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СЕРИЯ ХИМИИ И ТЕХНОЛОГИИ

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

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

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NEW TRENDS IN THE IDENTIFICATION OF THE TRADITIONALFOOD PRODUCTS OF KAZAKHSTAN

Abstract. Requirements for the traditional food producers and their relationship with regional brands or products with geographical indications (GI) are discussed.The development of the so-called regional or territorial brands that promote products produced in a given region meets consumer demand in the terms of traceability of the provenance of the good. Moreover, there is an emerging potential demand for the traditional food products that have a stronger link with the area of production and the traditional method of production, as it happens, for example, for the European Union GIs.The GIs food labels guarantee consumers the origin and the method of production. The potential of Kazakhstan's organic dairy products have opportunities for the identificationofa significant value of the healthy nutrition and meet requirements of quality labels for agricultural products and foodstuffs: Protected Designation of Origin (PDO), Protected Geographical Indication (PGI) and Traditional Specialty Guaranteed (TSG). For instance, TSGs system of protection co-exists with individual EU member countries systems of recognition, two Italian TSGs are protected under the EU TSG system, while around 5,000 food products/recipes are recorded in the Italian '*prodotti alimentary tradizionali'* list. In the presented review, the branded dairy foods that produced in Kazakhstan are described, such as: "made in Kazakhstan", "irimshik", "shubat", "koumiss", "saumal"et al. These new trends allow to promote and to support the agricultural products. Organic food and beverages with a geographical indication will positively improve food industry, social and environmental consequences.

Keywords: dairyproducts,organic products, geographical indication, regional brand, PDO, PGI, TSGindicators.

INTRODUCTION

Recently, an increased consumer's demand for differentiated food is emerging, which is mainly focused on different value adding food attributes: healthiness, organic farming and processing method of production and/or traditional local links. These – above the mandatory safety and hygiene- attributes are value adding characteristics which can create value in the supply chain when properly signaled to the final consumers, through public labels and/or private brands - who are willing to pay a price premium for them [13].

In Kazakhstan have been recently introduced a policy framework,which aims to address this emerging demand providing a legal context to avoid unfair competition among producers and to provide clear information to final consumer through certification systems. At present time framework covers products from organic farming and the "made in Kazakhstan" labelling system assuring the provenance of the produce.

The increasing trend in organic food consumption is observed all over the world, including Kazakhstan, where producers are adapting their supply to satisfy the growing demand in the domestic market [12]. Bothlarge-scale companies and small private farms are engaged in the production of organic products, which are sold through restaurants, cafes, supermarkets and specialized shops.

In 2015, the Kazakhstan Government adopted the Law "On the production of organic products." This Law regulates the relations between producers of organic products, and the other agents operating along the supply chain. According to the international organic farming standards: synthetic substances, pesticides, hormones, antibiotics, food additives, and genetically modified organisms (GMO) are forbidden: The production, processing,and marketing rules have been defined by the Order of the Minister of Agriculture of the Republic of Kazakhstan dated May 23, 2016 No. 230, registered in the Ministry of Justice of the Republic of Kazakhstan on July 4, 2016 No. 13875.The compliance with the defined organic methods of production standards is under public Authorities control by means of inspections and preventive control in accordance with the Entrepreneurship Code of the Republic of Kazakhstan. Only having obtained a conformity certification, food islabelled with the national public label of certified organic products [20].

The demand for food having beneficial effects on human health is also increasing in Kazakhstan. For example, in 2010 the first dairy factory of the Kazakh Academy of Nutrition "Amiran" was founded, aiming at producing "healthy and functional food products" [22].

The same organization manages the label "product.kz" ("Made in Kazakhstan"): it characterizes goods produced in the Republic of Kazakhstan, aiming at increasing public confidence in domestic goods [14, 15].

Given thatfood tourism is growing in Kazakhstan, which is strictly related to the consumption of products with a strong link with the visited geographical area. Local products are also often demanded by consumers far from the production areas (e.g. in bistro restaurants supplying traditional food [10].

The development of the so-called regional or territorial brands, which promotes products produced in a given regionmeets consumer demand in the terms of traceability of the provenance of the good. Moreover, there is an emerging potential demand for traditional foodproductswhich have a stronger link with the area of production and the traditional method of production, as it happens, for example,forthe European Union Geographical Indications (GIs) [5, 6].

Based on a long dating system of protection of food GIs in the Mediterranean European countries – particularly in Italy, France and Spain - the European Union (EU) food quality policy, has established a European public system of protection an labelling for agricultural products and foodstuffs GI (protected denomination of origin, PDO, and protected geographical indications, PGI) and traditional food products (TSG), since 1992 [7].

Overall, GIs represent an important element of culture, identity, and heritage and are characterized by both historical and geographical dimensions. The increasing attention shown in the past 25 years by academics, politicians, and food system agents, and their recognition through geographical indications, stems from their implications on economic, legal, political and social grounds [11].

The GIs food labels guarantee consumers about the origin and the method of production. Target analyses and analytical procedures, together with the chemometric tools can be used to discriminate foods from different areas and/or production methods [4].

Along with the geographical indication, the concepts of PDO, PGI and TSG used in Europe also presuppose the consideration and legal protection of methods of production, recipes, and traditions. Consequently, some work is needed to register and protect the names of places of origin of goods and strengthen legislation to protect intellectual property and collective trademarks [8,19].

Another direction that requires a significant attention is national brands. As examples, the brands “made in Kazakhstan”, “irimshik”, “shubat”, “koumiss”, “saumal”et al are available. The work purpose is a review of the food products that traditionally available on the territory of Kazakhstan with a geographical indications. In each region, it can be discovered a few similar products that will be as the drivers for the development of ecotourism and rural areas.

MATERIALS AND METHODS

This review article is based on the study of the European scheme of GIs – PDOs and PGIs - and TSG, for instance in Italy, the analysis of information on the development of brands with the name of the place of production of goods, the experience of world markets in the production and promotion of food products with GI, brand products with GI and the importance of this work for Kazakhstan, not only for the local food industry, but for the social sphere as a whole.

RESULTS AND DISCUSSION

1. The geographical indications for the terroir characteristics of the food products.

The rationale of the EU GIs system of recognition and protection is the concept of *terroir*, i.e. the link between the characteristics of both the traditional area of production and the historically-linked method of production (the so-called human factors well rooted in the culture of the traditional area of production) and the food quality attributes. Accordingly, and in line with the 2015 revision of the Lisbon Treaty on GIs, two different GI types are defined: the Protected Designation of Origin (PDO), and the Protected Geographical indications (PGI). PDOs have a stronger link with the terroir than the PGIs: i) for PDOs *terroir* characterize all food quality attributes and, consequently, all the production stages (farming, processing, packaging) take place in the traditional area of production, while ii) for PGIs the link is weaker and has to be proved for at least one quality attribute or food product’s reputation; in this case, only one stage of the production has to take place in the traditional area.

The main characteristics of the EU GIs system are the followings:

i) the present time Regulation (EC Regulation 1151/2012) emphasizes the relevant role that GIs can play in the creation of value in their specific supply chains and as a rural development tool, while in the past the intellectual property right administrative protection from frauds and from imitation of the protected name prevailed;

ii) the system of legal protection is a *sui generis* system, which is public, protects the GI for an unlimited time span, assures that the protected name will name become a generic name and strongly protects consumers -at least in the EU market- from misleading information (e.g. GI name translation and use of ‘type’, ‘like’ are not allowed);

iii) aiming at increasing the consumer awareness of the over than 1,350 PDOs and PGIs registered in the DOOR database, the use of the EU PDO or PGI label is mandatory for all PDOs and PGIs since 2016;

iv) the GI supply is based on a certification system, under public authority supervision which controls that the method of production both takes place in-the traditional area and complies with the defined historically-linked code of practice.

In the WTO international context, the food GI definition is similar to the EU PGI one (TRIPS agreement art. 22.1), but the issue of the international protection of the GI food products is not yet fully accommodated, several conflicts arising. In brief, the level of protection varies among different products’ category (it is generally higher for wines and spirits than for food products) and ii) and, among countries. While some non-EU countries adopt a *sui generis* system, others protect their GIs under trademark legal systems. However, the increasing number of bilateral agreements on mutual recognition and protection of GIs - which have been signed or are under negotiation - between the EU and a non-EU country and, since 2006, the European Union opening to non-EU GIs of the EU register of GIs (DOOR database), show the possible coexistence of both systems in the international context and the potential market opportunities in terms of international trade. For example, Italian food GIs overall turnover reached 6,4 billion euros in 2016 (around 5% of the food industry value of production) and 3.1 billion where exported both to other EU counties and to non-EU ones.

While the PDO and PGI system for geographical indications recognition and protection is exclusively managed at the EU level, traditional food products, having lost their link with a given area of production but maintaining their link with the traditional method of production, are protected by the Traditional Specialty Guaranteed (TSG) system. It has to be pointed out that TSGs are not GIs, and the property right to use the protected name is assured to all the producers who comply with the code of practice, independently from the place of production. TSGs system of protection co-exists with individual EU member countries systems of recognition (for example, two Italian TSGs are protected under the EU TSG system, while around 5,000 food products/recipes are recorded in the Italian ‘*prodotti alimentary tradizionali’* list [3].

2. Branded food products of Kazakhstan

Priority commodity positions in Kazakhstan for the assignment of labels in accordance with the European scheme as products of PDO, PGI, are:Shymkent beer, Saryagash water, sublimed powder koumiss Saumal, Rakhat chocolate, national sour-milk products - koumiss and shubat.

Regional products are a cultural tradition, technologies that have been developed for centuries, pride and motivation. An important role in promoting such products, both on the domestic and foreign markets, can be played by a geographical indication.

Products of “Eurasia Invest LTD” LLP - dry mare milk "Saumal" - received a declaration of compliance with the requirements of the Eurasian Customs Union for Security. The international document gives the right to sell the product both on the territory of the Eurasian Economic Union (EAEU), and export to abroad countries [21].

As a result of freeze-drying of mare's and camel’s milk, powder remains, which when re-diluted with water retain practically all the beneficial properties of milk[16, 17].

The composition of any kind of milk includes two groups of proteins - whey and caseins. The casein group is quite problematic for the children's stomach, since it does not dissolve in water. When digested, this casein forms a clot, which is difficult and not always qualitatively absorbed by the body. Hence, disorders of the gastrointestinal tract and allergic reactions.But whey proteins are easily absorbed. In milk, there are two types - albumin and globulin. The first contains a valuable irreplaceable amino acid tryptophan, which is not found in any other protein. The second is the carrier of immune bodies. Immunoglobulins have the ability to "glue" foreign proteins and cells of microorganisms, thus providing antibacterial protection to newborns [18].

In this regard, the dietary supplements powder of carrot and holy thistle(*Silybum*) can be used as the fortification sources of antioxidants, flavonoids and various vitamins [2].

Of course, caseins are also needed for the human body; it's all about their quantity. If the ratio of caseins and albumins in cow's milk is 80 to 20%, then in female milk it is 72%. In mare, the balance is ideal - 50 to 50%. As a result, saumal is easily digested by the stomach, without causing allergic reactions. It is recommended to use milk powder, dissolved in water, obtained from sources located in the resort area of Saryagash. It is possible to talk about the beneficial effect of two natural resources of Kazakhstan - the natural water of Saryagash and Saumal - on each other. Even at the first tasting, patients positively assessed the taste of the drink, its beneficial tonic effect on the body.

Interest in mare milk in the world has been growing in recent decades, and therefore this product "Saumal" is promising, and significantly expanding the sales market, it can be attributed to products with a geographical indication, as well as water Saryagash.

As for national fermented dairy products such as koumiss and shubat, it is difficult or even wrong to say today that the potential of goods with the name of the place of production is realized. Much more serious work is needed on the domestic and foreign markets, it is necessary to acquaint the foreign consumer with these goods, ensure compliance with the declared quality standards and ensure the protection of intellectual property [1].

For the assessment to the European criteria for GIsthe work to be done in this direction consists of the following steps, after having identified the institutional context:

1. Development of standards and regulations
- Define the historically-linked method of production
- Implementation and management of the internal control system
- Conflict resolution and arbitration
- Identification of the tradition-based production area

2. Ensure production
- Technical support of production processes
- Training of manufacturers and further training
- Introduction of innovations in the production process

3. Marketing support
- Development and implementation of collective marketing campaigns
- Ensuring a balance of marginality along the value chain
- Development, promotion and updating
- Market analysis, sales optimization
- Support for individual marketing campaigns of manufacturers

4. Protection of interests
- Counteraction to counterfeit goods

- Ensuring that all positions are taken into account when managing the production of the product, ensuring high confidence between participants [9].

CONCLUSION

This review highlights the social success of branded eco-products that with certain marketing support and legal protection can be assigned the signs of PDO, PGI, TSG.

In the above mentionedKazakhstan brand eco-products some attributes inherent in GI products are traced: typicality and uniqueness connected with the territory; reputation among consumers, mainly in the export markets in developed countries, but they are not guaranteed by legal processes.

This is a new direction for Kazakhstan to promote and support agricultural products, organic food and beverages with a geographical indication will positively increase food industry, social and environmental consequences.Thus, further work is needed to identify thebranded organic products with high commercial potential and support for the ecotourism.

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ҚАЗАҚСТАННЫҢ ДӘСТҮРЛІ АЗЫҚ-ТҮЛІК ӨНІМДЕРДІ СӘЙКЕСТЕНДІРУ ЖАҢА ТЕНДЕНЦИЯЛАРЫ

Аннотация. Дәстүрлі азық-түлік өндірушілеріне қойылатын талаптар мен олардың аймақтық брендтермен немесе географиялық көрсеткіштерге ие (GI) өнімдермен өзара қарым-қатынасы талқыланады. Регионалдық және территориалық деп аталатын, осы аймақта өндірілген өнімді ілгерілететін брендтердің дамуы тауарларды қадағалау тұрғысынан тұтынушылық сұранысты қанағаттандырады. Сонымен қатар, дәстүрлі азық-түлікке жаңа потенциалды сұраныс пайда болады, мысалы, GI Европалық Одақ үшін болып жатқандай, өндіріс және дәстүрлі өндіріспен берік байланысқа ие. GIs өнімдерінің заттаңбалары тұтынушыларға шығу тегі мен өндірістік әдісті қамтамасыз етеді. Қазақстандық органикалық сүт өнімдерінің потенциалы салауатты тамақтанудың маңызды құнын анықтау және ауыл шаруашылығы өнімдері мен азық-түлік үшін сапалы этикеткалар талаптарына сай мүмкіндігі бар: шығу тегінің қорғалған белгісі (PDO), географиялық көрсеткіш (PGI) және дәстүрлі арнайы кепілдік (TSG) қорғалған. Мысалы, қорғау жүйесі TSG жеке ЕО мүше мемлекеттердің тану жүйелерін, ЕО TSG жүйесі мен «prodotti alimal tradizionali» итальяндық тізімінде жазылған шамамен 5000 тағамдар / рецепт бойынша қорғалған екі итальяндық TSG бар. Көрсетілген шолуда «Қазақстанда жасалған», «ірімшік», «шұбат», «қымыз», «саумал»,т.б. Қазақстанда шығарылатын фирмалық сүт өнімдерісипатталған. Бұл жаңа әзірлемелер ауыл шаруашылығы өнімдерін ілгерілету және қолдауға мүмкіндік береді. Географилық нұсқаулары бар органикалық азық-түліктер мен сусындар тағам өнеркәсібін, әлеуметтік және экологиялық салдарына оң әсер ете отырып жақсартады.

Түйінді сөздер: сүт өнімдері, органикалық өнімдер, географиялық көрсеткіштер, аймақтық брендтер, PDO, PGI, TSG индикаторлары.

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НОВЫЕ ТЕНДЕНЦИИ В ИДЕНТИФИКАЦИИ ТРАДИЦИОННОЙ ПИЩЕВОЙ ПРОДУКЦИИ КАЗАХСТАНА

Аннотация. Обсуждаются требования к традиционным производителям продуктов питания и их связь с региональными брендами или продуктами с географическими показателями (GI). Развитие так называемых региональных или территориальных брендов, которые продвигают продукцию, произведенную в данном регионе, удовлетворяет потребительский спрос в терминах прослеживаемости происхождения товара. Кроме того, появляется новый потенциальный спрос на традиционные пищевые продукты, которые имеют более прочную связь с производством и традиционным способом производства, как это происходит, например, для GI Европейского Союза. Этикетки продуктов GIs гарантируют потребителям происхождение и способ производства. Потенциал органических молочных продуктов Казахстана имеет возможности для определения значимой ценности здорового питания и удовлетворения требований к этикеткам качества для сельскохозяйственной продукции и продуктов питания: защищенное обозначение происхождения (PDO), охраняемая географическая индикация (PGI) и традиционная специальная гарантия (TSG). Например, система защиты TSG существует с системами распознавания отдельных стран-членов ЕС, два итальянских TSG защищены в рамках системы TSG ЕС, а около 5000 пищевых продуктов / рецептов записаны в итальянском списке «prodottialimaltradizionali». В представленном обзоре описаны фирменные молочные продукты, производимые в Казахстане, такие как: «сделано в Казахстане», «иримшик», «шубат», «кумыс», «саумал» и др. Эти новые тенденции позволяют продвигать и поддерживать сельскохозяйственную продукцию. Органические продукты питания и напитки с географическим указанием будут положительно улучшать пищевую промышленность, социальные и экологические последствия.

Ключевые слова: молочные продукты, органические продукты, географические показатели, региональные бренды, PDO, PGI, TSG показатели.

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STUDY OF HYDRO PURIFICATION ANDHYDROIZOMERIZATIONSTRAIGHT-RUN GASOLINE FRACTION OVER MODIFIED Ni (Co)-Mo- Al_2O_3- CATALYSTS

Abstract. The article presents the results of studies of hydropurificationand hydroisomerization of a straight-run gasoline fraction on new zeolite-containing alumonickel (cobalt) molybdenum catalysts modified with phosphorus and (rare earth element) REE: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18) and $NiO-MoO_3$-$Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-3). The effect of temperature, pressure and the volume flow rate of the feedstock was studied. Investigation of the processes of hydroprocessing of straight-run gasoline was carried out in a high-pressure flow system with a stationary catalyst bed at temperatures of 320-400^{0}C, a pressure of 3.0 -4.0 MPa and a feed rate of 0.5-3.0hr^{-1}.

At hydroprocessing of straight-run gasoline with high hydrodesulfurizing activity the catalyst KGO-18 possesses. The sulfur content of the catalyst decreased from 0.0080 (reference gasoline) to 0.0015% with an increase in temperature to 400^{o}C. After hydroprocessing the straight-run gasoline fraction on the KGO-3 catalyst at 400°C, the octane number of the hydro-upgraded gasoline rises from 79.0 (reference gasoline) to 92.4 research method (RM) and from 62.4 to 77.0 motor method (MM). Under these conditions, the octane number of hydrotreated gasoline on the catalyst KGO-18 is increased in comparison with the initial from 78.9 to 90.7 (RM) and by the motor method from 60.9 to 71.7.

Electron microscopic studies have shown that the modified Ni (Co)-Mo-Al_2O_3 catalysts are highly disperse, the metal components of the active phase are predominantly in the oxidized state, forming cluster-associates on the surface whose dispersion and structure and state are determined by the nature of the catalyst components.

Key words: zeolite, straight run gasoline, catalyst, hydrotreatment.

Introduction

In the oil refining industry, hydropurification and hydroisomerization processes are widely used to produce high-quality motor fuels, which are one of the main processes widely used in the oil refining industry.

In connection with the deepening of the processing of high-sulfur oil, there is a growing need to improve the existing catalysts for the hydrotreating of oil fractions. In accordance with modern requirements, a significant limitation of the sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is necessary. The known industrial catalysts do not provide the required degree of hydrotreating. In many countries, catalysts are being searched for increasing the depth of removal of sulfur-containing compounds and improving the technology for the production of motor fuels.

The problem of choosing the most effective catalyst is complex and requires in each case an individual approach. Recently, specific catalytic systems for the hydroprocessing of a specific type of raw material have been purposefully developed [1-19].

In this paper, the results of hydropurification and hydroisomerization studies of a straight-run gasoline fraction on new zeolite-containing alumonickel (cobalt) molybdenum catalysts modified with phosphorus and REE: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18) and $NiO-MoO_3-Ce_2O_3$- $P_2O_5-Al_2O_3$-ZSM (KGO-3).

Experimental part

New modified zeolite-containing catalysts of CGO were developed. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolite ZSM with aqueous solutions of nickel (cobalt) nitrate, ammonium paramolybdate and the introduction of modifying additives. After molding, the catalyst was dried at 150°C and calcined at 550°C for 5 hours.

New zeolite-containing modified catalysts were synthesized for the process of hydrotreating gasoline fractions of oil:$CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18);$NiO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-3).

Investigation of the processes of hydroprocessing straight-run gasoline in a high-pressure flow system with a stationary catalyst bed at temperatures of 320-400^{0}C, a pressure of 3.0-4.0 MPa and a volumetric feed rate of 2hr^{-1}. The hydrocarbon composition of the reaction products was analyzed on chromatographs "Chromatec-Crystal" and "Chromium-5". Analysis of sulfur content in feedstock and products was carried out in «Oilsert International» LLP (Almaty).

To study the structure and state of the catalyst surface, the electron microscopy method was used [20, 21].

Results and discussion

When hydrolyzing the gasoline fraction on the catalyst KGO-3 at 320^{0}C at V = 2.0hr^{-1} and P = 4.0MPa, the content of isoalkanes increases from 40.3% (initial fraction) to 44.0%, with an increase in temperature to 400^{0}C, their amount slightly reduced to 37.5% (Table 1). Under these conditions, the proportion of aromatic hydrocarbons in the resulting catalyst varies from 14.7 to 29.4%. The content of naphthenic hydrocarbons in the catalyst is 19.4-22.5%, olefinic hydrocarbons - 4.2 - 6.1%. The yield of the liquid phase with increasing temperature from 320 to 400^{0}C decreases from 80.0 to 75.0%.The octane number of hydrotreated gasoline in these conditions rises from 79.0 (reference gasoline) to 92.4 (RM) and from 60.9 to 77.0 (MM). After processing the gasoline fraction with an initial sulfur content of 0.0080% on the catalyst KGO -3, the mass fraction of sulfur in the catalyst decreased to 0.0039% with an increase in temperature to 400 ° C.

Table 1 - Effect of temperature on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3

Products,%	T˚C				
	Initialgasoline	320	350	380	400
Paraffins C_5-C_6	25,7	14,5	8,5	5,1	6,9
Iso-alkanes	40,3	44,0	42,2	46,2	37,5
Olefins	5,1	4,3	6,1	4,2	4,4
Aromatichydrocarbons	8,9	14,7	23,2	25,1	29,4
Naphthenichydrocarbons	20,0	22,5	20,0	19,4	21,8
Yield of the liquid phase	-	80,0	78,5	78,6	75,0
Octane number by research method	79,0	85,6	87,9	89,1	92,4
Octane number by motor method	60,9	71,9	73,4	74,2	77,0
Massfractionofsulfur,%	0,0080	0,0064	0,0060	0, 0057	0,0039
Note: P=4,0MPa, V=2,0ч$^{-1}$					

The influence of pressure on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3 at V = 2.0 hr^{-1} and T = 400^{0}C was studied (Table 2). With an increase in pressure in the interval 2.5-4.0 MPa, the amount of isoalkanes is 37.2-38.9%, the concentration of naphthenic hydrocarbons decreases from 17.0% to 21.9%.The concentration of aromatic hydrocarbons in the resulting catalyst ranges from 29.4-30.9%, olefins - 3.4-9.0%. The yield of the liquid phase is 70.0-75.0%. The octane number of gasoline enriched at 4.0 MPa is 92.4 (RM) and 77.0 (MM). When hydrolyzing the gasoline fraction, the sulfur content of the final product decreases from 0.0080% (reference gasoline) to 0.0039% at 4.0 MPa.

Table 2 - Influence of pressure on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3

Products,%	Pressure, MPa				
	Initial gasoline	2,5	3,0	3,5	4,0
Paraffins C_5-C_6	25,7	8,5	4,2	8,7	6,9
Iso-alkanes	40,3	37,8	38,9	37,2	37,5
Olefins	5,1	3,4	9,0	6,3	4,4
Aromatichydrocarbons	8,9	30,9	30,9	30,8	29,4
Naphthenichydrocarbons	20,0	19,8	17,0	17,0	21,8
Yield of the liquid phase	-	70,0	70,0	72,0	75,0
Octane number by research method	79,0	90,0	91,0	91,5	92,4
Octane number by motor method	60,9	75,4	74,9	76,5	77,0
Massfractionofsulfur,%	0,0080	0,0061	0,0057	0,0049	0,0039
Note: P=4,0MPa, V=2,0hr^{-1}: V=2,0hr^{-1}andT= 400^{0}C.					

During the hydroprocessing of the gasoline fraction on the catalyst KGO-3 (P = 4.0 MPa and 400°C), when the volumetric feed rate of the feed varies from 1.0 to 2.5 hr^{-1}, the content of isoalkanes in the catalyst varies from 31.4 to 37.5% the concentration of aromatic hydrocarbons is 29.0-30.7%, of naphthenic hydrocarbons is from 15.4 to 21.8%. The amount of olefinic hydrocarbons varies between 2.7-4.4%. The octane number of the gasoline produced increases with hydrotreating on the catalyst KGO-compared to the initial (79.0) to 92.4-93.7 (RM). The yield of the liquid phase is 75.0-78.0%. When hydrolyzing the gasoline fraction on the catalyst KGO-3, the sulfur content in the final product decreases from 0.0080% (reference gasoline) to 0.0039% at 4.0 MPa (Table 3)

Table 3 - Influence of the space velocity on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3.

Products,%	Volumetricspeed, h^{-1}			
	Initial gasoline	1.0	1.5	2.0
Paraffins C_5-C_6	25,7	20,2	17,4	6,9
Iso-alkanes	40,3	31,4	33,8	37,5
Olefins	5,1	2,7	2,7	4,4
Aromatichydrocarbons	8,9	29,0	30,7	29,4
Naphthenichydrocarbons	20,0	16,6	15,4	21,8
Yield of the liquid phase	-	78,0	77,0	75,0
Octane number by research method	79,0	93,7	93,5	92,4
Octane number by motor method	60,9	77,4	77,6	77,0
Massfractionofsulfur,%	0,0080	0,0037	0,0039	0,0039
Note: P= 4.0MPa, 400˚C				

When studying the influence of temperature on the process of hydroprocessing of straight-run gasoline on the catalyst KGO-18, it was shown that in the temperature range 320-350^{0}C the maximum amount of isoalkanes is 39.7-38.2% (Table 4). At higher temperatures, the yield of isoalkanes decreases to 34.4% at 400 ^{0}C. The content of aromatic hydrocarbons in the catalyst under these conditions increases from 15.2 to 24.8%, the yield of naphthenic hydrocarbons decreases from 26.1 to 24.0%. The amount of olefinic hydrocarbons varies within the range of 4.6-7.6%. The yield of hydro-upgraded gasoline decreases from 70.7 to 60.5% with increasing temperature from 320 to 400^{0}C.The octane number of hydrotreated gasoline is increased compared with the original from 79.0 to 90.7 (MI) and by the motor method from 60.9 to 71.7. The sulfur content of the catalyst decreased from 0.0080 (reference gasoline) to 0.0015% with an increase in temperature to 400^{o}C.

Table 4 - Effect of temperature on the process of hydroprocessing straight-run gasoline on catalyst KGO-18

Products,%	T˚C				
	Initialgasoline	320	350	380	400
Paraffins C_5-C_6	27,3	11,4	15,1	12,5	12,2
Iso-alkanes	36,8	39,7	38,2	34,0	34,4
Olefins	4,8	7,6	5,6	5,4	4,6
Aromatichydrocarbons	9,2	15,2	18,7	20,9	24,8
Naphthenichydrocarbons	21,9	26,1	22,3	27,2	24,0
Yield of the liquid phase	-	70,7	68,3	65,0	60,5
Octane number by research method	79,0	82,6	84,9	88,1	90,7
Octane number by motor method	60,9	67,8	67,7	68,5	71,7
Massfractionofsulfur,%	0,0080	0,0049	0,0026	0,0030	0,0015
Note: P=4,0MPa, V=2,0hr^{-1}					

Table 5 shows the results obtained in a study of the effect of pressure on the process of hydroprocessing straight-run gasoline on the catalyst KGO-18. Studies have shown that in the pressure range 2.5-4.0 MPa, the content of isoalkanes in the catalyst increases from 31.2 to 38.8%. The amount of aromatic hydrocarbons in this pressure range increases from 25.8% to 32.8%, while a decrease in the yield of naphthenic hydrocarbons from 30.1% to 22.9%. The content of olefinic hydrocarbons is 5.3-6.2%.The yield of hydro-upgraded gasoline increases with increasing pressure from 58.0 to 90.0%. The octane number of hydro-upgraded gasoline is increased compared to the initial from 79.0 to 90.7 by the research method and by the motor method from 60.9 to 71.7. The sulfur content of the catalyst decreased from 0.0080 to 0.0015% as the temperature increased to 400^{0}C.

Table 5 - Influence of pressure on the process of hydroprocessing
of straight-run gasoline on the catalyst KGO-18 at T = 400°C, V = 2.0 h^{-1}

Products,%	P, MPa				
	Initialgasoline	2,5	3,0	3,5	4,0
Paraffins C_5-C_6	27,3	7,6	12,6	7,6	7,2
Iso-alkanes	36,8	31,2	32,0	37,8	38,8
Olefins	4,8	5,3	5,5	3,0	6,2
Aromatichydrocarbons	9,2	25,8	26,9	31,3	32,8
Naphthenichydrocarbons	21,9	30,1	22,9	20,3	22,9
Yield of the liquid phase		58,0	70,0	75,0	90,0
Octane number by research method	79,0	87,7	91,5	88,2	90,7
Octane number by motor method	60,9	70,3	72,3	72,5	71,7
Massfractionofsulfur,%	0,0080	0,0013	0,0013	0,0012	0,0015
Note: V=2,0hr^{-1}andT= 400^{0}C.					

When hydrolyzing the gasoline fraction on the catalyst KGO-18 (P = 4.0 MPa and 400°C) with an increase in the feed rate of feed from 0.5 to 3.0 hr^{-1}, the content of isoalkanes in the catalyst increases from 31.3 to 35.0 %, the amount of aromatic hydrocarbons is 25.7-32.8%, the yield of naphthenic hydrocarbons is 26.3-34.9%, of olefinic hydrocarbons varies between 5.8-6.3% (Table 6). The octane number of the produced gasoline increases with hydrotreating on the catalyst KGO-18 in comparison with the initial (79.0) to 89.2-90.7 (RM).The yield of the liquid phase fluctuates within the limits of 80.4-94.6%. During hydroprocessing of the gasoline fraction on the catalyst KGO-18 at P = 4.0 MPa and 400^{0}C and sulfur feed rates of 0.5 hr^{-1} sulfur-containing compounds in the final product were not detected. With an increase in feed rate, the residual sulfur content fluctuates between 0.0012 and 0.0026% (Table 6).

Table 6- Influence of the volumetric feed rate on the process
of hydroprocessing of straight-run gasoline on the catalyst KGO-18

Products,%	V, ч$^{-1}$					
		0,5	1,0	2,0	2,5	3,0
Paraffins C_5-C_6	27,3	3,5	8,2	3,2	7,9	6,5
Iso-alkanes	36,8	31,3	30,0	22,8	34,3	35,0
Olefins	4,8	6,3	6,2	6,2	5,8	5,7
Aromatichydrocarbons	9,2	25,8	27,7	32,8	25,7	26,2
Naphthenichydrocarbons	21,9	33,1	27,9	34,9	26,3	26,6
Yield of the liquid phase	-	94,6	93,8	90,0	86,4	80,4
Octane number by research method	79,0	89,7	89,2	90,7	90,7	92,1
Octane number by motor method	60,9	71,5	68,9	71,7	72,1	71,5
Massfractionofsulfur,%	0,0080	-	0,0012	0,0015	0,0024	0,0026
Note: P=4,0MPaand400˚C						

The conducted studies of the process of hydroprocessing of the straight-run gasoline fraction allowed to establish that the catalyst KGO-18 possesses higher hydrodesulfurizing activity in comparison with the catalyst KGO-3: the residual sulfur content at 400°C is 0.0015 and 0.0039%, respectively. Under these conditions, the octane number of gasoline hydroprocessed on the catalyst KGO-18 is 90.7 (RM), and the gasoline produced on the catalyst KGO-3 has an octane number of 92.4 (RM). The observed increase in the octane number is mainly due to the enhancement of the process of hydroisomerization of n-alkanes and the increase in the content of aromatic hydrocarbons.

The activity of the catalysts is related to the surface structure, composition and state of the active sites. An electron-microscopic study was made of the structure and state of the active sites of catalysts KGO-3 and KGO-18.

According to the electron microscopy data, the catalysts are highly disperse, the metal components of the active phase are predominantly in the oxidized state, forming cluster-associates on the surface, the dispersion, structure and state of which is determined by the nature of the catalyst components.

The KGO-3 catalyst is characterized by the presence of clusters with d = 3.0 - 4.0 nm, which are formed by finely dispersed particles with d <0.05 nm, which include NiSi2 and Ni2O3. In addition, there are single particles with signs of hexagonal faceting with d ≈ 15.0-30.0 nm, consisting of the compounds $AlNi_2Si$, AlNi, Ge_2O_3, MoO $(OH)_2$, $AlMo_3$, $MoSi_2$, Al_3Ce and $CeAlO_3$ (Figure 1).

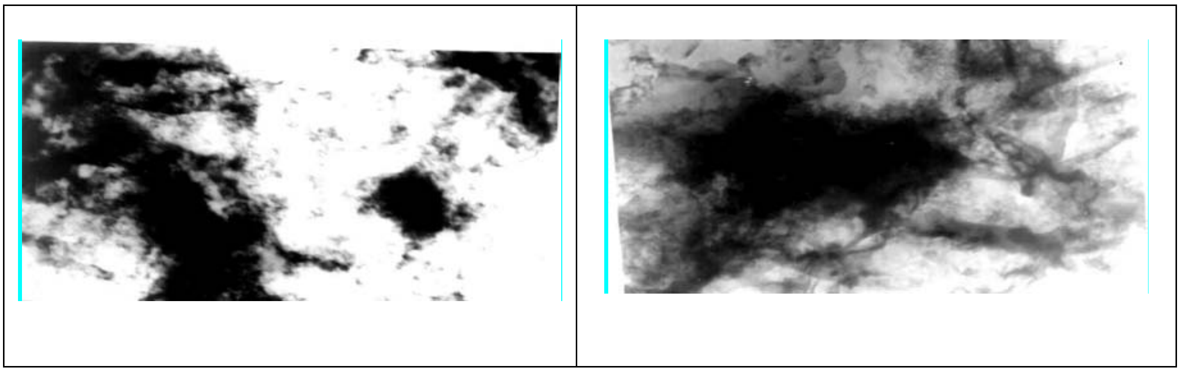

Figure 1 - Electron microscopic RMages of the catalyst KGO-3

Clusters of highly dispersed particles of various shapes with d = 50-200 nm, consisting of $Co_2Mo_3O_8$, CeP_2O_7, $AlPO_4$, CoOOH, $MoOPO_4$, α-Co (P_2O_7), Ce $(MoO_4)_2$, are found on the surface of the catalyst KGO-18 (Fig. 2). In addition, there are 4-5 nm particles formed by Ge4 (P2O7) 3, CoSi, MoP, $MoSi_2$, $Ge_6O_{11}$and $CoMoP_2$.

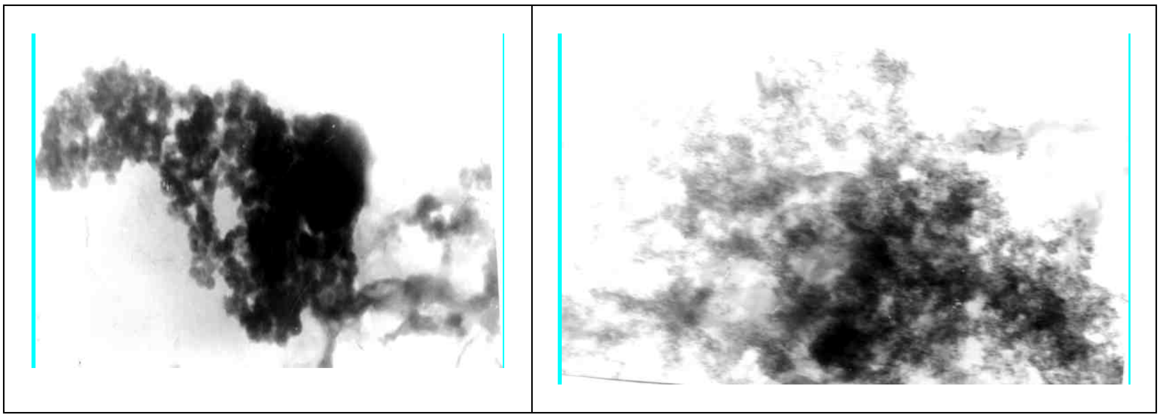

Figure 2 - Electron microscopic RMages of the catalyst KGO-18

It should be noted that the detected structures of AlNi2Si, AlMo3, AlNi, MoSi2, Al3Ce and CeAlO3 NiSi2 indicate the introduction of metals-active phase components into the zeolite structure with the formation of new centers that can function as Lewis acid sites [22, 23].

Conclusions. Thus, modified zeolite-containing catalysts for the hydroprocessing of gasoline fractions $CoO\text{-}MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{-}Al_2O_3\text{-}ZSM$ and $NiO\text{-}MoO_3\text{-}Ce_2O_3$ $\text{-}P_2O_5\text{-}Al_2O_3\text{-}ZSM$ have been developed and synthesized, which hydrotreating and hydroisomerization in one step. The developed catalysts for activity in hydrotreatment processes of gasoline fractions of petroleum exceed the known industrial catalysts [1, 2]. The catalysts make it possible to obtain low-sulfur gasoline, and also to increase its octane number.

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МОДИФИЦИРЛЕНГЕН Ni(Co)-Mo- Al_2O_3КАТАЛИЗАТОРЛАРЫНДА ТУРА АЙДАЛҒАН БЕНЗИН ФРАКЦИЯСЫН ГИДРОИЗОМЕРЛЕУ ЖӘНЕ ГИДРООҢДЕУ

Аннотация.Жұмыста жаңа цеолитқұрамды алюмоникель (кобальт) молибден, СЖЭ және фосформен модифицирленген $CoO\text{-}MoO_3$- $Ce_2O_3\text{-}P_2O_5\text{-}Al_2O_3$-ZSM (КГО-18); $CoO\text{-}MoO_3\text{-}La_2O_3\text{-}P_2O_5\text{-}Al_2O_3$-ZSM(КГО-20) жәнеCoO-$MoO_3\text{-}Ce_2O_3\text{-}P_2O_5\text{-}Al_2O_3$-ZSM-HY (КГО-16) катализаторларында тура айдалған бензин фракцияларын гидротазалау мен гидроизомерлеудің зерттеу нәтижелері көрсетілген. Шикізаттың көлемдікберілужылдамдығы мен қысымының температураға әсері зерттелді. Тура айдалған бензинді ағымды қондырғыда жоғары қысымда катализатордың стационарлы қабатының температурасы 320-400^{0}С, қысымы 3,0-4,0 МПа шикізаттың көлемдік берілу жылдамдығы 0,5-3,0 сағ$^{-1}$ гидроөңдеу процесі жүргізілді.Тура айдалған бензинді гидроөңдегенде жоғары күкіртсіздендіру активтілігіне КГО-18 катализаторы иеболды. Температураны 400^{0}С көтергенде сұйытықтағы күкірттің құрамы 0,0080 (Бастапқы бензин) 0,0015%-ға дейін төмендеді. 400^{0}С-та КГО-3 катализаторында тура айдалған бензин фракциясын гидроөңдегеннен кейін гидрожақсартылған бензиннің октан саны 79,0 (бастапқы бензин) 92,4 (З.Ә) және 62,4-тен 77,0 (М.Ә.) Осы жағдайда КГО-18 катализаторында гидрожақсартылған бензинді бастапқы мен салыстырсақ октан саны 78,9-дан 90,7(З.Ә) жәнемоторлы әдіспен 60,9-дан 71,7-ге өскен.

Электронды микроскопиялық зерттеулер модификацияленген Ni (Co) -Mo-Al_2O_3 катализаторларының жоғары дисперсті екенін көрсетті, белсенді фазаның металл компоненттері негізінен тотыққан күйде болып, бетінде кластерлі-ассоциаттар түзеді, дисперстілігі, құрылымы мен күйі катализатордың компоненттерінің табиғаты бойынша анықталады.

Түйін сөздер: цеолит, тура айдалған бензин, катализатор, гидроөңдеу.

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ИССЛЕДОВАНИЕ ГИДРООЧИСТКИ И ГИДРОИЗОМЕРИЗАЦИИ ПРЯМОГОННОЙ БЕНЗИНОВОЙ ФРАКЦИИ НА МОДИФИЦИРОВАННЫХ Ni(Co)-Mo- Al_2O_3- КАТАЛИЗАТОРАХ

Аннотация. В работе приведены результаты исследований гидроочистки и гидроизомеризации прямогонной бензиновой фракции на новых цеолитсодержащих алюмоникель (кобальт) молибденовых катализаторах, модифицированных фосфором и РЗЭ: $CoO\text{-}MoO_3$- $Ce_2O_3\text{-}P_2O_5\text{-}Al_2O_3$-ZSM (КГО-18) иNiO-$MoO_3$- $Ce_2O_3\text{-}P_2O_5\text{-}Al_2O_3$-ZSM (КГО-3). Исследовано влияние температуры, давления и объемной скорости подачи сырья. Исследование процессов гидропереработкипрямогонного бензина проводилосьв проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400^{0}С, давлении 3,0 -4,0 МПа и объемной скорости подачи сырья 0,5- 3,0ч$^{-1}$.

При гидропереработке прямогонного бензина высокой гидрообессеривающей активностью обладает катализатор КГО-18. Содержание серы в катализате с ростом температуры до 400^{o}С снизилось с 0,0080 (исходный бензин) до 0,0015%.После гидропереработки прямогонной бензиновой фракции на катализаторе КГО-3 при 400^{0}С октановое число гидрооблагороженного бензина растет от 79,0 (исходный бензин) до 92,4 (И.М) и от 62,4 до 77,0 (М.М).В этих условиях на катализаторе КГО-18 октановое число гидрооблагораженного бензина повышается по сравнению с исходным от 78,9 до 90,7 (ИМ) и по моторному методу от 60,9 до 71,7.

Электронно-микроскопические исследования показали что модифицированные Ni(Co)-Mo-Al_2O_3 катализаторы являются высокодисперсными, компоненты металлов активной фазы находятся преимущественно в окисленном состоянии, образуя на поверхности кластеры-ассоциаты, дисперсность, структура и состояние которых определяется природой компонентов катализатора.

Ключевые слова: цеолит, прямогонный бензин, катализатор, гидроочистка.

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THE STUDY OF THE CHEMICAL COMPOSITION OF *THYMUS EREMITA* KLOK. AND *THYMUS RASITATUS* KLOK. FROM THE KARAGANDA REGION

Abstract. Possible reduction of stocks of medicinal plant raw materials of creeping thyme (Thymus serpyllum L.) and thyme vulgaris (Thymus vulgaris L.) leads to the need to expand the raw material base of official medicinal plants due to additional plant sources and their integrated use. Therefore, we conducted a comprehensive study of the contents of various classes of biologically active substances in the herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok., which are endemic species growing in the territory of the Karaganda region. It has been established that herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok. contain a significant number of different classes of biologically active substances, namely terpenoids, flavonoids, phenolcarboxylic acids, tannins, triterpene compounds, water-soluble polysaccharides, pectin substances, amino acids and organic acids. The presence of these substances and the content of a large list of important mineral elements determine the promise of their use in pharmacy and medicine.

Keywords: herbs, *Thymus eremita* Klok., *Thymus rasitatus* Klok., essential oils, biologically active substances, macro- and microelements, radionuclides.

Introduction. In terms of developing and introducing into the practical health care an original effective phytomedication, plants of the Thymus family (Thymus L.) of the family Lamiaceae are of undoubted interest. The genus Thymus is popular in traditional medicine of many countries and peoples as a valuable medicinal raw material. Various types of biological activity of plants of the thyme species have been described by the results of scientific research [1, 2, 3, 4, 5, 6]. *Thymus serpyllum* L. and *Thymus vulgaris* L. are included in the State Pharmacopoeia of the Republic of Kazakhstan as medicinal plants [7]. At the same time, a possible reduction in stocks of medicinal plant raw materials leads to the need to expand the raw-material base of official medicinal plants through additional plant sources and their integrated use. At the moment, other species of plants of the genus Thymus L. have been applied only in folk medicine.

The flora of Central Kazakhstan includes 12 species of plants of the genus Thymus, of which 5 species are endemic, including *Thymus rasitatus* Klok. and *Thymus eremita* Klok. [8]. The chemical composition and biological properties of these species have not been practically studied for their possible use [9, 10].

The aim of our work is the chemical study of various classes of biologically active substances of endemic species of *Thymus rasitatus* Klok. and *Thymus eremita* Klok., growing in the territory of the Karaganda region.

Materials and methods. The aerial part (thin stems, leaves, flowers) of the plants used in this study were collected in populations of the Karaganda region of the Republic of Kazakhstan: *Thymus rasitatus* Klok. in the mountains of Karkaralinsk (N 49 ° 57407 '; E 75 ° 30976'), *Thymus eremita* Klok. in the vicinity of the town of Balkhash in the mountains of Bektauata (N 47 ° 2554 ', E 74 ° 4738'), in June 2016 in phase of blossoming – flowering. The collected samples were dried, crushed and stored in accordance with the requirements of the State Pharmacopoeia of the Republic of Kazakhstan for medicinal plants.

The commodity analysis of herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok. is given in accordance with the requirements of the State Pharmacopoeia of the Republic of Kazakhstan.

All samples of essential oils were obtained by hydrodistillation of the air-dried overground part of the raw material on the Clevenger apparatus [7]. The component composition of essential oils Genus of Thymus rasitatus and Thymus eremita was determined by GC-mass spectroscopy using an Agilent GC System 7890A gas chromatograph coupled with the Agilent 5975C mass-selective detector (MSD). The analysis was carried out under the following conditions: HP-5MS capillary column 30 m x 0.25 mm id, 0.25 µm), the isotherm of the furnace at 70°C for 2 min, then from 70°C to 270°C at 20°C/min, then hold 270°C for 30 min, the carrier gas (helium) at a flow rate of 2 ml/min – splitless, the temperature of the evaporator was 250°C and the detector temperature was 230°C. The mass spectra were recorded using an ionization energy of 70 eV and a separation temperature of 280°C, acquisition mass range m/z of 10-650. Identification of the components was carried out by comparing their recorded mass spectra with data stored in the NIST 2011 MS Bundle mass spectrum library (G1033A) of the GC-MS data system.

The content of flavonoids, phenol carboxylic acids, tannins, triterpene compounds, water-soluble polysaccharides, pectic substances, amino acids, organic acids, bioelements and radionuclides in the samples was determined using the methods described in the State Pharmacopoeias of the Republic of Kazakhstan, Russian Federation and described in the work [11].

The mineral composition of plant raw materials was studied by evaporation with the use of emission spectral analysis in the «EcoNus» testing laboratory (Karaganda, Kazakhstan).

The determination of radionuclides (Cs, Sr) in the two samples of plant raw materials was carried out by a radiochemical method without ashing in the beta spectrum at the «Ecoexpert» test center (Karaganda, Kazakhstan).

Results and discussion. A complex study of the main groups of biologically active compounds of the aboveground part of two endemic species *Thymus rasitatus* Klok. and *Thymus eremita* Klok., growing on the territory of the Karaganda region, is being conducted for the first time, and is the first stage of phytochemical research of these plant species. A commodity analysis of herbs of Thymus rasitatus Klok. and Thymus eremita Klok. was carried out, according to the results presented in Table 1, it was established that the samples of plant raw materials under investigation comply with the requirements of the GF RK.

Table 1 - Results of commodity analysis of herbs of Thymus rasitatus Klok. and Thymus eremita Klok.

Name of plant	Foreign impurities,% not more than 2%	Weight loss during drying,% no more 13 %	Total ash,% no more 12 %	Ash, insoluble in hydrochloric acid,% not more than 3,5%	Microbiological purity in accordance with the requirements of the GF RK
Thymus rasitatus Klok.	1,26	5,51	5,28	2,33	within the normal range
Thymus eremita Klok.	1,0	5,6	6,38	2,93	within the normal range

The results of determining the quantitative content of individual classes of biologically active substances in herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok. are presented in Table 2.

As can be seen from Table 2, the yield of essential oil from *Thymus rasitatus* Klok. was 0.60%, of *Thymus eremita* Klok.- 0.30%, in terms of air-dried raw materials.

Based on the results of the study of the component composition of the essential oils of the test samples by the method of chromatography-mass spectrometry (Table 2), it has been established that (±) - trans-nerolidol (14.55%), trans-geraniol acetate (13.91%), β-linalool (12.66%), trans-geraniol (9.50%), γ-terpineol (8.27%), 1.8-cineol (5.99%), cis-geraniol acetate (4.21%), cis- geraniol (3.49%), endo-borneol (3.01%) are the main components of essential oil of *Thymus rasitatus. Thymus eremita* Klok. essential oil contains the following main components: β-linalol (25.94%), α-terpeneol (12.27%), 1.8-cineole (10.46%), (±) -trans-nerolidol (7.17%), endo -Borneol (5.67%), β-myrcen (3.66%).

Table 2 - Content of the main groups of biologically active substances in herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok., growing in the territory of the Karaganda region

Name of plant	Essential oil, %	Flavonoids, %	Phenolcarboxylic acids, %	Tannins, %	Triterpene compounds,%	Water-soluble polysaccharides, %	Pectin substances, %	Amino acids, %	Organic acids, %
Thymus rasitatus Klok.	0,60 ±0,02	2,88 ±0,03	1,81 ±0,05	19,83 ±0,49	1,19 ±0,09	5,35 ±0,14	8,95 ±0,29	0,70 ±0,05	6,31 ±0,19
Thymus eremita Klok.	0,30 ±0,03	2,89 ±0,04	1,06 ±0,05	13,29 ±0,19	0,55 ±0,03	2,89 ±0,11	9,34 ±0,21	0,94 ±0,03	5,98 ±0,19

Table 2 - Chemical composition of essential oils of two species of *Thymus* L.

№	t_r (min)	Component	Area (%)	
			Th. rasitatus	*Th. eremita*
1	10.801	*α*-Pinene	1.70	1.21
2	11.408	Camphene	2.23	2.16
3	12.360	*β*-Terpinene	1.44	1.30
4	12.418	*β*-Pinene	2.10	-
5	12.584	1-octen-3-ol	-	0.52
6	13.017	*β*-Myrcen	-	**3.66**
7	13.846	(+)-4-Carene	0.16	0.42
8	14.128	*o*-Cymene	0.58	3.97
9	14.229	Limonene	0.87	0.83
10	14.301	1,8-Cineole	**5.99**	**10.46**
11	14.957	*cis*-*β*-Ocimene	2.29	1.46
12	15.297	*γ*-Terpinene	0.38	0.95
13	15.571	*cis*-*β*-Terpineol	0.14	0.10
14	16.639	*β*-Linalool	**12.66**	**25.94**
15	18.002	(+)-Camphor	0.46	1.28
16	18.233	Nerol oxide	0.17	-
17	18.659	endo-Borneol	**3.01**	**5.67**
18	19.020	(-)-Terpinen-4-ol	0.63	1.39
19	19.186	*cis*-Verbenol	0.05	-
20	19.431	*α*-Terpineol	**8.27**	**12.27**
21	20.528	*cis*-Geraniol	**3.49**	1.24
22	20.701	Thymol methyl ether	-	1.18
23	20.896	*β*-Citral	1.60	1.31
24	21.292	*trans*-Geraniol	**9.50**	-
25	21.740	*α*-Citral	2.62	-
26	22.180	*iso*-Bornyl acetate	0.21	0.21
27	22.440	Thymol	0.42	1.48
28	22.815	Carvacrol	-	-
29	24.287	(*R*)-Lavandulyl acetate	-	0.33
30	24.294	*cis*-Geraniol acetate	**4.21**	-
31	24.821	*trans*-Geraniol acetate	**13.91**	-
32	24.900	(-)-*β*-Bourbonene	0.17	0.37
33	25.816	Caryophyllene	0.64	2.32
34	26.675	Humulene	-	0.22
35	27.361	*β*-Copaene	0.32	0.40
36	27.765	*γ*-Elemene	0.10	0.31
1	2	3	4	5
37	29.374	(±)-*trans*-Nerolidol	**14.55**	**7.17**
38	29.785	(-)-Spathulenol	0.75	1.30
39	29.922	Caryophyllene oxide	0.70	2.24
40	31.279	*α*-*epi*-Cadinol	0.17	0.20
41	31.711	Juniper camphor	0.36	1.47
Total			96,85	95,34

Both plant objects contain an equal amount of flavonoids (in the form of cynaroside), however, the herb of *Thymus rasitatus* Klok. is characterized by a relatively high content of phenolcarboxylic acids (in the form of rosmarinic acid), tannins, triterpene compounds, water-soluble polysaccharides (in the form of apple acid) and organic acids, and the herb of Thymus eremita Klok.contains relatively more pectin substances and amino acids.

A study of the mineral composition of the herbs of *Thymus rasitatus* Klok. and Thymus eremita Klok. showed the presence of 43 bioelements (Table 4). In the herb of *Thymus rasitatus Klok.* herbs, iron (1245.51 mg / kg), phosphorus (861.88 mg / kg) and aluminum (680.90 mg / kg) were identified in significant amounts. Herb of *Thymus eremita* Klok. contains approximately identical concentrations of iron (1013.74 mg / kg), phosphorus (905.92 mg / kg) and aluminum (618.00 mg / kg). All values comply with the requirements of the GF RK.

Table 4 - Mineral elements of plants Thymus eremita Klok. and Thymus rasitatus Klok.

№	Chemical element	Content (%)	
		Th. *rasitatus*	Th. *eremita*
1	Aluminum	680,90	618,00
2	Barium	252,84	450,52
3	Beryllium	1,10	<0,80
4	Bor	28,56	21,09
5	Vanadium	<5	<5
6	Bismuth	<1	<1
7	Tungsten	<2	<2
8	Gallium	<3	<3
9	Hafnium	<5	<5
10	Germanium	<3	<3
11	Iron	1245,51	1013,74
12	Gold	<10	<10
13	Indium	<5	<5
14	Ytterbium	<0,50	<0,50
15	Yttrium	3,16	<3
16	Cadmium	<3	<3
17	Cobalt	<1	<1
18	Lanthanum	<5	<5
19	Lithium	1,83	<1
1	2	3	4
20	Manganese	242,96	165,42
21	Copper	18,73	12,79
22	Molybdenum	<1,50	<1,50
23	Arsenic	<5	<5
24	Nickel	<10	<10
25	Niobium	<5	<5
26	Tin	<1	<1
27	Platinum	<10	<10
28	Plumbum	23,45	<10
29	Silver	<0,10	<0,10
30	Scandium	<1	<1
31	Strontium	77,56	71,13
32	Antimony	<5	<5
33	Thallium	<10	<10
34	Tantalum	<10	<10
35	Tellurium	<20	<20
36	Titanium	108,91	110,72
37	Thorium	<2	<2
38	Uranus	<500	<500
39	Phosphorus	861,88	905,92
40	Chromium	29,41	28,45
41	Zinc	75,20	47,62
42	Cerium	<20	<20
43	Zirconium	2,39	2,74

The content of radionuclides (Cs, Sr) in the two investigated samples of plant raw materials complies with the requirements of the State Pharmacopeia of the Republic of Kazakhstan (table 5).

Table 5 - Results of determination of radionuclides in raw materials Thymus eremita Klok. and Thymus rasitatus Klok.

Name of plant	Contents of Cr-137, Bq/kg		Contents of Sr-90, Bq/kg	
	Permissible content of normative documents	Actual results	Permissible content of normative documents	Actual results
Thymus rasitatus Klok.	200 Bq/kg	12 Bq/kg	100 Bq/kg	< 15 Bq/kg
Thymus eremita Klok.	200 Bq/kg	9 Bq/kg	100 Bq/kg	< 11 Bq/kg

Thus, the obtained data make it possible to note that the herbs of *Thymus rasitatus* Klok. and *Thymus eremita* Klok. contain a significant number of different classes of biologically active substances, namely, terpenoids, flavonoids, phenol carboxylic acids, tannins, triterpene compounds, water-soluble polysaccharides, pectins, amino acids and organic acids. The presence of these substances and the content of a large list of important mineral elements indicate the need for further pharmacological and phytochemical studies of these types of plant raw materials, to assess their biological activity with the aim of developing new domestic medicines and more detailed study of the raw materials base to meet the needs of the pharmaceutical industry.

Conclusions.

1. Comprehensive study of the contents of various classes of biologically active substances in the herb *Thymus rasitatus* Klok. and herb *Thymus eremita* Klok., growing in the territory of the Karaganda region, was carried out.

2. It has been established that herbs of Thymus rasitatus Klok. and Thymus eremita Klok. contain a significant number of different classes of biologically active substances, namely terpenoids, flavonoids, phenolcarboxylic acids, tannins, triterpene compounds, water-soluble polysaccharides, pectin substances, amino acids and organic acids. The presence of these substances and the content of a large list of important mineral elements determine the promise of their use in pharmacy and medicine.

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ҚАРАҒАНДЫ ӨҢІРІНДЕГІ *THYMUS EREMITA* KLOK. ЖӘНЕ *THYMUS RASITATUS* KLOK. ӨСІМДІКТЕРІНІҢ ХИМИЯЛЫҚ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Дәрілік өсімдік Thymus serpyllum L. және Thymus vulgaris L. шикізатының қорының ықтимал төмендеуі қосымша өсімдік көздері арқылы ресми дәрілік өсімдіктердің шикізат базасын кеңейту қажеттілігіне әкеледі. Сондықтан Қарағанды облысы аумағында өсетін эндемикалық шөп түрлеріңде *Thymus rasitatus* Klok. және *Thymus eremita* Klok. биологиялық белсенді заттардың әртүрлі сыныптарының мазмұнын жан-жақты зерттеу жүргізілді. *Thymus rasitatus* Klok. және *Thymus eremita* Klok. шөптің құрамында биологиялық белсенді заттардың әртүрлі сыныптары бар, атап айтқанда, терпеноидтер, флавоноидтар, фенолкарбон қышқылдары, таниндер, тритерпен қосылыстары, суда еритін полисахаридтер, пектикалық заттар, амин қышқылдары мен органикалық қышқылдар бар. Бұл заттардың болуы және маңызды минералды элементтердің үлкен тізімінің мазмұны оларды фармацияда және медицинада пайдалану туралы уәдесін анықтайды.

Түйінді сөздер: шөп, Thymus eremita Klok, Thymus rasitatus Klok., эфир майы, биологиялық белсенді заттар, макро- және микроэлементтер, радионуклидтер.

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ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА *THYMUS EREMITA* KLOK. И *THYMUS RASITATUS* KLOK. КАРАГАНДИНСКОГО РЕГИОНА

Аннотация. Возможное сокращение запасов лекарственного растительного сырья тимьяна ползучего (*Thymus serpyllum* L.) и тимьяна обыкновенного (*Thymus vulgaris* L.) приводит к необходимости расширения сырьевой базы официнальных лекарственных растений за счет дополнительных растительных источников и комплексного их использования. Поэтому нами проведено комплексное изучение содержания различных классов биологически активных веществ в траве тимьяна бритого (*Thymus rasitatus* Klok.) и тимьяна пустынника (*Thymus eremita* Klok.), эндемичных видах произрастающих на территории Карагандинского региона. Установлено, что трава тимьяна бритого и трава тимьяна пустынника содержат значительное количество различных классов биологически активных веществ, а именно, терпеноидов, флавоноидов, фенолкарбоновых кислот, дубильных веществ, тритерпеновых соединений, водорастворимых полисаха-ридов, пектиновых веществ, аминокислот и органических кислот. Наличие которых, в комплексе с количественным содержанием многих важнейших минеральных элементов, определяют перспективность их использования в фармации и медицине.

Ключевые слова: трава, *Thymus eremita* Klok., *Thymus rasitatus* Klok., эфирные масла, биологически активные вещества, макро- и микроэлементы, радионуклиды.

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CATALYZED BY PALLADIUM COMPLEXES THE CYCLOADDITION OF HYDRAZONES TO FULLERENEC_{60}

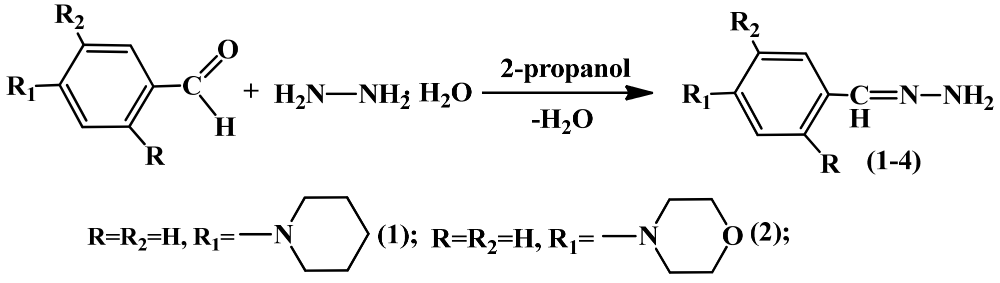
Abstract. The article is devoted to the development of a preparatively convenient method for the synthesis of new methanofullerenes by the catalytic cyclo coupling of hydrazones to fullereneC_{60}. The catalyst used was Pd(acac)$_2$-PPh$_3$-AlEt$_3$. The reactions were carried out under conditions of generating substituted diazomethanes in situ by oxidation of the hydrazones of the corresponding aldehydes with MnO_2. The use of complexes of transition metals in this reaction makes it possible to direct the cycloaddition of the diazo compounds to fullerenes towards the production of individual methanofullerenes. Initially, the synthesis of the initial arylhydrazones by the interaction of substituted benzaldehydes (salicylic aldehyde, 5-bromosalicyl aldehyde, 4-morpholino-benzaldehyde, 4-piperidine benzaldehyde) with an excess of hydrazine hydrate in isopropyl alcohol was carried out. The reaction of the reaction of diazoarylaldehydes with fullerene C_{60} was monitored by HPLC. It is shown that the use of the catalyst Pd(acac)$_2$-PPh$_3$-AlEt$_3$ in a ratio of 1:4:4 leads to the formation of exclusively methanofullerenes with yields of 40-95%. The composition and purity of the methanofullerenes obtained are confirmed by MALDI-TOF and HPLC mass spectrometry, and the structure by NMR^{1}H spectroscopy. The mechanism of formation of methanofullerene is discussed.

Keywords: fullereneC_{60}, aromatic aldehydes, diazoarylaldehydes, cycloaddition, catalyst Pd(acac)$_2$-PPh$_3$-AlEt$_3$.

At present, the world science pays ever more attention to the prospects for the development of fundamental and applied research in the field of chemistry of carbon clusters. The organic chemistry of fullerene has acquired a special perspective and is developing [1,2]. The presence of a fullerene fragment in the structure of compounds provides a significant improvement or appearance of qualitatively new mechanical, chemical, physical, biological and other properties associated with the manifestation of nanoscalefactors[3], immunomodulating [4], antioxidant [5], andothertypesofactivity. Functionalization of fullerenes is mainly carried out using classical reagents and methods widely used in synthetic practice [6-13]. We previously studied the reactions of the [2 + 3]-cycloaddition-the three-component condensation of C_{60} fullerene, N-methylglycine (sarcosine) and various functionally substituted aromatic aldehydes under Prato reaction conditions, leading to the formation of new fulleropyrrolidines [14-17].

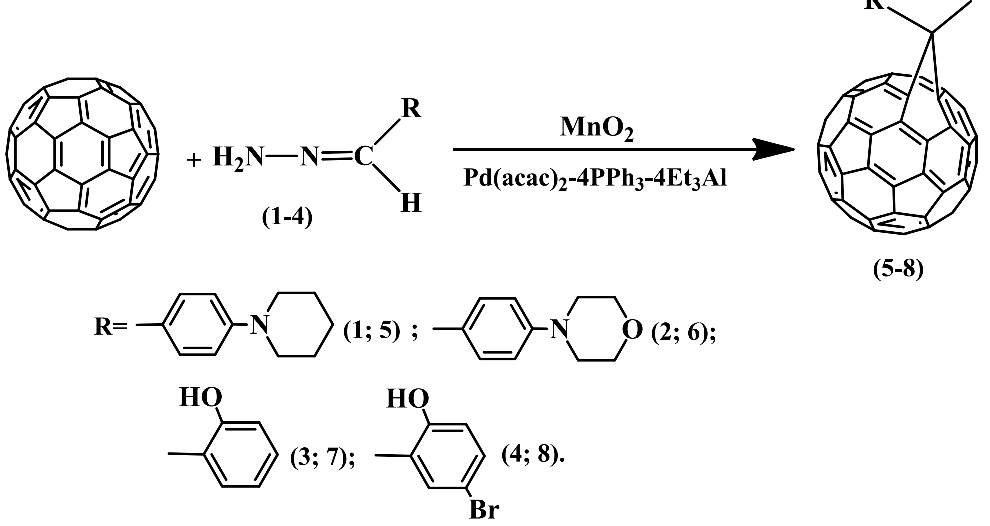
One of the most commonly used methods for the synthesis of practically important functionally substituted fullerene derivatives has been and still is the reaction of carbon clusters with *in situ* generated α-halocarbanions (the Bingel-Hirsch reaction) leading to methanofullerenes [18]. Along with this method of synthesis of fullerocyclopropanes, a wide application in synthetic practice has found methods based on cycloaddition to carbon clusters of diazocompounds.However, the main disadvantage of this reaction is its low selectivity. Meanwhile, the use of transition metal complexes in this reaction makes it possible to direct the cycloaddition of diazo compounds to fullerenes towards the production of individual methanofullerenes.

In this connection, it seemed to us of interest to study the catalytic cycloaddition of diazoarylhydrazones to C60-fullerene catalyzed by palladium complexes. Initially, we synthesized the initial arylhydrazones by the interaction of substituted benzaldehydes (salicylic aldehyde, 5-bromosalicyl aldehyde, 4-morpholinobenzaldehyde, 4-piperidine benzaldehyde) with excess hydrazine hydrate in isopropyl alcohol medium with heating for 6-10 hours. Theyieldsofhydrazones (1-4) 45-95%.



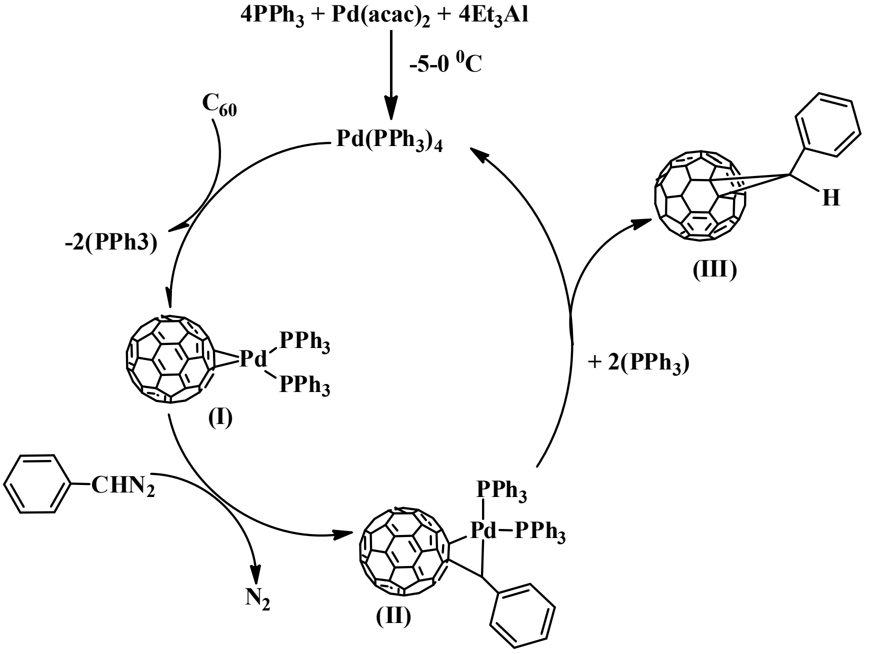
R=OH, R_1=R_2=H (3); R=OH, R_1=H, R_2=Br (4)

Next, we carried out for the first time the cyclic addition of diazoarylhydrazones (1-4) to fullerene C_{60} under the action of the three-component catalyst $Pd(acac)_2$-PPh_3-$AlEt_3$ under the conditions of using the procedure for the generation of substituted diazomethanes by oxidation of the corresponding aldehydes with MnO_2. The use of the catalyst $Pd(acac)_2$-PPh_3-$AlEt_3$ in the ratio 1:4:4 leads to the formation of methanofullerenes (5-8) with yields of 40-95%.

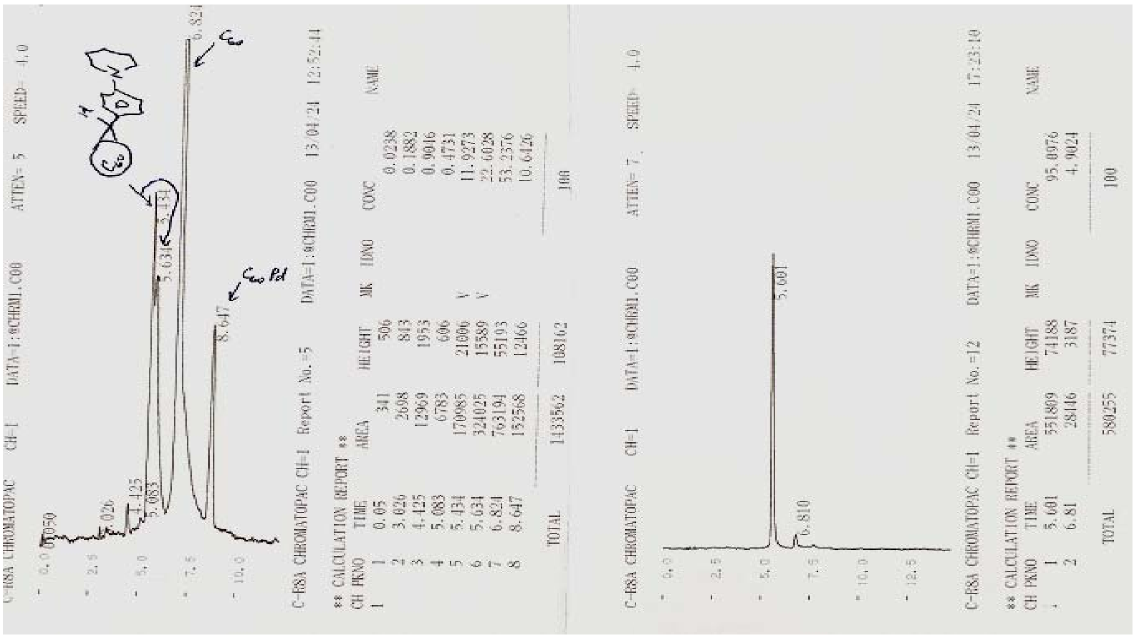


On the basis of the literature data, we give below a scheme-the proposed mechanism of cycloaddition of diazomethane to C_{60} involving Pd complexes. The likely mechanism of the catalytic action of the phosphine complex Pd on the cycloaddition of diazomethanes to fullerene C_{60} is based on the results of numerous experiments [19, 20].

According to the data of the authors [19, 20], the oxidative addition of fullerene C_{60} to the central catalyst atom ($Pd(PPh_3)_4$) proceeds to form the palladium of the cyclopropane complex $C_{60}Pd$ (PPh_3) (**I**), which is confirmed by the presence of a single signal with a chemical shift δp 25.23 m. e. in the ^1H NMR spectrum of the complex (**I**) obtained and the color change of the fullerene solution from violet-purple to dark green. Further, diazomethane reacts with the complex (**I**) via a polarized Pd-C bond with the simultaneous elimination of N_2 and the formation of intermediate fulleropalladiumcyclobutane (**II**), which under the reaction conditions is transformed into the target methanofullerene (**III**) with regeneration of the initial Pd complex.



The reaction of diazoarylaldehydes (1-4) with fullerene C_{60} under the action of the $Pd(acac)_2$-PPh_3-$AlEt_3$catalyst was monitored by HPLC. The reaction products were analyzed on an Altex chromatograph (model 330) (USA) with a UV detector at a wavelength of 313 nm. Figure 1 shows the chromatograms of Compound (5) for the reaction time in 2 h and 4 h.



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```
C-R8A CHROMATOPAC CH=1  Report No.=5      DATA=1:@CHRM1.C00   13/04/24  12:52:44

** CALCULATION REPORT **
CH PKNO      TIME        AREA       HEIGHT    MK   IDNO      CONC             NAME
1     1      0.05          341         506                     0.0238
      2      3.026        2698         843                     0.1882
      3      4.425       12969        1953                     0.9046
      4      5.083        6783         606                     0.4731
      5      5.434      170985       21006    V               11.9273
      6      5.634      324025       15589    V               22.6028
      7      6.824      763194       55193                    53.2376
      8      8.647      152568       12466                    10.6426
                     ----------  ---------               -----------
          TOTAL        1433562      108162                   100
```

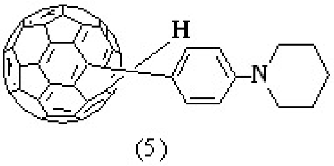
```
C-R8A CHROMATOPAC    CH=1      DATA=1:@CHRM1.C00       ATTEN= 7    SPEED=  4.0
```

```
C-R8A CHROMATOPAC CH=1  Report No.=12     DATA=1:@CHRM1.C00   13/04/24  17:23:10

** CALCULATION REPORT **
CH PKNO      TIME        AREA       HEIGHT    MK   IDNO      CONC             NAME
1     1      5.601      551809       74188                    95.0976
      2      6.81        28446        3187                     4.9024
                     ----------  ---------               -----------
          TOTAL         580255       77374                   100
```

A B

Figure 1 - Chromatograms of compound (5): A - after 2 h; (B) - after 4 h



(5)

The structure of the compounds obtained was studied using 1- (4- (piperidine) phenyl)-1aH-1(2)a-homo(C60-Ih) [5,6] fullerene (5) using mass spectrometry (MALDI-TOF/TOF). Mass spectra (5) contain peaks of molecular ions with m / z 892.097 (calculated at 893.120) (Fig. 2).

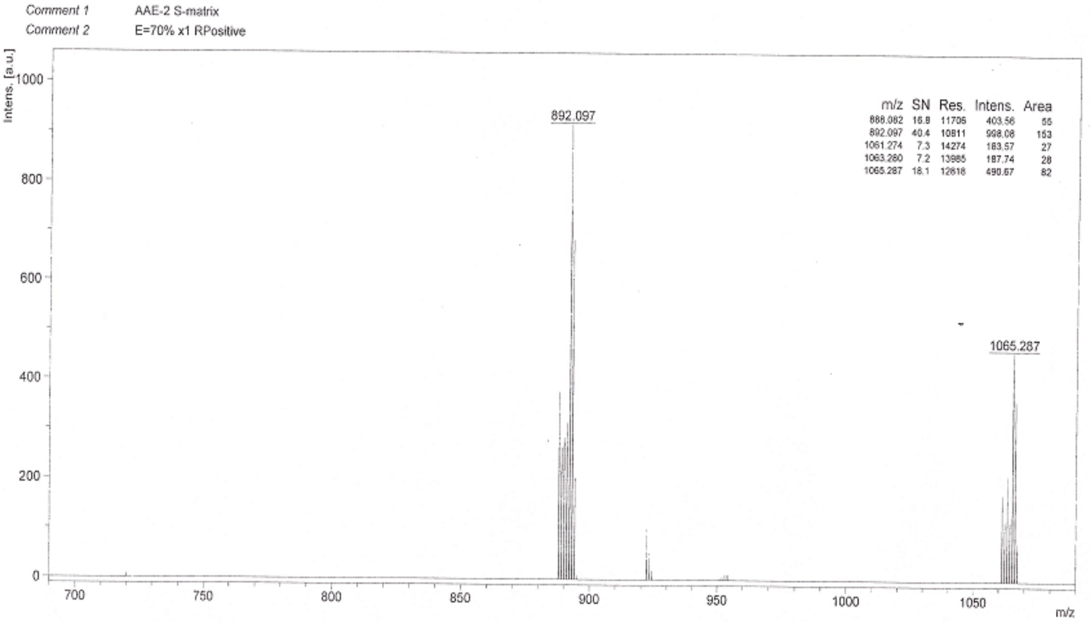


Figure 2 - Mass spectrum of 1-(4-(piperidine)phenyl)-1aH-(2)a-homo(C_{60}-I_h) [5,6] fullerene (5)

Thus, the synthesis was carried out and the catalytic cycloaddition of arylhydrazones to C_{60} fullerene was carried out using the metal complex catalyst $Pd(acac)_2$-PPh_3-$AlEt_3$. It is shown that the use of the catalyst $Pd(acac)_2$-PPh_3-$AlEt_3$ in a ratio of 1: 4: 4 leads to the formation of exclusively methanofullerenes with yields of 40-95%. The proposed method is based on the generation of diazoalkanes in situ by oxidation of arylhydrazones with MnO_2 and using catalytic amounts of the palladium complex, the reaction is carried out at room temperature in a solution of o-dichlorobenzene.

Experimental part

The ^1H NMR spectrum of compounds (5) was taken on a JEOLFX90Q spectrometer (90 and 22 MHz). The analysis of addition products was carried out by HPLC on an Altex chromatograph (model 330) (USA) with a UV detector at a wavelength of 313 nm. The components of the mixture were separated on a metal column of 250x8 mm PLgel 100 Å with sorbent grains 5 mkm at room temperature. The mobile phase is toluene, the flow rate is 0.2 ml/min. Mass spectra were obtained on a MALDI-TOF/TOF instrument.

1-(4-(Hydrazonomethyl) phenyl) piperidine (1). To a solution of 0.2 g (0.001 mol) of 4-(piperidin-1-yl)benzaldehyde in 10 ml of 2-propanol, 0.25 g (0.005 mol) hydrazine hydrate. The reaction mixture was heated at 70 °C for 3-4 h. The precipitate which formed was filtered off, washed with 2-propanol and recrystallized from 2-propanol, 0.19 g (95%) of compound (1) was obtained, m.p. 155-156 °C. Found (%): C, 70.95; H, 8.48; N, 20.72. $C_{12}H_{17}N_3$. Calculated (%): C, 70.90; H, 8.43; N, 20.67.

4-(4-(Hydrazonomethyl)phenyl)morpholine (2) was prepared analogously to compound (1) from 1 g (0.005 mol) of 4-morpholylbenzaldehyde and 1.3 g (0.026 mol) of hydrazine hydrate. 0.83 g (81%) of the compound (2.23) is obtained, m.p. 159-160^{0}C. Found (%): C, 64.42; H, 7.42; N, 20.52. $C_{11}H_{15}N_3O$. Calculated (%): C, 64.37; H, 4.37; N, 20.47.

2-(Hydrazonomethyl) phenol (3) was prepared analogously to compound (1) from 2 g (0.0164 mol) of salicylic aldehyde and 4.1 g (0.082 mol) of hydrazine hydrate. 1 g (45%) of the compound (3.24) was obtained, m.p. 82°C. Found (%): C, 61.80; H, 5.97; N, 20.63. $C_7H_8N_{20}$. Calculated (%): C, 61.75; H, 5.92; N, 20.58.

5-**Bromo-2-(hydrazonomethyl) phenol (4)** was prepared analogously to compound (1) from 1 g (0.005 mol) of 5-bromo-2-hydroxybenzaldehyde and 1.24g (0.025 mol) of hydrazine hydrate. 0.6 g (56%)

of the compound (3.25) is obtained, m.p. 247^{0}C. Found (%): C, 39.15; H, 3.33; N, 13.08. $C_7H_7N_2OBr$. Calculated (%): C, 39.10; H, 3.28; N, 13.03.

1-(4-(piperidine)phenyl)-1aH-1(2)a-homo(C_{60}-I_h)[5,6]-fullerene (5). A solution containing 0.1 ml (0.00278 mmol) of $Pd(acac)_2$ in 0.4 ml of o-dichlorobenzene and 0.2 ml (0.00556 mmol) of PPh_3 in 0.42 ml of o-dichlorobenzene was charged to the glass reactor. In dry argon flow at -5°C and with stirring, 0.4 ml (0.01112 mmol) of Et_3Al in 0.1 ml of toluene was added, while the color from slightly yellow to slightly brown. 10 mg (0.0139 mmol) of C_{60} fullerene in 2 ml of chlorobenzene were added to the obtained catalyst at room temperature, and the solution acquired a dark green color. 8.46 mg (0.0417 mmol) of 1-(4-(hydrazonomethyl)phenyl) piperidine were added to the resulting fullerene complex in 9.4 ml of CH_2Cl_2 and in small portions 0.2 mmol of MnO_2. After 1 hour, the reaction mass was treated with an aqueous solution of 5% HCl, 7 ml of toluene was added and the organic layer was passed through a column with a small amount of silica gel. The reaction products and the C_{60} fullerene were separated by preparative HPLC, eluent-toluene. The product was a brown powdered substance 11.4 mg (95%).

1-(4-(Morpholyl)-phenyl)-1a*H*-1(2)a-homo(C_{60}-*I_h*)[5,6]fullerene(6), 1-(4-(2-hydroxyphenyl)-1aH-1(2)a-homo(C60-Ih)[5,6] fullerene (7) and 1-(4-(5-bromo-2-hydroxy-phenyl)-1aH-1(2)a-homo(C_{60}-*I_h*)[5,6] fullerene (8) were prepared analogously to compound (5) and are brown powders with yields of 95%, 45% and 51%, respectively.

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C_{60} ФУЛЛЕРЕНГЕ ГИДРАЗОНДАРДЫҢ ПАЛЛАДИЙ КОМПЛЕСТЕРІМЕН КАТАЛИЗДЕНЕТІН ЦИКЛОҚОСЫЛУЫ

Аннотация. Мақала C_{60}-фуллеренге гидразондарды каталитикалық циклоқосумен жаңа метанофуллерендер синтезінің препаратты тиімді әдісін әзірлеуіне арналған. Катализатор ретінде композициялық катализатор $Pd(acac)_2$-PPh_3-$AlEt_3$ қолданылды. Реакциялар MnO_2 көмегімен сәйкес альдегидтертің гидразондарының тотығуы нәтижесінде орынбасылған диазометандардың *in situ* генерациялануы әдісін қолдану жағдайында жүргізілді. Ауыспалы металдардың комплекстерінің қолданылуыдиазоқосылыстардың фуллеренге циклоқосылуреакциясын жеке метанофуллерендерді алубағыттынқамтамасыз етеді. Алдымен изопропилді спирт ортасында гидразингидраттың артық мөлшері қатысында орын басылған бензальдегидттермен (салицил альдегиді, 5-бромсалицилді алдегид, 4-морфолинобензальдегид, 4-пиперидинбен-зальдегид)әрекеттесуі нәтижесінде бастапқы арилгидразондар синтезі жүргізілді. Диазоарилальдегидтердің фуллерен C_{60}-пен әрекеттестіру реакциясын ЖТСХ арқылы тексеріліп отырылды. $Pd(acac)_2$-PPh_3-$AlEt_3$ катализаторын 1:4:4 қатысында қолдану тек қана метано-фуллерендердің 40-95% шығымен түзілуіне әкелетінікөрсетілді. Алынған метнофуллерендердің құрылымы ЯМР^{1}Нспектро-скопиямен, құрамы мен тазалығы масс-спектрометрия MALDI-TOF және ЖТСХ әдістерімен расталған.Метанофуллереннің түзілуінің механизмі талқынылады.

Түйін сөздер: C_{60}-фуллерен, ароматтық альдегидтер, диазоарилальде-гидтер, циклоқосылу, катализатор $Pd(acac)_2$-PPh_3-$AlEt_3$.

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КАТАЛИЗИРУЕМОЕ КОМПЛЕКСАМИ ПАЛЛАДИЯЦИКЛОПРИСОЕДИНЕНИЕ ГИДРАЗОНОВ К ФУЛЛЕРЕНУ C_{60}

Аннотация. Статья посвящена разработке препаративно удобного способа синтеза новых метанофуллеренов каталитическим цикло присоединением гидразонов к фуллеренуC_{60}. В качестве катализатора использовалась композиция $Pd(acac)_2$-PPh_3-$AlEt_3$. Реакции проводились в условиях генерирования замещенных диазометанов*insitu* окислением гидразонов соответствующих альдегидов с помощью MnO_2. Использование комплексов переходных металлов в этой реакции позволяет направить циклоприсоединениедиазосоединений к фуллеренам в сторону получения индивидуальных метанофуллеренов. Вначале осуществлен синтез исходныхарилгидразонов взаимо-действием замещенных бензальдегидов (салициловый альдегид, 5-бромсалициловый альдегид, 4-морфолино-бензальдегид, 4-пиперидинбензальдегид) с избытком гидразингидрата в среде изопропилового спирта. Реакцию взаимодействия диазоарилальдегидов с фуллереном C_{60} контролировали методом ВЭЖХ. Показано, что исполь-зование катализатора $Pd(acac)_2$-PPh_3-$AlEt_3$ в соотношении 1:4:4 приводит к образованию исключительно метано-фуллеренов с выходами 40-95%. Состав и чистота полученных метанофуллеренов подтверждены данными масс-спектрометрии MALDI-TOF и ВЭЖХ, а строение - методом ЯМР^{1}Н-спектроскопии. Обсуждается механизм образования метанофуллерена.

Ключевые слова: C_{60}-фуллерен, ароматические альдегиды,диазоарилальдегиды, циклоприсоединение, катализатор $Pd(acac)_2$-PPh_3-$AlEt_3$.

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PROMISINGDIRECTIONSOFREDUCING SPECIFIC ENERGY COSTSIN GRINDING

Abstract. The grinding process is widely used in various technologies and is characterized by high energy consumption. Besides, there is anirretrievable loss of high-quality steel due to the wear of the working elements of grinders.

High energy costs occur not only due to the large volumes of processed materials, but also due to the extremely low efficiency of grinding machines, especially mills, the efficiency coefficientof which is at best several percents. Especially sharply the efficiency coefficientisreducing and the mills'drive capacityisincreasingwith an increase in the milling fineness of the material.

Despite the new methods of grinding: electro-hydraulic, ultrasonic, gravitational, light beam grinding, etc., in all designs of industrial units the grinding, is carried out by mechanical methods, such as crushing, cracking, impact, attrition, breakage or a combination of these methods.

There iscarried out the analysis of energy costs for formation of new surfaces, elastic and plastic deformations, for formation of various kinds of defects in the crystal structure (mainly dislocations), forfriction of the material's particles between themselves and the walls of the grinding chamber. It is noted that a small part of the input energy is consumed by different kinds of radiation (acoustic waves, exoelectronic emission, etc.), which always accompany the destruction.

From the analysis carried out it follows that the lowest energy intensity of the grinding process is achieved in grinding due to impact and slightly worse - due to crushing.When grinding by impact, the loading of the material should be pulsed with the steepest front.The loads must be dosed, corresponding to the strength and endurance of the defective zones.

To the working zone of the mill the starting material should be supplied in small volumes and even better piece by piece, and after grinding - quickly removed from the milling zone to the classifier. Therefore, any mill should operate in a closed cycle.

The classifier must be of highefficiency, so that to the finished product there came the particles of only smaller than the near-mesh grain, and the large fraction,returned to re-milling, contained as few particles of the finished product as possible.

Keywords: grinders, mills, energy costs, milling fineness, crushing, cracking, attrition, breakage, impact, classifier, closed cycle.

Introduction. Intensification of technological processes with reducing the energy costs for their implementation is an urgent task of modern production. One of the main ways to solve this problem is the creation and implementation of new high-performance machines and devices with low energy consumption.

The problem of reducing energy costs and increasing the efficiency is particularly acute in carrying out the grinding process. This process is widely used in various technologies and is characterized by high energy consumption, while the equipment for its implementation is cumbersome and has low efficiency.

Large energy consumption in the process of grinding is confirmed by the fact that about $5 \div 10\,\%$ of the world's electricity is spent on this process [1,p.8; 2, p. 6], and even more, according to the statistical data on the United Statesmining industry [3, 4]. Besides, the irretrievable losses of high-quality steel due to wear of the working elements of grindersare about 4 million tons per year. The mills'drive capacity in fine grinding of cement production, mining and other industries reaches up to 25MW [5, 6]. The size of mills at present has reached the limit of an economically viable size.

High energy costs occur not only due to the large volumes of processed materials, but also due to the extremely low efficiency of grinding machines, especially mills, the efficiency coefficientof which is at best several percents. Especially sharply the efficiency coefficientisreducing and the mills'drive capacityisincreasingwith an increase in the milling fineness of the material.

At the same time, by the studies of recent years, there has been revealed quite a number of mechanochemical phenomena, which are observed in fine and ultrafine grinding [7, p. 21-24]. For example, with the increase in the cementmilling fineness,thereincreases the rate of its setting and there sharply increases the strength of the agglomerate. Rocks, such as granite, schoeniteandothers, acquire cementingpropertiesin this grinding.With the increase in the milling fineness of some substances,thereincreases not only the rate, but also the degree of their dissolution. Some pigments, depending on the milling fineness, change their color. With fine grinding of ores, the process of extracting minerals is very fast, with high completeness of their extraction.In a number of works [7, p. 22] there is noted the possibility of direct metal recovery by a mechanochemical method. This is not at all a complete list of phenomena, on the basis of which it is possible to create new high-performance technologies. However, economically it is possible only on the condition of considerable reduction of costs for grinding of the materials.

The research methodology is to carry out the analysis of the main energy consumption items in grinding and to develop the recommendations onrational organization of the grinding technology with optimal process conditions.

Research results. In all designs of industrial unitsthe grinding is carried out by mechanical methods, such as crushing, cracking, impact, attrition, breakage or a combination of these methods.

In addition to mechanical methods, recently there have been proposed new methods of grinding: electrohydraulic, ultrasonic, gravitational, grinding with a light beam, obtained by means of a quantum generator, cavitational, grinding by rapidly changing high and low temperatures, grinding by a compressed gaseous mediumenergy, radiative and electromagnetic softening and others.However, the new methods have not yet come beyond the laboratory studies, and in the nearestfuture, the main units will remain mills, in which the grinding of the material is carried out by mechanical methods[2,p.8]. Hence, to reduce the energy consumption and to improve the efficiency of the grinding process, it is necessary to further improve the existing grinding units and create the fundamentally new designs.

Let's consider the main possible energy consumption items in grinding.

When grinding,theenergy is spent not only on the formation of new surfaces, but also on the elastic and plastic deformations, on the formation of various kinds of defects in the crystal structure (mainly dislocations), on the friction of material particles between themselves and the walls of the grinding chamber. A small part of the input energy is consumed by different kinds of radiation (acoustic waves, exoelectronic emission, etc.), which always accompany the destruction[2, p.153]. The value of each of the energy loss factors is not a constant value and varies quite sharply, depending on the nature of the material being destructed, the scale factor and the organization of the grinding process in each specific unit. Letusconsiderinmoredetaileachoftheaboveitems.

With the destruction of a piece of material, the new surfaces appear, with the layer of molecules of these surfaces acquiring the excess energy, the so-called "surface energy of the body." This energy must be transferred to the body from the outside. The amount of surface energy, depending on the formed surface, is determined by the following dependence [8]:

$$A = A_{уд}\Delta S \qquad (1)$$

whereA – the work, spent on the increment ΔS of the surface; $A_{уд}$ – the work, spent on the formation of a unit of a new surface.

Theoretical calculations and experimental studies, conducted by many researchers,lead to paradoxical conclusions that the real strength of most minerals is two or three orders of magnitude less than the theoretical strength, while the real energy intensity of the destruction of these minerals is three or more orders of magnitude more than the theoretical energy intensity of the formation of a new surface [2, p. 34].

The differences between the theoretical strength of solids and the real one were explained by the works of A. Griffiths and A. Ioffe [9, p. 45-53; 10, p. 145-163]. According to the theory of Griffiths, strength is determined not by regular properties of the solid, but by defects, "inhabiting" it, primarily cracks.Based on this theory, he was the first to formulate an energy strength criterion, according to which a crack in a stressed body with fixed boundaries begins to develop at the moment, when it becomes energetically "profitable"tothe body, namely, when the reduction of the deformation energy of the whole body, which occurred as a result of the crack opening, exceeds the energy of the surface, formed during this opening.

Later on, the results of a series of original studies werepublishedby other scientists, having explained the nature of plastic deformation as a result of kinetic processes, occurring at the atomic level, which are associated with a discrete model of matterstructure. The defects, in this case, are in the atomic structure of the substance itself, for example, vacancies, dislocations, disclinations in crystals [11, p. 140-146; 12, p. 104- 114].

The material destruction process is to be considered as a multi-stage one and as interrelated at different scale levels. For example, it is necessary to consider the collective effects of dislocation systems, disclinations, further cracks, etc. Thus, in [13, 8] in general, the whole process of destruction is proposed to be divided into the following stages: preparatory, embryonic cracks, microcracks, macrocracks, the growth of main cracks. In certain cases, some stages may be missing.

The essential influence on energy costs in grinding is also made by the method of loading pieces of material. Thus, during compression, the elastic deformations in the milled body occur due to its loading in quasi-static or dynamic modes. In this case, the entire volume of the body is subjected to loading. At the same time, it is known that compression is far from being a rational method of destruction, and finally, the destruction occurs in those points of the body, where the tensile stresses are createdabove the critical ones.The entire volume of the piece is subjected to loading, and the work of external forces by the time of destruction becomes close to the value, when it is possible to destroy the whole sample into separate tiny particles, but the destruction occurs only on separate planes with a weakened bond.Therefore, the rest of the energy of elastic deformation, accumulated in the body, will pass into heat, that is, will be irretrievably lost. To reduce the energy consumption for elastic deformations, it would be very promising to carry out the local limit loading of the initial piece in the place of destruction.In this case, in the body the stress gradient will be observed, due to which the energy selectivity of destructionwillbeincreasing. Pilot studies of this method are being carried out in Russia under the leadership of Yu. D. Krasnikovfor the purpose of organizing the destruction of rocks with lower energy costs [14].

Some researchers [15, pp. 68–71] prove that under high speed impact loading, the compression force occurs in a certain section so fast that the crack is formed before the equilibrium distribution of energyissetinthe particle,which is necessary for making a rupture. The experimental studies on impact destruction of glass balls, given in [16, p. 1053-1060], proved that the average work of grinding by impact is approximately 42% of the grinding work by crushing.Inpaper [17] Ye. M. Gutiyar also proves that under dynamic loading of materials the stresses arising are twice higher than under static loading.Apparently, this can be explained by the fact that under high-speed dynamic loading the elastic deformation, uniform throughout the whole volume, is not yet achieved, but due to a larger stress gradient, the destruction begins in the weakened places (sections).Itshould be noted that this position is also theoretically proved in the classical course of resistance of materials [18 p. 516; 19].

When grinding materials by force loading, in addition to elastic deformations, the pieces will be subjected to plastic deformations. G. S. Khodakov [1, p. 124–126] showed in his studies that even such fragile rocks like quartzite and jaspiliteundergo plastic deformation. Thermal losses in the maximum plastic deformation can be more than a half of the entire work of destruction for most materials.

At high loading rates of the body under grinding, the plastic deformation is localized in a relatively small number of atomic layers, located directly in the region of formation of future fracture surfaces. Thus, in order to reduce the costs for plastic deformation, it is also necessary to increase the speed of loading the material with the optimally applied load.

In addition to energy losses for elastic and plastic deformations, a certain part of the energy will be spent on the formation of new defects in the crystal structure. The main part in this process will be occupied by the formation of dislocations. It should be noted that dislocations have a great influence on the strength of crystals.Under the influence of an external load, dislocations easily move, interact with each other and with other defects, unite and come to the surface of the crystal. The very displacement of the structure by at least one row of atoms weakens the crystal, in addition, the dislocations contribute to the formation of embryonic cracks, developing further into cracks of destruction [20, p. 312].

For over a hundred years many researchers have been trying to identify the patterns, permitting to quantify the energy intensity of the grinding process. The first attempt to identify the energy costs for grinding was made by P. Rittinger. According to his hypothesis, it follows that the work, spent on grinding, is proportional to the size of the newly formed surface in the materialunder grinding:

$$A_{пов} = k_{пов}\delta^2 \tag{2}$$

where $k_{пов}$ – the coefficient of proportionality.

By the supporters of this hypothesis,there were conducted numerous studies that prove the validity of the assumption of proportionality of the grinding work to the newly formed surface. However, this hypothesis does not take into account many factors, affecting the consumption energy and, above all, the energy, spent on deformation of the body without destruction.

A bit later, F. Kick and V. Kirpichev [20; 21] independently from each other put forward the hypothesis that the energy, required to obtain the similar changes in the configuration of geometrically similar bodies of the same technological structure, is changing just like the weight or volume of these bodies. Therefore, the work for grinding one piece of size δ will be equal to:

$$A_{об} = k_{об}\delta^3 \tag{3}$$

where $k_{об}$ – the coefficient of proportionality.

The experimental test has shown that the hypothesis of Kick-Kirpichevis more or less true in crushing and completely inadequate in milling.F. Bond [20], believing that the full work should include the work of deformation and formation of new surfaces, proposed to consider the work, spent on the piecegrinding,to be proportional to the geometric average of the volume and surface of the piece:

$$A = A_{об} + A_{пов} = k_Б\delta^{2,5} \tag{4}$$

For ball and rod mills, for hammer crushers and other designs of grinders in thegrinding of certain rocks and ores, on the basis of experimental studies,there were obtained the specific values of the proportionality coefficient $k_Б$ (the so-called W-index of work according to F. Bond).The industrial tests have shown good convergence of recommendations for calculation of energy costs in crushing and milling by Bond's method, which ensured its application in practical calculations.

P. A. Rebinder [20; 21] also combined the hypotheses of Rittinger and Kick-Kirpichev, considering that the destruction occurs after deformation of the piece, and the total work of crushing is equal to the sum of deformation work and new surfaces'formation work:

$$A = A_{об} + A_{пов} = k_{об}\delta^3 + k_{пов}\delta^2 \tag{5}$$

From the physical point of view, the formula of P. A.Rebinder is more correct, since it indicates the multifactorial nature of the destruction process. However, to be limited to only two factors that determine the energy intensity of the grinding process would be wrong, since in the implementation of grindingthere are a lot of other processes, proceeding simultaneously, which can consume a significant part of energy.Let's consider the main ones of them. The significant power consumption in grinding is associated with plastic deformations. Thus, in the work of G. S. Khodakov [1, p.87-89] it is shown that almost all materials are subjected to plastic deformations, no matter how fragile they are.Thus, the analysis of the surface layer of quartz particles after grinding shows that it has not a crystalline, but an amorphous structure, and the thickness of this layer depends on the time and medium, in which the grinding was performed.The calculations show that energy losses on plastic deformations are most significant at a large specific surface area of the material to be destroyed and during a long stay in the grinding zone, i.e. in fine grinding.Even such a fragile material as quartzite is subjected to plastic deformation and the energy losses for its maximum plastic deformation is about half of the entire work of destruction, and for such plastic rocks as marble and limestone – more than 80%. Since with the existing methods of grinding the plastic deformation occurs throughout the whole volume of the destroyed body, the volume of the plastic deformation region of the material's piece is proportional to the volume of this piece:

$$A_{пл} = k_{пл}\delta^3 \tag{6}$$

In addition to energy dissipation for elastic and plastic deformation, as well as energy consumption fornew surfaces' formation, a certain part of the energy will be accumulated by the body in the form of energy of various newly formed defects in the crystal structure. The decisive role in this process will be played by dislocations. The calculations, given in the literature [2, p. 34-35], show that the maximum energy density that the body can store due to dislocation distortions of the crystal structure is of the order

$$B_{к.д.\max} \approx 10^7 \ Дж/м^3 \tag{7}$$

The formation of crystal structure defects will occur in the entire volume of the material, hence the energy of defects, accumulated by the material, is proportional to δ^3, and these losses can be recorded as:

$$A_{д} = k_{д}\delta^3 \tag{8}$$

The most significant energy consumption (especially in ball mills) occurs due to external friction, which is caused by resistance, arising between the particles, contacting under the action of the compressive load, with their relative movement in the plane of contact.External friction is the result of mechanical engagement and molecular adhesion between the surfaces and further elastic and plastic displacement and scratching of the material out, with the subsequent destruction and restoration of molecular bridges between the friction surfaces.Thebulk of energy costs for external friction is not"accumulated " by the material's particles and all the more does not go to the formation of new surfaces, but dissipates into heat. Therefore, the larger the layer of material in the industrial apparatus and the higher the relative speed of the friction surfaces, the higher the energy consumption for external friction.This is confirmed by the works of German scientists of G. Rumpf's school [22, p. 79-85], which showed that the main energy losses in ball mills occur due to interaction of the material's particles.

According to calculations, made by Revnivtsev, the costs for friction of one piece are proportional to the linear size δ of the latter in the degree of 2.5. Then the costs for friction will be:

$$A_{тр} = k_{тр}\delta^{2,5} \tag{9}$$

To complete the physical picture of costs for grinding, it is necessary to take into account the costs, associated with various types of radiation. First of all, these include the acoustic waves. In the general balance of energy consumption for grinding they are small. Since radiation comes as a rule from the surface layers of the newly formed surface, these costs can be taken into account by the following expression:

$$A_{изл} = k_{изл}\delta^2 \tag{10}$$

Deeming, that we have considered all the main known energy costs for grinding, the total costs will be equal to the amount of costs for volume and plastic deformations, formation of defects, formation of a new surface, external friction and radiation:

$$\begin{aligned} A &= A_{об} + A_{пов} + A_{пл} + A_{д} + A_{тр} + A_{изл} = \\ &= k_{об}\delta^3 + k_{пов}\delta^2 + k_{пл}\delta^3 + k_{д}\delta^3 + k_{тр}\delta^{2,5} + k_{изл}\delta^2 \end{aligned} \tag{11}$$

Each of the terms of this equation reflects a certain type of energy costs for processes, taking place in the grinder, and only the fourth term of the formula takes into account the useful work, spent on the formation of new surfaces. The percentage of each of the members of series (11) is not a constant value and will vary for different cases, depending on the nature of the material to be destructed, its size, the grinder's design and geometrical parameters.

The analysis of published works shows that in fine grinding of materials in the industrial designs of mills the value of useful costs, determined by the second member of the formula, does not exceed 3 percent of the total energy costs.

Of course, for further development of the grinding technology, it is necessary to develop successfully such sciences as solid state physics, fracture mechanics, etc. As for making some new "laws" of crushing, here the followingshould be noted. The natural heterogeneity of the materials, subjected to grinding, the unevenness of the stress field in the volume of the loaded piece, its anisotropy, multi-scale defects plus a variety of external factors (shape, material location, nature of movement of the machine's working parts, location of the crushed materialpieces, etc.) – make the problem of making the law of crushing, reflecting all aspects of modern technologies in terms of physics of this process, firstly, super-complex due to agreat number of parameters, and secondly, useless, because even in the hypothetical case, to use the record of a full formula of such a law would be impossible due to itsvastnesses.

In such a situation, it is quite natural that instead of the physical law for practical application there are more acceptablesimple statistical dependencies, convenient and describing close enough the phenomena in a certain range of each of the parameters of a certain design of agrinder.

However, the main task, facing both the theory and the practice of grinding, is to reduce the energy consumption in the implementation of this process. For this purpose, it is necessary to create fundamentally new, incomparably more effective methods of grinding, taking into account both the features of the natural properties of a particular material and the specifics of its further processing.First of all, it is necessary to work on the creation of more advanced designs of mills, in which the irretrievable energy losses, indicated in equation (11) by the first, third, fifth and sixth members,could be reduced to a minimum. The ways to solve this problem can be found in a detailed analysis of energy consumption items for specific structures, currently operated in the industrial production of grinding units [23-32].

Our critical analysis of the grinding process shows that the process of fine grinding (milling) is very energy-intensive, although the share of energy, spent on the disintegration of particles itself is very small and is equal to several percents. This occurs primarily due to imperfection of organization of the grinding processitself and due tolow efficiency of the equipment,applied for these purposes.

To reduce energy costs, a rational organization of the grinding process should be provided, with optimal process conditions without excessive overgrinding with minimal effort and a high degree of destruction in one working cycle.

The lowest energy intensity of the grinding process is achieved in grinding by impact and slightly worse - by crushing.

When grinding by impact, the loading of the material should be pulsed with the steepest front; the loads should be dosed, corresponding to the strength and endurance of the defective zones.

To the working zone of the mill the starting material should be supplied in small volumes and even better piece by piece, and after grinding - quickly removed from the milling zone to the classifier. Therefore, any mill should operate in a closed cycle.

The classifier must be of highefficiency, so that to the finished product there came the particles of only smaller than the near-mesh grain, and the large fraction, returned forre-milling, contained as few particles of the finished product as possible.

Conclusions.

For the process of grinding solid materials there iscarried out the analysis of energy costs for formation of new surfaces, elastic and plastic deformations,formation of various kinds of defects in the crystal structure, for friction of the material's particles between themselves and the walls of the grinding chamber, as well as for various kinds of radiation (acoustic waves, exoelectronic emission, etc.), which always accompany the destruction.

It is noted that the lowest energy intensity of the grinding process is achieved in grinding by impact and slightly worse -by crushing.

The recommendations are developed for organization of the optimal implementation of the processes of grinding and classification of solid materials.

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ҰСАҚТАУ БАРЫСЫНДАҒЫ МЕНШІКТІ ЭНЕРГИЯ ШЫҒЫНДАРЫН ТӨМЕНДЕТУДІҢ КЕЛЕШЕКТІ БАҒЫТТАРЫ

Аннотация. Ұсақтау процесі әр түрлі технологияларда кеңінен қолданыс табады және жоғары энергия тұтынумен ерекшеленеді. Одан басқа, ұсақтағыштың жұмыс элементтерінің тозуына байланысты жоғары сапалы болаттың қайтарымсыз жоғалулары болады.

Жоғары энергетикалық шығындар тек өңделетін материалдардың ауқымды көлемінен ғана емес, ұсақтаушы машиналардың аса төмен тиімділігімен түсіндіріледі, олардың пайдалы әсер коэффициенті (ПӘК) әрі кетсе бірнеше пайызды құрайды. Әсіресе материалдың ұнтақтық жұқалығы үлкеюімен диірменнің жетегінің қуаты артып бірден ПӘК-і төмендейді.

Ұсақтаудың жаңа әдістеріне қарамастан: электргидравликалық, ультрадыбысты, гравитационды, жарық сәулесімен ұсақтау және т.б., өнеркәсіптік агрегаттардың барлық конструкцияларында ұсақтау мыжғылау, уату, соққы, ұнтақтау, сындыру сияқты механикалық тәсілдермен немесе осы тәсілдерді үйлестірумен жүзеге асырылады.

Жаңа беттердің пайда болуына кететін энергия шығындарына, серпімділік және пластикалық деформациясына, кристалды құрылымның әр түрлі ақау түрлерінің пайда болуына (негізінен дислокация), ұсақтағыш камера қабырғалары мен материал бөлшектерінің өзара үйкелісіне сараптама жүргізілді. Жеткізілетін энергияның шамалы бөлігі әрқашан қиратуларды сүйемелдейтін әр түрлі сәулеленулерге (акусттикалық толқындарға, экзоэлектронды эмиссияға) жұмсалатыны атап көрсетілді.

Жүргізілген сараптамадан ұсақтау процесінің неғұрлым төмен энергия сыйымдылығы соққы есебінен ұсақтау кезінде және біршама нашар мыжғылау есебінен қол жеткізілетінін аңғаруға болады. Соққылаумен ұсақтау кезінде материалдың жүктелуі импульсты максималды кілт аймақты болуы қажет. Жүктеме ақаулы аймақтың төзімділігі мен беріктілігіне сәйкес мөлшерлі болуы қажет.

Диірменнің жұмыс аймағына бастапқы материал шағын көлемде түсуі қажет, даналап болса тіптен жақсы және ұсақталғаннан соң ұнтақтау аймағынан жылдам шеттетіліп классификаторға жөнелтілуі қажет. Сәйкесінше, кез-келген диірмен тұйық циклда жұмыс жасауы қажет.

Дайын өнімге тек шектес бидайдан кіші бөлшектер түсу үшін, ал майдалауға қайтарылатын ірі фракция дайын өнімнің мүмкіндігінше аз бөлшегін құрауы үшін классификатор жоғары тиімділікке ие болуы қажет.

Түйін сөздер: ұсақтағыштар, диірмендер, энерго шығындар, ұнтақтыңжұқалығы, мыжғылау, уату, майдалау, сындырылу, соққы, классификатор, тұйық цикл.

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ПЕРСПЕКТИВНЫЕ НАПРАВЛЕНИЯ СНИЖЕНИЯ УДЕЛЬНЫХ ЭНЕРГОЗАТРАТ ПРИ ИЗМЕЛЬЧЕНИИ

Аннотация. Процесс измельчения находит широкое применение в различных технологиях и отличается высоким энергопотреблением. Кроме того, происходит безвозвратная потеря высококачественной стали из-за износа рабочих элементов измельчителей.

Высокие энергетические затраты объясняются не только большими объемами перерабатываемых материалов, но и чрезвычайно низкой эффективностью измельчающих машин, особенно мельниц, коэффициент полезного действия (КПД) которых составляет в лучшем случае несколько процентов. Особенно резко снижается КПД и возрастает мощность привода мельниц с увеличением тонины помола материала.

Несмотря на новые способы измельчения: электрогидравлический, ультразвуковой, гравитационный, измельчение световым лучом и т.д., во всех конструкциях промышленных агрегатов измельчение осуществляется механическими способами, такими как раздавливание, раскалывание, удар, истирание, разламывание или сочетанием этих способов.

Проведен анализ затрат энергии на образование новых поверхностей, на упругие и пластические деформации, на образование различного рода дефектов кристаллической структуры (в основном дислокаций), на трение частиц материала между собой и стенками измельчающей камеры. Отмечено, что незначительная часть подводимой энергии расходуется наразличного рода излучения (акустические волны, экзоэлектронную эмиссию и т.д.), которые всегда сопровождают разрушение.

Из проведенного анализа следует, что наиболее низкая энергоемкость процесса измельчения достигается при измельчении за счет удара и несколько хуже за счет раздавливания.При измельчении ударом нагружение материала должно быть импульсным с максимально крутым фронтом.Нагрузки должны быть дозированными соответствующими прочности и выносливости дефектных зон.

В рабочую зону мельницы исходный материал должен поступать в небольших объемах, а еще лучше поштучно и после измельчения быстро удаляться из зоны помола в классификатор. Следовательно, любая мельница должна работать в замкнутом цикле.

Классификатор должен обладать высокой эффективностью, чтобы в готовый продукт попадали частицы только меньше граничного зерна, а возвращаемая на домол крупная фракция содержала как можно меньше частиц готового продукта.

Ключевые слова: измельчители, мельницы, энергозатраты,тонина помола, раздавливание, раскалывание, истирание, разламывание, удар, классификатор, замкнутый цикл

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OBTAINING AND STABILIZATION OF NANOSULFUR

Abstract. On the basis of sodium thiosulfate in the presence of sodium sulfite and solid organic acids – citric and oxalic - sulfur nanoparticles were synthesized. By the method of spectrophotometry, it was shown that efficient for the synthesis of sulfur is the using of the molar ratio of $[Na_2S_2O_3]/[Na_2SO_3]$ 1:0.5 and of the catalyst is oxalic acid. Nonionic polymer polyethylene glycol (PEG) was used for stabilizing sulfur particles. By methods of light scattering, electron and light microscopy it is shown that the stabilizing effect of the polymer is achieved at a concentration of 10^{-3}base-mol/L, and a further increasing of the concentration of PEG leads to aggregation processes. The size of the obtained particles is determined on the Zetasizer Nano device. It was found that in the presence of PEG concentrations of 10^{-3} - 10^{-2}base-mol/L, the size of sulfur particles decreases from 321.8 nm to 259.1 nm and 270.4 nm, respectively.

Key words: sulfur, nanoparticles, stabilization, polyethylene glycol.

Interaction

With the development of industry, demand for elemental sulfur as raw material for many chemical products is continuously increasing. There are various applications of sulfur nanoparticles in nowadays, the most important fields of applications are: in electrochemistry, sulfur nanoparticle was used to enhance the electrochemical activity of lithium batterythrough a solution-based technique; as catalysis, for example, elemental sulfur nanoparticles can dramatically enhance the rate of Cr(VI) reduction; in medical sphere, using of anticancer, antibacterial properties of sulfur nanoparticles significantly increasing too.

It is known that sodium thiosulfate in an acidic medium decomposes with the release of sulfur in a finely dispersed state. The stability of the sulfur produced depends on the initial amounts of sodium thiosulfate and acid. According to this method, we previously synthesized colloidal sulfur particles [5]. It is shown that the size of the obtained colloidal sulfur particles increases from 250 nm to 4500 nm in 90 hours after the beginning of the experiment with some subsequent reduction. The increase in the particle size is justified by the aggregation of sulfur particles, and the decrease by the stabilizing action of the acid.

Aggregation of sulfur particles is a completely expected phenomenon due to its high hydrophobicity. Meanwhile, the preservation of the dispersion sulfur particles is very important in its practical use, since the magnitude of its adsorption on the stems and leaves of plants, tissues of living organisms will be determined by the specific surface of the powder particles. In this regard, the aim of the study is the synthesis and stabilization of nanosulfur.

Experimental part

Synthesis of sulfur particles was carried out according to the procedure described in [5]. We use solutions of sodium thiosulfate and sodium sulfite with a concentration of 0.001 mol / L. The use of such low concentrations of starting reagents is due to the fact that the abundant formation of a sulfur precipitate makes it difficult to measure the optical density of a sulfur suspension. Solid organic acids (SOA) were used as a catalyst for the synthesis process: citric and oxalic.

For the synthesis on solid substrates glass and polyethylene plateswere used, which were washed in distilled water and ethyl alcohol before using. Then the starting solutions of sodium thiosulfate and sodium sulfite (0.5 ml each) were mixed on the surface of the substrates, after 60 minutes the substrate with the resulting sulfurwas washed with distilled water and air-dried.

To stabilize the synthesized sulfur in the solution volume, a solution of polyethylene glycol (PEG) was introduced into the reaction mixture. The polymer solution was mixed with a solution of thiosulfate, then a sulfite solution and solid acid crystals were added to the resulting mixture.

Results and discussion

The process of sulfur formation is accompanied by turbidity of the reaction mixture, so the most convenient method for studying this process is spectrophotometry. Table 1 presents data on sulfur synthesis using various molar ratios [$Na_2S_2O_3$]/[Na_2SO_3] and two solid organic acids: citric and oxalic. As can be seen from the table, the use of different ratios of the initial reagents causes significant differences in the optical density of these systems: at [$Na_2S_2O_3$]/[Na_2SO_3] equal to 1: 1, the optical density of the mixture is in the range 0.08-0.12. When switching to a system with the ratio [$Na_2S_2O_3$]/[Na_2SO_3] equal to 1: 0.5, the optical density increases significantly, so the initial reagents were used in the ratio 1: 0.5. In addition, the data in Table 1 show that when usingoxalic acid as the catalyst for the reaction, the optical density of the system is higher than in the presence of citric acid.

Table1 - Ratio of reagents for obtaining nanoparticles of sulfur

№ of exp	Ratio [$Na_2S_2O_3$]/ [Na_2SO_3]	Mass of citric acid, g	Mass of oxalic acid, g	D
1	1:1	0,2	-	0,08
2	1:1	-	0,2	0,12
3	1:0,5	0,2	-	0,36
4	1:0,5	-	0,2	0,40

The advantage of using solid organic acids for sulfur synthesis indicates the possibility of intensifying the synthesis process by using solid substrates of various types. The results of experiments on the use of plates of glass and polyethylene as substrates are shown in Fig. 1.

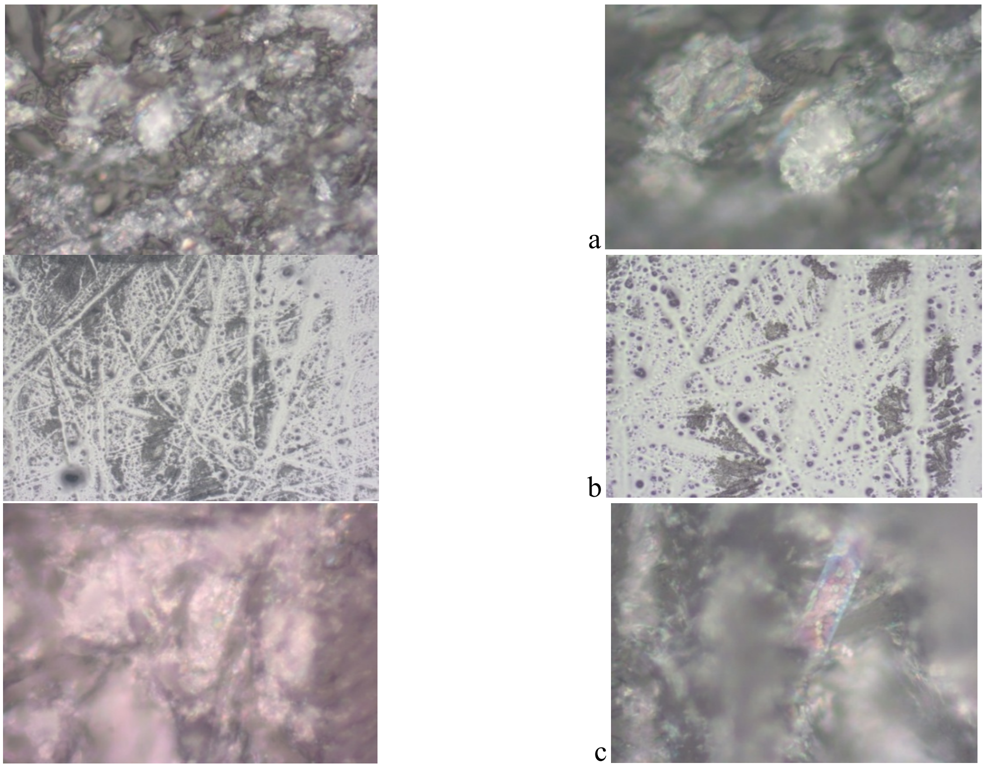


Figure 1 - Preparation of sulfur particles on the surface of glass (a) and polyethylene (b, c) in the presence of oxalic (a, c) and citric (b) acids. Magnification: x1000

As can be seen from Fig. 1a, on the surface of the glass the sulfur particles are in the form of large aggregates. On the surface of the polymer material (Fig. 1b, c), the sulfur particles are distributed more evenly. This difference in the distribution of sulfur particles on polymeric and inorganic materials can be explained by the high affinity of hydrophobic sulfur to the polyethylene substrate. At the same time, attention is drawn to the formation of an openwork mesh on the polymer when citric acid is used as a catalyst. This probably can also be due to the different hydrophobicity of the SOA molecules: citric acid is a tribasic acid, and oxalic is a dibasic acid.

Therefore, a more hydrophobic oxalic acid contributes to a more even distribution of sulfur particles on the non-polar surface. Nevertheless, the absence of separate sulfur particles on the light microscopy data indicates that the process of their aggravation has proceeded, which is a consequence of the high hydrophobicity of the sulfur particles.

Various high- and low-molecular surfactants can be used to stabilize and modify sulfur particles [6-8]. The use of a high molecular weight compound - polyethylene glycol (PEG) as a stabilizer can be very effective, since the -OH groups of the polymer can provide a high degree of lyophilization to the treated sulfur particles. The use of the PEG solution in the concentration range 10^{-5}-10^{-2} base-mol /L (Figure 2) showed that the polymer exerts a significant stabilizing effect on the system. If in the absence of PEG in the reaction mixture a monotonic increase in the optical density is observed with time, then in the presence of PEG, the optical density growth stops after 4-5 minutes after mixing the initial reagents, sodium thiosulfate,and sodium sulfite. In this case, the optical density of the mixture (D) in the presence of a PEG concentration of 10^{-3} base-mol /L is much higher than when using a lower-concentration PEG solution - 10^{-5}base-mol / L, and increasing the concentration from 10^{-3} to 10^{-2}, the base-mole / L does not show any difference in the D values, which may be due to the achievement in the case of PEG use of a concentration of 10^{-3}base-mole / L of the amount of polymer necessary to protect the sulfur particles from aggregation.

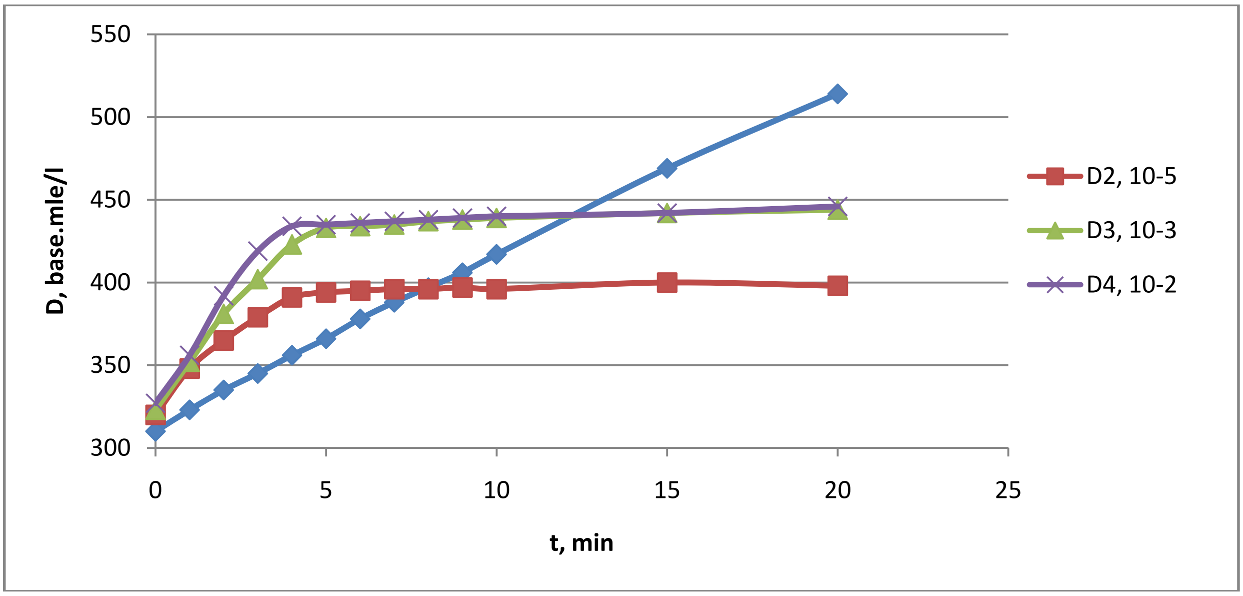
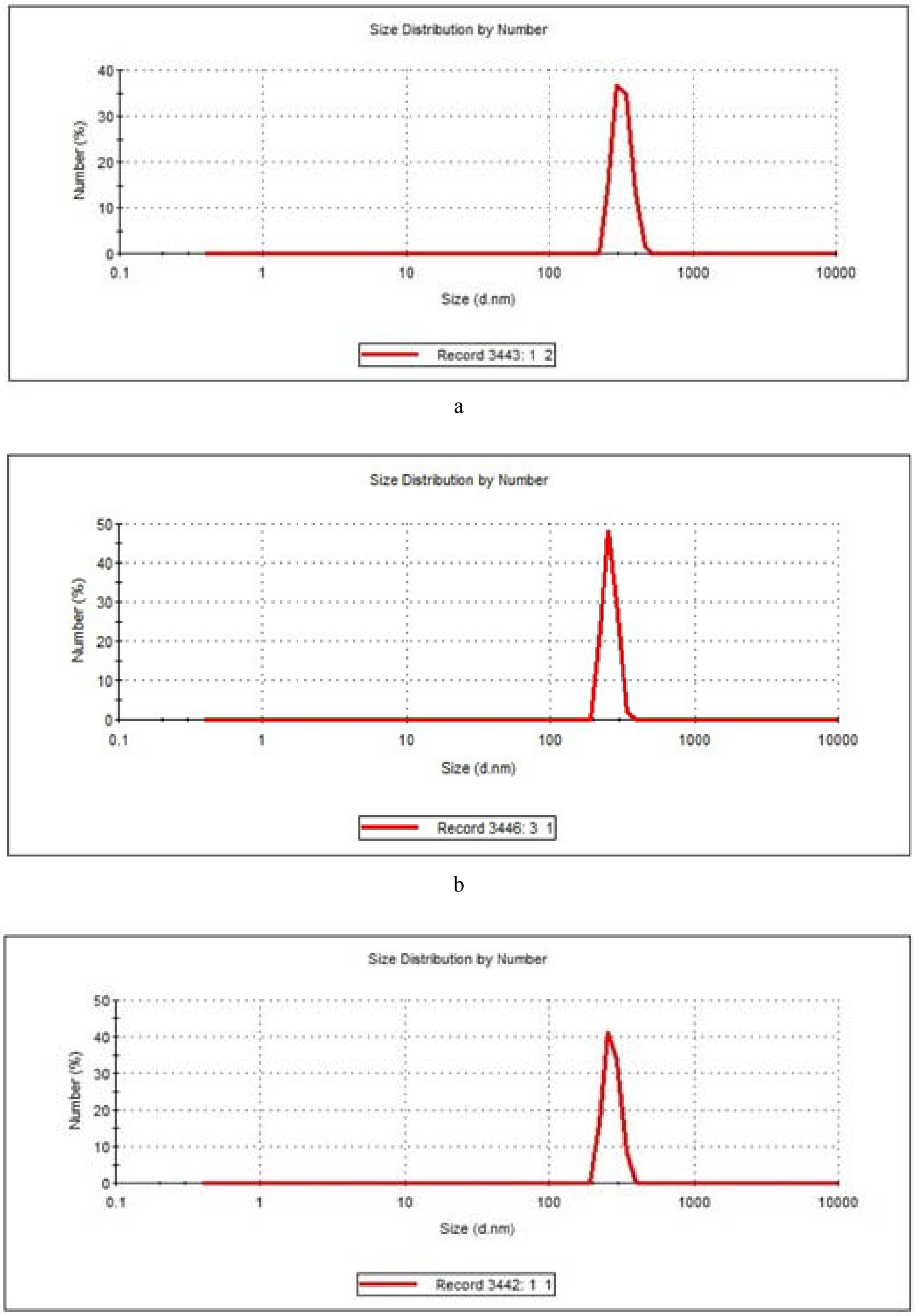


Figure 2 - The change in the optical density of the sulfur suspension in time in the absence (1) and the presence of PEG concentrations of 10^{-5}base-mol/L(2); 10^{-3} base-mol/L (3) and 10^{-2} base-mol/L (4)

The method of dynamic light scattering determines the size of the obtained sulfur particles. The particle size distribution of the sulfur obtained in the absence and presence of PEG (Figure 3) shows that the most probable particle size of sulfur without the addition of a stabilizer is 321.8 nm. Introduction to the PEG system of concentration 10^{-3} base-mol/Lleads to a reduction in particle size to 259.1 nm. In the case of PEG, a concentration of 10^{-2} base.mole / L, the average particle size is 270.4 nm. Another difference in the distribution curves in the absence and presence of PEG is the height and width of the peaks. If the scattering intensity for sulfur particles in the absence of a stabilizer was 36%, then in the presence of a polymer it rises to 48% and 41% in solutions with a PEG concentration of 10^{-3} and 10^{-2} base-mol/L, respectively. In addition, the width of the peaks here is much less than in the case of an unstabilized sulfur suspension, that is, in these mixtures, the particles are predominantly close in size to each other. From these data, it follows that at a PEG concentration of 10-3 base-mol/L, a significant stabilizing effect is achieved in the system. A further increase in the concentration of the polymer can cause the system to become unstable due to flocculation processes as a result of hydrophobic interactions between the "loops" and "tails" of adsorbed polymer macromolecules.



a

b

c

Figure 3 - The size distribution curves of sulfur particles in the absence (a) and in the presence of PEG concentrations of 10^{-3} base-mol/L(b) and 10^{-2} base-mol/L (c)

In figure 4 shows electron microscopic images of sulfur particles obtained in the presence of various concentrations of PEG. The smallest particles in the photographs are also observed at a PEG concentration of 10^{-3} base-mol/L.

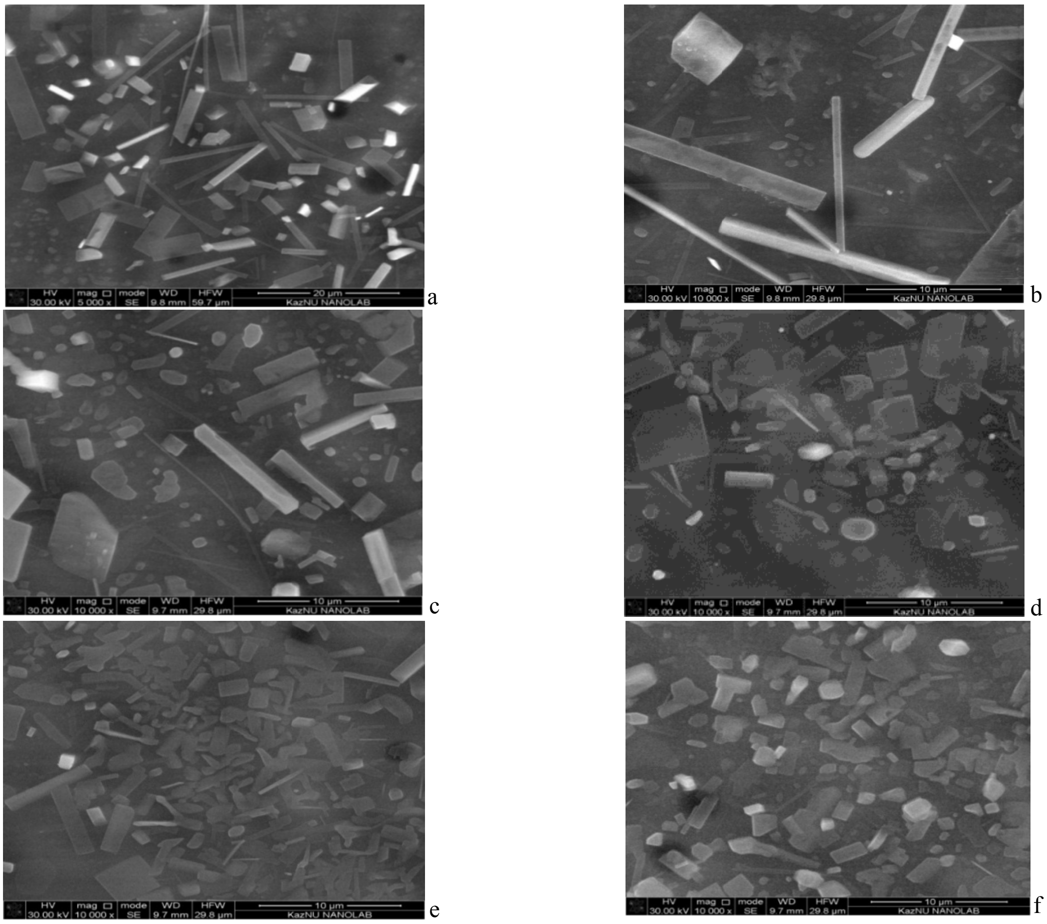


Figure 4 - Electron microscopic images of sulfur particles obtained in the absence of (a, b) and in the presence of PEG concentrations of 10^{-5} base-mol/L (c); 10-4 mol / l (d); 10^{-3} base-mol/L (e) and 10^{-2} base-mol/L (f)

The electron microscopy data also confirm the assumption of the protective effect of PEG (Figure 4). As can be seen from Fig. 4, the introduction of a solution of PEG into the reaction mixture decrease particle size of sulfur. The stabilizing effect of a nonionic polymer-PEGmay be due to adsorption of macromolecules by non-polar regions on the surface of sulfur particles. In this case, the polar functional groups of the polymer will be turned into a solution, imparting hydrophilicity to the sulfur particles. However, one should take into account the need to select a sufficient polymer concentration for the stabilization of dispersed particles. The lack of polymer cannot provide complete protection of particles from sticking, and excess leads to aggregation. At the same time, it should be noted that, in order to intensify the stabilization processes, it is probably necessary to study the kinetics of the process.

Conclusion

On the basis of sodium thiosulfate and sodium sulfite in the presence of solid organic acids - citric and oxalic - sulfur nanoparticles have been synthesized. Comparison of the effect of catalysts shows that the use of oxalic acid is more effective for the synthesis of sulfur. To stabilize the sulfur nanoparticles was used a nonionic polymer, polyethylene glycol. It is shown that the stabilizing effect of the polymer is achieved at a concentration of 10^{-3}base-mol/L. The size of the particles obtained is determined by light scattering. It was found that in the presence of PEG with concentrations 10^{-3} to10^{-2} base-mole /Ll, the particle size of sulfur decreases from 321.8 nm to 259.1 nm and 270.4 nm, respectively.

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НАНОКҮКІРТТІ АЛУ ЖӘНЕ ТҰРАҚТАНДЫРУ

Аннотация. Натрий тиосульфаты негізінде натрий сульфиты және қатты органикалық қышқылдар – лимон және қымыздық қышқылдары - қатысуымен күкірттің нанобөлшектері синтезделген. Спектрофото-метрия әдісімен күкіртті синтездеу үшін [Na2S2O3]/[Na2SO3] 1:0,5 мольдік арақатынасын және катализатор ретінде қымыздық қышқылын пайдаланудың тиімділігі көрсетілді. Күкіртті тұрақтандыру үшін иондық емес полимер - полиэтиленгликоль (ПЭГ) таңдалынды. Сәулені шашырату, электрондық микроскопия және сәуле микроскопиясы әдістерімен полимердің тұрақтандыру әрекеті оның 10-3 негіз-моль/л концентрациясында іске асатындығы, ал концентрацияны одан әрі ұлғайту агрегациялық үдерістерге апаратындығы көрсетілді. Zetasizer Nano құрылығысында алынған бөлшектердің өлшемі анықталды. Концентрациясы 10-3 - 10-2 негіз-моль/л ПЭГ қатысында күкірт бөлшектерінің өлшемі 321,8 нм-ден 259,1 нм және 270,4 нм-ге дейін төмен-дейтіндігі көрсетілді.

Түйін сөздер: күкірт, нанобөлшектер, тұрақтандыру, полиэтиленгликоль.

УДК 544.77

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ПОЛУЧЕНИЕ И СТАБИЛИЗАЦИЯ НАНОСЕРЫ

Аннотация. На основе тиосульфата натрия в присутствии сульфита натрия и твердых органических кислот – лимонной и щавелевой - синтезированы наночастицы серы. Методом спектрофотометрии показано, что эффективным для синтеза серы является использование мольного соотношения [$Na_2S_2O_3$]/[Na_2SO_3] 1:0,5 и катализатора - щавелевой кислоты.

Для стабилизации серы использовали неионный полимер полиэтиленгликоль (ПЭГ). Методами свето-рассеяния, электронной и световой микроскопии показано, что стабилизирующее действие полимера дости-гается при концентрации 10^{-3} осново-моль/л, а дальнейшее увеличение концентрации ПЭГ ведет к агрега-ционым процессам. На приборе Zetasizer Nano определен размер полученных частиц. Установлено, что в присутствии ПЭГ концентрации 10^{-3} - 10^{-2} осново-моль/л размер частиц серы уменьшается от 321,8 нм до 259,1 нм и 270,4 нм соответственно.

Ключевые слова: сера, наночастицы, стабилизация, полиэтиленгликоль.

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THE RMODYNAMIC ASSESSMENT OF SMELTING OF MANGANESE AND CHROMIUM FERROALLOYS BASED ON THE ANALYSIS OF THEIR STATE DIAGRAMS

Abstract. This paper proposes a technique for extracting thermodynamic data from state diagrams, which are based on the modified Schroeder-Le Chatelier equation allowing to describe the lines of phase equilibria of binary systems by mathematical expressions. We showed the possibility to apply the equation of dependence of the Bjerrum-Guggenheim coefficient for the area of iron crystallization on the activity of iron of an ideal solution α-γ for binary systems Fe-Si, Fe-Cr, Fe-Mn, Fe-Al. The calculated partial excess entropy, enthalpy and the Gibbs energies of mixing of the liquidus components of the said systems are proposed.

Key words: complex alloys, ferrosilicoaluminum, modified Schroeder- Le Chatelier equation, Bjerrum-Guggenheim coefficient, partial excess enthalpy (ΔH^E), entropy (ΔS^E) and the Gibbs energy of mixing (G^M) of liquidus component.

When smelting steel and special alloys, the ferroalloys obtained by alloying ferrosilicium and aluminum, produced from very scarce materials such as quartzite, metal shavings, bauxite, etc., are used as a reducing agent and a deoxidizing agent. For the first time in the world practice, a process for obtaining complex silicon-aluminum alloys under the general name of ferrosilicoaluminum has been developed.

When using ferrosilicoaluminum as a metal reducing agent while smelting refined grades of Mn, Cr and Ti the question arises as to how exactly aluminum and silicon in a complex will behave themselves in these alloys, since an alien metal (aluminum - when smelting ferromanganese and a low-carbon ferrochrome, and silicium - when smelting ferrotitanium) is additionally introduced into the system. Whether strong heteropolar (ionic, covalent, metallic) bonds of aluminum in the melts of Mn-Si-Fe, Si-Cr-Fe systems, and those of silicium - in the melt of Al-Ti-Fe system will be formed. If in the corresponding systems in the field of compositions of traditional refined ferroalloys they will experience negative deviations from ideality and they are not inclined to form various complex associates, then there will not be any obstacle in using a novel ferrosilicoaluminum in metallurgy as a metal reducing agent.

The state diagrams clearly reflect the nature of the interaction of components in the melt, its phase composition and the structure of alloys under conditions of stable thermodynamic equilibrium. Consequently, they contain all the fundamental and important data on the thermodynamic properties of phases and components.

The analysis of the state diagrams and the developed technique of mathematical description of the phase equilibrium line in terms of the Bjerrum-Guggenheim concept (Φ) showed that since this coefficient characterizes a degree of deviation of the energy state of a given component under equilibrium conditions from ideality, then using it, it is possible to determine a magnitude and a sign of the exchange energy between the components, and this deviation being the greater, the stronger the interparticle interaction between the components is ($\Phi > 1$ is a negative deviation from ideality, $\Phi < 1$, is a positive deviation from ideality) [1-3].

The developed technique of mathematical description of the lines of phase equilibria allowed to solve the direct Gibbs problem correctly, namely, to obtain an analytical dependence of the phase compositions on the temperature at phase equilibria based on the laws of phase formation. It is shown that by means of the osmotic Bjerrum-Guggenheim coefficient (Φ_i), a real equilibrium in the system under study can be determined in detail and its correct analytical expression be obtained [4-6].

The solution of the inverse Gibbs problem is in extracting the thermodynamic information contained in the state diagram provided that the mathematical problem of phase equilibria is solved correctly [7].

We have solved the first stage of the Gibbs inverse problem, i.e., we have obtained the modified Schroeder-Le Chatelier equation, allowing to describe analytically the liquidus and solidus lines. In this connection, let us consider the way of deriving analytical expressions for the partial excess enthalpy ($\Delta H^{M(E)}$) and entropy(ΔS^E) of mixing the liquidus component in the systems with the ratio of $\Phi_i = A_i + B_i \cdot a_i$.

The difference between the thermodynamic mixing function G^M for a real solution and the value of this function for an ideal solution $G_{id}^{'м}$ at the same T and p is called an excess thermodynamic function.

Therefore,

$$\Delta G_i^E = RT\ln j_i. \tag{1}$$

The relationship between the activity coefficient and the Bjerrum-Guggenheim coefficient is established as follows:

$$\Phi_i = \frac{\Delta G_{m,i}^{S\to L}}{\Delta G_{m,i}^{id}} = \frac{\Delta\mu_i^L - \Delta\mu_i^S}{\Delta\mu_{i,id}^L - \Delta\mu_{i,id}^S} = \frac{\ln(a_i^L/a_i^S)}{\ln(x_i^L/x_i^S)} = 1 + \frac{\ln\gamma_i^L/\ln\gamma_i^S}{\ln x_i^L/\ln x_i^S}, \tag{2}$$

where $\Delta G_{m,i}^{S\to L}$ is the Gibbs energy of melting of the component relates to its ideal component $\Delta G_{m,i,id}^{S\to L}$ = $RT\ln X_i^L - RT\ln X_i^S$.

Let us express the coefficient of activity in terms of the Bjerrum-Guggenheim osmotic coefficient. In the physicochemical literature, this coefficient is called an osmotic coefficient [8] and it establishes a relationship between the activity and concentration of the component in the solution, which substantially differs from the analogous relationship between the activity coefficient and concentration:

$$\ln a_i = \Phi_i \ln x_i.$$

Since we are considering the variation of the quantity F_i along the line of phase equilibria, hence, it depends on the temperature and on the composition of equilibrium phases. At the same time, as can be seen from expression (2), this quantity is a dimensionless quantity. Its identity with a well-known osmosis is shown below.

The thermodynamic classification of solutions is based on the nature of the equations for the chemical potentials of the solution components. In an ideal solution, the following expression is true for each component:

$$\mu_i^{id}(T,P,X) = \mu_i^0(T,P) + RT\ln X_i, \tag{3}$$

where μ_i^0 - is a standard chemical potential of an i-th substance in a standard state; X_i - is the molar concentration of the i-component in the solution; member $RT\ln X_i$ - corresponds to a change of the chemical potential due to the mixing (when forming an ideal solution).

By analogy with equation (3), the dependence of chemical potentials of a nonideal solution on the concentration can be written [7] in the form of:

$$\mu_i(T,P,X) = \mu_i^0(T,P) + RT\ln\gamma_i X_i, \tag{4}$$

where γ_i is an activity coefficient.

The general condition of ideality is that for an ideal solution throughout the entire concentration range the following condition is satisfied:

$$\gamma_i(T,P,X_1,\ldots,X_{k-1}) = 1 \ (i = 1,2,\ldots,k).$$

An advantage of using the coefficient of activity is that it allows to preserve a formal similarity of the expressions for the thermodynamic properties of real solutions with the equations for nonideal solutions. The activity coefficient of a solvent in contrast to the activity coefficients of the dissolved components from purely arithmetic considerations is not the most suitable function for measuring deviations from ideality. Therefore, instead of the activity coefficient for the solvent, it is more convenient to use another correction factor called the osmotic coefficient of Bjerrum-Guggenheim [9, 10], which is introduced in the following way:

$$\mu_1(T,P,X) = \mu_1^0(T,P) + \Phi_1 \cdot RT \cdot \ln X_1, \tag{5}$$

where Φ_1 is the osmotic coefficient of Bjerrum and Guggenheim of a solvent $\Phi \to 1$ at $X_1 \to 1$ and $X_{2,3} \ldots \to 0$.

Comparing the expression $\ln a_i = \Phi_i \ln x_i$ with equation (5), we will find that

$$\Phi - 1 = \frac{\ln\gamma_i}{\ln X_i} \text{ or } \Phi = \frac{\ln a_i}{\ln X_i}. \tag{6}$$

Therefore, the activity coefficient can be expressed as follows:

$$\ln j_i = (\Phi - 1)\ln x_i.$$

To calculate the partial excess thermodynamic mixing functions of the liquidus component we have the initial data:

$$\Phi_i = A_i + B_i \cdot a_i; \tag{7}$$

$$a_i = \exp\left[\frac{\Delta H_{m,i}}{R}\left(\frac{1}{T_{m,1}} - \frac{1}{T}\right)\right]; \tag{8}$$

$$\ln x_i = \frac{\Delta H_{m,i}}{R \cdot \Phi_i} \cdot \left(\frac{1}{T_{m,1}} - \frac{1}{T}\right)_0; \tag{9}$$

$$\left(\frac{d\Delta G_i^E}{dT}\right)_{x,p} = -\Delta S_i^E;\ \Delta G_i^E = \Delta H_i^{E(M)} - T\Delta S_i^E. \tag{10}$$

When differentiating function ΔG_i^E with respect to T at x = const

$$(\Delta G_i^E) = -\Delta S_i^E = [RT(\Phi_i - 1)\ln x] = R\cdot \ln x(\Phi_i - 1 + T\cdot \Phi'_i) =$$

$$R\ln x(\Phi_i - 1 + T\cdot B_i\cdot a_i\cdot \frac{\Delta H_{m,i}}{R}\cdot\frac{1}{T^2}); \qquad (11)$$

$$\Delta S_i^E = -R\ln x(\Phi_i - 1 + B_i\cdot a_i\,\frac{\Delta H_{m,i}}{RT}); \qquad (12)$$

$$\Delta H_i^{E(M)} = -B_i\cdot a_i\cdot \Delta H_{m,i}\cdot \ln x_i. \qquad (13)$$

For Fe-Mn, Fe-Cr, Fe-Si, Fe-Al systems under consideration we assumed the following thermodynamic characteristics of iron: $\Delta H_{melt,\,Fe}$= 15190.384 J/mole, $T_{melt,\,Fe}$= 1811 K [11].

Calculation of excess thermodynamic mixing functions in Mn-based systems.

The initial data are taken from [12] and presented in Table 1.

Table 1 - Input parameters for calculating thermodynamic data in Fe-Mn system

No. in sequence	T,K	$X^L_{op.\ Fe}$	LnX^L_{Fe}	Φ'_{Fe}	Φ''_{Fe}	a^L_{Fe}	1/T
1	1749	0.875	0	1.991	-0.136	1	5.534
2	1723	0.821	5.1512E-05	2.502	-0.153	0.992	5.577
3	1698	0.755	8.2152E-05	2.869	-0.165	0.986	5.608
4	1673	0.686	0.00010884	3.239	-0.178	0.98	5.64
5	1648	0.617	0.00013234	3.611	-0.190	0.975	5.672
6	1623	0.542	0.00015321	3.984	-0.203	0.969	5.704
7	1598	0.469	0.0001719	4.36	-0.215	0.963	5.737
8	1573	0.401	0.00018877	4.738	-0.228	0.957	5.770
9	1548	0.325	0.00020408	5.118	-0.241	0.951	5.803
10	1523	0.232	0.00021807	5.5	-0.254	0.946	5.837

Equation Φ'' for γ-Fe: $\Phi''_{Fe}=-2.33+2.194\cdot a_i$.

The thermodynamic characteristics of iron in Fe-Mn melt calculated by equations (11-13) are presented in Table 2 and in figure 1.

Table 2 - Calculated thermodynamic data of γ-Fe in Fe-Mn melt

No. in sequence	T,K	ΔH kJ/g·at.	ΔS kJ/g·at·K	ΔG kJ/mole
1	1749	0	0	0
2	1723	-0.0017	467.954159	-0.07555
3	1698	-0.0027	797.632826	-0.13165
4	1673	-0.00356	1123.464	-0.18956
5	1648	-0.0043	1445.416054	-0.24934
6	1623	-0.00495	1763.457148	-0.31102
7	1598	-0.00552	2077.555229	-0.37464
8	1573	-0.00603	2387.678037	-0.44026
9	1548	-0.00647	2693.793106	-0.50791
10	1523	-0.00688	2995.867768	-0.57764

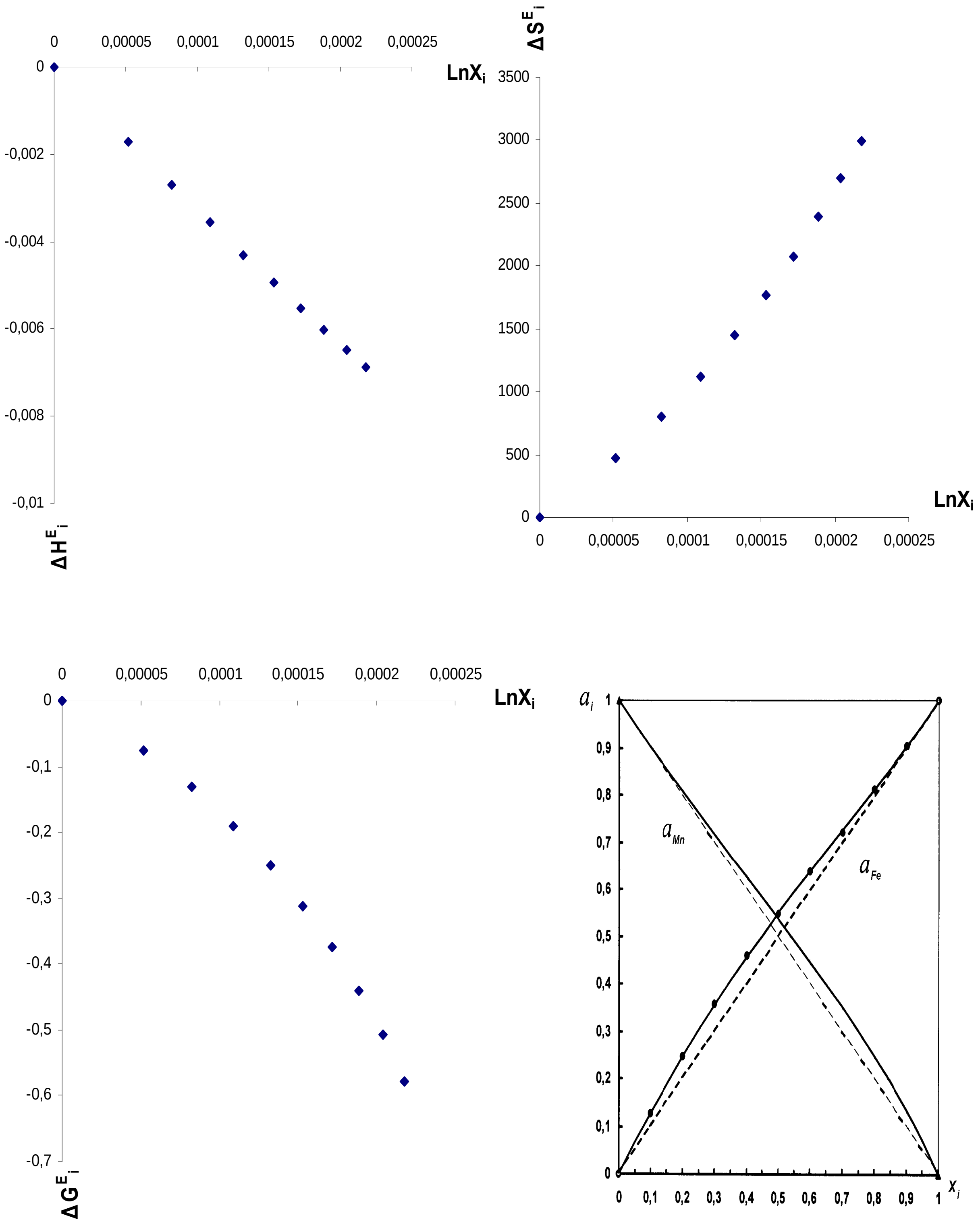

Figure 1 - Partial excess entropy, enthalpy and the Gibbs energy of mixing of the liquidus components in Fe-Mn system

Calculation of excess thermodynamic mixing functions in Cr-based systems

The initial data are taken from [12] and presented in Table 3.

Table 3 - Input parameters for calculating thermodynamic data in Fe-Cr system

No. in sequence	T,K	$X_{opt}^{L}{}_{.Fe}$	$LnX^{L}{}_{Fe}$	Φ'_{Fe}	Φ''_{Fe}	$a^{L}{}_{Fe}$	1/T
1	1812	1	0	0.154	0.104	1	5.518764
2	1803	0.983	-5.4526E-05	0.145415	0.092303	0.99498	5.546312
3	1793	0.959	-0.00013484	0.135827	0.079238	0.989372	5.577245
4	1783	0.935	-0.00024809	0.126186	0.066101	0.983734	5.608525
5	1773	0.905	-0.00041931	0.116492	0.052893	0.978065	5.640158
6	1763	0.88	-0.00070744	0.106745	0.039612	0.972365	5.67215
7	1753	0.855	-0.00129236	0.096944	0.026258	0.966634	5.704507
8	1743	0.825	-0.00311079	0.08709	0.012831	0.960872	5.737235

The crystallization area of α-Fe is described by the equation: Φ''_{Fe}= -2.226+2.33·a_i.

The thermodynamic characteristics of iron in Fe-Cr melt calculated by equations (11-13) are presented in Fig. 2 and Table 4.

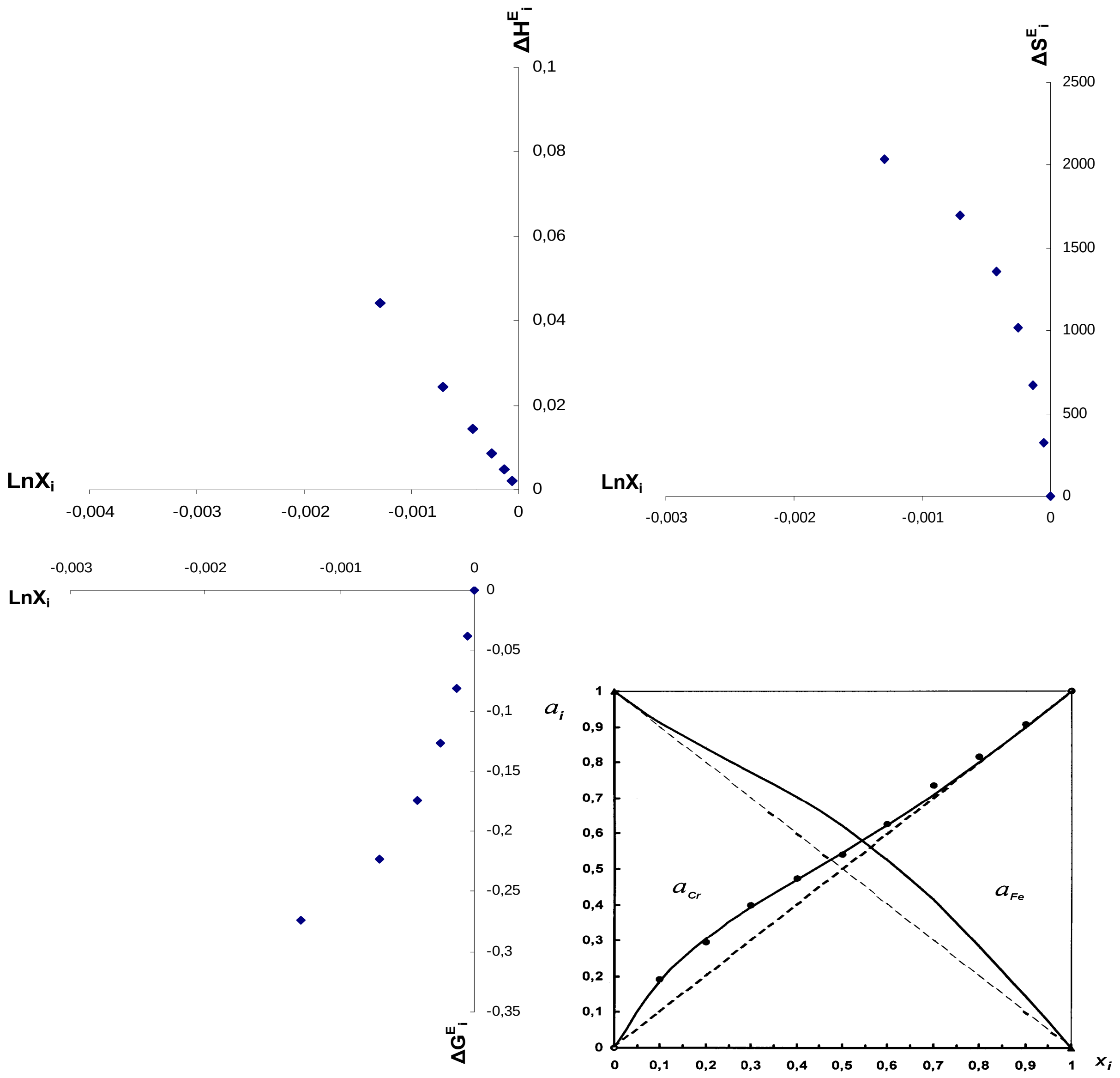

Figure 2 - Partial excess entropy, enthalpy and the Gibbs energy of mixing of the liquidus components in Fe-Cr system

Table 4 - Calculated thermodynamic data of α-Fe in Fe-Cr melt

No. in sequence	T,K	ΔH kJ/g·at.	ΔS kJ/g·at·K	ΔG kJ/mole
1	1812	0	0	0
2	1803	0.00192	319.5202762	-0.03789
3	1793	0.004722	670.7393355	-0.08159
4	1783	0.008638	1017.922868	-0.12702
5	1773	0.014515	1361.037675	-0.17422
6	1763	0.024346	1700.050331	-0.22322
7	1753	0.044214	2034.927181	-0.27408
8	1743	0.105791	2365.63435	-0.32683

Calculation of excess thermodynamic mixing functions in Si-based systems

The initial data are taken from [12] and presented in Table 5.

Table 5 - Input parameters for calculating thermodynamic data in Fe-Si system

No. in sequence	T,K	$X^{L}_{opt.\ Fe}$	LnX^{L}_{Fe}	Φ'_{Fe}	Φ''_{Fe}	a^{L}_{Fe}	1/T
1	2	3	4	5	6	7	8
2	1811	1	0	1.151	0.39	1	5.552
3	1773	0.955	-3.80722E-05	1.345	0.420	0.984	5.640
4	1733	0.91	-8.75179E-05	1.624	0.454	0.961	5.770
5	1693	0.87	-0.00013	1.913	0.489	0.937	5.906
6	1653	0.835	-0.00017	2.218	0.525	0.913	6.049
7	1613	0.805	-0.00021	2.514	0.561	0.888	6.199
8	1573	0.775	-0.00024	2.826	0.598	0.863	6.357
9	1533	0.748	-0.00027	3.174	0.633	0.837	6.523
10	1493	0.705	-0.00032	3.841	0.644	0.811	6.697
11	1485	0.69	-0.00033	4.012	0.647	0.804	6.743

The crystallization area of α-Fe is described by the equation:

$$\Phi''_{Fe}=1.8685+1.4711\cdot a_i$$

and that for the area of the ordered phase α_2-Fe by

$$\Phi''_{Fe}=0.98655+0.4216\cdot a_i$$

The thermodynamic characteristics of iron in Fe-Si melt calculated by equations (11-13) are presented in Table 6 and in Fig. 3.

Table 6 - Calculated thermodynamic data of α and α_2 -Fe in Fe- Si melt

No. in sequence	T,K	ΔH kJ/g·at.	ΔS kJ/g·at·K	ΔG kJ/mole
1	1811	0	0	0
2	1773	-0.000837	-624.71	-0.077
3	1733	-0.00187	-1481.49	-0.180
4	1693	-0.00276	-2295.06	-0.275
5	1653	-0.00352	-3064.01	-0.359
6	1613	-0.00418	-3786.88	-0.432
7	1573	-0.00473	-4462.19	-0.492
8	1533	-0.0015	-1458.67	-0.541
9	1493	-0.00168	-1623.72	-0.619
10	1485	-0.00173	-1662.67	-0.638

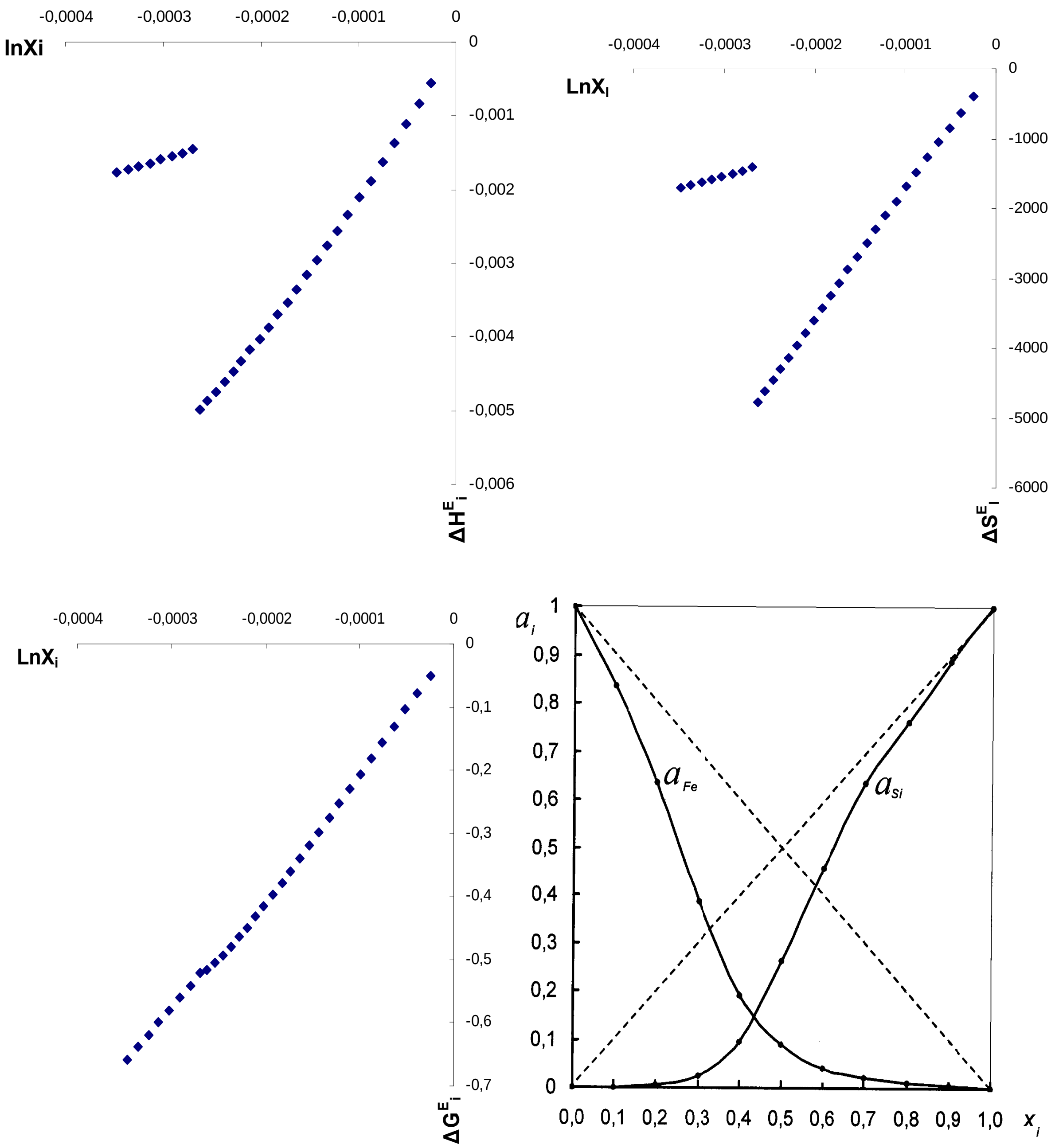

Figure 3 - Partial excess entropy, enthalpy and the Gibbs energy of mixing of the liquidus components in Fe-Si system

Calculation of excess thermodynamic mixing functions in Al-based systems

The initial data are taken from [4] and presented in Table 7.
The crystallization area of α-Fe is described by the equation:

$$\Phi''_{Fe}=0.3989+0.0495\cdot a_i,$$

Table 7 - Input parameters for calculating thermodynamic data in Fe-Al system

No. in sequence	T,K	$X^{L}_{opt.\,Fe}$	LnX^{L}_{Fe}	Φ'_{Fe}	Φ''_{Fe}	a^{L}_{Fe}	1/T
1	1811	1.0	0	0.7033	-0.3494	1	5.534
2	1773	0.808	-4.3E-05	0.764	-0.350	0.980	5.640
3	1733	0.684	-9.7E-05	0.837	-0.351	0.957	5.77
4	1693	0.608	-0.00015	0.911	-0.352	0.934	5.906
5	1653	0.551	-0.00021	0.987	-0.353	0.910	6.049
6	1613	0.505	-0.00027	1.065	-0.355	0.885	6.199
7	1573	0.466	-0.00034	1.116	0.435	0.860	6.357
8	1533	0.428	-0.00041	1.052	0.405	0.834	6.523
9	1493	0.387	-0.00048	0.986	0.374	0.808	6.697
10	1488	0.376	-0.0005	0.969	0.367	0.803	6.723

and that for the region of the ordered phase α_2-Fe is described by:

$$\Phi''_{Fe}=-0.5715+1.1707\cdot a_i.$$

The thermodynamic characteristics of iron in Fe-Al melt calculated by equations (11-13) are presented in Fig. 4 and table 8.

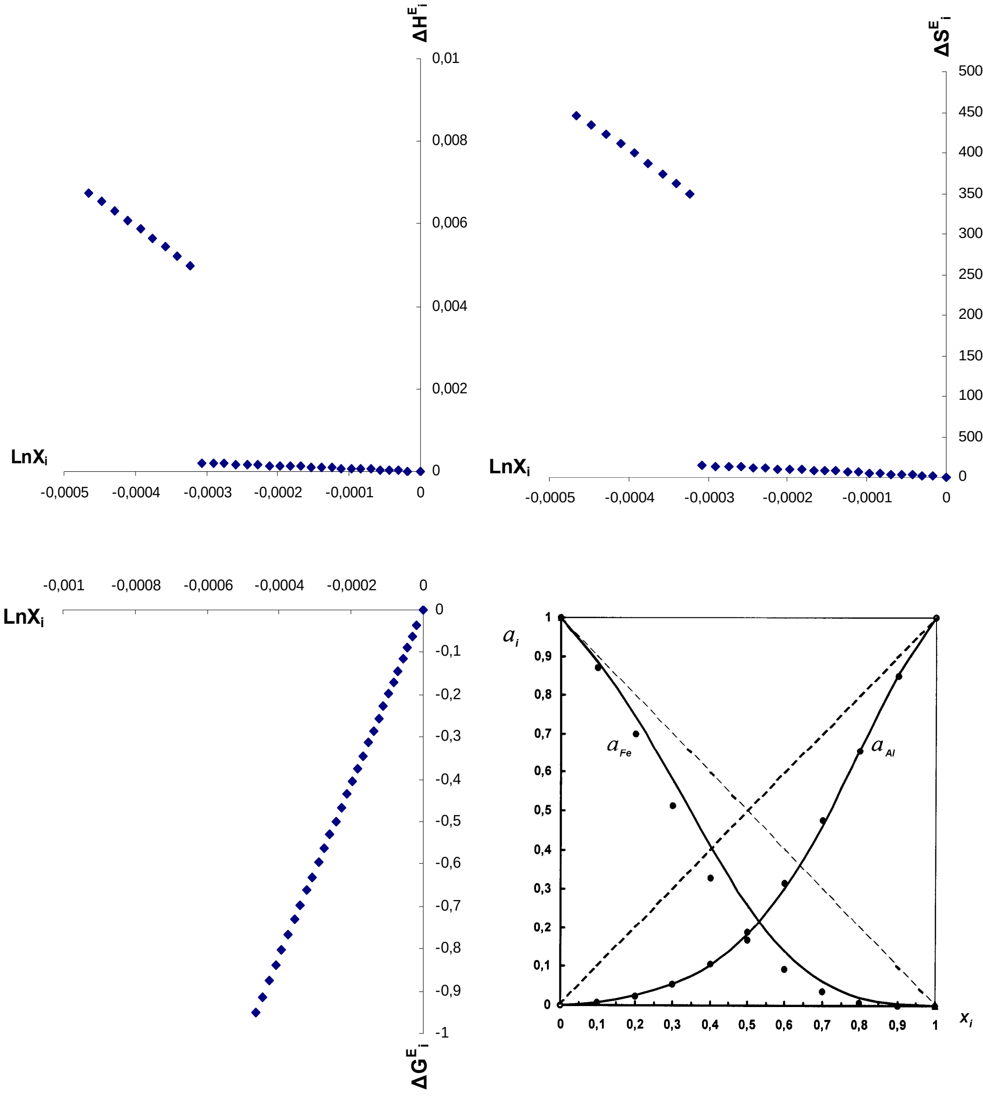

Figure 4 - Partial excess entropy, enthalpy and the Gibbs energy of mixing of the liquidus components in Fe-Al system

Table 8 - Calculated thermodynamic data of α and α_2 -Fe in Fe- Al melt

No. in sequence	T, K	ΔH kJ/g·at.	ΔS kJ/g·at·K	ΔG kJ/mole
1	1811	0	0	0
2	1773	3.2E-05	25.2	-0.089
3	1733	6.02E-05	53.6	-0.198
4	1693	8.85E-05	80.6	-0.314
5	1653	0.00012	106.1	-0.435
6	1613	0.00016	130.0	-0.563
7	1573	0.0002	3619.0	-0.696
8	1533	0.00565	4111.1	-0.839
9	1493	0.00653	4563.1	-0.989
10	1488	0.00674	4669.8	-1.028

Thus, by the example of Fe-Cr, Fe-Si, Fe-Al, Fe-Mn state diagrams, we illustrated the technique for solving the inverse Gibbs problem - extraction of the thermodynamic information directly from the state diagram.

The thermodynamic characteristics of solutions with positive and negative deviations from ideality have been calculated. In doing so we have found that in metal systems of Fe-Cr, Fe-Si, Fe-Al impurity elements Si and Al in the region of rich in chromium alloys exhibit positive deviations from ideality.

This fact allows to draw conclusions about the possibility of deep refining of ferrochromium from these elements, especially aluminum, using a complex alloy of ferrosilicoaluminum (FSA), since the above elements have extremely low solubility in the leading element (chromium) and in this respect using of FSA as a reducing agent does not cause certain difficulties.

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КҮЙ ДИАГРАММАСЫНА ТАЛДАУ ЖАСАУ НЕГІЗІНДЕ МАРГАНЕЦТІ ЖӘНЕ ХРОМДЫ ФЕРРОҚОРЫТПАЛАРДЫ БАЛҚЫТУҒА ТЕРМОДИНАМИКАЛЫҚ БАҒАЛАУ

Аннотация. Бұл жұмыста бинарлы жүйелердің фазалық тепе-теңдік сызықтарын математикалық өрнекпен сипаттауға мүмкіндік беретін Шредер-Ле-Шателье түрлендірілген теңдеуі негізіндегі күй диаграммасынан термодинамикалық деректерді бөліп шығару әдістемесі ұсынылған. Fe-Si, Fe-Cr, Fe-Mn, Fe-Al бинарлы жүйелері үшін идеалды α-γ ерітіндісінің темір белсенділігінен темірдің кристалдану облысына Бьеррумм-Гуггенгейм коэффициентінің тәуелділік теңдеуінің жарамдылығы көрсетілген. Аталған жүйелердің есептік парциалды шектен тысэнтропиялары, энтальпиялары және ликвидус компоненттерінің араласуының Гиббс энергиясы ұсынылған.

Түйін сөздер: кешенді қорытпалар, ферросиликоалюминий, Шредер-Ле-Шателье түрлендірілген теңдеуі, Бьеррумм-Гуггенгейм коэффициенті, парциалды шектен тыс энтальпия (ΔH^E), энтропия (ΔS^E) және ликвидус компонентінің араласуының Гиббс энергиясы (ΔG^M).

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ТЕРМОДИНАМИЧЕСКАЯ ОЦЕНКА ВЫПЛАВКИ МАРГАНЦЕВЫХ И ХРОМИСТЫХ ФЕРРОСПЛАВОВ НА ОСНОВЕ АНАЛИЗА ИХ ДИАГРАММ СОСТОЯНИЯ

Аннотация. В работе предложена методика извлечения термодинамических данных из диаграмм состояния в основе которых лежит модифицированное уравнение Шредера-Ле-Шателье, позволяющее математическими выражениями описывать линии фазовых равновесий бинарных систем. Показана применимость уравнения зависимости коэффициента Бъеррума-Гуггенгейма для области кристаллизации железа от активности железа идеального α-γ раствора для бинарных систем Fe-Si, Fe-Cr, Fe-Mn, Fe-Al. Предложены расчетные парциальные избыточные энтропии, энтальпии и энергии Гиббса смешения ликвидусных компопнентов указанных систем.

Ключевые слова: комплексные сплавы, ферросиликоалюминий, модифицированное уравнение Шредера-Ле-Шателье, коэффициент Бьеррумма-Гуггенгейма, парциальная избыточная энтальпия (ΔH^E), энтропия (ΔS^E) и энергия Гиббса смешения (ΔG^M) ликвидусного компонента.

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USING HERDERS FOR OIL SPILL RESPONSE IN THE SEA

Abstract. The article is devoted to the study of the capabilities, optimal conditions and efficiency of using herders for in-situ burning of oil as an oil spill response technique in the Kazakhstan Sector of the Caspian Sea (KSCS). The in-situ burning of spilled oil is considered as a preferred approach to fight large-scale oil spills offshore, when the oil slick spreads over large distances under the action of wind and currents, which also results in a greater spill area and greater spilled oil volume due to water absorption. Herders, or chemical oil-collectors, are used in the world practice for contracting oil slicks and their thickening before oil combustion. This study was conducted to determine the feasibility of using in the Kazakhstan sector of the Caspian Sea those herding agents that have proven to be effective for other types of oil and other marine conditions. The herding performance, suitability and efficiency of Siltech OP-40 and ThickSlick 6535 herders were investigated for Kashagan oil in artificial sea water with salinity level of KSCS.

Key words: oil spill, herders, dispersants, Kashagan, Kazakhstan sector of Caspian Sea, salinity, in-situ burning.

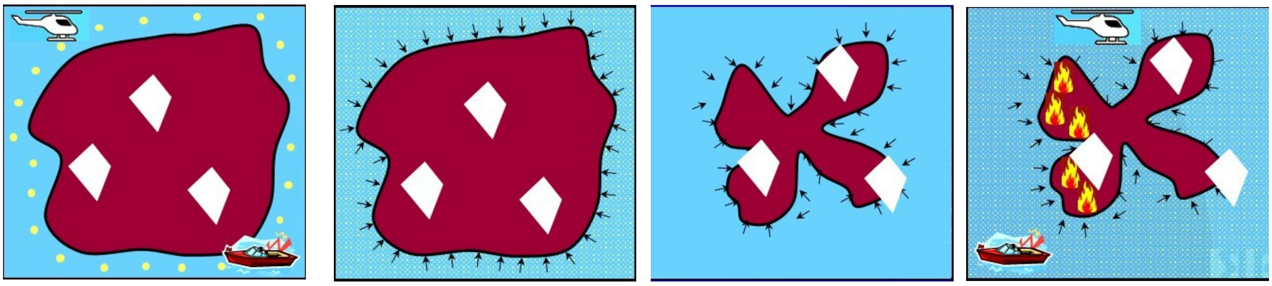
The Kashagan offshore oil field is located in the northern part of the Kazakhstan sector of the Caspian Sea. The distinctive features of the Northern Caspian are low depth of 2-6 m, low salinity of about 6 ‰ and ice cover in winter. Therefore, the methods for oil spills response, developed for open seas with large depth, 33-35 ‰ salinity and minimum fluctuations in water temperature, require significant adaptation to the conditions of the northern part of the Caspian Sea. The above facts necessitate additional studies to select the most suitable methods using chemical agents for oil spill response to find the conditions that provide the greatest positive effect.

Previously, the capability of using dispersants for the oil spills response [1,2] was investigated for Kashagan oil and for the conditions of the northern Caspian [3,4]. Based on the results of these works, the Ministry of Energy of the Republic of Kazakhstan approved the Method for Determination of Dispersants for inclusion on the list of dispersants for the liquidation of oil spills in the sea and inland water bodies of the Republic of Kazakhstan [5]. Also, the Ministry of Energy of the RK approved a list of admissible dispersants, including 5 dispersants [6].

Chemical collectors or herders are surfactants having two ends: hydr and hydrophobic. Herders are designed to contract the oil slick and prevent the oil spreading. The herders are applied to the water surface adjacent to the oil slick, thereby reducing surface tension at the oil/water interface. Reduction of the surface tension of water contributes to the tightening of the oil slick, which in turn leads to an increase in the thickness of the stain to the values sufficiently high for ignition and further combustion of oil.

The possibilities of using herders for oil spill response have been studied since the 1970s, but were considered from the standpoint of their use to restrain oil for subsequent mechanical collection [7,8]. Beginning in 2004, they began to explore more specifically the possibility of using them to contract oil stains before burning oil in cold seawater, especially in ice conditions [8,9].

The principle of the herder action is shown in Fig. 1.



A small amount of herder is sprayed onto the water around the perimeter of the oil slick

Herder rapidly spreads over the water surface, forming a monolayer

Herder changes the surface properties of water - the area of the oil film is reduced

After oil compression, the spots are ignited on the windward side using the Helitorch

Figure 1 - Effect of the herder on an oil slick [5]

In our opinion, the largest number of effective studies on chemical collectors - herders was conducted by Jan Buist, who developed a technique for small-scale testing of herders [10-12]. Over the past period, he carried out a number of tests to burn different types of oil in various natural and climatic conditions [6-7], including the use of herders, which allowed him to establish their comparative characteristics. The most effective herders, based on the results of the studies of Buist et al., are ThickSlick 6535 and Siltech OP-40. Both these chemical collectors were included in the list of herders allowed for use by the U.S. Environmental Protection Agency and currently, they are the most well-known in the world and commercially available chemicals.

A brief description of these collectors is presented in the following table [8].

Table 1 - Herders for testing on Kashagan oil

Herder Indicators	ThickSlick 6535	Siltech OP-40
Manufacturer	Desmi Inc.	Siltech Corp.
Composition	65% sorbitan monolaurate and 35% 2-ethyl butanol	3-(polyoxyethylene)propyl-heptamethyltrisiloxane
Density, г/см^3 (60°F = 15.6°C	0.975	0.988
Solubilbity in water	Partial miscibility	Partial miscibility
pH	6.45	10.1
Kinematic viscosity, cSt	24.70	8.27
Dinamic viscosity, mPa*s (cP)	25.35	8.37
Freezing point	-1,7°C (21,2°F)	-59°C (-74,2°F)
Flash Point	> 82°C (180°F)	> 82°C (180°F)

In this regard, we were interested in studying the behavior of these ThickSlick 6535 and Siltech OP-40 as herders for Kashagan oil in the water of the North Caspian.

MATERIALS AND EQUIPMENT

We used crude degassed Kashagan oil, density 0.802 g/ml, viscosity at 15°C 3.02 mPa*s.

In the initial stage of the study, weathering was carried out at 60°C. The density of oil increased to 0.803 g/ml, the viscosity under those conditions was 3.11 mPa*s.

For the second stage of the study, it was used oil stripped at a temperature of 200 °C. The density of the oil was 0.865 g/ml, and the viscosity – 22.6 mPa*s.

The herders are known to act differently on different types of oil. Thus, to establish comparative characteristics, the Buzachi oil with density 0.920 g/ml and viscosity 427.2 mPa*s was chosen as an alternative variant.

The experimental basin with an area of 1 m^2 was used for research. For each experiment, the pool was tightened with a freshly washed new plastic film, fastening them with large clips over the sides of the pool.

The tests were carried out at water temperatures of 5°C (+/- 2°C), 15°C (+/- 2°C). The water temperature of 5°C was maintained by adding ice pieces to water as needed. The water temperature was measured in the persistent extended tracking mode by using a thermometer.

Figure 2 - Pool for experiments with herders, on the right - a thermometer

Water for experiments with a salinity of 6‰, 12‰, 18‰ was prepared by dissolving sea salt in water.

Quantitative experimental data:

- The water volume of the corresponding salinity is 20 liters;
- Oil volume - 100 ml. The exact mass of oil was measured by weighing the cylinder with oil before and after pouring oil out of the cylinder, and calculating the difference between these two values; the exact value of the volume was calculated from the oil density.

The herder volume was 150 µl (micropipettes were used for sampling). Just as in the case of oil, the exact mass of the herder was determined by the difference between the total and empty micropipettes, and the exact value of the volume was determined from the density.

EXPERIMENTAL METHOD

We put water in the pool, create the appropriate temperature, pour 100 ml of oil, let the spot spread over the surface of the pool, add 150 µl of herder at the edges of the spot.

Results of experiments with oil weathered at 60°C

The oil produced from the Kashagan field is very light, quickly spreads over the surface of the water, tending to the edges of the basin, making it difficult to fix the zero point. We had to repeat the experiment several times to introduce the herder in time.

Fig. 3 shows photographs (real and black and white format) characterizing the results of experiments on the use of two types of herders for Kashagan oil, weathered at 60°C, at a temperature of 5°C and a salinity of 6‰.

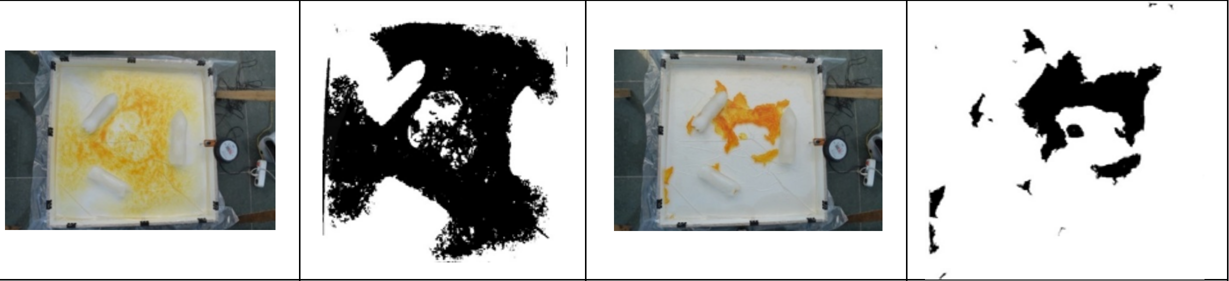
From Fig. 3 it can be seen that both herders act as oil collectors, since the area of oil spots decreases in all cases. In the course of the test, it was established that the effect of the herder is independent of the salinity of the water. The effectiveness of the action of chemical collectors in these experiments was not very high due to low density of oil. Nevertheless, of the two types studied the OP-40 herder is more effective. In turn, this herder showed the best result at a temperature of 15°C, because it was able to reach the maximum thickness of the oil film.

Herder ThickSlick, salinity 6‰, temperature 5°C, oil, weathered at 60°C

Real photo | Black and white format | Real photo | Black and white format

0 min | After 1 min

Herder OP-40, salinity 6‰, temperature 5°C, oil, weathered at 60°C



Real photo | Black and white format | Real photo | Black and white format

0 min | After 1 min

Figure 3 - Images of oil spots before and after the application of two types of herders at a temperature of 5°C and a salinity of 6‰

In Table 2 there are given the results of experiments and their processing on the application of herders to Kashagan oil weathered at 60°C. The areas and thickness of the spots at 15°C calculated are shown.

Table 2 - Experimental and calculated data on the determination of the area and thickness of the spot at 15°C after the application of herders to Kashagan oil weathered at 60°C

#	Test conditions	Number of white pixels	Number of black pixels	Spot area,%	Spot area, cm^2	Spot thickness, mm
Thick Slick						
1	00 min, 15°C, 6‰ TS	1088629	7625048	0,1249	1249,33	0,8004
2	01 min, 15°C, 6‰ TS	1246566	7349821	0,1450	1450,10	0,6896
3	05 min, 15°C, 6‰ TS	828634	7908811	0,0948	948,37	1,0544
4	30 min, 15°C, 6‰ TS	728408	7962083	0,0838	838,17	1,1931
5	60 min, 15°C, 6‰ TS	703439	7869412	0,0821	820,54	1,2187
6	90 min, 15°C, 6‰ TS	703546	7987086	0,0810	809,55	1,2353
7	120 min, 15°C, 6‰ TS	716835	7926290	0,0829	829,37	1,2057
OP-40						
1	00 min, 15°C, 6‰ OP-40	1425047	7218113	0,1649	1648,76	0,6065
2	01 min, 15°C, 6‰ OP-40	381624	8714547	0,0420	419,54	2,3835
3	05 min, 15°C, 6‰ OP-40	320863	8559331	0,0361	361,32	2,7676
4	30 min, 15°C, 6‰ OP-40	356232	8467190	0,0404	403,73	2,4769
5	60 min, 15°C, 6‰ OP-40	511166	7921378	0,0606	606,18	1,6497
6	90 min, 15°C, 6‰ OP-40	669823	8139010	0,0760	760,40	1,3151
7	120 min, 15°C, 6‰ OP-40	669648	7973795	0,0775	774,75	1,2907

Fig. 4 presents the data characterizing the effectiveness of two herders on Kashagan oil weathered at 60 °C. It is clear that the OP-40 is a more effective herder. It is also seen that after 40 min the activity of the OP-40 herder decreases, while the ThickSlick herder retains this feature for 2 hours.

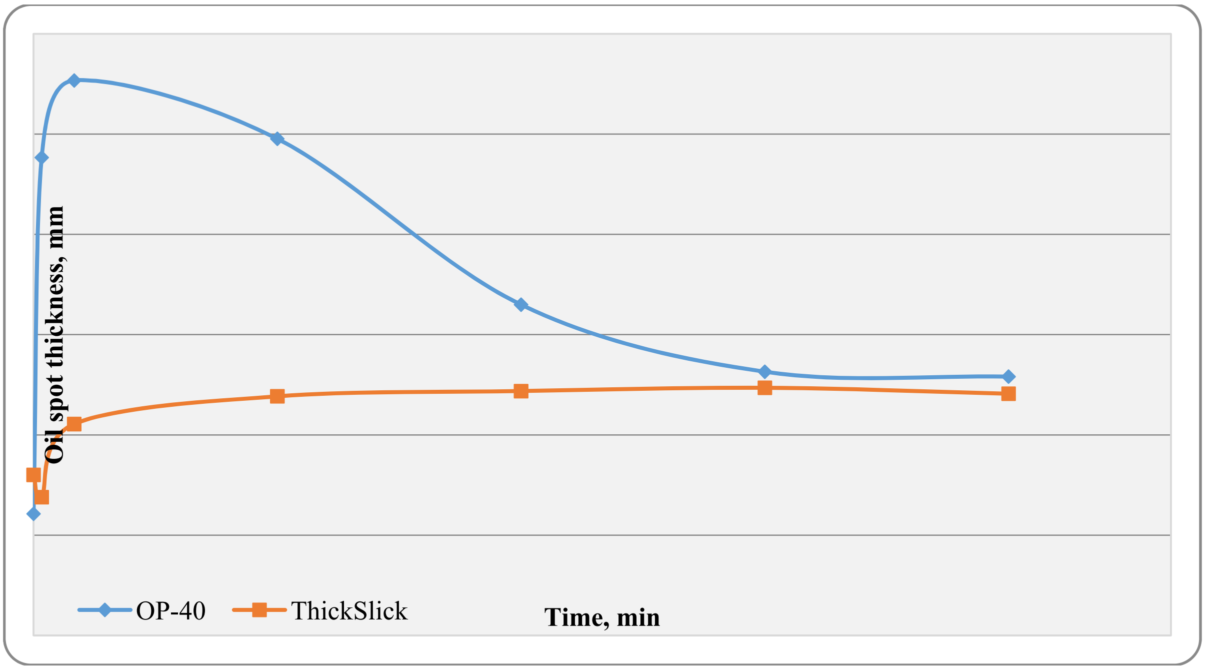


Figure 4 - Efficiency of herders in relation to Kashagan oil weathered at 60°C

Results of experiments with oil, stripped at 200°C

In real-life conditions, after an oil spill, a certain time passes before the response begins, during which the light fractions can evaporate and the oil becomes more viscous. To bring the experimental data closer to the real conditions, the oil was stripped at 200°C. The oil density increased to 0.865 g/ml, and the viscosity increased to 22.6 mPa*s.

The results of the herder effect on the oil stripped at 200°C at 5°C are shown in Table. 3.

Table 3 - Experimental and calculated data on the determination of the area and thickness of the spot at 5°C after the application of herders to Kashagan oil stripped at 200°C

#	Test conditions	Number of white pixels	Number of black pixels	Spot area,%	Spot area, cm^2	Spot thickness, mm
Thick Slick						
1	00 min, 5°C, 6‰ TS	4932840	2747585	0,6423	6422,61	0,1557
2	01 min, 5°C, 6‰ TS	3074019	4786767	0,3911	3910,57	0,2557
3	05 min, 5°C, 6‰ TS	3085968	4956569	0,3837	3837,06	0,2606
4	10 min, 5°C, 6‰ TS	3063227	4664084	0,3964	3964,16	0,2523
5	30 min, 5°C, 6‰ TS	3036094	4758240	0,3895	3895,26	0,2567
6	60 min, 5°C, 6‰ TS	2958613	4592571	0,3918	3918,08	0,2552
7	90 min, 5°C, 6‰ TS	2959968	4901942	0,3765	3764,95	0,2656
OP-40						
1	00 минут, 5°C, 6‰ OP-40	2151907	6627301	0,2451	2451,14	0,4080
2	01 min, 5°C, 6‰ OP-40	1538319	7386747	0,1724	1723,59	0,5802
3	05 min, 5°C, 6‰ OP-40	1199200	7327123	0,1406	1406,47	0,7110
4	10 min, 5°C, 6‰ OP-40	1107462	7552195	0,1279	1278,88	0,7819
5	30 min, 5°C, 6‰ OP-40	1024073	7735862	0,1169	1169,04	0,8554
6	60 min, 5°C, 6‰ OP-40	1022606	7714868	0,1170	1170,37	0,8544
7	90 min, 5°C, 6‰ OP-40	1016577	7767356	0,1157	1157,31	0,8641

Fig. 5 demonstrates the data characterizing the effectiveness of herders at 5°C in relation to Kashagan oil stripped at 200°C. The data show firstly, that the efficiency of the herders quite quickly reaches a peak (maximum) value; secondly, both herders retain the oil collecting ability for an hour and a half, and thirdly, the OP-40 is more efficient than ThickSlick. In the course of this experiment, the OP-40 herder was able to achieve a maximum thickness of the oil film of 0.85-0.86 mm.

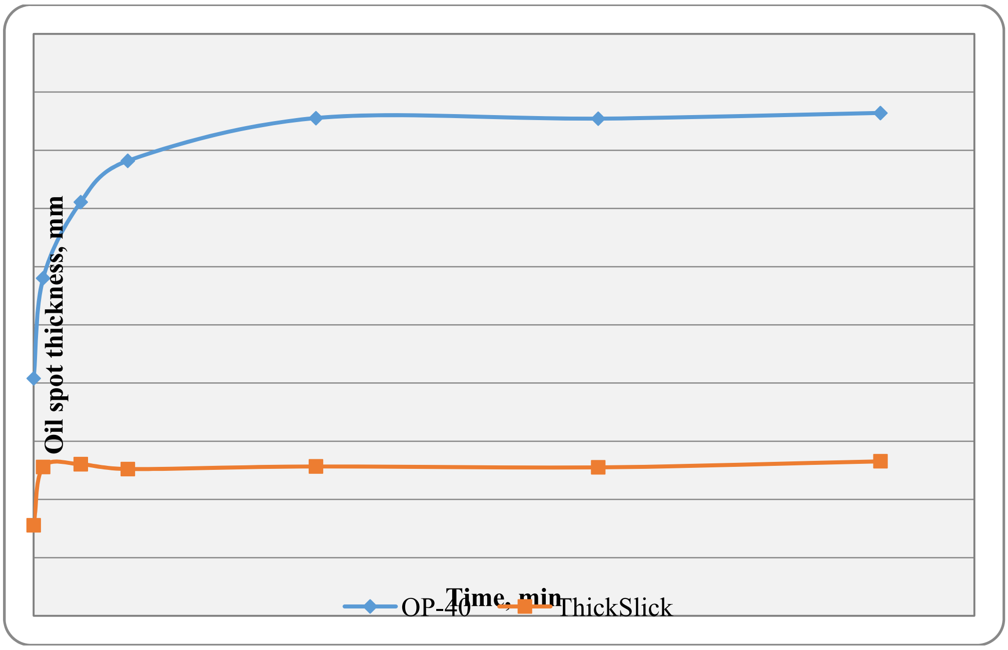


Figure 5 - Efficiency of herders at 5 °C in relation to Kashagan oil stripped at 200 °C

Fig. 6 shows photos describing the effect of the OP-40 herder at 15°C and a salinity of 6‰ on Kashagan oil stripped at 200°C.

			
Real photo	Black and white format	Real photo	Black and white format
0 min		After 1 min	

Figure 6 - Photographs and black and white images of oil spots for oil stripped at 200°C: OP-40 herder, 15°C; salinity 6‰

The results of the herder impact on the oil stripped at 200°C at 15°C are shown in Table. 4.

Table 4 - Experimental and calculated data on the determination of the area and thickness of the oil spot at 5°C after herder application to Kashagan oil stripped at 200°C

#	**Test conditions**	**Number of white pixels**	**Number of black pixels**	**Spot area,%**	**Spot area , cm^2**	**Spot thickness, mm**
1	2	3	4	5	6	7
Thick Slick						
1	00 min, 5°C, 6‰ TS	1711573	7457102	0,1867	1866,76	0,5357
2	01 min, 5°C, 6‰ TS	1212779	7786793	0,1348	1347,60	0,7421
3	05 min, 5°C, 6‰ TS	1227626	7965183	0,1335	1335,42	0,7488

Продолжение таблицы 4

1	2	3	4	5	6	7
4	10 min, 5°C, 6‰ TS	1018576	8198153	0,1105	1105,14	0,9049
5	30 min, 5°C, 6‰ TS	1237076	7883121	0,1356	1356,41	0,7372
6	60 min, 5°C, 6‰ TS	1003368	8164454	0,1094	1094,45	0,9137
7	90 min, 5°C, 6‰ TS	1013537	7097312	0,1250	1249,61	0,8003
OP-40						
1	00 min, 5°C, 6‰ OP-40	1563154	7531985	0,1719	1718,67	0,5818
2	01 min, 5°C, 6‰ OP-40	369848	8534342	0,0415	415,36	2,4075
3	05 min, 5°C, 6‰ OP-40	272525	8895435	0,0297	297,26	3,3641
4	10 min, 5°C, 6‰ OP-40	271338	8701935	0,0302	302,38	3,3070
5	30 min, 5°C, 6‰ OP-40	271229	8848742	0,0297	297,40	3,3625
6	60 min, 5°C, 6‰ OP-40	272666	8798668	0,0301	300,58	3,3269
7	90 min, 5°C, 6‰ OP-40	275081	8965908	0,0298	297,67	3,3594

Fig. 7 shows the efficiency of the herders when exposed to Kashagan oil stripped at 200°C at 15°C. The nature of the action of the herders in time is approximately the same for both temperatures: the area of the spot decreases and becomes stable for 1.5 - 2 hours, while the thickness of the oil spot increases.

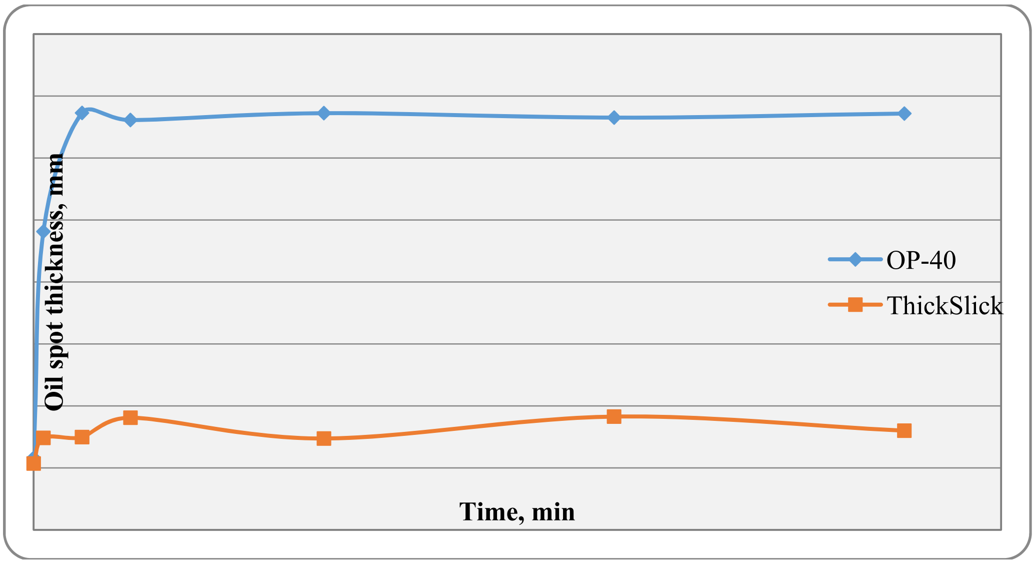


Figure 7 - Efficiency of herders influence at 15 °C to Kashagan oil stripped at 200 °C

With increasing temperature, both herders become more effective. Thus, for the temperature rising from 5 to 15°C the thickness of the oil slick increased from 0.26 to 0.80 mm for Thick Slick herder and from 0.86 to 3.36 mm for OP-40 herder. The effect of water temperature on the effectiveness of herders is shown in Table. 5.

Table 5 - Effect of temperature on the efficiency of herders applied to stripped Kashagan oil

#	Herder	Herder action time, min	Temperature	Spot thickness, mm
1	ThickSlick	60	5°C	0,2552
			15°C	0,9137
2	OP-40	60	5°C	0,8544
			15°C	3,3269

To assess the impact of herders on different types of oil, experiments were conducted with oil from the Buzachi field at 15°C. The results of calculating the efficiency are shown in the Fig. 8. As the data of this figure show, the efficiency of both herders applied to Buzachi oil is higher as compared to the results of Kashagan oil. Of the two herders, ThickSlick herder in this experiment showed a better result than the OP-40.

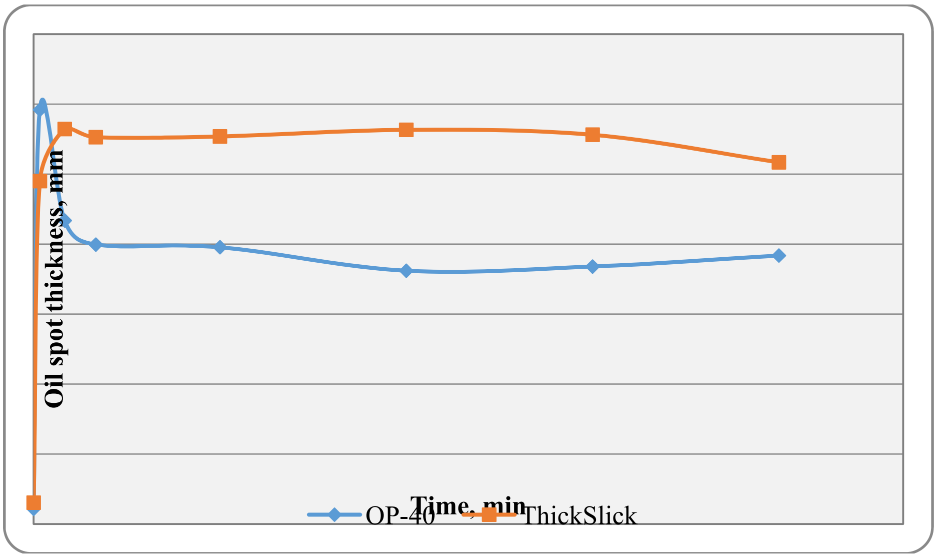


Figure 8 - Efficiency of the herders applied to oil from the Buzachi field at 15°C

CONCLUSIONS

Thus, the following conclusions are drawn on the basis of the experimental studies :

1. ThickSlick 6535 and Siltech OP-40 herders are effective for contracting and thickening Kashagan oil spot.
2. Herders showed the best result on Kashagan oil, stripped at 200°C: oil density increased to 0.865 g/ml.
3. Of the two herders studied the most effective is Siltech OP-40.
4. The herder’s action is independent of the salinity of the seawater.
5. The maximum effect of the herder is reached in 40 minutes. Herders retain their activity for one hour from the time they are applied to the water surface.
6. The efficiency of herders increases with rising temperature.
7. Both herders produce higher impact on Buzachi field oil, which has higher density of 0.920 g/ml and viscosity 427.2 mPa*s.

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ТЕҢІЗГЕ ТӨГІЛГЕН МҰНАЙДЫ ЖОЮДА ХЕРДЕРЛЕРДІ ПАЙДАЛАНУДЫҢ МҮМКІНДІКТЕРІ

Аннотация: Бұл зерттеу Каспий теңізінің қазақстандық секторында (КТҚС) мұнай төгілуін жою үшін өртеу әдісін пайдаланған кезде, хердерлерді қолдану мүмкіндіктерін, оңтайлы шарттарын және тиімділігін зертеуге арналған. Теңізге төгілген мұнайды жоюдың өртеу әдісі теңізде үлкен төгіліс болған жағдайда, жел мен ағын әсерінен мұнай жолағы үлкен қашықтыққа тез тарап, жайылу аймағы және төгілген мұнай көлемі суды сіңіру арқылы айтарлықтай ұлғайған кезде ерекше басымдыққа ие болатын әдіс. Дүниежүзілік тәжірибеде су бетіне төгілген мұнайды өртер алдында жиыстырып, қалыңдығын арттыру үшін хердерлер немесе химиялық жинағыштар пайдаланылады. Зертеу, басқа теңіздер мен мұнайларда жақсы нәтиже көрсеткен хердерлерді Каспий теңізінің қазақстандық секторында пайдалану мүмкіндіктерін анықтау мақсатында жүргізілді. Тұздылығы КТҚС жағдайына сәйкес келетін жасанды теңіз суында қашаған мұнайы үшін Siltech OP-40 және ThickSlick 6535 хердерлерін оңтайлы әрі тиімді пайдалану шарттары анықталды.

Түйін сөздер: мұнайдың төгілуі, хердерлер, диспергенттер, Қашаған, Каспий теңізінің қазақстандық секторы, судың тұздылығы, мұнайды өртеу.

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ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ХЕРДЕРОВ ПРИ ЛИКВИДАЦИИ РАЗЛИВОВ НЕФТИ НА МОРЕ

Аннотация: Исследование посвящено изучению возможностей, оптимальных условий и эффективности применения хердеров при сжигании нефти в качестве метода ликвидации разливов нефти в казахстанском секторе Каспийского моря (КСКМ). Метод сжигания нефти на море является одним из предпочтительных методов в случае больших разливов нефти на море, когда под действием ветра и течений нефтяное пятно быстро распространяется на большие расстояния, при этом значительно увеличиваются и площадь разлива, и объем разлитой нефти вследствие поглощения воды. Хердеры, или химические собиратели, используются в мировой практике для стягивания нефтяного пятна и его утолщения перед проведением сжигания. Исследование проведено с целью определения возможности применения наиболее эффективных, используемых с другими нефтями и в других морских условиях хердеров в условиях казахстанского сектора Каспийского моря. Определены условия и эффективность хердеров Siltech OP-40 и ThickSlick 6535 для кашаганской нефти в искусственной морской воде с соленостью, характерной для КСКМ.

Ключевые слова: разлив нефти, хердеры, диспергенты, Кашаган, казахстанский сектор Каспийского моря, соленость воды, сжигание нефти.

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HYDROTREATING OF VARIOUS PETROL FRACTIONS OVER MODIFIED ALUMOCOBALTMOLYDBDENIC CATALYSTS

Abstract. The paper presents the results of a study of hydrotreating of various gasoline fractions (straight-run gasoline, catalytic cracking gasoline, coking gasoline) on alumo-cobalt-molybdenum catalysts modified with additives of zeolites ZSM-5 and HY, phosphorus and rare earth elements:CoO-MoO_3- Ce_2O_3-P_2O_5-Al_2O_3-ZSM (КGO-18);CoO-MoO_3-La_2O_3-P_2O_5-Al_2O_3-ZSM(KGO-20)иCoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3-ZSM-HY (КGO-16).

The results obtained during the hydroprocessing of various types of gasoline on the catalyst KGO-18 show that the highest amount of isoalkanes is observed during the processing of catalytic cracking gasoline. In the catalyst obtained on the catalyst KGO-18 at 320-380°C 40,3-48,1% of isoalkanes were found, whereas when processing straight-run and gasoline coking, the content of isoalkanes is 34,0-39,7%and 33,9-37%. The octane number after hydrofining of straight-run gasoline and catalytic cracking gasoline is almost the same and is 90,7 and 90,5 (RM), respectively. In the case of coking gasoline, the octane number of fuel produced is lower than when processing other types of gasoline – 83,1 (MM). When studying the process of hydroprocessing of various gasoline fractions over the catalyst KGO-18, it was found that the highest degree of hydrodesulfurization is observed when processing coking gasoline – 87,3%, straight-run gasoline – 81,3% and catalytic cracking gasoline – 75,4%.Modified zeolite-containing alumo-cobalt-molybdenum catalysts for hydroprocessing gasoline fractions in one stage conduct hydrotreating, hydroisomerization, hydrogenation and allow to obtain low-sulfur high-octane gasoline.

Key words: zeolite, straight run gasoline, catalytic cracking gasoline, coking gasoline, catalyst, hydrotreatment.

Introduction

Different gasoline fractions of oil contain a significant amount of linear alkanes, which are characterized by low detonation resistance, which does not allow them to be used directly as motor gasoline. In the world production of motor gasoline, there is a constant tendency to increase the content of isoparaffins with high octane numbers and better ecological characteristics in comparison with aromatic hydrocarbons, limitations on the content of aromatic hydrocarbons, especially benzene (≤1%), olefins and sulfur are provided.

To obtain high-quality motor fuels from sulphurous, paraffinic oils, the use of catalytic hydroprocessing processes is necessary: hydrotreatment, hydroisomerization,and hydrogenation. In this regard, the process of hydroisomerization is one of the methods for improving the performance characteristics of light gasoline fractions.

Toughening the requirements for the quality of motor fuels leads to the need for significant changes in available technologies for processing low-grade gasoline fractions using new high-performance catalysts. It is very promising to create one-stage technologies that allow one-stage hydrotreating, hydroisomerization and hydrogenation processes. Existing industrial catalysts for processing petroleum fractions do not meet the increased requirements for the quality of motor fuels. In this regard, the creation of new catalysts for directed single-stage hydroprocessing of oil and its fractions in high-quality fuel will remain an urgent task now and in the near future [1-20]. In this paper, we present the results of a study of the hydroprocessing of various gasoline fractions (straight-run gasoline, catalytic cracking gasoline, coking gasoline) on alumo-cobalt-molybdenum catalysts modified with additives of zeolites ZSM-5 and HY, phosphorus and rare earth elements.

Experimental part

Zeolite-containing alumina catalysts were prepared. impregnation of a mixture of aluminum hydroxide and zeolites with aqueous solutions of cobalt, molybdenum and modifying additives. After molding, the catalyst was dried at 150°C and calcined at 550°C for 5 hours. Catalysts of the following compositions were prepared: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18); $CoO-MoO_3-La_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-20) and $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM-HY (KGO-16).

Synthesized modified zeolite-containing catalysts were used to study the hydroprocessing of various types of gasoline. The process was carried out in a high-pressure flow unit with a stationary catalyst bed at temperatures of 320-400^{0}C, a pressure of 4,0 MPa and a space feed rate of 2h^{-1}.The hydrocarbon composition of the reaction products was analyzed on chromatographs "Chromatec-Crystal" and "Chrom-5". Analysis of sulfur content in feedstock and products was carried out in LLP "Oilsert International" (Almaty) and laboratory of physico-chemical methods of "D.V. SokolskyIFCE".

Results and discussion

On the catalyst KGO-18, the process of hydroprocessing various types of gasoline was studied. Hydrogen processing of straight-run gasoline on KGO-18 catalyst showed that in the temperature range 320-350°C, the resulting catalyst contains 39,7-38,2% of isoalkanes (Table 1). At higher temperatures, the yield of isoalkanes decreases to 34,4% at 400°C. The amount of aromatic hydrocarbons in the catalyst under these conditions increases from 15,2 to 24,8%, the yield of naphthenic hydrocarbons decreases from 26,1 to 24,0%.he concentration of olefinic hydrocarbons varies within the range of 4,6-7,6%. The yield of hydro-upgraded gasoline decreases from 70,7 to 60,5% with increasing temperature from 320 to 400^{o}C. The octane number of hydrotreated gasoline is increased compared with the original from 78,9 to 90,7 (MM) and by the motor method from 60,9 to 71,7. The sulfur content of the catalyst decreased from 0,0080 (reference gasoline) to 0,0015% with an increase in temperature to 400^{o}C.

Table 1 - Effect of temperature on the process of hydroprocessing of straight-run gasoline on the catalyst KGO-18

Products,%	T^{o}C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	27,3	11,4	15,1	12,5	12,2
Isoalkanes	36,8	39,7	38,2	34,0	34,4
Oleffin	4,8	7,6	5,6	5,4	4,6
Aromatichydrocarbons	9,2	15,2	18,7	20,9	24,8
Naphthenichydrocarbons	21,9	26,1	22,3	27,2	24,0
Yield of the liquid phase	-	70,7	68,3	65,0	60,5
The octane number for research method	78,9	82,6	84,9	88,1	90,7
Octane number by motor method	60,9	67,8	67,7	68,5	71,7
Massfractionofsulfur,%	0,0080	0,0049	0,0026	0,0030	0,0015
Note: P = 4.0MPa, V = 2.0 h^{-1}					

The results of a study of the hydroprocessing of catalyticcracked gasoline using the catalyst KGO-18 showed that with an increase in temperature from 320 to 400^{0}C, the yield of liquid catalyst varies from 80,0 to 68,5% (Table 2). When hydrolyzing catalyticcracked gasoline on the catalyst KGO-18 at 320-350^{0}C, the amount of isoalkanes increases from 25,4 to 42,6-48,1% in comparison with the initial one. The content of aromatic and naphthenic hydrocarbons varies from 30.1 to 36,1%, from 7,0 to 10,4%, respectively. The amount of olefinic hydrocarbons under these conditions drops sharply from 31,2 to 4,3-3,3%. The octane number of the With an increase in temperature from 350 to 400oC, the content of isoalkanes decreases to 39,9% (400^{0}C). The yield of naphthenic and olefinic hydrocarbons under these conditions also decreases to 6,7 and 2,9%, respectively, the amount of aromatic hydrocarbons increases to 43,1%.

The octane number of the refined gasoline obtained at 400°C is 90,5 (RM) and 83,4 (MM). It should be noted that in gasoline hydro-enriched on catalyst KGO-18 at 320^{0}C, the sulfur content is 0,0110% (in the initial 0,0134%), and at 400^{0}C – 0,0033%, which indicates a sufficiently high hydrodesulfurizing activity of this catalyst, produced gasoline practically does not change.

Table 2 - Effect of temperature on the process of hydroprocessing
of catalytic cracking gasoline on catalyst KGO-18

Products,%	T,^{o}C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	6,3	6,9	8,2	7,3	7,4
Isoalkanes	25,4	42,6	48,1	40,3	39,9
Oleffin	31,2	4,3	3,3	3,4	2,9
Aromatichydrocarbons	30,1	36,1	30,0	40,3	43,1
Naphthenichydrocarbons	7,0	10,1	10,4	8,7	6,7
Yield of the liquid phase	-	80,0	75,0	71,0	68,5
The octane number for research method	88,7	87,9	88,7	90,4	90,5
Octane number by motor method	80,1	80,9	83,2	82,5	83,4
Massfractionofsulfur,%	0,0134	0,0110	0,0077	0,0053	0,0033
Note: P = 4.0MPa, V = 2.0 h^{-1}					

When hydrolyzing coking gasoline on the catalyst KGO-18 with an increase in temperature from 320 to 400^{o}C, the content of isoalkanes increases from 23,6% (initial), reaching a maximum value of 39,7% at 380°C, slightly decreasing to 37,1% at 400°C. Under these conditions, the yield of aromatic hydrocarbons increases to 18,6% (400°C). The amount of olefins in the resulting product is significantly reduced compared to the initial (24,2%) and varies within the range of 6,5-9,0%. The octane number of the refined gasoline obtained at 400^{o}C is 82,6 (RM) and 66,8 (MM). The yield of liquid catalyst is 75,5-82,6%. The sulfur content of the catalyst after hydroprocessing decreased from 0,7127 in the initial gasoline to 0,0906% (Table 3).

Table 3 - Effect of temperature on the process of hydroprocessing of coking gasoline on the catalyst KGO-18

Products,%	T,^{o}C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	27,2	26,2	20,9	24,7	19,1
Isoalkanes	23,6	35,6	38,7	33,9	37,1
Oleffin	24,2	9,0	8,0	8,1	6,5
Aromatichydrocarbons	8,9	13,2	10,6	14,9	18,6
Naphthenichydrocarbons	16,2	16,0	21,8	18,4	18,7
Yield of the liquid phase	-	82,6	78,2	76,1	75,5
The octane number for research method	84,0	80,9	80,6	81,4	82,6
Octane number by motor method	64,7	65,2	64,4	65,0	66,8
Massfractionofsulfur,%	0,7127	0,0950	0,0930	0,0908	0,0906
Note: P = 4.0MPa, V = 2.0 h^{-1}					

Analysis of the results obtained during the hydroprocessing of various types of gasoline on the catalyst KGO-18 shows that the highest amount of isoalkanes is observed during the processing of catalytic cracking gasoline. In the catalyst obtained at 320-380^{o}C 40,3-48,1% of isoalkanes were found, whereas when processing straight-run and gasoline coking, their quantity is 34,0-39,7% and 33,9-38,7%, respectively. The octane number of gasoline after hydrofining of straight-run gasoline and catalytic cracking gasoline is almost the same and equal to 90,7 and 90,5 (RM), respectively. In the case of coking gasoline, the octane number of fuel produced is lower than when processing other types of gasoline – 83,1 (MM).

The results obtained by studying the process of hydroprocessing of various gasoline fractions on the catalyst KGO-18 show that the highest degree of hydrodesulfurization is observed during the processing of coking gasoline and is 87,3%, whereas for straight-run gasoline and catalytic cracking gasoline this figure is lower – 81,3 % and 75,4% respectively.

The process of hydroprocessing straight-run gasoline was also investigated on the catalysts KGO-20 and KGO-16.Comparison of the composition of the initial gasoline and the resulting products of hydroprocessing of straight-run gasoline on the catalyst KGO-20 at 320°C shows that the content of isoalkanes increases from 36,8 to 39,3%, aromatic hydrocarbons from 9,2 to 14,9%, olefins from 4,8 to 6.8%, and naphthenes, from 21,9 to 24,5%. At the same time, there is a decrease in the number of paraffins from 27,3 to 14,5%. The octane number by the research method after hydrotreating the straight-run gasoline on the catalyst KGO-20 increased: according to the research method - from 78,9 to 81,4, on the motor - from 60,9 to 66,3. With an increase in temperature from 320 to 400°C, an insignificant decrease in the yield of isoalkanes to 36,2% is observed.The yield of aromatic hydrocarbons is increased to 20,1%. The content of olefins varies between 4,0-7,4%. Under these conditions, the octane number according to the research method after hydrotreating the straight-run gasoline reaches a maximum value of 89,3 for the motor one – 73,4 (Table 4).

Studies have shown that the residual sulfur content after hydroprocessing straight-run gasoline on the catalyst KGO-20 has decreased from 0,0080 in the initial gasoline to 0,0028% (Table 4).

Table 4 - Effect of temperature on the process of hydroprocessing of straight-run gasoline on the catalyst KGO-20.

Products,%	T,°C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	27,3	14,5	7,1	4,3	16,7
Isoalkanes	36,8	39,3	40,4	33,4	36,2
Oleffin	4,8	6,8	7,0	7,4	4,0
Aromatichydrocarbons	9,2	14,9	17,8	23,1	20,1
Naphthenichydrocarbons	21,9	24,5	27,7	31,8	23,0
Yield of the liquid phase	-	77,0	49,0	44,5	55,0
The octane number for research method	78,9	81,4	84,9	88,3	89,3
Octane number by motor method	60,9	66,3	69,4	69,2	73,4
Mass fraction of sulfur,%j	0,0080	0,0072	0,0062	0,0056	0,0028
Note: P = 4.0MPa, V = 2.0 h^{-1}					

Table 5 - Effect of temperature on the process of hydroprocessing straight-run gasoline on the catalyst KGO-16

Products,%	T°C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	27,5	17,0	12,7	12,8	14,2
Isoalkanes	39,8	41,3	40,0	36,9	39,8
Oleffin	5,8	5,6	6,3	5,6	6,2
Aromatichydrocarbons	8,7	12,9	15,7	22,8	19,7
Naphthenichydrocarbons	18,2	23,2	25,3	21,9	20,1
Yield of the liquid phase	-	77,0	67,0	65,0	60,0
The octane number for research method	79,2	84,0	86,4	85,2	87,3
Octane number by motor method	61,1	68,7	71,0	70,8	72,7
Massfractionofsulfur,%	0,0080	0,0036	0,0027	0,0023	0,0016
Note: P = 4.0MPa, V = 2.0 h^{-1}					

At P = 4.0 MPa, V = 2,0 h-1, the process of hydroprocessing a straight-run gasoline fraction with a sulfur content of 0,0080% on a catalyst KGO-16 was studied (Table 5). The yield of the liquid phase decreases from 83.5 to 70.0% with increasing temperature from 320 to 400^{0}C. When hydrolyzing gasoline on KGO-16 catalyst in the temperature range 320-400^{o}C, the maximum isoalkane content in the resulting catalyst is observed at 320^{0}C and is equal to 41,3%. It should be noted that the amount of isoalkanes in the catalyst obtained after hydroprocessing depends little on the process temperature and is equal to 36,9-41,3%, which is higher than in the original gasoline fraction. The amount of aromatic hydrocarbons rises from 8.7 to 19.7% with an increase in the process temperature to 400°C. The amount of olefins slightly increases compared with the original from 5,8 to 6.2%. The amount of naphthenic hydrocarbons in the resulting catalyst varies between 20,1-25,3%. The octane number of enriched gasoline increases in comparison with the initial from 19,2 to 87,3 (IM) and from 61,1 to 72,7 (MM). The content of sulfur in the catalyst with an increase in temperature to 400°C decreased compared with the initial from 0,0080 to 0, 0016%.

Comparison of the results obtained in the study of the process of hydroprocessing the straight-run gasoline fraction shows that the catalysts KGO-16 and KGO-18 possess the highest hydrodesulfurizing activity. The degree of hydrodesulfurization on the catalyst KGO-18 is 81,3%, for KGO-16 80,0%, for KGO-2065%.

When hydrotreating straight-run gasoline (octane number 79,2) on the catalysts KGO-16, KGO-18 and KGO-20, an increase in the octane number compared with the original: 87.3; 90,7 and 89,3 respectively. This is mainly due to the increase in the content of isoalkanes in hydro-upgraded gasoline.

When hydrolyzing catalyticcracked gasoline on KGO-16 catalyst with an increase in temperature to 320-350°C, the content of isoalkanes increases from 25,4 to 47,5% (Table 6). With a further increase in temperature, there is a decrease in the amountof isoalkanes formed to 40,3% (400°C). Under these conditions, the amount of aromatic hydrocarbons in the produced gasoline rises from 30,1 to 35,0%.The content of naphthenic hydrocarbons in the catalyst is small and varies between 6,1 and 8,3%. The content of olefins in the catalyst decreases from 31,2 to 8,0%. The yield of the liquid phase with an increase in temperature in the range 320-400^{0}C varies in the range 95.0-100%. The octane number of catalyticcracked gasoline enriched at 400°C is 86,1 (RM) and 79,6 (MM). When hydrotreating gasoline catalytic cracking, the sulfur content in the final product is reduced from 0,0134% (reference gasoline) to 0,0029%.

Table 6 - Effect of temperature on the process of hydroprocessing of catalytic cracking gasoline on the catalyst KGO-16

Products,%	T°C				
	Source gasoline	320	350	380	400
Paraffin C_5-C_6	6,3	8,8	9,2	10,6	8,1
Isoalkanes	25,4	47,5	47,3	43,0	40,3
Oleffin	31,2	12,1	7,6	5,0	8,0
Aromatichydrocarbons	30,1	25,5	29,4	32,6	35,0
Naphthenichydrocarbons	7,0	6,1	6,6	8,1	8,3
Yield of the liquid phase	-	100	97,5	95,5	95
The octane number for research method	88,7	86,2	85,2	85,4	86,1
Octane number by motor method	80,1	81,0	79,0	78,0	79,6
Massfractionofsulfur,%	0,0134	0,0048	0,0047	0,0035	0,0029
Note: P = 4.0MPa, V = 2.0 h^{-1}					

In the study of the process of hydroprocessing of catalytic cracking gasoline, it was shown that the catalysts of KGO have a sufficiently high hydrodesulfurizing activity. The degree of hydrodesulfurization on the catalyst KGO-18 is 75,4%, at KGO-16 – 78,4%. In the hydrotreating of catalytic cracking gasoline (octane number 88,7 (RM), a slight decrease in the octane number to 86,1 (RM) is observed on the catalyst KGO-16, while at the KGO-18 the octane number of the upgraded gasoline increases to 90,5 (RM).

We have previously shown that the activity of hydroprocessing catalysts of various petroleum fractions is related to the surface structure, phase composition and the state of the modifying additives [8]. An electron microscopic study was made of the structure and state of the active centers of the KGO catalysts promoted by Ce, Co, Mo, etc. Studies have shown that on the surface of these catalysts, there are several types of surface structures that differ significantly in both size and chemical state of the components.

According to electron microscopy, the thermodesorption of ammonia and X-ray diffraction catalysts are highly dispersed, the metal components of the active phase are predominantly in the oxidized state, forming cluster-associates on the surface whose dispersion and structure and state are determined by the nature of the catalyst components [8].

Conclusions. When hydroprocessing various types of gasoline on the catalyst KGO-18, the highest content of isoalkanes is observed during the processing of catalytic cracking gasoline. 40,3-48,1% of isoalkanes were found in the catalyst obtained on the catalyst KGO-18 at 320-380°C, whereas in the process of straight-run and gasoline coking, the content of isoalkanes is 34,0-39,7% and 33,9 – 38,7%. The octane number of gasoline after hydrofining of straight-run gasoline and catalytic cracking gasoline is almost the same and is 90,7 and 90,5 (RM), respectively.Modified zeolite-containing alumo-cobalt-molybdenum catalysts for hydroprocessing gasoline fractions in one stage conduct hydrotreating, hydroisomerization, hydrogenation and allow to obtain low-sulfur high-octane gasoline.

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БЕНЗИННІҢ ӘРТҮРЛІ ФРАКЦИЯЛАРЫН МОДИФИЦИРЛЕНГЕН АЛЮМОКОБАЛЬТМОЛИБДЕН КАТАЛИЗАТОРАЛАРЫНДА ГИДРОЖАҚСАРТУ

Аннотация.Жұмыста ZSM-5 және HY цеолит қоспалары, фосфор мен сирек кездесетін элементтермен модифицирленген алюмокобальтмолибден катализаторларында: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (КГО-18); $CoO-MoO_3-La_2O_3-P_2O_5-Al_2O_3$-ZSM(КГО-20) және $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM-HY(КГО-16) бензиннің әртүрлі фракцияларын (тура айдалған бензин, каталитикалық крекинг бензині және кокстеу бензині) гидроөңдеу зерттеулерінің нәтижелері берілген.

КГО-18 катализаторында бензиннің әртүрлі фракцияларын гидроөңдеуден алынған нәтижелері көрсеткендей,изоалкандардың ең жоғары үлесі каталитикалық крекинг бензинін өңдегенде байқалды. КГО-18 катализаторындағы 320-380°С–та алынған катализаттағы изоалкандар мөлшері 40,3-48,1%болса, ал тура айдалған бензин мен кокстеу бензиндерін өңдегенде алынған изоалкандар 34,0-39,7% және33,9-38,7%-ды құрады. Тура айдалған бензин мен каталитикалық крекинг бензинін гидрожақсартудан соң октан саны іс жүзінде бірдей, яғни 90,7 мен 90,5–ке (ЗӘ) тең. Ал өңделген кокстеу бензинінің октан саны басқа өңделген бензин фракцияларынан қарағанда төмен, яғни 83,1-ге тең (ЗӘ).КГО-18 катализаторында бензиннің әртүрлі фракцияларынгидроөңдеу процесінің зерттеулері байқатқандай,ең жоғары гидрокүкіртсіздендіру кокстеу бензинін өңдеуде жүзеге асты, яғни 87,3%-ға тең болды. Ал тура айдалған бензинде 81,3% болса, каталитикалық крекинг бензинінде 75,4%-ды құрады.

Түйін сөздер: цеолит, тура айдалған бензин, каталитикалық крекинг бензині, кокстеу бензині, катализатор, гидротазалау

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ГИДРООБЛАГОРАЖИВАНИЕ РАЗЛИЧНЫХ БЕНЗИНОВЫХ ФРАКЦИЙ НАМОДИФИЦИРОВАННЫХ АЛЮМОКОБАЛЬТМОЛИБДЕНОВЫХКАТАЛИЗАТОРАХ

Аннотация. В работе приведены результаты исследования гидропереработки различных бензиновых фракций (прямогонный бензин, бензин каталитического крекинга, бензин коксования) на алюмокобальтмолибденовых катализаторах, модифицированных добавками цеолитов ZSM-5 и HY, фосфора и редкоземельных элементов:$CoO-MoO_3$- $Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (КГО-18);$CoO-MoO_3-La_2O_3-P_2O_5-Al_2O_3$-ZSM(КГО-20) и $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM-HY (КГО-16).

Результаты, полученные при гидропереработке различных видов бензина на катализаторе КГО-18, показывают, что наиболее высокое количество изоалканов наблюдается при переработке бензина каталитического крекинга. В катализате, полученном на катализаторе КГО-18 при 320-380^{o}С обнаружено 40,3-48,1% изоалканов, тогда как при переработке прямогонного и бензина коксования содержание изоалканов составляет 34,0-39,7% и 33,9 - 38,7%. Октановое число после гидрооблагораживания прямогонного бензина и бензина каталитического крекинга практически одинаково и составляет 90,7 и 90,5 (ИМ) соответственно. В случае бензина коксования октановое число получаемого топлива ниже, чем при переработке других видов бензинов - 83,1(ИМ). При исследовании процесса гидропереработкиразличных бензиновых фракции на катализаторе КГО-18 установлено, что наиболее высокая степень гидрообессеривания наблюдается при переработке бензина коксования - 87,3%, прямогонного бензина - 81,3% и бензина каталитического крекинга - 75,4%.Бензин фракцияларын гидроөңдеуде модифицирленген цеолитқұрамды алюмокобальтмолибден катализаторлары бір сатыда гидротазалау,гидроизомерлеу, гидрлеу реакцияларын жүргізіп, аз күкіртті жоғары октанды бензин алуға мүмкіндік береді.

Ключевые слова: цеолит, прямогонный бензин, бензин каталитического крекинга, бензин коксования, катализатор, гидроочистка

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DEVELOPMENT OF TECHNOLOGY FOR THE COMPLEX ISOLATION OF BIOLOGICAL ACTIVE SUBSTANCES FROM PLANTS OF THE GENUS HAPLOPHYLLUM A. JUSS

Abstract: In this study, a complex study of plants of the genus Haplophyllum A.Juss of a sort H. Perforatum Kar et Kir. The main parameters or raw material quality: preparation raw material (grinding, sieve analysis); humidity, total ash, ash is insoluble 10 % HCl, sulphate ash, extractives.

Macro- and microelement composition of total ash is analyzed. Qualitative reactions and chromatographic analysis methods, the main classes of natural compounds in raw materials and their quantitative contents have been identified.

Keywords: Rutaceae, Haplophyllum, moisture, ash, coumarins, Perforatum, flavonoids, terpenoids.

Introduction

The stirpes Rutaceae includes 150 genera and about 900 species are widely distributed in tropical, subtropical and heat-sensitized regions of both hemispheres. Most of the representatives of the stirpes grow in the South of the USA (California, Florida) in the Mediterranean countries (Spain, Italy, Morocco, etc.), Brazil, Argentina, Japan, China, South Africa and the arid regions of Australia [1; 201].

Rutaceae - occur mainly as evergreen trees or bushes, sometimes lianas, very rarely perennial (ruta - Ruta, ash - Dictamnus, haplophyllum - Haplophyllum) and annual grasses [2; 240].

Plants of the genus Haplophyllum A. Juss (stirpes Rutaceae) on a global scale are represented by approximately 70 species, which are distributed from the Mediterranean to Western Siberia. There are 23 species of Haplophyllum growing on the territory of the Central Asian countries [3; 229].

The main active components of the plant genus Haplophyllum A. Juss are:

- coumarins (collinin, obtusifol, obtusinin, obtusinol, obtosozid, daurosid D, ostol, 6-methoxy-7-(3',3'-dimethylallyloxy) coumarin, 5-hydroxy-7-methoxycoumarin, scopoletin, isoskopoltin, bungenediol, skimianin , umbelliferone, and daurozides A and B);
- flavonoids (haplozid A, 7-O-glycoside haplogenin, haplozid D, haplozid F, 7-O-β-D- (6acetyl-'), glucopyranoside 3,5,4'-trihydroxy-8,3' - dimethoxyflavone, 7-O-α-L-rhamnopyranosyl, glycosides of quercetin, kaempferol, isoramnetin, 7-glucoside of 3'-methyl ester of gossipetin);
- alkaloids (acetamide, folifin, evoxin, haplotin, candecin, palmatin, magnophlarin, haplophin, buharaine, bucharidine, robustin, folimin, 4-methoxy-N-methylquinolone-2, robustinine, dictamnin, skimmianin, dubinin, dubamine, haplopherin, foliosin);
- terpenoids;
- steroids (sitosterol, stigmasterol, camperterol);
- essential oils;
- carboxylic acids;
- lignans (eudesmine, variantcoside, diphyllin, pluviatil, suicilactone, yusticidin B, daurinol);
- tannins;
- amides;
- carbohydrates (glucose, galactose, mannose, xylose, arabinose, rhamnose);

- saponins;
- higher aliphatic alcohols (n-triacontanol) and a number of other BAS (Biologically active substances) [4; 13].

Table 1 - the biologically active substances of plants of the genus Haplophyllum [5; 6].

Kind of plant	Dedicated connections		
	Coumarins	Flavonoids	Lignans
Haplophyllum Perforatum Kar et Kir	scopoletin, scopiolin, haploperoside A, haploperoside B, x haploperoside C, haploperoside D, haploperoside E	haplogenin, limocitrine, limocitrine-7-O-β-D- (6 "-O-acetyl) -glucopyranoside, haplozid A, haplozid B, haplozid C, haplozid D, haplozid E	eudesmine
Haplophyllum Obtusifolium Ledeb	scopoletin, 6-methoxy-7-γ, γ-di-methylal-liloxicumarin, obtusinol, obtusinin, otosozid, feruloylskopolin fraxetin, kapensin, obtusicin, obtusiprenin, otusiprenol, obtusidine, obtusipholine, fraxetine-7-O-glucoside		yusticidin B, diphyllin
Haplophyllum Davuricum (L.) G. Don	umbelliferon, scopoletin, 5,7-dihydroxyquarium, skimmin, daurozide A, daurozide B, daurozide D	haplogenin, haplozid B, haplozid D	yusticidin B, diphyllin daurinol
Haplophyllum Latifolium Kar et Kir	-	haplogenin, haplozid B, haplozid D	-
Haplophyllum Versicolor Fisch. Et Mey	-	-	variantcoside

From the data presented in Table 1, the common feature of all the species of studied for the content of coumarins is the presence of scopoetin, scopolin, haploperoside *Haplophyllum Perforatum Kar et Kir*, haploperoside B, haploperoside C, haploperoside D, haploperoside E. The content of flavonoids: haplogenin, limocitrine, limocitrine-7-O-β-D- (6 "-O-acetyl) -glucopyranoside, haplozid A, haplozid B, haplozid C, haplozid D, haplozid E. Content of lignans: eudemin.

Table 2 - the quantitative content of coumarins during flowering and fruiting [5; 7].

Coumarins	The yield of coumarins (in% of the weight of an air-dry plant)	
	Flowering period	Fruiting period
scopoletin,	-	trace amounts (<0,004%)
6-methoxy-7-γ, γ-dimethyl-lyloxycoumarin	0,023	trace amounts (<0,004%)
Obtusinol		
Obtusinin	trace amounts (<0,004%)	-
Obtusoside	0,08	0,19
Feruloylskopolin	0,054	0,27
Thraxetine	-	0,005
Capensin	0,018	0,14
Obtusicin	0,84	0,17
Obtusiprenin	0,025	0,26
Obtusiprenol	-	0,023
Obtusidine	-	0,025
Thraxetine-7-O-glucoside	-	0,013
	-	0,006

The data obtained by us and other researchers show that the qualitative and quantitative compositions of coumarins of the studied plant species vary greatly depending on the ecological-geographic, soil-climatic conditions, as well as the vegetation period and the plant organ. The same species of this genus, growing in different geographical areas, may contain different in quality and quantity composition of coumarins.

As can be seen from the data presented in Table 2, the greatest amount of coumarins is extracted during the flowering period, rather than during the fruiting period, since during the fruiting period the yield of coumarins decreases.

In the flora of Kazakhstan, there are more than 70 species of plants, many species have plant medicinal plants and may be required for the pharmaceutical industry of the Republic. Therefore, the study of the chemical composition of pensions is not only scientific, but also practical [4; 12].

Various species of Haplophyllum (H.Dubium, H.Bucharicum, H.Bungei, H.Davuricum, H.Foliosum, H.Obtusifolium, H.Latifolium H.Perforatum and others) have long been used in folk medicine for the treatment of skin, as well as an antidote for poisoning, antipyretic, analgesic, laxative, for diseases of the stomach and spleen. Extracts of some species show antitumor and cytotoxic activity. Therefore, they attract the attention of researchers as potential sources of biologically active substances. The objects of our study are the species Haplophyllum Perforatum [4; 14].

In plant resources under the editorship of Sokolov P.D. information on the chemical composition and useful properties of this plant species is presented. Phenyl carboxylic acids and their derivatives: methyl ester of n-coumaric (n-hydroxycinnamic) acid. Lignans: (8R, 8'R 4, 4'-dimethylglylignolide-9.9 ".The plant roots contain alkaloids (in %) 0.047, skimianin 0.009, evoxin, haplopin. Containment in the aerial part of plants: steroids (in %) sitosterol 0.07; alkaloids (in %) 0.04-0.05; skimianin 0.14, haplatin 0.001, evoxin 0.04, haplopin 0.001, haplamide 0.003, haplamidine, glycopein, 7-isopentenyloxy-γ-pharagin. Phenyl carboxylic acids and their derivatives: methyl ester of n-hydroxycinnamic (n-coumaric) acid. In the stems of the plant contain: alkaloids 0.23%. In the leaves of the plant contain: alkaloids (in %) 0.04-0.6, skimianin 0.005-0.6, hapsolein 0.06, dubamine, haplatin.

Useful properties. The content of n-hydroxycinnamic acid methyl ester in the aerial part of plants shows estrogenic activity [5; 13].

And in plant resources under the editorship of Budantsev A.L. information on the chemical composition and useful properties of this plant species is also presented. The roots contain:

- terpenoids (fraksinellon);
- alkaloids (robustin, dictamnin, γ-pharagin, skimianin, evoxin, haplozidine 0.01%, haplosinin 0.003%);
- coumarins (seselin);
- flavonoids (haplogenin, limocitrin, haplozid C).

The leaves of the plant contain:

- flavonoids (7,3'-dimethyl ether of dihydroquercetin, 3,6-dimethyl ester of quercetin (axillarin), 3,5,7-trimethyl ester of kaempferol, 7-O-β-D-methyl glucuronide of 3'4'-dimethyl ester of lutheline , 7,3'-dimethyl ether and 3'-methyl esters of luteolin).

In the flowers and fruits are found essential oil in its composition includes monoterpenoids, hydrocarbons.

Water extract is used externally for dermatoses, eczema, varicose veins, alopecia, asthenia, anemia [6; 234,235].

Result and Discussion

The size of the medicinal plant material is determined by the method of sieve analysis.

The investigated plants were crushed to a particle size within 0.5mm in flowers (420.759), 1mm in stems (316.488), according to the regulatory documentation.

Good quality - compliance of medicinal raw materials, products, medicines with technical requirements of NTD.

All indicators of good-quality were determined by the methods of the GF RK, the European Pharmacopoeia and other literary sources.

Table 3 - Sieve analysis of H.Perforatum plant

Sifter №	Mass (*H.Perforatum*) = 600g		Mass (*H.Perforatum*) = 500g	
	H.Perforatum (flowers)		*H.Perforatum* (stems)	
	Mass, g	%	Mass, g	%
10	-	-	-	-
8	-	-	-	-
6	9,545	1,59	21,352	4,27
4	19,696	3,28	27,640	5,53
2	35,348	5,89	40,552	8,11
1	72,443	12,07	316,488	63,3
0,5	420,759	70,13	28,263	5,65
0,3	12,928	2,15	24,499	4,9
0,2	9,863	1,64	16,020	3,2
0,25	6,454	1,08	11,125	2,23
0,1	5,132	0,86	7,085	1,42
Remain	3,552	0,59	2,120	0,42
Losses	4,280	0,71	4,856	0,97

Table 4 - Numerical indicators of benignity of a plant of H. Perforatum species

Indicators of good quality	Plant H. Perforatum	
	Flowers	Stems
Humidity, %	5,74	5,83
Total ash, %	6,74	6,38
Sulphated ash, %	11,25	12,43
Ashes insoluble in 10% HCl	9,56	10,18
Containment of detective substances (70% alcohol)	44,06	32,59

As can be seen from the data presented in table 3, the moisture content in the stems (5.83%) is greater than for the flowers of the plant (5.74%). The total ash of the plant was 6.74%. The ash insoluble in 10% HCl was 9.56% in flowers, 10.18% in stems. And the distribution of extractive substances in the plant was H. Perforatum in flowers 44.06%, stems 32.59%.

The solvent, which should be taken when extractives are determined, is indicated in the relevant specification for this type of raw material. Usually, it is the same solvent that is used when preparing a tincture or extract from this raw material.

Extractive substances show the content of the likely active substances in the raw materials, which can later be processed. As can be seen from the data, the greatest amount of extractive substances is extracted by the flowers of this plant. The obtained data testify to the quality of the raw materials and the profitability of using the BAS complex. Figure 1 shows a benign chart of the distribution of H. Perforatum Kar.et Kir.

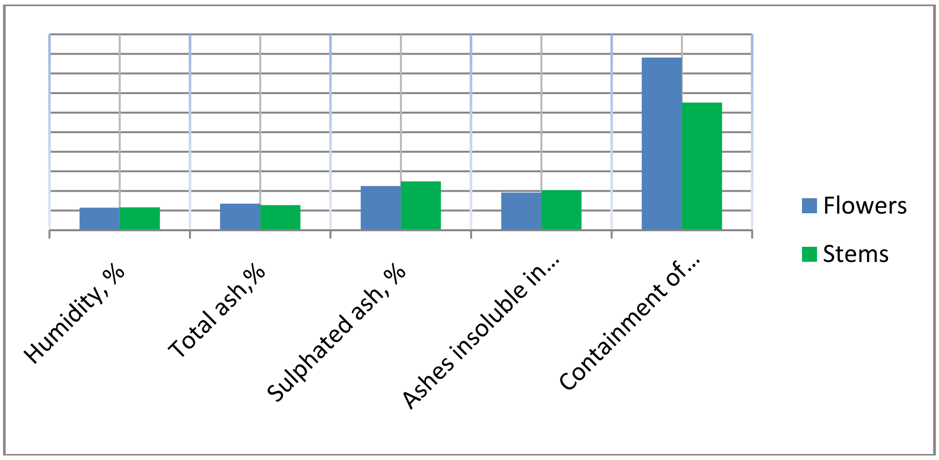

Figure 1 - Diagram of the assimilation of Haplophyllum Perforatum.

In the plant raw material, the ash of total, sulfate ash, ashes is insoluble in 10% HCl, which is the residue after treatment with the total HCl ash and consists mainly of silicates, which are a natural component for some objects, but more often the result of contamination of the raw materials with sand, earth and stones.

Mineral elements by their content in the plant are divided into macro elements, microelements and ultra microelements. Macroelements include Na, K, Ca, Mg, Cl, P; their content in the ashes is measured in hundredths of a percent. Microelements: Zn, Cu, Ni, Mn, Cu. Along with the "biometals" - elements that make up living organisms (for example, sodium, potassium, calcium, magnesium, iron, zinc), they can be referred to heavy metals - cadmium, lead, chrome, mercury and other d-elements, content which, according to the gradation of Vinogradova A.P., corresponds to the level of microelements in plants.

The study was carried out by the method of atomic absorption analysis on the basis of the Center for Physical and Chemical Methods of Research and Analysis (CPCMRA). The data are presented in table 5.

Table 5 - Macro- (K, Ca, Na, and Mg) content and microelements (Cu, Cd, Pb, Fe, Mn, Ni, Zn) in the plant H. Perforatum

Microelements	Flowers of a plant, %	The stems of the plant, %
Cd	$0,0227\cdot10^{-3}$	0
Pb	$0,1636\cdot10^{-3}$	$0,1487\cdot10^{-3}$
Fe	$5,2048\cdot10^{-3}$	$3,3864\cdot10^{-3}$
Mn	$0,6036\cdot10^{-3}$	$0,2767\cdot10^{-3}$
Ni	$0,2569\cdot10^{-3}$	$0,2301\cdot10^{-3}$
Zn	$2,7284\cdot10^{-3}$	$208,680\cdot10^{-3}$
Cu	$0,3671\cdot10^{-3}$	$0,3691\cdot10^{-3}$
Macroelements		
K	$473.370\cdot10^{-3}$	$432.30\cdot10^{-3}$
Ca	$395.880\cdot10^{-3}$	$157.890\cdot10^{-3}$
Na	$23.5525\cdot10^{-3}$	$28.2150\cdot10^{-3}$
Mg	$91.180\cdot10^{-3}$	$45.7025\cdot10^{-3}$

The largest number of macro and microelements is the flowers of the plant. In the stems and flowers of the plant, the dominant macro elements are K. In the flowers and stems of the plant, there is an increased content of macroelements like K, Ca. And the content of macroelements K, Ca, Na is explained by the fact that in saline conditions the Na +, K + concentration is increased, and they diffuse rapidly into the interior and easily saturate the cell sap.

A comparative phytochemical analysis for qualitative reactions and chromatographic analysis for the main classes of biologically active substances was carried out. The results are shown in Table 6.

Table 6 - Phytochemical analysis of the plant Haplophyllum A. Juss

BAS	*Developers*	Flowers	Stems
Carbohydrates	o-Toluidine	Light-brown envelope	Light-brown envelope
Tannins	JAK	Blue shading	Black-blue staining
Phenolic compounds	$FeCl_3$, 3%	Green	Dark green
Flavonoids	NH_3, 5%	bright yellow	yellow-green
	$AlCl_3$	pale yellow	bright yellow
	SiHNO	-	-
	$AgNO_3$, 1%	reddish-brown	reddish-brown
	NaOH, 5%	-	-
Carotenoids	$KMnO_4$ (Potassium permanganate)	decolorization	decolorization
	Phosphorus-molybdic acid	blue	green
Amino acids	$C_9H_6O_4$	pale purple	light purple
Carboxylic acids	(ninhydrin)	yellow-brown	brown
	CH_4N_2O (urea)	-	-
	$MgAc_2$	-	-

As can be seen from the data presented in table 6, in the accumulation of Haplophyllum A. Juss there are the main groups of biologically active substances. Carbohydrates, phenolic compounds, tannins, flavonoids, carotenoids, amino acids and carboxylic acids were found.

The method of the two-story paper chromatography in the use of reliable samples in flowers, and packages from flavonoids were occupied by quercetin and rutin; from the corners – cane sugar and glucose; from amino acids - as the so-called and all-alone α-amino acids.

An important parameter for obtaining the plant extract is the ratio of raw materials and solvent from 1:4 to 1:8. For 5 grams of raw material (flowers and stems of H. Perforatum Kar.et Kir) Pour in different volumes and different percentages of ethyl alcohol, when using a curing agent 1:6, and instill 24 hours without decontamination at a temperature of 24-25°C. These parameters are presented in table 7.

Table 7 - Determination of the optimum extragent for extraction

Mass of raw material, g *const*		5	5	5
*Solvents (*extragent*s)*		30% ethanol	50% ethanol	70% ethanol
Extraction temperature, ˚C const		24-25°C	24-25°C	24-25°C
Weight of dry extract, g	Flowers	0,1253	0,1625	0,0941
	Stems	*0,3442*	*0,5661*	*0,3824*
Extraction amount, %	Flowers	2,51	3,25	1,88
	Stems	6,88	11,32	7,65

As a result of comparative studies it was found that the optimal extragent is 50 % ethyl alcohol for flowers, 70 % ethyl alcohol for stems. When the ratio of raw materials: extragent 1: 6, the amount of dry extract in flowers was 3.25 %, and in stems 7.65 %.

One of the important parameters in the technology of obtaining extracts is also the ratio of the selected extragent to the raw material. To determine the optimum volume, the ratio of raw materials and solvent is changed from 1:4 to 1:8, pouring on 5 g of vegetable raw materials 70 % and 50 % ethyl alcohol. At this time constant of extraction (24 hours) and temperature (24-25° C), the following results were obtained. This is presented in the form of a table 8.

Table 8 - Determination of the optimal ratio

Mass of raw material, g *const*		5	5	5
Ratio of raw materials (g) and extraction (ml)		1:4	1:6	1:8
Extraction temperature, ˚C const		24-25°C	24-25°C	24-25°C
Weight of dry extract, g	Flowers	0,291	0,1625	0,2462
	Stems	0,1001	1,234	*0,3824*
Extraction amount, %	Flowers	5,82	3,25	4,92
	Stems	2,002	24,68	7,65

The data presented on the table show that the ratio of 1:6 with the extragent chosen was optimal, in flowers the amount of extract was 3.25%, and in stems 7.65%.

Table 9 - Determination of the optimal time

Mass of raw material, g *const*		5	5	5
Extraction time		12	24	48
Extraction temperature, ˚C const		24-25°C	24-25°C	24-25°C
Weight of dry extract, g	Flowers	1,618	0,1625	1,1125
	Stems	0,9864	1,8515	*0,3824*
Extraction amount, %	Flowers	32,36	3,25	22,25
	Stems	19,73	37,03	7,65

As a result, it was found that the optimal time was 24 hours with the extragent selected, the mass of the dry extract was 0.11625g in flowers and 0.3824g in stems.

The carried out researches allowed to determine the optimum values of the parameters influencing the extraction of biologically active substances from the plant H. Perforatum Kar.et Kir. stirpes Rutaceae.

Conclusions

Based on the results of the study, the following conclusions can be drawn:

The numerical parameters of the raw materials are determined: sieve analysis, moisture content, total ash, fly ash soluble in 10 % HCl, sulfate ash, extractives regulating the quality of raw materials complies with the norms of the State Pharmacopoeia of the Republic of Kazakhstan.

Methods of spectral analysis established for the plant H. Perforatum 4 macro- and 7 microelements. Qualitative methods of analysis include carbohydrates, tannins, flavonoids, phenolic compounds, carotenoids, amino acids and carboxylic acids.

The technology of extraction of the extract from the studied type of raw material, its ratio, temperature and time is worked out. The following parameters were chosen as the optimal condition: extragent 50 % ethyl alcohol in flowers, 70 % ethyl alcohol in stems, extraction ratio 1:6, extraction time 24 hours, temperature 24-25°C.

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HAPLOPHYLLUM A. JUSS ШӨБІНЕН БИОЛОГИЯЛЫҚ БЕЛСЕНДІ ЗАТТАРДЫҢ КЕШЕНДІ БӨЛІНУ ТЕХНОЛОГИЯСЫН ДАМЫТУ

Аннотация. Бұл зерттеуде Rutaceae тұқымдасына жататын *Haplophyllum A.Juss* өсімдігінің *H.Perforatum Kar et Kir* түріне комлексті зерттеу жүргізілді. Шикізат сапалылығының маңызды параметрлері қаралды. Олар: шикізат дайындау (майдалау, електен өткізу зерттеуі); ылғалдылық, жалпы күлділік, 10 % HCl-да ерімейтін күлділік, сульфатты күлділік, зерттеліпп отырған өсімдік түрлерінен экстрагенттің табиғатын, оның шикізатпен қатынасын, экстрактілеу уақыты мен жиілігін өзгерте отырып, биологиялық белсенді кешенді алу технологиясы өңделді.

Жалпы күлділіліктің макро- және микроэлементтік құрамы зерттелді. Сапалық реакция және хроматографиялық талдау әдісімен шикізаттағы табиғат қосылыстарының маңызды класстары жіктелді және олардың сапалық құрамы анықтады.

Түйін сөздер: Rutaceae, Haplophyllum, ылғалдылық, күлділік, кумариндер, Perforatum, флаваноидтар, терпеноидтар.

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РАЗРАБОТКА ТЕХНОЛОГИИ КОМПЛЕКСНОГО ВЫДЕЛЕНИЯ БИОЛОГИЧЕСКИХ АКТИВНЫХ ВЕЩЕСТВ ИЗ РАСТЕНИЙ РОДА HAPLOPHYLLUM A. JUSS

Аннотация. В данном исследовании проведено комплексное исследование растения рода *Haplophyllum A.Juss вида H. Perforatum Kar et Kir.* Рассмотрены основные параметры качества сырья: подготовка сырья (измельчение, ситовой анализ); влажность, общая зола, зола не растворимая в 10 % HCl, сульфатная зола, экстрактивные вещества.

Проанализирован макро- и микроэлементный состав общей золы. Качественными реакциями и хроматографическими методами анализа идентифицированы основные классы природных соединений в сырье и определено их количественные содержание. В сырье определены основные технологические параметры получение экстракта.

Ключевые слова: Rutaceae, *Haplophyllum*, *влажность, зольность, кумарины, Perforatum, флаваноиды, терпеноиды.*

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METHODS OF CARRYING OUT FLOTATION PROCESSES

Abstract. Within the scope of work on separation of polymer waste by the flotation method, there has been made a review of methods for carrying out flotation processes and the equipment used. There have been considered the existing schemes for classification of flotation processes by objects, interfacial boundaries, design features of flotators, aeration method, technological purpose, and there has been done the analysis of the completeness of accounting for all characteristic features.

Based on the analysis done, there has been suggested the classification of flotation processes by the following types: extraction of the valuable (target) component, type of the raw material, type of devices, process mode in the apparatus, interfacial surfaces. Among the methods of flotation separation on interfacial surfaces, the phase foam flotation is most widely presented in the industry. By the method of feeding gas to the liquid, flotation is divided into pneumatic, pneumomechanical, cascade, ejector, vacuum, pressure, electrical, reagent and thermal.

Flotation devices are also proposed to be classified by type into trough (direct flow), chamber (cascade) and column (tank) ones.

When choosing the most suitable flotation method for a particular task, it is necessary to take into account all types of flotation and know the features, advantages and disadvantages of each of them. The suggested scheme for classification of flotation processes lets us systematize and characterize completely most of the existing flotation processes.

Keywords: flotation, classification, raw materials, concentrate, target component, process mode, interfacial surface, aeration, equipment.

Introduction. Flotation as a method of mineral concentration is known since the 19th century. The English inventor William Haynes was the first who patented the use of oil flotation on February 23, 1860 [1]. Flotation varies by objects, interfacial boundaries, design features of flotators, aeration method, technological purposeand other characteristics [2–5].

Recently, the flotation process on the basis of various wettability is used to sort plastics. It is very promising because of the simplicity of hardware design and reliability in operation. It can be used to separate plastics with fairly close or equal densities. This requires the presence of surfactants and gas bubbles in the working volume of the device.

The purpose of this article is to review the methods of carrying out flotation processes and the equipment used, as well as to develop the flotation process classification scheme, ensuring the completeness of accounting for all characteristic features.

Study methods. Each of the considered methods of carrying out the flotation process has its own specific features of carrying out the studies.

Study results.

In the existing literary sources, there is a description of flotation types only by separate features. In the mining encyclopedia [6] there is a flotation process classification scheme, shown in figure 1. But it also does not contain a complete list of features and is difficult for perception.

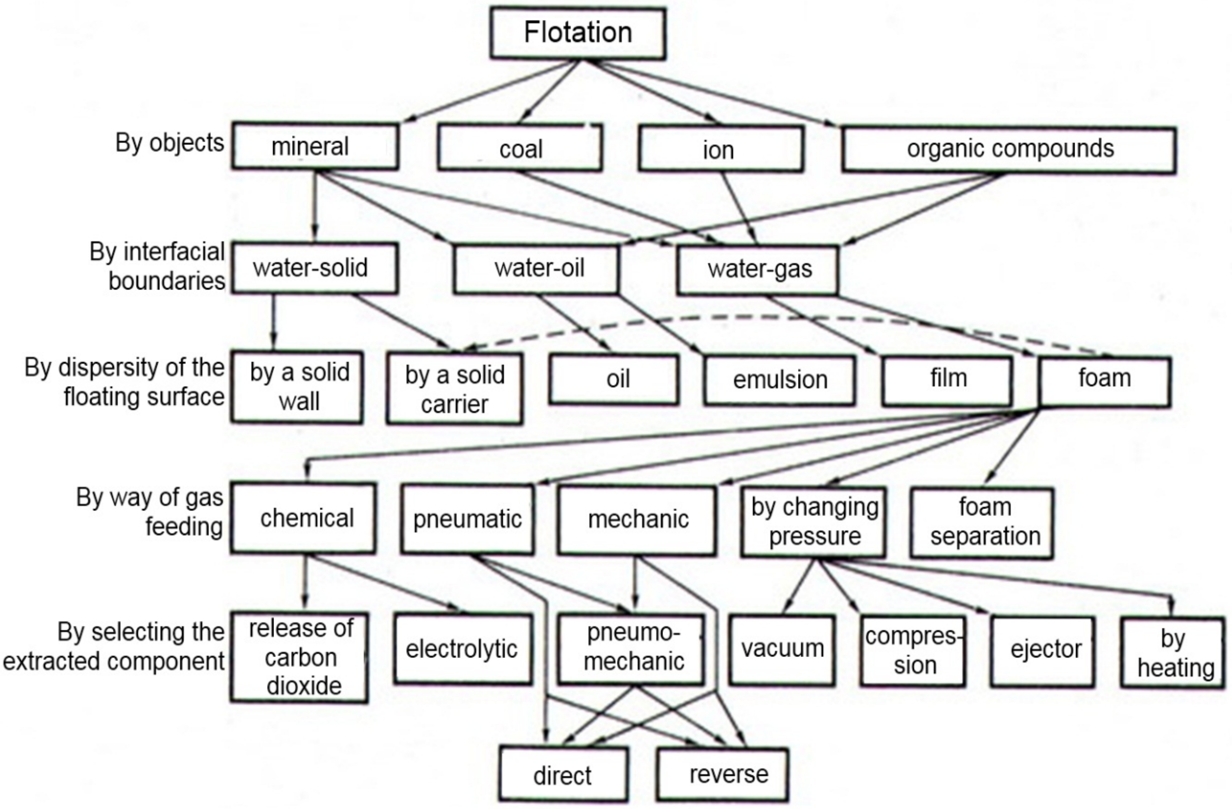

Figure 1 –Classification of flotation

Therefore, based on the literature data on flotation methods and their hardware design, the authors proposed the most complete scheme for classification of existing flotation processes, shown in figure 2.

The proposed scheme includes the following types of classification. By the extraction of a valuable (target) component, flotation can be direct or reverse; selective or collective. ***Direct*** flotation is an operation, in which the extracted useful material is concentrated in foam [7-9]. If during flotation the gangue is extracted into the foam and the concentrate is a chamber product, such flotation is called ***reverse*** [10, 11].

During the flotation of ores with obtaining several concentrates, depending on the order of separation of valuable components, there are distinguished selective and collective types of flotation. At the beginning of flotation process development, there was used only separation of gangue and target components, extracted into a collective (generic) concentrate with its following separation. Such flotation is called ***collective.*** Later on, there were developed the methods of separation into several products with the release of valuable components into various concentrates– so there appeared the ***selective*** flotation [12, 13].

Depending on the type of extracted material, flotation is divided into ***organic*** [10, 14, 15], ***mineral*** [16] and ***ion*** [17–20].

Flotation separation is carried out on the following phase interfaces:

– liquid-liquid (oil and emulsion flotation);

- liquid-gas (film and foam flotation);

– liquid-solid (coagulation and flotation with a carrier).

Oil flotation consists in different wetting of separated particles by immiscible liquids, dispersed in water in the form of small drops [15]. As a result, there are formed "particle – oil" complexes, floating to the surface. In Mariupol (1904) such a process was applied for the purpose of graphite ore concentration. Subsequently, this method was improved: the oil was dispersed to ***an emulsion***, which made it possible to extract fine tailings [21].

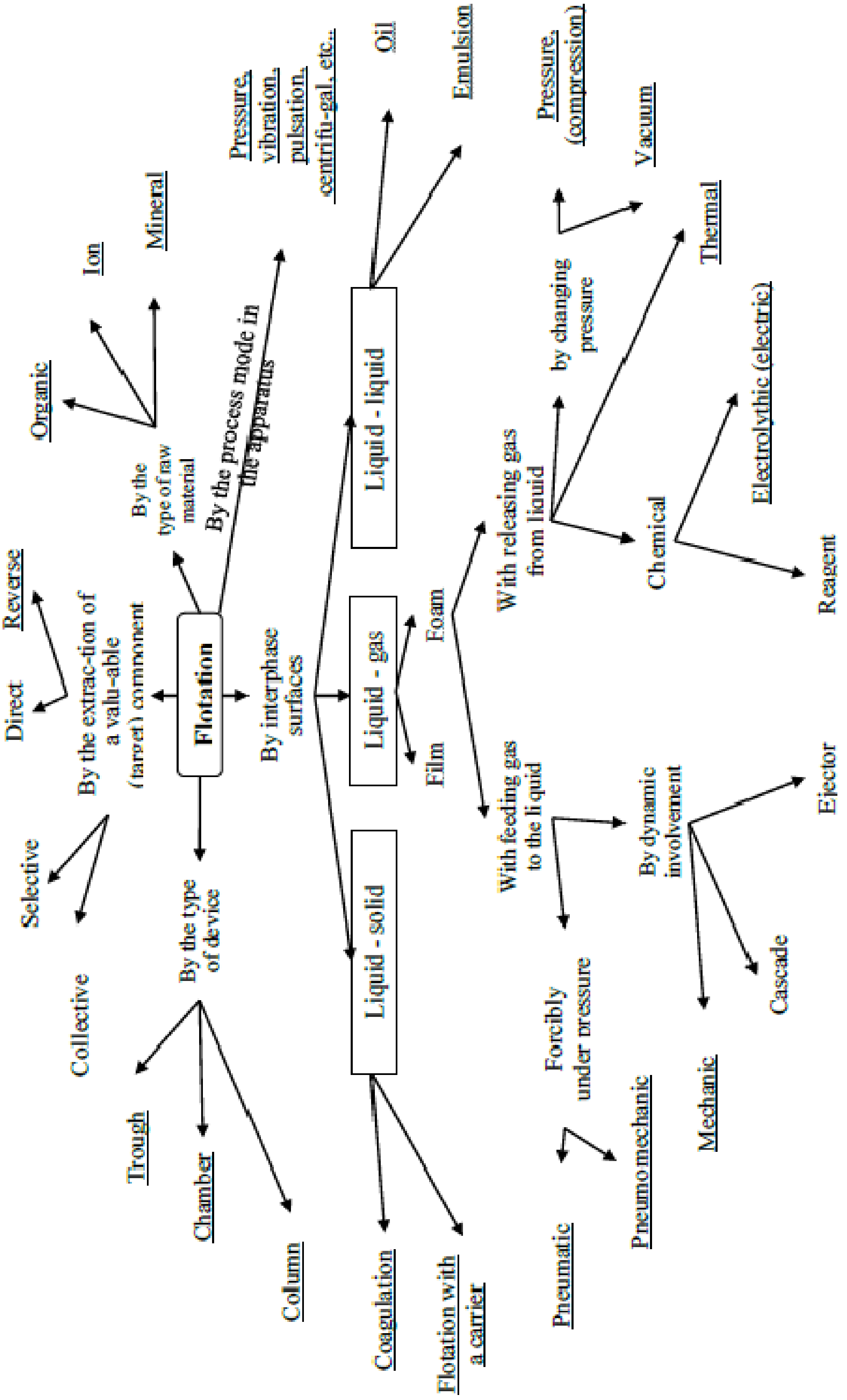

Figure 2 – Classification of flotation

During ***film*** flotation, the separated particles are poured from a certain height to the surface of the working fluid [22-25]. Non-wetted particles are kept on its surface and separated as a concentrate, while those wetted with water – sink and get into another product.

Oil and film flotation have low efficiency. Foam flotation is most widely presented in the industry.

Foam flotation is carried out in a three–phase medium "particles –liquid-gas", which contains flotation reagents. The flotation principle is as follows. In an aqueous medium, the gas bubble and the particle's hydrophobic surface, the adhesion (adherence) of which to liquid is less than the cohesion (repulsion) of liquid, come together. The water layer, separating them, reaches a certain thickness, at which it becomes unstable and spontaneously breaks. Then the particle and the bubble stick together. Due to the fact that the density of "bubble-particle" complexes is less than the density of liquid, they float to its surface and form a foam product that is withdrawn from the flotation machine. Wetted particles do not adhere to the bubbles, remaining in the volume of liquid, or settle to the bottom [26, 27]. This method was first patented by brothers Arthur and Adolf Bessel (Germany, 1877).) [28].

The foam layer can be formed in two ways - when feeding gas to the liquid or when gas being released from the liquid. Gas is fed to the liquid either forcedly under pressure (pneumatic and pneumomechanical flotation), or with dynamic involvement (mechanical, cascade, ejector flotation).

By the method of feeding gas to the liquid, as a defining feature of classification of flotation machines, there are distinguished the following methods of flotation [4]:

– ***pneumatic*** – flotation by gas bubbles, appearing, when gas is passed through porous aerators (branch pipes, filters, porous plates, caps, etc.)[29, 30];

– ***pneumomechanical*** – flotation by bubbles, formed during dispersion of the compressed gas, fed by mechanical agitators [31];

– ***mechanical*** – flotation by bubbles, drawn into the liquid from atmosphere, with intensive mixing of liquid by various agitators [31, 32, 33];

– ***cascade*** – flotation by bubbles, drawn into liquid from atmosphere as a result of the jet of the same liquid, falling into it from a certain height [34];

– ***ejector***– flotation by bubbles, drawn into liquid from atmosphere as a result of the flow of a jet of the same liquid at a high speed in a tube with a narrowing and air access gap [35, 36, 37].

Gas is separated from the liquid thermally, chemically (reagent or electroflotation) and by changing the pressure (pressure, vacuum):

– ***vacuum*** – flotation by gas bubbles, dissolved in the liquid, which are released under vacuum [38, 39];

– ***pressure*** (compression) – flotation by bubbles, released at atmospheric pressure from oversaturated under pressure solutions of gases in the liquid [40, 41];

– ***electroflotation*** – flotation by bubbles, arising in electrolysis, usually on the cathode [42, 43];

– ***reagent*** – flotation by bubbles, which are obtained as a result of the influence of acids or alkalis on the liquid;

– ***thermal*** – flotation by bubbles, released from the liquid as a result of its heating above the boiling point of the liquid, oversaturated with gas.

Reagent and thermal methods of flotation are very expensive and recently do not find a wide practical application. There are also combined methods of flotation, in which the liquid is aerated in several ways [44–46].

In machines of ***mechanical***type, air from the atmosphere is sucked due to the mechanical action of the mixer-aerator blades on the pulp. Strong mixing in the chamber creates the pulp turbulent flows in it. The pulp has a horizontal circular motion around the impeller shaft and a vertical circulation. Large air bubbles, trapped in the working fluid, are broken by a stirrer and pulp flows into small bubbles. Mechanical floatation is characterized by a variability of air suction with time, high power consumption, strong agitation of the pulp.

The specific feature of ***pneumomechanical*** flotation devices is that in such devices the impeller rotates only to hold the particles in suspended state and to disperse the air, supplied to the device from the blower, which makes it possible, in comparison with mechanical flotation devices, to ensure constant air flow in the device regardless of the wear of aerators. With this method, strong mixing of the pulp is carried out too.

Pneumatic flotation is characterized by the design simplicity, low cost (no impellers, pumps are needed). However, it is characterized by frequent clogging of aerator holes, the difficulty of uniform aeration. The efficiency of pneumatic flotation depends on the holes and material of the aerator, pressure and air flow, duration of the process, depth of liquid in the apparatus [47]. The low efficiency of separation is determined by the fact that when air is supplied through aerators, there are appearing large bubbles (1–3 mm) [48]. However, currently there are developed the aerators, providing a fine aeration (up to 0.3 mm). With such aerators there are equipped modern flotation devices with pneumatic aeration [49], and their use in pneumatic flotators increases the efficiency.

Gas separation from the solution with changing the pressure is applied for liquids that contain very small particles. This possibility was grounded by Klassen [50]. In this case, bubbles appear on the surface of the particles. This is done, in accordance with Henry's law, by reducing the solubility of gas in liquids with a decrease in pressure. The essence of the method is in formation of an oversaturated gas solution in the liquid. When pressure is released, from the solution there begin to separate the gas bubbles, which float hydrophobic particles. There are distinguished vacuum and pressure types of flotation.

By the method of ***vacuum*** flotation, the liquid under atmospheric pressure is saturated with air in the aeration chamber, and then transferred to the flotation unit, where the vacuum pump maintains the vacuum of 30-40 kPa. The bubbles released in this case float part of the dispersed particles to the surface. The advantages of vacuum flotation are that the process is carried out in a still medium, the possibility of destruction of flotation complexes is minimal and energy costs are low. The disadvantages of vacuum flotation include a limited by small pressure difference amount of liquid saturation with gas. This limits its application to separation of suspended particles with a concentration of up to 0.3 kg/m^3. One more disadvantage of vacuum flotation is the presence of sealed reservoirs with scraper mechanisms, which causes certain structural and operational difficulties.

Pressure flotation devices are more common than vacuum ones. Pressure flotation makes it possible to separate the material with a concentration of suspensions in liquid up to 5 kg/m^3. They are simple and reliable in operation. The saturation of liquid with gas occurs at elevated pressures in pressure tanks. The flotation unit operates at atmospheric pressure in this case. The solubility of gas in it decreases, and in the entire volume there are released the bubbles, which collide with the particles and float them.

Electroflotation is a process of separation of particles, suspended in liquid, by gas bubbles of hydrogen and oxygen, released during electrolysis. This method has distinctive features, which at the same time are its advantages. During electrolysis the finely dispersed gases are released [51, 52]. The bubbles of electrolysis gases are the same in size, they are little inclined to coalescence and during their residence in liquid they retain their diameters.

Electroflotation is a complex hydro-mechanical and electrochemical process. The speed and efficiency of this process is significantly influenced by the density of the electric current. The most serious drawback of the electroflotation separation method is that as electricity passes through the liquid, salt deposits occur on the electrodes, which can provoke a complete stop of the process. The electrodes work more effectively in an acidic medium. Uneven gas release on the electrodes leads to the concentration of bubbles in certain areas of the flotation device. Because of this, it produces the undesirable circulation of liquid [53, 54].

The process of electro-flotation, apparently, will not receive widespread adoption in large-tonnage production. This is primarily due to the low performance of electric flotators, as well as their instability, caused by the latch-up of the interelectrode area [55, 56].

Flotation devices are also classified by type to trough (direct-flow), chamber (cascade) and column (tank).

Flotation devices of a ***trough*** type have a form of a bath, stretched in length. The working fluid is supplied from one side and goes out on the other side together with the sludge. The foam is taken along the entire length through the side boards into the troughs (usually by gravity). The height of the working fluid is regulated by the intensity of discharge.

Chamber [57] flotation devices consist of separate chambers, with one or more aerators used in each of them. Among the features of chamber machines there are: the need to adjust the height of the working fluid in each chamber; lowering the level of the working fluid along the machine, due to which in each chamber there are different heights of foam threshold and foam scraper blades.

Flotation apparatuses of ***column*** type [2, 58-81] are vertical tanks of different sections (round, elliptical or rectangular). The foam product is removed from the top and the sediment - from the bottom of the column. Power is supplied most often to the middle part of the column.

Flotation in the column apparatus is carried out with the counter-current movement of the bubbles and the working fluid. The liquid is discharged through the discharge pipe at the bottom of the column, and bubbles float towards it. On the surface of liquid they form the foam, which is withdrawn at the top of the column. The speed of the working fluid should be less than the relative speed (float) of the bubbles. The high velocity of liquid can result in the accumulation of bubbles, their coalescence and the release of gas locks.

The flotation column is smaller in size than other flotation units of the same capacity; it is generally free of moving parts, which reduces the energy consumption and maintenance costs. The main difficulties, arising during the operation of column apparatus are associated with clogging of aerators [81].

Chamber machines can be of mechanical and pneumomechanical types, trough machines – of any other types, column machines - of a pneumatic type only.

The mode of motion of bubbles and particles is a significant factor, affecting the possibility of flotation complex formation, flotation intensity and energy consumption of the process. The probability of collision of a bubble and a particle, as well as the formation of a flotation complex depends on the relative speed of their movement, the duration of contact and the forces of inertia. By the mode of movement of phases in the machine, flotation is also divided into numerous types: pressure, vibration, pulsation, centrifugal, etc. In this work we'll consider only those modes of movement of phases, which are most commonly found in the basic designs of flotation machines.

In mechanical and pneumomechanical machines the nature of liquid and solid phases' motion is similar to perfect mixing. This is necessary to maintain the suspension in a suspended state, to disperse the bubbles and increase the time they stay in the working volume of the apparatus. However, intensive mixing can cause the destruction of the bubble – particle complex due to the inertia forces, especially during the flotation of large particles [2]. In addition, the use of the impeller reduces the efficiency of the flotation unit, since a significant part of the energy is used to maintain the working medium in a suspended state, which is not directly related to the flotation process.

The counter-flow of the working fluid and bubbles in the column apparatus reduces the speed of the constrained (group) motion of bubbles, which increases their residence time in the working fluid, the efficiency of gas use and the specific productivity of the flotator. In the column, the forces of inertia are insignificant due to the absence of mechanical devices and low turbulence of flows.

As it can be seen from the listed types, flotation is a complex and multi-faceted process. When choosing the most suitable method of flotation for a particular task, it is necessary to take into account all types of flotation and know the features, advantages and disadvantages of each of them. The suggested scheme for classification of flotation methods lets us systematize and characterize completely most of the existing flotation processes.

Conclusions. There have been made a review and analysis of methods for carrying out flotation processes and the equipment used. The existing schemes of classification of flotation processes do not contain a complete list of features and are difficult for perception.

There has been suggested the classification of flotation processes, the main components of which are the methods of extraction of a valuable (target) component, the type of raw materials, the type of devices used, the process modes in the apparatus, the interfacial surfaces used. The suggested scheme for classification of flotation methods lets us systematize and characterize completely most of the existing flotation processes.

Foam flotation is noted as a method, most widely used in the industry. There have been considered the designs of flotation machines.

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ФЛОТАЦИЯЛЫҚПРОЦЕССТЕРДІЖҮРГІЗУӘДІСТЕРІ

Аннотация. Флотация арқылы полимерлік қалдықтарды бөліп шығару бойынша жұмыстардың шеңберінде флотациялық үрдістерді және қолданылатын жабдықты жүргізу әдістеріне шолу жасалды. Нысандар, фазааралық шекара, флотаторлардың конструктивті белгілері, аэрациялау тәсілдері, технологиялық тағайындалулары бойынша қолданыстағы флотациялау процесстерінің классификациялық сұлбасы қарастырылды және оларға тән барлық белгілерді есепке алынып талданды.

Жүргізілген талдаудан кейін флотация процестерін келесі типтер бойынша жіктеу ұсынылады: бағалы (мақсатты) компонентті алу бойынша, шикізат түрі бойынша, құрылғылардың түрі бойынша, аппараттардағы процестің бойынша, фазааралық беттер бойынша. Фазаларды беттік бойымен бөлумен флотационды бөлу әдістерінің ішінде көбікті флотация өнеркәсіпте кеңінен ұсынылған. Газды сұйықтыққа беру тәсілі бойынша флотация пневматикалық, пневмомеханикалық, каскадты, эжекторлы, вакуумды, қысымды, электрофлотациялық, реагентті және термиялық болып бөлінеді.

Флотациялық аппараттар типі бойынша жіктелу (тік сызық), камералы (каскад), баған (шанда) бойынша ұсынылады.

Белгілі бір тапсырма үшін флотацияның ең қолайлы әдісін таңдағанда, флотацияның барлық түрлерін ескеріп, әрқайсысының ерекшеліктерін, артықшылықтарын және кемшіліктерін білу қажет. Флотациялық әдістерді жіктеудің ұсынылған сұлбасы қолданыстағы флотация процестерінің көпшілігін жүйелеуге және сипаттауға мүмкіндік береді.

Түйін сөздер: флотация, классификация, шикізат, концентрат, мақсатты компонент, процесс тәртібі, фазааралық бет, аэрация, жабдық.

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МЕТОДЫ ПРОВЕДЕНИЯ ФЛОТАЦИОННЫХ ПРОЦЕССОВ

Аннотация. В рамках проведения работы по разделению полимерных отходов методом флотации проведен обзор методов проведения флотационных процессов и применяемого оборудования. Рассмотрены существующие схемы классификации процессов флотации по объектам, межфазным границам, конструктивным признакам флотаторов, способу аэрации, технологическому назначениюи выполнен анализ полноты учета всех характерных признаков.

Исходя из проведенного анализа, предложена классификация процессов флотации по следующим типам: по извлечению ценного (целевого) компонента, по виду сырья, по типу устройств, по режиму процесса в аппарате, по межфазным поверхностям. Среди методов флотационного разделения на поверхностях раздела фазпенная флотация наиболее широко представлена в промышленности.По способу подачи газа в жидкость флотация подразделяется на пневматическую, пневмомеханическую, каскадную, эжекторную, вакуумную, напорную, электрофлотацию, реагентную и термическую.

Флотационные аппараты предложено также классифицировать по типу накорытные (прямоточные),камерные (каскадные),колонные (чановые).

При выборе наиболее подходящего способа флотации для той или иной задачи необходимо учитывать все типы флотации и знать особенности, достоинства и недостатки каждого из них. Предлагаемая схемаклассификации методов флотации позволяет полностью систематизировать и охарактеризовать большинство существующих процессов флотации.

Ключевые слова: флотация, классификация, сырье, концентрат, целевой компонент, режим процесса, межфазная поверхность, аэрация, оборудование.

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STUDY OF THE PARTICLE DYNAMICS IN IMPACT-CENTRIFUGAL MILLS

Abstract. Proceeding from the analysis of operation of impact-centrifugal mills, requiring extremely high energy costs, of particular interest is the search for sources, enabling to minimize these costs. Along with the structural elements and assemblies, as well as the technological service, a great role here is played by the influence of the dynamics of particles, formed during grinding. In its turn, the velocity nature of crushed particles' motion is a function of such variables as the design of impingement elements, the direction of impact, the particle's configuration and the material, to which it belongs, as well as a number of other factors.

The paper presents the analysis of design schemes of impact-throwing type mills with different shape and location of accelerating blades. There is considered the common case of the material's particle motion along the accelerating arc blade, located in the horizontal plane, and there is given the design scheme.There is graphically considered the direction of the total velocity of a particle at different location of blades, and there is suggested the dependence of the particle's impact impulse on the particle's descent angle. There are obtained the laws of material's particle motion in the impact-centrifugal mill with the blades of arc profile of variable radius, there are established the basic laws, permitting to determine the impact impulse and, accordingly, the grinding efficiency, depending on the blade profile.

Keywords: the impact-centrifugal mills,thedesign scheme, the particle**,** the velocity, the motion, the operating device, the rotating rotor, the impact impulse, the profile, the efficiency.

Introduction.

Grinding processes are very common in many industries. These, in particular, include: the production of building materials, food production, pharmacology, recycling.

A. Griffiths and A. Ioffe made a significant contribution to the study of fracture mechanics [1, 2]. Taking into account their work, many researchers studied the physical bases of the processes of destruction [3 – 5], laying the Foundation for modern hypotheses and assumptions. Particularly important attention was paid to the problems associated with specifying the grinding work, since this process itself is very energy-intensive. The first attempt to identify the energy costs of grinding was made by P. Rittinger. According to his hypothesis, it follows that the work spent on grinding is proportional to the size of the newly formed surface in the crushed material. A bit later, F. Kick and V. Kirpichev [6 – 8], independently from each other, put forward a hypothesis that the energy, required to obtain similar changes in the configuration of geometrically similar bodies of the same technological structure, change like the weight or volume of these bodies. P. A. Rebinder [6, 7] combined the hypotheses of Rittinger and Kick-Kirpichev, considering that the destruction occurs after the piece's deformation and the total work of crushing is the sum of the work of deformation and the work of new surfaces' formation.

The above researchers laid the foundations of fracture mechanics, established the laws for specifying the fracture work, however, in spite of this, currently there is no clear theory of this process. This is determined both by the complexity of the phenomena, observed in the material during destruction, and by the practically infinite variations in the properties of the materials themselves, such as hardness, density, plasticity and many others.

At the same time, many researchers note that for most materials, especially for fragile and fragile-flexible, the most acceptable in terms of energy efficiency are such methods of grinding as crushing and impact [9 – 15]. Upon impact, in the material there occur considerable short - term internal forces, which result in the appearance and development of cracks that destroy the integrity of the material. Therefore, impact mills are widely used in grinding of various materials [11,12, 15].

Basically, the working body of such mills is a rotating rotor, usually in the form of a disk with the accelerating blades, installed on it. When the rotor rotates, the crushed material, fed into its inner cavity, moves under the influence of inertial forces along the accelerating blades from the center of rotation to the periphery. Breaking off from the blades at a certain speed, the material's particles hit the fixed impact surface and break down into smaller parts [16 – 18].

The efficiency of impact grinding depends on the speed, at which the particle hits the impingement element, and the angle between the velocity vector and the normal to the impingement surface in the impact point of the particle. The greater the speed of the particle at the time of impact and the closer the impact angle in relation to the normal to the impact surface to zero, the more effective the grinding process. Therefore, we can assume that the grinding efficiency is affected by the profile and location of the blade. In addition, it should be noted that when the abrasive particles move along the blade, there is an intense abrasion of its surface. In this regard, the task is to select such parameters of the blade profile, at which the pressure on it will be minimal, which, in its turn, will reduce the friction force and increase the durability of the blade.

Typical designs of rotors in impact-throwing type mills in most cases are provided with radial accelerating blades (Fig.1, a) [16-18]. These blades are easy to manufacture and therefore they are widely used in rotary mills. The results of studies of the material's movement in mills with radial blades are presented in many works [16–20].

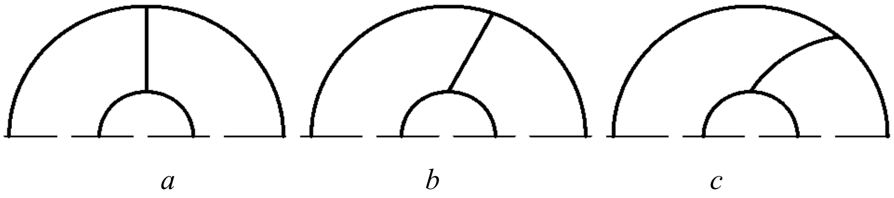


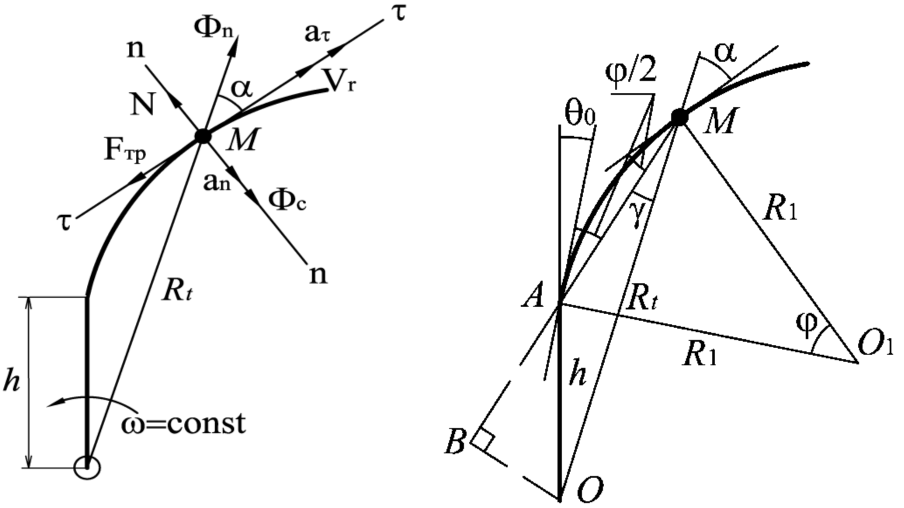
Figure 1 – The design schemes of impact-throwing type mills with different shape and location of accelerating blades

Therefore, the purpose of further research was to investigate the material's particle dynamics in impact type mills with arc blades of variable radius; to determine the influence of geometric characteristics of impact-centrifugal mills with different types of blades on the efficiency of impact grinding.

Study methods. To carry out the studies, there were used the numerical and analytical methods with the use of computers.

Studyresults. The material to be ground, before reaching the blade, is fed into the central part of the rotor, from where, under the influence of centrifugal forces, it moves to the inter-blade space. Despite the fact that the material is supplied as a continuous flow, it can be considered that the movement of particles along the blades occurs separately, since their speed in the radial direction is constantly increasing, so they move apart from each other. Also, in [21] it is pointed out that for mill sizes of grinded pieces of material of the order of 10 mm, mill loading cannot be considered a bulk medium, it is allowed to consider the motion of single particles.

Let's consider the general case of the material's particle movement along the accelerating arc blade, located in a horizontal plane (Fig. 2). Here we believe that the blade has a constant curvature radius R_1, and the particle is presented by a material point M.



h – a distance from the rotor center to the beginning of blades, R_t – the radius-vector module n

Figure 2 -Thedesignscheme

Let the particle be in any point of the blade surface. Here we assume that the rotor rotates at a constant angular velocity ω. In relative motion, the particle will be affected by the centrifugal inertial force Φ_n, the Coriolis inertial force Φ_c, the force of the particle's friction on the blade surface $F_{тр}$ and the reaction of the support surface N. The force of aerodynamic resistance will be neglected by us, since the centrifugal force of inertia is by an order of magnitude more than the force of aerodynamic resistance. The particle's motion along the blade in the axial direction of the rotor, i.e. across the blade, is not considered, since the value of gravity force at operating frequencies of the mill rotor rotation is by orders of magnitude less than the values of inertial forces.

The system of equations, describing the motion of a particle along the arc blade in a natural coordinate system (Fig. 2), will be written as:

$$m\ddot{s} = m\omega^2 R_t \cos\alpha - Nf\,,$$

$$m\frac{\dot{s}^2}{R_1} = -N - m\omega^2 R_t \sin\alpha + 2m\omega\dot{s}\,, \tag{1}$$

where m – the mass of a particle, s – the arc coordinate, measured from the beginning of the blade, ω – the mill rotor angular velocity, f – the coefficient of sliding friction, N – the support's reaction.

The system of equations (1) completely describes the motion of particle M, if we know explicit expressions for the radius vector modulusR_t, $\cos\alpha$ and $\sin\alpha$ as a function of the generalized coordinate s. These expressions are easy to find with the help of Fig. 2. From the right triangle OBM we obtain

$$R_t^{\,2} = \left(h\sin(\theta_0 + \frac{\varphi}{2})\right)^2 + \left(h\cos(\theta_0 + \frac{\varphi}{2}) + 2R_1 \sin\frac{\varphi}{2}\right)^2. \tag{2}$$

Angle θ_0 is the inclination angle of the tangent to the starting point of the blade. This angle specifies the orientation of the blade curvature radius R1 in the plane of the rotor.

FromFig. 2 itfollowsthat

$$\cos\alpha = \frac{1}{R_t}\left(h\cos(\theta_0 + \varphi) + R_1 \sin\varphi\right),$$

$$\sin\alpha = \frac{1}{R_t}\left(h\sin(\theta_0 + \varphi) + R_1(1 - \cos\varphi)\right). \tag{3}$$

Taking into account that the angular coordinate $\varphi = s/R_1$ from system **Ошибка! Источник ссылки не найден.**, with taking into account **Ошибка! Источник ссылки не найден.**, we derive the equation of the particle motion as

$$\ddot{s} = \omega^2 \left(h\cos(\theta_0 + \frac{s}{R_1}) + R_1 \sin\frac{s}{R_1} \right) - f\frac{N}{m}, \tag{4}$$

where the support reaction

$$N = m\left(2\omega\dot{s} - \frac{\dot{s}^2}{R_1} - \omega^2 (h\sin(\theta_0 + \frac{s}{R_1}) + R_1 - R_1\cos\frac{s}{R_1}) \right).$$

From the nonlinear differential equation (4) it is possible to obtain special cases of the particle motion along the rectilinear inclined and radial blades. For this, it is needed to carry out the limiting transition $R_1 \to \infty$. As a result, we obtain a linear differential equation of the particle's motion along the rectilinear inclined blade:

$$\ddot{s} = \omega^2 \left(h\cos\theta_0 + s \right) - f\,N/m,$$
$$N = m(2\omega\dot{s} - \omega^2 h\sin\theta_0). \tag{5}$$

If the blade is radial, i.e. $\theta_0 = 0$, then the equation of motion has the form:

$$\ddot{s} = \omega^2 \left(h + s \right) - f\,N/m,$$
$$N = m\,2\,\omega\,\dot{s}. \tag{6}$$

The solution of equations (5) and (6) can be obtained in the analytical form, equation (4) is integrated numerically, but the determination of the particle's position on the blade as a function of time is of no interest, since for grinding efficiency analysis it is necessary to know the full speed of the particle at the time of its descent from the blade and the direction of this speed. The analysis of equation (4) shows that the friction force component is much smaller than the inertial component, hence it can be concluded that the friction force will not significantly affect the magnitude and direction of the total speed of the particle, so in further calculations it will be neglected. In this case, we can obtain the first integral of motion for equation **Ошибка! Источник ссылки не найден.** which makes it possible to determine the reaction of a support surface N as a function of the particle's position on the blade s.

$$\frac{\dot{s}^2}{2} = \omega^2 \left(hR_1 (\sin(\theta_0 + \frac{s}{R_1}) - \sin(\theta_0)) + R_1{}^2 (1 - \cos\frac{s}{R_1}) \right), \tag{7}$$

The integrals, similar to (7), are obtained for rectilinear inclined and radial blades by integrating equations (5) and (6) or by performing a limit transition $R_1 \to \infty$ for equation **Ошибка! Источник ссылки не найден.**.

$$\frac{\dot{s}^2}{2} = \omega^2 \left(h\cos\theta_0 s + \frac{s^2}{2} \right), \tag{8}$$

$$\frac{\dot{s}^2}{2} = \omega^2 \left(hs + \frac{s^2}{2} \right). \tag{9}$$

Equation **Ошибка! Источник ссылки не найден.** can be derived by writing the theorem of the particle kinetic energy change in the rotating coordinate system

$$\frac{m\dot{s}^2}{2}=\frac{m\omega^2 R_t^2}{2}-\frac{m\omega^2 h^2}{2}, \tag{10}$$

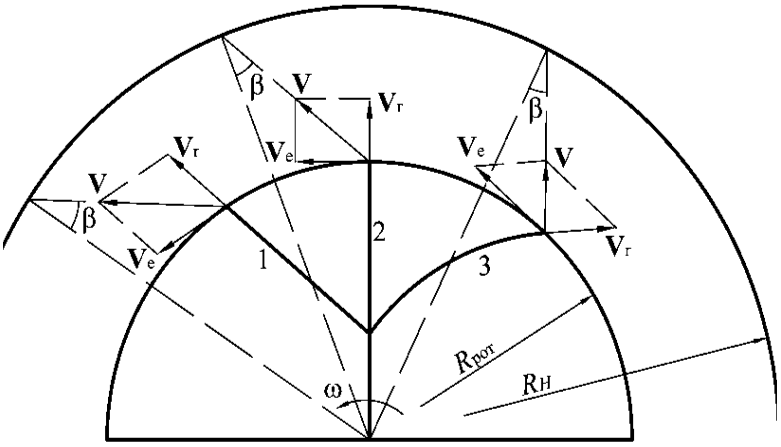
where in the right part there is recorded the work of the centrifugal inertial force during the particle's relocation from the initial position h to the current position R_t. Then from (10) we have

$$\dot{s}^2=\omega^2\left(R_t^2-h^2\right). \tag{11}$$

By putting expression (2) into equation (11), we obtain (7). Expression (11) leads to an important conclusion: the particle's relative velocity module during its departure from the rotor (when $R_t = R_{\text{рот}}$) does not depend on the profile and location of the accelerating blade.

$$\dot{s}\equiv V_r=\omega\sqrt{R_{\text{рот}}^2-h^2}=\text{const}. \tag{12}$$

The direction of the relative velocity vector, of course, will depend on the shape and location of the blade (Fig.3).



$R_{\text{рот}}$ – the rotor radius; R_H –the impingement surface radius.

Figure 3 - The direction of the particle's total velocity at various blade positions

Let's decompose the particle's total velocity at the moment of its descent from the blade to the radial component v_n and the tangent component v_τ:

$$v_n=V_r\cos\alpha_c,\ v_\tau=\omega R_{\text{рот}}-V_r\sin\alpha_c., \tag{13}$$

where α_c – the angle value α at the time of descent of the particle from the blade (the angle of descent) is determined by formulas (3). Then the square of the particle's total velocity, with taking into account (12), will be

$$v^2 = v_n^2 + v_\tau^2 = 2\omega^2 R_{\text{рот}}^2\left(1-\sqrt{1-\left(h/R_{\text{рот}}\right)^2}\sin\alpha_{\text{с}}\right) - \omega^2 h^2. \qquad (14)$$

The formula shows that for the blade, at the end of which $\sin\alpha_{\text{c}} = 0$ (for example, a radial blade), the square of the particle's total velocity at the moment of its descent from the blade will be

$$v_{\text{п}}{}^2 = 2\omega^2 R_{\text{рот}}^2 - \omega^2 h^2.$$

The rate of descent of a particle from a rectilinear inclined blade will depend on the direction of the slope of this blade (in the direction of the angular velocity ω or opposite to it, Fig. 3). The limit transition $R_1 \to \infty$ for such a blade, according to (3), gives $\sin\alpha_{\text{c}} = h/R_{\text{рот}}\sin\theta_0$ and, in accordance with formula (14), the total speed of the particle with the passing blade inclination $v > v_{\text{п}}$ (since the blade inclination angle θ_0 in this case is negative) and $v < v_{\text{п}}$ with the blade inclination in the direction, opposite to the angular velocity ω. Similar conclusions can be made for the arc blade.

The value of the particle's total velocity says nothing about the grinding process efficiency, since the impact impulse accounts for only part of this velocity. The impact impulse can be determined by the formula

$$p = mv\cos\beta, \qquad (15)$$

whereβ – the angle between the vector of total velocity and the normal to the surface in the point of impact of the particle (Fig.4).

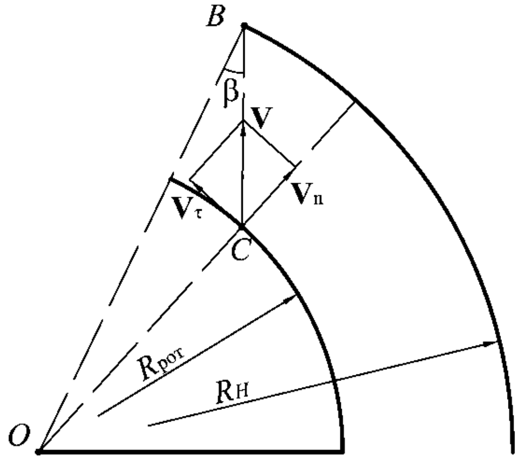


Figure 4- Determination of the particle's impact impulse.

Using the sine theorem for triangle *OBC* (Fig. 9), we derive

$$\cos\beta = \sqrt{1-\left(\frac{R_{\text{рот}}}{R_H}\right)^2\left(\frac{v_\tau}{v}\right)^2}, \qquad (16)$$

whereR_H – the radius of the mill's impingement surface.

Then the particle's impact impulse (15), with taking into account (14) and (16), will be

$$p = m\sqrt{v_n^2 + v_\tau^2\left(1 - \left(R_{\text{рот}}/R_H\right)^2\right)}\,. \tag{17}$$

In formula (17) the first summand under the root determines the contribution of the radial component of the total velocity; the second summand - the contribution of the tangential component. If to solve the problem for extremum of the impact impulse function (17), then the particle's descent angle, at which the maximum impact impulse will be reached, at a specified $R_{\text{рот}}/R_H$ ratio, is determined by the formula

$$\sin\alpha_{\text{c}}^{\max} = \frac{1-(R_H/R_{\text{рот}})^2}{\sqrt{1-(h/R_{\text{рот}})^2}}\,. \tag{18}$$

The maximum impact impulse here will be

$$p_{\max} = m\omega\sqrt{R_H^2 - h^2}\,. \tag{19}$$

The analysis of formula (17) showed that with increasing the radius of the impingement surface, the impact impulse maximum is shifted towards the negative values of angles of the particle's descent from the blade (for example, if the blade is inclined in the direction of the angular velocity). The dependence of the impact impulse on the angle of the particle's descent from the blade for different values of$k = R_H/R_{\text{рот}}$ is shown in Fig. 5.

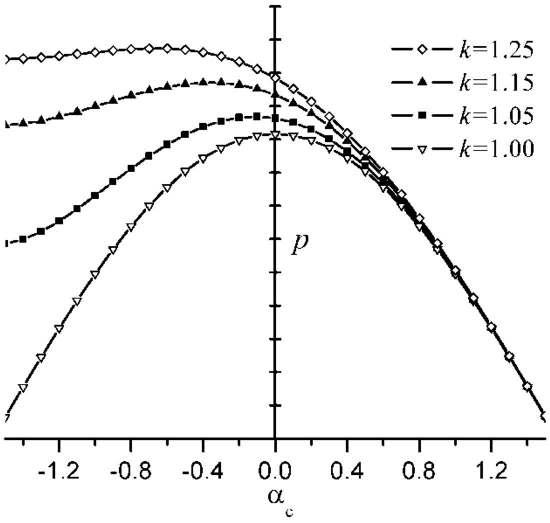


Figure 5 - Dependence of the particle's impact impulse on the angle of the particle's descent

From the figure it is seen that the impact impulse increases with increasing radius of the impingement surface, but in practice to achieve an increase in the impact impulse in this way is difficult, since during the particle's movement in the space between the rotor and the impingement surface there are appearing the air flows that greatly slow down the speed of the particle, so the gap between the rotor and the impingement surface is usually made minimum, so that $k = R_H/R_{\text{рот}}$ does not exceed 1.05. If to assume $R_{\text{рот}}/R_H = 1$, then formula (17), with taking into account (12), can be approximately written as

$$p = mV_r\,\cos\alpha_{\text{c}} = m\omega\sqrt{R_{\text{рот}}^2 - h^2}\,\cos\alpha_{\text{c}}\,. \tag{20}$$

From formula (20) (and from Fig. 4) it is seen that at $R_{\text{рот}}/R_H \approx 1$ the maximum impact impulse is achieved during the particle's descent from the blade, having $\alpha_c = 0$. This value α_c can be achieved either on the radial blade or on the arc blade, at the end of which the tangent to this blade τ will coincide with the radius vector R_t. Thearcblade,providing$\alpha_c = 0$, isshowninFig. 6.

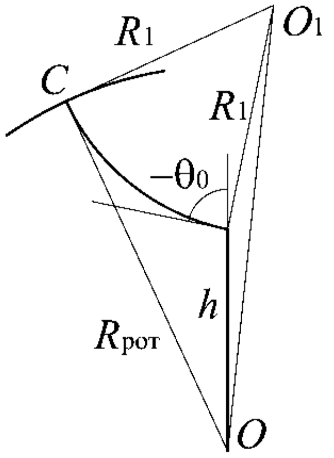


Figure 6 - Determination of the arc blade's optimal angle of inclination θ_0

From the right triangle OO_1C in Fig. 6 we can determine the dependence of the arc blade's angle of inclination θ_0 from the radius of its curvature, which will provide $\alpha_c = 0$.

$$\sin\theta_0 = -\frac{R_{\text{рот}}^2 - h^2}{2h}\frac{1}{R_1}. \tag{21}$$

The sign "–" in formula (21) shows that to ensure the condition $\alpha_c = 0$, the blade must be tilted in the direction of the angular velocity ω. From formula (21), we obtain the possible range of variation of the curvature radius

$$\frac{R_{\text{рот}}^2 - h^2}{2h} \le R_1 < \infty, \tag{22}$$

with the angle θ_0 changing from $-\pi/2$ to 0.

Conclusions. In the course of research there were obtained the laws of motion of the material's particles in an impact -centrifugal mill with blades of an arc profile of variable radius, there were established the basic mechanisms that allow to determine the impact impulse and, accordingly, the efficiency of grinding, depending on the profile of the blade.

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СОҚҚЫЛЫ-ОРТАДАН ТЕПКІШ ДИІРМЕНДЕРДЕГІ БӨЛШЕКТЕРДІҢ ДИНАМИКАСЫН ЗЕРТТЕУ

Аннотация. Аса энергия шығынды болып келетін соққылы-ортадан тепкіш диірмендердің жұмысына талдау негізінде, осы шығындарды азайтатын көздерді іздестіру ерекше қызығушылық тудырады. Құрылымдық элементтер мен түйіндермен қатар, технологиялық сервиспен қатар, бөлшектердің динамикасының әсері маңызды рөл атқарады. Өз кезегінде, ұсақталған бөлшектердің қозғалыс жылдамдығының сипаты айналдыру элементтерінің конструкциясы, әсер ету бағыты, бөлшектердің конфигурациясы және оған тиесілі материал, сондай-ақ бірқатар басқа факторлар сияқты айнымалылардың функциясы болып табылады.

Жұмыста әртүрлі пішіндегі соққылы-лақтырылған типтегі диірмендердің есептік сұлбаларына және жылдамдатқыш пышақтардың орналасуына талдау жүргізілді. Горизонталь жазықтығында орналасқан доғалық жылдамдатқыш жүзі бойындағы материалдың бөлшектерінің қозғалысы қарастырылды және есептеу сұлбасы берілді. Бөлшектердің әртүрлі орналасуы бар бөлшектердің жалпы жылдамдық бағыты графикалық түрде қарастырылды және бөлшектің әсер ету серпінін бөлшектердің кету бұрышына тәуелділігі ұсынылды. Бөлшектердің әртүрлі орналасуы бар бөлшектердің жалпы жылдамдық бағыты графикалық түрде қарастырылады және бөлшектің әсер ету серпінін бөлшектердің кету бұрышына тәуелділігі ұсынылады. Айнымалы радиустардың доғалы профилінің пышақтарымен соққы-ортадан тепкіш диірмендегі материалдық бөлшектердің қозғалысы туралы заңдар алынып, пышақтың бейініне байланысты әсер ету импульсін және, тиісінше, тегістеу тиімділігін анықтауға мүмкіндік беретін негізгі заңдылықтар орнатылды.

Түйін сөздер:соққылы-ортадан тепкіш диірмендер, есептік сұлба, бөлшек, жылдамдық, қозғалыс, жұмыс органы, айналмалы ротор, соққылы импульс, профиль, тиімділік.

УДК621.926

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ИССЛЕДОВАНИЕ ДИНАМИКИ ЧАСТИЦ В УДАРНО-ЦЕНТРОБЕЖНЫХ МЕЛЬНИЦАХ

Аннотация. Исходя из анализа работы ударно-центробежных мельниц, являющихся энергозатратными, особый интерес представляет поиск источников, позволяющих свести к минимуму эти затраты. Наряду с конструктивными элементами и узлами, а также технологическим сервисом, большую роль при этом играет влияние динамики частиц, движущихся в роторах мельниц. В свою очередь, скоростной характер движения измельченных частиц является функцией от таких переменных, как конструкция отбойных элементов, направление удара, конфигурация частицы и материал, к которому она принадлежит, а также ряда других факторов.

В работе выполнен анализ расчетных схем мельниц ударно-метательного типа с различными формами и расположением разгонных лопаток. Рассмотрен общий случай движения частицы материала по дуговой разгонной лопатке расположенной в горизонтальной плоскости и приведена расчетная схема. Графически рассмотрено направление полной скорости частицы при различном расположении лопаток и предложена зависимость ударного импульса частицы от угла схода частицы. Получены законы движения частиц материала в ударно-центробежной мельнице с лопатками дугового профиля переменного радиуса, установлены основные закономерности, позволяющие определить ударный импульс и, соответственно, эффективность измельчения в зависимости от профиля лопатки.

Ключевые слова: ударно-центробежные мельницы, расчетная схема, частица, скорость, движение, рабочий орган, вращающийся ротор, ударный импульс, профиль, эффективность.

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TRIPHENYLPHOSPHINE ANION RADICAL

Abstract. According to the experimental data, the scheme of transformations of triphenylphosphine interaction with alkali metals should include stage of one-electron transfer from metal and the formation of a primary triphenylphosphine anion-radical $Ph_3P \xrightarrow{M} Ph_3P^{\overset{-}{\bullet}} M^+$.

Therefore, during the lecture on organoelemental chemistry for students of chemical specialties of higher educational institutions should be noted that in the preparation of organic derivatives of alkali metals and tetraphenyl diphosphine from triphenylphosphine in a reaction with alkali metals, at the first stage the anion- radical of triphenylphosphine is formed.

The EPR spectrum of the anion radical of tetraphenyl diphosphine formed during the decomposition reaction of the triphenylphosphine-potassium anion-radical in 1,2-dimethoxyethane was studied.

Key words: anion-radical, triphenylphosphine, tetraphenyl diphosphine, electron paramagnetic resonance, organoelemental chemistry.

The most common types of organic derivatives of trivalent phosphorus are the phosphines R_3P, R_2PH, and RPH_2 in the molecule of which phosphorus is directly attached to the carbon. Hydrogen atoms with phosphorus have quite pronounced acidic properties in order to interact with metallic sodium, giving a salt (sodium phosphide) and hydrogen. Thus, during the reaction of phenylphosphine with sodium, the phenylphosphide anion $C_6H_5PH^-$ is formed, which is a strong nucleophilic reagent [1]

$$2C_6H_5PH_2 + 2\,Na \longrightarrow \underset{\substack{\text{sodium phenylphosphide}\\ \text{(good nucleophile)}}}{2\,C_6H_5PH^-Na^+} + H_2$$

Summarizing the study of the reduction of triphenylphosphine with an alkali metal, Brit and Kaiser [2] proposed a triphenylphosphine splitting scheme that does not include the formation of an anion radical (AR).

In the reduction of triphenylphosphine with alkali metals (K and Na) in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) at -70 °C with the EPR method, we found an almost identical EPR spectrum [3], as Il'yasov did [4] with electrochemical restoration, Fig.1. In DME, the spectrum is described by the following hyperfine structure constants (HFS):

$$a_p = a_н^{para} = 2{,}5 \text{ гс},\ a_н^{ortho} = 1{,}25 \text{ gauss}$$

An analysis of the hyperfine structure of the spectrum shows that the unpaired electron is uniformly delocalized throughout the molecule. In Figure 1, under the spectrum, quantum numbers corresponding to the projections of the total spin 3 para-protons (I_H=1/2) and one nucleus of phosphorus (I_P=1/2).

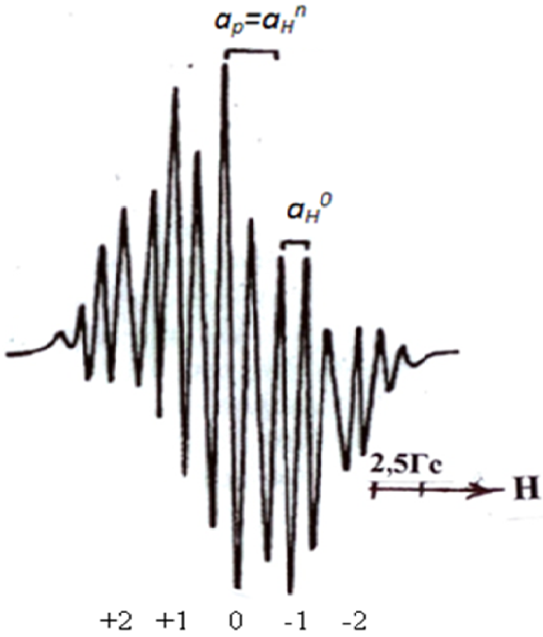
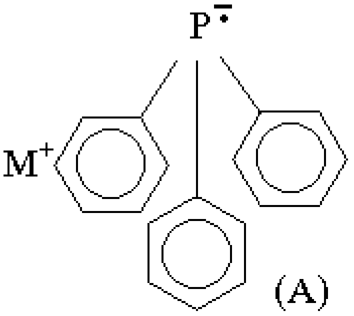


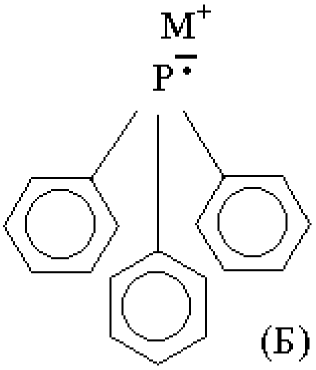
Figure 1 - EPR Spectrum of the anion radical of triphenylphosphine - potassium in DME at -60^{o}C

In this connection, one can imagine two ways of locating the metal cation near the AR, which ensure a uniform distribution of the unpaired electron over the phenyl rings. In structure A, the cation is located near the phenyl nucleus and migrates at a high frequency between all three equivalent positions. In structure B, the cation is attached to the phosphorus atom and occupies a stationary symmetrical position with respect to the phenyl rings. This arrangement of the cation will also ensure a uniform distribution of the density of the unpaired electron throughout the molecule.

In favor of the second structure is the absence of the effect of a decrease in temperature on the nature of the electron delocalization. This means that the motion of the cation does not have a significant effect on the nature of delocalization of the unpaired electron.

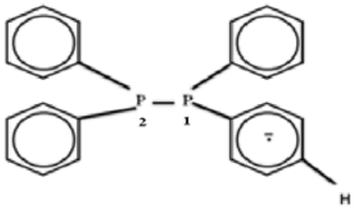


(A)



(Б)

Primary anion radicals are of low stability and turn into secondary radical anions as the temperature rises. This is evidently manifested in a change in the green coloring of the primary anion radicals to yellow. Figure 2 shows the EPR spectrum of the secondary anion radical. An analysis of a simple hyperfine structure shows that an unpaired electron interacts with two nuclei with an HFS constant of 7.15 gauss, with two cores with an HFS constant of 4 gauss and with one core with a HFS constant of 1.25 gauss.



We supposed that the HFS constant of 7.15 gauss refers to a single proton in the para-position of phenoxyl and to a phosphorus atom (I_P=1/2). Then the HFS constant of 4 gauss is naturally attributed to two ortho-protons. The magnitude of the constants and the nature of the distribution that should be reconstructed on their basis correspond to the parameters obtained by Gerson when studying the dimethylphenylphosphine anion radical [5].

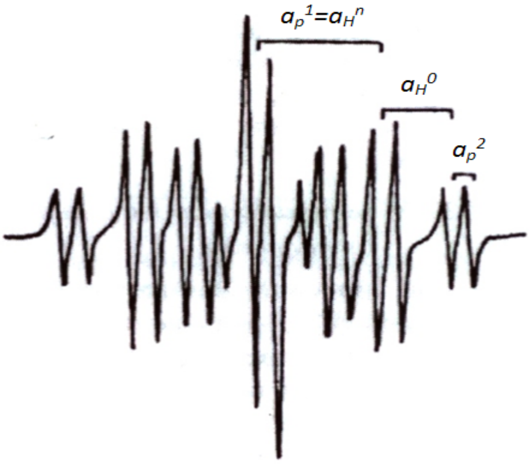


Figure 2 - EPR spectrum of tetraphenyl diphosphin
the decay of triphenylphosphine-potassium AR

According to the data of Britt and Kaiser [6], noting the formation of diphosphines, the EPR spectrum of the secondary anion radical can be attributed to the AR of tetraphenyldiphosphine. This assumption makes it possible to classify the doublet splitting with the HFS constant of 1.25 gauss to the second atom of phosphorus.

To confirm the above assumptions, we investigated the EPR spectrum of AR of secondary particle obtained from paradeuterated triphenylphosphine. Analysis of the obtained spectrum, Figure 3, convincingly confirmed the assignment of the HFS constants. The triplet spectrum has become a doublet, which confirms the equality of the HFS constants from phosphorus and proton in the para-position. The splitting constant for deuterium in accordance with the ratio of the magnetic moments of the proton and deuteron is 1.1 gauss and is close to the interaction constant with the second phosphorus atom.

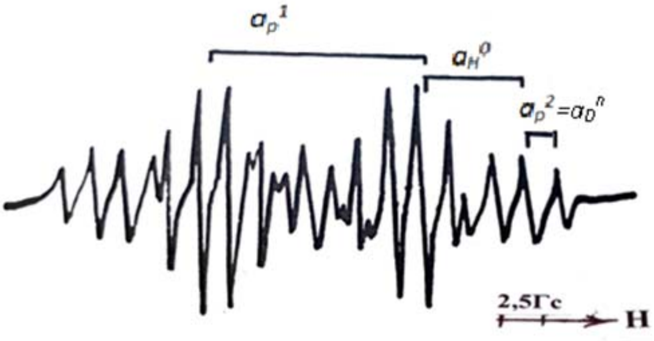


Figure 3-EPR spectrum of AR of the para-deuterotetraphenyl diphosphine formed during the decomposition of AR of para-deuterotriphenylphosphine-potassium in DME (at -30^{0}C)

The obtained results indicate a change in the site of cation localization upon transition from triphenylphosphine AR to tetraphenyldiphosphine AR. In AR of tetraphenyl diphosphine, the cation is located near one phenyl nucleus, and the frequency of its migration to other phenyl rings is small in comparison with the splitting values.

As follows from the experimental data, the scheme of transformations of triphenylphosphine in the interaction with alkali metals [2] should include a single electron transfer from the metal and the formation of the primary anion radical of triphenylphosphine

$$Ph_3P \xrightarrow{M} Ph_3P^{\bar{\cdot}}M^+ \qquad (1)$$

Anion radical of
triphenylphosphine

Therefore, during the lecture on organoelemental chemistry [7-10] for students of chemical specialties of higher educational institutions, it should be noted that iupon receiving the organic derivatives of alkali metals and tetraphenyl diphosphine from triphenylphosphine with alkali metals, the anion radical of triphenylphosphine (1) of the very first stage is formed.

Conclusions

1. As follows from the experimental data, the scheme of transformations of triphenylphosphine in the interaction with alkali metals should include a single electron transfer from the metal and the formation of the primary triphenylphosphine anion radical.
2. The EPR spectrum of the anion radical of tetraphenyl diphosphine formed during the decomposition reaction of the triphenylphosphine-potassium anion radical in 1,2-dimethoxyethane was studied.

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ҮШФЕНИЛФОСФИННІҢ АНИОН-РАДИКАЛЫ

Аннотация. Тәжірибелік зерттеулерден үшфенилфосфиннің сілтілік металдармен әсерлесу кезінде, оған металдан бір электронның ауысуы орын алады, осының нәтижесінде анион-радикал деп аталатын бөлшек түзіледі $Ph_3P \xrightarrow{M} Ph_3P^{\bar{\bullet}} M^+$.

Сондықтан, химия мамандығы студенттеріне элементорганикалық химиядан дәріс оқу кезінде сілтілік металдардың органикалық туындыларын және төртфенилекіфосфинді үшфенилфосфиннен сілтілік металдармен әсерлесуі кезінде, алғашқы сәтте үшфенилфосфин анион-радикалының түзілетіндігін ескерту керек.

Үшфенилфосфин – калий анион-радикалының 1,2-екіметоксиэтанда ыдырауы кезінде төртфенилекіфосфин анион-радикалының түзілуінің ЭПР спектрі зерттелген.

Түйін сөздер: анион-радикал, үшфенилфосфин, төртфенилекфосфин, электрондық парамагниттік резонанс, элементорганикалық химия.

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АНИОН-РАДИКАЛ ТРИФЕНИЛ-ФОСФИНА

Аннотация. Как следует из экспериментальных данных, схема превращений трифенилфосфина при взаимодействии с щелочным металлами должна включать стадию одноэлектронного переноса от металла и образование первичного анион-радикала трифенилфосфина $Ph_3P \xrightarrow{M} Ph_3P^{\overset{-}{\bullet}} M^+$.

Поэтому, в ходе чтения лекции по элементоорганической химии для студентов химических специальностей высших учебных заведений следует отметить, что при получении органических производных щелочных металлов и тетрафенилдифосфина из трифенилфосфина с щелочными металлами образуется анион-радикал трифенилфосфина самой первой стадии.

Изучен спектр ЭПР анион-радикала тетрафенилдифосфина, образующегося в ходе реакции распада анион-радикала трифенилфосфин-калия в 1,2-диметоксиэтане.

Ключевые слова: анион-радикал, трифенилфосфин, тетрафенилдифосфин, электронный парамагнитный резонанс, элементоорганическая химия.

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HYDROGEN ENERGETICS CURRENT STATE AND HYDROGEN PRODUCTION METHODS

Abstract. Review about hydrogen energetics current state and obtaining hydrogen methods are given with using literature sources from near and far abroad. It is shown that hydrogen energy is an alternative to traditional energy based on natural resources and describes the technical aspects of hydrogen production methods. We described industrial methods three categories for producing hydrogen - an environmentally friendly energy carrier. It is shown that the first category includes hydrogen production thermochemical methods, one of which is natural gas steam reforming. Along with this, methods for methane partial oxidation, autothermal reforming, and steam and gas coal conversion are considered.

The second group of methods for the hydrogen production is represented by electrolytic methods. Among them, a noteworthy method is the electrolysis of water. At present, the promising hydrogen production technology is standard electrolysis, decomposing water into its components - hydrogen and oxygen with the passage of electric current.

In recent years, other methods of producing hydrogen have been developed and are being developed. Biomass gasification and biomass pyrolysis methods are described, it is shown how these methods differ.It is shown that all the methods considered have their own advantages and disadvantages.

Keywords: hydrogen, energy, energy carrier, reforming, electrolysis, biomass.

One of the modern scientific and technical research topical issues is the development of affordable, environmentally friendly, cheap types of energy. The search for clean fuels is crucial and vital for survival since in subsequent years (the next 40-50 years) there will be big environmental problems associated with climate change, depletion of the ozone layer and other adverse consequences for the planet. The results of mandatory monitoring indicate an annual increase in emissions of carbon dioxide and carbon monoxide into the atmosphere. The amount of carbon dioxide emissions in the biosphere is about 30 billion tons per year. This gas is a major component of greenhouse gases and has a significant adverse impact on the environment [1].

There is a hypothesis that if the change in the concentration of carbon dioxide when using natural resources increases the temperature by 0.60°C for 100 years, then until 2075 this change will be equal to 5.40°C [2-3].

In addressing these issues, it is clear that alternative energy sources should be used in place of traditional energy sources. And it is unlikely that hydrogen energy will be equivalent to alternative sources of energy. Ecologically pure hydrogen fuel, its inexhaustibility (water), but also a lot of opportunities for using hydrogen - all this shows the advantages of using hydrogen as a fuel. Compared with organic fuel, hydrogen has a very large amount of energy, and the amount of heat released when burning 1 ton of hydrogen is equal to the amount of heat burned for 3.5 tons of organic fuel.

The ability of hydrogen to catalytically oxidize at low temperatures, in this case, the direct oxidation of chemical energy to electrical energy opens the way for the use of hydrogen in power engineering. Devices that make it possible to realize such functions are fuel cells or electrochemical energy generators characterized by a very high efficiency factor (70 to 80%), which is 2.0-2.5 times higher than the thermal coefficient of efficiency of the engine.

Nevertheless, the current state of hydrogen technology does not completely replace traditional energetic. The reason for this is that there is no free hydrogen in the earth, and its production requires chemical raw materials and energy sources. In short, hydrogen is an energy carrier, not fuel.

Hydrogen is the most common chemical element in the universe (93% atomic percent and one of the most common elements on Earth is 15.52% atomic percent).The main sources of hydrogen on Earth are water and organic compounds: oil, natural gas, and biomass.Hydrogen has unique properties, and its properties can be used in many different areas [4-7].

Let's take a closer look at the basic methods of obtaining hydrogen. At present, $368 \cdot 10^{12}$ m^3 of hydrogen is produced worldwide [8].

Depending on the technological characteristics of the recovery and extraction of hydrogen from its compounds, we decided to divide it into three categories [9-11].

Let us first consider the thermochemical methods of producing hydrogen.One of them is steam reforming of natural gas. This method involves the conversion of natural gas under the action of various oxidants (CO_2, H_2O, O_2, air and their mixtures). As a result, the product contains a large amount of H_2 and CO [12-18]. This method is highly productive and cheap, so the amount of hydrogen produced by this method is 85% of the hydrogen produced in the world, and in the United States - even 95%.

The production of hydrogen in the steam reforming of natural gas is carried out in three stages. First of all, methane is reformed at 500-950°C and 3 MPa pressure in the presence of a catalyst (usually Ni), in this case, a synthesis gas ($CO + 3H_2$ mixture) is formed:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206 \text{ kJ / mol (for 1 mole of } CH_4) \tag{1}$$

The reforming reaction is usually endothermic and requires the supply of heat from outside, which in turn is generated by the combustion of a portion of natural gas (about 25%) or separated from exhaust gases (for example, gas from a hydrogen purification system). Then the resulting synthesis gas reacts with an excess of water vapor, and at this time an additional amount of hydrogen is formed by the following reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 42 \text{ kJ / mol CO} \tag{2}$$

This reaction takes place at temperatures below the reforming reaction (usually below 600°C). The reaction proceeds in several stages, each of which occurs at a temperature below its previous stage. At high temperatures (350-475°C), the degree of conversion of CO to hydrogen is also high; at this stage, an iron-based catalyst can be used. In the following steps, a copper-based catalyst is used at a lower temperature (200-250°C); and the CO concentration in the synthesis gas is significantly reduced. The gas produced during steam reforming mainly comprises (H_2) is hydrogen (70-80%) and a small amount of CH_4 (2-6%), CO (7-10%) and CO_2 (6-14%) [16,18].

The final stage of the process is devoted to the purification of hydrogen, purification degree depends on the volume of application of hydrogen. For the purification of hydrogen, pressure-reducing adsorption systems or Pd-membranes are used to remove water vapor, CH_4, CO_2, N_2,and CO. The purity of hydrogen obtained by such purification reaches 99.999% [16]. In this case, an oxidation system is mainly used, introducing air into the produced gas through the catalyst bed. The oxidation of hydrogen also requires the following reaction at a certain temperature:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \tag{3}$$

Then the amount of CO decreases to the required level [16]. In some cases, the use of calcium oxide as a sorbent will reduce the amount of CO_2 and CO and increase the hydrogen content. The gas content is 90% H_2, 10% CH_4 and 0.5% CO_2.

Main drawbacks of hydrogen obtaining method from natural gas are:

- a large amount of air emissions, higher costs of hydrogen and required CO_2-gas formation. All this increases the valueof hydrogen;
- low installations productivity, the complexity of obtaining hydrogen peroxide by this method;
- The presence of CO in hydrogen composition, which means the need for additional purification for use in fuel cells production.

Another type of thermochemical methods of hydrogen extraction is methane incomplete oxidation. Methane or other hydrocarbons (for example, oil) are oxidized in this process, as a consequence of the following reaction, CO and H_2 are formed:

$$CH_4 + 1/2O_2 \rightarrow CO + H_2 + 36 \text{ MJ/kmol } CH_4 \quad (4)$$

The reaction does not require exothermic or external heat, so there is no need to use heat exchangers. Since the temperature is very high, the catalyst is also not needed.But you can use a catalyst to increase the flow of hydrogen (based on 1 mole of methane) or improve useful factor of the system. Unlike the steam reformer, the reactor designed for oxidation is more compact and its useful coefficient is higher (70-80%).Although the reactor itself is cheaper than a reformer, a working reactor and hydrogen purification systems are expensive. Taking into account these factors, it is necessary to invent cheaper hydrogen purification technologies [16,17,19].

Another type of reforming is autothermal. The outlet temperature of the reactor is 950-100 °C, and the gas pressure reaches 100 MPa [19]. Unlike steam reforming, there is no need to import external heat for autothermal reforming, since the reaction is exothermic and, accordingly, autoreformers are more affordable and cheaper. However, due to the need to purify exhaust gases, hydrogen production will be more expensive, and the beneficial effect will be reduced (65-75%) [18]. From these questions follows, from the ecological point of view, hydrogen production from natural hydrocarbon raw materials seems to be the same as from fossil fuels. This is due to the fact that in the latter case, harmful emissions into the atmosphere are formed when fuel is used, and in the first case these emissions are formed, but they are formed during the evaporation of hydrogen. Summarizing these reasons, basic scientific and technical research in the field of hydrogen extraction from natural resources should be aimed at improving the processes of capturing or disinfecting gases, especially carbon dioxide, in the production of new technologies.

Based on these views, it can be concluded that the method of obtaining hydrogen from coal by conversion of water and gas is significantly more promising.

Now let's move on to this method. Hydrogen can be obtained by various methods of coal gasification (for example, gasification in a fixed, liquid layer or a stream). In practice, high-temperature gasification is more effective because at that time the level of carbon dioxide is high, and the formation of high-flammable waste and phenol in large quantities is prevented [19].Typically, the gasification of carbon occurs when the temperature is 1200-1350°C and is carried out in accordance with the following equation [9, 10, 16, 17, 19, 20]:

$$C \text{ (solid)} + H_2O + \text{heat} \rightarrow CO + H_2. \quad (5)$$

The reaction requires endothermic and external heating; this situation was also observed during natural gas reforming. The formed CO can then be used as an additional element for the production of hydrogen by interaction with water vapor:

$$CO + H_2O \rightarrow H_2 + CO_2. \quad (6)$$

At present, much attention is paid to improving methods of extracting hydrogen from solid fuels, since coal reserves still remain in sufficient quantities(According to British Petroleum Corp., coal reserves in 2008 amounted to 826 billion tons) [21].

In the United States, there is a national program called "Hydrogen production from coal," which reads as follows:introduction of hydrogen energy technologies into the industry will reduce the amount of greenhouse gases released into the environment and improve the ecological purity and productionenergy efficiency [22].

Carbon gas processing plants are currently environmentally friendly, and the coefficient of useful use (39-44%) is higher than solid waste for processing solid fuel. A significant disadvantage of this method is the low hydrogen content in the synthesis gas (usually 40% (volume) percent) [21].

The second group of methods for obtaining hydrogen are electrolytic methods. Requiring attention - electrolysis of water.

A promising technology of hydrogen production in the modern world is the standard electrolysis, which breaks down the water into components - hydrogen and oxygen under the influence of electric current:

$$2H_2O + \text{electric current} \rightarrow O_2 + 2H_2. \qquad (7)$$

The doubtless advantages of this method are:

- an inexhaustible resource of raw materials (water);
- clean from an environmental point of view;
- possibility of having a wide range of productivity structures;
- ease of use and work;
- very high degree of hydrogen produced purity, as well as pure distribution and valuable gaseous products - gas oxygen.

At present, there are three technologies of hydrogen electrolytic reduction [13, 23-25] and their differences in the following: types of electrolyte (alkaline-aqueous solutions, protonionic membranes, with solid polymer electrolytes); solid oxide electrolyte - ceramics Zr-Y (with the conductivity of oxygen ions). Electrolytes filled with various electrolytes dissolve in different ways.

Electrolysis with an alkaline electrolyte is accompanied by the following chemical reactions [23]:

$$\text{Cathode reaction: } 2H_2O + 2e \rightarrow H_2 + 2OH^-$$

$$\text{Anode reaction: } 2OH^- \rightarrow 1/2O_2 + 2e$$

$$\text{Total reaction: } H_2O + \text{electric current} \rightarrow H_2 + 1/2O_2. \qquad (10)$$

And if a polymer proton membrane is present in the cell, the water decay occurs as a result of the following reactions [23, 26]:

$$\text{Anode reaction: } H_2O \rightarrow 1/2O_2 + 2H^+ + 2e \qquad (11)$$

$$\text{Cathode reaction: } 2H^+ + 2e \rightarrow H_2 \qquad (12)$$

$$\text{Total reaction: } H_2O + \text{electric current} \rightarrow H_2 + \tfrac{1}{2}\,O_2. \qquad (13)$$

Solid oxide ceramic materials are used in solid oxide electrolysers as electrolytes (usually stabilized with yttrium oxide).In such cells, cathodic water absorbs electrons from the outer layer and forms hydrogen, as well as negative oxygen ions, which in turn transfer electrons to the outer chains in the anode and become oxygen in the gas [26]. The problem is that cells with a solid oxide ceramic electrolyte function operate at high temperatures (about 800-1000°C), and electrolysers equipped with protonionic membranes function at 80-200°C, an electrolyser filled with an alkaline electrolyte at 50-200°C. These differences are associated with the use of heat obtained at high temperatures from other sources in the activity of these cells (including nuclear energy), thereby reducing energy costs for electrolysis.

In some works [27] new types of electrolyzer are proposed. In this type, the anode and cathode chambers are placed separately; they have a cathode and an anode, whereas the second pair of electrodes is usually made of a ruthenium oxide material that does not interact with short-circuited oxygen.

The cost of hydrogen hydrolysis will affect the cost of electricity [13,23].Therefore, modern research of wastewater technology should be focused on the search for new electrode materials and electrolytes, which save energy and increase the efficiency of the process.

To reduce energy costs and associated financial costs, it is necessary to use methods that generate electricity without reducing costs. The value of hydrogen obtained at that time is also small. Such technologies are primarily associated with the production of energy from alternative sources - the Sun, Wind, Hydrothermal. The use of solar energy is a promising method. In this case, both hydrogen and electrical energy must be taken from renewable sources - water and the Sun. For example, consider the production of hydrogen by photolitical methods.In the case of electrochemical water splitting, the anode generally is a compound having a semiconductor effect, and electrolyte and electron-hole pairs are formed at the anode boundary under the influence of light, these pairs contribute to the oxidation and reduction reactions of water, and as a result, hydrogen and oxygen form from the water. Fusikima and Honda in 1972 for the first time described the device built into the H_2SO_4 solution, first combining the TiO_2-photoanode and the Pt-cathode. This information is then presented in this paper [28].As a result of the use of semiconductor photovoltaics, various studies have been carried out to increase the efficiency of hydrogen evolution from water.

It is not necessary to completely decompose water during photoelectrolysis to produce hydrogen.It is sufficient to conduct a cathodic reaction in which only hydrogen is formed:

$$2H_2O + 2e^- \rightarrow 2OH- + H_2\uparrow \qquad (14)$$

The free electrons that are necessary for this reaction can be obtained from other reactions, and not only from anodic oxidation, for example, from the oxidation of sulfide ions or other compounds [29]. In this regard, as a photoanode, as a rule, a compound that absorbs light well but with a smaller forbidden band (for example, AIIBVI, AIIIBV, SnS, etc.) is used, rather than semiconductor metal oxides with a band gap in the range 2.7 to 3.2 eV. From a theoretical point of view, this method contributes to the efficiency of the process of converting solar energy into hydrogen energy [28].

The creation of photovoltaic systems, which can be used for semiconductor anodes sensitive to the visible spectrum of solar radiation and effective absorption of hydrogen cathodes, is a new direction in the creation of a solar irradiation and accumulation system [28].

One of the most important ways of obtaining hydrogen is the decomposition of water at high temperatures. Thermolysis of water by the direct method:

$$H_2O \rightarrow H_2 + 1/2O_2 \qquad (15)$$

To conduct this reaction, the temperature must be above 2500°C, and hydrogen and oxygen must be separated by efficient methods [30, 16]. The problem of separation of hydrogen and oxygen from each other is realized by using thermochemical cycles at extremely low temperatures [19, 16, 18] or thermochemical hybrid processes of thermal decomposition of water [16,30], in this case we use nuclear reactors heat and other solar collectors heat sources [31].

In the production of hydrogen, the cycles of reactions of chemically active compounds arising at high temperatures in a thermochemical process, such as iodine and sulfur, are used. More than 100 chemical cycles are recommended for this process. The most effective and promising method for these cycles is the use of iodine and sulfur reactions. This method was proposed by General Atomics in mid-1970. In this system, water reacts with SO_2 and iodine (I_2), which leads to the formation of sulfuric acid and iodide (HI):

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad (16)$$

At a temperature of 800-1000°C in a thermal nuclear reactor, sulfuric acid decomposes in water into sulfur dioxide (SO_2) and oxygen, and HI decomposes into hydrogen and iodine:

$$H_2SO_4 + \text{heat} \rightarrow H_2O + SO_2 + 1/2O_2 \qquad (17)$$

$$2HI + \text{heat} \rightarrow H_2 + I_2. \qquad (18)$$

$$\text{Total reaction: } H_2O + \text{heat} \rightarrow H_2 + 1/2O_2 \qquad (19)$$

Iodine and SO_2 react with water again, and oxygen is removed from the system or collected for use in production. In the modern world in reactor designs, the maximum operating temperature is about ≈ 827°C [12].

The thermochemical hybrid process is a combined cycle process that combines the thermochemical and electrolytic reactions of water decomposition and allows the electrons to react at low temperatures [12]. Modern nuclear reactors or solar energy concentrators can serve as a source of energy necessary for the reaction. It was suggested that the main contribution to the development of hydrogen energy will take place if an industrial hybrid thermochemical process is established [32].

Technology based on thermal ionization of water vapor also requires attention.This method is the basis for the thermal decomposition of the leading and conventional water, as well as the basis of technology aimed at burning highly heated water vapor [33]. The main stages of this technology include special preparation and activation of water, heat treatment of high heated steam, its thermonuclear activation, subsequent dissociation (using this catalyst this pair of H_2 and O_2) and burning on a special catalyst surface.

The most important sources of energy production when extracting hydrogen from biomass are wood and wood waste, agricultural crops,and waste generated during processing, solid waste in the city, food industry waste, algae, etc. Biomass is of great interest for hydrogen production. First, biomass is considered one of the many uses of renewable resources. According to The International Institute for Applied Systems Analysis, the biomass potential in the world is about 250 billion GJ. It is expected that this potential by 2050will grow to 350 billion GJ [23].

Secondly, biomass is a substance consisting of organic components formed by the absorption of carbon dioxide from the atmosphere after photosynthesis. Since the first types of biomass are renewed, carbon dioxide and other types of carbon can be used in the atmosphere as energy or material. Since the CO_2 concentration in this cycle is theoretically stable, it can be expected that the future biomass will become the main source of renewable energy [34].

Thirdly, comparing some other methods of obtaining hydrogen and taking into account the geographical location, biomass is relatively common in the world.

Fourth, in addition to the heat released during the production of hydrogen, biomass can be valuable as auxiliary products: glues, black powder, activated carbon, polymers, fertilizers, ethanol, various acids, Fisher-Tropys diesel fuel, paraffin, and methanol. Energy and biomass products are likely to satisfy the demand for them in the future. Removal of hydrogen from biomass is divided into two groups, one of which is pyrolysis of biomass.

Pyrolysis is the heating of biomass at a pressure of 0.1-0.5 MPa at a temperature equal to 650-800 K. As a result, solid and liquid products are formed [35,36]. Depending on the nature of the pyrolysis biomass, H_2, CH_4, CO, CO_2 and other gases are present in the gas products.Liquid products contain resins and oils that store the liquid form at room temperature. Solid products consist mainly of flammable substances in the form of residues that are formedfrom the rectification of coal, as well as from some pure carbon and some other inert substances. Pyrolysis of biomass is mainly concentrated on biofuel, but also during high-temperature pyrolysis and when the volatile phase is stabilized, hydrogen is formed by the following reaction:

$$\text{biomass} + \text{heat} \rightarrow H_2 + CH_4 + CO + \text{other products} \tag{20}$$

Methane and a couple of other hydrocarbons can then be modified to produce hydrogen by steam:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{21}$$

and then the amount of hydrogen increases as a result of the interaction of CO_2 with water:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{22}$$

Liquid pyrolysis products can also be used to extract hydrogen. Depending on their solubility in water, they are divided into two fractions. The water-soluble fraction is used to extract hydrogen and the insoluble fraction is used to absorb the adhesives [37].

Hydrogen is also produced by gasification of biomass.Gasification is the thermal treatment of biomass by a large number of gaseous substances, and a small amount of resin and ash. This process is essentially similar to gasification of coal and is carried out at 950-1500 K [38, 39]. Unlike gas cleaning of biomass it is carried out in the presence of oxygen or air. This biomass conversion process is based on the following reaction:

$$\text{biomass} + \text{heat} + \text{vapor} \rightarrow H_2 + CH_4 + CO + CO_2 + \text{light and heavy hydrocarbons} + \text{carbon flammable waste generated during rectification} \tag{23}$$

The gasification process can be considered as one of the types of pyrolysis, but at very high temperatures, since it is necessary to optimize the formation of the gas phase, and pyrolysis is aimed at obtaining biomass. Gas products obtained during gasification are then converted to hydrogen under the influence of water vapor. Hydrogen can be produced biochemically. Biochemical production of hydrogen (biohydrogen) as a substance of the metabolism of microorganisms is a relatively new technology. This method allows extracting hydrogen from renewable sources. This, in turn, contributes to the development of hydrogen energy in the future [36]. The production of biohydrogen can be divided into several groups:1) direct biophotolysis; 2) indirect biophotolysis; 3) biological shift of the gas-water reaction 4) fermentation [40].

The hydrogen production by direct bio-photolysis is a biological process using photosynthetic microalgae, which is aimed at converting solar energy into hydrogen in the form of chemical energy [41].

$$2H_2O + \text{solar energy} \rightarrow 2H_2 + O_2. \tag{24}$$

Two photosynthetic systems are necessary for photosynthesis:1) I photosystem (PSI), which actually produces a CO_2 gas reducer and II photosystem (PSII) - system of water decomposition and oxygen separation. In a biophytolytic process, two water protons with PSI recovers CO_2 gas or releases hydrogen in the presence of hydrogenase.Since green plants do not contain hydrogenase, only the CO_2 reduction reaction takes place. In contrast, green and cyanobacterial (blue-green) microbes contain hydrogenases that are capable of producing hydrogen.In this process, the electrons formed as a result of the absorption of the light energy of the PSII system are converted to ferredoxin (Fd). This replacement occurs for the production of hydrogen as a result of the use of solar energy absorbed by the PSI system.

Since the hydrogenase is sensitive to oxygen, it is necessary to maintain the oxygen content at low levels (<0.1%) in order to prolong hydrogen production [42].

Indirect biophytolysis consists of the following four stages:1) biomass production by photosynthesis; 2) biomass concentration; 3) deep fermentation of anaerobic, resulting in the formation of algae cells 4 moles of H2, which is calculated for 1 mole of glucose and 2 moles of acetate; 4) conversion of two moles of acetate to hydrogen.

Usually in indirect biophotosynthesis cyanobacteria are used, in this case, hydrogen is obtained by the following reactions [40]:

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \tag{25}$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2 \tag{26}$$

The production rate of hydrogen produced by indirect bio-photolysis can be compared with the production of hydrogen on the basis of hydrogenase with the help of green algae [42].

Hydrogen-rich carbohydrate compounds (eg, glucose, starch, etc.) can be obtained at temperatures of 30 to 80 °C and at atmospheric pressure, especially in the dark, by fermentation [36, 43].

In contrast to the usual process of bio-photolysis, in which only hydrogen is released, the difference in this method lies mainly in the fact that the fermentation products are hydrogen and CO_2.

However, the formation of other gases (CH_4, H_2S) takes place depending on the materials used and the reactions occurring in the process. The amount of hydrogen released affects the direction of fermentation and the resulting liquid products. For example, when glucose is used, and acetic acid is the final product of fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \tag{27}$$

(In this reaction, from 1 mole of glucose, 4 moles of H2).

And if fatty acids are formed as the final product:

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2OOH + 2H_2 + CO_2(28)$$

(from 1 mole of glucose, 2 moles of H_2).

But usually, in fact, 1 mole of glucose does not form 4 moles of hydrogen, because the fermentation product contains acetic acid and fatty acid ester [44].

In the dark, the amount of hydrogen produced by the fermentation method depends on the average pH, the time of hydraulic confinement and the partial gas pressure. For optimum hydrogen production conditions, it is necessary to keep the pH at 5-6 [36].

Alanaerobiumhydrogeniformanshaloalkaliphilic bacteria can produce 5- and 6-carbon sugars from hydrogen-containing hemicellulose and cellulose [45].

In addition to pure sugars and industrial raw materials, raw materials for the production of fermented hydrogen are considered (for example, agricultural and food waste and solid organic waste, including urban and agricultural waste and sewage sludge).However, the production of hydrogen from these raw materials has a number of disadvantages, one of which is the low yield of hydrogen. This method is currently realized by simple fermentation of sugar [46].

By combining photo fermentation in the dark, you can double the yield of hydrogen in a two-stage hybrid system. In the first stage anaerobic bacteria decompose glucose or starch acetate with enzymatic metabolism, and the resulting acetate is subjected to hydrogen direct photosynthetic bacterial changes in the second stage [47].

Conclusion

In industry today, only natural gas conversion, coal gasification and water electrolysis are used. Steam conversion of natural gas is one of the cheapest ways to use natural fuels, and CO_2 emissions in this method are extremely low. Water electrolysis is more expensive and is used only to produce hydrogen peroxide. If natural gas cost increasingis predicted, coal gasification method can be an alternative method of producing hydrogen starting around 2030. Biomass gasification and its pyrolysis for hydrogen production are at the research stage, but in the coming decades these methods are likely to become alternative methods of hydrogen production.

Biomass gasification and its pyrolysis for hydrogen production are at the research stage, but in the coming decades these methods are likely to become alternative methods of hydrogen production. According to the long-term International Energy Agency forecast, hydrogen, obtained by biomass gasification, will compete at a price with fully restored hydrogen, and its price will be the lowest among the extracted raw materials.

Biomass gasification is the simplest and most economical way of producing renewable hydrogen. This technology is likely to be the most advanced technology in the future. Hydrogen production from renewable sources (wind energy, solar energy, hydrothermal energy, etc.) will be economically advantageous for countries with a large number of renewable energy sources, for remote areas without natural resources and for less populated areas (for example, peninsula and islands) or for the accumulation of a huge amount energy from renewable energy sources.

In the long term, it will be necessary to produce hydrogen by a method without separating CO_2 or by separating a very small amount of.Electrolysis using renewable hydrogen electricity, using the sun, wind, hydrothermal energy, is maximum possible option, but these methods are not suitable for using hydrogen as an energy carrier. Before achieving this goal, the extraction of hydrogen from natural resources is very important, but the conservation and fixing of CO_2 gases are mandatory, especially in terms of environmental safety.

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СУТЕКТІК ЭНЕРГЕТИКАНЫҢ ҚАЗІРГІ ЗАМАНДАҒЫ ЖАҒДАЙЫ ЖӘНЕ СУТЕКТІ АЛУ ӘДІСТЕРІ

Аннотация. Бірқатар алыс және жақын шетелдік әдебиет көздеріне сүйене отырып, сутектік энергетика-ның қазіргі замандағы жағдайы туралы және сутекті алу әдістері жайында шолу жасалған. Сутектік энергетиканың табиғи қазба байлықтарға негізделген дәстүрлі энергетиканың баламалы түрі болып табылатыны көрсетілген және сутекті алу әдістерінің техникалық аспектері сипатталған. Экологиялық тұрғыдан таза болып табылатын энергия тасымалдаушы – сутектің өндірістік алыну әдістерінің үш категориясы сипатталған. Бірінші категорияға сутекті өндірудің термохимиялық жолдары қарайтыны, оның бірі – табиғи газдың булы риформингі екені көрсетілген. Бұл әдіс табиғи газды әртүрлі тотықтырғыштармен әсер ету арқылы конверсиялауды көздейді. Сонымен қатар метанды толық емес түрде тотықтыру, автотермалды риформинг, көмірді сулы-газды конверсиялау әдістері қарастырылған.

Сутекті өндіру әдістерінің екінші тобын электролиттік әдістер құрайды. Оны ішінде көңіл бөлуді талап ететіні – су электролизі. Қазіргі заманда сутекті алудың келешегі бар технологиясы – суды электр тогының әсерімен құрамдас бөліктеріне - сутекке және оттекке ыдырататын стандартты электролиз.

Кейінгі жылдары сутекті алудың басқа да әдістері жасалып, дамып келеді. Олардың ішінде биомассаны газдандыру және оның пиролизін жүргізу, олардың бір-бірінен айырмашылығы қарастырылған. Барлық әдістердің өзіндік артықшылықтары мен кемшіліктерінің бар екені көрсетілген.

Түйін сөздер: сутек, энергетика, энергия тасымалдаушы, риформинг, электролиз, биомасса

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СОВРЕМЕННОЕ СОСТОЯНИЕ ВОДОРОДНОЙ ЭНЕРГЕТИКИ И СПОСОБЫ ПОЛУЧЕНИЯ ВОДОРОДА

Аннотация. Проведен обзор о современном состоянии водородной энергетики и способах получения водорода с использованием литературных источников ближнего и дальнего зарубежья. Показано, что водородная энергетика является альтернативой традиционной энергетике, основанной на природных ископаемых и описаны технические аспекты способов получения водорода. Приведено описание трех категории промышленных методов получения водорода – экологически чистого энергоносителя. Показано, что к первой категории относятся термохимические способы получения водорода, одним из которых является паровой риформинг природного газа. Наряду с этим рассмотрены способы частичного окисления метана, автотермальный риформинг, парогазовая конверсия угля.

Вторую группу способов получения водорода представляют электролитические методы. Среди них заслуживающий внимания способ – электролиз воды. В настоящее время перспективная технология получения водорода – стандартный электролиз, разлагающий воду на ее составляющие – водород и кислород при пропускании электрического тока.

В последние годы разрабатываются и развиваются другие способы получения водорода. Описаны способы газификации биомассы и пиролиз биомассы, рассмотрены их различияя. Показано, что все рассмотренные методы имеют свои как преимущества, так и недостатки.

Ключевые слова: водород, энергетика, энергоноситель,, риформинг, электролиз, биомасса.

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ISOMERIZATION OF LIGHT FRACTION OF STRAIGHT-RUN GASOLINE ON Pt-AND Pd-CATALYSTS SUPPORTED ON PILLARED BY Al, AlZr AND Ti MONTMORILLONITE IN Na-AND Ca-FORMS

Abstract. The paper presents data on isomerization of the light fraction of straight-run gasoline on the zeolite-free and mordenite-containing Pt and Pd- catalysts supported on activated and pillared by Al, AlZr and Ti montmorillonite in Na- and Ca-forms. The catalysts were characterized by BET, X-ray phase,and elemental analysis, and their acid properties were determined by thermal desorption of ammonia. It is shown that the isomerization of the light fraction of straight-run gasoline over mordenite-containing Pd / AlZrCaHMM, Pt / Al (2.5) NaHMM and Pt / Ti (5.0) NaHMM catalysts at different temperatures leads to a significant change in the composition of gasoline and an increase in octane numbers. The greatest amount of isomers produced during the isomerization of the light fraction of gasoline was found on a Pt / Al catalyst (26.48%), followed by Pd / AlZr (23.56%), followed by Pt / Ti (23.15%). A comparison of the results on the acidity of the catalysts studied and their strength distribution shows that a correlation is observed between the total number of weak and medium acid sites and the isomerizing activity of the catalysts studied. For further practical use in the process of isomerization of light n-alkanes, 0.35% Pt / Al (2.5) NaHMM catalyst is proposed. The catalyst is characterized by a high yield of isomers, increased selectivity of isomerization of n-alkanes, operates at atmospheric pressure and a temperature of 350 ° C, and is characterized by increased stability.

Key words: the isomerization, straight-run gasoline, easy n- alkanes, mordenite, a pillarization, Pt and Pd-catalysts, octane numbers, selectivity.

Introduction. The process of an isomerization of paraffin hydrocarbons of oil has acquired high relevance in connection with the transition to use of more effective and ecologically safe fuels [1-4] in recent years. One of the ecologically safest ways of improvement of anti-detonation properties of straight-run gasolines is the use of process of a catalytic isomerization of n- alkanes with receiving high-octane isomers on effective Pt and Pd-catalysts [5-8]. Pt, Pd and Ni-catalysts on pillared montmorillonite have perfectly proved in this process [9-12]. On the example of the process of an isomerization of n- hexane it has been shown that the main advantage of these catalysts their high selectivity to isomers is represented. It has been noticed that on the developed catalysts at temperatures of 250-300^{0}C reactions of hydrocracking practically don't go, and only at more high temperatures in products of reaction there are small amounts gaseous C_1-C_3 of the hydrocarbons which are formed as a result of hydrocracking [13,14].

The isomerization of the real light fractions of oil consisting generally of pentanes of C_5 and C_6 hexanes gains the increasing value in connection with toughening of ecological requirements to motor fuels and need of production of alkylgasolines with high octane number [15,16]. Earlier it has been shown that on reduction of stationary isomerization activity in reaction of hydroconversion of n-hexane the developed Pt-and Pd-catalysts on pillared with various oxides montmorillonite it is possible to arrange in following row: Pt/Al (2,5) NaHMM (53.0%)>Pd/Al:Zr(1:1)CaHMM (35,0%)> Pt/Ti (5,0) NaHMM+ HM (34,0 of %)>Pd/Al:Zr (3:1) CaHMM(31,0%)>0,1%Pt/Al(5,0)NaHMM+HM(20,2%). Due to stated, the present article is devoted to a research of properties of the mordenitecontaining Pt-and Pd-catalysts supported on pillared Al, AlZrandTi the activated montmorillonite in an isomerization of easy fraction of straight-run gasoline (b.b. - 70^{0}C) depending on temperature.

Experimental part Clay of Tagandeposit (Kazakhstan), containing up to 95% of montmorillonite (MM) in Na-and Ca-forms transferred to the H-form processing 0,1n H_2SO_4 solution with the subsequent washing from SO_4^{2-}ions. The activated clay was formed, dried in a thin layer at first at the room temperature, then at 150^{0}C and further subjected to calcinating at 500^{0}C. The prepared MM in H-form was used as initial material for a pillaring.

Introduction in interlayered spaces of montmorillonite aluminum, aluminum - zirconium and titanic complexes was carried out by the known techniques. Synthesis of Al-ZrCAHMM was carried out sequential:at first pillared by Al, and then by Zr. The received pillared clays separated bycentrifugation, washed before negative reaction to Cl - ions, formed, dried at first at the room temperature, then at 150^{0}C and further subjected to calcinating at 500^{0}C.

Pt-and Pd-catalysts on the basis of the modified clays in the mix with mordenite (15%, with the module 20) prepared by an impregnation method on moisture capacity of carriers water H_2PtCl_6 or $PdCl_2$ solutions. Samples formed, dried on air and in a drying cabinet, calcinated at temperatures of 200, 400 and 500^{0}C with decomposition of salts to oxides and the subsequent reduction of oxides to a metal state when processing by hydrogen at temperatures of 200 and 450^{0}C. Content of platinum and palladium in catalysts was 0,35mas. %. Tests of catalysts carried out in flowing laboratory installation with a volume of catalyst of 5 ml at temperatures of 250-400^{0}C, mass loading on hydrocarbon raw materials 0,8h^{-1}, pressure of hydrogen 1 atm and a molar ratio hydrogen: hydrocarbons, equal 3,5. Products of reaction were analyzed on the gas chromatograph"Chromos GH-1000" supplied with a capillary column 100 m long, diameter 0,25mm and the flame-ionization detector.

Physical and chemical characteristics of the prepared samples have been determined by the X-ray method, the element analysis, low-temperature adsorption of N_2 by BET method on the ACCUSORB device, and acid properties - an ammonia thermal desorption method.

Results and their discussion

According to the X-ray phase analysis(RFA) all catalysts contain the reflexes characteristic for Ca- and Na-forms of the MM (2,50; 4,45; 14,6), quartz (3,34), mordenite (3,44; 3,96; 6,5; 9,08; 10,2), platinum or palladium and also oxides of pillared ions-Al_2O_3, TiO_2 – anatase, the tetragonal phase ZrO_2 (3,00 and 1,84). According to RFA on 0,35%Pt/Ti (2,5) NAHMM-catalyst besides the above-named phases metal Ti (ASTM 5-682) and metal Pt is identified (ASTM 4-802 on reflexes 2,26; 1,95; 1,39). According to a data of X-ray fluorescent analysis except the elements making a basis of aluminosilicates Al, Si, O, the catalyst contains small amounts of Mg, Ca, Fe, insignificant quantities of Na, S, Cl (table 1). Besides according to the element analysis, in 0,35% Pt/Ti (5.0) NaHMM+HM –catalyst 0,26% of Pt, 9,9% of Ti are found.

Table 1 - The elemental analysis of Pt and Pd-catalysts supported on pillared MM and modified by mordenite.
0.35%Pt/Ti(5.0)NaHMM+HM

Element	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**S**	**Cl**	**Ca**	**Ti**	**Fe**	**Pt**	**Total**
Specter 1	9,04	48,18	0,08	0,71	11,59	19,68	0,04	0,17	0,20	9,81	0,19	0,32	100
Specter2	8,24	48,9	0,10	0,72	1198	19,62	0,04	0,19	0,19	9,85	0,31	0,28	100
Specter3	8,45	48,81	0,9	0,74	10,84	20,32	0,00	0,12	0,19	10,06	0,19	0,18	100
Average	**8,58**	**48,49**	**0,09**	**0,72**	**11,47**	**19,87**	**0,03**	**0,16**	**0,19**	**9,90**	**0,23**	**0,26**	**100**

0,35%Pd/AlZrCaHMM+HM

Specter	**O**	**Na**	**Mg**	**Al**	**Si**	**S**	**Cl**	**Ti**	**Fe**	**Zr**	**Pd**	**Total**
Specter1	49,55	0,09	0,87	15,32	23,72	0,06	0,14	0,09	0,69	9,36	0,14	100,00
Specter2	49,46	0,07	0,82	14,34	24,78	0,06	0,10	0,14	0,74	9,34	0,14	100,00
Specter3	49,79	0,09	0,84	13,92	24,67	0,05	0,11	0,11	0,79	9,43	0,22	100,00
Average	**49,60**	**0,08**	**0,84**	**14,53**	**24,39**	**0,06**	**0,12**	**0,11**	**0,74**	**9,38**	**0,17**	**100,00**

0,35% Pt/Al(2,5) NaHMM+HM

Specter	**O**	**Na**	**Mg**	**Al**	**Si**	**S**	**Cl**	**Ca**	**Fe**		**Pt**	**Total**
Specter1	51,51	0,13	1,30	24,20	21,91	0,03	0,07	0,18	0,42		0,24	100,00
Specter2	51,65	0,13	1,27	24,76	21,33	0,02	0,05	0,17	0,39		0,27	100,00
Specter3	51,99	0,16	1,35	23,44	22,07	0,04	0,05	0,20	0,39		0,30	100,00
Average	**51,7**	**0,14**	**1,31**	**24,13**	**21,77**	**0,03**	**0,06**	**0,19**	**0,40**		**0,27**	**100,00**

The elemental analysis of the 0,35%Pd/AlZrCaHMM+HM-catalyst has also shown decrease in concentration of alkaline and alkaline-earthmetals in the course of activation, pillaring and supporting active metal. The amount of sodium in the ready catalyst doesn't exceed 0,08mas. %. From data of table 1 it is visible that the average content of palladium in powder of the catalyst is 0,17% that in ~ 2 times are lower, than calculated. Besides, small amounts of chlorine are found in powder of the catalyst, other results of quantitative elementalanalysis of the catalyst in comparison with the support after palladium introduction practically don't change. Similar results have been received in case of 0,35%Pt/Al (2,5) NaHMM+HM –catalyst. According to the analysis the amount of platinum in this catalyst is 0,27% that is close to the introduced his quantity.

Textural properties of three studied catalysts are characterized by small decrease in a specific surface of the catalyst when supporting platinum from 172,7 to 169,0 m^2/g in a case 0,35%Pt/Al (2,5) NaHMM+HM (table 2) and from 190,7 to 182,7m^2/g for 0,35%Pt/Ti (5) NaHMM+HM. The support of these catalysts differs in the considerable maintenance of micropores which quantity grows when supporting platinum. In case of the Pd-catalyst supported on pillared by Al and Zr montmorillonite in Ca-form more essential reduction of a specific surface area and decreaseof quantity of microporesis observed.

Table 2 – Comparative structural and adsorptive properties of Al (2,5) NaHMM+HM, Ti (5) NaHMM+HM, AlZr (1:1) CaHMM+HM, 0,35%Pt/Al (2,5) NaHMM+HM, 0,35%Pt/Ti (5) NaHMM+HM and 0.35% Pd/AlZrCaHMM+HM- catalysts

Sample	$S_{av.,\ m}^{2}$/g	Total true volume of a pores, cm^3/g	Relative quantity, %	
			Micropores 0-20 Å	Mesopores 20-80 Å
Al(2,5)NaHMM+HM	172,7	0,161	38,7	61,3
0,35%Pt/Al(2,5)NaHMM+HM	169,0	0,194	46,9	53,1
Ti(5)NaHMM+HM	190,7	0,190	32,2	67,8
0,35%Pt/Ti(5)NaHMM+HM	182,7	0,176	33,7	66,3
AlZr (1:1) CaHMM+HM	249,9	0,167	70,7	29,3
0.35% PdAlZrCaHMM+HM	228,6	0,153	54,0	46,0

It is possible to see the growth of the amountof microporesand the decrease of amount of a mesopores when supporting platinum by comparison of curves of distribution of a poresby the sizes in the support and in Pt/Al (2,5) NaHMM+ HM - the catalyst (fig. 1).

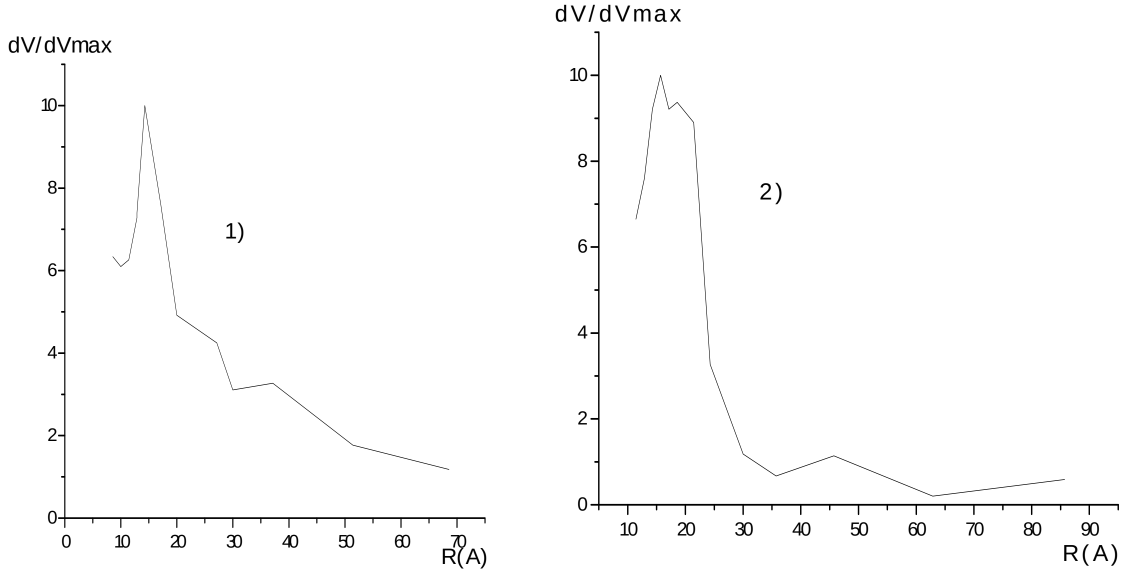

Figure 1- Distributions of a poreson their effective radiuses on Al(2,5)NaHMM+HM and 0,35Pt/Al (2,5) NaHMM+HM-catalysts. 1)Al(2,5) NaHMM+15%HM; 2)0,35Pt/Al (2,5) NaHMM+15%HM

The listed above samples of catalysts, optimum on the isomerization activity, have been tested in an isomerization of easy fraction of straight-run gasoline (b.b.-70^0C). Light fraction of straight-run gasoline (b.b. – 70^0C) according to the chromatografy analysis contains C_3-C_{15}-hydrocarbons which on to group composition consist from 15,9mass. % of paraffins, 12,5mass. % of isoparaffins, 1,0mass % of aromatic compounds, 13,6mass. % of naftens and 43,9mass. % of olefins. The total number of the identified compounds in initial light gasoline is 87,0% (table 3).

Table 3 - The group composition of initiallight fraction of straight-run gasoline, in mass. %

Group on C-hydro-carbon	Paraffins	Isoparaffins	Aromatic compounds	Naphtenes	Olefines	Oxygen-containing	Sum on C-group
1	0,001	0,000	0,000	0,000	0,000	0,000	0,001
3	0.030	0.000	0.000	0.000	0.000	0.000	0.030
4	2,270	0,438	0,000	0,000	0,498	0,000	3,205
5	11,748	0.049	0.000	0.000	0.353	0.000	12.151
6	0,000	0,000	0,000	0.000	0,203	0.000	0,203
7	0,000	6,087	0,000	8,614	41,458	0,000	56,159
8	0,000	4,146	0,913	4,880	0,149	0,000	10,088
9	0,791	1,495	0,013	0,082	1,338	0,000	3,719
10	1,040	0,271	0,044	0,052	0,000	0,000	1,407
11	0,043	0,006	0,045	0,000	0,000	0,000	0,094
12	0,013	0,000	0,000	0,000	0,000	0,000	0,013
15	0,002	0,000	0,000	0,000	0,000	0,000	0,,002
Сумма	15,937	12,491	1,0158	13,628	43,999	0	87,072

The octane number of this fraction by a research method is equal 41,8 units. Influence of temperature of an isomerization on the group composition of light fraction of straight-run gasoline and change of the octane numbers in the course of hydroconversion on the studied catalysts is presented in tables 4 and 5.

Table 4 - Influence of temperature and the nature of catalysts on the group composition of light fraction of gasoline in the course of a catalytic isomerization

Sample	T,^{0}C	Paraffins	Isoparaffins	Aromatics	Naphtenes	Olefines	Oxygencontaining
0,35%Pd/AlZrCaHMM+HM	250	0.807	23.565	0.160	6.158	27.834	24.871
	300	0.181	10.543	8.697	17.292	31.713	0
	350	8.727	7.522	9.116	6.309	31.481	13.321
	400	14.912	21.046	3.743	3.068	42.916	0.287
0,35%Pt/Al(2,5)NaHMM+HM	250	0.667	10.401	1.787	19.032	55.836	0
	300	6.935	5.460	2.757	8.337	59.706	10.834
	350	24.530	26.484	6.854	24.523	1.193	0
	400	3.812	2.483	4.973	2.857	9.442	52.661
0,35%Pt/Ti(5.0)NaHMM+HM	250	6.896	23.151	0.998	21.457	40.641	0
	300	9.368	19.364	3.808	9.807	50.585	0
	350	7.227	9.184	9.221	12.655	52.299	0.004
	400	4.022	4.154	10.046	2.426	21.782	0

The isomerization of light fraction of straight-run gasoline on 0,35% Pd/AlZrCaHMM+HM - catalyst at various temperatures leads to essential change of composition of gasoline and increase its octane numbers (table 4,5). At 250^0C the amount of the isoparaffins which is formed fromlightfraction of straight-run gasoline on Pd/AlZrCaHMM+HM considerably grows from 12,49 to 23,56 mas. %, and amount of paraffin and aromatic hydrocarbons decreases (paraffin from 15,93 to 0,80 mas.% and aromatic hydrocarbons from 1,01 to 0,16 mas. %). Such change of composition of gasoline is followed by growth of octane number for 29 units by a research method and for 13 units by a motor method. Temperature increase of an isomerization on 0,35%Pd/AlZrCaHMM - the catalyst to 300^0C decreases the amount of paraffins from 15,93 to 0,18mas. % in comparison with the initial composition oflightfraction of straight-run gasoline. In these conditions, the amounts ofisoparaffinsand olefinesalso decreaseby2 and 12% accordingly. At the same time, the content of aromatic compounds grows more, than by 8 times. The increase of octane number makes 11 units by a research method possibly due to increasein the amount of aromatic hydrocarbons. At 350^0C the content of paraffins and naphtenes decreases almost twice, and the amount of aromatic hydrocarbons grows from 1,01 to 9,11mas. %. On this catalyst at 350^0C the increase of octane number makes 25 units by a research method. At 400^0C the amount of paraffin decreases, and isomers grows from 12,49 to 21,04mas. %. However anincreaseof the octane number of gasoline in these conditions small (5 units) in comparison with octane number of initial gasoline that is possible caused by the decreaseof a quantity of the identified compounds for 10,5%. It is possible to draw a conclusion on isomerization ability of the studied catalysts by the amount of the isomers which are formed in process in comparison with their quantity in initial gasoline. The greatest number of isomers, equal 26,48%, is found on the Pt/Al-catalyst at 350^0C (table 4), it is followed by Pd/AlZr (23,56%) at 250^0C, and further Pt/Ti (23,15%) at 250^0C. The largest value of conversion of hydrocarbons about which it is possible to make a conclusion isanincreaseof octane numbers was observed on the Pt/Ti-catalyst (table 5)

Table 5 - Influence of temperature and the nature of catalysts on the value of octane numbers of light fraction of gasoline after an isomerization

Catalyst	T,^{0}C	O.n.byresearch method	Increase of o.n.	O.n. by motor method
0,35%Pd/AlZrCaHMM+HM	250	70.96	29,1	63.23
	300	52.81	10,95	40.62
	350	67.15	25,29	53.62
	400	46.75	4,89	42.38
0,35%Pt/Al(2,5)NaHMM+HM	250	46.83	4,97	50.68
	300	67.82	25,96	53.10
	350	53.52	11,66	51.06
	400	34.57	7,29	37.44
0,35%Pt/Ti(5.0)NaHMM+HM	250	54.02	12,16	58.0
	300	74.81	32,95	60.78
	350	60.03	28,20	55.59
	400	33.20	8,66	30.92
Initial gasoline		41.86		50.32

On reduction of a increase of octane numbers of the studied catalysts settle down in the sequence: Pt/Ti(33,0)>Pd/AlZr(29,1)> Pt/Al(26,0). The highest increase in o.n., equal to 33.0, was observed on Pt / Ti-catalyst at 300^0C. All studied catalysts provide a high increase of o. n. not only due to the formation of isoalkanes, but also aromatic compounds with high o. n.From data table.4 it can be seen that the quantity of aromatic compounds increases with increasing temperature on all catalysts, but the greatest quantity is formed on Pt/Ti-catalyst at 350 and 400^0C-9.2 and 10.0%, which explains the raised increase of o.n. gasoline on this catalyst.

It is known that the selectivity of the isomerizing action of bifunctional catalysts is determined by the ratio of acidic and hydro-dehydrating activities of the catalyst. In this regard, it is of interest to compare the acidic properties of the studied catalysts (table.6) according to NH3 thermal desorption data.

When modifying mordenite Pt and Pd-catalysts, supported on pillared MM, redistribution of the acid centers for the strength is observed (figure 2 and table 6). This is illustratedby figure 2 on the example of Pd/AlZr.

From figure 2 it can be seen that the introduction of mordenite in Pd/AlZrCaHMM-catalysts a small decrease in the total number of acid centers of different strengths is observed, regardless of the content of Pd.

So, for the 0,1%Pd-catalyst the total acidity decreases from 220,3 to 211,0 mcmol NH3/g, and in case of the 0,35%Pd-catalyst mordenite reduces acidity from 249,3 to 230,0 mcmol of NH3/g. Such reduction of the total acidity is followed by redistribution of a.c.on strength. At the introduction of the mordenitethe quantity of weak a. c. decreases, and keeping of middle and strong increases.

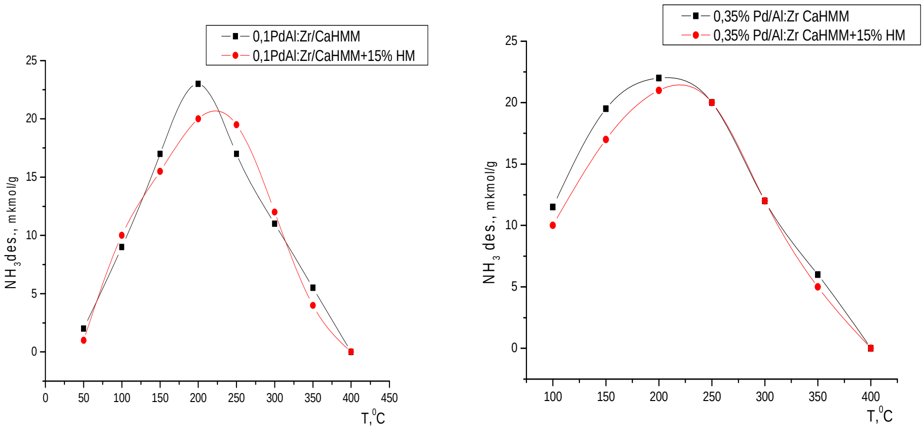

Figure 2 - Curves of thermal desorption of NH3 from Pd/AlZrCaHMM-catalysts with various quantity of Pd and modificationby mordenite

Table 6 – Distribution of acid centers in the mordenite containing Pt-and Pd-catalysts supported on pillared Al, Al-Zr and Ti montmorillonite

Sample	Quantity of acid centers	Acid centers			
		Weak <200^{0}C	Middle 200-300^{0}C	Strong> 300^{0}C	Total acidity
0,35%Pt/Al(2,5)NaHMM+HM	%	49,81	40,19	10,0	100
	mcmolNH$_3$/g	106,89	86,24	21,46	214,6
0,35%Pd/Al:Zr CaHMM +HM	%	44,51	42,55	12,94	100
	mcmolNH$_3$/g	102,38	97,87	29,76	230,0
0,35%Pt/Ti(5.0) NaHMM+HM	%	45.42	44.06	10.52	100
	mcmolNH$_3$/g	84.10	81.58	19.48	185.2

Comparison of results on acidity of the studied catalysts shows that on reduction of total acidity catalysts it is possible to arrange in the following row: Pd/AlZrCaHMM+HM (230,0 mcmol NH$_3$/g)> Pt/Al(2,5)NaHMM+HM(214.6)> Pt/Ti(5.0) NaHMM+HM (185.2). The same row on the decrease of the sum of the weak and middle acid centers is observed for studied catalysts:Pd/AlZr (200,25)> Pt/Al(193,13)>Pt/Ti (165,68 mcmol NH3/g). In the same sequence, the catalysts are arranged to reduce the content of isomers formed during the hydroconversion of the light fraction of straight-run gasoline, which indicates that the isomerizing activity is determined by the sum of weak and medium acid centers at which isomerization is carried out.

Now the most modern of technologies of a skeletal isomerization of n- alkanes which are already used in the industry [17-21] are the technologies with the use of Pt-catalysts on sulfated oxides of metals developed in the late 90-ies by firms UOP (USA) - and JSC NPP Neftekhim (Russia, Krasnodar). Comparison of the results received on the catalysts developed by us will be carried out with data on sulfated zirconium oxide catalysts of UOP and JSC “Neftekhim” (table 7). From table 7 it is visible that depth of processing of light alkanes on the example of n-hexane which was defined as the relation 2,2ДМБ/ΣC$_6$, masses %, (depth of isomerization of n-hexane, DIH), hesitates in ~ identical limits 30-32 and 30-31 on the RussianСИ-2 catalysts in process of Izomalk-2 at two different plants while in JSC Ufaneftekhim depth of an isomerization of n-hexane was 18-22 that is possibly connected with more high temperature of the process. On the similar catalyst of UOP of the brandPI-242 value of DIH was 20-27 that is also explained by more high temperature of process.

The laboratory and enlarged laboratory researches of the catalyst developed in IFCE have shown higher depth of an isomerization of hexane equal 28-39mass. %, in comparison with modern Pt/ZrO$_2$catalysts. Despite more high temperature of carrying out process of an isomerization, the selectivity on isomers remain very high -98-99%. The developed catalyst is characterized by increased stability, easily regenerated and is certainly of interest for practical use.

Table 7 - Indicators of isomerization process of n-alkanes on industrial UOP, JSC NPP "Neftekhim" and ITKE catalysts

Catalyst	**Petroleum refining plant**	**Process**	**Processparameters**	**Octane number**	**Depthofanisomerization, %**
Pt/ZrO$_2$-SO$_4$(СИ-2)	CJSC RyazanskayaOilRefinery	Isomalk-2	T=130^{0}C P=2,8-2,9 MPa	83-84	DIH=30-32
Pt/ZrO$_2$-SO$_4$(СИ-2)	JSC Ufaneftekhim	Isomalk-2	T=170-180^{0}C P=3 MPa	81-82	DIH=18-22
Pt/ZrO$_2$-SO$_4$(СИ-2)	Kirishinefteorgsintez	Isomalk-2		85	DIH=30-31
Pt/ZrO$_2$-SO$_4$ (PI-242)	UOP	Par-Isom	T=140-190^{0}C	81-83	DIH=20-27
Pd/AlZrCaHMM+HM	Laboratory of Institute of fuel, catalysis and electrochemistry	Isomeriza-tionn - hexane	T=300- 350^{0}C		DIH=28-39

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Al, AlZr ЖӘНЕ Ті-мен ПИЛЛАРИРЛЕНГЕН Na- ЖӘНЕ Са-ФОРМАЛЫ МОНТМОРИЛЛОНИТКЕ ЕНГІЗІЛГЕН Pt- ЖӘНЕ Pd-КАТАЛИЗАТОРЛАРЫНДАҒЫ ТІКЕЛЕЙ АЙДАЛҒАН БЕНЗИННІҢ ЖЕҢІЛ ФРАКЦИЯСЫНЫҢ ИЗОМЕРИЗАЦИЯСЫ

Аннотация. Бұл жұмыста Al, AlZr және Ті-мен пилларирленген және белсендірілген Na- және Са-формалы монтмориллонитке енгізілген цеолитсіз және морденитқұрамдыPt- және Pd-катализаторларындағы тікелей айдалған бензиннің жеңіл фракциясының изомерленуі бойынша мәліметтер келтірілген. Катализаторларға БЭТ, рентгенфазалық және элементтік талдау әдістерімен сипаттама берілді, аммиак термодесорбциясы бойынша олардың қышқылдық қасиеттері анықталды. Бензиннің жеңіл фракциясын изомерлеу процесінде пайда болатын изомерлердің көбірек саны Pt/Al(26,48%), сосын Pd/AlZr(23,56%), одан кейін Pt/Ti (23,15%) катализаторларында табылды. Зерттелген катализаторлардың қышқылдық нәтижелері мен олардың күштері бойынша таралуын салыстырғанда, әлсіз және орташа қышқылды орталықтардың суммалық мөлшері мен зерттелген катализаторлардың изомерлеу белсенділігі арасында өзара байланыс болатыны көрсетілді. Бұдан әрі қарай жеңіл қ-алкандарды изомерлеу процестерінде қолдану үшін 0,35%Pt/Al(2,5)NaHMM-катализаторы ұсынылды.

Түйін сөздер: изомерлеу, тікелей айдалған бензин, жеңілқ-алкандар, морденит, пилларирлеу,Pt мен Pd-катализаторлары,октан саны, селективтілік.

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ИЗОМЕРИЗАЦИЯ ЛЕГКОЙ ФРАКЦИИ ПРЯМОГОННОГО БЕНЗИНА НА Pt- И Pd-КАТАЛИЗАТОРАХ, НАНЕСЕННЫХ НА ПИЛЛАРИРОВАННЫЙ Al, AlZr И Ti МОНТМОРИЛЛОНИТ В Na- И Са-ФОРМАХ

Аннотация. В работе приведены данные по изомеризации легкой фракции прямогонного бензина на бесцеолитных и морденитсодержащих Pt и Pd-катализаторах, нанесенных на активированный и пиллaрированныйAl, AlZrи Ti монтмориллонит в Na- и Ca-формах. Катализаторы охарактеризованы методами БЭТ, рентгенофазового и элементного анализа, определены их кислотные свойства по термодесорбции аммиакаНаибольшее количество изомеров, образующихся в процессе изомеризации легкой фракции бензина, найдено на Pt/Al-катализаторе (26,48%), за ним следует Pd/AlZr(23,56%), а далее Pt/Ti (23,15%). Сопоставление результатов по кислотности изученных катализаторов и их распределению по силе показывает, что наблюдается корреляция между суммарным количеством слабых и средних кислотных центров и изомеризующей активностью изученных катализаторов. Для дальнейшего практического использования в процессе изомеризации легких н-алкановпредложен 0,35%Pt/Al(2,5)NaHMM-катализатор.

Ключевые слова: изомеризация, прямогонный бензин, легкие н-алканы, морденит, пилларирование, Pt и Pd-катализаторы, октановые числа, селективность.

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DETERMINATION OF VANADIUM IN THE PRECASPIAN REGION'S OIL BY THE EPR-SPECTROSCOPY METHOD

Abstract. In the article of 1977, it is considered the preparation of anisotropic EPR spectrum of a vanadyl ion complex consisting of 8 lines of hyperfine structure, as a result of a decrease in the viscosity of Karazhanbas oil. In recent years, lectures on EPR spectroscopy have been given in the subjects of petroleum chemistry and petroleum geology for students of higher educational institutions. The practical side of this lecture should begin with a simple isotropic vanadium spectrum. A method is proposed for determining vanadium and FR in crude oils at a temperature of liquid nitrogen. An important scientific and practical result of the proposed new method for the determination of vanadium in crude oils, in contrast to the method of American authors, is a reduction in nitrogen consumption, and an additional advantage of the method consists in reducing the cost of the process, since the use of an expensive temperature attachment is excluded. The EPR method is also proposed to estimate the total amount of vanadium in oil zones based on the interaction of V_2O_5 with concentrated hydrochloric acid. The standard photocolorimetric method for the determination of vanadium in oil ash can be replaced by a more rapid and selective EPR technique.

Keywords: organic free radicals, vanadyl ion VO^{2+}, electron paramagnetic resonance, isotropic vanadium spectrum, anisotropic vanadium spectrum.

The first report on the paramagnetism of crude oils was made by N.S. Garifiyanov and B.M. Kozyrev in 1956 [1] who, while studying the oil of the Bavly field in the EPR spectrum, found a single absorption line with a g-factor equal to 2 (Fig. 1). H.K. Gutovsky and co-workers [2] found that most crude oils produce an EPR spectrum, this spectrum consisting of a single line with a g-factor of 2.009, a width of about 4.5 Oe, and hyperfine structure lines.

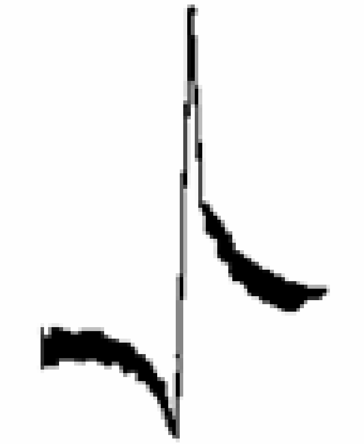

Figure 1-Electronic paramagnetic resonance in oil samples of the Bavly deposit (Tataria).
A single line is due to the free radical (R ·) of the asphaltene structure [2]

The latter was attributed to a paramagnetic vanadyl ion, and the singlet was due to free carbon bonds in condensed aromatic structures in colloidal particles of asphaltenes (Fig. 2).

A large number of lines indicates the anisotropic nature of the hyperfine interaction of an unpaired electron with the nuclear magnetic moment of the vanadium (spin of the nucleus - I_v=7/2). The anisotropy of hyperfine interaction is caused by the high viscosity of the oil.

R. Nasirov and S.P. Solodovnikov [3,4] found that dissolution of oil in toluene (1:3.55) and heating to 120 °C in a vacuum sealed ampoule result in the complex anisotropic spectrum transforming into a simple isotropic spectrum consisting of 8 hyperfine structure lines (HFS) due to the interaction of an unpaired electron with the nuclear magnetic moment of the vanadium (nuclear spin - I_v=7/2), as is seen in Fig. 3. The narrow (ΔH = 7±0.5 G) intense line at the center of the spectrum belongs to the so-called "free radical" (R•).

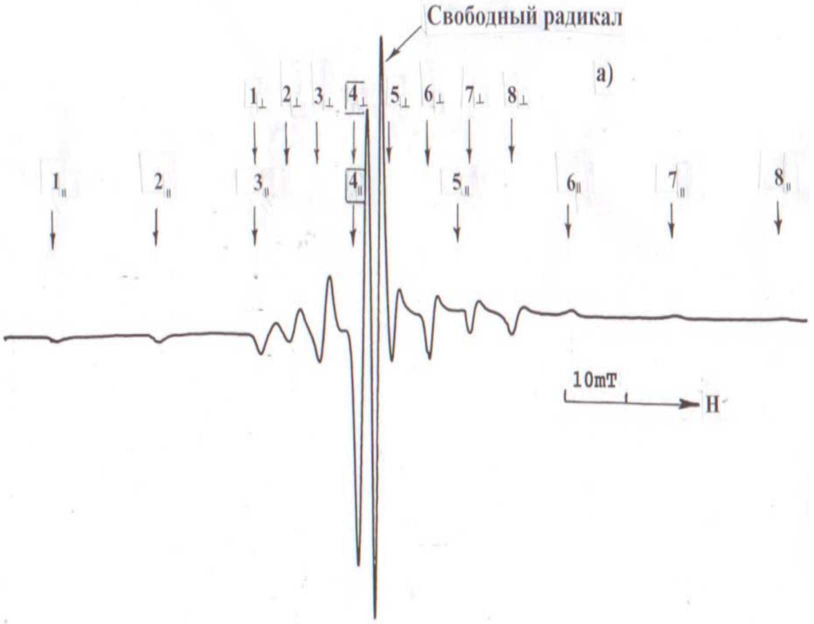

Figure 2- EPR spectrum of the Karazhanbas oil (well No. 851) at room temperature: the hyperfine lines I_{II}-8_{II} and 1⊥-8⊥ belong to the oxo-vanadyl VO^{2+} cations, and the single line in the high field refers to the free radical

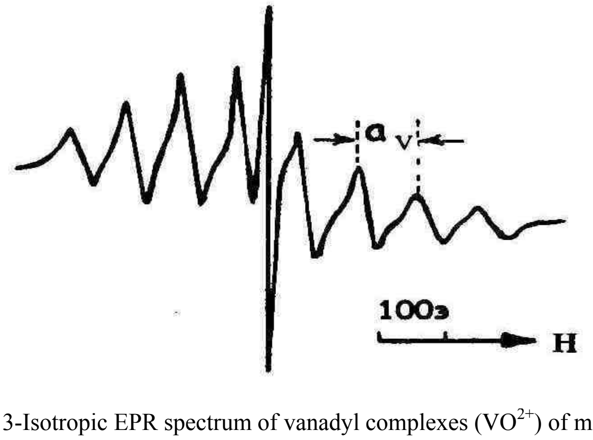

Figure 3-Isotropic EPR spectrum of vanadyl complexes (VO^{2+}) of mixtures of the Karazhanbas oil with toluene (1:3.55) at + 120 °C

EPR spectra were recorded on the E-12 spectrometer of the "Varian" company at a frequency of 9000 MHz with a magnetic field strength of 3000 Oe. As a standard, the Urikhtau oil of the Emba region with a vanadium content of 28 g/t was used. For measurements, a double resonator was used, which makes it possible to monitor the recordings of each spectrum with the help of the "Strong pich" reference sample included in the instrument. The amount of vanadium in the investigated oil samples was determined directly from the EPR spectra with the hyperfine structure of the complexes of tetravalent vanadium (see Fig. 4). The lines of HFS $1_{II} – 8_{II}$ and $1_{\perp} – 8_{\perp}$ belong to the oxo-vanadyl VO^{2+} cations. Of the two intense central lines, the line in the low field refers to the highest peak of $4_{\perp}$ HFS VO^{2+}, and a single line in the high field - to the "coal" free radical. To determine the V^{4+} content, the amplitude of the most intense line of the spectrum, which is adjacent to a single line of the free radical in the region of a weaker magnetic field, was measured.

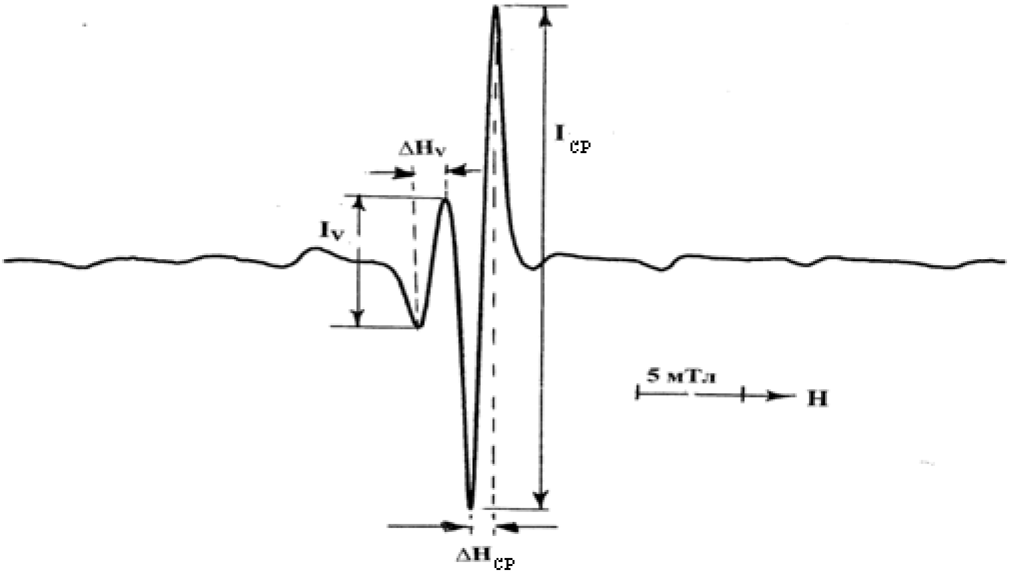

Figure 4-The central parts of the EPR spectrum (at liquid nitrogen temperature) of the oil of the Urikhtau deposit, well # 8: I_v - the amplitude of the vanadium signal, I_{CP} - the amplitude of the FR signal

The V^{4+} content was determined by comparing the spectral amplitudes of the investigated sample I_V and the standard $I_{ст}$ by the formula: $C_V = I_V I_{э.ст}/I_{ст}\ I_э$, where $I_{э.ст}$ - the amplitude of the reference sample line when recording the standard spectrum; $I_э$ - the amplitude of the same line when recording the spectrum of the sample. It was assumed that the widths of the spectral lines of the sample and the standard are the same.

On the recommendation of the American authors [5], the EPR spectra of V^{4+} are measured at a temperature of -90^0C, at which the oil hardens, and the amplitude of the measured signal does not depend on the viscosity of the oil. Thermostating of the sample was carried out by blowing it with nitrogen gas, heated to a given temperature.

Of particular interest was the effect on the accuracy of the determination of vanadium in oils extracted from different wells, the use of liquid nitrogen temperature (-196°C), which greatly expands the possibilities of laboratory determination of vanadium and increases the efficiency of the method.

Before using liquid nitrogen as a coolant in the determination of vanadium, it was necessary to investigate the nature of the saturation curves of EPR signals V^{4+} depending on the power P of ultra-high frequency, since such a dependence exists.

Figure 5 shows the saturation curves of the V^{4+} EPR signal as a function of the square root of the UHF power taken in a special double resonator at various temperatures.

In the first case, a quartz Dewar vessel (Figure 6) containing an ampoule with oil in liquid nitrogen was located in one resonator, in the second resonator, there was the standard "Strong pitch" of the E-12 spectrometer of the Varian company, used to monitor the UHF power.

In the second case, in the determination of vanadium at -90^0C, a quartz vacuum-treated tube with the oil sample was used in one resonator through which nitrogen vapors of the corresponding temperature were blown, in the second resonator, there was a standard.

Since, in the absence of saturation, the intensity of the EPR signal is $I \approx \sqrt{P}$, the intensity of the standard was a relative measure used as the scale of abscissas in Fig. 5.

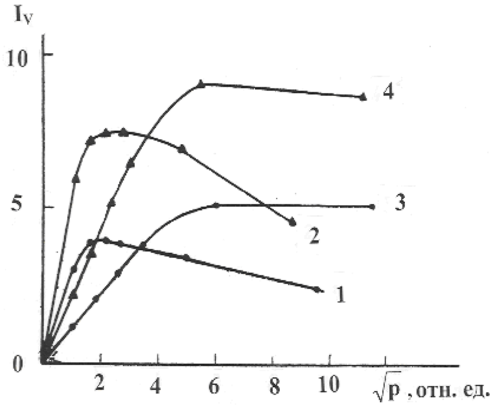

Figure 5 - Dependence of intensity change I EPR V^{4+} of oil of the South-East Kamyshitovoye field on $\sqrt{P}$.
Well 1: 1 - at -196 °C, 3- at -90 °C; well 16: 2 - at -196 °C, 4 - at -90 °C

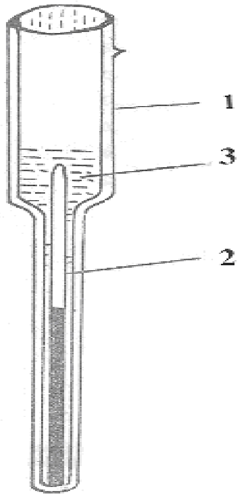

Figure 6-System for measuring EPR spectra of oils at liquid nitrogen temperature:
1 - Dewar vessel; 2 - ampoule with oil; 3 - liquid nitrogen

Table 1- Results of the V^{4+} determination in the region of linear dependence of I on $\sqrt{P}$ on the South-East Kamyshitovoye deposit

N of well	V^{4+}, g/t	
	-90^0C	-196^0C
1	25.0	25.0
2	68.6	40.0
3	10.3	10.6
4	16.8	16.5
5	15.5	15.7
14	36.7	34.7
16	71.0	68.3
19	24.6	24.1
21	11.2	10.5
110	71.1	70.8
111	34.3	35.0
115	14.5	14.1
117	10.9	10.2
123	10.2	10.3
120	11.6	10.6

As can be seen from Figure 5, there is a significant region of linear dependence of I on $\sqrt{P}$, in which a correct determination of the V^{4+} vanadium content is possible at both -90 °C and -196 °C. Regardless of the concentration of vanadium (see wells 1 and 16 in Table 1), the regions of linear dependence for the same temperature are approximately the same, but differ significantly at different temperatures: at -196 °C, the linear section is about 3 times shorter than at -90 °C.

Table 1 presents a good correspondence of the data, which makes it possible to recommend the use of liquid nitrogen as a coolant in mass laboratory determinations of vanadium.

In order to improve the standard photocolorimetric method for determination of vanadium in oil ash, a more rapid method was proposed for estimating the total amount of vanadium in oil ash, based on the interaction of V_2O_5 with concentrated hydrochloric acid according to the following scheme:

$$V_2O_5 + 6HCl \leftrightarrow 2VOCl_2 + Cl_2 + 3H_2O\,.$$

Figure 7 shows the anisotropic EPR spectrum of vanadium chloride formed from reactive vanadium oxide. The same spectrum was obtained from the ash of Kalamkas oil, well N 52 (Fig. 7) and other oils. The concentration of vanadium in the studied oil ash (Table 2) of the Caspian region is determined from the anisotropic EPR spectrum of the formed vanadium chloride by the methods of [6-8]. As can be seen from Table. 2, the results of determining the content of vanadium in oil ash by the chemical method and EPR and XRF methods are consistent. The advantage of the EPR method for determining the total vanadium from oil ash is its productivity, selectivity, high accuracy and reliability in comparison with conventionally used photocolorimetric methods.

Table 2-Vanadium content in oils and their ash, %

Oil	Ash output	Vanadium content		Vanadium cfontent per ash
		по РФА	по ЭПР	
Kalamkas, 52	0.087	0.015	0.0148	17.5
Botakhan, 68	0.037	0.0025	0.0022	12.9
Karazhanbas, 851	0.09	0.029	0.026	28.9

The results of these studies on the determination of vanadium in crude oils using EPR-radiospectroscopy were used by geologists and scientists of the All-Russian Petroleum Research Exploration Institute (VNIGRI) as reference samples for calculating the geological reserves of vanadium in the Karazhanbas, North Buzachinsky, Kalamkas and Zhalgiztobe oil fields of the Mangyshlak region (Act on the Use of Materials by R. Nasirov in the works on calculating the reserves of vanadium in the oil deposits of the Mangyshlak region, 24.03.1992, №08-signed by the head of the department of the VNIGRI, doctor of geological and mineralogical sciences, laureate of the State award, V.V. Gribkov) [9].

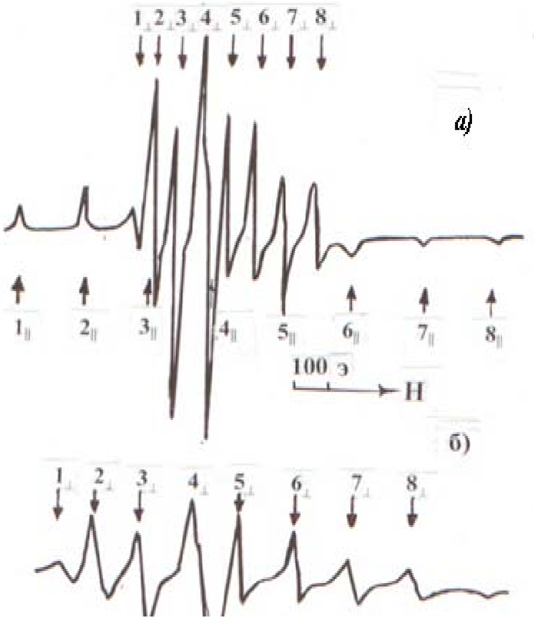

Figure 7- EPR spectra of vanadyl chloride at -196 °C, obtained: a) from V_2O_5 b) from the ash of Kalamkas oil, well N 52 (here are recorded the hyperfine lines $1_\perp - 8_\perp$ of vanadyl ion)

The developed method "The results of determination of tetravalent vanadium in oils by the EPR spectroscopy" is also recommended for students of higher education institutions studying in the specialties "Geology and geochemistry of oil and gas" [10] and "Oil and gas chemistry" [11]. In these textbooks, EPR spectroscopy is widely used not only in petrochemistry, but also in other geological and geochemical studies, in particular, in the allocation of oil strata on the relationship between the concentration of ions of divalent manganese, vanadium V^{4+} and FR in rocks

The presence of porphyrins with vanadium in the form of vanadyl ion VO^{2+} is evidence in favor of the theory of the organic origin of oil (chemofossilia). pigments with a porphyrin structure (plant chlorophyll, animal hemoglobin) are considered as biological precursors of oil porphyrins widely distributed in nature [12]. Allocated from vanadylporphyrin concentrates of Karazhanbas oil, free porphyrins were used by us to obtain complex copper compounds [13]. In order to establish the structure of the oil porphyrins in the EPR spectrum, hyperfine splitting from the interaction of an unpaired electron with copper nuclei and four atoms of ^{14}N pyrolic rings was observed.

Conclusions.

1. It was found that dissolution of oil in toluene (1:3.55) and heating to 120 °C in a vacuum-sealed ampoule result in the complex anisotropic spectrum transforming into a simple isotropic spectrum consisting of 8 hyperfine structure lines (HFS), caused by the interaction of the unpaired electron with the nuclear magnetic moment of the vanadium (the nuclear spin I_v=7/2).
2. 2. For the first time a new method for determination of vanadium and FR in crude oils at liquid nitrogen temperature is proposed. An important scientific and practical result of the new proposed method for the determination of vanadium in crude oils, in contrast to the method of American authors, is a reduction in nitrogen consumption, and an additional advantage of the method is to reduce the cost of the process, since the use of an expensive temperature attachment is excluded.
3. The advantage of the EPR method for determining the total vanadium in oil ash is its productivity, selectivity, high accuracy and reliability in comparison with conventionally used photocolorimetric methods.
4. The developed method "The results of determination of tetravalent vanadium in oils by the EPR spectroscopy" is also recommended for students of higher educational institutions studying in the specialization of "Geology and geochemistry of oil and gas" and "Oil and gas chemistry".

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ЭПР СПЕКТРОСКОПИЯ КӨМЕГІМЕН КАСПИЙ МАҢЫНДАҒЫ МҰНАЙЛАРДАҒЫ ВАНАДИЙДІ АНЫҚТАУ

Аннотация. Мақалада 1977 жылы мұнайдың тұтқырлығын азайту нәтижесінде төрт валентті ванадий ионы комплексінің 8-желіден тұратын тәжірибелік изотропты ЭПР-спектрі алынғаны сөз болады. Соңғы жыдары мұнай химиясы және геологиясы пәндері бойынша студенттерге ЭПР – спектроскопиядан дәрістер оқыла бастады, ал дәрістің практикалық негізі осы жәй изотропты спектрден бастау алынуы керек. Ванадийді және еркін радикалды мұнайларда сұйық азот температурасында анықтау әдісі ұсынылады. Зертхана жағдайында ванадийді жаппай анықтау кезінде ұсынылған әдістің американдық ғалымдардың ұсынысынан өзгешілігі азотты көп шығындамайды, температура қондырғысын қажет етпейтіндігі және экспресті болатындығы. Сол сияқты бұл жұмыста ЭПР әдісі мұнайдың күліндегі жалпы ванадийді анықтауға болатындығы тәжірибе негізінде дәлелденді және қазіргі кезде қолданылып жүрген фотокололиметрлік әдісті толық ығыстырады.

Түйін сөздер: органикалық еркін радикалдар, ванадил ионы VO^{2+}, электрондық парамагниттік резонанс, ванадийдің изотропты спектрі, ванадийдің анизотропты спектрі.

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ОПРЕДЕЛЕНИЕ ВАНАДИЯ В НЕФТЯХ ПРИКАСПИЙСКОГО РЕГИОНА МЕТОДОМ ЭПР-СПЕКТРОСКОПИИ

Аннотация. В статье 1977 года рассматривается получение изотропного спектра ЭПР комплексного иона ванадила, состоящего из 8 линий сверхтонкой структуры, в результате уменьшения вязкости Каражанбасской нефти. В последние годы по предметам: химии нефти и геологии нефти для студентов высших учебных заведений читаются лекции по ЭПР – спектроскопии. Практическая сторона этой лекции должна начинаться с простого изотропного спектра ванадия. В работе предлагается способ определения ванадия и СР в сырых нефтях при температуре жидкого азота. Важным научно-практическим результатом предлагаемого нового способа определения ванадия в сырых нефтях, в отличие от метода американских авторов является снижение расхода азота, а дополнительное преимущество способа заключается в удешевлении процесса, так как исключается применение дорогостоящей температурной приставки при массовых лабораторных определениях ванадия. Так же предлагается метод ЭПР для оценки общего количества ванадия в золах нефти, основанной на взаимодействии V_2O_5с концентрированной соляной кислотой. Стандартный фотоколориметрический метод определения ванадия в золах нефтей можно заменить более экспрессной и избирательной методикой ЭПР.

Ключевые слова: органические свободные радикалы, ион ванадила VO^{2+}, электронный парамагнитный резонанс, изотропный спектр ванадия, анизотропный спектр ванадия.

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CATALYTIC CONVERSION OF METHANE INTO OLEFINS

Abstract. The worldwide use of olefins in the chemical industry is growing every year. This is due to increased consumption of olefins for the production of chemically important products, such as polyethylene, ethylene glycol, acetaldehyde and vinyl chloride. In the present work, the activity of the developed heteropolyacid (HPA) catalysts based on phosphorus and tungsten in the oxidative conversion of methane to olefins was studied. The developed catalysts were applied to various natural and synthetic carriers. The process of oxidative conversion of methane was studied by varying the reaction temperature, the ratio of the reacting components, the space velocity, and the effect of the addition of water vapor to the reaction mixture. When 5% of the HPA was applied to natural carriers, ethane, ethylene, hydrogen and propylene were observed in the reaction mixture. The same activity was observed for catalysts deposited on synthetic carriers. It has been established that the optimal conditions for the oxidative conversion of methane on a catalyst of 5% HPA applied to a natural carrier are: T = 1073K, W = 3900h^{-1}, $CH_4 : O_2$ = 2 : 1. The positive effect of the addition of water vapor to the reaction mixture was determined.

Key words: catalytic oxidation, catalysts, methane, olefins.

Introduction

Chemistry of lower alkanes is one of the most rapidly developing scientific fields [1-8]. The most important source of alkanes in nature is natural gas, mineral hydrocarbon raw materials - oil and associated oil gases. Natural gas consists of 95 percent methane [9]. Therefore, in the modern petrochemical industry, saturated hydrocarbons are the basis for obtaining a variety of organic compounds, an important raw material in the processes of obtaining intermediates for the production of plastics, rubbers, synthetic fibers, detergents and many other substances.

It is estimated that over the next decades, the world situation will be when half of the existing oil reserves will be spent and the expected production come into conflict with the growing demand for oil [10]. The clash of these trends could lead to a shortage of oil, increase in the price of this kind resource and will become a powerful resource and a prerequisite for the transition to alternative energy sources. According to numerous forecasts of Russian and foreign analysts in the next 10-20 years the situation has changed in favor of the priority of gas demand. Natural, economic and political factors, which together determine the inevitability of change in the structure of world power balance in favor of growth in the share of gas are at the heart of this process. Therefore, the widespread use of gas in areas focused on the consumption of petroleum products is important program of the world economy, which is undoubtedly important for Kazakhstan. The full range of products produced from petroleum, can be synthesized by direct route from natural gas. The cost of such substances as synthesis gas, H_2, ethylene, formaldehyde, and benzene is 10-100 times higher than the original gas. They are the basic raw material for the synthesis of methanol, polyethylene, alcohols, acids, liquid motor fuel, dimethyl ether, ammonia fertilizer and hundreds of other compounds necessary for the development of chemical industry.

The problem of processing of natural gas into organic compounds solved by steam, carbon dioxide and oxidative conversion of alkanes to synthesis gas with subsequent production a mixture of paraffin, olefins and alcohols [11,12]. Co-conversion of methane with C_3-C_4 hydrocarbons with formation of mono- and polycyclic aromatic hydrocarbons, oxidative dimerization of methane to ethylene and ethane, selective oxidation of methane to methanol can serve as example of one-step conversion of methane [13,14]. Produced hydrocarbons are readily oxidized to carbon dioxide and water in the presence of oxygen, which significantly reduces the selectivity of the reaction at high conversion of methane. This leads to a higher cost of hydrocarbons produced from methane than analogs of petroleum origin. In general, one-step methane conversion processes are at the level of laboratory research, and finding new ways of effective utilization of natural gas is an urgent task.

We have developed polyoxide catalysts based on molybdenum, chromium and gallium, applied to natural clays for catalytic oxidation of propane butane mixture into oxygenates and olefins [15-17].

Light olefins are the most important building blocks for polymers and a variety of intermediate products. The world demand for ethylene and propylene exceeds 180 MTA (about 2/3 of ethylene production) with annual growth of 4-5% in the next decade [18].

The oxidative conversion of alkanes to ethylene in place of the use of petroleum feedstock is of practical interest, since ethylene and propylene are the basis for the production of approximately 50% of all organic products in the chemical industry. At present, their annual output is one of the main indicators of the potential of industrial development. It is known that the petrochemical potential of many countries is estimated by the volume of production of ethylene and propylene, which are the basic raw materials for the production of polyethylene, polypropylene, plastics and other products. The literature reports an increase in ethylene prices and an increase in olefin production in Asia, Europe and America [19]. Expansion of production and construction of new petrochemical complexes is also in Russia and China. For Kazakhstan, which has huge reserves of natural gas, a significant part of which is flared, the development and implementation of technologies for processing alkanes is a strategic task.

There are two main ways of producing valuable chemicals from methane - indirect and direct conversion. Currently, the most commonly used method is indirect conversion, i.e. methane is first converted to a synthesis gas with various C/H ratios by either reforming or partial oxidation, and then the synthesis gas is converted to raw chemicals by Fischer-Tropsch synthesis, converting the synthesis gas to an olefin, converting the synthesis gas to gasoline , synthesis of ammonia or many other processes. However, indirect conversion of methane is always accompanied by complicated installations, high production costs and, in particular, large CO_2 emissions. Consequently, the study of the direct conversion of methane into valuable chemicals has recently attracted special attention [20].

Experimental

Catalyst preparation

The method of catalyst preparation has been previously developed in the laboratory of oxidative catalysis of JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry" [21]. The catalysts were prepared by the capillary impregnation method of mixed aqueous solutions of nitrate salts of metals, supported on carriers.

Characterization techniques

The analysis of the initial mixture and reaction products was carried out using a chromatograph "Chromos GC-1000" with the "Chromos" software and on a chromatograph "Agilent Technologies 6890N" (USA) with computer software. Chromatograph "Chromos GC-1000" is equipped with packed and capillary columns. The packed column is used for the analysis of H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3-C_4 hydrocarbons, CO and CO_2. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. Carrier gas velocity Ar = 10 ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve V = f (S) was constructed, where V - amount of substance in ml, S - peak area in cm^2. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was ± 3.0%.

Results and discussion

The influence of nature of carriers, as well as reaction temperature during partial oxidation of methane on catalysts supported on various natural and synthetic carriers on the basis of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ was investigated. The reaction was investigated under the following conditions: the ratio of initial reaction mixture $CH_4:O_2 = 7:1$ (36.0%: 5.0%, the rest - Ar); $V = 7800\ h^{-1}$ by varying the reaction temperature from 873 to 1173 K. The formation of hydrogen, as well as the C_2, C_3, and C_4 hydrocarbons occurred in this temperature range. Conversion (X) of methane was varied from 0.5 to 35.6%.

When supporting of 5% HPA on natural carriers: TC, EKC, diatomite, CC, TWC, ZE conversion of methane was varied from 2.7 to 15.6%. Selectivity (S) on the main product - ethylene varied from 6.2 to 41.9%. At 1023 K on the catalyst supported on ZE observed the formation of ethane with yield (Y) 3%, 44.4% selectivity at 6.7% conversion of methane. With further increase of reaction temperature to 1173 K the yield of ethane decreased to 1.6% (selectivity 23.9%). Starting from 1073-1123 K there was the formation of ethylene. Conversion at the same time kept constant and the selectivity of ethylene increased from 33.6 to 40.1%. Hydrogen began to form at 973 K increasing at higher temperatures, the selectivity of its grown from 15.3% to 24.7%. Propylene was also observed in small amounts in the reaction products.

Effect of synthetic carriers on the activity of 5% $H_3PW_{12}O_{40}$ catalyst in reaction of partial conversion of methane was investigated. It was investigated a series of synthetic carriers: CaA, Siral-10, Siral-20, Siral-30, NaX, AlSi and 20% Al_2O_3+80% H-ZSM-5. Hydrogen, C_2, C_3, and C_4 hydrocarbons, and CO are formed on synthetic carriers as well as on natural in this temperature range. Conversion of methane was varied from 1.3 to 19.7%.

Comparing the data obtained on 5% $H_3PW_{12}O_{40}$ catalyst supported on synthetic and natural carriers, revealed that the optimal catalyst leading ODM reaction toward the formation of C_2 hydrocarbons is 5% HPA, supported on East Kazakhstan zeolite. At 1023 K observed the formation of 3% ethane and 2.7% ethylene at 1123 K. 5.17% hydrogen at 900°C formed on the catalyst supported on TWC.

Table 1 - The influence of ratio of $CH_4:O_2$ in oxidative conversion of methane on 5.0% HPA/NC catalyst

Concentration $CH_4:O_2$, %	Ratio, $CH_4:O_2$	X_{CH4}, %	Yield, %		
			H_2	C_2H_6	C_2H_4
50,0 : 50,0	1,0 : 1,0	significant formation of hydrogen with sparks			
67,0 : 33,0	2,0 : 1,0	14,0	28,0	2,8	10,8
75,0 : 25,0	3,0 : 1,0	22,0	-	2,75	9,12
80,0 : 20,0	4,0 : 1,0	significant formation of hydrogen with sparks			
84,0 : 16,0	5,0 : 1,0	15,0	-	1,4	5,2
Note - T = 1073 K, $V = 3900\ h^{-1}$.					

Series of experiments at a space velocity of reaction 3900 h^{-1} and the temperature range 973-1173 K on the investigation of reactants ratio $CH_4 : O_2$ with in 1 : 1, 2 : 1, 3 : 1, 4 : 1, 5 : 1 was performed (Table 1). It was determined that the highest yield of ethylene 10,8% is observed at ratio of $CH_4 : O_2 = 2 : 1$ at reaction temperature 1073 K.

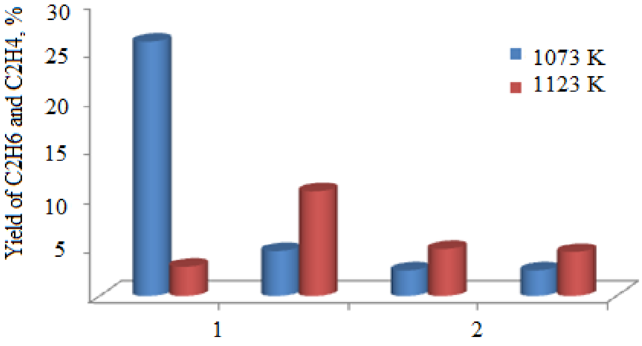
Effect of the changes in space velocity (1000, 3900, 10000, 12000 and 15000 h^{-1}) of process on the catalytic activity in oxidative conversion of methane was investigated. It was determined experimentally that the best in the conversion of methane to 28% H_2 and 13,6% C_2 hydrocarbons is space velocity 3900 h^{-1} and contact time 0.9 s (Table 2).

Addition of water vapor into the reaction mixture at a ratio of $CH_4 : H_2O = 1: 0.5$, space velocity 3900 h^{-1} and the temperature range of 973-1173 K, $CH_4 : O_2 = 2: 1$ was examined. It was shown that with the addition of water vapor into the reaction mixture ethylene yield remained constant at 10,8% at 1073 K.

Table 2 - Effect of space velocity on the performance of process of oxidative conversion of CH_4 on 5,0% HPA/NC catalyst

Space velocity, h^{-1}	X_{CH4}, %	Yield, %		
		H_2	C_2H_6	C_2H_4
1000	13	26	1,9	8,8
3900	13,9	28	2,8	10,8
10000	6,6	4,3	3,0	3,2
12000	15,0		4,0	8,1
15000	20,0		1,0	1,2
Note - T = 1073 K, V = 3900 h^{-1}, $CH_4 : O_2 = 2 : 1$.				

Also, we investigated the increase in the volume of catalyst to 5ml and decrease of space velocity to 1560 h^{-1} which shows that with increase of catalyst sample the yield of ethane and ethylene at 1073K was respectively 26% and 4,6% with sharp decrease of ethane up to 3% and increase of ethylene to 10,7% with increase in the reaction temperature on 50 K (Figure 1). It was shown that the yield of ethane and ethylene at 1073 K was 2,6% with slight increase in the amount of ethane to 4,8% and ethylene 4,5% at raise of reaction temperature to 1123 K with increase of space velocity up to 3900 h^{-1}.



1 - 1560 h^{-1}, 2 - 3900 h^{-1}. Catalyst – 5ml

Figure 1 - Effect of space velocity and temperature of reaction in the oxidative conversion of CH_4 on 5,0% HPA/NC catalyst

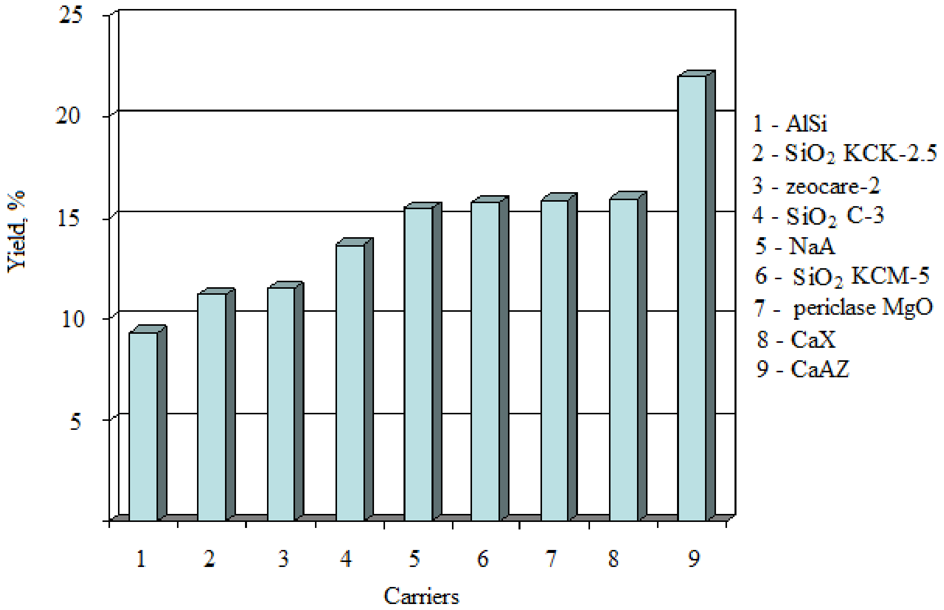
Thus, the optimal conditions for the oxidative conversion of methane on 5% HPA/TWC catalyst were determined: the ratio of reactants $CH_4 : O_2 = 2 : 1$, 1073 K temperature and space velocity 3900 h^{-1}.

On the example of 5-15% catalysts based on $H_4SiW_{12}O_{40}$ and its salts on aluminosilicate was established the formation of C_2H_6, C_2H_4, CO_2, H_2, the ratio of which was determined by temperature of reaction in oxidative dimerization of methane (ODM). The ratio $C_2H_4:C_2H_6$ in products increased toward the formation of C_2H_4 with increasing temperature and transition from high-percentage to low-percentage catalysts. Catalysts 5% $H_4SiW_{12}O_{40}$/AlSi (S_{C2H4} = 51.5%, $S_{C2\text{-}HC}$ = 80.0%) and 15% $H_3PW_{12}O_{40}$/AlSi (S_{C2H4} = 39.2%, $S_{C2\text{-}HC}$ = 60.2%) had a maximum selectivity by C_2-hydrocarbons. CaAZ, CaX, minerals containing MgO, SiO_2, and NaA can be recommended as a carrier. The yield of C_2H_4 from CH_4 achieved 13,5-18,5% at conversion of CH_4 23-32% and the ratio of C_2H_4: C_2H_6 3,6-7,5, Figure 2.

The studied cations as part of HPC form series on the effectiveness of influence on yield of C_2H_4 (%) from CH_4:

-for 5% $[SiW_{12}]/SiO_2$: Na (13,7) > Mg (11,9) > Ce (11,1) > Cd (10,7) > Ni (10,0) > Pb (9,7) > Ca (6,9) > Cr (8,1) > Fe (7,3) > Bi (7,0);

-for 5%$[PW_{12}]/SiO_2$: Mg (14,2) > Cs (12,7) > Pb (11,7) > Ba (10,0) > Cr (9,8).



The composition of reaction mixture, % vol.:CH_4 - 20,5; O_2 - 15,4; Ar - 64,1; water vapor.

Figure 2 – Effect of the nature of carrier of 5% [SiW_{12}] catalysts on conversion and yield of C_2 hydrocarbons in oxidative dimerization of methane

The transition from supported HPA to their salts optimized ODM process. It was shown that Y and S formation of C_2H_4 increases with increasing ratio of CH_4:O_2 from 1:1 to (1,5-30):1 on 0,5% $H_4SiW_{12}O_{40}$/AlSi), Table 3. The composition of mixture, mol: CH_4 - 0018-0-0,0031, O_2 - 0,0013, inert gas - 008-0-0,004 is optimal for synthesis of C_2H_4. The positive effect has introduction of water vapor (CH_4:O_2 = 1:0,21, mol) into reaction mixture.

Table 3 – Influence of CH_4 and O_2 in mixture on yield and selectivity of C_2 hydrocarbons on 0,5% $H_4SiW_{12}O_{40}$/AlSi

Composition of reaction mixture, mol	Yield, %		Selectivity, %	
	C_2H_6	C_2H_4	C_2H_6	C_2H_4
CH_4-0,0013, O_2-0,0013, Ar-0,006	2,2	9,5	5,9	25,7
CH_4-0,0018, O_2-0,0013, Ar-0,0056	3,4	8,8	16,6	43,0
CH_4-0,0031, O_2-0,0013, Ar-0,0042	3,1	10,2	11,2	38,6
CH_4-0,0044, O_2-0,0013, Ar-0,0030	3,0	8,9	48,0	20,9
CH_4-0,0018, O_2-0,0004, Ar-0,0065	5,1	5,2	28,4	29,0
CH_4-0,0018, O_2-0,0004, Ar-0,006	4,1	7,4	13,6	24,6
Note – T=750°C, τ=0,46s. By-products: CH_2O, H_2, CO_2.				

ODM process can be intensified by additional oxidative dehydrogenation of ODM product - C_2H_6 into C_2H_4.

Conclusion

Thus, it follows from the above results that optimization of the ODM process can be achieved by rigorous selection of the process parameters of the reaction, by improving the composition of the supported catalysts, for example, by substituting the protons of the HPA for metal cations of Groups I and II, by applying GPC to silicon-containing carriers (SiO_2, pentasils, aluminosilicates, and synthetic zeolites).

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МЕТАННЫҢ ОЛЕФИНДЕРГЕ ДЕЙІН КАТАЛИТИКАЛЫҚ КОНВЕРСИЯСЫ

Аннотация. Химия өндірісінде олефиндердің әлемдік Қолданылуы жыл өткен сайын өсуде. Бұл полиэтилен, этиленгликоль, ацетальдегид және винилхлорид секілді химиялық маңызды өнімдерді өндіруге арналған олефиндерді Қолданылуының артуымен байланысты. Ұсынылған жұмыста метанның олефиндерге тотығу конверсиясында фосфор және вольфрам негізіндегі жасалынған гетерополиқышқылды (ГПҚ) катализаторлардың белсенділігіне зерттеулер жүргізілді. Әр түрлі синтетикалық және табиғи тасымалдағышқа отырғызылған катализаторлар жасалынды. Метанның тотыға айналу үрдісі барысында әр түрлі температура мен көлемдік жылдамдықта реакцияға түсетін компоненттердің Қатынасы, сондай-ақ реакциялық Қоспаға су буының әсері зерттелді. Табиғи тасымалдағышқа 5% ГПҚ енгізгенде реакциялық Қоспадан этан, этилен, сутек және пропилен түзілгені байқалды. Синтетикалық тасымалдағышқа отырғызылған катализаторлар үшін де осындай белсенділік байқалды. Метанның тотыға айналу конверсиясы үшін табиғи тасымалдағышқа отырғызылған 5% ГПҚ катализаторының оңтайлы жағдайының шарттары Т = 1073К, W=3900 сағ$^{-1}$, $CH_4 : O_2 = 2 : 1$ болып табылады. Реакциялық қоспаға су буын қосқандағы әсері оң нәтиже көрсететіні анықталды.

Түйін сөздер: каталитикалық тотығу, катализаторлар, метан, олефиндер.

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КАТАЛИТИЧЕСКАЯ КОНВЕРСИЯ МЕТАНА В ОЛЕФИНЫ

Аннотация. Мировое применение олефинов в химической промышленности растет с каждым годом. Это связано с увеличением потребления олефинов для производства химически важных продуктов, таких как полиэтилен, этиленгликоль, ацетальдегид и винил хлорид. В представленной работе проведено исследование активности разработанных гетерополикислотных (ГПК) катализаторов на основе фосфора и вольфрама в окислительной конверсии метана в олефины. Разработанные катализаторы были нанесены на различные природные и синтетические носители. Процесс окислительного превращения метана исследовался при варьировании температуры реакции соотношение реагирующих компонентов, объемной скорости, а также изучено влияние добавление паров воды в реакционную смесь. При нанесении 5% ГПК на природные носители в реакционной смеси наблюдалось образование этана, этилена, водорода и пропилена. Такая же активность наблюдалась и для катализаторов нанесенных на синтетические носители. Установлено, что оптимальными условиями окислительной конверсии метана на катализаторе 5% ГПК нанесенном на природный носитель являются: Т = 1073К, W=3900ч$^{-1}$, $CH_4 : O_2 = 2 : 1$. Определено положительное влияние добавления паров воды в реакционную смесь.

Ключевые слова: каталитическое окисление, катализаторы, метан, олефины.

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FORMATTIVE EVALUATION IS AN UNINTERRUPTABLE PART OF THE TRAINING PROCESS ON LESSONS OF CHEMISTRY

Abstract. In recent years, the world pedagogy is in the process of rethinking the system for assessing students' learning achievements, since evaluation is one of the main stages of the educational process. One of the goals of the school is to create conditions conducive to the pursuit of self-education, self-knowledge of the individual, the development of motivation to achieve success, that is, the formation of key competencies of students. According to the State Program for the Development of Education in the Republic of Kazakhstan for 2011-2020, when evaluating students' learning achievements it is important to focus on the process of developing the key competencies of the future specialist. And for this it is necessary to make significant changes to the traditional system of knowledge assessment.

Keywords: formative evaluation, summary estimation, criterion estimation, teacher assessment, self-evaluation.

INTRODUCTION

One of the significant indicators of the effectiveness of secondary education is the level of educational achievements of students, which demonstrates how the educational activity in the school functions, develops, affects the students and their effectiveness. Therefore, the level of the potential in improving the quality of education depends on how well the system of assessing the educational achievements of students is built up. (1) In the National Plan "100 concrete steps", the Head of State pointed out, as a fundamental basis for economic growth, improving the quality of human capital based on OECD standards.

MAIN PART

The implementation of the OECD direction provides for the updating of standards and evaluation systems for the development of functional literacy of students. In the OECD report "Review of the national educational policy. Secondary Education in Kazakhstan "(2014) proposed a number of measures aimed at improving the quality, relevance and frequency of the assessment in the classroom. In particular, the introduction of a criteria-based assessment system, the definition of evaluation criteria for high-level thinking skills, the training of teachers, the conduct of national standardized testing at the end of each stage of education, the establishment of an effective and reliable data collection system, etc. It also indicates the need for effective use of the results of the conducted evaluation. (5) Criterial evaluation is the process of correlating the learning outcomes actually achieved by students with the expected learning outcomes on the basis of clearly defined criteria. The purpose of the criterial evaluation is to obtain objective information about the results of training the students on the basis of evaluation criteria and to provide it to all interested participants for further improvement of the educational process. To collect data on progress and progress in learning during the school year, two types of evaluation are carried out: formative assessment and summary evaluation. The cumulative assessment, in turn, includes procedures for cumulative assessment for the section / cross-cutting theme, a quarter and level of education.

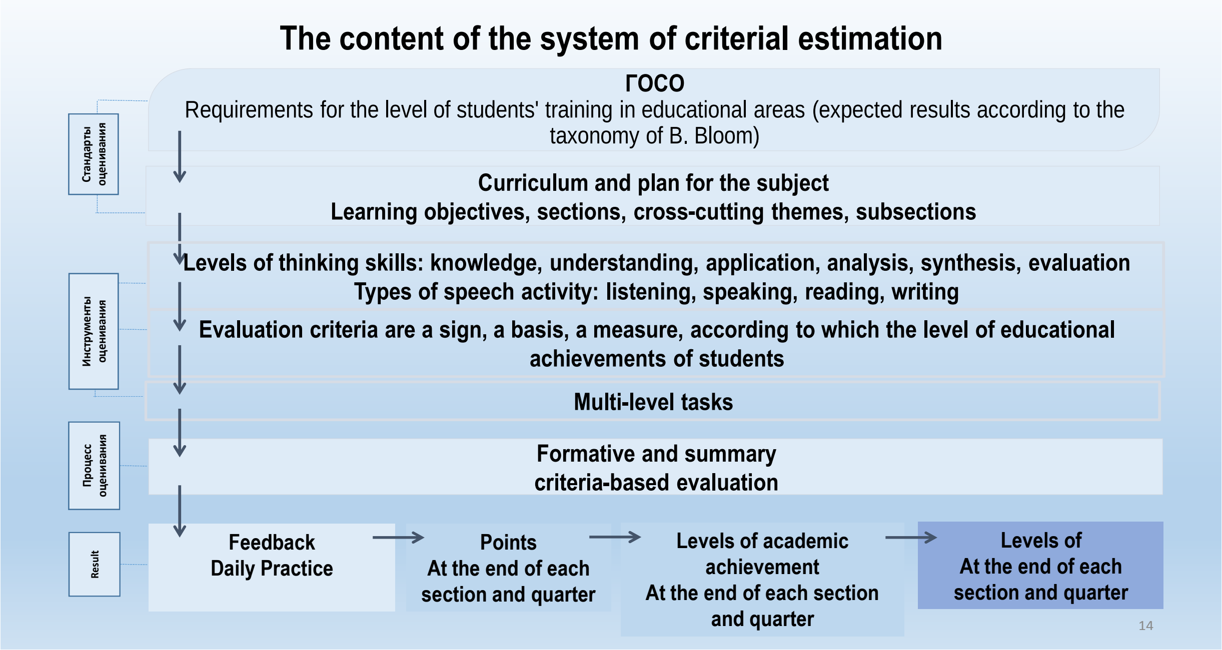
Table 1 - Two types of estimation

Formative	Summative
is made during training (with the help of small independent works, tests, etc.)	at the end of the studied topic or section (with the help of control or credit work)
helps the student to adjust his work, achieve better results	allows students to demonstrate their achievements on the topic
allows the teacher to accumulate information about the assimilation of the material by each student, to analyze it and plan further work, that is, to carry out a more qualitative learning process	gives the teacher the opportunity to make a final judgment about the students' achievements, to set the final marks

The developed system of criterial estimation, which integrates the best Kazakhstani and international experience, allows us to proceed to the implementation of the assigned tasks in the lessons, in particular chemistry.

The content of the system of criterial evaluation is determined by standards, processes, tools and evaluation results. (3)

(Figure 1).



The content of the system of criterial estimation

Стандарты оценивания

ГОСО

Requirements for the level of students' training in educational areas (expected results according to the taxonomy of B. Bloom)

Curriculum and plan for the subject
Learning objectives, sections, cross-cutting themes, subsections

Инструменты оценивания

Levels of thinking skills: knowledge, understanding, application, analysis, synthesis, evaluation
Types of speech activity: listening, speaking, reading, writing

Evaluation criteria are a sign, a basis, a measure, according to which the level of educational achievements of students

Multi-level tasks

Процесс оценивания

Formative and summary criteria-based evaluation

Result

Feedback
Daily Practice

Points
At the end of each section and quarter

Levels of academic achievement
At the end of each section and quarter

Levels of
At the end of each section and quarter

14

Figure 1 - The process of formative estimation

Formative assessment is a process that has a direct impact on the growth and development of learning achievements and provides feedback between the teacher and the learner. Formative evaluation takes on an increasingly important role in international practice and is generally defined as the assessment used to adapt teaching and learning to the needs of learners (Black and William, 1998; Ashcroft and Foreman-Pack, 1994; Taras, 2005). At the same time, analysis of the literature suggests that the description of the structural elements of formative evaluation is treated ambiguously and can vary depending on the objectives and conditions of application.

Structure of Formative Assessment:

Structure of Formative OECD Assessment / International Conference of the Center for Research in Education and Innovation (2008) :

- Create a culture in the classroom
- Formulate learning objectives
- Use a variety of teaching methods to meet the different needs of students
- Use different approaches to assessing students' understanding of the material
- Provide feedback to learners and adapt the learning process to identified needs

- Actively involve learners in the learning process

Black and William (2010):

- Design effective discussion in the classroom, apply questions and assignments that can be used as evidence of learning outcomes
- Provide feedback, which is aimed at developing students
- Clarify evaluation criteria and expected results
- Encourage the development of learners as creators of their own learning
- Use trainees as sources and resources for mutual learning

Clarke (2013):

- Develop a culture of learning
- Engage students in the planning phase
- Make assessment criteria together with students who know the learning objectives
- Use discussions and discussions in class
- Promote effective feedback from students, peers and teachers. (6)

Thus, as the general elements among the presented structures of formative evaluation can be identified: the active involvement of students in the assessment process, the adaptation of teaching to the needs of students, the provision of quality and constructive feedback. Therefore, formative evaluation is the practice of the teacher, which allows you to integrate learning and assessment through a set of interrelated elements in the lesson. Expected results and learning objectives for each section of the curriculum determine the content of the practice of formative evaluation. In this case, the process of formative evaluation will not be standardized, i.e. each teacher can independently determine his own practice and be responsible for its results. The process of formative evaluation in the activities of the teacher involves the implementation of the following stages:

- Planning and organization of formative evaluation;
- choice of methods of formative evaluation;
- providing feedback;
- analysis of the results of formative evaluation.

Planning and organization of formative evaluation

In order to plan an effective process of formative evaluation that meets the needs of students, the teacher is given the opportunity to independently determine the form, content and frequency, as well as tools for formative evaluation. The teacher needs to include in the learning processes and formative evaluation all the objectives of the training according to the curriculum. To this end, collections of assignments for formative evaluation have been prepared to help the teacher, including evaluation criteria for the purposes of training, sample assignments with descriptors. The collections of formative evaluation are used as a source for the selection of tasks in the planning of the lesson and do not require printing. For the independent development of tasks of formative evaluation, the teacher is recommended:

- Study the curriculum, curriculum and conduct learning goals analysis;
- Draw up evaluation criteria based on training objectives according to the curriculum;
- To distribute the evaluation criteria according to the levels of cognitive skills in order to ensure a differentiated approach to the formulation of tasks;
- Develop a task in accordance with the evaluation criteria;
- Draw up descriptors to the task, which describe the main stages of its implementation.

Teacher develops or selects tasks in accordance with the needs of the students and the context of training. (1)

3. Experimental part.

Examples of the formative task on the subject "Chemistry" Grade 7

Section 7.1A Introduction to Chemistry. Pure substances and mixtures

Subject Chemistry subject

The purpose of the training 7.1.1.1 To know what the science of chemistry is studying

Evaluation Criteria

- Formulates the definition of chemistry as a science

Level of Cognitive Skills: Knowledge and Understanding

Exercise 1

Using the proposed set of words, formulate the definition of chemistry as a science:

Chemistry, substances, science, properties, transformations, about, structure, them, and

Descriptor *Learning*

- formulates the definition of chemistry as a science, placing the proposed set of words in the correct sequence.
- understands the meaning of the word "Chemistry"
- Concludes on the science of chemistryЗадание 2

Indicate suggestions where it comes to chemistryИз древесины делают бумагу

1) Combustion of iron is accompanied by a crackle and a "firework" of sparks
2) Potatoes belong to the family of solanaceous
3) Health is the main value of a person
4) Petrol is obtained from oil

Descriptor *Learning*

- correctly indicates the proposals in which we are talking about chemistry
- Fills his choice

Activity 3

Insert the missed words in the sentence (using paragraph 1)

Substances, elements, experiment, processing, science.

1. The subject of studying chemistry are chemical ...., the simple and complex substances they form.
2. Chemical .... allows theoretical knowledge to be confirmed in practice.
3. The tasks of chemistry and chemical industry are .... natural and synthetic raw materials, release of various materials and products.
4. To obtain many food products use a variety of chemical ....
5. Chemistry is an experimental ....

Descriptor trainee - defines suitable words in the sentence

- justifies his answer (2)

Section 7.1.V. Change in the state of substances

Subject: Aggregate state of substances

The purpose of study: To know the various aggregate states of substances and to be able to explain the structure of solid, liquid, gaseous substances according to the kinetic theory of particles.

Evaluation Criterion: Studying

Distinguishes the aggregate state of matter

Level of Cognitive Skills: Knowledge and Understanding

Exercise 1

Divide the substances according to their aggregate state into three groups:

Ice, oxygen, air, tea, ice cream, chocolate, chalk, nail, water, nitrogen, sugar, cola, board, milk, oil.

Gaseous	Liquid	Solid

Descriptor *Learning*

1. Distinguishes gaseous substances
2. Distinguishes solids
3. Distinguishes liquid substances
4.Hows to place the proposed substances in the appropriate columns

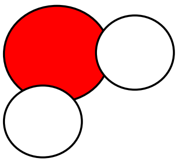
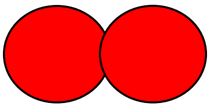
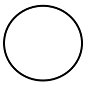
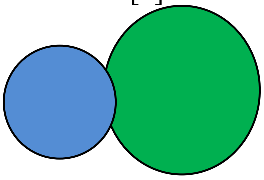
Activity 2

Which statements do you think are correct (yes) and which ones are wrong (no)

1. In the solid state between particles, the attraction is strong
2. Liquid substances retain volume
3. Gaseous substances have no shape and volume
4. In a solid matter, particles can freely move relative to each other

5. In gaseous substances, the particles move rapidly
Descriptor *Learning*
1. Explains the position of particles in gaseous substances
2. Explains the position of particles in solids
3. Explains the position of particles in liquid substances
4. Understands the features of motion and interaction between particles of matter
5. Establishes the relationship between the arrangement of particles and their aggregate state
Activity 3
Establish compliance (using the scheme number 1 in the textbook, page
1. Steam formation A. Burning of a candle
2. Crystallization B. Formation of dew
3. Melting C. The formation of frost
4. Condensation C. Boiling water
Descriptor *Learning*
- correlates processes with natural phenomena
Activity 4
A-ice B-water with water vapor
1 level
Correlate models of the state of atoms with the aggregate state of matter
Level 2
1) The forces of attraction between the particles are insignificant
2) Weak forces of attraction between molecules
3) The attraction between particles is strong
3 level
1) particles freely move relative to each other during transfusion take the form of a vessel
2) the particles move quickly and chaotically, the substances do not have a shape and volume
3) the particles make constant oscillatory movements, retain their shape and volume
Descriptor *Learning*
1 distinguishes models of solids
2 distinguishes between gas models
3 distinguishes between models of liquids
4 knows the peculiarities of the arrangement of particles in substances with different aggregate states
5 establishes the relationship between the arrangement of particles and their aggregate state. (2)
Section. 7.2 A

The theme of Atoms and molecules. Chemical elements
The purpose of study 7.1.2.1 is to describe the difference between atoms and molecules
Level of skills and thinking Understanding
Evaluation criteria Describes the difference between atoms and molecules
The task
Molecules consist of smaller particles - atoms.
Consider the drawing.
Write out, under what figures are the molecules depicted, and under which - atoms? [2]

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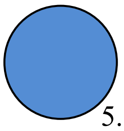
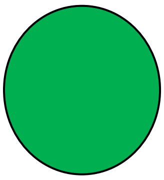
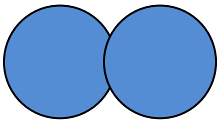


5. 6. 7.

Molecules: Atoms:

Criteria

Describes the difference between atoms and molecules

Descriptors

Correctly marks the picture of all the molecules.

Correctly marks the picture of all atoms. (2)

The descriptors used for assignments must be clear and precise, so that the teacher's decision during the assessment is objective. Descriptors allow you to determine at which stage of the assignment the student is experiencing difficulties. This helps to provide feedback to students. According to the theory of formative evaluation (William, 2007), three positions of the organization are assumed, taking into account the participants in the process: teacher assessment, self-evaluation and mutual evaluation. (6)

Teacher assessment.

Much of what is reflected in this manual characterizes the teacher's assessment process. Therefore, on how well the teacher can understand the proposed recommendations, adapt, apply and improve them depends the success of his practice of formative evaluation.

Self-evaluation.

CONCLUSION

At school it is necessary to instill skills and accumulate experience of self-evaluation among students. The main focus in the organization of self-evaluation of students is given to stimulating self-regulation and independent learning. Self-evaluation of students helps self-analysis of strengths and weaknesses in the learning process. It is important to teach the learner to objectively determine what he knows and what skills he owns, determine his own gaps, which he as a result wants to achieve. However, there are cases when the self-esteem of students is excessively overstated or understated. This reduces the overall positive effect of self-assessment in class. Teachers can help such students be more objective. (4)

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ФОРМАТИВТІ БАҒАЛАУ - ХИМИЯ САБАҚТАРЫНДА ОҚЫТУ ПРОЦЕСІНІҢ АЖЫРАМАС БӨЛІГІ

Аннотация. Соңғы жылдары әлемдік педагогика оқушылардың оқу жетістіктерін бағалау жүйесін қайта қарастырады, өйткені бағалау - оқу процесінің негізгі кезеңдерінің бірі. Мектептің мақсаттарының бірі - өздігінен білім алу, жеке тұлғаның өзін-өзі тану, табысқа жету үшін ынталандыру, яғни студенттердің негізгі құзіреттіліктерін қалыптастыру үшін жағдай жасау. Қазақстан Республикасында білім беруді дамытудың 2011-2020 жылдарға арналған мемлекеттік бағдарламасына сәйкес, оқушылардың оқу жетістіктерін бағалау кезінде болашақ маманның негізгі құзыреттерін дамыту процесіне баса назар аудару керек. Бұл үшін білімнің дәстүрлі жүйесін бағалауға елеулі өзгерістер енгізу қажет.

Түйін сөздер: қалыптастырушы бағалау, қорытынды баға, критериалды бағалау, мұғалімдерді бағалау, өзін-өзі бағалау.

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HYDROGENATION OF AROMATIC HYDROCARBONS IN GASOLINE FRACTIONS OVER SUPPORTED CATALYSTS UNDER PRESSURE

Abstract. The aim of the work was to study the process of hydrodearomatization of gasoline fractions under increased hydrogen pressure. It has been used Rh-Pt (9:1)/Al_2O_3 catalyst in the work. It has been studied the hydrogenation of two gasoline fractions of "Atyrau Oil Refinery" LLP (Hydrogenizate KU GBD and Stable Catalysate LG). Technological parameters of the process of hydrodearomatization for the production of environmentally friendly fuels, containing no benzene and low in aromatic hydrocarbons have been worked out (pressure, temperature). Data on group composition of organic substances in gasolines demonstrate that after catalytic hydrogenation benzene in final samples of two fractions is absent. For hydrogenizate, the aromatic content decreased from 11.12 weight % to 2.20 weight %. For stable catalysate, the amount of aromatics decreased from 51.5 weight % to 10.96 weight %. The catalyst was studied by BET, porometry and EM methods, which established a uniform formation of nanoscale particles on the catalyst surface.

Key words: catalysts, hydrogenation, hydrodearomatization, aromatic hydrocarbons, benzene, gasoline.

Introduction

Technical progress in various fields of machine building, machine operation and laws for the protection of the biosphere tighten the requirements for the quality of fuels and oils. Continuously deteriorating environmental conditions in the world dictate the need to operate clean and quality fuel. The quality of fuels depends largely on the hydrocarbon composition. Aromatic hydrocarbons in fuels are represented by monoaromatic compounds: benzene, toluene, xylene isomers, and polyaromatic compounds - naphthalene, tetralin and other condensed aromatic compounds.

The product of incomplete combustion of benzene is benzpyrene - a strong carcinogen. When burning 1 liter of gasoline in the exhaust gas, benzpyrene is formed up to 81 μg and in case of 1 liter of diesel fuel - up to 170 μg. By the standards of gasoline EURO-6, it is provided the benzene content is less than 0.1% and amounts of aromatic hydrocarbons up to 11%.

When moving to new standards, the problem arises of removing benzene from gasoline, which can not be separated by conventional physical methods. One of the methods for improving the operational properties of fuels is their hydrodearomatization, which consists in the hydrogenation of benzene and polycyclic aromatic hydrocarbons contained in gasoline fractions in the presence of effective catalysts.

Catalytic hydrogenation of aromatic hydrocarbons allows changing the chemical structure of hydrocarbons in the desired direction and improving the performance of motor fuels [1-8]. Development and introduction of technology of hydrodearomatization of fuel fractions of oils and fuels will improve the operational properties of domestic gasolines and the ecological situation in the Republic.

In the process of exploitation of fuels and low quality oils, except harmful emissions into the atmosphere, there is also rapid wear of the equipment due to the deposition of carbon from polycyclic aromatic hydrocarbons and the service life of the equipment reduces approximately to 30%. Reducing the amount of aromatic hydrocarbons in car fuels will extend the service life of the machines.

Leading countries are engaged in the problem of hydrodearomatization of refined products. These countries are: Russian Federation, USA, Great Britain, France, Germany, Poland, Japan, China [9-15]. In the oil refining industry, hydrogenation processes are carried out under harsh conditions (high temperature and hydrogen pressure) on metal oxide catalysts, where Co, Mo, Ni, Cu, W and other transition metals are used as the metal. Catalytic systems based on platinum group metals, especially Pt, Pd, Rh and Ru are the most effective and selective catalysts for hydro - dehydrogenation reactions [11-20].

In the industry use both catalysts on the basis of metals of group VIII and sulphidic, however on the last one the hydrogenation of benzene and aromatic hydrocarbons is carried out in more stringent conditions.

Recently Pt-Pd catalysts have been intensively used for the hydrotreating of petroleum products, especially for the reduction of benzene in gasolines and aromatics in diesel fuels, so they are closely watched by researchers. The addition of Pd to Pt/Al_2O_3 leads to an increase not only the activity, but also the stability in the hydrogenation of benzene. By varying the nature of the carrier, modifying the catalysts reach a uniform distribution of the metals on carriers, optimum acidity and stability against sulfur-containing compounds.

Taking into account the toughened measures currently applied to motor fuels, the transition to European quality standards for fuels, as well as the modernization of Kazakhstan's oil refineries, carrying out research in this area is relevant and timely.

The purpose of this work is to study the catalytic hydrodearomatization of two gasoline fractions of "Atyrau Oil Refinery" LLP to reduce the content of benzene and aromatic hydrocarbons by hydrogenating them on supported catalysts based on Group VIII metals.

Experimental

In this work it has been used a catalyst based on the metals of the platinum group Pt and Rh. At preparation of catalysts were used $RhCl_3 \cdot 3H_2O$, $H_2PtCl_6 \cdot 6H_2O$ of "chemically pure" mark. Solutions of these compounds were applied by the adsorption method on the prepared carrier Al_2O_3. A mixture of aqueous solutions of two metals was applied at preparation of bimetallic catalysts. The catalyst samples were filtered off and dried at 100-110°C to constant weight. The reduction of supported catalysts was carried out in a quartz tube with electrical heating in a hydrogen stream at 200°C for 4 hours, then the catalysts were cooled in a hydrogen stream until room temperature.

The experiment was carried out on a kinetic installation - the autoclave of "Amar Equipment" in the isobaric-isothermal regime. Analysis of the initial compounds and reaction products was carried out on the Crystallux 4000M chromatograph: column Zebron ZB-1 filled with dimethylsiloxane, column length is 30 mm, column diameter is 0.53 mm.

The catalysts were studied by physicochemical methods of analysis: measurement of the catalyst surface (BET), electron microscopy (EM). The surface of the catalysts was examined by the BET method on nitrogen adsorption by "Accusorb" instrument. Electron microscopy of samples was studied by means of electron microscope EM-125K by replica with extraction using microdiffraction (160,000 magnification).

Results and discussion

It has been studied the hydrogenation of benzene and aromatic hydrocarbons contained in two gasoline fractions of "Atyrau Oil Refinery" LLP - Hydrogenizate KU GBD and Stable Catalysate LG. The content of benzene in them is 2.54% and 5.17%, and aromatics are 11.12% and 51.5%, respectively.

As the catalyst used Rh-Pt(9:1)/Al_2O_3, which showed the greatest efficiency in the hydrogenation of individual benzene and toluene [2]. The effect of temperature and hydrogen pressure was studied on the process of hydrogenation of benzene and aromatics for two gasoline fractions.

Data on hydrogenation of sample of gasoline №1, the hydrogenizate KU GBD in the temperature range of 25-200°C are presented in table 1. At 25°C after the experiment, the catalysate contains 0.05% benzene, at higher temperatures benzene is absent, i.e. its conversion reached to 100%. The content of aromatic hydrocarbons decreased from 11.12% to 2.30-3.05%.

According to the results of table 1, it can be concluded that, on the effective catalyst Rh-Pt (9:1)/Al_2O_3, benzene can be hydrogenated at low temperatures, which is important for the industrial conduct of such a process, since the industry uses temperatures 150-400°C.

Table 1 - Hydrogenation of the fraction of Hydrogenizate KU GBD at various temperatures and 3 MPa

Temperature	The content of benzene,%		Aromatic content,%	
	Initial	After experiment	Initial	After experiment
25	2,54	0,03	11,12	3,05
50		-		2,30
100		-		2,63
150		-		2,20
200		-		2,53

When the hydrogen pressure is changed from 2.5 to 4.0 MPa, the time of the catalytic treatment of the Hydrogenizate KU GBD decreases from 65.0 to 32 minutes (picture 1). The presence of benzene in this case after the experiment in the amount of 0.06% was observed at 2.5 MPa, with other hydrogen pressure values there are no traces of benzene. The content of aromatic compounds after hydrogenation of gasoline on this catalyst varies between 1.23 - 4.65%.

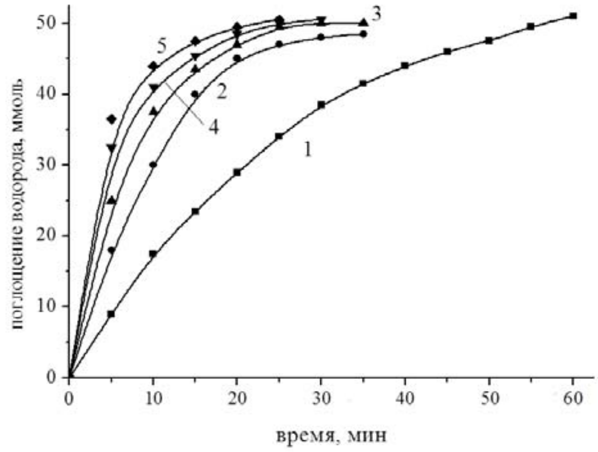


Figure 1 - Hydrogenation of gasoline (Hydrogenizate KU GBD) at different hydrogen pressures on Rh-Pt (9:1)/Al_2O_3 catalyst at 50°C. a - 1 - 2.0 MPa; 2-2.5 MPa; 3 - 3.0 MPa; 4 -3.5 MPa; 5 - 4.0 MPa

At hydrogenation of the second sample of gasoline (Stable catalysate LG) in the range of hydrogen pressures from 0.5 to 4.0 MPa, the reaction order of the hydrogenation of gasoline on Rh-Pt(9:1)/Al_2O_3 catalyst is on hydrogen, calculated from the bilogarithmic dependence of the rate from the pressure is equal to 1 (Figure 2, a). Benzene with initial content of 5.17% was completely hydrogenated and removed from this gasoline fraction, the aromatic content decreased from 51% to 10-14%.

An increase in temperature from 25 to 150°C increases the rate of hydrogenation of the second sample of gasoline (Figure 2,b) and the apparent activation energy is 40.8 KJ/mol. Benzene with initial content of 5.17% was completely removed from this gasoline fraction, and the aromatic content decreased from 51% to 10-15%. It should be noted for Stable catalysate LG, as well as for Hydrogenizate KU GBD, that is already at 50°C benzene is fully hydrogenated.

Studies of the influence of temperature and hydrogen pressure made it possible to select the optimal parameters for the production of environmentally friendly fuels without benzene and with a low content of aromatic hydrocarbons - temperature 50°C and pressure 3 MPa.

Data on group composition of organic substances in two gasolines of initial fractions and after hydrogenation on Rh-Pt(9:1)/Al_2O_3 catalyst are presented in table 2, P = 3 MPa, T = 50°C.

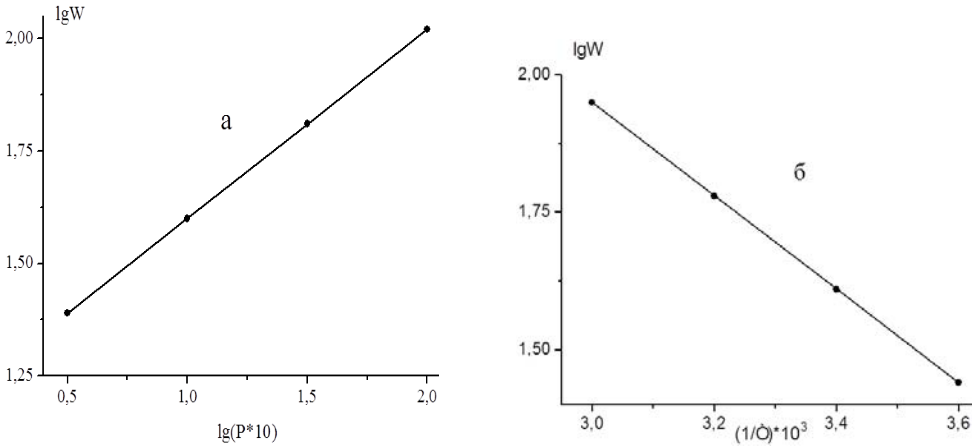


Figure 2 - Hydrogenation of Stable catalysate LG on Rh-Pt (9:1)/Al_2O_3 at 4.0 MPa. a - bilogarithmic dependence of rate from pressure; b - dependence of the logarithm of rate from reciprocal temperature

In the initial Hydrogenizate KU GBD benzene was 2.22 wt.% (2.54 vol.%), after hydrogenation benzene was not detected in the samples - i.e. it was completely hydrogenated, the amount of toluene was decreased from 2.81 wt.% (3.25 vol%) to 0.54 wt.% (0.64 vol%). The aromatic content in the initial gasoline was 13.70 wt.% (11.12% by volume), after hydrogenation it became 2.26 wt.% (2.07% by volume).

It should be noted that the amount of olefins decreased almost 2 times from 0.47 wt.% (0.50% by volume) to 0.28 wt.% (0.28% by volume), which is very favorable for gasoline, since the presence of olefins leads to instability (in chemical terms, polymerization and oligomerization reactions proceeds).

In addition, the content of isoparaffins increased from 35.79 wt.% (28.94% by volume) to 44.26 wt.% (45.04% by volume), which is favorable for the octane number. It is possible that the hydroisomerization reaction proceeds on this catalyst.

For the Stable catalysate LG, the benzene content in the initial state was 4.53 wt.% (5.17% by volume), after the reaction the benzene content was 0.15 wt. % (0.19% by volume), i.e. conversion of benzene equal to 97%. The content of toluene after hydrogenation decreased from 19.65 wt.% (22.63% by volume) to 12.99 wt.% (15.01% by volume). The amount of aromatics decreased from 51.5 wt. % (49.19% by volume) to 10.96 wt. % (11.32% by volume).

Table 2 - Group composition of gasoline fractions of initial and after hydrogenation on Rh-Pt (9:1)/Al_2O_3 catalyst at 3 MPa, 50°C

Sample Name	Unit of measure	The content of the defined indicator						
		Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Benzene	Toluene
Hydrogeni-zate KU GBD initial)	% weight	30,44	35,79	0,47	30,03	13,70	2,22	2,81
	% volume	31,97	28,94	0,50	27,46	11,12	2,54	3,25
Rh-Pt (90:10)/ Al_2O_3	% weight	29,47	44,26	0,28	23,77	2,26	-	0,54
	% volume	30,46	45,04	0,28	22,19	2,07	-	0,64
Stable catalysate (initial)	% weight	16,17	29,57	0,78	1,95	51,5	4,53	19,65
	% volume	19,14	33,66	0,84	1,90	49,19	5,17	22,63
Rh-Pt (90:10)/ Al_2O_3	% weight	14,71	51,75	0,74	12,08	11,96	0,15	12,99
	% volume	16,12	54,51	0,75	11,78	10,32	0,19	15,01

The amount of paraffins also decreased from 16.17 wt.% (19.14% by volume) to 14.71wt. % (16.12% by volume). And the content of isoparaffins increased from 29.57 wt.% (33.66% by volume) to 51.75

wt.% (54.51% by volume). Apparently there has been a reaction of isomerization of paraffins into isoparaffins. The amount of olefins practically did not change. The content of naphthenes increased sharply from 1.95 wt. % (1.90% by volume) to 12.08 wt. % (11.78% by volume).

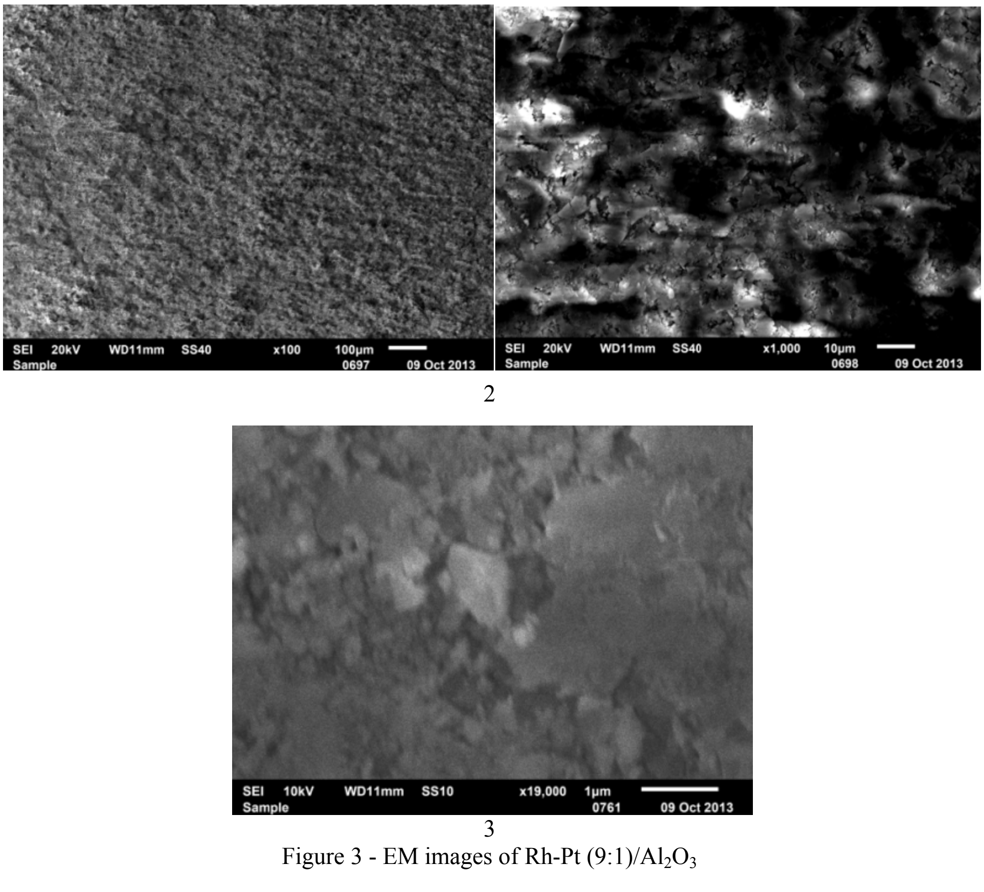
Gasoline fraction Stable catalysate LG treated in the process of hydrodearomatization was studied for octane number in LLP "Independent Expertise Center for Oil Products ORGANIC". The data on the analysis are given in Table 3. The octane number by the research method (RM) after treatment of Stable catalysate was unchanged and equal to 94 units. And the octane number by the motor method (MM) increased from 82.6 to 82.7. This indicates that the catalytic treatment of gasoline does not decrease the octane number.

Table 3 - Octane number of gasoline fraction of Stable catalysate LG before and after catalytic treatment

Gasoline sample	Octane number RM	Octane number MM
Initial (sample 1)	94	82,6
After experiment (sample 2)	94	82,7

The characteristics of the catalyst determined by method BET and porometry showed a well developed surface - the surface area of the Rh-Pt(9:1)/Al_2O_3 catalyst - 138 m^2/g, the pore diameter - 4-14 Å, the catalyst pore volume - 313.28 ml/g.

The surface of catalysts was studied by scanning electron microscopy. In pictures of different increase of the Rh-Pt (9:1)/Al_2O_3 catalyst (fig. 3) is shown the uniform surface of the carrier, on which agglomerates of active metals are viewed.



2

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Figure 3 - EM images of Rh-Pt (9:1)/Al_2O_3

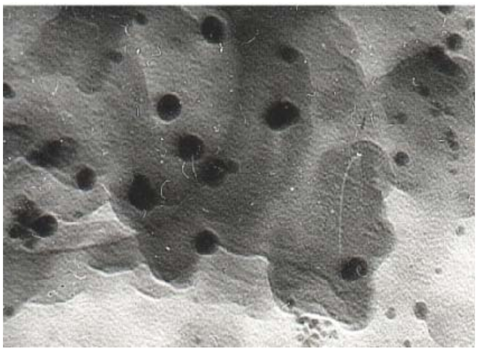

Figure 4 - EM image of 2% Rh-Pt (9:1)/Al_2O_3 (increase 160,000)

In the transmission electron microscopy photo, Rh-Pt(9:1)/Al_2O_3 catalyst is represented by finely dispersed particles of 2-2,5 nm in size and a small number of denser and larger particles of 50 nm, microdiffraction pictures of which are represented by diffuse rings corresponding to metals (Fig. 4). Metal particles are distributed on the surface of oxide of aluminum and represent the mixed bimetallic Rh-Pt agglomerates together with Rh particles. The high activity of the catalyst is perhaps caused by formation of alloys of these metals.

Conclusions

Thus, a highly efficient catalyst for the hydrogenation of gasolines has been synthesized, which makes it possible to completely remove benzene, and also 2-4 times to reduce the content of aromatic compounds. The catalyst is tested in the process of hydrogenation of gasolines of two fractions of LLP "Atyrau Oil Refinery": Hydrogenizate KU GBD and Stable catalysate LG. By method of studying the effect of temperature and hydrogen pressure for two gasoline fractions were chosen the optimal parameters (temperature 50°C and pressure 3 MPa) for the production of environmentally friendly fuels, which do not contain benzene and with low aromatic hydrocarbons content.

Data on the group composition of organic substances in gasolines indicate that for hydrogenizate, the aromatic content decreased from 13.70 wt.% to 2.26 wt.%. For stable catalysate, the amount of aromatics decreased from 51.5 wt.% to 10.96 wt.%. The amount of olefins decreased almost 2 times, and the content of isoparaffins increased from 35.79 wt.% to 44.26 wt.%, which is favorable for the octane number. Furthermore, the content of isoparaffins also increased from 29.57 wt.% to 51.75 wt.%.

By BET method, porometry and EM was established a uniform formation of metal particles in zero degree of valence on the surface of catalysts, the composition and nano-sized particles of metals of group VIII were determined.

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БЕНЗИН ФРАКЦИЯЛАРЫНДАҒЫ ХОШ ИІСТІ КӨМІРСУТЕКТЕРДІ ЖОҒАРЫ ҚЫСЫМДА ОТЫРҒЫЗЫЛҒЫН КАТАЛИЗАТОРЛАРДЫ ҚОЛДАНУ АРҚЫЛЫ СУТЕКТЕНДІРУ

Аннотация. Жұмыстың мақсаты - бензин фракцияларын сутектендіру процесін сутегінің жоғары қысымында зерттеу. Жұмыс барысында Rh-Pt(9:1)/Al_2O_3 катализаторы қолданылды. ЖШС «Атырау мұнай өңдеу зауытының» екі бензин фракциялары сутектендіру процесі бойынша зерттелінді (Гидрогенизат КУ ГБД және Тұрақты катализат ЛГ). Құрамында бензол жоқ және төмен мөлшердегі хош иісті көмірсутектері бар экологиялық таза жанармайлар өндіру үшін гидродеароматизация процесінің технологиялық параметрлері жасалынды (қысым, температура). Жанармайдағы органикалық қосылыстардың топтық құрамының көрсеткіштері бойынша каталитикалық сутектендіру процесінен соң бензол компоненті екі бензин фракцияларының құрамынан толығымен жойылды. Гидрогенизат фракциясы бойынша хош иісті көмірсутектер мөлшері 11,12 мас.%-дан 2,20 мас.%-ға дейін төмендеді. Тұрақты катализат фракциясы бойынша хош иісті көмірсутектер мөлшері 51,5 мас. %-дан 10,96 мас. %-ға дейін төмендеді. Катализаторлар БЭТ әдісі, порометрия және электрондық микроскопта зерттелінді.

Түйін сөздер: катализаторлар, сутектендіру, гидродеароматизация, хош иісті көмірсутектер, бензол, бензин.

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ГИДРИРОВАНИЕ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ В БЕНЗИНОВЫХ ФРАКЦИЯХ НА НАНЕСЕННЫХ КАТАЛИЗАТОРАХ ПОД ДАВЛЕНИЕМ

Аннотация. Целью работы являлось изучение процесса гидродеароматизации бензиновых фракций при повышенном давлении водорода. В работе использовался Rh-Pt(9:1)/Al_2O_3 катализатор. Изучено гидрирование двух бензиновых фракций ТОО «Атырауский нефтеперерабатывающий завод» (Гидрогенизат КУ ГБД и Стабильный катализат ЛГ) Отработаны технологические параметры процесса гидродеароматизации для производства экологически чистых топлив, не содержащие бензол и с низким содержанием ароматических углеводородов (давление, температура). Данные по групповому составу органических веществ в бензинах свидетельствуют о том, что после каталитического гидрирования бензол в конечных пробах двух фракций отсутствует. Для гидрогенизата содержание ароматики снизилось с 11,12 мас.% до 2,20 мас.%. Для стабильного катализата количество ароматики уменьшилось с 51,5 мас.% до 10,96 мас.%. Катализатор исследован методами БЭТ, порометрии и ЭМ, которые установилио равномерное образование на поверхности катализаторов наноразмерных частиц.

Ключевые слова: катализаторы, гидрирование, гидродеароматизация, ароматические углеводороды, бензол, бензин.

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