring 0.151 g (1.12 mol) of anisaldehyde was added dropwise in 5 ml of methanol. The reaction mixture was stirred for 4 hours at 60-65 °C. The precipitate formed was filtered off and recrystallized from ethanol. $C_{23}H_{22}N_4O_2$, yield 56%, melting point 171-172 ºC, $[\alpha]^{24}_D$ +250 (*c* 0.16; $CHCl_3$). UV-spectrum (EtOH, λ_{max}/nm (log ε): 215 (2.78), 238 (2.82), 305 (2.74). IR-spectrum (KBr, ν, cm^{-1}): 3235 (-NH), 3006, 2841 (-C-H), 2964, 2927, (-OCH_3 of phenyl fragment), 1618, 1605 (-C=N), 1572, 1513, 1462, 1424 (-C-C), 1293, 1249 (-C=N-N), 1175 (-N-N).

^{1}H NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 2.72, (3H, s, CH_3CN), 2.79 (3H, s, -CH_3), 3.89 (3H, s, -OCH_3), 4,00 (3H, s, -OCH_3), 6,96 (1H, d, *J*=8.7, H-6), 6.99 (1H, q, *J*=6.8, H-3'), 7.01 (1H, q, *J*=6.8, H-5'), 7.73 ppm (1H, d, *J*=5.3, H-4), 7.84 (1H, q, *J*=8.8, H-2'), 7.86 (1H, q, *J*=8.8, H-6'), 8.07 (1H, d, *J*=8.7, H-5), 8.32 (1H, d, *J*=5.3, H-3), 8.32 (1H, br. s, H-16), 10.51 (1H, br. s, NH). ^{13}C NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): s. 141.6 (C-1); d. 139.0 (C-3); d. 112.3 (C-4); s. 116.9 (C-4a); s. 128.14 (C-4b); d. 124.29 (C-5); d. 105.44 (C-6); s.162.05 (C-7); s. 110.22 (C-8); s. 140.33 (C-8a); s. 134.86 (C-9a); q. 19.84 (CH_3CN); q. 55.56 (OCH_3); q. 56.44 (OCH_3); q. 20.42 (CH_3); s. 167.24 (C=N); d. 157.2 (CH=N); s. 128.1 (C-1'); d. 114.40 (C-3',5'); d. 130.27 (C-2',6'). Mass-spectrum, *m/z* (I_{rel}, %): 355 (100), 356 (22), 386 (20), 387 (8). Found, *m/z*: 386.1739 $[M]^+$. $C_{23}H_{22}N_4O_2$. Calculated, *m/z*: 386.1737. Elemental analysis: found, %: C 71.07; H 6.13; N 14.32. $C_{23}H_{22}N_4O_2$. Calculated, %: C 71.45; H 5.72; N 14.51.

8-((*E*)-1-((*E*)-(2-fluorobenzylidene)hydrazono)ethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole (5). To a solution of 0.1 g (0.37 mol) of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole **3** in 10 ml of methanol, while stirring 0.092 g (2 mol) of 2-fluorobenzaldehyde was added dropwise in 5 ml of methanol. The reaction mixture was stirred for 4 hours at 60-65 °C. The precipitate formed was filtered and recrystallized from ethanol. Yield 82%, $C_{22}H_{19}N_4OF$, melting point 166-168 ºC, $[\alpha]^{24}_D$ +62.5 (*c* 0.16; chloroform). UV-spectrum (EtOH), λ_{max}/nm (log ε): 209 (3.03), 245 (3.08), 300 (2.87), 342 (2.69) nm. IR-spectrum (KBr, ν, cm^{-1}): 3274 (-NH), 3044, 2840 (-C-H), 2997, 2977 (-OCH_3 of phenyl fragment), 1622, 1604 (-C=N), 1577, 1484, 1459 (-C-C), 1295, 1283 (-C=N-N), 1236 (-C-F), 1170 (-N-N). ^{1}H NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 2.72, (3H, s, CH_3CN), 2.81 (3H, s, CH_3), 4,01 (3H, s, OCH_3), 6,97 (1H, d, *J*=8.7, H-6), 7.16 (1H, ddd, *J*=10.3, 8.4, 0.9, H-3'), 7.27 (1H, td, *J*=7.6, 0.9, H-5'), 7.46 (1H, dddd, *J*=8.4, 7.6, 5.4, 1.6, H-4'), 7.74 (1H, d, *J*=5.4, H-4), 8.09 (1H, d, *J*=8.7, H-5), 8.19 (1H, td, *J*=7.6, 1.6, H-6'), 8.34 (1H, d, *J*=5.4, H-3), 8.73 (1H, br.s, H-16), 10.53 (1H, br.s, NH). ^{13}C NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): s.141.6 (C-1); d. 139.0 (C-3); d. 112.3 (C-4); s. 116.97 (C-4a); s. 128.20 (C-4b); d. 124.61 (C-5); d. 105.47 (C-6); s. 160.10 (C-7); s. 109.94 (C-8); s. 140.40 (C-8a); s. 134.86 (C-9a); q. 19.94 (CH_3CN); q. 20.21 (CH_3); q. 56.43 (OCH_3); s. 167.68 (C=N); d. 150.43 (CH=N); s. 122.49 (C-1', J_F=9.8); s. 162.16 (C-2', J_F=5.2), d. 116.14 (C-3', J_F=2.1); d. 132.60 (C-4', J_F=8.5); d. 124.56 (C-5', J_F=3.8); d. 127.77 (C-6', J_F=2.5). In the ^{19}F NMR spectrum, the only signal of the fluorine phenyl fragment of the compound (E)-1-(2-fluorophenyl)hydrazone)ethyl)-7-methoxy-1-methyl-9H-pyrido[3,4-b]indole-8-yl **5** was observed. Mass spectrum, *m/z* (I_{rel}, %): 343 (100), 374 (58), 344 (23), 237 (21), 375 (15). Found, *m/z*: 374.1537 $[M]^+$. $C_{22}H_{19}FN_4O$. Calculated, *m/z*: 374.1535. Elemental analysis: found, %: C 69.61; H 5.61; N 14.40. $C_{22}H_{19}FN_4O$. Calculated, %: C 70.47; H 5.11; N 14.96.

8-((*E*)-1-((*E*)-(2,4-dimethoxybenzylidene)hydrazono)ethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole (6). To a solution of 0.15 g (0.56 mol) of (*E*)-8-(1-hydrazonoethyl)-7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*] indole **3** in 20 ml of methanol 0.186 g (1.12 mol) of 2,4-dimethoxybenzaldehyde was added dropwise with stirring in 5 ml of methanol. The reaction mixture was stirred for 4 hours at a temperature of 60-65 °C. The precipitate formed was filtered and recrystallized from ethanol. Yield 75%, $C_{24}H_{24}N_4O_3$, $[\alpha]^{24}_D$ +125 (*c* 0.16; chloroform). UV-spectrum (EtOH, λ_{max}/nm (log ε): 216 (2.78), 236 (3.26), 293 (2.26), 317 (2.17). IR-spectrum (KBr, ν, cm^{-1}): 3220 (-NH), 3178, 3107, 3004, 2851, 2837 (-C-H), 2970, 2926 (-OCH_3 of phenyl fragment), 1623, 1606 (-C=N), 1570, 1462, 1421 (-C-C), 1290, 1271, 1226 (-C=N-N), 1173 (-N-N).

^{1}H NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 2.54, (3H, s, CH_3CN); 2.68 (3H, s, -CH_3); 3.70 (3H, s, -OCH_3); 3.71 (3H, s, -OCH_3); 3.95 (3H, s, OCH_3); 6.18 (1H, dd, *J* = 8.7, H-3'), 6.32 (1H, d, *J* = 8.8, H-6'), 6,94 (1H, d, *J*=8.7, H-6); 7.73 (1H, d, *J* = 5.3, H-4), 8.04 (1H, d, *J* = 8.7, H-5), 8.32 (1H, d, *J* = 5.3, H-3), 8.69 (1H, d, *J* = 6.8, H-5’), 8.76 (1H, br. s, H-16), 10.56 (1H, br. s, NH). ^{13}C NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): s.129.1 (C-1'); d.139.28 (C-3); d.112.43 (C-4); s.115.49 (C-4a); s.117.07 (C-4b); d.123.31 (C-5); d.105.34 (C-6); s.162.34 (C-7); s.110.60 (C-8); s.141.73 (C-8a); s.135.65 (C-9a); q.24.33 (CH_3CN); q.56.40 (OCH_3); q.55.57 (OCH_3); q.56.52 (OCH_3); q.20.31 (CH_3); d.98.39 (C-6'); d.28.52 (C-3',5'); d.155.01 (CH=N); s.163.59 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 385 (100), 416 (32), 386 (26), 237 (11), 417 (9). Found, *m/z*: 416.1843 $[M]^+$. $C_{24}H_{24}N_4O_3$. Calculated, *m/z*: 416.1840. Elemental analysis: found, %: C 68.99; H 6.34; N 13.03. $C_{24}H_{24}N_4O_3$. Calculated, %: C 69.21; H 5.82; N 13.45.

In conclusion, new methods for the preparation of harmine derivatives substituted at position C-8 were elaborated which allow subsequent modification of 8-acetylharmine to new *N*-arylidenehydrazones of harmine, the molecular structure of which was established on the basis of elemental analysis and spectral data (IR-, UV-, ^{1}H-, ^{13}C-, ^{19}F-, ^{15}N- NMR).

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ГАРМИН ГИДРАЗОН ТУЫНДЫЛАРЫНЫҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫСЫ

Аннотация. Алкалоидтардың молекулаларын түрлендіру биологиялық белсенділік спектрі бастапқы затпен салыстырғанда айтарлықтай кеңейетін әрі түрі өзгеретін қосылыстарды алуға кең мүмкіндік беретіні белгілі.

Жаңа синтондар мен биологиялық белсенді қосылыстарды іздеу және олардың негізінде әсер ету спектрі белгіленген тиімді дәрілік құралдарды іздестіру мақсатында гармин алкалоидының химиялық түрлендірілуі жүргізілді. β-карболин типтес гармин алкалоиды Оңтүстік Қазақстанда кеңінен таралған кәдімгі адыраспан (*Peganum harmala* L.) шикізатының құрамында кездеседі.

Әдеби деректерге сәйкес гармин индолды алкалоиды кең фармакологиялық белсенділік спектріне ие. Гармин неврологиялық аурулар кезінде нейропротекторлық белсенділік танытып, орталық жүйке жүйесіне әсер етеді, А моноаминоксидазаны тежейді. Гармин туындылары микробқа қарсы белсенділікке ие, ал оның суда еритін түрі – гармин гидрохлоридінің депрессияға, гипоксияға (гипобариялық гипоксия) және паркинсонизмге қарсы әсері бар.

Соңғы жылдары гидразондар синтезі нысаналы қосылыстардың айтарлықтай биологиялық белсенділігімен ғана емес, олардың негізінде әртүрлі гетероциклдерді, оның ішінде энергия сыйымды материалдарды синтездеу мүмкіндігімен де назар аудартатынын атап өткен жөн.

Осыған байланысты біздің тарапымыздан жаңа биологиялық белсенді қосылыстар алу мақсатында қолжетімді гармин алкалоидын трансформациялау жөніндегі зерттеулер жалғасуда.

Жұмыста 8-ацетилгармин молекуласы негізіндегі синтездің нәтижелері ұсынылған. 8-ацетилгарминнің гидразин гидратымен өзара әрекеттесуі кезінде шығымы 69% (*E*)-8-(1-гидразоноэтил)-7-метокси-1-метил-9*H*-пиридо[3,4-*b*]индол алынды. Метанолда қайнатқан кезде (*E*)-8-(1-гидразоноэтил)-7-метокси-1-метил-9*H*-пиридо[3,4-*b*]индолдың функционалдық түрде алмастырылған ароматикалық альдегидтермен (анис альдегиді, 2-фторбензальдегид, 2,4-диметоксибензальдегид) реакциясы шығымдары 56-82% тиісті N-арилиденгидразондардың туындауына алып келетіні көрсетілді. Синтезделген қосылыстардың құрылысы бір өлшемді ^{1}H, ^{13}C және DEPT ЯМР әдістерімен, сондай-ақ COSY, HMQC, HMBC екі өлшемді спектрлерінің, элементтік талдау және масс-спектрлердің деректерімен сипатталған. Протондардың үш байланыс арқылы протондармен корреляция схемалары және протондардың COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C, ^{1}H-^{15}N) бір байланыс арқылы көміртекті атомдармен корреляция схемалары ұсынылған, гарминнің жаңа туындыларының құрылымдарын растайтын гомо және гетероядролық өзара әрекеттесулер анықталды. Жұмыста заманауи физика-химиялық және спектроскопиялық зерттеу әдістерін қолдану алынған қосылыстардың құрылысы мен қасиеттерін сенімді әрі бірмағыналы сипаттауға мүмкіндік берді.

Түйін сөздер: гармин, 8-ацетилгармин гидразонтуындысы, N-арилиденгидразон туындылары, ЯМР спектрлер, екі өлшемді спектрлері.

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СИНТЕЗ И СТРОЕНИЕ ГИДРАЗОНПРОИЗВОДНЫХ ГАРМИНА

Аннотация. Известно, что модификация молекул алкалоидов дает широкую возможность получения соединений, спектр биологической активности которых значительно расширяется и видоизменяется по сравнению с исходным веществом.

С целью поиска новых синтонов и биологически активных соединений и изыскания на их основе эффективных лекарственных средств заданного спектра действия проведена химическая модификация алкалоида гармина. Алкалоид β-карболинового типа гармин содержится в сырье гармалы обыкновенной (*Peganum harmala* L.), широко распространённом в Южном Казахстане.

Согласно литературным данным, индольный алкалоид гармин обладает широким спектром фармакологической активности. Гармин оказывает влияние на центральную нервную систему, проявляя нейропротекторную активность при нейрологических заболеваниях, ингибирует моноаминоксидазу А. Производные гармина обладают антимикробной активностью, а его водорастворимая форма –гидрохлорид гармина обладает антидепрессивным, противогипоксическим (гипобарическая гипоксия) и антипаркинсоническим действием.

Следует отметить, что в последние годы синтез гидразонов привлекает внимание не только значительной биологической активностью целевых соединений, но и возможностью синтеза на их основе разнообразных гетероциклов, в том числе энергоемких материалов.

В связи с этим нами продолжаются исследования по трансформации доступного алкалоида гармина с целью получения новых биологически активных соединений.

В работе представлены результаты синтеза на основе молекулы 8-ацетилгармина. При взаимодействии 8-ацетилгармина с гидразин гидратом получено (*E*)-8-(1-гидразоноэтил)-7-метокси-1-метил-9*H*-пиридо [3,4-*b*]индол с выходом 69%. Показано, что реакция (*E*)-8-(1-гидразоноэтил)-7-метокси-1-метил-9*H*-пиридо[3,4-*b*]индола с функционально замещёнными ароматическими альдегидами (анисовый альдегид, 2-фторбензальдегид, 2,4-диметоксибензальдегид) при кипячении в метаноле приводит к образованию соответствующих N-арилиденгидразонов с выходами 56-82%. Строение синтезированных соединений охарактеризованы методами ЯМР одномерной ^{1}H, ^{13}C и DEPT, а также данными двумерных спектров COSY, HMQC, HMBC, элементного анализа и масс-спектров. Представлены схемы корреляций протонов с протонами через три связи и схемы корреляций протонов с углеродными атомами через одну связи COSY (^{1}H -^{1}H) и HMQC (^{1}H-^{13}C, ^{1}H-^{15}N), установлены гомо- и гетероядерные взаимодействия, подтверждающие структуры новых производных гармина. Применение в работе современных физико-химических и спектроскопических методов исследования позволили надежно и однозначно охарактеризовать строение и свойства полученных соединений.

Ключевые слова: гармин, гидразонпроизводное 8-ацетилгармина, N-арилиденгидразоны, ЯМР спектры, двумерные спектры.

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SELECTIVE CATALYTIC OXIDATION AND STEAM OXYGEN CONVERSION OF METHANE INTO SYNTHESIS GAS

Abstract. The results of the stability study of the developed dispersed optimal composition Pt-Ru = 1 : 1 (Pt: Ru = 0.7 : 0.3, at.%) of the catalyst in the reaction of selective catalytic oxidation (SCO) and steam oxygen conversion (SOC) of methane into synthesis gas at millisecond contact times are presented. Methods of catalyst regeneration were determined. During the study of the stability of a low-percentage granular sample of 1.0% Pt-Ru/2% Ce/(θ+α)Al_2O_3 catalytic system in the process of oxidation of methane, regeneration methods were found that allow stable conduct of the process of SCO and SOC of methane for 410 hours. As a result of the process, a synthesis gas was obtained with a ratio of H_2/CO = 2.0 without the formation of CO_2, which is most suitable for its use in the Fischer-Tropsch synthesis of methanol and hydrocarbons. It is assumed that the reaction of SCO of CH_4 proceeds by a direct mechanism involving reduced Pt^0, Ru^0 and Pt-Ru nanoclusters detected by TEM research after testing the stability of the developed Pt: Ru (1:1) catalyst on a carrier.

Keywords: Pt-Ru catalyst, selective catalytic oxidation, steam oxygen conversion, methane, synthesis gas.

Introduction. Synthesis gas is the main raw material for producing a wide range of petrochemical products. Correlation of the ratio of H_2 and CO in the composition of synthesis gas makes it possible to obtain liquid hydrocarbons or oxygenates, CH_3OH, CH_3COOH, CH_2O and C_2H_6O. The process of SCO of methane which proceeds with a molar ratio of hydrogen to carbon monoxide equal to 2.0, could become a reaction, an alternative reaction of steam reforming of methane for the production of synthesis gas. An alternative reaction of steam reforming of methane to obtain syngas can be the process SCO of methane which proceeds with an optimal molar ratio of hydrogen to carbon oxide equal to 2.0.

The creation of large-scale production in natural gas production areas would significantly reduce the cost of target products and reduce environmental pollution. Obtaining a synthesis gas by direct oxidation of CH_4 with a lack of oxygen and millisecond contact times is a relatively new reaction, first performed by M. Pretre, which plays an important role in petrochemical syntheses. Researchers returned to the study of this process in the 90 years thanks to the use of a reactor with block porous catalysts during the process in a micro-reactor when secondary reactions are prevented.

In 1992, Schmidt investigated reduced Pt, Pd, and Rh catalysts in selective catalytic oxidation at an excess of methane, high temperature, and a contact time of 0.01 - 0.004 s to form a synthesis gas with high selectivity for hydrogen and carbon monoxide. Among the studied compositions, the best results were shown on Rh catalysts carried to Al_2O_3 [1-3].

It is known that platinum group metals are more active than Fe, Co, Ni, and are less prone to carbon deposition. Most of the known compositions of catalysts for SCO of methane include noble metals with a content of ≥1% of metals in the active phase. To achieve high performance in the production of synthesis gas in the process of methane co-production at high volume velocity without the formation of CO_2 with a ratio of hydrogen to carbon monoxide equal to 2, the catalyst must provide both a high conversion of methane and selectivity for the target product [4-15].

We studied Pt, Ru, and Pt-Ru/2%Ce/(θ+α)-Al_2O_3 catalytic systems with varying Pt to Ru ratios in the reaction of SCO of methane into synthesis gas at millisecond contact times [16-20]. Determined that at contact times of 3.0 - 4.0 millisecond the conversion of methane at 1173K varies from 96 to 100%, the selectivity for hydrogen is 100% and for CO is 95-100%. It was found that 100% conversion of methane by direct mechanism into synthesis gas with 100% selectivity for hydrogen and carbon monoxide was achieved at the atomic ratio Pt : Ru = 2 : 1 or 1 : 1 (32.4 and 45.3 at.% Ru in a mixture of Pt-Ru) and the contact time is 4.0 millisecond. Physical and chemical methods determined that the introduction of ruthenium in a platinum catalytic system with a ratio of metals Pt : Ru = 2 : 1 (0.68 Pt: 0.32 Ru. weight.%) increases oxygen adsorption in the second temperature region, and the surface is stabilized in a uniform state. It is assumed that on Pt: Ru (2:1. 1:1) catalysts, the reaction of SCO of CH_4 proceeds by a direct mechanism with the participation of reduced Pt-Ru clusters that have the greatest ability to absorb atomic hydrogen.

This paper presents data on the stability of the developed Pt-Ru = 1 : 1 (Pt : Ru = 0.7 : 0.3 at.%) catalyst. The activity of the catalyst was studied in the reactions of SCO and SOC of methane into synthesis gas at low contact times. As a result of the conducted research, the methods of catalyst regeneration were determined.

Experimental

Catalyst preparation

Pt-Ru catalysts supported on 2%Ce/(θ+α)-Al_2O_3 have been prepared by incipient wetness on (θ+α)-Al_2O_3 (100-200 μm, S = 57.7 m^2/g) from water solutions of salts with subsequent heating and reduction with H_2+Ar at 623-1023 K. Tests were carried out in a continuous flow quartz micro reactor by a literature technique.

The activity of the developed catalytic systems in the process SCO of methane was determined in a catalytic flow unit at atmospheric pressure in a quartz microreactor with an internal diameter of 0.45 cm. 10 mg of the catalyst suspension was thoroughly mixed with quartz powder (particle size 0.2 mm in a ratio of 1: 43, height 20 mm). Then, larger quartz particles (1÷2 mm) were added to the reactor from above to a total layer height of 70 mm. After that, the initial reaction mixture was fed under the following conditions: CH_4:O_2:Ar = 2.0 : 1.0 : 97.0. (%) T = 1173K, V = $9\cdot10^5$ h^{-1}, $\tau = 0.004$ s. In the process the SOC of methane: $CH_4 : O_2 : H_2O$: Ar = 2.0 : 1.0 : 2.0 : 95.0, %, T = 1073 – 1173 K, V = $1\cdot10^5$ - $9\cdot10^5$ h^{-1}.

Characterization techniques

Analysis of the initial mixture and the reaction products was performed using "Chromos GC-1000" (Russia) chromatograph, which was equipped with packed and capillary columns. The packed column is used for the analysis of H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3-C_4 hydrocarbons, CO and CO_2. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. The speed of the carrier gas Ar is 10 ml / min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve V = f (S) was constructed, where V - amount of substance in ml, S - peak area in cm^2. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was ± 3.0%.

Physico-chemical research

Electron microscopic characteristics of the catalysts were obtained using the EMK-125 K microscope (1990, USSR) at an accelerating voltage of 75 kV. The morphology, particle size and their chemical composition was investigated by increasing to 120,000 times by using the replica technique with extraction with the use of microdiffraction of electrons. Carbon replicas were sprayed in a vacuum universal post, then the catalyst carrier was dissolved in HF. Identification of micro-diffraction patterns was carried out using the jspds card file of 1986.

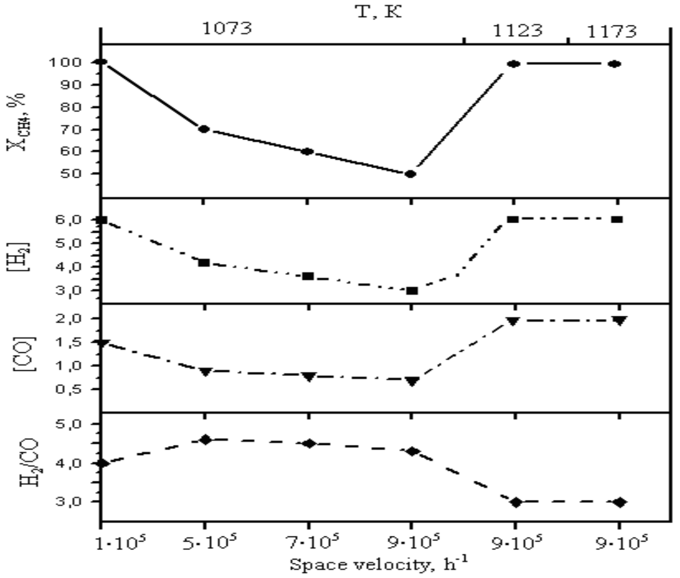
Results and discussion. A priori, it is known that the addition of water vapor to the reaction mixture reduces the formation of carbon on the surface of the catalysts. In modern installations at a pressure of 2 MPa or higher, the residual content of CH_4 after steam conversion is 8-10%. In order to achieve a residual content of methane within 0.5% the conversion is usually carried out in 2 stages. Stage 1: under pressure and stage 2: steam-air conversion in the presence of air oxygen. This results in a sin gas of stoichiometric composition and eliminates the need for separation of products after the reaction.

To study the activity of catalytic systems synthesized by capillary impregnation in the SOC reaction the effect of the concentration of added water vapor in the initial reaction mixture in the SOC was first performed by 2.0% CH_4 + 1.0% O_2 + Ar + H_2O at $V = 9\cdot10^5$ h^{-1}, $\tau = 4{,}0$ ms. It was found that when adding small amounts of water vapor to the reaction system with a ratio of $CH_4 : H_2O = 1: 0.5$ with an increase in temperature from 1023 to 1173 K, there was a gradual increase in the conversion of methane from 70 to 90%, S for H_2 from 23.8 at 1023 K to the maximum 100% value at 1173 K, without the formation by-product of a CO_2. The ratio of hydrogen to carbon monoxide vary from 3.3 to 5.0. At higher ratio of $CH_4 : H_2O = 1 : 1$ with increasing the temperature of reaction from 1023 to 1123 and 1173 K was also observed an increase conversion of methane and selectivity of H_2 respectively, from 97.5% and 18.8 to maximum 100% of the values without the formation of CO_2 with a ratio of H_2/CO from 3.0 to 3.6.

When the added water vapors increased to the ratio $CH_4 : H_2O = 1: 2$, as the temperature increased from 1023 to 1123 K, all parameters of process also increased. The conversion of methane and selectivity of hydrogen increased from 62.5 and 26.6 to the maximum 100% values, and the selectivity for CO ranged from 88.8 – 98.2% with the appearance of small amounts of CO_2 in the reaction system (0.013 – 0.023%). As the temperature increased, the H_2/CO ratio decreased from 10.0 to 4.6.

Thus, determined that the preferred process for converting of methane is SOC of CH_4 with a ratio of $CH_4 : H_2O = 1 : 1$. The addition of 2.0% water to the reaction system increases to the maximum values conversion of methane, selectivity for H_2 and CO (100%) at a temperature 50^0C lower than at the SCO of methane to produce a synthesis gas with a ratio of $H_2/CO = 3.0$ without the formation of CO_2.

A study of the effect of changes the volume velocity and temperature of the process SOC of methane $CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0$,% on the conversion of methane, the concentration of H_2 and CO by the catalytic system 1.0%Pt-Ru (1:1)/2%Ce/(θ+α)–Al_2O_3 at T = 1073 – 1173 K, $V = 1\cdot10^5 - 9\cdot10^5$ h^{-1}. As can be seen from figure 1, the reaction of SOC of methane at 1073 K with an increase the volume velocity from $1\cdot10^5$ h^{-1} to $9\cdot10^5$ h^{-1} X_{CH4}, the concentration of H_2 and CO decreases. However, when the temperature of process increases to 1123 and 1173 K, all the parameters of process increase again to the initial maximum values. The ratio H_2/CO was 3.0-4.5.

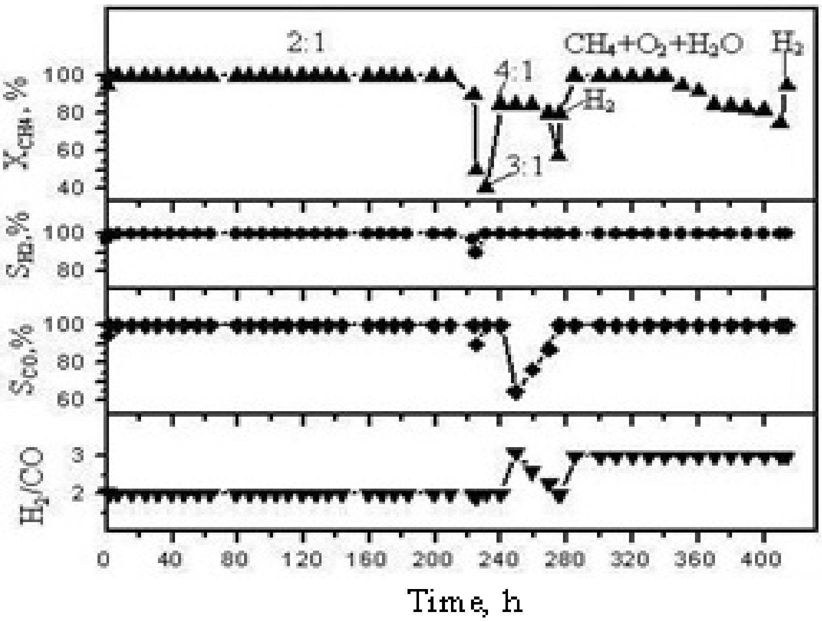


Experimental conditions: SOC of $CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0$.%, T = 1073 – 1173 K, $V = 1\cdot10^5 - 9\cdot10^5$ h^{-1}

Figure 1 - Influence of the volume velocity on change of X_{CH4}, $[H_2]$, [CO] in the SOC of methane by 1.0%Pt-Ru (1:1)/ 2%Ce/(θ+α)-Al_2O_3

Thus, determined that the process of SOC of methane with the optimum ratio of $CH_4 : H_2O = 1 : 1$ proceeds with complete conversion of the initial methane and maximum selectivity for the main products of the reaction without formation of CO_2 at 1123 K and volume velocity of $9 \cdot 10^5$ h^{-1} and decreasing the temperature of the reaction to 1073 K and volume velocity of $1 \cdot 10^5$ h^{-1} on 1.0%Pt-Ru (1:1)/ 2%Ce/(θ+α)-Al_2O_3 catalyst.

It is known that one of the most important characteristics of catalysts is their stability. We tested the stability of the developed optimal composition of Pt-Ru = 1 : 1 of the catalytic system in the processes of SCO and SOC of methane in synthesis gas at low contact times. From the data in figure 2 shows that up to 225 hours the developed catalyst does not lose its activity in the reaction of methane SCO. Then the conversion of methane was gradually reduced and the test was performed with a change in the concentration of the initial reaction mixture at $CH_4 : O_2 = 3 : 1$ and $CH_4 : O_2 = 4 : 1$.



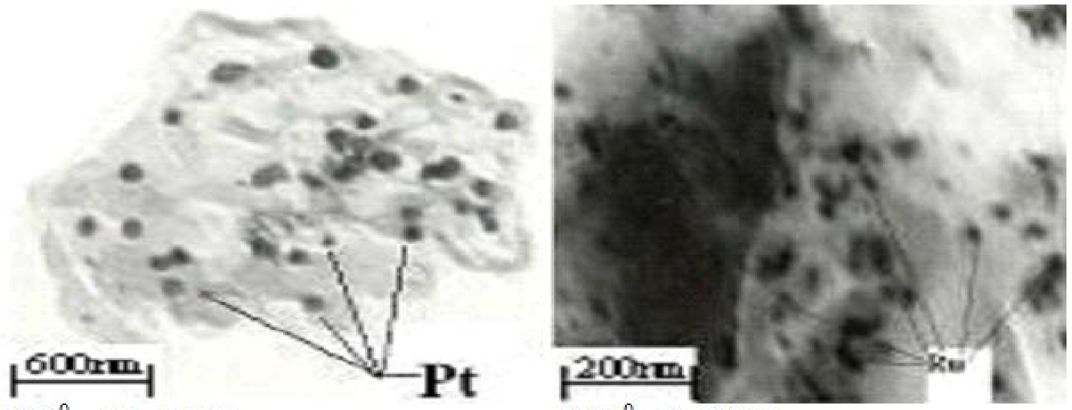
Condition the process of SCO of methane: $CH_4 : O_2 : Ar = 2.0 : 1.0 : 97.0$, %, T = 1173 K, $V = 9 \cdot 10^5 h^{-1}$, $\tau = 0.004$ s and SOC of methane $CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0$, %, T = 1073 K, $V = 1 \cdot 10^5 h^{-1}$, $\tau = 0.036$ s

Figure 2 – Change conversion of methane, selectivity of H_2 and CO, ratio of H_2/CO on 1.0 % Pt-Ru (1:1)/2%Ce/(θ+α)Al_2O_3 catalyst in time

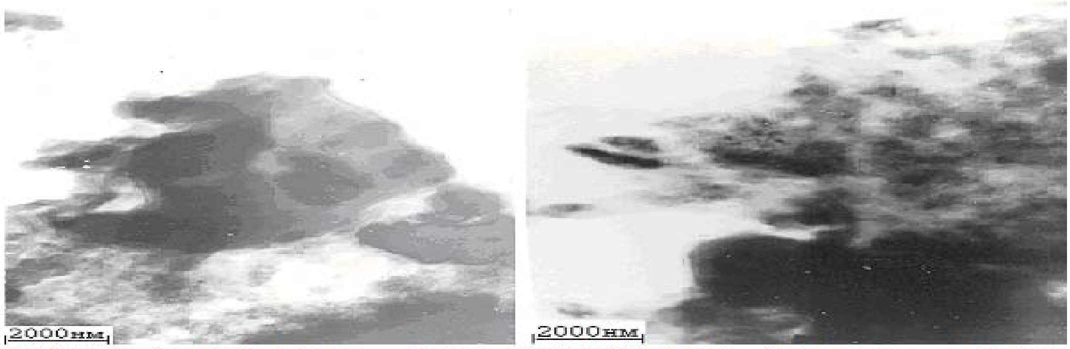
After that updating of catalyst was performed by regeneration in mixture of H_2+Ar. Determined that the most optimal is adding in the reaction mixture of water vapors. Then only the activity returned to its starting value. Next, the process of SOC of CH_4 was conducted at the concentration of water vapors found experimentally, which was optimal. It should be noted that in these processes use only 10 milligrams of a catalyst diluted four hundred times with quartz.

Thus, it is established that the developed catalytic system 1.0%Pt-Ru(at. %)/2%Ce/(θ+α)-Al_2O_3 selectively works without losing its activity for 414 hours in the reaction of SCO and SOC of methane into synthesis gas.

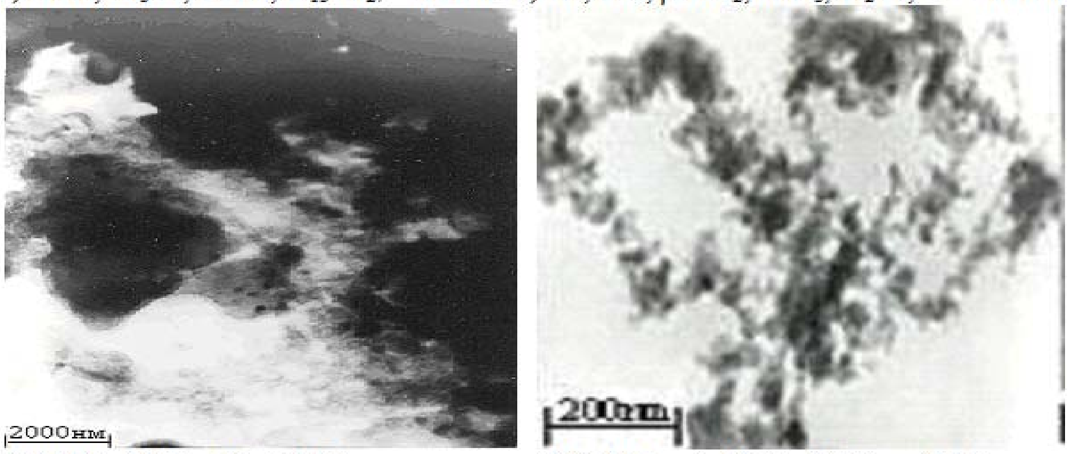
The following data are presented for 1.0% Pt-Ru catalyst, which is the most active with a ratio of 1 : 1 at a regeneration temperature of 573 K (figure 3). It can be seen that the catalyst contains from phases of both platinum and ruthenium, as well as their oxides, but also with adsorbed platinum and ruthenium by diffractograms, it was determined that bimetallic Pt-Ru nanoclusters are formed. These data indicate that the active catalyst among the compositions studied by us differs in that separate adsorption occurs on the detected Pt-Ru clusters. It is assumed that dissociation of methane can occur on one side of the platinum cluster, and oxygen activation can occur on the other side of the ruthenium cluster.



a) Pt^0 – 7,5 - 15 nm. b) Ru^0 – 6 - 10 nm.



c) AlRu, Al_3Ce, Pt-Ru, $Pt_{13}Ru_{27}$ – 10 nm. d) Ru, PtO, β-PtO_2, $AlPt_3$, Pt_2Ce, – 5 - 10 nm.



e) Al_6Ru, Al_2Pt, - 20 - 30 nm. f) $CeAlO_3$ – 3-10 nm, Ce_6O_{11} – 5 nm

Figure 3 - Electron microscopic photos of various phases reduced in H_2 at 573 K
1.0% Pt-Ru/2%Ce/(θ+α)-Al_2O_3 (a, b, c, d, e, f) catalysts

Conclusion. During the study of the stability of a low-percentage granular sample of 1.0% Pt-Ru/2% Ce/(θ+α)Al_2O_3 catalytic system in the process of oxidation of methane, regeneration methods were found that allow stable conduct of the process of SCO and SOC of methane for 410 hours. As a result of the process, a synthesis gas was obtained with a ratio of $H_2/CO = 2.0$ without the formation of CO_2, which is most suitable for its use in the Fischer-Tropsch synthesis of methanol and hydrocarbons. It is assumed that the reaction of SCO of CH_4 proceeds by a direct mechanism involving reduced Pt^0, Ru^0 and Pt-Ru nanoclusters detected by TEM research after testing the stability of the developed Pt: Ru (1:1) catalyst on a carrier.

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МЕТАННЫҢ СИНТЕЗ-ГАЗҒА ДЕЙІН СЕЛЕКТИВТІ КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ ЖӘНЕ БУ ОТТЕКТІ КОНВЕРСИЯЛАНУЫ

Аннотация. Синтез-газ мұнай-химия өнімдерінің кең спектрін өндіру үшін негізгі шикізат болып саналады. Синтез-газ құрамындағы H_2 және CO арақатынасының корреляциясы сұйық көмірсутектерді немесе CH_3OH оксигенаттарын, CHCOOH, CH_2O және C_2H_6O. Синтез-газды алумен метанның бу риформингінің баламалы реакциясы сутегі оксидіне оңтайлы молярлық қатынасына 2,0 тең болатын метанның бөліну үдерісі болуы мүмкін.

Табиғи газ өндіру аудандарында ірі ауқымды өндіріс құру мақсатты өнімнің өзіндік құнын айтарлықтай төмендетуге және қоршаған ортаның ластануын төмендетуге мүмкіндік берер еді. Оттегінің жетіспеуі барысында және контактінің миллисекунд уақытында CH_4 тікелей тотығу жолымен синтез-газды алу мұнай-химия синтезінде маңызды рөл атқаратын М. Претре алғаш рет жүзеге асырған салыстырмалы жаңа реакция болып саналады. Зерттеушілер 90-жылдары бұл үдерісті зерттеуге блок кеуекті катализаторлары бар реакторды микрореактор үдерісі барысында екінші реакциялардың алдын алу барысында пайдалану арқылы назарға алған болатын.

Зерттеу жүргізу үшін $2\%Ce/(\theta+\alpha)-Al_2O_3$ тасымалдағышына қондырылған Pt-, Ru және Pt-Ru каталитикалық жүйелердің сериясы дайындалды. Каталитикалық жүйелер элементтерді тасымалдағышқа $/(\theta+\alpha)-Al_2O_3$ (100 − 200 мкм, Sуд = 57,7 $м^2/г$) металл тұздарының алдын ала дайындалған су ерітінділері негізінде $Ce(NO_3)_3\cdot 6H_2O$, $Ru(OH)Cl_3$ және $H_2PtCl_6\cdot 6H_2O$ арқылы ауаның ылғал сыйымдылығы бойынша капиллярлы сіңдіру әдісімен жүзеге асып, 873 К 3 сағат бойы ауада біртіндеп кептіріліп, ауада біртіндеп қыздырылады. 10 мг катализатордың үлгісі кварц ұнтағымен мұқият араластырылады (бөлшектер өлшемі 1:43 қатынасында 0,2 мм, қабат биіктігі 20 мм). Содан кейін жоғарыдан реакторға қосылған бөлшектер ірі кварц (12 мм) дейінгі жалпы биіктігі қабатының 70 мм. болатын ұнтақпен жабылады.

Содан кейін микрореакторға метанның талғамды каталитикалық тотығу үдерісінің бастапқы реакциялық қоспасы мынадай жағдайларда жіберіледі: $CH_4:O_2:Ar = 2,0 : 1,0 : 97,0$, (%), T = 1173K, $V = 9\cdot 10^5$ $сағ^{-1}$, τ = 0,004 с. Метанның бу оттекті конверсия процесін жүргізу кезінде: $CH_4 : O_2 : H_2O : Ar = 2,0 : 1,0 : 2,0 : 95,0$, %, T = 1073 – 1173 K, $V = 1\cdot 10^5 - 9\cdot 10^5$ $сағ^{-1}$.

Бастапқы реакциялық қоспаны және алынған үдеріс өнімдерін талдау «Хроматэк Кристалл 5000.1» хроматографын пайдалана отырып, «Хроматэк Аналитик 2,5» бағдарламалық қамтамасыз ету арқылы жүргізілді. Жылу өткізгіштігі бойынша детекторы бар диатомитті тасымалдағышта гептадеканның 20% құрамының фазасымен толтырылған капиллярлы баған пайдаланылды. Сынамаларды іріктеу реакция басталған сәттен, 1 минуттан кейін автоматты түрде жүргізілді. Алынған өнімдердің концентрациясы қол жеткізілген калибрлеу графиктері негізінде анықталды.

Катализаторлардың электронды-микроскопиялық сипаттамалары 75 kV үдеткіш кернеу кезінде ЭМК – 125 К (1990, КСРО) микроскопында алынды. Морфологиясы, бөлшектер өлшемі және олардың химиялық құрамы электрондардың микродифракциясын қолдана отырып, экстракциямен реплик әдісімен 120000 есеге дейін ұлғаю барысында зерттелді. Көмір репликалары вакуумдық әмбебап постта шаңды, содан кейін катализаторлардың тасымалдаушысы HF-да ерітілді. Микродифракциялық картиналарды идентификациялау 1996 ж. JSPDS картотекасы бойынша жүргізілді.

Pt-Ru = 1 : 1 (Pt : Ru = 0,7 : 0,3, ат.%) катализатордың талғамды каталитикалық тотығу (ТКТ) реакциясында және бу оттекті конверсиясында (БОК) метанның синтез-газға жанасу уақытының миллисекунд кезіндегі зерттеу нәтижелері көрсетілген. Төмен пайыздық түйіршіктелген үлгінің тұрақтылығын зерттеу барысында 1,0% $Pt-Ru/2\%Ce/(\theta+\alpha)Al_2O_3$ каталитикалық жүйенің метанның ТКТ және БОК үдерісінде 410 сағат ішінде тұрақты жүргізуге мүмкіндік беретін регенерациялау тәсілдері анықталды. Үдеріс нәтижесінде $H_2/CO = 2,0$ арақатынасымен CO_2 түзілмей синтез-газ алынды, бұл Фишер-Тропш бойынша метанол мен көмірсутектер синтезінде пайдалануда аса қолайлы екені белгілі. CH_4-ның ТКТ реакциясы Pt:Ru (1:1) катализатордың тұрақтылығын сынаудан кейін ЭМ зерттеу барысында айқындалған нанокластерлердің қалпына келтірілген Pt^0, Ru^0 және Pt-Ru қатысуымен тікелей механизм бойынша өтеді деген болжам жасалды.

Түйін сөздер: Pt-Ru катализаторы, талғамды каталитикалық тотықтыру, бу оттекті конверсия, метан, синтез-газ.

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СЕЛЕКТИВНОЕ КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ И ПАРОКИСЛОРОДНАЯ КОНВЕРСИЯ МЕТАНА В СИНТЕЗ-ГАЗ

Аннотация. Синтез-газ является основным сырьем для производства широкого спектра нефтехимической продукции. Корреляция соотношения H_2 и CO в составе синтез-газа позволяет получать жидкие углеводороды или оксигенаты CH_3OH, CH_3COOH, CH_2O и C_2H_6O. Процесс получения метана, протекающий при молярном соотношении водорода к монооксиду углерода, равном 2,0, может стать реакцией, альтернативной реакции парового риформинга метана для получения синтез-газа. Альтернативной реакцией парового риформинга метана с получением синтез-газа может быть процесс выделения метана, протекающий с оптимальным молярным отношением водорода к оксиду углерода, равным 2,0. Создание крупномасштабного производства в районах добычи природного газа позволило бы значительно снизить себестоимость целевой продукции и снизить загрязнение окружающей среды. Получение синтез-газа путем прямого окисления CH_4 при недостатке кислорода и миллисекундном времени контакта является относительно новой реакцией, впервые осуществленной М. Претре, которая играет важную роль в нефтехимическом синтезе. Исследователи вернулись к изучению этого процесса в 90-е годы благодаря использованию реактора с блочными пористыми катализаторами во время процесса в микрореакторе, когда вторичные реакции предотвращаются.

Для проведения исследований была приготовлена серия Pt-, Ru- и Pt-Ru каталитических систем, нанесенных на 2%Ce/(θ+α)−Al_2O_3. Каталитические системы были приготовлены методом последовательного внесения элементов на носитель (θ+α)−Al_2O_3 (100 − 200 мкм, $S_{уд}$ = 57,7 м^2/г) из заранее приготовленных водных растворов солей металлов $Ce(NO_3)_3 \cdot 6H_2O$, $Ru(OH)Cl_3$ и $H_2PtCl_6 \cdot 6H_2O$ методом капиллярной пропитки на воздухе по влагоемкости с последующим постепенным прогревом на воздухе при 873 К 3 ч. Активность разработанных каталитических систем в процессе СКО метана определяли в каталитической проточной установке при атмосферном давлении в кварцевом микрореакторе с внутренним диаметром 0,45 см. 10 мг навеска катализатора тщательно перемешивалась с порошком кварца (размер частиц 0,2 мм в соотношении 1:43, высота слоя 20 мм). Затем сверху в реактор добавлялись частицы более крупного кварца (1÷2 мм) до общей высоты слоя 70 мм. После этого подавалась исходная реакционная смесь при следующих условиях: CH_4:O_2:Ar = 2,0 : 1,0 : 97,0, (%), при T = 1173К, $V = 9 \cdot 10^5$ ч$^{-1}$, τ = 0,004 с. При процессе ПКК метана: CH_4 : O_2 : H_2O : Ar = 2,0 : 1,0 : 2,0 : 95,0, %, T = 1073 – 1173 К, $V = 1 \cdot 10^5$ - $9 \cdot 10^5$ ч$^{-1}$. Анализ исходной реакционной смеси и полученных продуктов процесса проводили с использованием хроматографа «Хроматэк Кристалл 5000.1» с программным обеспечением «Хроматэк Аналитик 2,5», снабженного автоматическим газовым дозатором, подключенным непосредственно к установке по окислению метана в синтез-газ. Использовалась капиллярная колонка, заполненная фазой состава 20% гептадекана на диатомитовом носителе с детектором по теплопроводности. Отбор проб проводился автоматически через 1 минуту после начала реакции. Концентрации полученных продуктов определяли на основе полученных калибровочных графиков. Электронно - микроскопические характеристики катализаторов получены на микроскопе ЭМК – 125 К (1990, СССР) при ускоряющем напряжении 75 kV. Морфология, размер частиц и их химический состав исследовались при увеличении до 120000 раз методом реплик с экстракцией с применением микродифракции электронов. Угольные реплики напылялись в вакуумном универсальном посту, затем носитель катализаторов растворялся в HF. Идентификация микродифракционных картин проводилась по картотеке JSPDS 1986 г.

В представленной работе приведены данные по изучению стабильной работы разработанной Pt-Ru = 1:1 (Pt:Ru = 0,7:0,3, ат.%) каталитической системы. Активность катализатора исследована в реакции селективного каталитического окисления (СКО) и парокислородной конверсии (ПКК) метана в синтез-газ при малых временах контакта. В процессе исследования стабильности низкопроцентного гранулированного образца 1,0%Pt-Ru/2%Ce/(θ+α)Al_2O_3 каталитической системы в процессе окисления метана найдены способы регенерации, позволяющие стабильно проводить процесс СКО и ПКК метана в течение 410 часов. В результате процесса получен синтез-газ с соотношением H_2/CO = 2,0 без образования CO_2, что наиболее подходит для его использования в синтезах метанола и углеводородов по Фишеру-Тропшу. Предполагется, что реакция СКО CH_4 протекает по прямому механизму с участием восстановленных Pt^0, Ru^0 и Pt-Ru нанокластеров, обнаруженных ЭМ исследованием после испытания стабильности разработанного Pt:Ru (1:1) катализатора на носителе.

Ключевые слова: Pt-Ru нанесенный катализатор, селективное каталитическое окисление, парокислородная конверсия, метан, сингаз.

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PRODUCTION OF SULFOCATIONITE BY MODIFICATION OF NATURAL COAL WITH CONCENTRATED SULFURIC ACID

Abstract. Monitoring the content of rare metals in environmental objects at the level of their maximum permissible concentrations is an important environmental task. The widely used physicochemical methods do not always provide a direct solution to this problem because of the influence of the matrix composition of the sample on the results of the determinations, as well as low concentrations of the determined elements. This article proposes a new modified sulfonated charcoal based on coal from the Shubarkul deposit for sorption of rare metal ions from water bodies. Concentrated sulfuric acid (H_2SO_4) is used as a modifier. The synthesis of new highly permeable cross-linked, sulfonated cation exchangers and their composition, structure by chemical and physical methods was investigated. The static exchange capacity (SEC) of sulfonated coal was calculated. The article shows an increase in SEC from the concentration used in the modification of H_2SO_4. During the synthesis, the static exchange capacity of sulfonated coal increases at 240 min. heating up. The temperature stability of sulfonated coal is higher to (100-120 °) C. Sulfonated coal refers to medium acid cation exchangers, which work effectively at pH 2-14. The resulting sorption materials are recommended for use in treatment plants for the removal of rare metal ions.

Key words: natural coal, modified coal, sorption, rare metal ion, sulfonated coal, water purification.

Introduction. The extraction of rare metals is possible from ash and slag dumps of energy enterprises. In the scientific works of Krasnov, O.S. and Salikhova V.A. It is noted that the processing of ash and slag waste in industrial production can produce from one to several tens of tons of rare metals per year. Thus, the associated beneficial components in the processing of coal can be considered a promising mineral resource base for a number of rare metals [1]. The global problem of effective and cheap treatment of wastewater and drinking water from rare metal ions is of great importance. Common methods of water purification are various sorption options based on the absorption of harmful substances by various sorbents [2-6,7]. The ion-exchange method using natural and synthetic ion-exchange materials, which makes it possible to extract these metals from wastewater, attracts much attention [8, 9]. Most sorbents that have not been used yet are very expensive and have a limited exposure with a relatively narrow range of effects. The method of manufacturing these sorbents is complex and takes more time [10,11]. In this regard, a promising direction is the creation of new effective types of sulfocationionites from cheap local raw materials of fossil coals [12,13]. The large-scale use of sorbents based on carbon raw materials for the sorption of rare and rare-earth metal ions requires the targeted modification of cheap types of organic raw materials: fossil solid fuels, natural and industrial organic waste [14].

New sulfocationionite was obtained by chemical modification of coal from the Tengiz field with concentrated sulfuric acid [15]. The sorption and kinetic properties of V^{2+}, Mo^{2+}, and W^{2+} ions were studied. Sulfonation of brown coals and modification of sulfonated coal, which can be used for chemical treatment of water, are proposed. For example, there is a known method for producing sulfonated coal, in which coal grits are treated with oleum in solfatar at a temperature of 110-140 ° C [16]. Several technologies for coal sulfonation are also available for chemical treatment of water [17-20]. The method of acid activation is most effective for the preparation of sorbents from this natural material.

This article describes sulfonated coal as a simple way to purify rare metal ions from drinking and wastewater. The method is based on the modification by sulfuric acid of a carbon carrier, which is coal from the Shubarkul basin deposit, as a cheap local carbon sorbent. The presence on the altered carbon surface of sulfo groups will enhance the selectivity of the extraction of rare metal ions.

Experimental part. Coal Sulphonation. Heat treatment of coal of the Shubarkul deposit was carried out at a temperature of 110 ° C for 2 hours in an oven until the moisture content was not more than 1%. After heat treatment, the coal was treated with concentrated 96% sulfuric acid, with different ratios of solid and liquid phases (Table 1.).

Table 1 - Conditions for sulfonation of coal

№	Mass ratio, Coal: H_2SO_4	T °C	t, min
1	1:3	60 - 180	30 - 6
2	1:2,5		
3	1:2		
4	1:1.5		
5	1:1		
6	1:0.5		

After coal modification, a loose black product was formed, which was washed in a 5% NaOH solution in order to remove unreacted substances.

Results and its discussion. According to laboratory results, the static exchange capacity (SEC) was calculated according to the method [21]. In figure 1. shows an increase in SEC from the concentration used in the modification of H_2SO_4. An increase in acid concentration above 2.5 mol does not affect a further increase in SEC. With an increase in temperature to 120 ° C, SEC is the highest (Fig.2.), With a further increase in temperature its value decreases. During synthesis, a heating time of up to 240 min (Fig. 3.) Increases the SEC of sulfonated coal.

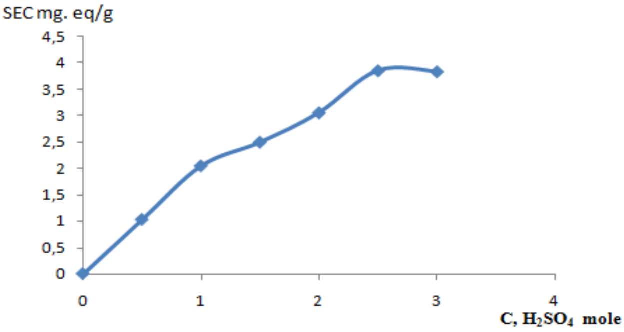

Figure 1 - Dependence of static exchange capacity of sulfonated coal on the concentration of sulfonating agent

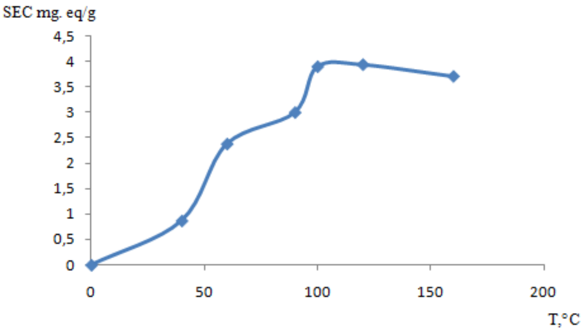

Figure 2 - Dependence of static exchange capacity of coal-based sulfocationite on the temperature of heating

The temperature stability of sulfonated coal is higher up to (100–120) ° C. Moreover, as a rule, the H form of ion exchangers is less stable than salt form.

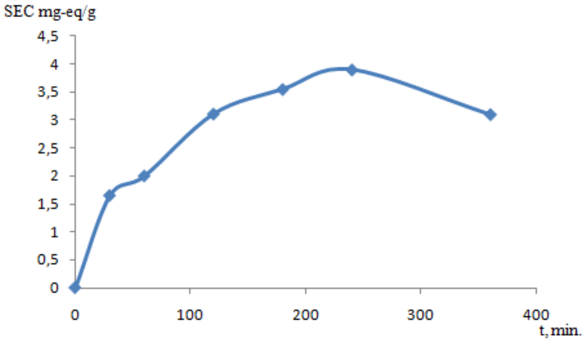

Figure 3 - Dependence of the static exchange capacity of sulfonated coal on heating time

Static exchange capacity – the number of milliequivalents of an ion absorbed over a given time of 1 g of dry ion exchange. As can be seen from figure 4, sulfocationionite absorbs 3.90 mg-eq/g in 240 minutes.

Sulfonated coal refers to medium acid cation exchangers, which work effectively at pH 2-14.

Conclusion. In this study, a new modified sorbent is available that is effective with sorption capacity for rare metal ions based on sulfonated Shubarkul coal. The article shows an increase in SEC from the concentration used in the modification of H_2SO_4. During the synthesis, the SEC of sulfonated coal increases at 240 min. heating up. The temperature stability of sulfonated coal is higher to (100-120°) C. Sulfonated coal refers to medium acid cation exchangers, which work effectively at pH 2-14. The resulting sorption materials are recommended for use in treatment plants for the removal of rare metal ions.

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ТАБИҒИ КӨМІРДІ КОНЦЕНТРЛІ КҮКІРТ ҚЫШҚЫЛЫМЕН МОДИФИКАЦИЯЛАУ АРҚЫЛЫ СУЛЬФОКАТИОНИТ АЛУ

Аннотация. Қоршаған орта нысандарындағы сирек кездесетін металдардың мүмкіндігі шектеулі концентрациясының деңгейін бақылау экологиялық маңызды мәселелердің бірі саналады. Сынаққа алынған заттың матрицалық құрамы нәтижеге әсер ететіндігінен және анықталатын элементтердің концентрациясы төмен болғандықтан кеңінен қолданылатын физико-химиялық әдістер көбінесе мәселенің түрлі шешімін айқындай алмайды. Бұл мақалада су нысандарынан сирек кездесетін металл иондарын сорып алу үшін Шұбаркөл кен орнындағы көмірге негізделген жаңа модифицирленген көмір ұсынылады. Модификатор ретінде концентрацияланған күкірт қышқылы (H_2SO_4) қолданылады. Өткізгіш жаңа, сульфатталған катион алмастырғыштардың синтезі және олардың құрамы, құрылымы химиялық және физикалық әдістермен зерттелді. Шұбаркөл кен орнының көмірін термиялық өңдеу, ылғалдылығы 1%-дан асқанға дейін пеште 2 сағат 110°С температурада жүргізілді. Термиялық өңдеуден кейін көмір концентрацияланған 96% күкірт қышқылымен, қатты және сұйық фазалардың түрлі қатынасы негізінде өңделді. Көмірді модификациялаудан кейін борпылдақ қара өнім пайда болды, модифицирленген көмірден реакцияланбаған заттарды кетіру үшін 5% NaOH ерітіндісімен жуылды. Статикалық алмасу сыйымдылығы – берілген уақыт ішінде 1 г құрғақ ион алмастырғышқа сіңген ионның саны. Сульфатталған көмірдің статикалық алмасу сыйымдылығы есептелді. Мақалада H_2SO_4 модификациясында қолданылатын концентрациядан статикалық алмасу сыйымдылығының жоғарылау деңгейі көрсетілген. Синтездеу кезінде сульфатталған көмірдің статикалық мөлшері 240 мин. жоғарылайды. Сульфатталған көмірдің температуралық тұрақтылығы (100-120°С) жоғары. Сульфатталған көмір pH 2-14 аралығында тиімді жұмыс істейтін орташа қышқылдық катион алмастырғыштарға жатады.

Энергетикалық кәсіпорындардың күл мен қож (шлак) үйінділерінен сирек металдарды алуға болады. О.С. Краснов пен В.А. Салихованың ғылыми еңбектерінде көрсетілгендей, күл мен қож (шлак) қалдықтарын өнеркәсіптік өндірісте қайта өңдеу жылына бір тоннадан бірнеше ондаған тоннаға дейін сирек металдарды шығара алады. Сонымен, көмірді қайта өңдеуге байланысты пайдалы компоненттер бірқатар сирек кездесетін металдар үшін перспективті минералды-шикізат базасы деп санауға болады. Ағынды және ауыз суларды сирек кездесетін металл иондарынан тиімді және арзан тазартудың жаһандық мәселесі үлкен мәнге ие болып отыр. Суды тазартудың кең таралған әдістері – түрлі сорбенттермен зиянды заттарды сіңіруге негізделген түрлі сорбциялық нұсқалар. Табиғи және синтетикалық ион алмасу материалдарын қолданатын ион алмасу әдісі бұл металды ағынды сулардан алуға мүмкіндік береді. Әлі қолданылмаған сорбенттердің көпшілігі өте қымбат және шектеулі әсерге ие, олардың әсер ету тиімділігі өте аз. Бұл сорбенттерді өндіру әдісі күрделі және көп уақытты қажет етеді. Осыған байланысты арзан жергілікті қазбалы көмір шикізатынан сульфатокиониттердің жаңа тиімді түрлерін құру перспективалы бағыт болып саналады. Сирек және сирек кездесетін металл иондарын сорбциялау үшін көміртегі шикізатына негізделген сорбенттерді кеңінен қолдану органикалық шикізаттың арзан түрлерін мақсатты түрлендіруді талап етеді: қазбалы қатты отындар, табиғи және өнеркәсіптік органикалық қалдықтар. Суды химиялық тазартуда көмір сульфанизациясының бірнеше технологиялары да бар. Қышқылдандыру әдісі осы табиғи материалдан сорбенттерді дайындау үшін тиімді саналады. Бұл мақалада сульфатталған көмір сирек кездесетін металл иондарын ауызсу мен ағынды сулардан тазартудың қарапайым әдісі ретінде сипатталады. Бұл әдіс арзан жергілікті Шұбаркөл бассейнінен алынған көмірді күкірт қышқылымен модифицирлеуге негізделген. Өзгертілген көміртегі бетінде сульфо топтардың болуына байланысты сирек кездесетін металл иондарын сорып алу селективтілігін арттырады.

Түйін сөздер: табиғи көмір, модификацияланған көмір, сорбция, сирек кездесетін металл ионы, сульфатталған көмір, суды тазарту.

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ПОЛУЧЕНИЕ СУЛЬФОКАТИОНИТА ПУТЕМ МОДИФИКАЦИИ ПРИРОДНОГО УГЛЯ КОНЦЕНТРИРОВАННОЙ СЕРНОЙ КИСЛОТОЙ

Аннотация. Контроль содержания редких металлов в объектах окружающей среды на уровне их предельно допустимых концентраций является важной экологической задачей. Широко используемые физико-химические методы не всегда обеспечивают прямое решение этой задачи из-за влияния матричного состава пробы на результаты определений, а также низких концентраций определяемых элементов. В данной статье предложен новый модифицированный сульфоуголь на основе угля Шубаркульского месторождения для сорбции ионов редких металлов из водных объектов. В качестве модификатора используется концентрированная серная кислота (H_2SO_4). Был исследован синтез новых высокопроницаемых сшитых, сульфосодержащих катионитов и их состав, структура химическими и физическими методами. Термическую обработку угля Шубаркульского месторождения проводили при температуре 110 °C в течение 2 часов в сушильном шкафу до тех пор, пока содержание влаги составило не более 1 %. После термообработки уголь обрабатывали концентрированной 96% серной кислотой при различном соотношении твердой и жидкой фазы. После модификации угля образовался рыхлый продукт черного цвета, который промывали в 5 % растворе NaOH с целью удаления не прореагировавших веществ. Статическая обменная емкость – количество миллиэквивалентов иона, поглощенное за определенное время 1 г сухого ионита. Рассчитывали статическую обменную емкость сульфоугля. В статье показано увеличение статической обменной емкости от концентрации использованной при модифицировании H_2SO_4. Во время синтеза увеличивается статическая обменная емкость сульфоугля при 240 мин. нагревании. Температурная устойчивость сульфоугля выше до $(100\text{-}120^{\circ})$C. Сульфоуголь относят к среднекислотным катионитам, которые эффективно работают при показателях pH 2-14.

Извлечение редких металлов возможно из золо-шлаковых отвалов энергетических предприятий. В научных работах Краснова О.С. и Салихова В.А. отмечается, что переработка золо-шлаковых отходов на промышленном производстве может дать от одного до нескольких десятков тонн редких металлов в год. Таким образом, попутные полезные компоненты при переработке углей можно считать перспективной минерально-сырьевой базой ряда редких металлов. Всемирная проблема эффективной и дешевой очистки сточных и питьевых вод от ионов редких металлов имеет большое значение. Распространенными методами очистки воды являются различные варианты сорбции, основанные на поглощении вредных веществ различными сорбентами. Большое внимание привлекает ионообменный метод с использованием природных и синтетических ионообменных материалов, позволяющий извлекать эти металлы из сточных вод. Большинство сорбентов, которые до сих пор не использовались, очень дорогие и имеют ограниченную экспозицию с относительно узким диапазоном эффектов. Способ изготовления этих сорбентов сложен и занимает больше времени. В этой связи перспективным направлением является создание новых эффективных видов сульфокатионитов из дешевого местного сырья ископаемых углей. Крупномасштабное использование сорбентов на основе углеродного сырья в целях сорбции ионов редких и редкоземельных металлов требует целенаправленного модифицирования дешевых видов органического сырья: ископаемых твердых топлив, природных и техногенных органических отходов. Несколько технологий для сульфирования угля также доступно применяется для химической очистки воды. Способ кислотной активации является наиболее эффективным для приготовления сорбентов из данного природного материала. В настоящей статье описан сульфированный уголь как простой способ очистки питьевых и сточных вод от ионов редких металлов. Способ основан на модифицировании серной кислотой углеродного носителя, представляющего собой уголь из месторождения Шубаркульского бассейна, в качестве дешевого местного углеродного сорбента. Присутствие на измененной углеродной поверхности сульфогрупп позволит усилить селективность извлечения ионов редких металлов.

Ключевые слова: природный уголь, модифицированный уголь, сорбция, ион редкого металла, сульфированный уголь, очистка воды.

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CATALYTIC PROCESSING OF PROPANE INTO IMPORTANT PETROCHEMICAL PRODUCTS

Abstract. In the Republic of Kazakhstan, despite the huge reserves of hydrocarbon raw materials, it is mainly consumed in the form of domestic, industrial and motor fuels, remains are burned as part of the exhaust gases, or again driven into the oil-bearing strata. Propane, which is in the composition of associated gases and formed in petrochemical, in the first case, either burned or used as fuel after separation. In the second case, it is partially used in petrochemicals, as well as municipal or motor fuel, the rest is exported. In order to identify the ability of the developed catalysts to regeneration or reoxidation and determine the energy characteristics of hydrogen and oxygen, the study was carried out by the methods TPR and TPO, as well as by TEM, XRD and BET for determine the morphology, particle size and their chemical composition. In the present work it is shown that on the developed $5\%V/(\Theta+\alpha)Al_2O_3$ catalyst the process of oxidative conversion of propane passes with the formation of 24.5% ethylene and 27.5% hydrogen under the optimal conditions: 66.5% C_3H_8 + 33.5% CO_2, $T = 700^oC$, $W = 1000\ h^{-1}$ and $C_3H_8 : CO_2 = 2 : 1$.

Key words: catalytic oxidation, propane, ethylene, hydrogen, carbon dioxide.

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

According to the annual Statistical Review of World Energy – 2018, published by British Petroleum (BP) at the end of 2017, proven natural gas reserves in the world are estimated at 193.5 trillion cubic meters. Kazakhstan ranks 15th in the world and 4th in the CIS of natural gas reserves. The prospects for the development of the global gas processing industry are associated with the creation and introduction of new catalytic environmentally friendly technologies for producing of olefins, based on production of polymers, alcohols and motor fuels. Gas processing plants in Kazakhstan are currently engaged mainly in the purification of gases from water, impurities of carbon dioxide and hydrogen sulfide for their use for domestic purposes. This situation is associated with the lack or absence of new catalytic technologies for the directed processing of light C_1-C_4 alkanes. There are no production facilities for the production of olefins, plastics, motor fuels and other products whose demand is met by imports. Therefore, an important task is the intensive development of the industrial processing of light hydrocarbon raw materials, the reserves of which far exceed oil reserves.

It is known that vanadium compounds [1-4] are widely used for homogeneous and heterogeneous catalysis, especially in selective oxidation of light alkanes, which are one of the most effective catalysts.

Thus, the authors of [1] investigated the activity of vanadium catalysts deposited in the oxidation of propane. It was determined that the yield of propylene was 10% with 30% conversion of propane.

In [2], V_2O_5/SiO_2 catalysts promoted by a fluoride anion and obtained by successive addition of different amounts of F-were investigated. The performance and structure of the catalysts were greatly influenced by the sequence of fluoride impregnation and the method of obtaining catalysts. Oxidative dehydrogenation of propane was carried out in a reactor with a fixed bed with a continuous flow at atmospheric pressure, a temperature range of 400 - 600°C and a ratio of gases supplied: 10% C_3H_8 : 5% O_2 : 85% Ar.

The total flow rate of the reaction gas mixture was 50 ml/min, the mass of the catalyst was 200 mg, the volume velocity was 9000 h^{-1}. For VOC-F catalyst at 540°C selectivity of propene amounted to 64.16% in the conversion of propane of 14.76%. Compared to the V-Si-O catalyst, propene selectivity increased by 9.89% and a small increase in C_3H_8 conversion was found.

Increasing atmospheric CO_2 levels have a negative impact on the environment. The chemical use of CO_2, one of the main greenhouse gases, is an important step towards green chemistry. The main problem associated with the use of CO_2 is the thermodynamic stability of this molecule. One of the technologies that is gaining strength and importance in the scientific world is the use of CO_2 as an oxidizer for catalytic oxidative transformation at high temperatures [5-8].

Previously, we investigated the process of oxidative conversion of light alkanes into olefins in the presence of oxygen on different types of catalysts [9-18].

The paper presents the data of the activity of the developed deposited catalyst based on vanadium, capable of conducting the process of oxidative conversion of propane into ethylene and hydrogen, using CO_2 as an oxidizer.

Experimental

Catalyst preparation

The catalytic systems were synthesized by the method of impregnation in air. The developed compositions of catalysts were prepared by capillary impregnation of mixed aqueous solutions of metal salts supported on carriers by moisture capacity, followed by drying at T = 200°C for 2 h. Calcinations of samples at T = 500°C for 2 h in air was carried out for decomposition of supported metal salts and corresponding volatilization of nitrates from the catalyst surface.

Characterization techniques

Analysis of the initial mixture and the reaction products was performed using "Chromos GC-1000" (Russia) chromatograph, which was equipped with packed and capillary columns. The packed column is used for the analysis of H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3-C_4 hydrocarbons, CO and CO_2. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. The speed of the carrier gas Ar is 10 ml / min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve V = f (S) was constructed, where V - amount of substance in ml, S - peak area in cm^2. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was ± 3.0%.

Physico-chemical research

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

XRD analysis was performed on a Siemens Spellman DF3 diffractometer using CuKa1 (λ = 1,5406 Å) radiation by powder method in the angle range $2\theta = 5 - 100°$.

Thermoprogrammed oxidation (TPO) and thermoprogrammed regeneration (TPR) of the developed catalysts was investigated on the analyzer "Chemosorb".

Morphology, particles size, chemical composition of initial and worked out catalysts were performed on transmission electron microscope TEM-125K with enlargement up to 66000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in universal vacuum station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns was carried out by means of ASTM cart index (Ukraine).

Results and discussion. The methods for synthesis of the developed catalysts were determined and the physicochemical characteristics of the catalysts were established. Developed 5% V/(ϴ+α)Al_2O_3 catalyst was studied by the BET, XRD, TEM, TPR and TPO methods.

The results of the studies on the determination of the surface area of the developed catalysts it is established that with increasing percentage of vanadium on the carrier equally increases the surface area of the catalytic system (figure 1).

It is known that the larger the specific surface area of the catalyst, the greater the number of active centers are on the surface, the greater the activity of the catalyst. It is assumed that this dependence is associated with the activity of 5% V/(ϴ+α)Al_2O_3 catalyst in the oxidative conversion of propane to ethylene and hydrogen under optimal reaction conditions.

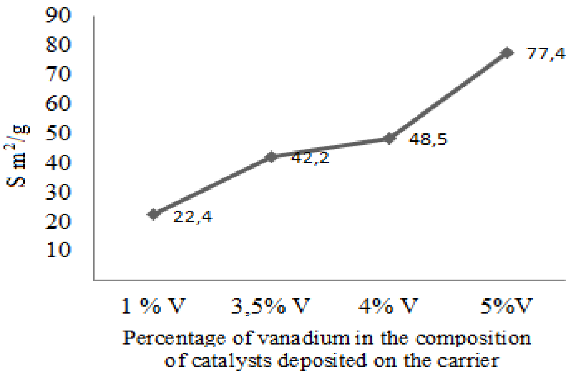


Figure 1 - Change in the specific surface area of vanadium in the composition of catalysts deposited on the carrier

Before the x-ray phase analysis of the samples, the literature sources were analyzed and the mechanisms of thermal decomposition of ammonium metavanadate and possible phases formed were determined [19.20].

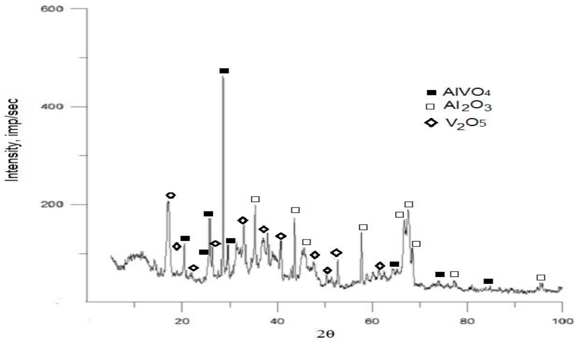


Figure 2 - XRD analysis of 5% V/(ϴ+α)Al_2O_3 catalyst

XRD analysis of 5% V/(ϴ+α)Al_2O_3 catalyst (figure 2) revealed the following phases: $AlVO_4$ (JSPDS, 11-0130), Al_2O_3 (JSPDS, 42-1468) and V_2O_5 (JSPDS, 41 -1426). It should be noted that the phase $AlVO_4$ (JSPDS, 11-0130) was detected only on a single-component vanadium catalyst. It is assumed that this detected phase of the aluminum-vanadium bond promotes the formation of ethylene and hydrogen during the oxidative transformation of propane.

This conclusion is also confirmed by electron microscopic studies of catalysts. The sample is presented mainly by aggregates of translucent particles of plate type, filling a significant part of the surface of the carrier. In figure 3a shows aggregates of translucent particles, the sizes of which vary from 50-70 nm to 100-200 nm. The microdiffraction pattern is represented by a large set of symmetrical and separate reflexes and can be attributed to a mixture of phases: V_6O_{11} (JCPDS, 18-1451), V_2O_5 (JCPDS, 19-1391), $AlVO_4$ (JCPDS, 25-26).

Figure 3b shows the units of the large semi-transparent particles with a size of 100-200 nm. The microdiffraction pattern is represented by a series of reflexes and individual reflexes and can be attributed to a mixture of phases: V_2O_5 (JCPDS, 19-1391), VOOH (JCPDS, 27-1366), $VO_{0.9}$ (JCPDS, 10-313).

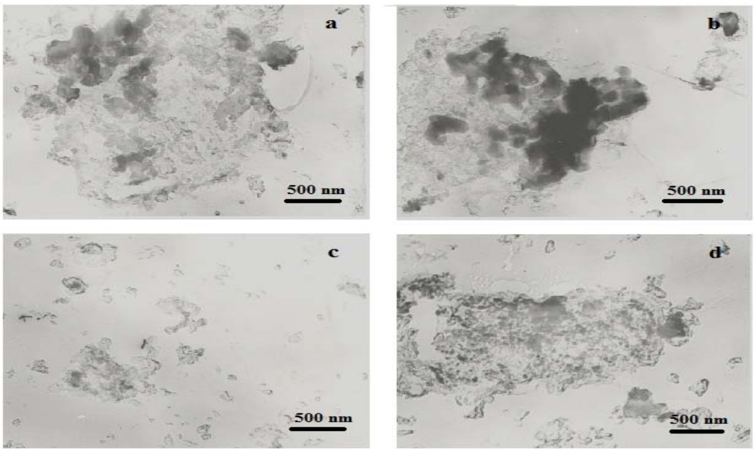


Figure 3 - TEM images of 5% $V/(\Theta+\alpha)Al_2O_3$ catalysts

Figure 3c shows a translucent particle size of 50-100 nm, filling the surface of the carrier. The microdiffraction pattern is represented by reflexes and can be attributed to a mixture of phases: VO_2 (JCPDS, 31-1439), $VO_2 \cdot H_2O$ (JCPDS, 18-445), V_6O_{13} (JCPDS, 27-1332), V_3O_4 (34-615).

Figure 3d shows the area of dense settlement of the carrier by small particles of 20-50 nm in size. There are several large particles exceeding 150 nm. Microdiffraction pattern is represented by reflexes, located on the rings, and individual reflexes, and can be attributed to a mixture of phases: $V_7O_{17} \cdot H_2O$ (JCPDS, 15-247) и γ-VO_2 (JCPDS, 35-361).

Figure 4 shows the TPR spectrum of the vanadium catalyst. Regeneration of hydrogen was carried out in the region of 400-1000°C with four clearly defined maxima, which on the basis of TEM and literature data can be associated with successive transitions V_2O_5 in V_6O_{13} ($Tmax^{I}$=700°C), V_6O_{13} in VO_2 (T_{max}^{II}=840°C), VO_2 in V_8O_{15} ($Tmax^{III}$=920°C) and then V_8O_{15} in V_2O_3 ($Tmax^{IV}$=980°C); shoulder 550°C corresponds to the regeneration weakly bound adsorbed oxygen. Theoretical calculations have shown that the amount of hydrogen absorbed in different peaks correlates well with the data of chromatographic analyses.

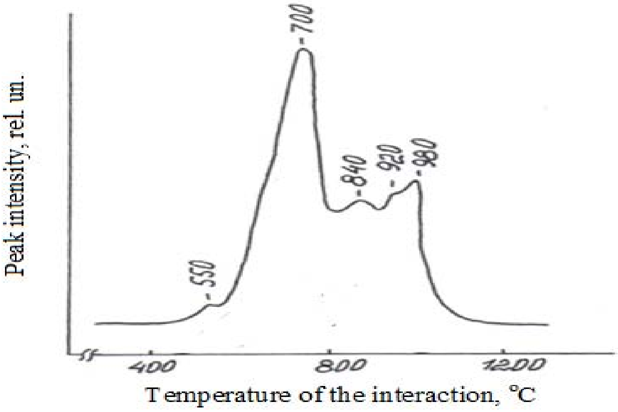


Figure 4 - TPR spectrum of $5\%V/(\theta+\alpha)Al_2O_3$ catalyst

It is known that the stable activity of the catalyst is ensured by the reversibility of the reduction and reoxidation processes in the surface deposited structures of vanadium oxide, so we studied the ability of the reduced catalysts to reoxidation under the influence of oxygen.

When treated with a mixture of 6% O_2+He catalyst oxygen absorption is starting from 100°C.

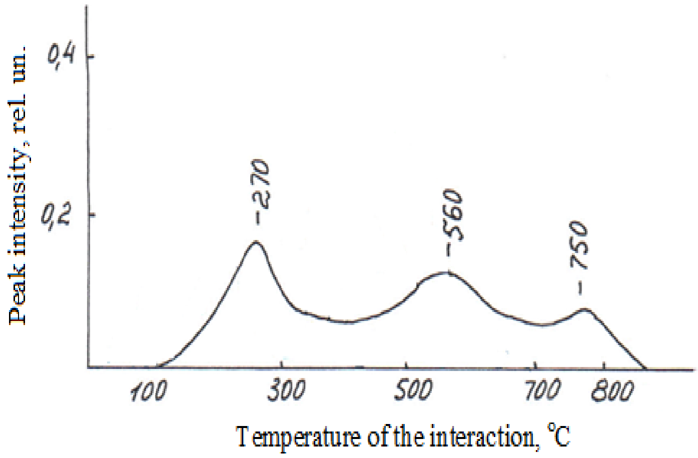


Figure 5 - TPO spectrum of 5%V/(θ+α)Al_2O_3 catalyst

It is assumed that the oxidation of reduced, coordination unsaturated vanadium oxides V^{4+} is with the formation of weakly adsorbed forms of oxygen and V_2O_5, as evidenced by the presence of several peaks of O_2 absorption:

$$O_{2\ (gas)} \rightarrow O_2^-{}_{(surface\ oxide)} \rightarrow O_2^-{}_{(\ ion\ in\ the\ lattice)}$$

From figure 5 it is seen that 5,0%V/(θ+α)Al_2O_3 the catalyst absorbs O_2 at maximum: T_{max}^{I} =270, T_{max}^{II} =560 and T_{max}^{III} =750°C.

The paper presents data of activity of the developed 5% V/(Θ+α)Al_2O_3 catalyst in the oxidation reaction of propane at W = 1000 h^{-1} with a change in T = 500 - 800°C and the ratio of the initial gases in the reaction mixture $C_3H_8 : CO_2$ = 1 : 1, 2 : 1 and 5 : 1.

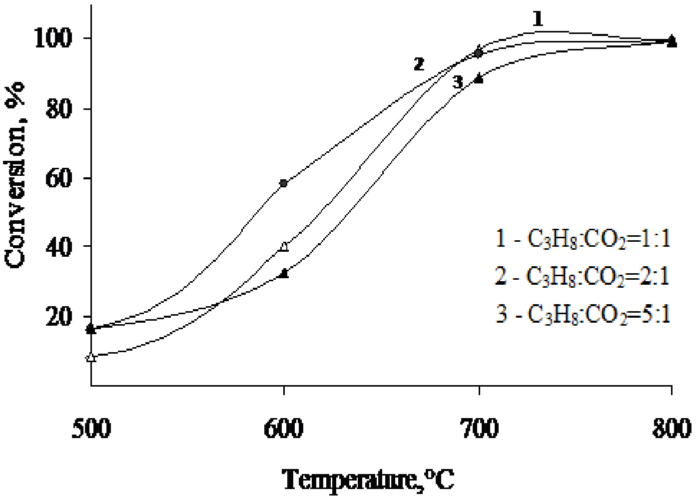
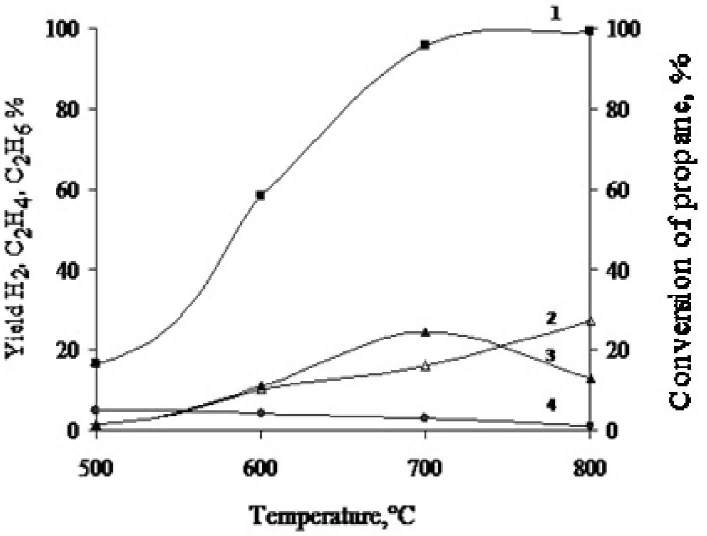


Figure 6 - Investigation of activity of 5%V/(Θ+α)Al_2O_3 catalyst
in the oxidation of propane at W = 1000 h^{-1}

It was found that the optimal ratio for the conversion of propane is $C_3H_8 : CO_2$ = 1 : 1 and $C_3H_8 : CO_2$ = = 2 : 1.

The study of the activity of the developed 5% V/(Θ+α)Al_2O_3 catalyst in the reaction of oxidative conversion of propane at W = 1000 h-1, $C_3H_8 : CO_2 = 2 : 1$ showed that with an increase of the reaction temperature, the yield of ethylene increases which reaches 24.5% at T = 700°C (figure 7).



1- X_{CH_4}; 2- H_2; 3- C_2H_4; 4- C_2H_6

Figure 7 - Investigation of 5% V/(Θ+α)Al_2O_3 catalyst activity
in the reaction of propane oxidation at W = 1000 h^{-1}, $C_3H_8 : CO_2 = 2 : 1$

As the reaction temperature increases, the yield of ethane decreases from 4.9% to 1.0%. It is assumed that the product of the reaction of catalytic oxidation of propane - ethane during the reaction has time to oxidize to ethylene. For the formation of 27.5% hydrogen, the optimum temperature is 800°C.

Conclusion

Thus, in the present work it is shown that on the developed 5% V/(Θ+α)Al_2O_3 catalyst using the methods of BET, XRD, TEM, TPR and TPO certain characteristics were found, namely, an increase in the specific surface area and the connection of the carrier with the active phase. It was found that the process of oxidative conversion of propane on the catalyst developed by 5% V/(Θ+α)Al_2O_3 passes with the formation of 24.5% ethylene and 27.5% hydrogen under the optimal conditions found by the experimental method: 66.5% C_3H_8 + 33.5% CO_2 ($C_3H_8 : CO_2 = 2 : 1$), T = 700°C, W = 1000 h^{-1}.

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ПРОПАНДЫ МАҢЫЗДЫ МҰНАЙ-ХИМИЯ ӨНІМДЕРІНЕ КАТАЛИТИКАЛЫҚ ӨҢДЕУ

Аннотация. Әлемдік мұнай қоры күн сайын заманауи технологияларды пайдалана отырып, үздіксіз өндіру және оларды қайта өңдеу есебінен азайып барады. Бүкіл әлем ғалымдары мұнай химиясын алмастырушы ретінде табиғи газдың орасан зор ресурстарын пайдалану үшін түрлі шикізат материалдары

мен әдістерін іздейді. Осыған байланысты мұнай-химия өнеркәсібі үшін шикізаттың баламалы көзі ретінде табиғи газға айтарлықтай көңіл бөлінді.

2017 жылдың соңында «British Petroleum» (BP) компаниясы жариялаған World Energy-2018 жыл сайынғы статистикалық шолуына сәйкес, әлемдегі дәлелденген табиғи газ қоры 193,5 трлн. текше метрге бағаланды. Қазақстан әлемде 15-орында және табиғи газ қоры бойынша ТМД-да 4-орында. Әлемдік газ өңдеу өнеркәсібін дамыту перспективалары полимер, спирт және мотор отындарын өндіруге негізделген олефиндерді алудың экологиялық таза каталитикалық жаңа технологияларын құру және енгізуге байланысты. Қазақстанның газ өңдеу зауыттары қазіргі уақытта газды судан, көмірқышқыл газы мен күкіртсутегі қоспаларынан, оларды тұрмыстық мақсатта пайдалану үшін тазартумен айналысады. Мұндай жағдай C1-C4 жеңіл алкандарды қайта өңдеуге бағытталған жаңа каталитикалық технологиялардың жетіспеушілігіне немесе жоқтығына байланысты. Мұнда олефиндер, пластмассалар, мотор отындарын және импорт есебінен қанағаттанатын басқа да өнімдерді өндіру бойынша өндірістік қуат жоқ. Сондықтан мұнай қорларынан едәуір асатын жеңіл көмірсутек шикізатын өнеркәсіптік қайта өңдеуді қарқынды дамыту маңызды міндет саналады.

Қазақстан Республикасында көмірсутек шикізатының орасан зор қорына қарамастан, ол негізінен тұрмыстық, өнеркәсіптік және моторлы отын түрінде тұтынылады, қалдықтар пайдаланылған газдардың құрамында жағылады немесе мұнай құятын қабаттарға қайта айдалады. Ілеспе газдардың құрамына кіретін және мұнай химиясында түзілетін Пропан бірінші жағдайда жағылады немесе сепарациядан кейін отын ретінде пайдаланылады. Екінші жағдайда ол ішінара мұнай химиясында, сондай-ақ коммуналдық немесе моторлы отынға пайдаланылады, қалғаны экспортқа шығады.

Жұмыста пропанның этиленге және сутекке тотығу үдерісін жүргізуге қабілетті ванадий негізінде дайындаған катализатордың белсенділігі туралы мәліметтер CO_2 тотықтырғыш қатысында жүретін реакцияға негізделген. Каталитикалық жүйелер ауада сіңдіру әдісімен синтезделді. Катализаторлардың дайындалған құрамы ауада T=200°C кезінде кептіре отырып 2 сағат, одан кейін T=500°C кезінде үлгілерді қыздыру арқылы ылғал сыйымдылығы бойынша тасымалдағыштарға отырғызылған металл тұздарының аралас су ерітінділерін капиллярлы сіңдіру әдісімен дайындалды.

Дайындалған катализаторлар Gapp V-Sorb 2800 (Қытай) талдағышында БЭТ әдісімен зерттелді. Газ тасымалдаушы ретінде гелий мен азот газдарының қоспасы қолданылды. БЭТ әдісі Наноғылым және нанотехнологиялар институтының перспективалы керамикалық және композиттік материалдар зертханасында «Демокритос» (Афины, Греция) өткізілді. Рентгенқұрылымдық талдау Siemens Spellman DF3 дифрактометрінде CuKa1 (λ = 1,5406 Å) сәулеленуін қолдану арқылы $2\theta = 5 - 100^{o}$ бұрыштар диапазонында ұнтақ әдісімен жүргізілді. Термобағдарламаланған тотығу және дайындалған катализаторларды термобағдарламаланған қалпына келтіру (тотықсыздандыру) «Хемосорб» талдағышында зерттелді. Бастапқы және өңделген катализаторлардың морфологиясын, бөлшектер мөлшерін, химиялық құрамын экстракциясы және микродифракциясы бар реплик әдісімен 66000 есеге дейін ұлғайта отырып, ТЭМ-125к жарық түсіретін электрондық микроскоппен жүргізді. Микродифракциялық картиналарды сәйкестендіру ASTM cart index (Украина) индексінің көмегімен жүргізілді.

Жұмыста пропанның этиленге және сутекке тотығу үдерісін жүргізуге қабілетті ванадий негізінде әзірленген катализатордың белсенділігі туралы мәліметтер CO_2 тотықтырғыш ретінде қолданылады. Әзірленген катализаторлардың регенерацияға немесе тотығуға қабілетін анықтау және сутегі мен оттегінің энергетикалық сипаттамаларын анықтау мақсатында тпд және ТПО әдістерімен, сондай-ақ бөлшектер морфологиясын, мөлшерін және олардың химиялық құрамын анықтау үшін ТЭМ, БЭТ және РФА әдістерімен зерттеулер жүргізілді.

Осы жұмыста $5\%V/(\Theta+\alpha)Al_2O_3$ катализаторѕуда пропанның тотығу конверсиясы үдерісі 24,5% этилен және 27,5% сутегі түзілуімен оңтайлы жағдайларда өтеді: 66,5% C_3H_8 + 33,5% CO_2, T = 700°C, W = 1000 $сағ^{-1}$ және $C_3H_8 : CO_2 = 2 : 1$.

Түйін сөздер: каталитикалық тотығу, пропан, этилен, сутегі, көмірқышқыл газ.

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КАТАЛИТИЧЕСКАЯ ПЕРЕРАБОТКА ПРОПАНА В ВАЖНЫЕ НЕФТЕХИМИЧЕСКИЕ ПРОДУКТЫ

Аннотация. Мировые запасы нефти с каждым днем сокращаются за счет непрерывной добычи и их переработки с использованием самых современных технологий. Ученые всего мира ищут различные сырьевые материалы и методы для использования огромных ресурсов природного газа в качестве заменителя нефтехимии. В этой связи значительное внимание уделяется природному газу как альтернативному источнику сырья для нефтехимической промышленности.

Согласно ежегодному статистическому обзору World Energy-2018, опубликованному компанией British Petroleum (BP) в конце 2017 года, доказанные запасы природного газа в мире оцениваются в 193,5 трлн кубометров. Казахстан занимает 15-е место в мире и 4-е место в СНГ по запасам природного газа. Перспективы развития мировой газоперерабатывающей промышленности связаны с созданием и внедрением новых каталитических, экологически чистых технологий получения олефинов, основанных на производстве полимеров, спиртов и моторных топлив. Газоперерабатывающие заводы Казахстана в настоящее время занимаются в основном очисткой газов от воды, примесей углекислого газа и сероводорода для их использования в бытовых целях. Такая ситуация связана с недостатком или отсутствием новых каталитических технологий направленной переработки легких алканов С1-С4. Здесь отсутствуют производственные мощности по производству олефинов, пластмасс, моторных топлив и других продуктов, спрос на которые удовлетворяется за счет импорта. Поэтому важной задачей является интенсивное развитие промышленной переработки легкого углеводородного сырья, запасы которого значительно превышают запасы нефти.

В Республике Казахстан, несмотря на огромные запасы углеводородного сырья, оно в основном потребляется в виде бытового, промышленного и моторного топлива, остатки сжигаются в составе отработанных газов или вновь загоняются в нефтеносные пласты. Пропан, который входит в состав попутных газов и образуется в нефтехимии, в первом случае либо сжигается, либо используется в качестве топлива после сепарации. Во втором случае он частично используется в нефтехимии, а также в коммунальном или моторном топливе, остальное идет на экспорт. Известно, что соединения ванадия широко применяются для гомогенного и гетерогенного катализа, особенно при селективном окислении легких алканов, которые являются одним из наиболее эффективных катализаторов.

В работе представлены данные об активности разработанного катализатора на основе ванадия, способного проводить процесс окислительного превращения пропана в этилен и водород, используя в качестве окислителя CO_2. Каталитические системы были синтезированы методом пропитки на воздухе. Разработанные составы катализаторов получали методом капиллярной пропитки смешанных водных растворов солей металлов, нанесенных на носители по влагоемкости, с последующей сушкой при $T=200^oC$ в течение 2 часов прокаливанием образцов при $T=500^oc$ в течение 2 часов на воздухе.

Удельную площадь поверхности и измерение распределения пор разработанных катализаторов исследовали методом БЭТ на анализаторе GAPP V-Sorb 2800 (Китай). В качестве газа-носителя использовался азот с гелием. Метод БЭТ проводился в Лаборатории перспективных керамических и композитных материалов Института нанонауки и нанотехнологий "Демокритос" (Афины, Греция). Рентгеноструктурный анализ проводился на дифрактометре Siemens Spellman DF3 с использованием излучения CuKa1 (λ = 1,5406 Å) порошковым методом в диапазоне углов $2\theta = 5 - 100^o$. Термопрограммированное окисление (ТПО) и термопрограммированное восстановление (ТПВ) разработанных катализаторов исследовались на анализаторе "Хемосорб". Морфологию, размер частиц, химический состав исходных и отработанных катализаторов проводили на просвечивающем электронном микроскопе ТЭМ-125к с увеличением до 66000 раз методом реплик с экстракцией и микродифракцией. Идентификация микродифракционных картин проводилась с помощью индекса ASTM cart index (Украина).

С целью выявления способности разработанных катализаторов к регенерации или окислению и определения энергетических характеристик водорода и кислорода были проведены исследования методами ТПД и ТПО, а также методами ТЭМ, РФА и БЭТ для определения морфологии, размера частиц и их химического состава.

В настоящей работе показано, что на разработанном 5%V/(Ѳ+α)Al_2O_3 катализаторе процесс окислительной конверсии пропана протекает с образованием 24,5% этилена и 27,5% водорода при оптимальных условиях: 66,5% C_3H_8 + 33,5% CO_2, T = 700°C, W = 1000 $ч^{-1}$ и $C_3H_8 : CO_2 = 2 : 1$.

Ключевые слова: каталитическое окисление, пропан, этилен, водород, углекислый газ.

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PRODUCTION OF CARBON COMPOSITE NANOFIBERS BASED ON COAL TAR AND TEXTILE CORD

Abstract. The article conducted experiments on the production of carbon nanofibers based on coal tar and textile cord by method electrospinning in a laboratory setup. Carbon nanofibers (CNFs) were obtained from textile cord carbonizate (TC) and coal tar (CT) from the Shubarkol deposit, and polymethylmethacrylate (PMMA) was used as a binder. The elemental composition was determined and the surface morphology of the samples was studied. As a result of energy dispersive X-ray spectroscopy and SEM microscopy, the chemical compositions of the CNF based on TC + PMMA were determined, which amounted to C-82.69%, O-1.72%, Si-0.46%, Al-15.14%, TC + CT + PMMA: C-88.43%, O-4.06%, Al-7.32%, S-0.19%, the diameter of carbon nanofibers ranged from 64.2 nm to 539.3 nm.

Keywords: carbon nanofiber, coal tar, nanocomposites, electrospinning, textile cord, polymethylmethacrylate.

Introduction. In recent decades, the unique properties of carbon fibers have expanded the scientific base and technology of composite materials [1]. Carbon may exist in the form of tubular microstructures called filaments or fibers. Carbon nanofibers are a class of materials in which curved graphene layers or nanoconuses are folded in the form of a quasi-one-dimensional filament, whose internal structure can be characterized by the angle α between the graphene layers and the fiber axis [2]. Due to their exceptional thermal, electrical, shielding and mechanical properties [3], they have found application in science-intensive industries: mechanical engineering, nuclear energy, aviation and astronautics, the military-industrial complex, construction, in addition, carbon fibers have the potential to be used in various new applications, such as electrodes, catalyst substrates, adsorbents, composites, etc. Composites based on CNFs can be used as promising materials in many fields, such as electrical devices, electrode materials for batteries and supercapacitors, as well as sensors and others because of their large surface area and relatively high electrical conductivity [4].

Carbon fibers have high atmospheric resistance, resistance to light and penetrating radiation. Carbon fibers are bio-resistant and bio-inert, heat resistant and difficult to combust. Of the properties of carbon fibers, a special place is occupied by a high modulus of elasticity and strength, low density, low coefficient of friction, and also high resistance to atmospheric influence and chemical reagents. In addition to high strength properties and low weight, carbon fibers and composites from them (carbon plastics) are black and conduct electricity well. In addition, carbon fibers have a very low, almost zero coefficient of linear expansion, which makes them indispensable in some special applications [5,6].

The global market for carbon fibers and materials based on them has been growing steadily in recent decades, and only in the last eight years has it grown five times in physical terms. Most carbon fiber is produced in a complex and multi-stage process from specially prepared polymer raw materials, mainly polyacrylonitrile or from viscose. As the feedstock, we used coal tar from the coal of the Shubarkol deposit, which are formed during the pyrolysis of the feedstock, as well as textile cord - waste from the processing of car tires, and polymethylmethacrylate was used as a binder.

The initial coal tar has the following characteristics: density at 20 °C - 1070 kg / m^3; viscosity at 80 °C - 2.9-3.3 conventional degrees; coking ability - 2.0-3.5%; flash point - 110-120 °C; softening temperature - 60-70 °C; the yield of volatiles is 83.0%, which are formed during the pyrolysis of raw materials. It is not electrically conductive and insoluble in water, it is soluble only in organic solvents (pyridine, benzene, etc.), and is resistant to acids [7].

Textile cord – is a filament of cord fiber with rubber particles. It is obtained by processing automobile tires into rubber crumb. A car wheel consists of rubber, metal cord (wire) and textile material to give the wheel strength and wear resistance. Textile cord consists of polyester – 60%, polyamide – 37%, viscose – 3.0%, the density of which is 0.1 g / cm^3.

One of the methods for producing chemical fibers is the formation of fibers from solutions under the influence of an electrostatic field (electrospinning of fibers). An electrical voltage of 10 to 30 kV is applied to the solution using a pump syringe. High voltage induces in the solution the same electric charges, which, as a result of the Coulomb electrostatic interaction, lead to the drawing of the solution into a thin stream [8]. The resulting jets are cured by evaporation of the solvent or as a result of cooling, turning into fibers, and drift to a grounded substrate under the action of electrostatic forces [9-11]. Electrospinning is a universal and effective method for producing continuous nanofibers from submicron diameters to nanometer diameters using a high-potential electric field [12,13]. The technology can be easily used in the laboratory and can be scaled to an industrial process [14]. The electrical conversion of nanofibers from polymer solutions or melts is of practical interest, since they have many potential applications [15].

Based on the foregoing, the goal of the forthcoming work was formulated, which is to obtain carbon fibers based on coal tar and textile cord by the method of electrospinning and the study of physicochemical properties.

Research methodology. CNF samples were obtained at the “Institute of Coal Chemistry and Technology” LLP (Nur-Sultan) by the method electrospinning under laboratory conditions.

As feedstock were used coal tar which was obtained from the coal «Shubarkol» deposit, textile cord and PMMA. Samples of textile cord were provided by «Kazakhstan Rubber Recycling» LLP (Nur-Sultan).

We have chosen the electrospinning method for obtaining CNFs, since this method is acceptable in the laboratory, and thin fibers are formed. Electrospinning is good in that, unlike the usual mechanical drawing of fibers from a solution, it does not impose high requirements on the chemistry of the process, does not require high temperatures for the fiber to solidify, which means that it allows the creation of fibers from long and complex molecules as a result of capillary and electrostatic forces. Also, the processes inside the solution, the charged drop itself lengthens, thins, and dries in flight.

The technology for producing carbon nanofibers includes the following stages: preparation of raw materials, formation, oxidation (to remove low molecular weight degradation products and the formation of crosslinked and cyclic structures), carbonization (to remove hydrogen and heteroatoms in the form of volatile compounds, the final formation of carbon fibers occurs).

To obtain nanofibers based on textile cord, the sample was carbonized at 400 °C in a rotary tube furnace in argon (figure 1).

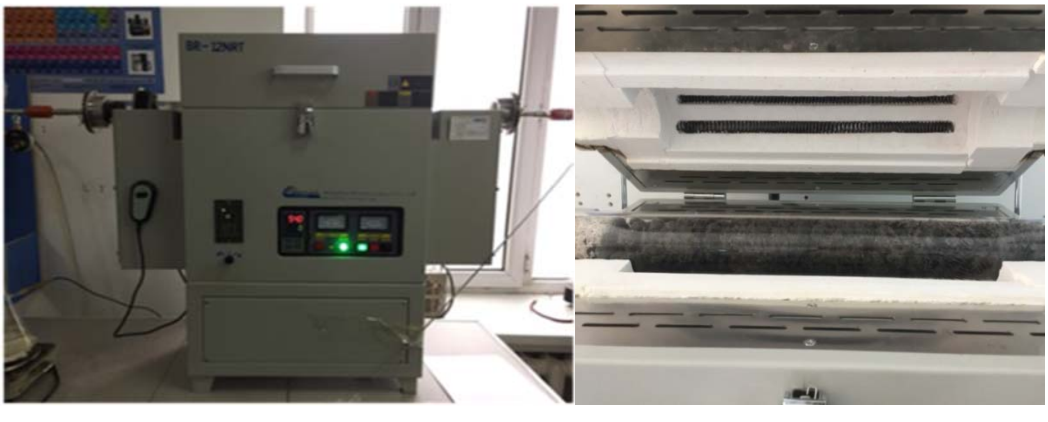


Figure 1 - High-temperature rotary tube furnace BR-12NRT


a) b)

Figure 2 – Samples of textile cord: a- initial, b-carbonized (400^{0}C)

The obtained carbonized textile cord is crushed and dissolved in 1,2-dichloroethane in an ultrasonic bath at 35 °C for 30 minutes, the frequency is 35 kHz. Polymethylmethacrylate is also soluble in 1,2-dichloroethane (mass fraction of 3%) in an ultrasonic bath under similar conditions. The prepared solutions obtained in the previous stages are mixed in 1:1 ratios in an ultrasonic bath at 35 °C for 40 minutes until a homogeneous mass is obtained. To obtain a nanofiber, dies are used in the form of a needle with a diameter of 0.6 mm. A pulsed high voltage voltage of 20-25 kV is applied to the die. A solution with a solvent is squeezed out of the die with a speed of 5-10 ml / h and precipitated onto a substrate. The distance between the substrate and the syringe was 20 - 30 cm. Next, the finished solutions are formed in the laboratory electrospinning unit [16]. For this the finished mixture is drawn into the syringe and installed on the pump motor, a charge is supplied to the tip of the syringe. Next, the engine turns on, and with the appearance of the first drop, the opposite charge is turned on. The charge of the same name is attracted to the substrate with the opposite charge and nanofibers are formed. Nanofibers are cured by evaporation of the solvent. High voltage is the basis of electroforming.

To obtain composite carbon nanofibers, coal tar and carbonized textile cord (1:1) are used, and polymethyl methacrylate is used as a binder, 1,2-dichloroethane is used as a solvent, the mixture of the starting products is dispersed in an ultrasonic bath at a temperature of 35 ^{0}C, frequency – 35 kHz, holding time 30 min, the prepared solution is placed in an electrospinning unit with a syringe, the set voltage is 20-25 kV.

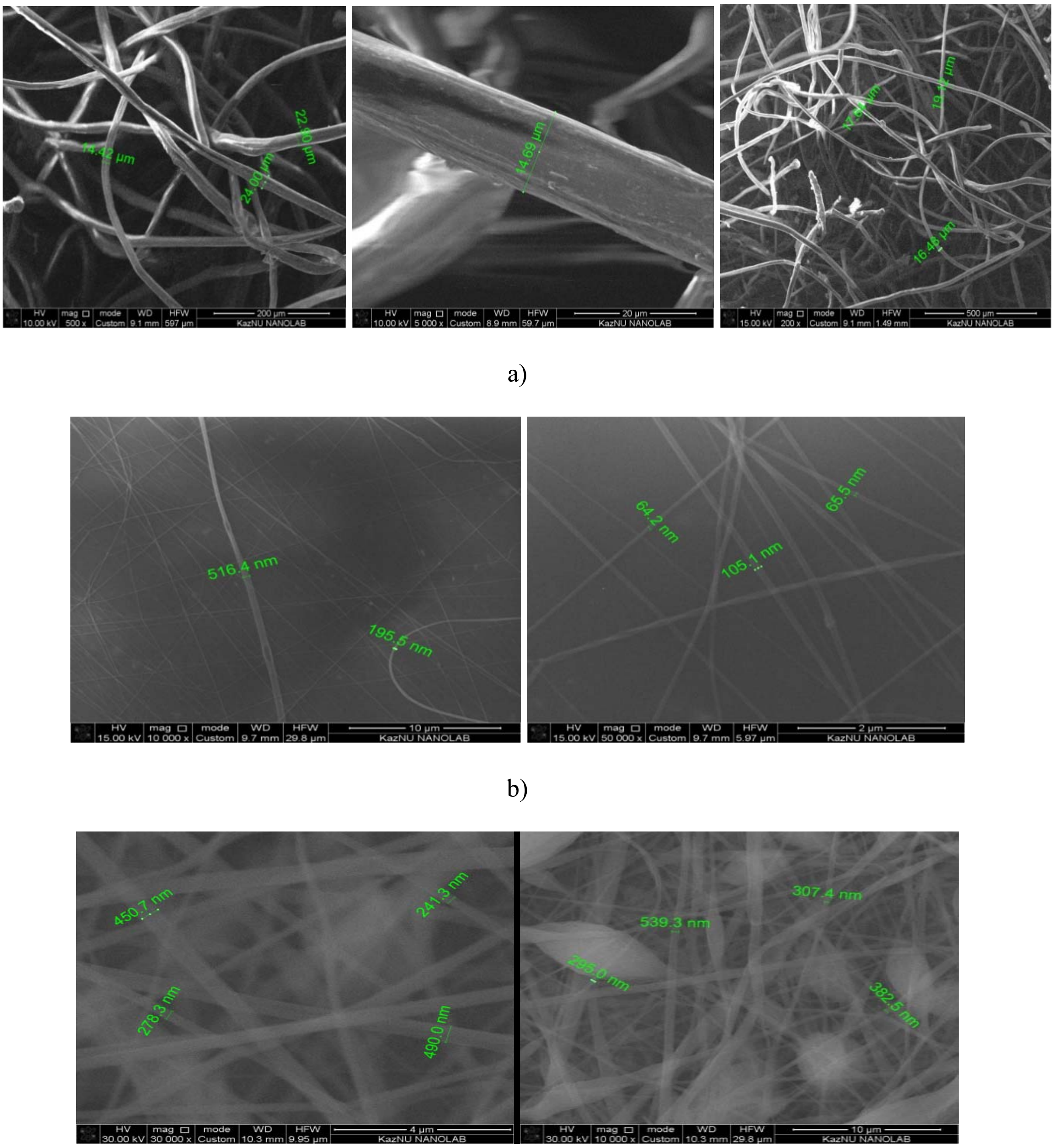
The elemental composition, structure, and dimension of the CNF were studied by energy dispersive X-ray spectroscopy on an SEM instrument (Quanta 3D 200i) with an attachment for energy dispersive analysis from EDAX. For the study, the samples were mounted on a copper holder using conductive adhesive paper. The energy of the exciting electron beam in the analysis was 15 keV, and the working distance was 15 mm. Humidity, ash content and volatility of the samples were determined on a thermogravimetric analyzer «Thermoster Eltra» (according to ASTM D7582-12).

Results and its discussion. The results of the elemental analysis, presented in table 1, show that after carbonization of the textile cord, most of the volatile components are removed in the form of gaseous products, respectively, the concentration of mineral components increases.

Table 1 – The chemical composition and physico-chemical characteristics of the initial, carbonized textile cord

Denomination	($W^r{}_t$),n %	(A^r), %	(V^d), %	The content of elements, %										
				C	Zn	S	O	Na	Al	Si	Cu	K	Ca	Fe
Initial Textile Cord	-	5,09	75.82	67,9	3,8	0,3	13,9	0,4	0,9	0,7	4,4	-	1,1	6,6
Carbonized Textile Cord (400^{0}C)	0,75	18,73	36,38	69.5	4.3	1.3	3.6	-	0.4	1.1	-	0.5	1.3	4.9

The results of a scanning electron microscope of the initial textile cord, also obtained by CNF based on TC + PMMA and TC + CT + PMMA, are shown in figure 2.



a)

b)

c)

Figure 2 – Electron-microscopic images of the samples: a) initial TC:
b) CNF based on TC + PMMA; c) TC + CT + PMMA

In Figure 2 (a), the fibers of the initial textile cord with a diameter size of 14.42-24.00 µm are clearly visible. In SEM images of CNFs obtained on the basis of TC + PMMA (figure 2(b)), the fiber diameter ranged from 64.2 nm to 516.4 nm, and in Figure 2 (c) CNFs with a diameter slightly higher from 241.3 nm to 539.3 nm are visible. The structural elements of nanofibers take the form of fibrils - filamentary formations, the length of which exceeds their diameter by more than one order. The cylindrical surface of the fibers is formed by hexagons. Due to the existence of penta- and heptagons, structural defects, the formation of bridges and the curvature of the cylindrical surface are observed (Fig. 3 (c)). The CNF obtained on the basis of TC + PMMA compared with TC + CT+PMMA turned out to be more even.

The results of the elemental analysis of the CNF are presented in table 2.

Table 2 - The elemental composition of CNF from TC + PMMA and TC +CT + PMMA

CNF	C, %	O, %	Si, %	Al, %	S, %
TC + PMMA	82,69	1,72	0,46	15,14	-
TC +CT + PMMA	88,43	4,06	-	7,32	0,19

As can be seen from the obtained data, CNF based on TC + CT + PMMA has 5.74% more carbon.

Thus, we obtained carbon nanofibers based on textile cord and “Shubarkul” coal tar using the electrospinning method.

The environmental effect of the study is to create an environmentally friendly technology based on the processing of secondary raw materials (coal tar and other coal wastes) to produce carbon fibers and composites based on them. The creation of this technology will help to solve the environmental aspect of the disposal of this type of waste with obtaining an economically viable product.

The proposed method is unique in that the raw materials that we use to produce carbon fibers are a renewable resource, compared with the technology for producing fibers from many other precursors (nylon, polyester, acrylic, polypropylene, etc.). The prospect of these studies lies in the possibility of large-scale production of carbon fibers from textile cord and coal tar, which will lead to the appearance on the Kazakhstan market of materials and composites based on them of domestic production.

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ТАСКӨМІР ШАЙЫРЫ МЕН ТОҚЫМА КОРД НЕГІЗІНДЕ КОМПОЗИТТІ КӨМІРТЕКТІ НАНОТАЛШЫҚ АЛУ

Аннотация. Мақалада электроспининг әдісі арқылы зертханалық қондырғыда тоқыма кордынан көміртекті наноталшықтар алу бойынша тәжірибелер көрсетілген. КНТ алуда тоқыма кордының карбонизаты (ТК), «Шұбаркөл» кен орны көмір шайыры (КШ) және полиметилметаакрилат (ПММА) қолданылды. КНТ алу үшін зертханалық жағдайда қолайлылығы себепті электроспиннинг әдісі қолданылды. Оның механикалық созу әдісінен артықшылығы үдерістің химиясына қатаң талап қойылмайды, талшықтың кебуі үшін жоғары температура қажет етпейді. Яғни, капиллярлық және электростатикалық күшінің нәтижесінде ұзын және күрделі молекулалардан талшық алуға мүмкіндік береді. Тоқыма корд негізінде наноталшық алу үшін үлгіні 400 ^{0}С температурада айналмалы түтік пеште аргон ортасында карбондау үдерісі жүргізілді. Алынған карбондалған тоқыма корды үгітіліп, ультрадыбыстық ваннада 35 ^{0}С температурада 30 мин. бойы 35 кГЦ жилікте 1,2-дихлорэтанда ерітілді. Полиметилметаакрилат (массалық үлесі 3 %) ерітіндісі де 1,2-дихлорэтанда ультрадыбыстық ваннадағыға ұқсас жағдайда дайындалды. Дайын ерітінділер 1:1 қатынаста араластырылып, ультрадыбыстық ваннада 35 ^{0}С температурада 40 мин бойы бірыңғай масса алынғанша ұсталды. Наноталшықты алу үшін арнайы ине тәрізді филлер қолданылады, диаметрі 0,6 мм. Оған жоғары вольтті кернеу 20-25 кВ беріледі. Фильерден ерітінді 5-10 мл/сағ жылдамдықта шығып, қабылдағышта қона бастайды. Фильер мен коллектор арасындағы қашықтық 200-бен 300 мм арасын қамтиды. Арықарай ерітінді электроспиннинг аппаратына беріледі, онда ерітінді шприцке жиналып, сорғыш қозғалтқышқа (двигатель) орналастырылады, шприц ұшына заряд беріліп, двигатель қосылады, бірінші тамшының пайда болуына қарама-қарсы заряд қосылады. Бірдей зарядтар қарсы зарядталған коллекторға тартылып, наноталшық түзеді. Еріткіш ұшқан кезде наноталшық түзіліп, жоғары кернеу электротүзілудің негізі болып саналады. Композитті наноталшық алу үшін таскөмір шайыры мен тоқыма корды (1:1), байланыстырғыш ретінде полиметилметакрилат, ал еріткіш ретінде 1,2-дихлорэтан қолданылды, алынған қоспа ультрадыбыстық ваннада 35 ^{0}С температурада, 35 кГЦ жилікте, 30 мин. бойы ұсталды, алынған ерітіндіден электоспиннинг әдісімен наноталшық алынды. Энергодисперсиялық рентгенді спектроскопия талдау нәтижесінде және СЭМ көмегімен КНТ құрамы мен морфологиясы анықталды, ТК+ПММА негізінде алынған КНТ құрамы С-82,69%, О-1,72%, Si-0,46%, Al-15,14%, ал ТК+КШ+ПММА: С-88,43%, О-4,06%, Al-7,32%, S-0,19 % көрсетті, КНТ диаметрі 64,2-539,3 нм. ТК+ПММА негізінде алынған көміртекті наноталшықтың ТК+ КШ+ПММА негізінде түзілген наноталшыққа қарағанда диаметрі кіші, бірыңғай наноталшық түзілді.

Түйін сөздер: көміртекті наноталшық (КНТ), таскөмір шайыры, нанокомпозиттер, электроспиннинг, тоқыма корды, полиметилметакрилат.

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ПОЛУЧЕНИЕ УГЛЕРОДНЫХ КОМПОЗИТНЫХ НАНОВОЛОКОН НА ОСНОВЕ КАМЕННОУГОЛЬНОЙ СМОЛЫ И ТЕКСТИЛЬНОГО КОРДА

Аннотация. В статье приведены результаты эксперимента по получению углеродных нановолокон на основе текстильного корда методом электроспиннинга на лабораторной установке. Были получены углеродные нановолокна (УНВ) из карбонизата текстильного корда (ТК), каменноугольной смолы (КС) месторождения «Шубарколь» и полиметилметакрилата (ПММА). Нами выбран метод электроспиннинга для получения УНВ, так как этот метод является приемлемым в лабораторных условиях: его преимущество в том, что, в отличие от обычного, механического вытягивания волокон из раствора, он не предъявляет высоких требований к химии процесса, не требует больших температур для затвердевания волокна, а, значит, позволяет создавать волокна из длинных и сложных молекул в результате борьбы капиллярных и электростатических сил. Для получения нановолокон на основе текстильного корда проводился процесс карбонизации образца при 400^0С во вращающейся трубчатой печи, в среде аргона. Полученный карбонизованный текстильный корд измельчается и растворяется в 1,2-дихлорэтане в ультразвуковой ванне при 35 ^{0}С в течение 30 мин, частота – 35 кГЦ. Полиметилметакрилат также растворяется в 1,2-дихлорэтане (массовая доля 3 %) в ультразвуковой ванне в аналогичных условиях. Готовые растворы, полученные в предыдущих стадиях, смешиваются в соотношениях 1:1 в ультразвуковой ванне при 35 ^{0}С в течение 40 мин до получения однородной массы. Для получения нановолокна использовался фильер в виде иглы диаметром 0,6 мм. К фильеру прикладывалось импульсное высоковольтное напряжение 20-25 кВ. Из фильеры выдавливали раствор с растворителем со скоростью 5 - 10 мл/час и осаждали на подложку. Далее готовые растворы формируются в лабораторной установке электроспиннинга, для этого готовая смесь набирается в шприц и устанавливается на насосный двиагатель, на кончик шприца подается заряд, далее включается двигатель, и с появлением первой капли включается противоположный заряд. Одноименный заряд притягивается на подложку с противоположным зарядом и образуются нановолокна. Нановолокна отверждаются за счет испарения растворителя. Расстояние между приемником и шприцем составило 20-30 см. Высокое напряжение являяется основой электроформования. Для получения композитных углеродных нановолокон использовались каменноугольная смола и текстильный корд (1:1), а в качестве связующего – полиметилметакрилат, в качестве растворителя – 1,2-дихлорэтан, смесь продуктов также подвергают диспергированию в ультразвуковой ванне при температуре 35 ^{0}С, частота – 35 кГЦ, время выдержки – 30 мин, приготовленный раствор помещают в установку электроспиннинга со шприцем, установленное напряжение – 20-25 кВ. Определен элементный состав и изучена морфология поверхности исследуемых образцов. В результате энергодисперсионной рентгеновской спектроскопии и СЭМ-микроскопии были определены химические составы УНВ на основе ТК+ПММА, который составил С-82,69%, О-1,72%, Si-0,46%, Al-15,14%, ТК+КС+ПММА: С-88,43%, О-4,06%, Al-7,32%, S-0,19 %, диаметр углеродных нановолокон составил от 64,2 нм до 539,3 нм. УНВ, полученные на основе ТК+ПММА, по сравнению ТК+ КС +ПММА, получились более ровными и с меньшим диаметром нановолокон.

Ключевые слова: углеродные нановолокно, каменноугольная смола, нанокомпозиты, электроспиннинг, текстильный корд, полиметилметакрилат.

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PREPARATION OF PHTHALONITRILE MONOMER WITH LOW MELTING POINT

Abstract. This article presents the results of the synthesis of para – and meta-hydroxyphenoxyphalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus and 4-(3-propargyloxyphenoxy) phthalonitrile, the introduction of which into the binder, allowed to achieve the necessary viscosity indicators without loss of heat resistance. At the first stage, it was proposed to obtain a monomer with a phenoxy group in phosphorus. For this purpose, we proposed the use of dimethylacetamide (DMAA) with K_2CO_3, but the product was hydrolytically unstable in the main medium, so it was impossible to isolate the desired monomer. To solve this problem, we conducted a number of experiments on the selection of synthesis conditions using various solvents. Comparing the T_{gt} of the obtained monomers, we found higher values for para-oriented phthalonitriles, which is probably due to higher structure symmetry, as well as an increase in glass transition temperature (T_{gt}) for phosphonate-based monomers. Due to the equally high thermal properties of the cured matrices, we decided to use 4-(3-hydroxyphenoxy) phthalonitrile as the main precursor, as well as phosphate chlorangidrides. Based on the calculated data, a pattern was identified that consists in a decrease in the T_{gt} of phosphorus-containing phthalonitriles when switching to aliphatic substituents in phosphorus. A decrease in the T_{gt} of monomers was found with an increase in the size of the aliphatic substituent. As a result of the experiment, we obtained 9 new phosphorus-containing phthalonitrile monomers with high yield that are resistant to hydrolysis, which is confirmed by the fact that the products were isolated by flash chromatography on silica gel, as well as two-dimensional TLC. The synthesized substances were glassy masses with T_{gt} = - 5-58 °C. The consistency of the approach involving the introduction of phosphate bridges into the structure of phthalonitriles was shown.

Key words: thermosetting polymers, temperature-time-transformation diagrams, isothermal transformation diagrams, thermal stability, thermal analysis, polymer composite materials (PCM).

Introduction. Intensive industrial development is impossible without progress in the field of materials science [1,2]. Recently, significant progress in its development has been achieved due to the use of qualitatively new special-purpose materials for the manufacture of machine parts and mechanisms that operate at a high level of loads, temperatures and sliding speeds, in aggressive and abrasive environments when using lubricants and cooling liquids and without them [3,4].

The most promising special-purpose materials are polymers and PCM based on them [3]. The presence of a wide range of polymer matrices, fillers and modifying systems allows us to obtain materials with the necessary level of properties, which vary in a wide range depending on the composition and technology of their production. Modern polymers and PCM based on them approach such structural materials as metals and their alloys by their physical and mechanical properties, while having a number of significant advantages: low cost of manufacturing products, a high level of chemical resistance, low weight, the ability to work in friction units without lubrication, and so on [4,5].

The paper considers a literature review on the scientific basis of obtaining composite materials in Kazakhstan, which shows the principal possibility of creating new composite films from alicyclic polyimide and polyethylene glycol with improved physical and mechanical properties [6]. For example, the authors point out that the resulting nanocomposites are tin dioxide nanoparticles immobilized in an inorganic polymer mesh of silicon dioxide and deposited carbon. At the same time, silicon dioxide provides high adhesive properties and prevents crystallization of the composite, while nano – and microparticles of tin and carbon dioxide determine gas-sensitive properties. The film-forming solutions obtained by Sol-gel technology contain tetraethoxysilane, tin salts (SnCl2·2H2O), silicic acid (SiO2·nH2O) and sodium silicic acid (Na2SiO3·9H2O). The resulting solutions were applied to metal substrates with subsequent heat treatment. Additional introduction of tetraethoxysilane into Sol solutions as a source of SiO2 allowed to obtain xerogels of oxide compositions of 5% wt. SnO2-95% wt. SiO2, 30% wt. SnO2-70 % wt. SiO2. The change in the content of elements shows that the microstructure of the obtained compounds changes as carbon nanoparticles build up [7].

The synthesis of phthalonitrile monomers is well studied and described in the literature and includes the stages of nucleophilic aromatic substitution between 4-nitrophthalonitrile and aromatic amides. To obtain a phthalonitrile monomer with a low melting point, it was proposed to introduce phosphate fragments into the structure of the monomer [8-10].

Experimental part and results. To obtain a phthalonitrile monomer with a low melting point, it was proposed to introduce phosphate fragments into the structure of the monomer [11-13] . For this purpose, we synthesized para – and meta-hydroxyphenoxyphalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus, and 4-(3-propargyloxyphenoxy) phthalonitrile, the introduction of which into the binder, presumably, would allow to achieve the necessary viscosity indicators without loss of heat resistance. The scheme of synthesis proposed in this paper is shown in figure 1 [14].

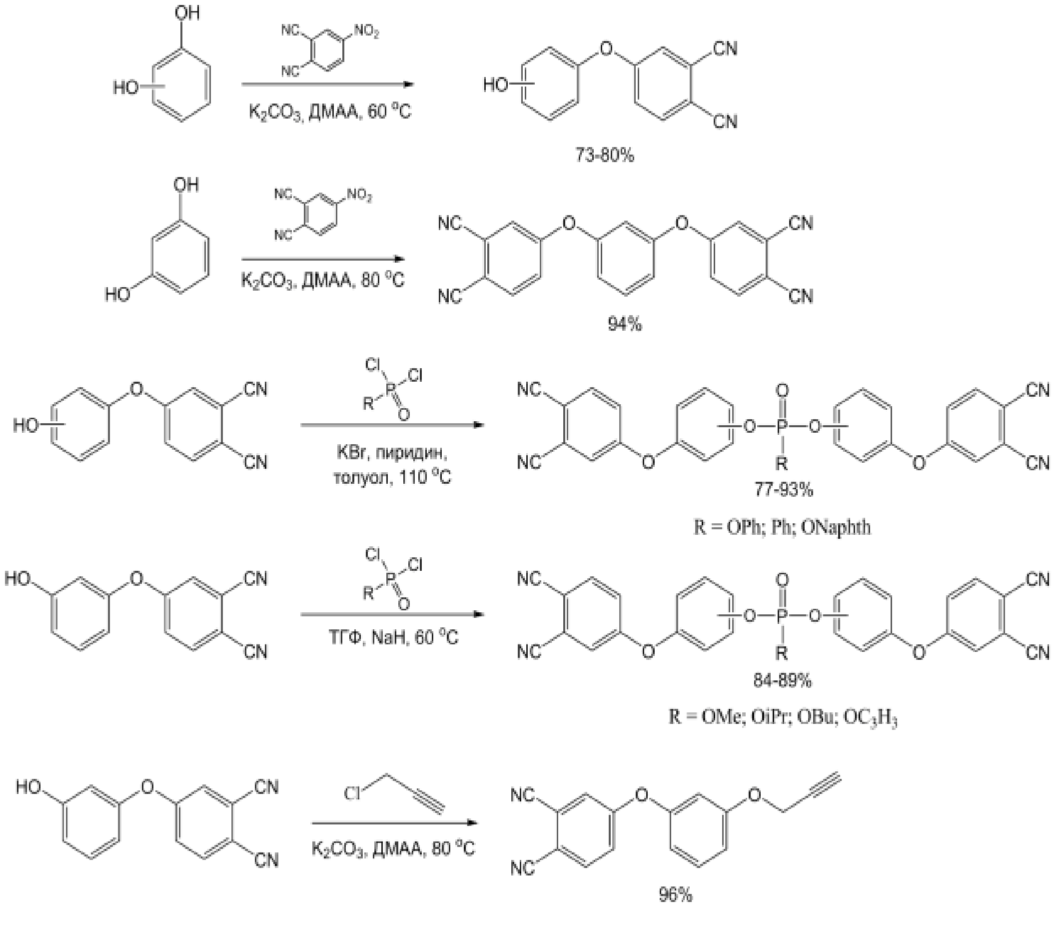


Figure 1 – Scheme of synthesis of phthalonitrile monomers

At the first stage, it was proposed to obtain monomer 1 with a phenoxy group in phosphorus. For this purpose, we proposed the use of dimethylacetamide (DMAA) with K_2CO_3, but the product was hydrolytically unstable in the main medium, so it was impossible to isolate the desired monomer. To solve this problem, we conducted a number of experiments on the selection of synthesis conditions using various solvents (table 1) [15].

Table 1 - Selection of optimal synthesis conditions

Solvent	Synthesis Condition	Result
DMA	K_2CO_3, 70 °C	Monomer hydrolysis
Toluene	Δ°C	The desired monomer (yield 81%)
Dichloroethane	Δ°C	4- (3-hydroxyphenoxy) phthalonitrile, insoluble
Bu_2O	Δ°C	A large number of by-products
	Addition of acid chloride to the precursor melt	A large number of by-products
Pyridine	Δ°C	The desired monomer (yield 67%)
THF (Tetrahydrofuran)	Δ°C	A large number of by-products

Thus, the desired monomer was obtained only when using toluene and pyridine as solvents, but the main disadvantage of pyridine is its high toxicity (LD_{Lo} = 500 mg / kg), whereas when using toluene, the reaction time is about a week. Since it is necessary to remove the released HCl to shift the equilibrium of the reaction, we proposed using toluene as a solvent with an equimolar amount of pyridine acid. Thus, it was possible to reduce the amount of pyridine used and reduce the reaction time to 24 hours.

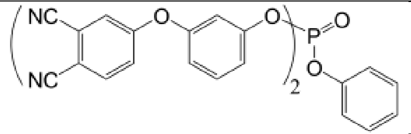
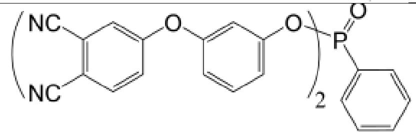
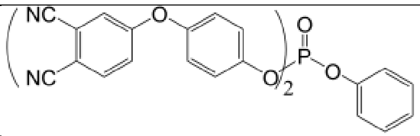
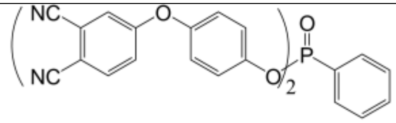
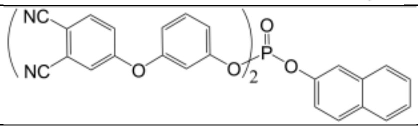
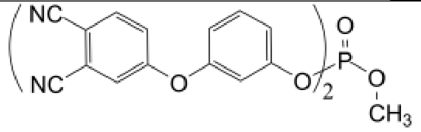
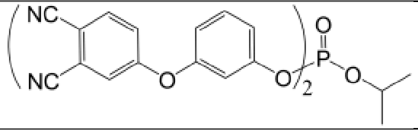
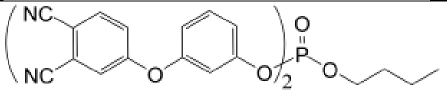
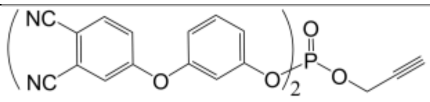
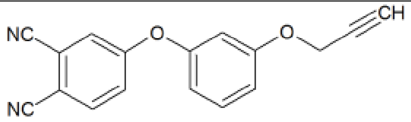
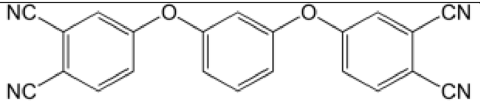
Comparing the T_{gt} of the obtained monomers 1-4 (table 2), we found higher values for para-oriented phthalonitriles, which is probably due to higher structure symmetry, as well as an increase in T_{gt} for phosphonate-based monomers. Due to the equally high thermal properties of the cured matrices, we decided to use 4-(3-hydroxyphenoxy) phthalonitrile as the main precursor, as well as phosphate chlorangidrides.

To study the General regularities, researchers from the laboratory of A. R. Khokhlov performed calculations that allow predicting the glass transition temperature of phosphorus-containing phthalonitriles [16]. Based on the calculated data, the expected pattern was revealed, which consists in a decrease in the T_{gt} of phosphorus-containing phthalonitriles when switching to aliphatic substituents in phosphorus. In addition, a decrease in the T_{gt} of monomers was found with an increase in the size of the aliphatic substituent.

In order to confirm the calculated model, as well as to study the changes in the properties of monomers and cured matrices depending on the size of the substituent in phosphorus, we attempted to obtain monomers 5-9 (table 2), using a similar scheme, but only monomer 5 (table 2) was obtained in this way. In other cases, after the addition of pyridine, a resin began to form in the reaction mixture, which makes it impossible to isolate the desired product. To solve this problem, we have tested batch addition of pyridine to the reaction mixture (10%), but the ultimate is the addition of 50% of a given amount of pyridine, then is quite fast (~ 10 minutes) formation of resin; in addition, the selection of the desired monomer difficult (yield ~5%). We also proposed the use of Et3N (triethylamine) instead of pyridine and THF as a solvent, as well as various combinations, but it was not possible to isolate the desired monomer in any of the cases. As a result, to obtain monomers 6-9(table 2), and study them, THF with NaH was used as a base with further isolation by flash chromatography. After studying the properties of monomers 6-9(table 2), it can be found that the lowest glass transition temperature is monomer 8(table 2), with a butyl group at phosphorus (T_{gt} = -5 °C), while monomer 6 (table 2), turns out to be crystalline, having a melting point of T_{mp} = 116 °C.

Discussion of results. As a result of the experiment, we obtained 9 new phosphorus-containing phthalonitrile monomers with a high yield, which are shown in table 6. they are resistant to hydrolysis, which is confirmed by the fact that the products were isolated by flash chromatography on silica gel, as well as two-dimensional Thin layer chromatography (TLC). The synthesized substances were glassy masses with T_{gt} = - 5-58 °C, which is significantly lower than for classical phthalonitriles[17,18] and lower than for oligomers [19,20]. In addition, monomer 6 was a crystalline substance with a T_{mp} = 116 °C, so the developed calculation method is not applicable. Thus, the consistency of the approach involving the introduction of phosphate bridges into the structure of phthalonitriles was shown. The thermal properties of the resulting monomers are shown in table 2.

Table 2 - Thermal properties of the obtained phthalonitrile monomers

№	Structure	T_{gt}/ T_{mp} (exp.), °C	T_{gt}/T_{mp} (calculated value), °C	ΔT, °C
1		22	49±11	27
2		42	48±7	6
3		20	-	-
4		46	-	-
5		58	61±7	3
6		116	43±8	73
7		5	33±5	28
8		-5	-	-
9		12	32±6	20
10		118	-	-
11		185		

Conclusion. The introduction of phosphate fragments into the structure of the monomer is proposed to obtain a phthalonitrile monomer with a low melting point. Para - and meta-hydroxyphenoxyphthalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus and 4-(3-proparhyloxyphenoxy) phthalonitrile were synthesized, the introduction of which into the binder allowed to achieve the necessary viscosity indices without loss of heat resistance. 9 new

phosphorus-containing phthalonitrile monomers resistant to hydrolysis were obtained. The synthesized substances were glassy masses with T_{gt} = - 5-58 °C. In addition, monomer 6 was a crystalline substance with T_{mp} = 116 °C, in connection with which the developed calculation method is not applicable. Thus, the consistency of the approach implying the introduction of phosphate bridges into the structure of phthalonitriles was shown.

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БАЛҚУ ТЕМПЕРАТУРАСЫ ТӨМЕН ФТАЛОНИТРИЛЬДІ МОНОМЕР АЛУ

Аннотация. Өнеркәсіп дамуындағы жоғары табысқа жоғары деңгейде жүктемемен қызмет атқаратын машина мен механизм бөлшектерін дайындау барысында арнайы мақсатта сапалы жаңа материалдарды пайдалану негізінде қол жеткізілді. Оның қатарына полимер және соның негізінде жасалған ПКМ жатқызуға болады.

Полимерлік матрица, толтырғыш және түрлендіргіш жүйелердің кең спектрі болуы тиіс қасиетке ие материалды алуға мүмкіндік береді. Олар құрамы мен дайындалу технологиясына орай түрліше келеді. Қазіргі заманғы полимерлер мен ПКМ физикалық-механикалық қасиетіне сәйкес, металл мен қорытпа сияқты конструкциялық материалдарға жақын келеді, бұл ретте өндіріс өнімінің төмен құны, химиялық төзімділіктің жоғары деңгейі, аз салмақ, майланбаған үйкеліс қондырғыларында жұмыс атқару мүмкіндігі сынды елеулі артықшылығы бар.

Фталонитрильді мономерлер синтезі зерттеген әдебиеттерде жете түсіндірілген әрі сипатталған және құрамында 4-нитрофталонитрилді және хош иісті диолдар арасындағы нуклеофильді хош иісті алмастыру сатылары бар. Балқу температурасы төмен фталонитрилді мономер алу үшін мономер құрылымына фосфатты фрагмент енгізу ұсынылды. Бұл үшін пара және мета-гидроксифеноксифталонитрилді, фосфор мен 4- (3-пропаргилоксифенокси) фталонитрилдегі түрлі алмастырғышы бар фосфорлы қышқыл хлоридтер синтезделді және оны байланыстырушы құрамға енгізу жылуға төзімділікті жоғалтпастан тұтқырлыққа қол жеткізуге мүмкіндік береді.

Бірінші кезеңде фосфордағы фенокси тобы бар мономер алу туралы ұсыным жасалды. Ол үшін біз k2co3 бар диметилацетамид (ДМАА) пайдалануды ұсындық, алайда өнім негізгі ортада гидролитикалық тұрақсыз болғандықтан, біз іздеген мономердің бөлінуі мүмкін емес еді. Осы мәселені шешу үшін түрлі еріткіштерді пайдалана отырып, синтездеу шарттарын таңдау бойынша бірқатар тәжірибе жүргіздік.

Алынған мономердің Тст-ін салыстыра отырып, пара-бағытталған фталонитрилге арналған жоғары мәнді айқындадық. Бұл құрылымның жоғары симметриясымен, сондай-ақ фосфонат негізіндегі мономерге арналған Tst-нің жоғарылауына байланысты болуы ықтимал. Қатырылған матрицаның термиялық қасиетінің бірдей жоғарылығын ескере отырып, негізгі прекурсор және фосфат хлориді ретінде 4- (3-гидроксифенокси) фталонитрилді қолданған жөн деп таптық.

Есептелген мәліметтер негізінде фосфор құрамындағы алифатты алмастырғыштарға өтуде құрамында фосфоры бар фталонитрилдердің Tst азаю үдерісін көрсететін заңдылық анықталды. Сонымен қатар, алифатты алмастырғыш мөлшері ұлғайғанда Тст мономердің төмендейтіні анықталды.

Тәжірибе нәтижесінде гидролизге төзімді 9 жаңа фосфорлы фталонитрилді мономерлер алынды, аталған өнімдер силикагельде флеш-хроматография әдісімен, сондай-ақ екіөлшемді ТСХ негізінде анықталды. Синтезделген заттар – Tst = -5-58 ° С болатын әйнек массалар, бұл классикалық фталонитрилге, олигомерге қарағанда айтарлықтай төмен. Сонымен қатар, мономер тпл = 116 °С кристалды зат болғандықтан есептік әдіс қолданылмайды. Фталонитрил құрылымына фосфат көпірін енгізуді білдіретін тәсілдің ауқымдылығы көрсетілді.

Түйін сөздер: термореактивті полимер, «температура-айналу уақыты» диаграммасы, изотермиялық түрлену диаграммасы, термиялық тұрақтылық, термиялық талдау, полимерлік композициялық материал (ПКМ).

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ПОЛУЧЕНИЯ ФТАЛОНИТРИЛЬНОГО МОНОМЕРА С НИЗКОЙ ТЕМПЕРАТУРОЙ ПЛАВЛЕНИЯ

Аннотация. Значительные успехи в развитии промышленности достигнуты за счет использования качественно новых материалов специального назначения для изготовления деталей машин и механизмов, работающих при высоком уровне нагрузок, в число которых можно отнести полимеры и ПКМ на их основе.

Наличие широкого спектра полимерных матриц, наполнителей и модифицирующих систем позволяет получать материалы с необходимым уровнем свойств, которые изменяются в широком интервале в зависимости от состава и технологии их получения. Современные полимеры и ПКМ на их основе по физико-механическим свойствам приближаются к таким конструкционным материалам, как металлы и их сплавы, имея при этом ряд существенных преимуществ: невысокая себестоимость изготовления изделий, высокий уровень химической стойкости, невысокая масса, возможность работы в узлах трения без смазывания.

Синтез фталонитрильных мономеров достаточно хорошо изучен и описан в литературе и включает в себя стадии нуклеофильного ароматического замещения между 4-нитрофталонитрилом и ароматическими диолами. Для получения фталонитрильного мономера с низкой температурой плавления было предложено введение фосфатных фрагментов в структуру мономера. Для этого были синтезированы пара- и мета-гидроксифеноксифталонитрил, фосфорсодержащие хлорангидриды с различными заместителями при фосфоре и 4-(3-пропаргилоксифенокси) фталонитрил, введение которого в состав связующего, предположительно, позволило бы достичь необходимых показателей вязкости без потери термостойкости.

На первом этапе было предложено получение мономера с фенокси-группой при фосфоре. Для этого нами было предложено использование диметилацетамида (ДМАА) с K_2CO_3, однако продукт оказался гидролитически нестабилен в основной среде, в связи с чем выделение искомого мономера было невозможно. Для решения этой проблемы нами был проведен ряд экспериментов по подбору условий синтеза с использованием различных растворителей.

Сравнив $T_{ст}$ полученных мономеров, мы обнаружили более высокие значения для пара-ориентированных фталонитрилов, что, вероятно, связано с более высокой симметрией структуры, а также возрастание $T_{ст}$ для мономеров на основе фосфонатов. Ввиду одинаково высоких термических свойств отвержденных матриц, нами было решено использовать 4-(3-гидроксифенокси) фталонитрил в качестве основного прекурсора, а также фосфатные хлорангидриды.

На основе расчетных данных была выявлена закономерность, заключающаяся в снижении $T_{ст}$ фосфорсодержащих фталонитрилов при переходе к алифатическим заместителям при фосфоре. Кроме того, было обнаружено снижение $T_{ст}$ мономеров при увеличении размера алифатического заместителя.

В результате эксперимента нами были получены с высоким выходом 9 новых, фосфорсодержащих фталонитрильных мономеров, устойчивых к гидролизу, что подтверждено тем, что продукты были выделены методом флеш-хроматографии на силикагеле, а также двумерной ТСХ. Синтезированные вещества представляли собой стеклообразные массы с $T_{ст}$ = -5-58 °C, что значительно ниже, чем для классических фталонитрилов и ниже, чем для олигомеров. Кроме того, мономер представлял собой кристаллическое вещество с $T_{пл}$ = 116 °C, в связи с чем разработанный расчетный метод неприменим. Таким образом была показана состоятельность подхода, подразумевающего введение фосфатных мостиков в структуру фталонитрилов.

Ключевые слова: термореактивные полимеры, диаграммы «температура-время-превращения», диаграммы изотермических превращений, термическая стабильность, термический анализ, полимерные композиционные материалы (ПКМ).

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CALCULATION OF HYDRAULIC RESISTANCE DURING FILTRATION DRYING OF RAW COTTON

Abstract. Textile, non-woven and other fiber materials have a great importance in the modern world economy. Cotton is one of the most valuable raw materials for the production of various industrial, food and household products. The movement of a gas stream through a porous structure of a material is a mixed problem of hydrodynamics. However, there are no theoretical foundations for the mixed hydrodynamic problem today. In this article, we propose the use of a filtration method for drying raw cotton and calculating the hydraulic resistance. To describe the hydrodynamics of gas movement through the porous structure of the material in scientific articles, the authors use theoretical dependencies of internal or external problems. Given that the intensity of heat and mass transfer determines the speed of movement of the heat agent relative to the elements of the porous layer, this paper presents the results of studies of pressure losses in the layer of cotton fiber from the point of view of the internal problem of hydrodynamics. Experimental studies on filtration of a heat agent through a stationary layer of cotton were conducted. due to the difference in bulk weight and different heights of the layer, they were represented as a functional dependence $\Delta P = f(v_0)$. The results obtained in dimensionless form allow us to predict the energy costs of creating a pressure drop (under the same hydrodynamic conditions) when designing a new drying equipment.

Keywords:cotton fiber, hydrodynamics, filtration drying, hydraulic resistance, porosity, active specific surface of the layer.

Introduction. According to the State program of industrial-innovative development of Kazakhstan for 2020 - 2025, a stable growth and competitiveness of the manufacturing sector will be achieved by creating a technologically advanced industry, the transformation and digitalization of the basic assets of functioning enterprises, focused on the creation of medium-and high-tech products with subsequent access to the global markets [1]. By 2021, the acreage of cotton in South Kazakhstan region is expected to increase by 100 thousand hectares, yield – 3000 kg/ha, and cotton production to 300 thousand tone/year. Therefore, high-quality storage and processing of raw cotton are the main factors. When processing raw cotton to obtain a more efficient and high-quality fiber, its humidity should be in the range of 8-9% [2,3]. In order to boost the cotton and textile industries of Kazakhstan, The law «on the development of the cotton industry» was adopted, and the free economic zone «Ontustik» was created for 2005-2030, which will contribute to the revival and development of the textile industry in Kazakhstan [4] .

At the present, the properties of raw materials deteriorate in cotton processing plants when using drying drums of type 2SB-10, SBT, SBO. As a result of subsequent technological processes, the fiber grade is reduced by 25% through mechanical action, a lot of energy is spent, the color of the fiber is lost, and the fiber twists, and the fiber microstructure deteriorates [5].

In the cotton-growing regions of Central Asia and Kazakhstan, drying drums of type 2SB-10, SBT, and SBO are mainly used for drying raw cotton, and various methods and drying devices are used for drying food and vegetable raw materials [6-8], which are not acceptable for drying raw cotton.

For this reason, experimental and theoretical studies of cotton drying, reducing the cost of technological processes for processing cotton fiber and improving their quality characteristics are of urgent importance for the economy of Kazakhstan. The integration of new highly efficient and resource-saving technologies for processing cotton raw materials into a finished product of high quality will be competitive not only in the domestic but also in foreign markets.

Analysis of literature sources [9-13] allows us to conclude that there is no comprehensive and systematic approach to the intensification of drying processes of wet cotton fiber, given that it contains mainly bound moisture, is a thermolabile material, and the drying process takes place in the second period.

Choosing the drying mode for raw cotton depends on the following parameters: color, fiber length, type of mechanical damage, and so on. During drying of raw cotton, it is important to choose the optimum mode of drying, since inadequate drying parameters, there is a fiber breakage, reducing its length, resulting in reduced fiber quality [2,3].

Experimental part and description of the installation. Theoretical analysis and design of drying systems are complicated by a number of factors, in particular, simultaneous heat and mass transfer to the surface and inside the material, moisture transfer within the material, while there are more than twenty different types of mechanisms for transferring moisture in a solid. Changes in the moisture content and temperature of the material are determined by heat and mass transfer between the surface of the body, the environment and the interior of the material to be dried.

To realize the process of drying raw cotton, as noted above, the industry uses drum type dryers and fluidized bed dryers, which are energy-consuming and expensive. Therefore, we had the task to develop a new type of dryer that will reduce the energy costs of the drying process.

Generalization of the results of experimental and theoretical studies of hydrodynamics and heat and mass transfer during filtration drying of raw cotton allowed us to propose a design of a drying plant that takes into account the physical and mechanical properties of raw cotton, improve the method for calculating the main structural dimensions of this installation and calculate the optimal technological parameters of the thermal agent.

We suggest using the concept of a drum-type filtration drying device for drying raw cotton (figure 1) [14].

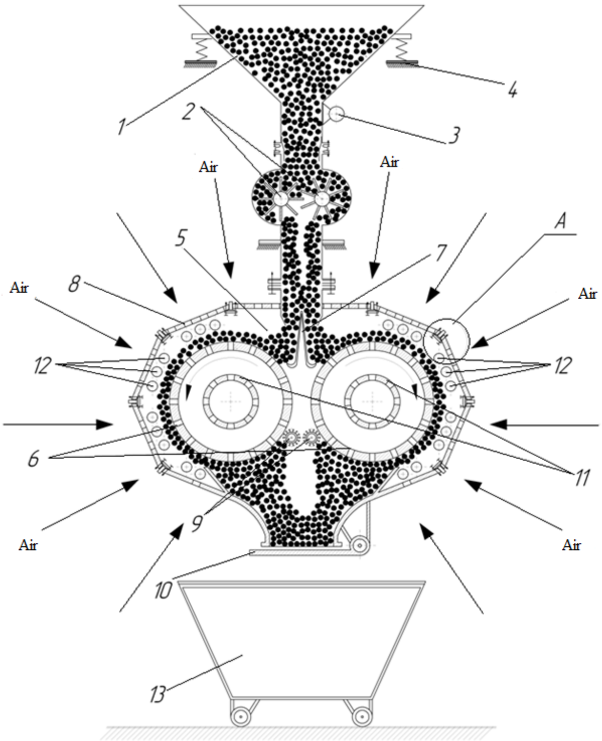

Figure 1 – The installation of the filtration drying of drum-type:
1 – bunker, 2 – proportioner, 3 – vibrator, 4 – springs, 5 – drying chamber, 6 – perforated drums, 7 – partition wall, 8 – perforated sheets, 9 – brushes, 10 – spring-loaded lid, 11 – perforated sleeves, 12 – warming system, 13 – container

Installation for the filtration drying of raw cotton consists of a bunker 1 which serves to feed a raw and in the lower part it includes a proportioner 2 and the vibrator 3, and the bunker 1 is mounted on a spring 4. The lower part of the hopper 1 is attached to the drying chamber 5 in which is placed parallel to the perforated drums 6 with a perforated sleeve 11. The perforated drums 6 with a partition 7. Warming system of heating agent 12 is located inside drying chamber 5. The outside of the perforated drum is equipped with 8 removable perforated sheets. Brushes 9 are installed on the drum 6 in the dry material discharge zone. In the lower part of the drying chamber 5, a spring-loaded lid 10 is installed, which serves for automatic unloading of dry material into the container 13. The Perforated drums are connected to the vacuum line through perforated sleeves 11. Container 13 is intended for dry material.

The installation works as follows. Include a vibrator 3 and a vacuum line, so that the heat agent passes through the perforated sheets 8, which ensure uniform drying of the material and facilitate the changeover of the installation for a different type of material, or for a different humidity. The air is heated directly in the drying chamber 5 by the warming system 12, which is placed directly in the drying chamber, which makes it possible to reduce heat loss to the environment. Due to the fact that the perforated sheets are washed by the ambient air, their temperatures are approximately equal to the ambient temperature.

Turn both the reels 6 and brush 9. The wet material enters the hopper 1 and with a dispenser 2 is fed to the drying chamber 5 into two of the perforated drum 6, between which the partition wall 7 and which rotate in opposite directions. Partition 7 serves to form a uniform layer of dispersed material. Due to the rarefaction, the wet material is firmly pressed against the perforated surface of the drum and rotates along with it in the direction shown in figure 1. 9 Brushes are used to clean the perforated partition from dry material particles. To prevent the hanging of wet material due to caking or compaction, and the formation of a so-called funnel, a vibrator 3 is installed on the hopper 1. The Amplitude and frequency of vibration of the vibrator 3 is set experimentally depending on the humidity and adhesive properties of the material being dried. Container 13 is intended for unloading dry material from the drying zone [14].

Theoretical part and discussion of results. One of the high-intensity methods of removing both free and bound moisture is the method of filtration drying of materials. This is due to the fact that during filtration drying, the heat agent is filtered through the porous structure of the wet material, which is placed on the perforated partition in the direction «wet material – perforated partition». The speed of movement of the heat agent in the pores and channels of a stationary layer of wet material determines the thickness of the boundary layer (hydrodynamic, thermal and diffusion) and, accordingly, the values of the heat and mass transfer coefficients. In addition, the surface of heat and mass transfer is the total surface of the pores and channels through which the heat agent is filtered. The filtration rate of the heat agent is determined based on technical and economic considerations, taking into account that its increase affects the growth of pressure loss. Moreover, the actual speed of movement of the heat agent relative to the layer elements is significantly higher than in the case of drying by any other methods (in the fluidized bed, during drying in pneumatic transport dryers, etc.). The large surface of heat and mass transfer and the speed of the heat agent in the pores and channels of the stationary layer of wet material provide high coefficients of heat and mass transfer and, accordingly, the intensity of the filtration method of drying [15].

At the same time, the total energy consumption for the filtration drying process consists of pressure losses in the stationary layer and heating of the heat agent (air) to a set temperature. Given the above, it is important to establish the dependence of pressure losses in a stationary layer of wet cotton fiber on the fictitious filtration rate of the heat agent, as an important factor determining the intensity and economic efficiency of filtration drying.

The movement of a gas flow through a porous structure of a material is a mixed problem of hydrodynamics. However, there are no theoretical foundations for a mixed problem of hydrodynamics today. to describe the hydrodynamics of gas movement through a porous structure of a material in scientific articles [9-13], the authors use theoretical dependencies of the internal or external problem.Given that the intensity of heat and mass transfer determines the speed of movement of a heat agent relative to the elements of a porous layer, in this paper we present the results of theoretical studies of pressure losses in a layer of cotton fiber from the point of view of the internal problem of hydrodynamics.The movement of a gas stream through a porous structure of a material is a mixed problem of hydrodynamics. However, there are no theoretical foundations for the mixed hydrodynamic problem today. To describe the hydrodynamics of gas movement through the porous structure of the material in scientific articles [9-13], the authors use theoretical dependencies of the internal or external problem.

Given that the intensity of heat and mass transfer determines the speed of movement of the heat agent relative to the elements of the porous layer, in this paper we present the results of theoretical studies of pressure losses in the cotton fiber layer from the point of view of the internal problem of hydrodynamics.

As shown by the researches, the stationary layer of cotton fiber during the application of a pressure drop, to ensure the appropriate filtration rate of the heat agent, due to the slight stiffness of individual randomly placed fibers in the experimental container, changes its height. This leads to a change in the equivalent diameter of the channels through which the heat agent moves, the porosity of the layer and, accordingly, the actual speed.Changing the actual filtration speed of the gas flow leads to an increase in the pressure loss in the layer ΔP and the height of the cotton fiber layer H-to an increase in the volume densityρ_l. Thatis:$H = f(\Delta \mathrm{P})$; $d_e = f(\Delta \mathrm{P})$; $\varepsilon = f(\Delta \mathrm{P})$; $\rho_l = f(\Delta \mathrm{P})$; $\Delta \mathrm{P} = f(v)$. At the same time, the only constant values are the weight of the fiber attachment and $G_v = const_v$ and the outer surface of all cotton fibers $F = const$.

The pressure loss in a porous stationary layer is determined based on the well-known Darcy-Weisbach dependence, because it takes into account all possible experimental variables [15,16]:

$$\Delta P = \lambda_l \cdot \frac{H}{d_e} \cdot \frac{\rho \cdot v^2}{2}, \tag{1}$$

where λ_l – is the coefficient of hydraulic resistance of the layer; ΔP – pressure loss in the material layer, Pa; H – layer height, m; d_e – equivalent diameter, m; ρ – the density of the gas flow, kg/m^3; υ – the actual speed of the gas flow, *m/s*.

$$d_e = \frac{4 \cdot \varepsilon_l}{a}, \tag{2}$$

where ε_l – isthe porosity of the layer, m^3/m^3; a – active specific surface of the layer, m^2/m^3; We define the initial specific surface of the fibera$_0$, which depends on the initial height of the stationary layer of cotton fiber and its volume:

$$\mathrm{a}_0 = \frac{F}{H_0 \cdot S} \tag{3}$$

where H_o – is starting height of the cotton fiber layer, m; S – cross-sectional area of the experimental container, m^2.

To define the starting specific surface area of all cotton fibersa$_0$assume that there are N identical fibers of length$L_v$in the experimental container. Then the outer surface of all particles can be represent as:

$$F = 2 \cdot (\mathrm{a} + b) \cdot L_v \cdot N, \tag{4}$$

where a and b – the middle width and thickness of the cotton lint, respectively,m.

Knowing the specific density of the cotton fiber$\rho_v$and the weight of the hitch $G_v$we find the volume of the cotton fiber:

$$V = \frac{G_v}{\rho_v} = a \cdot b \cdot L_v \cdot N, \tag{5}$$

where we define number of lints *N:*

$$N = \frac{G_v}{\rho_v \cdot a \cdot b \cdot L_v}, \tag{6}$$

so the surface of all the cotton lints:

$$F = 2 \cdot (\mathrm{a} + b) \cdot L_v \cdot \frac{G_v}{\rho_v \cdot a \cdot b \cdot L_v} = \frac{2 \cdot (\mathrm{a} + b) \cdot G_v}{\rho_v \cdot a \cdot b}. \tag{7}$$

We define the starting and current specific surfaces of a conditionally stationary layer of cotton fiber, which is located in the experimental container, as the ratio of the total surface to the volume:

$$a_0 = \frac{F}{S \cdot H_0} = \frac{2 \cdot (\mathrm{a} + b) \cdot G_v}{\rho_v \cdot a \cdot b \cdot S \cdot H_0}, \tag{8}$$

and the active specific surface of the cotton fiber is represented as:

$$a = a_0 \cdot \frac{H_0}{H} \tag{9}$$

where a_o, a – starting and active specific surfaces of the fiber layer, m^2/m^3; H_o – starting height of the fiber layer, m; H – current height of the fiber layer, depending on the pressure loss, m.

So:

$$a = a_0 \cdot \frac{H_0}{H} = \frac{2\cdot(\mathrm{a}+b)\cdot G_v}{\rho_v \cdot a \cdot b \cdot S \cdot H_0} \cdot \frac{H_0}{H} = \frac{2\cdot(\mathrm{a}+b)\cdot G_v}{\rho_v \cdot a \cdot b \cdot S \cdot H} \tag{10}$$

Let's express the weight of the cotton fiber attachment in terms of its volume and specific density:

$$G_v = V \cdot \rho_v = H_v \cdot S \cdot \rho_v \tag{11}$$

where H_v –isthe height of the fiber layer with densityρ_v, m.

Then the active specific surface of a conditionally stationary layer of cotton fiber can be represented as:

$$a = \frac{2\cdot(\mathrm{a}+b)\cdot G_v}{\rho_v \cdot a \cdot b \cdot S \cdot H} = \frac{2\cdot(\mathrm{a}+b)\cdot H_v \cdot S \cdot \rho_v}{\rho_v \cdot a \cdot b \cdot S \cdot H} = \frac{2\cdot(\mathrm{a}+b)}{a \cdot b} \cdot \frac{H_v}{H}, \tag{12}$$

and then equation (2) can be written as:

$$d_e = \frac{4\cdot\varepsilon_l}{a} = \frac{2\cdot a \cdot b \cdot \varepsilon_l}{(\mathrm{a}+b)} \cdot \frac{H}{H_v}, \tag{13}$$

and equations (1) using (13) can be represented as:

$$\Delta P = \lambda_l \cdot \frac{H}{d_e} \cdot \frac{\rho \cdot v^2}{2} = \lambda_l \cdot \frac{H \cdot (\mathrm{a}+b) \cdot H_v}{2 \cdot a \cdot b \cdot H \cdot \varepsilon_l} \cdot \frac{\rho \cdot v^2}{2} = \lambda_l \cdot \frac{(\mathrm{a}+b) \cdot H_v}{2 \cdot a \cdot b \cdot \varepsilon_l} \cdot \frac{\rho \cdot v^2}{2} \tag{14}$$

It is known that the coefficient of hydraulic resistance of the porous layer ξ is defined as a part of the speed pressure, that is, equation (14) can be represented as [17-20]:

$$\Delta P = \xi \cdot \frac{\rho \cdot v^2}{2} = \xi \cdot \frac{\rho \cdot v_0^2}{2 \cdot \varepsilon_l^2} \tag{15}$$

where ξ – is the coefficient of hydraulic resistance of the porous layer$\xi = \lambda_l \cdot \frac{(\mathrm{a}+b)\cdot H_v}{2 \cdot a \cdot b \cdot \varepsilon_l}$, v_0– fictitious heat agent filtration rate$v_0 = v \cdot \varepsilon$, $м/с$.

Approximation of experimental information by a power function allowed us to receive the following calculated dependence:

$$\varepsilon = \varepsilon_0 \cdot v_0^{-0.025} \tag{16}$$

The absolute value of the maximum relative error between the experimental data and the theoretically calculated data does not exceed 5.6%.

Generalization of experimental data on the hydrodynamics of filtering a thermal agent through a stationary layer of cotton was carried out in the form of dimensionless complexes$Eu = f(Re_\mathrm{e})$, and dependence of the hydraulic resistance coefficient of the layer $\xi = f(Re_\mathrm{e})$as functions of the Reynolds number:

$$\mathrm{Eu} = 84000 \cdot \mathrm{Re}_\mathrm{e}^{-1.18}, \tag{17}$$

where $\mathrm{Re_e}$ – is the equivalent value of the Reynolds number.

$$\mathrm{Re_e} = \frac{\mathrm{v} \cdot \mathrm{d_e} \cdot \rho}{\mu},$$

where μ – is coefficient of dynamic viscosity of the gas flow, $Pa \cdot s$;

The coefficient of hydraulic resistance of the cotton fiber layer was calculated based on experimental data from equation (15). Approximation of experimental information by a power function allowed us to receive the following calculated dependence:

$$\xi = 160000 \cdot \mathrm{Re}_\mathrm{e}^{-1.16} \tag{18}$$

Comparing the proportion of experimentally determined values of pressure losses in a conditionally stationary layer of cotton fiber to those theoretically calculated based on the dependence (17) on the Reynolds number, the absolute value of the relative error does not exceed 14.2%, which is explained by the complex structure and spontaneity of the formation of a stationary layer of cotton fiber, as well as the impact of the pressure drop on the height of the layer.

Conclusion. Received in dimensionless form, the calculated dependence (17) makes it possible to predict the energy costs of creating a pressure drop (under the same hydrodynamic conditions) when designing a new drying equipment, and the dependence (18) is convenient to use during the operation of the drying plant when it is necessary to change the technological parameters of the process, that is, to change the height of the cotton fiber layer or the filtration rate of the thermal agent.The Error between the theoretically calculated values and experimental data does not exceed 14.2%, which is quite acceptable for the design calculations of new drying equipment.Obtained in dimensionless form the calculated dependence (17) gives the possibility to predict the energy cost of creating the pressure differential (with the same hydrodynamic conditions) when designing new drying equipment, and the dependence (18) it is convenient to use during operation of the dryer when you need to change the process parameters, that is, change the height of the layer of cotton fibers or the filtration rate of the heat agent.The error between the theoretically calculated values and experimental data does not exceed 14.2%, which is quite acceptable for design calculations of new drying equipment.

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ШИТТІ МАҚТАНЫ СҮЗІП КЕПТІРУ БАРЫСЫНДА ГИДРАВЛИКАЛЫҚ КЕДЕРГІНІ ЕСЕПТЕУ

Аннотация. Қазіргі заманғы әлемдік экономикада тоқыма, тоқылмаған және басқа да талшықты материалдарды үлкен маңызға ие. Мақта – түрлі өнеркәсіп, азық-түлік және тұрмыстық өнімдерді өндіру үшін шикізаттың құнды түрінің бірі. Шитті мақтаны кептіру режимін таңдау түсі, талшықтың ұзындығы, механикалық зақымдану түрі және т.б. көрсеткіштерге байланысты болып келеді. Шитті мақтаны кептіру барысында кептірудің оңтайлы режимін таңдаған маңызды, өйткені кептірудің параметріне сәйкес келмесе талшық үзіліп, ұзындығы қысқарады, нәтижесінде талшықтың сапасы төмендейді.

Өнеркәсіпте шитті мақтаны кептіру үдерісін іске асыруда барабан түріндегі кептіргіштер мен энергия шығыны, қайнаған қабаттың қымбат кептіргіші қолданылады. Сондықтан кептіргіштің жаңа түрін әзірлеуді міндет етіп алдық, өйткені ол Кептіру үдерісіне энергетикалық шығындарды азайтуға мүмкіндік береді.

Шитті мақтаны сүзіп кептіру кезінде гидродинамика мен жылу және масса алмасудың эксперименттік және теориялық зерттеулерінің нәтижелерін қорыту шитті мақтаның физикалық-механикалық қасиеттеріне сай кептіру қондырғысының құрылымын ұсынуға, осы қондырғының негізгі конструктивтік өлшемдерін есептеу әдістемесін жетілдіруге және жылу агентінің оңтайлы технологиялық параметрін есептеуге мүмкіндік берді.

Біз шитті мақтаны кептіруге арналған барабан типті Сүзгіш кептіргіш орнатудың принципті схемасын пайдалануды ұсынамыз, ол еркін әрі байланысқан ылғалдың жоғары инсенсивті әдісі болып саналады. Бұл Сүзгіш кептіру кезінде жылу агенті «ылғалды материал-перфорацияланған қалқа «бағытында перфорацияланған қалқа орналасқан ылғалды материалдың кеуекті құрылымы арқылы сүзіледі. Ылғалды материалдың стационарлық қабат тесігі мен каналдарындағы жылу агентінің қозғалыс жылдамдығы шекаралық қабаттың қалыңдығын және тиісінше жылу және масайналым коэффициенттерінің мәнін анықтайды. Сонымен қатар, жылу және масса алмасу беті жылу агенті сүзетін тесіктер мен каналдардың жиынтық беті болып саналады. Жылу агентін сүзу жылдамдығы оның ұлғаюы қысымның жоғалуына әсер ететінін ескере отырып, техникалық-экономикалық пайымдарға сүйене отырып анықталады. Сонымен қатар, қабат элементіне қатысты жылу агентінің нақты қозғалыс жылдамдығы кез келген басқа әдістермен кептіру жағдайына қарағанда айтарлықтай жоғары. Жылу және масса алмасудың үлкен беті және ылғалды материалдың стационарлық қабатының поралары мен каналдарындағы жылу агентінің жылдамдығы жылу және масса берудің жоғары коэффициентін және тиісінше кептірудің сүзу тәсілінің қарқындылығын қамтамасыз етеді.

Материалдың кеуекті құрылымы арқылы газ ағынының қозғалысы гидродинамиканың аралас міндеті болып табылады. Алайда гидродинамиканың аралас есебінің теориялық негіздері бүгінде жоқ. Бұл мақалада шитті мақтаны кептірудің сүзгілеу әдісін пайдалану және гидравликалық кедергіні есептеу ұсынылады. Ғылыми мақалаларда материалдың кеуекті құрылымы арқылы газ қозғалысының гидродинамикасын сипаттау үшін авторлар ішкі немесе сыртқы есептің теориялық тәуелділігін пайдаланады. Жылу және масса алмасу қарқындылығы кеуекті қабаттың элементтеріне қатысты жылу агентінің қозғалыс жылдамдығын анықтайтынын ескере отырып, бұл жұмыста гидродинамиканың ішкі міндеті тұрғысынан мақта талшығының қабатындағы қысым шығынын зерттеу нәтижелері ұсынылған. Жылу агентін мақтаның стационарлы қабаты арқылы сүзу үшін эксперименталдық зерттеулер жүргізілді, өйткені үйіндінің салмағы мен қабаттың түрлі биіктігінің әртүрлілігіне байланысты $\Delta P = f(v_0)$ функционалдық тәуелділік түрінде көрсетілді. Алынған нәтижелер өлшемсіз жаңа кептіру жабдығын жобалау кезінде қысымның ауытқуын жасауға (бірдей гидродинамикалық жағдайда) арналған энергетикалық шығындарды болжауға мүмкіндік береді.

Түйін сөздер: мақта талшығы, гидродинамика, сүзіп кептіру, гидравликалық кедергі, кеуектілік, қабаттың белсенді беткі қабаты.

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РАСЧЕТ ГИДРАВЛИЧЕСКОГО СОПРОТИВЛЕНИЯ ПРИ ФИЛЬТРАЦИОННОЙ СУШКЕ ХЛОПКА-СЫРЦА

Аннотация. Текстиль, нетканые и другие волоконные материалы имеют большое значение в современной мировой экономике. Хлопок является одним из наиболее ценных видов сырья для производства различных промышленных, пищевых и бытовых продуктов. Выбор режима сушки хлопка-сырца зависит от следующих показателей: цвет, длина волокна, типа механического повреждения и тому подобное. Во время сушки хлопка-сырца важно выбрать оптимальный режим сушки, поскольку при несоответствующих параметрах сушки наблюдается обрыв волокна, уменьшение его длины, в результате чего снижается качество волокна.

Для реализации процесса сушки хлопка-сырца в промышленности используют сушилки барабанного типа и сушилки кипящего слоя, которые являются энергозатратными и дорогими. Поэтому перед нами стояла задача разработать новый тип сушилки, который позволит снизить энергетические затраты на процесс сушки.

Обобщение результатов экспериментальных и теоретических исследований гидродинамики и тепло - и массообмена при фильтрационной сушке хлопка-сырца позволили предложить конструкцию сушильной установки, которая учитывает физико-механические свойства хлопка-сырца, усовершенствовать методику расчета основных конструктивных размеров данной установки и рассчитать оптимальные технологические параметры теплового агента.

Нами предлагается использование принципиальной схемы установки фильтрационной сушки барабанного типа для сушки хлопка-сырца, которая является одним из высокоинтенсивных методов удаления как свободной, так и связанной влаги. Это обусловлено тем, что во время фильтрационной сушки тепловой агент фильтруется сквозь пористую структуру влажного материала, который размещен на перфорированной перегородке в направлении «влажный материал – перфорированная перегородка». Скорость движения теплового агента в порах и каналах стационарного слоя влажного материала определяет толщину пограничного слоя и соответственно значения коэффициентов тепло- и масоотдачи. Кроме этого, поверхностью тепло- и массообмена является суммарная поверхность пор и каналов, сквозь которые фильтруется тепловой агент. Скорость фильтрации теплового агента определяют исходя из технико-экономических соображений, учитывая то, что ее увеличение влияет на рост потери давления. Причем, действительная скорость движения теплового агента относительно элементов слоя значительно выше, чем в случае сушки любыми другими методами. Большая поверхность тепло- и массообмена и скорость теплового агента в порах и каналах стационарного слоя влажного материала обеспечивают высокие коэффициенты тепло - и массоотдачи и соответственно интенсивность фильтрационного способа сушки.

Движение газового потока сквозь пористую структуру материала представляет собой смешанную задачу гидродинамики. Однако теоретических основ смешанной задачи гидродинамики на сегодня не существует. В этой статье предлагается использование фильтрационного способа сушки хлопка-сырца и расчет гидравлического сопротивления. Для описания гидродинамики движения газа сквозь пористую структуру материала в научных статьях авторы используют теоретические зависимости внутренней или внешней задачи. Учитывая то, что интенсивность тепло- и массообмена определяет скорость движения теплового агента относительно элементов пористого слоя, в данной работе представлены результаты исследований потерь давления в слое волокна хлопка с точки зрения внутренней задачи гидродинамики. Проведены экспериментальные исследования по фильтрации теплового агента сквозь стационарный слой хлопка, из-за разности насыпного веса и различных высот слоя представляли в виде функциональной зависимости $\Delta P = f(v_0)$. Полученные результаты в безразмерной форме позволяют прогнозировать энергетические затраты на создание перепада давлений (при одинаковых гидродинамических условиях) при проектировании нового сушильного оборудования.

Ключевые слова: волокно хлопка, гидродинамика, фильтрационная сушка, гидравлическое сопротивление, пористость, активная удельная поверхность слоя.

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INVESTIGATION OF Ni-CONTAINING CATALYSTS FOR THE PURIFICATION OF EXHAUST GASES

Abstract. Results of the development of multicomponent oxide catalysts for the purification of exhaust gases based on Ni, Cu, and Cr supported on 2% Ce/θ-Al_2O_3 by varying the concentration of the active phase of catalyst are presented in paper. It was found that the highest degree of toluene conversion (up to 98.8 %) is observed on the three-component Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst with optimal metal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at GHSV = 5Ч10^3 h^{-1} and a temperature of 723 - 773 K. The presence of CeO_2 crystals, X-ray amorphous clusters (d = 20 – 100 E) of variable valence metal oxides NiO and CuO as well as solid metal solutions CuO (NiO) and aluminates was detected on the surface of optimum catalyst calcined at 873 K using XRD and transition electron microscopy methods. Preparation of polyoxide supported catalysts as well as study the influence of catalyst composition and modified additives on deep oxidation of toluene - a major component of toxic organic gaseous industry emissions, is the goal of research.

Key words: catalytic oxidation, toluene, purification, nickel, copper.

Introduction. The problem of chemical safety and sanitary air protection is particularly relevant due to the increase of harmful emissions of industrial enterprises, which have a strong toxic effect. Many chemical compounds (toluene, xylene, styrene, phenol, tricresol, mineral spirits, CO, etc.), which negatively affect the living organisms and flora are harmful toxic emissions from industrial plants. Under the Paris agreement, adopted on December 12, 2015 and signed on April 22, 2016, in addition to the United Nations Framework Convention on Climate Change (UNFCCC), developed countries and countries with economies in transition have to reduce or stabilize greenhouse gas emissions [1]. The content of harmful emissions above the MPC in industrial workshops and atmospheric air in the cities cause a negative impact on living organisms and lead to various diseases thereby creates a threat to the safety of the environment [2]. Toluene, xylene and ethyl-benzene are major part of the solvents used in various industries, which are present in gaseous emissions [3]. Toxic and adverse effect of harmful emissions on a living organism can be traced on the example of toluene - a major component of toxic organic gaseous emissions that are present in the emissions of furniture, paint, cable, printing and other industries. For example, the inhalation of toluene with a concentration of 250 mg m^{-3} for 2 h leads to a decrease in heart rate, disturbance of speech, movement coordination [4]. Prolonged inhalation of toluene, which is present in the composition of glue, varnishes, paints, etc., causes neurotoxic deviations that lead to clinical consequences - hallucinations, somnolence, suicide attempts, visual disturbances and seizures.

From the literature data [5] on the methods and apparatuses for neutralization of toxic emissions follows that deep catalytic oxidation is the most economical way for cleaning of gases from the emissions of complex composition [6]. Typically, the catalysts based on noble metals (Pt, Pd) [7], which have high activity (95-100 %) in complete oxidation of organic substances [8], are used mainly for cleaning of waste gas of industrial enterprises [9]. Catalysts based on Pt group metals have high activity at low temperatures, durability, heat resistance and ability to operate stably at high space velocities. Conditions of deficit and high cost of platinum group metals lead to the need to develop new approaches to the creation of highly effective polyoxide catalysts that do not contain noble metals capable exhibit a high thermal stability and poison-resistance and sustainable in the long term operation [10-15]. Creation of catalysts for gas purification, which do not contain noble metals or contain them in small amounts [16], is an important goal. In this context, the development of high-performance polyoxide catalysts, which do not contain precious metals, and technology for deep oxidation of toxic organic gaseous emissions from industry are relevant.

Experimental. Purification of exhaust gases from harmful organic impurities, in particular from toluene, was carried out on a flow installation, the implementation conditions of which are close to real conditions.

The granulated θ-Al_2O_3 (S = 100 m^2 g^{-1}, particle size between 40 and 50 μm) modified by Ce, which forms resistant surface $CeAlO_3$ perovskite up to 1,373 K was used as a carrier. Polyoxide catalysts were prepared by capillary impregnation of alumina modified with cerium by mixed aqueous solution of Ni, Cu and Cr nitrates by incipient wetness, followed by drying at 453 - 473 K (4 - 5 h) and calcination at 873 K (1 - 1.5 h) in air. The prepared oxide catalysts have been promoted with Pt and Pd (0.05%) to improve the activity and thermal stability.

Deep oxidation of toluene was carried out on the flow type PKU-2VD catalytic installation intended for testing of catalysts at pressures from atmospheric pressure up to 3.4 MPa in tubular reactor with fixed catalyst bed. Catalytic activity of catalysts was determined in flow installation at deep oxidation of toluene in air at various temperatures (523 – 773 K), space velocities (5 – 15Ч10^3 h^{-1}) and toluene concentration (320 mg m^{-3}) in the initial mixture.

Analysis of the initial mixture and reaction products were carried out using CHROMOS GC-1000 chromatograph. The rate of carrier gas (Ar) - 10 ml min^{-1}.

The phase composition of catalysts was determined by X-ray diffractometer DRON-4.7, Co – anode, 25 kV, 25 mA, 2θ – 5 – 80° (XRD). The morphology, particle size and chemical composition of the Ni-Cu-Cr catalysts were investigated using transmission electron microscope EM-125K at 80,000 times magnification by the replica method with extraction using microdiffraction (TEM). The surface of catalysts was determined by the BET method on the low temperature N_2 adsorption using the Accusorb apparatus (Micromeritics, USA).

Determination of the amount of adsorbed oxygen by catalysts, its characteristics, as well as the ability to interact with a reducing agent (H_2) were carried out by methods of temperature-programmed desorption of oxygen (TPD) and temperature-programmed reduction (TPR). Temperature-programmed reduction of catalysts after the formation in air at 873 K were carried out by passing a mixture of H_2 (10%) and He (90%) at 20 ml min^{-1} and the temperature rises at speeds of 8 K min^{-1} from 293 to 1,173 K (at 1,173 K temperature was stabilized).

Results and discussion. Investigation of the activity of polyoxide catalysts in the reaction of deep oxidation of toluene at 723 K and space velocity 5Ч10^3 h^{-1} is presented. The conversion of toluene increased with the complexity of the composition of catalysts. The lowest 57.0 % degree of toluene oxidation was observed on the 5% Ni/2% Ce/θ-Al_2O_3 catalyst, and the greatest 98.5% degree was observed on the three-component 9% Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst. The following series by activity in the reaction of deep oxidation of toluene was determined: Ni-Cu-Cr/2% Ce/θ-Al_2O_3 (98.5%) > Ni-Cu-Cr/θ-Al_2O_3 (92.0%) > Ni-Cu/2% Ce/θ-Al_2O_3 (84.0%) > Ni-Cr/2% Ce/θ-Al_2O_3 (75.0%) > Ni/2% Ce/θ-Al_2O_3 (57.0%). The largest conversion of toluene is observed on three-component Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst with an optimal ratio of metals Ni: Cu : Cr = 1.0 : 3.0 : 0.1 at T = 723 K. The degree of toluene oxidation reduces from 98.5 to 89.3% with the increase of space velocity from 5Ч10^3 to 15Ч10^3 h^{-1}, respectively.

Increasing the concentration of toluene from 100 to 320 mg m^{-3} in the initial mixture with air leads to a slight decrease in the degree of conversion of toluene on the two component Ni-Cu/2% Ce/θ-Al_2O_3 and Cu-Cr/2% Ce/θ-Al_2O_3 catalysts. A noticeable decrease in activity between two component oxide catalysts was found on the Ni-Cr-containing catalyst from 76.6 to 73.0%. Ni-Cu-Cr/2% Cr/θ-Al_2O_3 catalyst was the most stable.

Thus, the optimal conditions of deep oxidation of toluene on oxide Ni-, Cu- and Cr-containing catalysts over 2% Ce/θ-Al_2O_3 were determined. Degree of conversion of toluene reaches 98.5 – 98.8% on the Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst at temperatures of 723 - 773 K, GHSV - 5Ч10^3 h^{-1} and the concentration of toluene in the initial mixture with air – 100 - 320 mg m^{-3}.

The intensive reflections from CuO and less intensive from NiO, CeO_2, and θ-Al_2O_3 are observed in roentgenograms of the Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst heated at 873 K. Not only CeO_2 crystallization, but a sharp increase in the content of α-Al_2O_3 starting from 1,273 K is a result of heating of the Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst. Significant reduction of the total surface area of catalysts is due to heating. CeO_2 crystallization occurs to a lesser extent due to the small (2%) of Ce content (in carrier only). According to XRD the presence of CeO_2 crystals and X-ray amorphous clusters with diameters from 20 to 100 E, metal oxides of variable valence NiO, CuO, and solid solutions of metals CuO (NiO) is fixed on the surface of carrier in the process of catalyst synthesis after heating at 873 K. Phase transformations occur in the Ni-Cu-Cr catalyst upon heating in air above 1,273 K. Metal oxides react with alumina to form the Me-Al_2O_4 type aluminates with diameter from 200 to 1,000 E and the surface decreases sharply to 2 - 5 m^2. Reflexes from the θ-Al_2O_3, α-Al_2O_3, and CeO_2 are presented in the 2% Ce/θ-Al_2O_3, as well as in the carrier (quantification was performed by reflections 2.31 E, 1.74 E, 1.91 E, respectively). The intensity of CeO_2 reflexes increases slightly with increasing the Ce content in catalyst, and especially after the heating consistently at 873, 1,073, 1,273, 1,373 and 1,473 K. This indicates that crystallization of the amorphous cerium oxides happens as a result of heating. The same process is characteristic for supported on the 2% Ce/θ-Al_2O_3 catalysts, but to different degrees.

Thus, the use of X-ray diffraction analysis to study of polyoxide catalysts supported on 2% Ce/θ-Al_2O_3 showed that the active components are mainly in amorphous state in the initial catalysts; part of Ni and Cu is represented by Ni and Cu oxides [17].

The morphology and particle size of the developed catalysts were examined by transmission electron microscope on the EM-125K at magnification 80,000 times by the replica method with extraction using electron microdiffraction. It was found that single, double and triple metal oxides, the particle size of which are decreased from 50-80 E (Ce/Al_2O_3) to 20-30 E (Ni-Cu-Cr) are formed at complication the composition of three-component catalyst. The nanoparticles of metal oxides or their mixtures are formed after decomposition of nitrates of initial oxide Ni-Cu-Cr catalyst at 873 K according to electron microscopy and microdiffraction. Interaction of elements with θ-Al_2O_3 carrier with formation of larger copper and nickel aluminates of the AB_2O_4 and ABO_3 type occurs when the temperature rises [18].

Figure 1 shows the spectra of thermal desorption of oxygen from the oxide Ni-Cu-Cr/θ-Al_2O_3 after oxygen adsorption at 873 K. It is seen that the amount of oxygen released upon heating to 1,173 K (stabilizing temperature) increases with the complexity of the composition of mixed catalyst. Desorption curve has bends at 773 K and 923 K as well as maximum at 1,023 K, which is caused by desorption of the adsorbed oxygen (673 – 873 K) and decomposition (873-1,073 K) of copper and nickel oxides (up to Cu_2O, Ni_2O) and then mixed oxides (> 1,070 K).

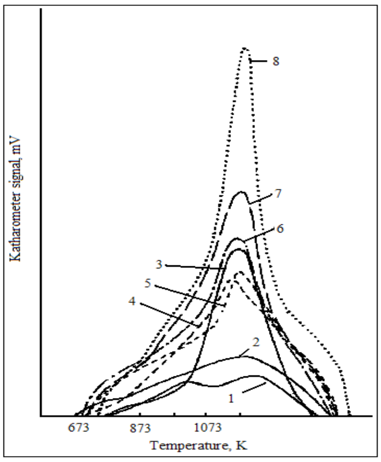

Figure 1 – Thermal desorption of oxygen from the catalysts on $A1_2O_3$ after heating in air:
1-5% Ni, 2-5% Cu, 3-5% Cr, 4-5% (Ni + Cr), 5-5% (Cu + Cr), 6-8-10% Ni-Cu-Cr at varying the deposition methods of catalysts:
6 - NH_4HCO_3, 7 - $A1(NO_3)_3$, 8 - NH_4HCO_3 + $A1(NO_3)_3$, T – 873 K, 1 h

The total amount of released oxygen (9.7 mmol from the 1.0 g of active phase) exceeds the probable sorption at each of oxides. This is obviously connected with the dissolving of oxides of superstoichiometric oxygen in formed solid solutions, which are released at lower temperatures [19]. The total amount of released oxygen (mainly due to weak adsorbed oxygen) from the Ni-Cu-Cr catalyst depends on the conditions of preparation of mixed carbonates and their decomposition. It is increased by 2 times when using $NH_4HCO_3 + Al(NO_3)_3$ in the precipitation of mixture.

Calculation of activation energy release of oxygen from the catalyst showed that it is 88 - 89 kJ/mol. Desorption energy from single copper oxides is 128 kJ/mol; from nickel oxides - 120 kJ/mol and from mixed oxides – 140 - 144 kJ/mol.

Heating of Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst at 1,473 K sharply reduces the release of oxygen in the area of decomposition of metal oxides for the initial and promoted contacts (Figure 2). The area of adsorbed oxygen completely disappears in the spectrum of Ni-Cu-Cr and Ni-Cu-Cr + Pt catalysts. The observed phenomenon can be explained by the fact that most of the metal oxides reacts with the carrier to form large (200 – 1,000 Å) $Ni(Cu)Al_2O_4$ aluminates (XRD and TEM), because of which the total surface area of contacts is reduced from 60 to 5 m^2 g^{-1} [20].

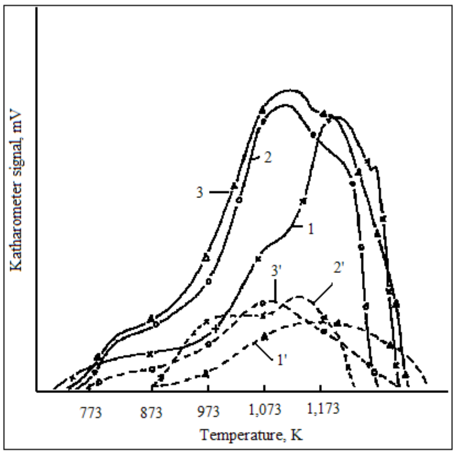

Figure 2 – Thermal desorption of oxygen from the Ni-Cu-Cr/2 % Ce/$A1_2O_3$ catalyst heated in oxygen and promoted with Pd and Pt: 1 - Ni-Cu-Cr/2 % Ce/$A1_2O_3$, 2 - Ni-Cu-Cr/2 % Ce/$A1_2O_3$ + Pd, 3 - Ni-Cu-Cr/2 % Ce/$A1_2O_3$ + Pt. 1^1, 2^1, 3^1 - catalysts after heating at 1,473 K, T – 873 K

The study of temperature-programmed reduction of Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalysts allowed to make one more step in understanding of reduction mechanism and elimination of oxygen from oxides, and to assess the ability of catalyst to absorb oxygen from gas phase.

Figure 3a shows that the TPR curve has four hydrogen absorption peaks: T_1 = 523 K, T_2 = 573 K, T_3 = 673 K and T_4 = 1,073 K corresponding to reduction of CuO (T_1), mixed oxides CuO-NiO (T_2), NiO (T_3) and formed partially Ni or Cu aluminates.

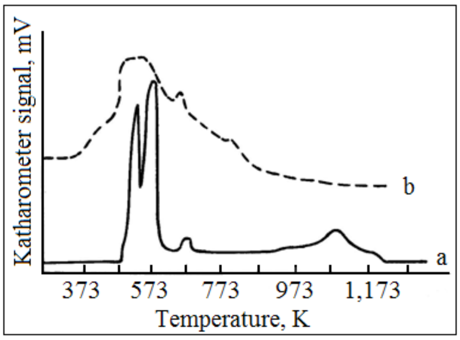

Figure 3 – TPR and TPO spectra of the initial Ni-Cu-Cr/Ce/θ-$A1_2O_3$ catalyst:
a - TPR of the initial catalyst, b - TPO after TPR up to 1,225 K

Temperature-programmed oxidation (TPO) of catalyst after its reduction up to 1,225 K (figure 3b) showed that oxygen is adsorbed easily, starting from 357 – 373 K, as a broad peak with T^1_m = 523 K, T^2_m = 673 K and T^3_m = 800 – 810 K, which corresponds to adsorption of it on surface (T^1_m) and formation of Ni and Cu oxides. Ni-Cu-Cr/Ce/θ-Al_2O_3 catalyst has undergone profound changes in the phase composition after heat treatment at 1,473 K 5 h (Figure 4a).

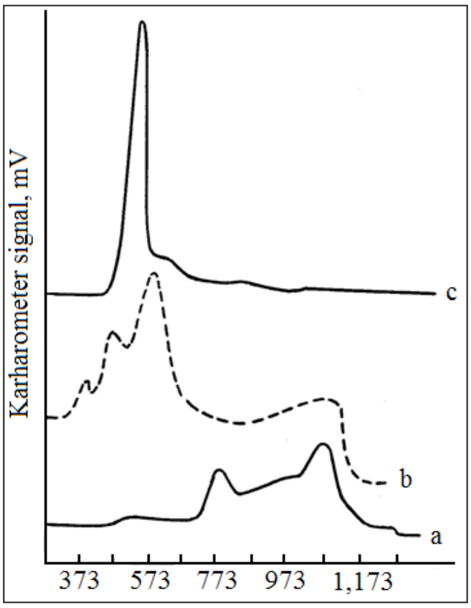

Figure 4 - TPR and TPO spectra of the Ni-Cu-Cr/Ce/θ-Al_2O_3 catalyst:
a - TPR of the initial catalyst, b - TPO of catalyst reduced up to 1,223 K,
c - TPR of catalyst after treatment in oxygen to 973 K, T - 1,473 K, 5 h

Weak bending of curve at 473 K is available in TPR spectrum. The main absorption of H_2 occurs at T_m = 773 and 1,073 K when Cu (Ni) aluminates are reduced. Cu(Ni)Al_2O_4 crystals (2,42 reflex) is also fixed according to XRD. If the reduction temperature of catalyst reaches 1,223 K, the adsorption of oxygen in the initial Ni-Cu-Cr catalyst is carried out at a temperature above than 373 K (figure 4b).

Subsequent temperature-programmed reduction of catalyst indicates on absorption of H_2 only as a single peak (Figure 4c). This indicates that a mixture of Ni(Cu) oxides, which are reduced at 523 K, is synthesized from aluminates.

Thus, Ni-Cu-Cr catalyst is a solid solution of copper and nickel oxides with chromium, included in it, according to the TPD and TPR results. Superstoichiometric surface oxygen with E_{des} = 88 - 89 kJ mol^{-1}, which reacts easily with reducing agents is adsorbed onto its surface. TPD curves and TPO data indicate on its presence in catalyst. Besides mixed oxides the less active Ni and Co aluminates are formed in the oxidation process at high temperatures in catalyst in an oxidizing atmosphere.

Conclusion. As a result of studies, it was found that the highest degree of toluene conversion (to 98.8 %) is observed on three-component Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst with optimal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at space velocity of 5Ч10^{3} h^{-1} and temperature 723 - 773 K. The binding energy of oxygen with surface and its reactivity on polyoxide catalysts were determined by the TPD, TPO and TPR methods. It was shown that formed Ni and Cu aluminates can be reduced to the initial oxides or their mixtures under the influence of H_2 at 973 - 1,223 K. Again, oxygen adsorption on Ni-Cu-Cr catalysts after decomposition of oxides occurs at low temperature (325 K). This point to high reactivity of adsorbed O_2^-, O^-, and lattice oxygen of dispersed oxides, as well as mixtures thereof, and its ability to easy reactivation.

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ШЫҒАРЫЛҒАН ГАЗДАРДЫ ТАЗАРТУ ҮШІН Ni-ҚҰРАМДЫ КАТАЛИЗАТОРЛАРДЫ ЗЕРТТЕУ

Аннотация. Химиялық қауіпсіздік және ауаны санитарлық қорғауда қатты улы әсер ететін өнеркәсіптік кәсіпорындардан шығарылатын зиянды қалдықтың артуы өзекті мәселе болып саналады. Өндірістік кәсіпорындардан шығатын зиянды улы қалдықтар, яғни көптеген химиялық қосылыстар (толуол, ксилол, стирол, фенол, трикрезол, минералды спирттер, СО және т.б.) тірі организмдер мен флораға теріс әсер тигізеді. Климаттың өзгеруі жөніндегі 2015 жылы 12 желтоқсанда қабылданған Париж келісіміне және 2016 жылы 22 сәуірде қол қойылған Біріккен Ұлттар Ұйымының конвенциясына сәйкес дамыған және экономикасы дамушы елдерде парниктік газдардың шығындысын азайтып, тұрақтандыру қажет. Өнеркәсіптік цехтардан шығарылған зиянды газдардың құрамы қаладағы атмосфералық ауада шекті рұқсат етілген концентрациядан жоғары болса, ол қоршаған ортаның қауіпсіздігіне, сондай-ақ тірі организмге теріс әсерін тигізеді және түрлі ауруларға әкеледі. Әртүрлі өндірістік салалардан шығарылған газдағы толуол, ксилол және этилбензол негізгі еріткіштертердің бөлігі болып саналады.

Өндірістік өнеркәсіптерден, мысалы жиһаз, бояу, лак, кабель, полиграфия салаларынан шығарылатын улы газ қалдықтары тірі ағзаларға теріс әсер тигізеді. Осындай органиканың негізгі компоненті – толуол. Мысалы, 2 сағат ішінде 250 мг м$^{-3}$ концентрациясы бар толуолды жұтқанда жүрек жиілігі төмендейді, сөйлеу бұзылып, қозғалыс баяулайды.

Желім, лак, бояудың және т.б. құрамында болатын толуолмен ұзақ дем алатын болса, нейротоксикалық ауытқу клиникалық салдарға, яғни галлюцинация, ұйқышылдық, өз-өзіне қол жұмсау мен көру кабілетінің бұзылуына және құрысуға әкеледі.

Органикалық заттардың толық тотығуы кезінде жоғары белсенділікке ие (95 - 100%) бағалы металдар негізіндегі (Pt, Pd) катализаторлар өнеркәсіптік өндірістерден шығарылған газдарды тазарту үшін қолданылады. Платина тобы металдарының қолжетімділігі мен бағасының жоғары болуы құрамында асыл металдары болмайтын, термотұрақтылығы жоғары, улануға қарсы және ұзақ уақыт аралығында эксплуатациялануға тұрақты, тиімділігі жоғары полиоксидті катализаторларды жасауға деген қажеттілік тудырады. Шығарылған газдарды тазалауға бағалы металдарсыз және құрамында бағалы металдар аз катализаторларды жасау басты мақсат болып саналады.

Өндірістік өнеркәсіптерден шығарылған улы органикалық газдарды толық тотығу технологияларын дамытуда құрамында бағалы металдары жоқ жоғары тиімді полиоксидті катализаторларды жасау да өзекті.

Көлемдік жылдамдығы 5Ч10^3 с$^{-1}$ мен температурасы 723 К-де толуолдың толық тотығу реакциясында полиоксидті катализаторлардың белсенділігін зерттеу жолдары көрсетілген. Катализаторлар құрамының көбеюі арқылы толуолдың конверсиясы жоғарылады. 5 Ni/2% Ce/θ-Al_2O_3 катализаторында толуолдың ең төменгі тотығу көрсеткіші 57.0% болса, ал керісінше үш компонентті 9% Ni-Cu-Cr/2% Ce/θ-Al_2O_3 катализаторда 98.5% ең жоғары тотығу дәрежесі байқалды.

Бастапқы қоспадағы ауа мен толуолдың концентрациясын 100-ден 320 мг$^{-3}$-ке дейін жоғарылатқанда екі компонентті Ni-Cu/2%Ce/θ-Al_2O_3 және Cu-Cr/2%Ce/θ-Al_2O_3 катализаторда толуол конверсиясының дәрежесі төмендейді.

Зерттеу нәтижесі барысында үш компонентті Ni-Cu-Cr/2% Ce/θ-Al_2O_3 катализаторда оңтайлы Ni : Cu : Cr = 1,0 : 3,0 : 0,1 қатынасында, 5Ч10^3 сағ$^{-1}$ көлемдік жылдамдықта және 723 - 773 К температурада толудың айналым дәрежесі анағұрлым (98.8%- дейін) жоғарылайды. Оттектің беттік қабатпен байланыс энергиясы және полиоксидті катализатордағы реакциялық қабілеттілігі ТБД, ТБТ және ТБТ әдістері арқылы анықталды. Түзілген Ni және Cu алюминаттары 973-1223 К аралығында H_2 әсерінен оксидтерге немесе олардың қоспаларына дейін тотықсызданатындығы анықталды.

Ni-Cu-Cr катализаторларында оттегінің адсорбциясы оксидтердің ыдырауынан кейін ең төменгі (325 К) температурада жүреді. Бұл дисперсті оксидтердің адсорбцияланған O_2^-, O^- және оттегі торларының жоғары қайта белсенділігін, сондай-ақ олардың қоспаларын оның жеңіл жолмен қайта қосылуға қабілеттілігін көрсетеді.

Түйін сөздер: каталитикалық тотығу, толуол, тазалау, никель, мыс.

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ИССЛЕДОВАНИЕ Ni-СОДЕРЖАЩИХ КАТАЛИЗАТОРОВ ДЛЯ ОЧИСТКИ ОТХОДЯЩИХ ГАЗОВ

Аннотация. Проблема химической безопасности и санитарной защиты воздуха особенно актуальна в связи с увеличением вредных выбросов промышленных предприятий, которые оказывают сильное токсическое воздействие. Многие химические соединения (толуол, ксилол, стирол, фенол, трикрезол, минеральные спирты, CO и т.д.), которые негативно влияют на живые организмы и флору, являются вредными токсичными выбросами от промышленных предприятий. В соответствии с Парижским соглашением, принятым 12 декабря 2015 года и подписанным 22 апреля 2016 года в дополнение к Рамочной конвенции Организации Объединенных Наций об изменении климата, развитые страны и страны с переходной экономикой должны сократить или стабилизировать выбросы парниковых газов. Содержание вредных выбросов выше ПДК в промышленных цехах и атмосферном воздухе в городах оказывает негативное воздействие на живые организмы и приводит к различным заболеваниям, тем самым создает угрозу безопасности окружающей среды. Толуол, ксилол и этилбензол являются основной частью растворителей, используемых в различных отраслях промышленности, которые присутствуют в газообразных выбросах. Токсичное и вредное воздействие вредных выбросов на живые организмы можно проследить на примере толуола - основного компонента токсичных органических газообразных выбросов, которые присутствуют в выбросах мебельной, лакокрасочной, кабельной, полиграфической и других отраслей промышленности. Например, вдыхание толуола с концентрацией 250 мг м$^{-3}$ в течение 2 ч приводит к снижению частоты сердечных сокращений, нарушению речи, координации движений. Длительное вдыхание толуола, который присутствует в составе клея, лаков, красок и т.д., вызывает нейротоксические отклонения, которые приводят к клиническим последствиям - галлюцинациям, сонливости, попыткам самоубийства, нарушениям зрения и судорогам.

Как правило, катализаторы на основе благородных металлов (Pt, Pd), которые обладают высокой активностью (95 - 100%) при полном окислении органических веществ, используются в основном для очистки отходящих газов промышленных предприятий. Условия дефицита и высокая стоимость металлов платиновой группы приводят к необходимости разработки новых подходов к созданию высокоэффективных полиоксидных катализаторов, не содержащих благородных металлов, способных проявлять высокую термостойкость и стойкость к отравлению и устойчивых в течение длительного срока эксплуатации. Создание катализаторов для очистки газов, которые не содержат благородных металлов или содержат их в небольших количествах, является важной целью. В этом контексте актуальны разработки высокоэффективных полиоксидных катализаторов, которые не содержат драгоценных металлов, а также технологии глубокого окисления токсичных органических газообразных выбросов промышленности.

Представлено исследование активности полиоксидных катализаторов в реакции глубокого окисления толуола при 723 К и объемной скорости 5Ч10^{3} ч$^{-1}$. Конверсия толуола возрастала с усложнением состава катализаторов. Самая низкая степень окисления толуола 57.0% наблюдалась на катализаторе 5% Ni/2% Ce/θ-Al_2O_3, а наибольшая степень 98.5% наблюдалась на трехкомпонентном 9% Ni-Cu-Cr/2% Ce/θ-Al_2O_3 катализаторе. Увеличение концентрации толуола от 100 до 320 мг м$^{-3}$ в исходной смеси с воздухом приводит к незначительному снижению степени превращения толуола на двухкомпонентных Ni-Cu/2% Ce/θ-Al_2O_3 и Cu-Cr/2% Ce/θ-Al_2O_3 катализаторах.

В результате исследований было установлено, что наибольшая степень превращения толуола (до 98.8%) наблюдается на трехкомпонентном катализаторе Ni-Cu-Cr/2% Ce/θ-Al_2O_3 с оптимальным соотношением Ni : Cu : Cr = 1,0 : 3,0 : 0,1 при объемной скорости 5Ч10^{3} ч$^{-1}$ и температуре 723 - 773 К. Энергию связи кислорода с поверхностью и его реакционную способность на полиоксидных катализаторах определяли методами ТПД, ТПО и ТПВ. Было показано, что образующиеся алюминаты Ni и Cu могут восстанавливаться до исходных оксидов или их смесей под воздействием H_2 при 973 - 1223 К. Адсорбция кислорода на катализаторах Ni-Cu-Cr после разложения оксидов происходит при низкой температуре (325 К). Это указывает на высокую реакционную способность адсорбированного O_2^-, O^- и кислорода решетки дисперсных оксидов, а также их смесей и его способность к легкой реактивации.

Ключевые слова: каталитическое окисление, толуол, очистка, никель, медь.

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INTERACTION OF THE Fe/γ-Al_2O_3 CATALYTIC SYSTEM WITH PROBE MOLECULES III. STUDY OF THE INTERACTION OF AMMONIA WITH γ-Al_2O_3 OXIDE AND THE Fe/γ-Al_2O_3 SYSTEM

Abstract. The work is devoted to the study of the interaction of heterogeneous catalytic systems with adsorbed molecules. It presents the results of the interaction of the initial γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system with ammonia obtained using IR spectroscopy and the method of temperature programmed desorption.

Lewis and Bronsted acid centers were detected on the surface of both γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system during their interaction with ammonia in the temperature range 293-773K using IR spectroscopy. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with ammonia.

It was found by ammonia TPD that adsorbed NH_3 is desorbed in the form of five peaks from the γ-Al_2O_3 surface on a temperature scale, and in the form of seven peaks from the surface of the Fe/γ-Al_2O_3 system. It was shown that the total amount of desorbed ammonia decreases markedly with increasing adsorption temperature. Moreover, for individual temperature peaks, the amount of adsorbed ammonia can either decrease, pass through an extremum, or remain approximately constant. The appearance of additional desorption peaks for the Fe/γ-Al_2O_3 system is associated with iron deposited on alumina.

Proceeding from the temperature range of existence of desorption peaks for γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system it was established that they contain weak acid centers (desorption temperature up to 523K), acidic centers of medium strength (desorption temperature from 523 to 613K) and strong acid sites (desorption temperature above 613K). The volume of desorbed ammonia in the indicated temperature ranges can serve as a quantitative measure of various types of acid sites.

Key words: heterogeneous catalysis, physicochemical research methods, adsorbed molecules.

Introduction. One of the most common and highly effective methods for studying acid-base centers on the surfaces of supports and heterogeneous catalysts are infrared spectroscopy [1-5] and temperature programmed desorption of ammonia [6, 7].

The use of IR spectroscopy for studying the donor-acceptor surface properties is based on the spectral probing method. The properties of adsorption centers are judged by the absorption spectra of the adsorbed molecules, as well as by the change in the position of the absorption bands observed during adsorption.

The position of the peak in the TPD method on the temperature scale and activation energy of the probe molecule give the possibility to assess the strength of the center that its area can serve as a measurement of the quantity of the various acid centers of various types.

This work is a continuation of studies on the interaction of a heterogeneous catalytic system with adsorbed molecules [8, 9].

Experimental. Fe/γ-Al_2O_3 system with an iron content of 3; 13 wt.% was prepared by impregnating [10-13] the initial γ-Al_2O_3 oxide with an aqueous solution of iron acetate, followed by drying and calcination in air.

IR spectroscopy

Sample preparation and obtaining IR spectra took place in several stages. At the first stage, the sample (a tablet with KBr filler) was placed in a sealed quartz cell and heated to 523K with simultaneous evacuation for 2 hours. Then, the temperature decreased to 293K. Next, ammonia purging began at the required temperature (from a given temperature range of 293-773 K) for 150 minutes. After that, a temperature of 293K was established then the cell was purged with an inert gas for 30 minutes and after that the IR spectrum was taken.

Equipment - Nicolet iS5 IR spectrometer, Thermo Scientific, USA. Operation mode: resolution 1 cm^{-1}, number of scans - 200.

Ammonia TPD

A chromatographic version of temperature programmed desorption was used. The sample with the molecules of the probe substance preliminarily adsorbed on it was subjected to heating at a certain constant speed in the flow of the carrier gas. During desorption, the substance in the gas phase passed through the cell of the thermal conductivity detector (TCD), and the resulting signal was recorded.

Conditions for preparing samples for ammonia adsorption:

- vacuum treatment 30 minutes;
- sample dehydration in a stream of dry argon (5 ml/min) at a temperature of 623K for 120 minutes.

Ammonia adsorption:

- ammonia feed rate 5 ml/min;
- adsorption duration one hour; temperature range 293-773K.

Programmed desorption of ammonia:

- temperature variation range from 293 to 773K;
- speed - 12K/min; carrier gas velocity (argon) - 75 ml/min;
- detector sensitivity 1:8.

Desorbed ammonia was detected by chromatograph's TCD and was recorded as a TPD spectrum. At certain temperatures, the TPD spectrum had maxima that characterized the adsorption sites of the sample. The amount of ammonia desorbed in the corresponding temperature range was determined by peak areas, having previously established how much NH_3 corresponds to the area unit.

Equipment - ″CETARAM″ thermo analyzer, France.

Results and discussion

Investigation of the Fe/γ-Al_2O_3 system by FTIR spectroscopy during NH_3 adsorption.

In the beginning, the interaction of γ-Al_2O_3 with NH_3 was studied in the range of 293-773K. The data obtained for γ-Al_2O_3 oxide were necessary as reference and comparison points when studying the Fe/γ-Al_2O_3 system. Figures 1-7 show the IR spectra of γ-Al_2O_3 oxide when interacting with ammonia at different temperatures and table 1 shows the results of their interpretation. In the initial γ-Al_2O_3 oxide and even after interaction with ammonia, the IR spectra contain absorption bands corresponding to -OH groups bound on the surface by hydrogen bonds, absorption bands from Al-O bonds, and also vibrations of CH bonds in the -CH, -CH_2, -CH_3 groups (in trace amounts). A small amount of hydrocarbons, apparently, remained in the γ-Al_2O_3 oxide after synthesis.

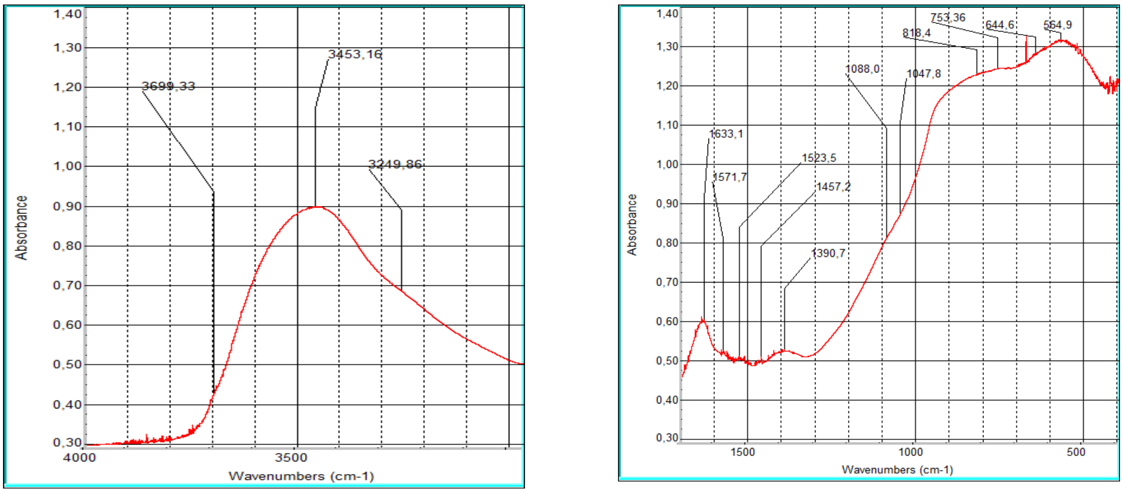


Figure 1 - IR spectrum of the initial γ-Al_2O_3 oxide

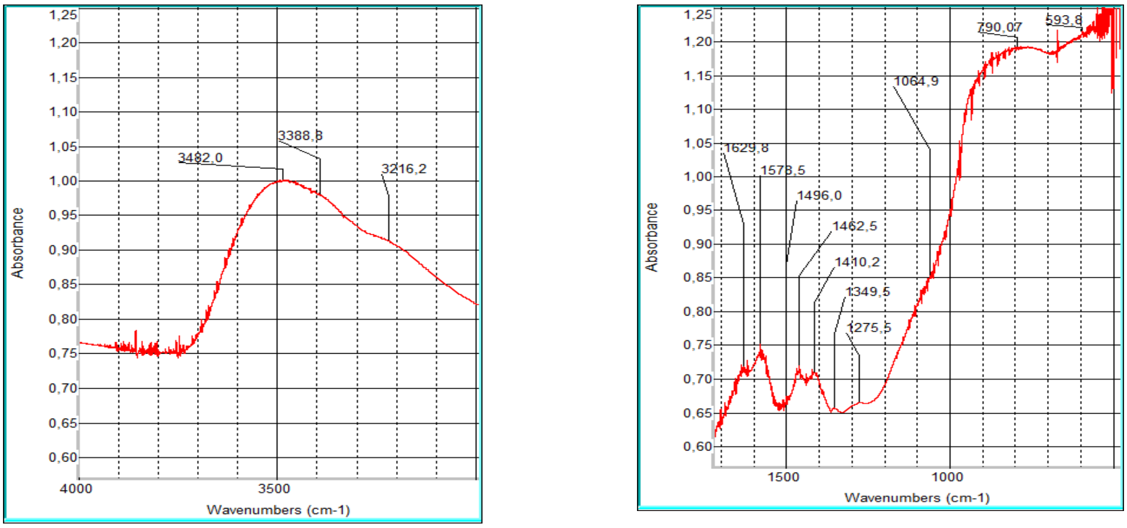


Figure 2 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 293K

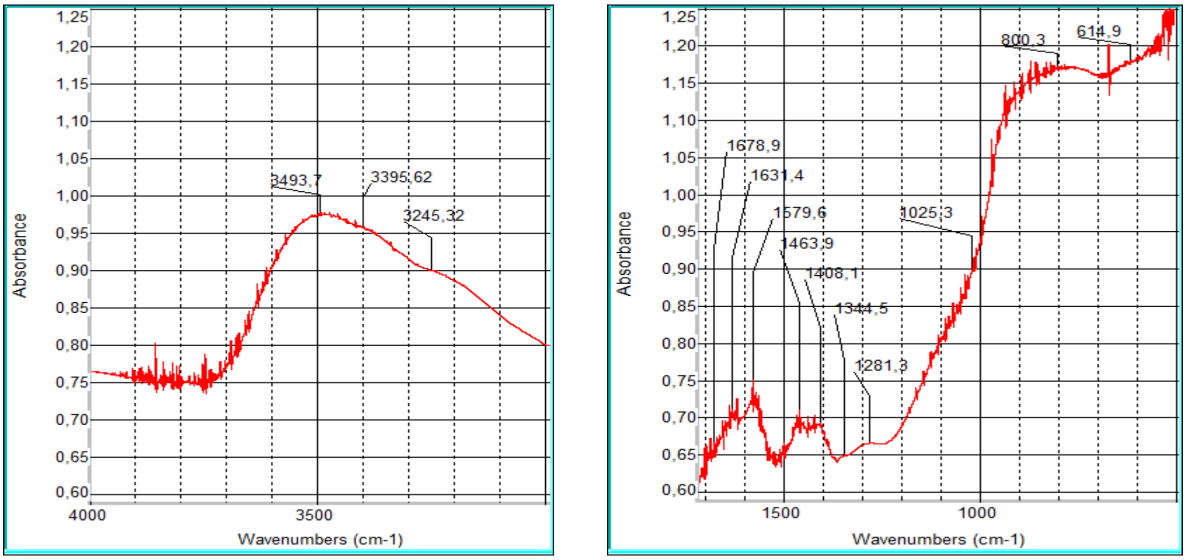


Figure 3 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 373K

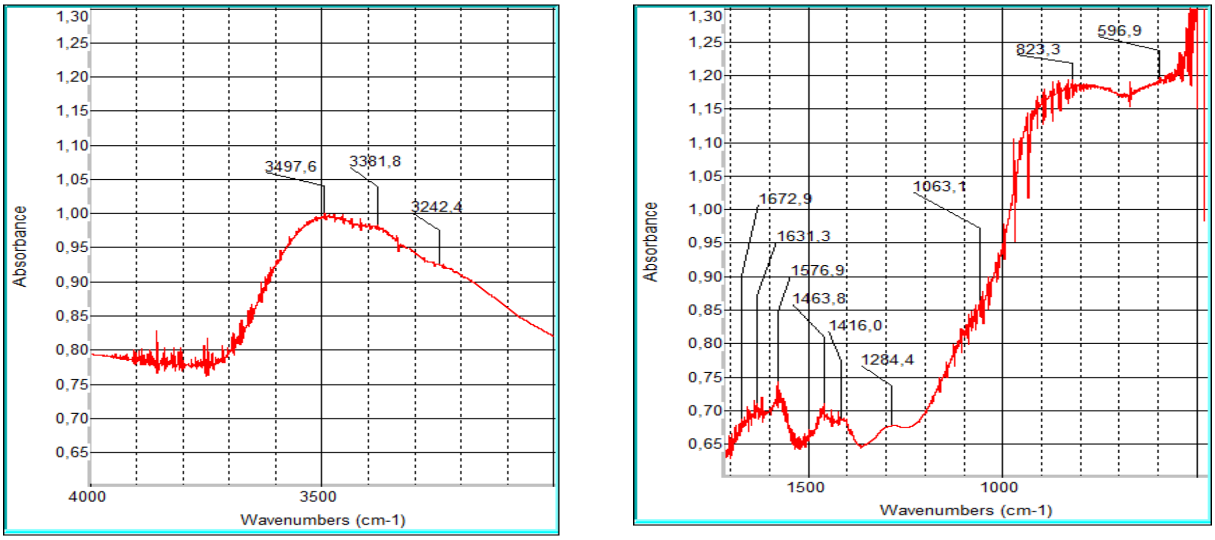


Figure 4 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 473K

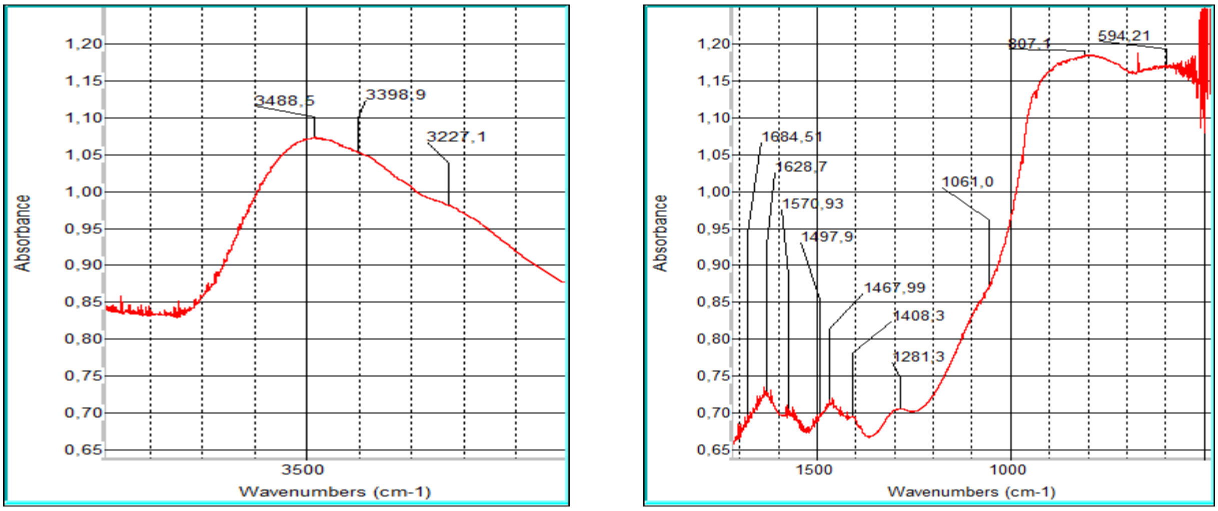


Figure 5 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 573K

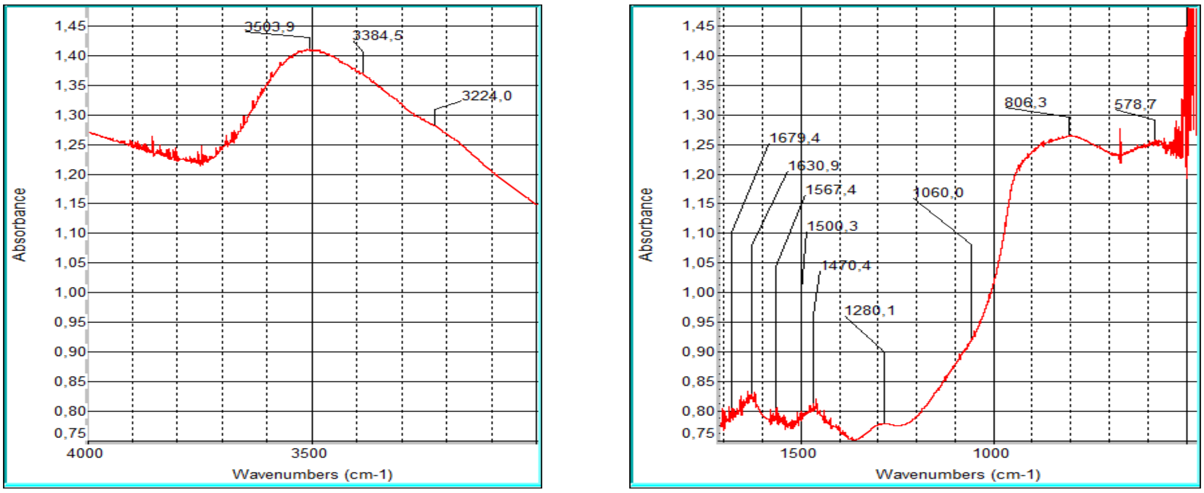


Figure 6 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 673K

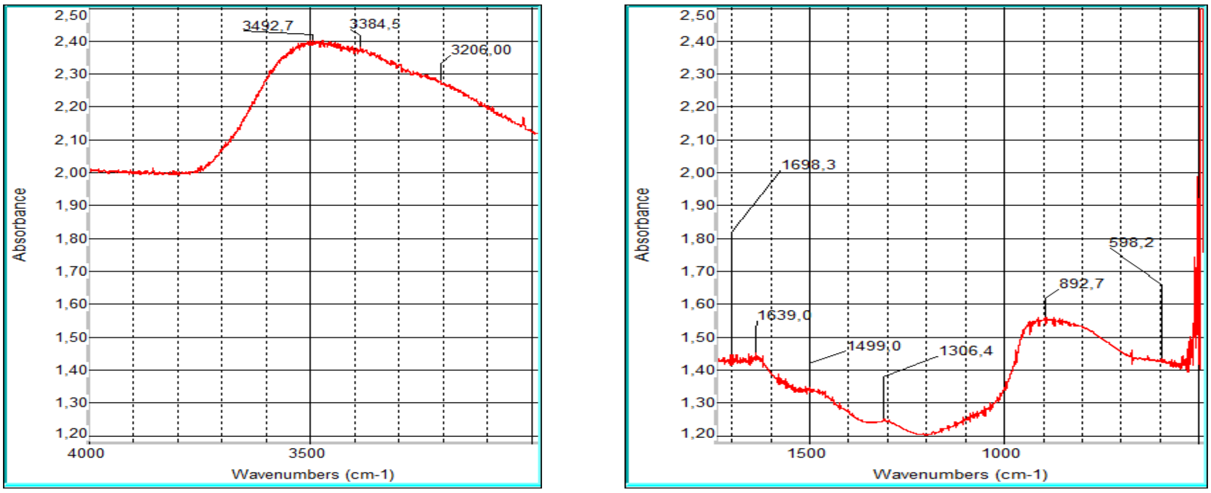


Figure 7 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 773K

Table 1 - Interpreted data of the IR spectra of γ-Al_2O_3 oxide
and the Fe/γ-Al_2O_3 system in the initial states,
and after their interaction with NH_3 in the range 293-773K

T, K	Absorption bands, cm^{-1}		Assignment of absorption bands
	Sample		
	γ-Al_2O_3	Fe/γ-Al_2O_3	
1	2	3	4
Initial states			
293	3699	3702	Stretching vibrations of bridging groups -OH bound to aluminum ions in octahedral and (or) tetrahedral coordination
	3453, 3250	3452, 3212	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
		3404, 3301,	Stretching vibrations of -OH groups bound on the surface of aluminum hydroxides by hydrogen bonds
	1633, 1571, 1524, 645	1632, 1584, 1526, 623	Bending vibrations of -OH groups bonded to the surface by hydrogen bonds
	1457, 1391	1468, 1400, 1358	Bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups (traces)
	1088, 1048	1068,	Stretching vibrations in -Al-O- groups in a tetrahedral and (or) octahedral coordination
	818, 753	804, 728	Bending vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination, possibly, in Al-O-Fe groups in the Fe/γ-Al_2O_3 system
	565	550	The stretching vibrations of the M-O bonds (M = Al; Fe)
Interaction of ammonia			
293	3482, 3216	3475, 3236	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1629, 1579, 594	1627, 1585, 631	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3389	3389	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1276	1692, 1270	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3178	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1496, 1463, 1410, 1350	1463, 1406	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1065	1066	Stretching vibrations related to Al-O bonds in -Al-O- groups
	790	834	Bending vibrations of -Al-O bonds in tetrahedra

Continuation of the table 1

1	2	3	4
373	3494, 3245	3479, 3229	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1580, 615	1627, 1584, 611	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3386	3383	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1679, 1281	1695, 1280	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3173	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1464, 1408, 1345	1463, 1405, 1351	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1025	1077	Stretching vibrations related to Al-O bonds in -Al-O- groups
	800	814	Bending vibrations of -Al-O bonds in tetrahedra
473	3498, 3242	3472, 3224	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1577, 597	1626, 1576, 617	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3382	3392	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1673, 1234	1674, 1273	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3163	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1464, 1416	1462, 1405	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1063	1069	Stretching vibrations related to Al-O bonds in -Al-O- groups
	823	813	Bending vibrations of -Al-O bonds in tetrahedra
573	3489, 3227	3472, 3250, 3221	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1629, 1571, 594	1619, 1564, 1543, 629	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3399	3361, 3310	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1685, 1281	1673, 1652, 1269	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3154	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1498,1468, 1408	1498, 1458, 1408	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1061	1058	Stretching vibrations related to Al-O bonds in -Al-O- groups
	807	812	Bending vibrations of -Al-O bonds in tetrahedra

Continuation of the table 1

1	2	3	4
673	3504, 3224	3481, 3239	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1567, 579	1620, 1548, 615	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3385	3374, 3310	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1679, 1280	1699, 1649, 1245	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3166	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1500, 1470	1490, 1463	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1060	1074	Stretching vibrations related to Al-O bonds in -Al-O- groups
	806	856	Bending vibrations of -Al-O bonds in tetrahedra
773	3493, 3206	3472, 3233	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1639, 598	1624	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3385	3328	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1698	1698, 1266	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3153	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1499, 1306	1479, 1306	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
		1080	Stretching vibrations related to Al-O bonds in -Al-O- groups
	893	924, 853, 804	Bending vibrations of -Al-O bonds in tetrahedra and, possibly, bonds in Al-O-Fe groups (for $Fe/\gamma-Al_2O_3$)

Absorption band related to the bridging -OH groups bound to aluminum ions in an octahedral coordination is also observed. However, upon interaction with ammonia, this absorption band disappears.

Absorption bands associated with the Lewis acid sites and with ammonium ions NH_4^+ (Bronsted sites) appear while interacting with ammonia. An increase in temperature causes noticeable decrease in the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers.

Further, the interaction of the $13\%Fe/\gamma-Al_2O_3$ system with NH_3 in the temperature range 293-773K was also studied using the Fourier-transform IR spectroscopy in the “In Situ” mode.

Figures 8-14 show the IR spectra of the $Fe/\gamma-Al_2O_3$ system interacting with ammonia and table 1 shows the results of their interpretation.

There are absorption bands related to -OH bridge groups bonded to aluminum ions in octahedral coordination, and absorption bands related to -OH groups bound on the surface by hydrogen bonds , absorption bands related to Al-O bonds in the initial $Fe/\gamma-Al_2O_3$ system, as well as in the initial $\gamma-Al_2O_3$ oxide. In addition, an absorption band related to Fe-O bonds is observed in the initial $Fe/\gamma-Al_2O_3$ system. This band disappears when interacting with ammonia.

It should be noted that in the $Fe/\gamma-Al_2O_3$ system (initial state) there are absorption bands belonging to the -OH groups on the surface of aluminum hydroxides. This is in good agreement with the data presented in our works [8, 9]. In that works were noted that during the synthesis of the $Fe/\gamma-Al_2O_3$ system by impregnation partial hydrolysis of aluminum oxide can occur as a result of which a certain amount of aluminum hydroxide is formed.

Absorption bands associated with the Lewis acid centers and with ammonium ions NH_4^+ (Bronsted centers) appear when the $Fe/\gamma-Al_2O_3$ system interacts with ammonia as in the case of the initial alumina. An increase in temperature, similarly to what was observed for $\gamma-Al_2O_3$ oxide, also leads to the decrease of the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers.

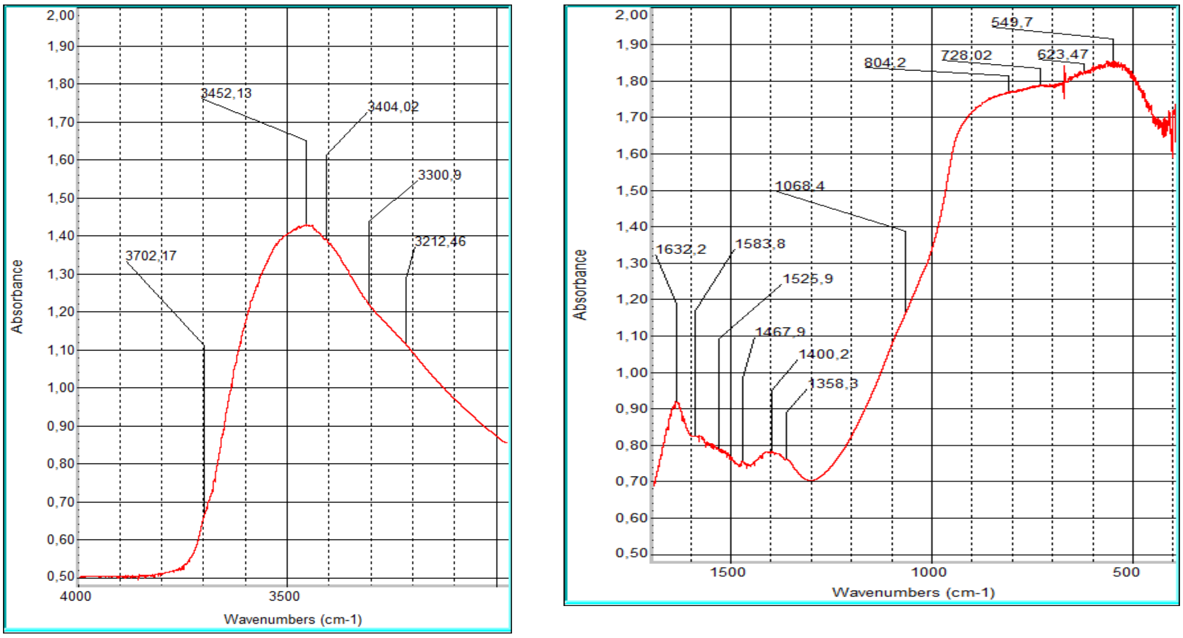


Figure 8 - IR spectrum of the initial 13%Fe/γ-Al_2O_3 system

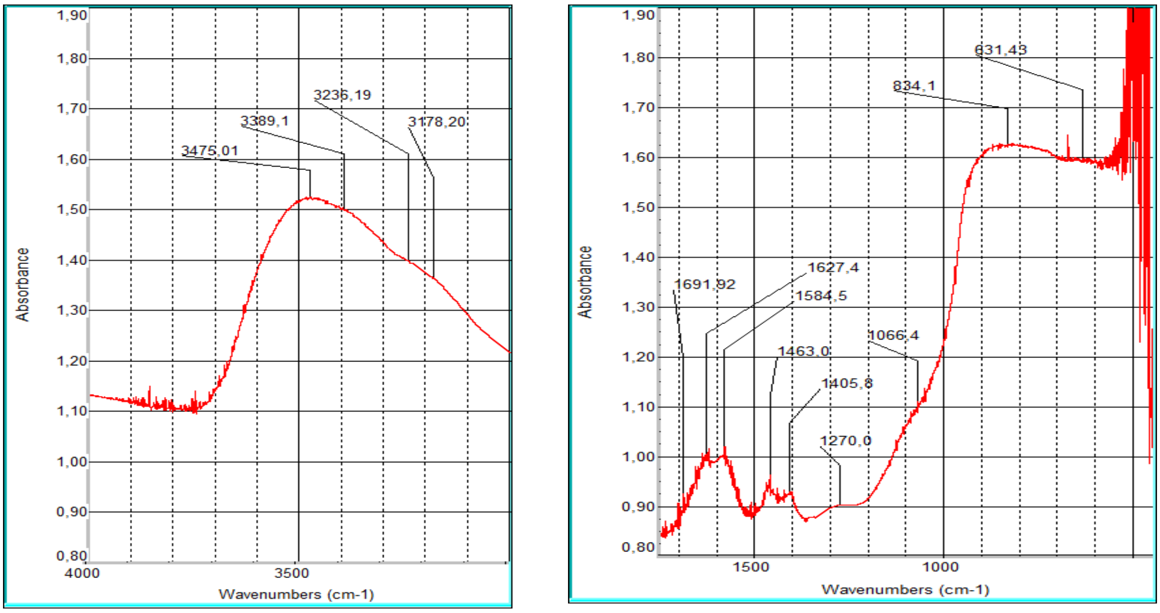


Figure 9 - IR spectrum of 13%Fe/γ-Al_2O_3 system after adsorption of ammonia at 293K

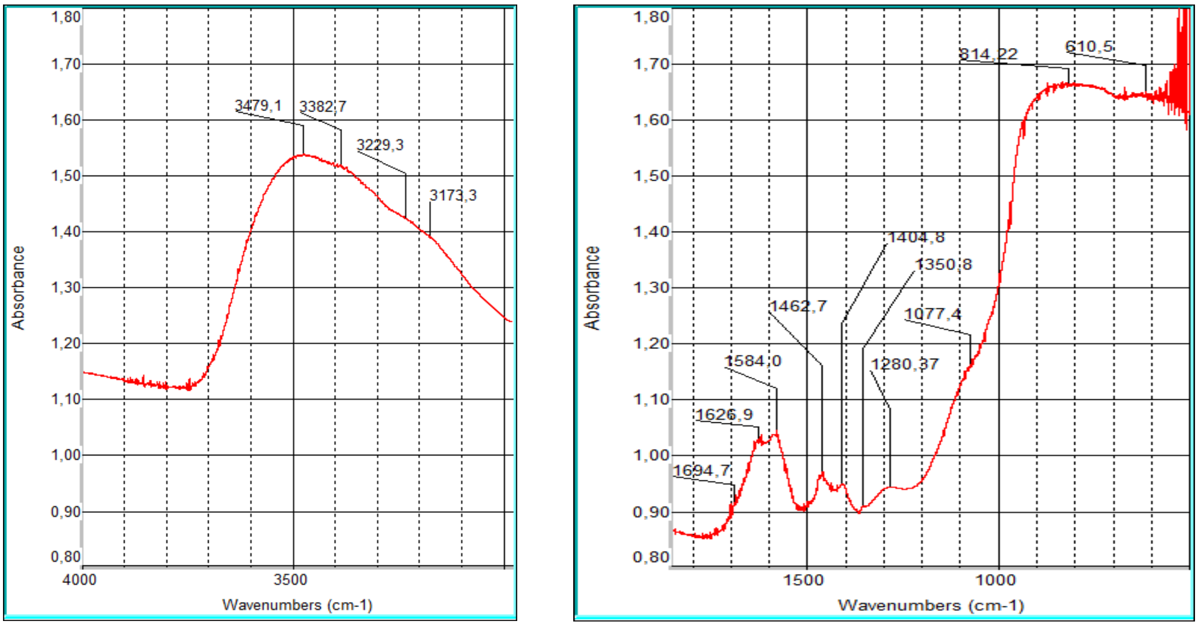


Figure 10 - IR spectrum of 13%Fe/γ-Al_2O_3 system after adsorption of ammonia at 373K

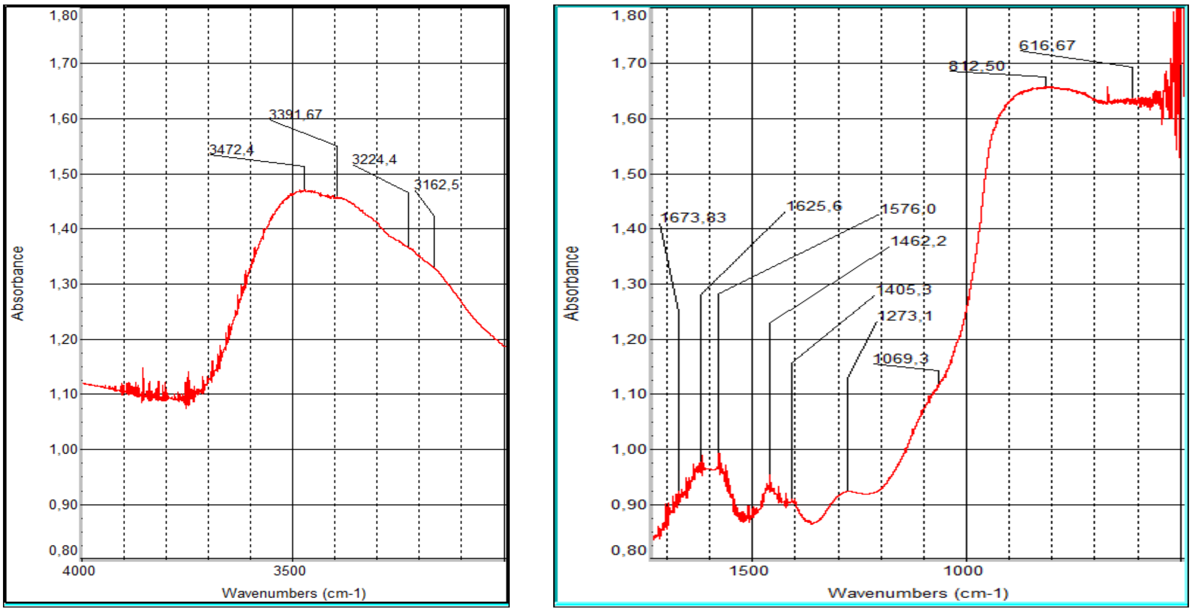


Figure 11 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 473K

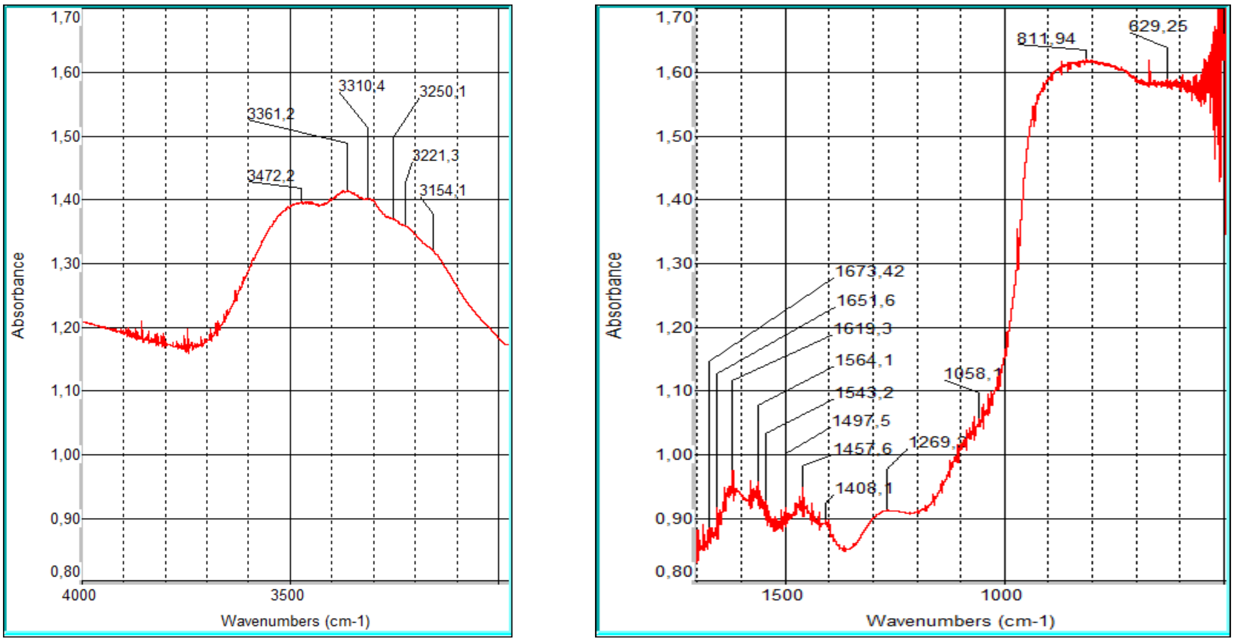


Figure 12 - IR spectrum of 13%Fe/γ-Al_2O_3 system after adsorption of ammonia at 573K

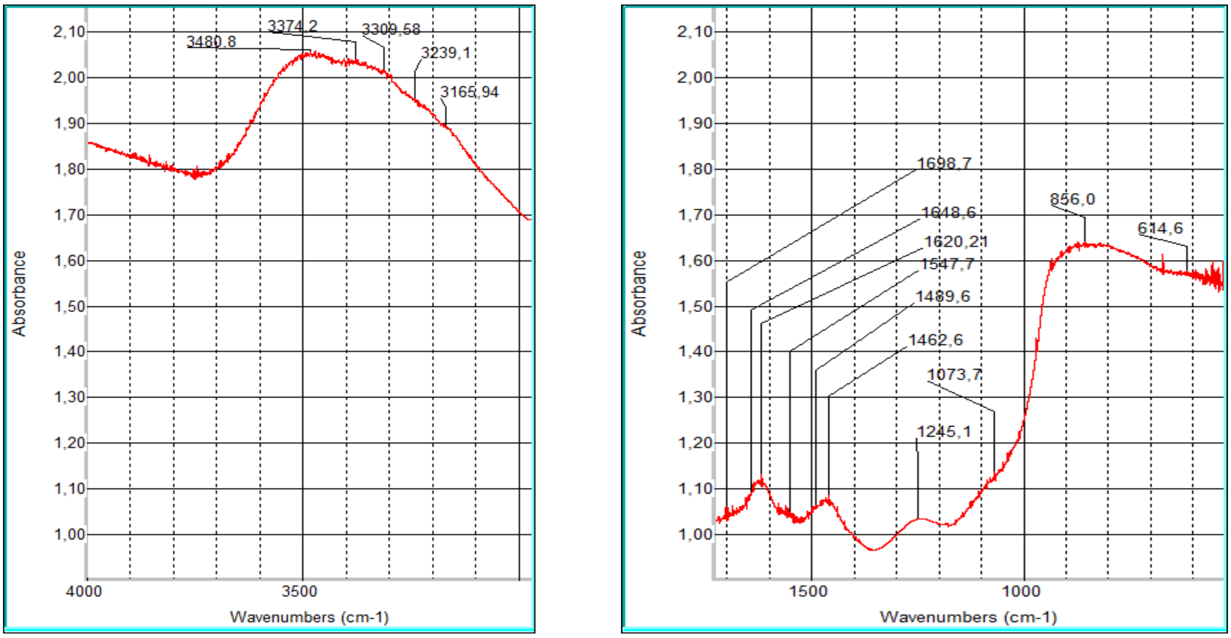


Figure 13 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 673K

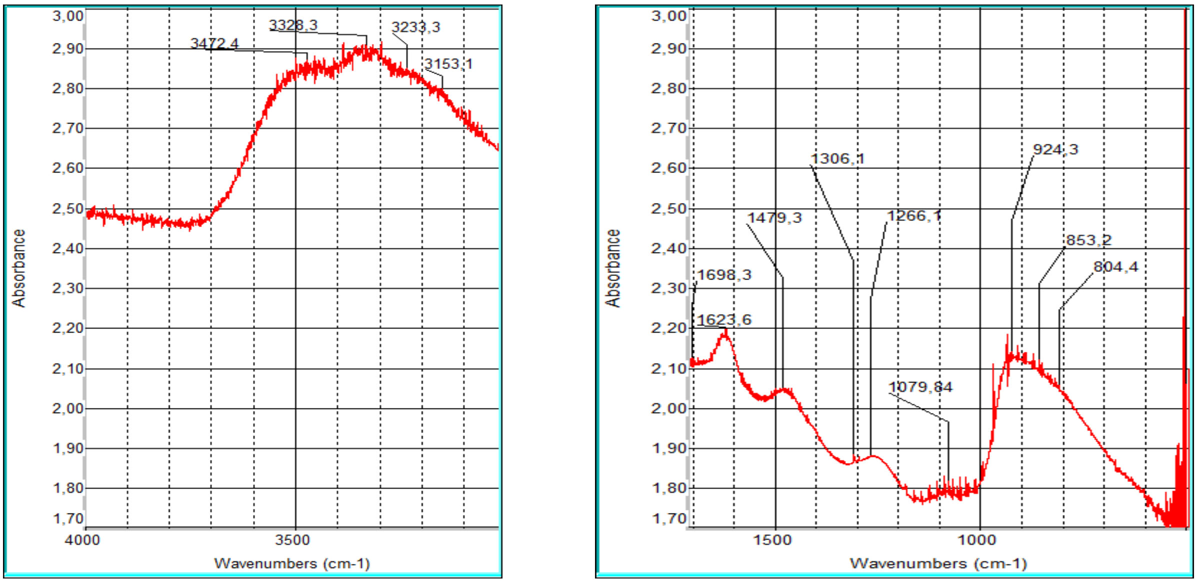


Figure 14 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 773K

At the same time, there are noticeable differences, in particular, the number of absorption bands corresponding to -OH groups bound on the surface by hydrogen bonds and absorption bands corresponding to Lewis centers increases, a band corresponding to stretching vibrations of N-H groups in ammonium ions NH_4^+ appears - Bronsted centers (table 1). In the case of alumina, only bending vibrations were observed. In addition, at 773 K, absorption bands are present in the long-wavelength region of the IR spectra, which can be attributed to bonds in the Al-O-Fe groups.

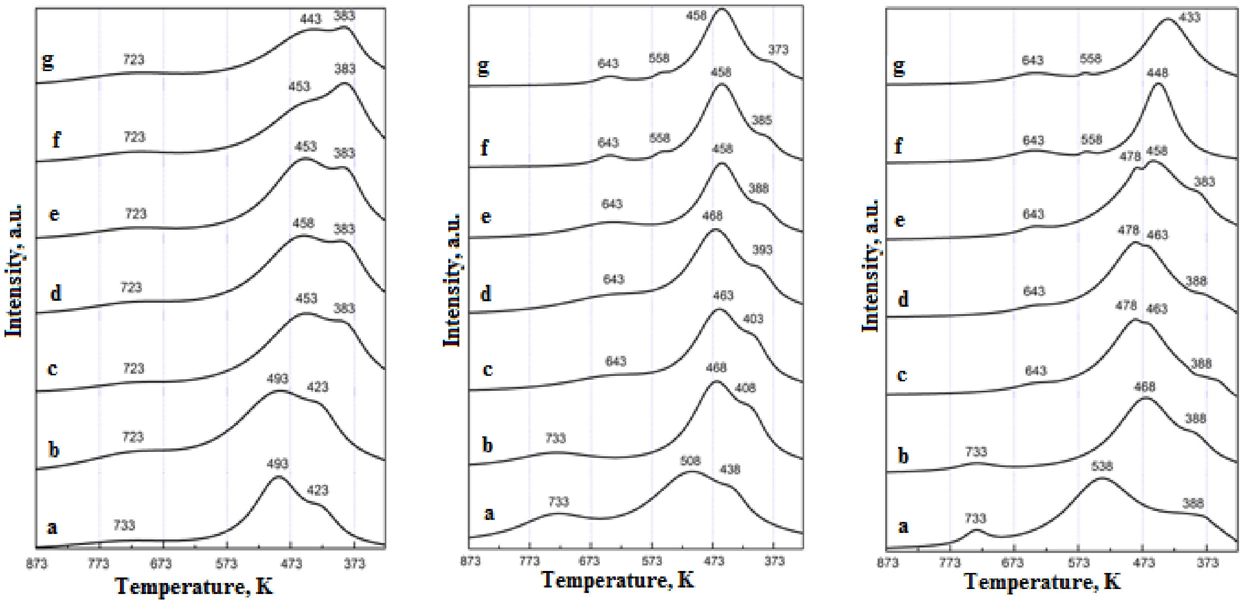
Study of the Fe/γ-Al_2O_3 system using temperature programmed desorption during ammonia adsorption

As it was already noted, the catalytic characteristics of heterogeneous systems correlate with the presence of acid centers of various nature on their surface and an important criterion is the quantity and strength of acid centers.

The properties of the surface of γ-Al_2O_3 oxide (as a reference point) and the Fe/γ-Al_2O_3 system were studied by temperature programmed desorption (TPD) in the temperature range 293-773K using an ammonia as a probe molecule.

The results of ammonia TPD for γ-Al_2O_3 oxide are shown in Figure 15(I) and are shown in table 2.

Adsorbed NH_3 is desorbed from the surface of γ-Al_2O_3 on a temperature scale in the form of five peaks, and the high-temperature peak E is much smaller in quantitative terms than the lower-temperature peak and, as the adsorption temperature rises its position practically does not shift (table 2). Peaks A and C are observed only at ammonia adsorption temperatures of 293, 373K. Peaks B and D appear starting from an adsorption temperature of 423K.



(I) (II) (III)

NH_3 adsorption temperature: a - 293K; b - 373K; c - 423K; d - 473K; e - 573K; f - 673K; g - 773K

Figure 15 - TPD-NH_3 profiles for γ-Al_2O_3 (I), 3%Fe/γ-Al_2O_3 (II) system and 13%Fe/γ-Al_2O_3 (III) system

Table 2 - The results of the study of TPD-NH_3 for γ-Al_2O_3 oxide

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K					Amount of desorbed NH_3, 10^{-4} mol/g					The total amount of desorbed NH_3, 10^{-4} mol/g
		A	B	C	D	E	A	B	C	D	E	
γ-Al_2O_3	293	423	-	493	-	733	4.82		6.00		0.78	11.60
	373	423	-	493	-	723	4.80		5.47		0.89	11.16
	423	-	383	-	453	723	-	4.03	-	4.71	0.96	9.60
	473	-	383	-	458	723	-	3.79	-	4.06	1.17	9.02
	573	-	383	-	453	723	-	3.71	-	4.02	0.98	8.71
	673	-	383	-	453	723	-	3.47	-	3.04	0.72	7.23
	773	-	383	-	443	723	-	2.73	-	2.67	0.67	6.07

For A, B, C, D peaks the amount of desorbed ammonia decreases with increasing adsorption temperature. For peak E this dependence has an extremal character with a maximum position at an adsorption temperature of 473 K.

It should be noted that with an increase in the adsorption temperature the total amount of desorbed ammonia decreases significantly (table 2).

The results of ammonia TPD for the Fe/γ-Al_2O_3 system with different iron contents are shown in Figure 15 (II, III) and in tables 3-4.

For the 3%Fe/γ-Al_2O_3 system (Figure 15 (II), table 3) the ammonia adsorbed in the temperature range 293-773K is desorbed on the temperature scale in the form of seven peaks (A′, B′, C′, D′, E′, F′, G′). Desorption temperature range for A′, B′, D′, E′ peaks is close to that observed for γ-Al_2O_3 oxide (peaks A, B, D, E) and the amount of desorbed ammonia also decreases with increasing adsorption temperature.

There are some peculiarities, in particular, the peak B′ appears at a higher adsorption temperature, and the peak D′- at a lower temperature, the peak E′ is observed only at adsorption temperatures of 293, 373K. Nevertheless, based on the obtained data, with a high degree of probability, it can be assumed that the adsorption of ammonia (A′, B′, D′, E′ desorption peaks) in the 3%Fe/γ-Al_2O_3 system occurs at the centers which are close in nature to adsorption characteristics of the γ-Al_2O_3 oxide centers.

At the same time, it should be paid attention to significant differences in the TPD spectra of γ-Al_2O_3 oxide and the 3%Fe/γ-Al_2O_3 system. In particular, the adsorption center to which the C′ peak corresponds has a noticeable temperature shift with respect to the C peaks and is present only at an adsorption temperature of 293K. In addition, in the TPD spectrum for the 3%Fe/γ-Al_2O_3 system F′ and G′ peaks appear in the temperature range of ammonia adsorption 423-773K (peak F′) and 673 - 773K (peak G′). Peaks F′ and G′ are located at desorption temperatures of 643 and 558K, respectively. Apparently, these desorption peaks can be associated with iron deposited on alumina.

Ammonia adsorbed in the temperature range 293-773K is also desorbed in the form of seven peaks (A″, B″, C′′, D″, E″, F″, G″) in case of the 13%Fe/γ-Al_2O_3 system (figure 18 (III), table 4). The desorption peaks of B″, D″, E″ are in the same temperature range as the of B, D, E peaks for γ-Al_2O_3 oxide, as well as B′, D′, E′ peaks in the case of the 3% Fe/γ-Al_2O_3 system. The F″, G″ and F′, G′ peaks are identical for the 13%Fe/γ-Al_2O_3 and 3%Fe/γ-Al_2O_3 systems.

The position on the temperature scale of peak A″ is significantly shifted to the high-temperature region. In addition, when ammonia is adsorbed in the range 423-573K the C″ desorption peak appears at 478K in the 13%Fe/γ-Al_2O_3 system, and the amount of desorbed ammonia for the D″ peak is extreme with a minimum position in the temperature range 473-573K. At the same time, for the 3%Fe/γ-Al_2O_3 system the amount of desorbed ammonia at the D′ peak decreases with increasing adsorption temperature.

Table 3 - TPD-NH_3 study results for γ-Al_2O_3 oxide

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K					Amount of desorbed NH_3, 10^{-4} mol/g					The total amount of desorbed NH_3, 10^{-4} mol/g
		A	B	C	D	E	A	B	C	D	E	
γ-Al_2O_3	293	423	-	493	-	733	4.82		6.00		0.78	11.60
	373	423	-	493	-	723	4.80		5.47		0.89	11.16
	423	-	383	-	453	723	-	4.03	-	4.71	0.96	9.60
	473	-	383	-	458	723	-	3.79	-	4.06	1.17	9.02
	573	-	383	-	453	723	-	3.71	-	4.02	0.98	8.71
	673	-	383	-	453	723	-	3.47	-	3.04	0.72	7.23
	773	-	383	-	443	723	-	2.73	-	2.67	0.67	6.07

Table 4 - TPD-NH_3 study results for Fe/γ-Al_2O_3 system

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K							Amount of desorbed NH_3, 10^{-4} mol/g							The total amount of desorbed NH_3, 10^{-4} mol/g
		A′	B′	C′	D′	E′	F′	G′	A′	B′	C′	D′	E′	F′	G′	
3%Fe/γ -Al_2O_3	293	438	-	508		733	-	-	5.20	-	6.59	-	0.80	-	-	12.59
	373	408	-	-	468	733	-	-	3.91	-	-	5.81	0.82	-	-	10.54
	423	403	-	-	463	-	643	-	3.66	-	-	5.71	-	0.81	-	10.18
	473	-	393	-	468	-	643	-	-	2.53	-	5.70	-	1.01	-	9.24
	573	-	389	-	458	-	643	-	-	2.44	-	5.70	-	1.01	-	9.15
	673	-	383	-	458	-	643	558	-	2.00	-	5.30	-	0.96	0.86	9.12
	773	-	373	-	458	-	643	558	-	1.85	-	5.19	-	0.97	0.88	8.79
13%Fe/γ -Al_2O_3		A″	B″	C″	D″	E″	F″	G″	A″	B″	C″	D″	E″	F″	G″	
	293	538	388	-	-	733	-	-	8.10	5.01	-	--	1.62	-	-	14.73
	373		388	-	468	733	-	-	-	2.90	-	7.06	1.20	-	-	11.16
	423		388	478	463	-	643	-	-	1.31	4.37	4.16	-	1.10	-	10.94
	473		388	478	463	-	643	-	-	1.25	3.86	3.38	-	1.15	-	9.64
	573		383	478	458	-	643	-	-	1.25	3.37	3.32	-	1.17	-	9.11
	673	-	-	-	448	-	643	558	-	-	-	6.82	-	1.05	0.88	8.75
	773	-	-	-	433	-	643	558	-	-	-	6.78	-	1.04	0.84	8.66

Conclusion. Investigations of the Fe/γ-Al_2O_3 system in the temperature range 273-773K using IR spectroscopy and the ammonia TPD method showed that its surface is inhomogeneous and represents a set of adsorption centers that differ in their characteristics.

On the surface of both γ-Al_2O_3 oxide (support) and the Fe/γ-Al_2O_3 system Lewis and Bronsted acid centers were detected using IR spectroscopy during their interaction with ammonia in the temperature range 293-773K. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with ammonia and with its growth decreases both for γ-Al_2O_3 and for the Fe/γ-Al_2O_3 system.

However, significant differences were identified. So, in the case of the Fe/γ-Al_2O_3 system:

- an increase in the number of absorption bands related to -OH groups joined on the surface by hydrogen bonds;
- an increase in the number of absorption bands related to Lewis acid centers;
- the appearance of a band corresponding to stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers (no stretching vibrations were observed in the case of alumina).

The observed features can be associated with the presence of an iron-containing component on the surface of the support. This statement is justified because the absorption band related to Fe-O bonds is observed in the initial Fe/γ-Al_2O_3 system, and when the Fe/γ-Al_2O_3 system interacts with ammonia at 773K, absorption bands are present in the long-wavelength region of the IR spectra, which are most likely relate to bonds in Al-O-Fe groups. In addition, the shift of the absorption bands corresponding to the Lewis acid centers in the frequency range also testifies to the effect of the iron-containing component on the adsorption centers.

As a result of studies of γ-Al_2O_3 oxide and 13%Fe/γ-Al_2O_3 systems using ammonia TPD, it was found that adsorbed NH_3 is desorbed in the form of five peaks from the γ-Al_2O_3 surface on a temperature scale, and from the surface of 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems - in the form of seven peaks. For all the samples studied the total amount of adsorbed ammonia decreases markedly with an increase in the adsorption temperature, and for individual temperature peaks the amount of adsorbed ammonia can decrease (peaks B, C, D, A′, B′, D′, B″, C″, E″), and pass through the extremum (peaks E, F′, D″, F″) or remain approximately constant (peaks A, E′, G′, G″).

As the adsorption temperature increases the desorption temperature for some of the peaks of γ-Al_2O_3 oxide and 13%Fe/γ-Al_2O_3 systems remains almost constant (peaks A, B, C, E′, F′, G′, B″, C″, E″, F″, G″) and for the other part of the peaks there is some tendency to lower the desorption temperature.

The appearance of additional desorption peaks (F′, G′, F″, G″) in the 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems, as well as a change in the position on the temperature scale of desorption peaks A″, C′, C″ can be associated with iron deposited on alumina. In particular, C′, F′, F″ peaks, possibly, relate to the adsorption of ammonia on -Al-O-Fe- type fragments, and the C″ peak on -Fe-O-Fe- type fragments, since the last peak is attributed to the 13%Fe/γ-Al_2O_3 system with a significantly higher iron content.

Investigations of the Fe/γ-Al_2O_3 system using Mössbauer spectroscopy [14] showed that the system depending on conditions can contain various forms of iron. The presence of several forms of iron in the system indicates the potential for the formation of catalytically active centers with different electronic characteristics and as a result different catalytic properties. Thus, each form of the iron cation on the support can be a specific active (adsorption) center.

Based on the temperature range for the existence of desorption peaks for γ-Al_2O_3 oxide and 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems, it follows that weak acid centers (desorption temperature up to 523K), acidic centers of medium strength (desorption temperature from 523 to 613K) and strong acid sites (desorption temperature above 613K) are present in them [15-17].

The volume of desorbed ammonia in the indicated temperature ranges can serve as a quantitative measure of various types of acid sites.

It should be noted that the total amount of adsorbed ammonia decreases markedly with increasing adsorption temperature and this is in good agreement with the data of IR spectroscopy, according to which the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers also depends on the temperature of interaction with ammonia and decreases with its growth.

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Fe/γ-Al_2O_3 КАТАЛИТИКАЛЫҚ ЖҮЙЕНІҢ ЗОНДТЫ МОЛЕКУЛАЛАРМЕН ӨЗАРА ҚАТЫНАСЫ III. γ-Al_2O_3 ОКСИДІ ЖӘНЕ Fe/γ-Al_2O_3 ЖҮЙЕСІНІҢ АММИАКПЕН ӨЗАРА ҚАТЫНАСЫН ЗЕРТТЕУ

Аннотация. Жұмыс гетерогенді каталитикалық жүйелердің адсорбцияланған молекулалармен әрекеттесуін зерттеуге арналған. Онда ИҚ спектроскопиясы мен термопрограммалық десорбция әдісімен алынған γ-Al_2O_3 оксиді мен Fe/γ-Al_2O_3 жүйесінің аммиакпен әрекеттесу нәтижелері келтірілген.

γ-Al_2O_3 оксиді мен Fe/γ-Al_2O_3 жүйесінің аммиакпен әрекеттесу кезінде екеуінің де бетіндегі ИК спектроскопиясын 293-773K температура аралығында қолдану арқылы Льюис және Бренстед қышқыл орталықтары анықталды. Осы орталықтарға сәйкес келетін сіңіру жолақтарының салыстырмалы қарқындылығы аммиакпен әрекеттесу температурасына байланысты.

Алайда айтарлықтай айырмашылықтар анықталды.

Fe / γ-Al_2O_3 жүйесіне қатысты:

– сутегі байланыстарымен біріккен –OH топтарына жататын сіңіру жолақтарының санының өсуі;

– Льюис қышқылы орталықтарына байланысты сіңіру жолақтарының санының артуы;

– NH_4^+ аммоний иондарындағы N-H тобының тербелісіне сәйкес келетін жолақтың пайда болуы – Бренстед орталықтары (алюминий оксиді жағдайында валенттік діріл байқалмады).

Байқалған ерекшеліктер тірек бетінде (γ-Al_2O_3) темір кездесетін компоненттің болуына байланысты. Бұл тұжырым негізделген, өйткені Fe-O байланыстарына қарай сіңіру диапазоны Fe/γ-Al_2O_3 бастапқы жүйесінде байқалады және Fe/γ-Al_2O_3 жүйесі аммиакпен 773K әрекеттескенде сіңіру жолақтары ИК спектрінің ұзын толқындар аймағында болады, олар Al-O-Fe топтарындағы байланыстарға қатысты болып келеді. Сонымен қатар, жиілік диапазонында Льюис қышқылы орталықтарына сәйкес келетін сіңіру жолақтарының ығысуы да құрамында темір бар компоненттің адсорбция орталықтарына әсер етуін дәлелдейді.

Алюминий оксиді γ-Al_2O_3 және 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 жүйелерін зерттеу нәтижесінде температуралық шкала бойынша 293-773K температуралық интервалында аммиактің ТПД көмегімен γ-Al_2O_3 бетінен адсорбцияланған NH_3 - беттік шкала бойынша бес шың түрінде десорбацияланатыны анықталды, ал 3% Fe/γ-Al_2O_3 және 13%Fe/γ-Al_2O_3 жүйе бетінен – жеті шың түрінде десорбацияланатыны анықталды.

Десорбцияланған аммиактың жалпы мөлшері адсорбция температурасының жоғарылауы негізінде айтарлықтай азаятындығы көрсетілді. Сонымен қатар, температураның жекелеген шыңы үшін адсорбцияланған аммиак мөлшері азайып, экстремумнан өтуі немесе шамамен өзгермеуі мүмкін. Fe/γ-Al_2O_3 жүйесі үшін қосымша десорбция шыңының пайда болуы алюминий оксидінің бетіндегі темірге байланысты.

γ-Al_2O_3 оксиді мен Fe/γ-Al_2O_3 жүйесі үшін десорбция шыңының температуралық диапазонын ескере отырып, олардың құрамында әлсіз қышқыл орталықтары (десорбция температурасы 523K дейін), орташа күштік қышқыл орталықтары (десорбция температурасы 523-тен 613K дейін) және күшті қышқыл орталықтары (десорбция температурасы 613K-тан жоғары) бар екені анықталды. Көрсетілген температура диапазонында десорбцияланған аммиактың мөлшері түрлі қышқыл орталықтарының сандық өлшемі ретінде қызмет ете алады.

Түйін сөздер: гетерогенді катализ, физика-химиялық зерттеу әдістері, адсорбцияланған молекулалар.

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ВЗАИМОДЕЙСТВИЕ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ Fe/γ-Al_2O_3 С МОЛЕКУЛАМИ-ЗОНДАМИ

III. ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ АММИАКА С ОКСИДОМ γ-Al_2O_3 И СИСТЕМОЙ Fe/γ-Al_2O_3

Аннотация. Работа посвящена исследованию взаимодействия гетерогенных каталитических систем с адсорбированными молекулами. В ней представлены результаты по взаимодействию с аммиаком исходного оксида γ-Al_2O_3 и системы Fe/γ-Al_2O_3, полученные с помощью ИК-спектроскопии и метода термопрограммированной десорбции.

С помощью ИК-спектроскопии на поверхности как оксида алюминия $\gamma\text{-}Al_2O_3$ (носитель), так и системы $Fe/\gamma\text{-}Al_2O_3$ при их взаимодействии с аммиаком в температурном интервале 293–773К были обнаружены кислотные центры Льюиса и Бренстеда. Относительная интенсивность полос поглощения, отвечающих этим центрам, зависит от температуры взаимодействия с аммиаком и с её ростом падает как для оксида $\gamma\text{-}Al_2O_3$, так и для системы $Fe/\gamma\text{-}Al_2O_3$.

Вместе с тем, выявлены и существенные различия.

Для системы $Fe/\gamma\text{-}Al_2O_3$ имеет место:

- увеличение количества полос поглощения, относящихся к группам –OH, объединённых на поверхности водородными связями;

- увеличение количества полос поглощения, относящихся к льюисовским кислотным центрам;

- появление полосы, отвечающей валентным колебаниям групп N-H в ионах аммония NH_4^+, - центры Бренстеда (в случае оксида алюминия валентных колебаний не наблюдалось).

Наблюдающиеся особенности связаны с присутствием на поверхности носителя (оксида алюминия $\gamma\text{-}Al_2O_3$) железосодержащей компоненты. Такое утверждение обосновано, поскольку в исходной системе $Fe/\gamma\text{-}Al_2O_3$ наблюдается полоса поглощения, относящаяся к связям Fe-O, а при взаимодействии системы $Fe/\gamma\text{-}Al_2O_3$ с аммиаком при 773К в длинноволновой области ИК-спектров присутствуют полосы поглощения, которые, вероятней всего, относятся к связям в группах Al-O-Fe. Кроме того, о влиянии железосодержащей компоненты на центры адсорбции свидетельствует и смещение по частотному диапазону полос поглощения, отвечающих льюисовским кислотным центрам.

В результате исследований оксида алюминия $\gamma\text{-}Al_2O_3$ и систем $3\%Fe/\gamma\text{-}Al_2O_3$, $13\%Fe/\gamma\text{-}Al_2O_3$ с помощью ТПД аммиака в температурном интервале 293 – 773К установлено, что с поверхности $\gamma\text{-}Al_2O_3$ адсорбированный NH_3 по температурной шкале десорбируется в виде пяти пиков, а с поверхности систем $3\%Fe/\gamma\text{-}Al_2O_3$ и $13\%Fe/\gamma\text{-}Al_2O_3$ – в виде семи.

Показано, что суммарное количество десорбированного аммиака заметно уменьшается с ростом температуры адсорбции. При этом для отдельных температурных пиков количество адсорбированного аммиака может как уменьшаться, так и проходить через экстремум или оставаться приблизительно постоянным. Появление дополнительных пиков десорбции для системы $Fe/\gamma\text{-}Al_2O_3$ связано с нанесённой на оксид алюминия железосодержащей компонентой.

Исходя из температурного интервала существования десорбционных пиков для оксида алюминия $\gamma\text{-}Al_2O_3$ и систем $3\%Fe/\gamma\text{-}Al_2O_3$, $13\%Fe/\gamma\text{-}Al_2O_3$ сделан вывод, что в них присутствуют слабые кислотные центры (температура десорбции до 523К), кислотные центры средней силы (температура десорбции от 523 до 613 К) и сильные кислотные центры (температура десорбции свыше 613К). Объем десорбированного аммиака в указанных температурных интервалах может служить количественной мерой кислотных центров различного типа.

Ключевые слова: гетерогенный катализ, физико-химические методы исследования, адсорбированные молекулы.

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СИНТЕЗ НАНОЧАСТИЦ МЕДИ

Аннотация. В кратком сообщении рассматривается возможность синтеза наночастиц меди осаждением в водных средах. Нами исследованы наночастицы меди, полученные способом химического восстановления ионов из раствора под действием восстановителя - боргидрида натрия, а также мы обеспечили усиление стабилизации наночастиц путем введения модифицирующей добавки – полиоксиэтиленсорбитанмоноолеата (Tween 80), которые эффективно мешают агрегации наночастиц в растворе. Размеры и свойства дисперсий наночастиц меди исследовали различными способами. Размер наночастиц и степень их агрегации исследовали с использованием анализатора размера Malvern Zetasizer Nano. УФ и видимые спектры поглощения были получены на двухлучевом спектрофотометрическом UV-1800.

Ключевые слова: наночастицы (НЧ), медь, синтез, поверхностно-активные вещества (ПАВ), частицы, растворы.

При синтезе наночастиц (НЧ) осаждением в водных средах, образуются крупные частицы (до нескольких микрометров), которые агрегируют и осаждаются. Для замедления роста и образования частиц нанометрового размера часто используют добавки различных поверхностно-активных веществ (ПАВ).

Для получения наночастиц меди использовали реакцию химического восстановления ионов Cu^{2+} из раствора под действием восстановителя – борогидрида натрия.

Образование зародышей кристаллизации меди в водных средах происходит практически мгновенно после смешивания реагентов. Однако дальнейший рост частиц, их агрегация и срастание протекают более длительное время. Стабилизирующая способность НЧ усиливается при введении ПАВ.

Для стабилизации НЧ меди использовали неионогенное ПАВ – моноолеат полиоксиэтилен-сорбитана (Tween 80). Молекулы неионогенных ПАВ, адсорбируясь на поверхности синтезируемых НЧ, экранируют их заряд. В то же время молекулы неионогенных ПАВ содержат полярные группы, что приводит к возникновению определенного заряда поверхности НЧ. Кроме того, при адсорбции молекул ПАВ создается стерический барьер, препятствующий сближению наночастиц и их агрегации.

Исследование размера и свойств дисперсий НЧ меди проводили с использованием различных методов. Размеры наночастиц, степень их агрегации исследовали с помощью анализатора размеров Malvern Zetasizer Nano (Великобритания). Спектры поглощения в УФ и видимой области получали на двухлучевом сканирующем спектрофотометре UV-1800 (Япония).

Для изучения скорости образования НЧ меди были получены спектры поглощения в УФ и видимой области в зависимости от времени синтеза. В течение первой минуты синтеза образуется большая часть НЧ меди. При дальнейшем выдерживании системы оптическая плотность увеличивается, но в меньшей степени. При проведении процесса синтеза более 20 мин спектры поглощения практически не изменяются. Это свидетельствует об установлении в системе квазиравновесия.

Так же было исследовано влияние концентрации данных компонентов для определения составов, устойчивых к седиментации дисперсий НЧ меди.

Чем больше концентрация ионов меди в исходном растворе, тем большее количество зародышей кристаллизации образуется при добавлении в раствор восстановителя. Однако при высокой концентрации может происходить неконтролируемый рост НЧ, приводящий к получению дисперсии достаточно крупных частиц с широким распределением по размерам, которые неустойчивы к агрегации и седиментации. Устойчивая к агрегации дисперсия НЧ меди образуется при концентрации ионов меди, не превышающей 0,3 моль/л.

Увеличение среднего размера одиночных частиц связано с тем, что содержание меди в системе увеличилось, а количество ПАВ осталось неизменным. Поэтому НЧ выросли до большего размера, до предельной адсорбции ПАВ на всей поверхности образовавшихся НЧ.

Экспериментальная часть. Для определения количества борогидрида натрия, необходимого для восстановления меди, использовали раствор $CuSO_4$ с концентрацией ионов меди 0,3 моль/л. Концентрация Tween 80 в растворе составляла 2 моль/л соответственно. Затем в данный раствор добавляли по 3,6 мл водного раствора борогидрида натрия с концентрацией 0,3 моль/л. Систему интенсивно перемешивали и с интервалом 1 мин измеряли оптическую плотность растворов при 400 нм. Значения оптической плотности возрастали при увеличении времени перемешивания до 20 мин и далее практически не изменялись. Рассматривали зависимость равновесной оптической плотности растворов при 400 нм от мольного соотношения борогидрида натрия и ионов меди. Полное восстановление меди происходило при мольном соотношении $NaBH_4/Cu^{2+}$, превышающем 15–18.

Для определения размеров образующихся НЧ меди были получены снимки образцов с помощью наносайзера – Malvern Zetasizer Nano (Великобритания).

Наночастицы меди, полученные путем химического восстановления ионов Cu^{2+} из раствора под действием восстановителя – борогидрида натрия, далее мы обеспечили усиление стабилизации наночастиц путем введения модифицирующей добавки – Tween 80, которые препятствуют агрегации наночастиц в растворе. Средний размер частиц 345,1 нм, самый наименьший размер частиц составил 70,33 нм. Средний размер НЧ меди без участия Tween 80 в системе составил 429 нм. Наименьший размер частиц составил 384,4 нм.

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МЫС НАНОБӨЛЕКТЕРІНІҢ СИНТЕЗІ

Аннотация. Қысқаша хабарламада су ортасында шөгумен мыс нанобөлшектерін синтездеу мүмкіндігі қарастырылады. Біз қалпына келтіруші – натрий боргидридінің әсерімен ерітіндіден иондарды химиялық қалпына келтіру тәсілімен алынған мыс нанобөлшектерін зерттейміз, сондай-ақ біз ерітіндідегі нанобөлшектердің агрегациясына тиімді кедергі келтіретін полиоксиэтиленсорбитанмоноолеат (Tween 80) модификациялық қоспасын енгізу жолымен нанобөлшектердің тұрақтануын күшейтуді қамтамасыз еттік. Мыс нанобөлшектері дисперсиясының өлшемдері мен қасиеттері әртүрлі тәсілдермен зерттелді. Нанобөлшектердің мөлшері және олардың агрегация дәрежесі Malvern Zetasizer Nano өлшемінің анализаторымен зерттелді. УК және көрінетін сіңіру спектрлері екі сәулелі спектрофотометриялық UV-1800 алынған.

Нанобөлшектерді (НБ) су ортасында шөгумен синтездеу кезінде агрегациялайтын және шөгетін ірі бөлшектер (бірнеше микрометрлерге дейін) пайда болады. Нанометр өлшемі бөлшектерінің өсуі мен түзілуін баяулату үшін әртүрлі беттік-белсенді заттардың (ББЗ) қоспаларын жиі қолданады.

Мыс нанобөлшектерін сулы ортада араластырғанда реагенттер лезде дерлік кейін пайда болады. Алайда агрегациялаудан соң, түйірлердің одан әрі өсуі көп уақыт алады.

Тұрақтанған нанобөлшектердің химиялық заттарды енгізуге қабілеті күшейеді.

Алайда жоғары шоғырлану кезінде агрегацияға және шөгуге тұрақсыз өлшемдері бойынша кең таралған жеткілікті ірі бөлшектердің диспергирлеуге әкелетін нанобөлшектердің бақыланбайтын өсуі болуы мүмкін.

Түйін сөздер: Нанобөлшектер (НБ), мыс, синтез, беттік-белсенді заттар (ББЗ), бөлшектер, ерітінділер.

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SYNTHESIS OF COPPER NANOPARTICLES

Abstract. The summary report considers the possibility of synthesis of copper nanoparticles by precipitation in aqueous media. Copper nanoparticles obtained by the method of chemical reduction of ions from solution under action of reducing agent – sodium borohydride have been studied, and also provided for strengthening stabilization of nanoparticles by introduction of modifying additive – polyoxyethylene sorbitan monooleate (Tween 80), which effectively interfere with aggregation of nanoparticles in solution. The size and properties of the copper nanoparticles dispersions were investigated in various ways. The size of the nanoparticles and their degree of aggregation were examined using a Malvern Zetasizer Nano (UK) size analyzer. UV and visible absorption spectra were obtained on a two-beam scanning spectrophotometric UV-1800 (Japan).

In the synthesis of nanoparticles by precipitation in aqueous media, quite large particles (up to a few micrometers) are formed, which aggregate and precipitate. Additives of various surfactants are often used to slow growth and form nanometer-sized particles.

Nucleation of copper in aqueous media occurs almost instantaneously after mixing of the reactants. However, further particle growth, aggregation, and growth take longer.

The stabilizing ability of the nanoparticles is enhanced by the introduction of surfactants.

The effect of the concentration of these components for determining compositions resistant to sedimentation of copper nanoparticles dispersions has also been investigated.

During the first minute of synthesis, most of the copper nanoparticles are formed. When the system is further held, the optical density increases, but to a lesser extent. When the synthesis process is carried out for more than 20 minutes, the absorption spectra are practically unchanged. This indicates the establishment of quasi-equilibrium in the system. In the system, at a high concentration of nanoparticles, aggregation of the aggregates and their subsequent sedimentation may occur.

The effect of the concentration of these components for determining compositions resistant to sedimentation of copper nanoparticles dispersions has also been investigated.

The greater the concentration of copper ions in the feed solution, the greater the amount of crystallization nuclei formed by adding a reducing agent to the solution. However, at a high concentration, uncontrolled growth of nanoparticles can occur, resulting in a dispersion of sufficiently large particles with a wide size distribution that are unstable to aggregation and sedimentation.

Key words: Nanoparticles, copper, synthesis, surfactants, particles, solutions.

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