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# Х А Б А Р Л А Р Ы

## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
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**FOOD SAFETY AND HACCP SYSTEM  
IN THE *PHYSALIS* CONFITURE PRODUCTION**

**Abstract.** The identification of hazards and the principles of the food safety management system are considered. Within the processing of the fruit and berry raws, the jam and confiture production technologies could assume Critical Control Points that will influence the final product safety. In the production of *Physalis* confiture with a lemon, a sugar and apple pectin, by taking into account the principles of the HACCP system, the technological processes are analyzed. *Physalis* as a natural antioxidant has a high nutritional value and useful features in medicine. In this regard it is important to keep all *Physalis* benefits in the confiture production. Each technological process step by step analyzed, and prerequisites of the Critical Control Points were determined. The most important production stages are: reception and sorting, cleaning and sterilization. For the avoiding of the negative factors, monitoring system, control and corrective actions on the base of the HACCP / MS ISO 22000:2018 Food safety management systems standard are offered.

**Key-words:** food safety, HACCP, confiture, *Physalis*, hazards, risks, prerequisite.

**Introduction**

Safety of food products is the concept according to which the food products will not cause any harm to the consumer if they are prepared and/or eaten according to the appropriate application. In this regard, for the supporting of the specified concept and regulations of the harmless productions, a safety management system of food is important. Investments into safety management systems of food are key prerequisite of reliable and stable supply of safe food products and growth of international trade [2].

HACCP (Hazard Analysis and Critical Control Points) system is a simple and logical control system based on the concept of preventing problems by identifying hazards, establishing critical control points and developing measures for monitoring, preventing and correcting them. It should be developed taking into account seven basic principles [4]:

1. Conduction of possible hazards analysis;
2. Identification of Critical Control Points (CCP).
3. Determination of Critical Limits for CCP.
4. Establishment of a monitoring system for control on CCP.
5. Setting of corrective actions.
6. Fixing of verification procedures.
7. Establishment of principles for maintaining records and documentation.

Within the processing of raw fruits and berry, the jam and confiture production technologies Critical Control Points that will influence the final product safety can be established.

To obtain confiture based on *Physalis*, following products are used: *Physalis* fruits, lemon, sugar and apple pectin.

The technological process of production of the confiture consists of: reception and sorting of initial products, cleaning, washing, grinding and mixing, filling, packing, sterilization, storage. There is a potential risk of hazard detection in each stage of the production of confiture.

The HACCP system should take into account all categories of potential risk: biological, chemical and physical hazards [8].

Biological risks include risks resulting from the action of living organisms including yeast (osmophilic yeast), microorganisms (pathogens), protozoa, parasites, etc., their toxins and waste products [3,5].

Chemical risks can be divided depending on the source of origin into three following groups:

1. Inadvertently ingested chemicals;

a) Agricultural chemicals: pesticides, herbicides, plant growth regulators, etc.

b) Chemicals used in enterprises: cleaning, washing and disinfecting agents, lubricating oils, etc.

c) Infections from the external environment: lead, arsenic, cadmium, mercury, etc.

2. Naturally occurring risk factors of products plant, animal or microbial metabolism, such as aflatoxins.

3. Chemicals intentionally added to food, such as preservatives, acids, food additives, substances that facilitate processing, etc.

Physical risks are associated with the presence of any physical material that is not present in the natural product or the food product, and which can cause disease or harm to the person who consumed the food product (glass, metal, plastic, etc.) [6].

## MATERIALS AND METHODS

For the preparation of the confiture following ingredients were used: *Physalis*, sugar, lemon and apple pectin. Organoleptic and physicochemical properties were analyzed in accordance with the GOST (State standard) 34447-2018 "Confiture" [9,10].

*Physalis* is a member of the Solanaceae family that owns a large number of edible plants: potatoes, tomatoes, eggplants and others. In recent years, *Physalis* has begun to firmly conquer the world markets due to its high nutritional value and the promise of its application in medicine in the treatment of malaria, hepatitis, rheumatism, arthritis, dermatitis, asthma, cardiovascular and oncological diseases, Alzheimer's disease, dementia and anti-fatigue. *Physalis* fruits contain all the essential and non-essential amino acids, in the largest number of essential L-valine and L-isoleucine, and of the interchangeable amino acids L-tyrosine. The phytoncide content makes the *Physalis* fruits as good physiological an antiseptic, they also contain polyphenols, ascorbic acid (vitamin C), carotenes (vitamin A), thiamine (vitamin B1), riboflavin (vitamin B2), niacin (vitamin B3), calcium, ferrum, phosphorus and other organic acids, macro- and microelements, tannins. The content of solids is in the range from 6% to 10%. *Physalis* fruits are used in the treatment of diseases of the gastrointestinal tract, chronic cholecystitis, in hypertension, as a multivitamin, and extracts of the *Physalis* have anti-inflammatory, hemostatic and analgesic effects. Due to the presence of water-soluble pectin and gelling properties, *Physalis* has been used in the cooking, in the preparation of jelly, marmalade, confiture, jam, yoghurt and soft drinks [1,7,11].

## Results and discussion

In the presented work, an analysis of the likely hazardous factors in the production of *Physalis* confiture is carried out. All stages of production were analyzed as sources of hazards: reception and sorting of initial products, cleaning, washing, grinding and mixing, filling, packing, sterilization, storage. The summarized results are presented in table 1.

Table 1- Hazard Analysis in the production of *Physalis* confiture

Name of operation	Process parameters	Considered factors	Controlled hazards	Preventive action	Responsible person
1. Reception and sorting of <i>Physalis</i> , sugar and lemon	<i>Physalis</i> berries must be fresh or frozen, quite ripe, clean, without foreign smell, without peduncles, heterogeneous in size and color, without any damage and disease. Lemon fruits are fresh, clean, not ugly, without mechanical damage, without damage by pests and diseases, with a pedunclet exactly cut at the base of the fruit	Microbiological	a) bacteria of the group of <i>Escherichia coli</i> (BGEC), b) pathogenic microorganisms	Control at the reception	Head of Laboratory
		Chemical	a) pesticides b) herbicides c) plant growth regulators	Input control	Head of Laboratory
		Physical	a) glass b) metal c) plastic	Control at the reception	Head of Laboratory
	Presence of microorganisms in sugar	Microbiological	Pathogens	Control at the reception	Head of Laboratory
		Chemical	a) mercury b) arsenic c) copper	Input control	Head of Laboratory
		Physical	a) glass b) metal c) plastic	Input control	Head of Laboratory
2. Cleaning	The remains of unsuitable parts of raw materials	microbiological	Bacteria, viruses, yeasts, moulds and viruses	Cleaning process control	Foreman
3. Washing	Detergent residues	Physical	At non-observance of the washing process, the berries which are not completely cleared from strangers can remain	Control of washing process	Foreman
4. Grinding and mixing	Metal fragments, personal belongings of staff	Physical	If the grinding and mixing processes are disregarded, foreign objects or particles can input into the finished product	Control grinding and mixing processes	Foreman
5. Filling	Contaminated packaging	Microbiological	Sterilizing	Control of the filling process into the packaging, the creation of aseptic conditions	Foreman
6. Packing	Presence of foreign objects	Physical	If the packing process is disregarded, foreign objects or particles can input into the finished product (rubber from the cover, glass, plastic).	Control of the packing process	Foreman
7. Sterilization	Incorrect compliance of the sterilization process	Microbiological	<i>Escherichiacoli</i> bacteria	Creating aseptic conditions Use of metal detector	Foreman
		Physical	Impurities Metal parts of equipment		
8. Storage	Package integrity	Microbiological	Temperature, °C Duration, h	Control of temperature-time variation	Foreman



The technological scheme for the obtaining of *Physalis* confiture with the identification of possible CCP (Critical Control Points) is presented in Figure 1.

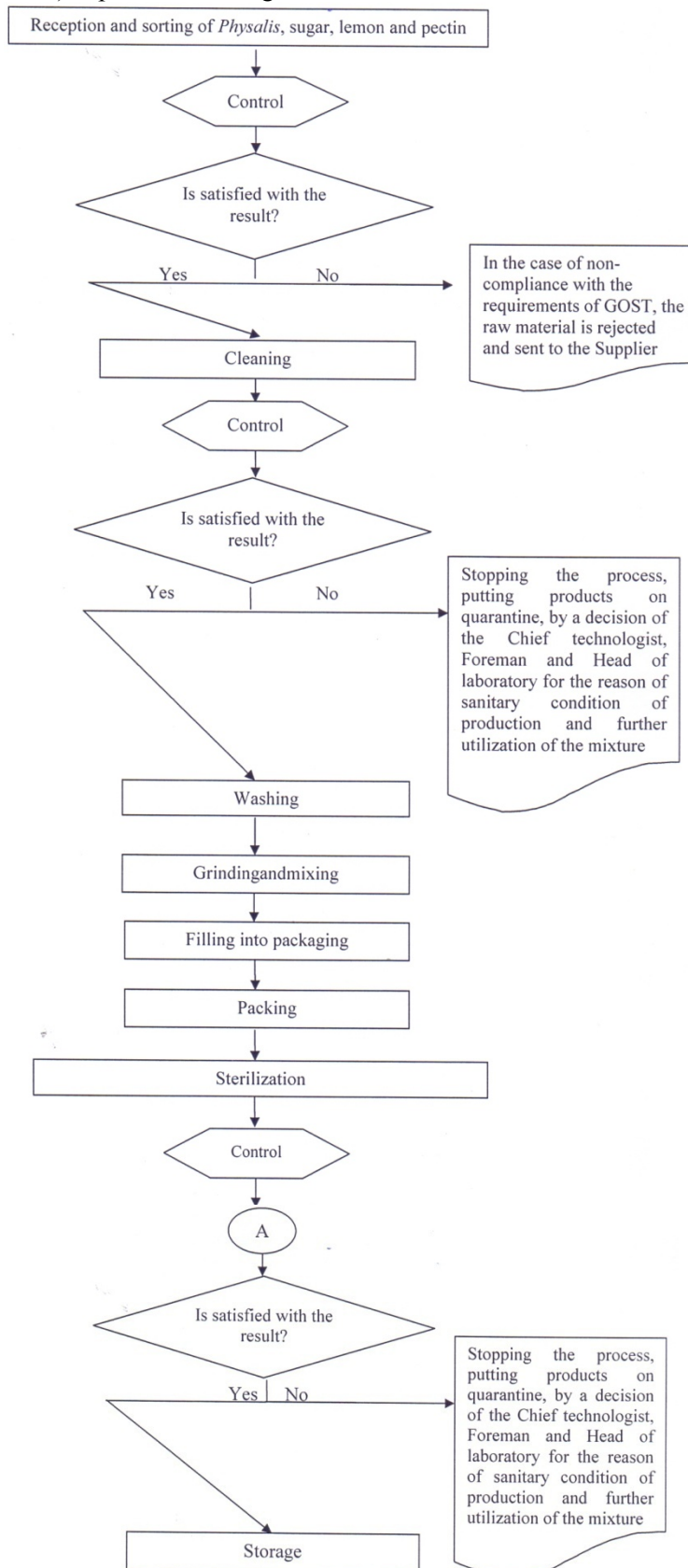


Figure 1 - Technological scheme of *Physalis* confiture production and CCPs

By analyzing of the Figure 1, three CCPs with high risks are identified: reception and sorting, cleaning and sterilization. These production stages and offered control actions are presented in the Table 2.

Table2 - Prerequisites of the CCPs risk assessment and control actions in the production of *Physalis* confiture

Prerequisite	Risk	Control actions	Degree of risk
CCP 1	Reception and sorting of <i>Physalis</i> , lemon, sugar and apple pectin	<i>Physalis</i> berries must be fresh or frozen, quite ripe, clean, without foreign smell, without peduncles, heterogeneous in size and color, without any damage and disease. The fruits of the lemon are fresh, clean, not deformed, without mechanical damage, without damage by pests and diseases, with a stems evenly cut off at the base of the fruit. More thorough visual inspection and laboratory analysis of berries and fruits.	High
CCP 2	Cleaning	Compliance strictly with the parameters of cleaning, identifying rotten, mismatching berries, cleaning of foreign objects	High
CCP 3	Sterilization	Control of sterilization parameters	High

## CONCLUSION

Thus, the analysis of the most possible dangers in the production of confiture from *Physalis* carried out, with potential prerequisites of the CCPs (Critical Control Points) istaken into account: biological, chemical, and physical risks. The dangerous factors and critical control points are determined. The most important production stages are: reception and sorting, cleaning and sterilization. As the checking operations are necessary visual inspection and laboratory analysis of berries and fruits. A monitoring system for the control of CCPs and corrective actions are also required. For the avoiding of the negative factors, monitoring system, control and corrective actions on the base of the HACCP / MS ISO 22000:2018 Food safety management systems standard are offered.

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### PHYSALIS КОНФИТЮРИ ӨНДІРІСІНДЕГІ ТАМАҚ ҚАУІПСІЗДІГІ ЖӘНЕ НАССР ЖҮЙЕСІ

**Аннотация.** Тамақ өнімдерінің қауіпсіздігін басқару жүйесінің қауіптілігі мен принциптері қарастырылады. Жеміс-жидек шикізатын өңдеу кезінде джем мен конфитюрді өндіру технологияларының соңғы өнімнің сапасына әсер ететін сыни бақылау нүктелері болуы мүмкін. Лимон, қант және алма пектині бар *Physalis* конфитюрасын өндіру кезінде ХАССП жүйесінің принциптерін есепке ала отырып, технологиялық үдерістер талданады. *Physalis* табиғи антиоксидант ретінде медицинада жоғары тағамдық құндылыққа және пайдалы қасиеттерге ие. Осыған байланысты конфитюралар өндірісіндегі *Physalis*-тің барлық артықшылықтарын сақтау маңызды. Әрбір технологиялық процесс кезең-кезеңімен талданады және сыни бақылау нүктелері анықталады. Өндірістің ең маңызды кезеңдері: қабылдау және сұрыптау, тазалау және зарарсыздандыру. Жағымсыз факторларды болдырмау үшін НАССР / ISO 22000: 2018 стандарты негізінде мониторинг, бақылау және түзету әрекеттері ұсынылады.

**Түйін сөздер:** тағам қауіпсіздігі, ХАССП, конфитюр, физалис, қауіптер, тәуекелдер, алғышарты.

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### ПИЩЕВАЯ БЕЗОПАСНОСТЬ И СИСТЕМА НАССР В ПРОИЗВОДСТВЕ КОНФИТЮРА *PHYSALIS*

**Аннотация.** Опасности и принципы системы управления безопасностью пищевых продуктов рассматриваются. Технологии производства джема и конфитюра при переработке плодово-ягодного сырья могут иметь критические контрольные точки, которые будут влиять на качество конечного продукта. При производстве конфитюра *Physalis* лимоном, сахаром и яблочным пектином, с учетом принципов системы ХАССП анализируются технологические процессы. *Physalis* как природный антиоксидант обладает высокой пищевой ценностью и полезными свойствами в медицине. В связи с этим важно сохранить все преимущества *Physalis* в производстве конфитюров. Каждый технологический процесс поэтапно анализируется, и определяются критические контрольные точки. Наиболее важными этапами производства являются: прием и сортировка, очистка

и стерилизация. Во избежание негативных факторов предлагаются системы мониторинга, контроля и корректирующие действия на основе стандарта HACCP / ISO 22000: 2018 системы управления безопасностью пищевых продуктов.

**Ключевые слова:** пищевая безопасность, HACCP, конфитюр, физалис, опасности, риски, пререквизит.

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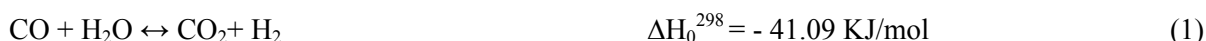
## **WATER-GAS SHIFT REACTION OVER THE POLYMETALLIC Fe-CONTAINING SUPPORTED CATALYSTS**

**Abstract.** The water-gas shift reaction over the polymetallic iron-containing catalysts modified by additives of the transition metals and supported on alumina was studied in the work. The effects of process temperature and nature of additives (Co or Cu) on behavior of the iron-containing catalysts in the process of interaction between water and carbon monoxide were investigated. It was observed that the synthesized iron-based catalysts modified by additives of copper/cobalt and transition metal of the 8<sup>th</sup> group of elements as the third component and supported on alumina perform the high activity and selectivity on hydrogen formation in the water-gas shift reaction. The optimum conditions for producing hydrogen by the water shift reaction over the synthesized catalysts are determined.

**Keywords:** Water-Gas Shift Reaction, Fe-containing Supported Catalyst, Hydrogen, Carbon Oxides.

### **1. INTRODUCTION**

The water-gas shift reaction (WGSR) discovered by Italian scientist Felice Fontana as early as 1780 [1] became well-known in the 1912 due to process of ammonia synthesis [2,3]. At present time, WGSR is widely used for hydrogen production from fossil and renewable carbonaceous raw materials – biomass. Hydrogen is used to enrich gas mixtures, production of ammonia, and also in oil refining and petrochemistry, and more recently in fuel cells [1, 4-5]. Hydrogen is considered as one of the most attractive types of future clean fuels, because it can be effectively stored and transported. Only water is formed as a side product when hydrogen is burned [6]. Water-gas shift reaction as well as the steam reforming of methane/other hydrocarbons is the most industrially developed method for hydrogen production. Overall reaction of water-gas shift is described by the following equation (1):



The same amount of carbon dioxide is formed in water-gas shift reaction and hydrocarbon fuel combustion; however carbon dioxide produced can be captured and then can be either stored or utilized. This fact permits to classify this reaction as a process with zero CO<sub>2</sub> emission [7].

WGSR reaction (Eq.1) runs with the release of heat and without changing the volume, therefore an increase in temperature will help to reduce the degree of CO conversion. There is no possibility to shift the reaction equilibrium to the right due to the pressure change. Nevertheless, growing the total pressure leads to an increase in the rate of reaching the equilibrium state. An increase in H<sub>2</sub>O /CO ratio enhances carbon monoxide conversion, however for reasons of cost reduction, a large excess of steam should be avoided. As for the iron-based catalysts, the minimum excess of steam is needed to prevent excessive catalyst reduction, which leads to methanation [8,9], for the copper catalysts this fact is not critical.

With taking into account the opposite effect of temperature on both the reaction completeness and rate, the various types of catalysts operating at different temperature ranges are used. They are divided on the high temperature (HT) and low temperature (LT) catalysts [10]. Traditionally, the iron-chromium and copper-zinc catalysts were used for facilitation of reaction in high and low temperature regions

respectively [1]. The typical composition of high temperature catalysts operating in temperature region within 310–450°C: 74.2% Fe<sub>2</sub>O<sub>3</sub>, 10% Cr<sub>2</sub>O<sub>3</sub>, 0.2% MgO and balance of variable composition. It is supposed that the active phase is the magnetite (Fe<sub>3</sub>O<sub>4</sub>) is formed during partial reduction of the initial catalyst, while Cr<sub>2</sub>O<sub>3</sub> improves the catalyst stability and prevents sintering the iron oxide. By using the high temperature catalysts it is possible to achieve residual concentration of CO in amount of 3%, which corresponds to the equilibrium concentration at 450°C [3,11]. Because of risk of leakage of toxic Cr(VI), the chromium-free catalysts should be developed. Aluminum was considered as an alternative, because it is textural promoter. Introduction of Al<sup>3+</sup> ions into iron oxide is easily feasible because they have similar ionic radii: 0.675Å and 0.690Å for Al<sup>3+</sup> and Fe<sup>3+</sup> respectively [12].

Low temperature process (LTS – Low Temperature Shift) is carried out in temperature range of 200-250°C. Because of water condensation negatively effects on catalyst activity, a lower limit of process temperature is determined by condensation temperature of water under specific pressure. The typical catalysts for LTS have the following composition: 32-33% CuO, 34-53% ZnO, 15-33% Al<sub>2</sub>O<sub>3</sub> [2]. The active centers in these catalysts are crystallites of CuO, while ZnO provides the structural stability and Al<sub>2</sub>O<sub>3</sub>, mainly inactive, provides dispersion of an active phase and prevents shrinking of catalyst granules [1]. Using the low temperature catalysts allows reaching the residual concentration of CO is 0.1% [8]. Another advantage of low temperature water gas shift catalysts is their low activity toward the side reactions. That has importance under elevated pressures [13,14]. Disadvantages of the low temperature catalysts are their susceptibility to poisoning by sulfurous compounds, halogens, and unsaturated hydrocarbons, pyrophoricity, low thermal stability, and complexity of their activation [15,16].

Despite of industrial development of WGS process, search for more active and efficient catalysts and optimal process parameters is still ongoing. In recent years, the technologies of catalysts preparation have been significantly improved. The catalysts are modified in order to provide the reaction in the middle range of temperatures and to achieve both high conversions of CO and selectivity [1,17]. As a rule, the middle temperature catalysts are the low temperature catalysts modified usually by iron oxide. They operate at higher temperatures – 275-350°C [18]. The catalysts supported on alumina contain sulfides of cobalt and copper or cobalt and nickel as the active ingredients. The feature of the catalysts is their sulfur resistant [19-20].

In addition to these types of catalysts, the acid gas shift catalysts and catalysts containing noble metals are developed [9]. The latter mainly include gold or platinum and are used in fuel cells.

In general, there is significant progress in the water-gas shift reaction including approaches to the methods of preparation and characterization, doping, improvement and evaluation of catalysts, in particular the nanocatalysts [1,6]. The data concerning WGS studies permanently published demonstrate a significant variety of the novel catalysts compositions and continuous interest in this field [7].

This work deals with testing the novel chromium-free, polymetallic alumina supported catalysts based on iron as main component of high temperature catalysts and modified by additives of cobalt or copper as the main components of low temperature catalysts and a noble metal – M<sub>1</sub> as a promoter. The catalysts were tested in the water-gas shift reaction under atmospheric pressure and varying temperature, gas hourly space velocity (GHSV), and steam to CO ratio (H<sub>2</sub>/CO).

## 2. EXPERIMENTAL

The WGS process – water-gas shift reaction was carrying out in a quartz flow reactor with fixed bed catalyst under atmospheric pressure. Volume of catalyst was 6 ml. Water was supplied with well-controlled rate using the syringe pump “Perfusor FM BRAUN” plugged to an unit via connecting tube equipped by heating system aimed for evaporating water. Steam was mixed with carbon monoxide (99.9% vol. purity) and argon (99.9% vol. purity) used as balance-gas (10 vol.%) incoming from cylinders. Gas velocities (carbon monoxide and argon) were regulated and controlled by means gas the mass-flow rate regulators (F201CV, series EL-FLOW). Gas hourly space velocity (GHSV) of inlet mixture of carbon monoxide and steam was varied within a range of 500-1500 h<sup>-1</sup>. Steam to carbon monoxide ratio – H<sub>2</sub>O/CO was varied from 1.0 to 1.6. Temperature was varied in the range of 200-400°C. Duration of catalysts testing was 8-20 hours.

Composition of inlet and outlet gas streams was determined by gas chromatograph Chromatec Crystal 5000.1 equipped with two TCD and with two packed columns, NaX 60/80 and Hayesep R 80/100, to detect CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>-C<sub>6</sub> hydrocarbons.

The catalysts with the following composition were prepared: 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> and 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> (wt.%), where M<sub>1</sub> – metal of the Group VIII. The catalysts were prepared by the impregnation method.

Conversion of CO (X<sub>CO</sub>,%) was calculated by formula given below:

$$X(CO) = \frac{V_{in}^{CO} - V_{out}^{CO}}{V_{in}^{CO}} \times 100\%,$$

where  $V_{in}^{CO}$  - mole fraction of CO in inlet stream,  $V_{out}^{CO}$  – mole fraction of CO in outlet stream.

Conversion of water was not calculated.

Yields of reaction products: hydrogen, carbon dioxide and methane, (Y<sub>H<sub>2</sub></sub>, Y<sub>CO<sub>2</sub></sub> and Y<sub>CH<sub>4</sub></sub> respectively) expressed as its amount (μmol) formed by gram of the catalyst per second (μmol/(g·s)).

### 3. RESULTS AND DISCUSSION

The important parameters of WGS process are reaction temperature and steam/CO ratio. The effect of temperature and H<sub>2</sub>O/CO on carbon monoxide conversion and products yields have been studied in WGS under atmospheric pressure over the synthesized catalysts

During testing the 10%Fe-Cu(1:1)-0.25%M/Al<sub>2</sub>O<sub>3</sub> catalyst in reaction of water-gas shift under atmospheric pressure, H<sub>2</sub>O/CO=1 and GHSV=1000 h<sup>-1</sup> it was observed that dependence of carbon monoxide conversion degree on temperature is characterized by maximum at 290°C (Fig.1). Conversion degree of CO at this temperature is 96.4%. Further increase in temperature to 310°C leads to slight decrease of carbon monoxide conversion to 95.0%, while at 340°C the degree of CO conversion is markedly decreased: X(CO)=88.0%. It is predictable taking into account the tendency of copper to thermal sintering at higher temperatures [2]. The reaction products are hydrogen and carbon dioxide only. Their yields and carbon monoxide conversion degree are symbatically changed. The yields of hydrogen and carbon dioxide reach at maximum 1.33 and 1.30 μmole/(g·s) respectively at temperature 290°C (Fig.1). The formation of methane was not detected in the whole investigated range of temperatures.

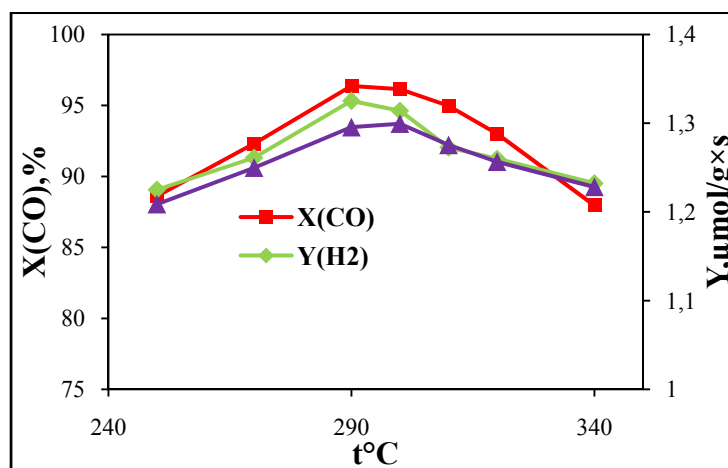


Figure 1 – Effect of temperature on WGS process parameters over 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

Testing the catalyst modified by cobalt – 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> under the same conditions showed that the maximum conversion degree is 94.6% was reached at 315°C. In contrast to copper containing catalyst, there was no significant decrease in degree of CO conversion with increase in temperature (Fig. 2). Yields of hydrogen and carbon dioxide are almost equal and get at maximum 1.29 μmole/(g·s) at t=315-320°C (Fig. 2). At temperature ≥ 320°C, the formation of insignificant amount of methane was occurred (less than 0.03%). At temperatures below 320°C, the formation of methane was not observed.

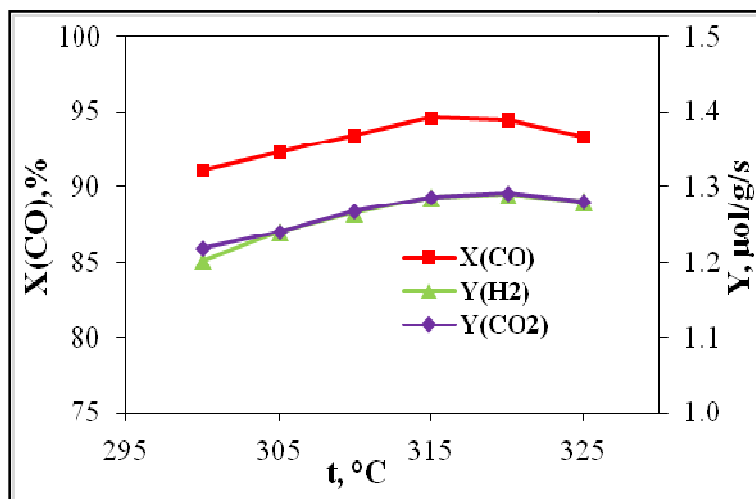


Figure 2 – Effect of temperature on WGSR process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

For the both catalysts, the effect of steam amount on water-gas shift reaction was studied. In industry, the water-gas shift reaction is carried out at the excessive H<sub>2</sub>O/CO ratios. Decreasing operating temperature and increasing steam/carbon ratio stimulate the growth of conversion degree regardless to operating pressure. It is well-known that the low steam/CO ratios can result in epy metallic iron formation, which causes increasing of methanation, carbon deposition, and Fischer – Tropsch reaction [6].

It was observed that a character of dependence of carbon monoxide conversion on molar ratio of H<sub>2</sub>O/CO was the opposite to the expected one. That requires the further study. However, the high value of feed conversion at a low steam to carbon monoxide ratio may indicate that the 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> is a perspective one to be used as the middle temperature catalyst for water-gas shift reaction accompanied with the steam economy.

At Fig.3 the dependence of carbon monoxide conversion degree on H<sub>2</sub>O/CO ratio over the iron-copper catalyst at t= 310°C and GHSV=1000 h<sup>-1</sup> is presented. With increase in H<sub>2</sub>O/CO ratio from 1 to 1.4 the conversion degree is decreased from 95.0 to 91.9% and accordingly the yields of hydrogen and carbon dioxide decreased from 1.27 and 1.28 to 1.22 μmol/(g·s) respectively.

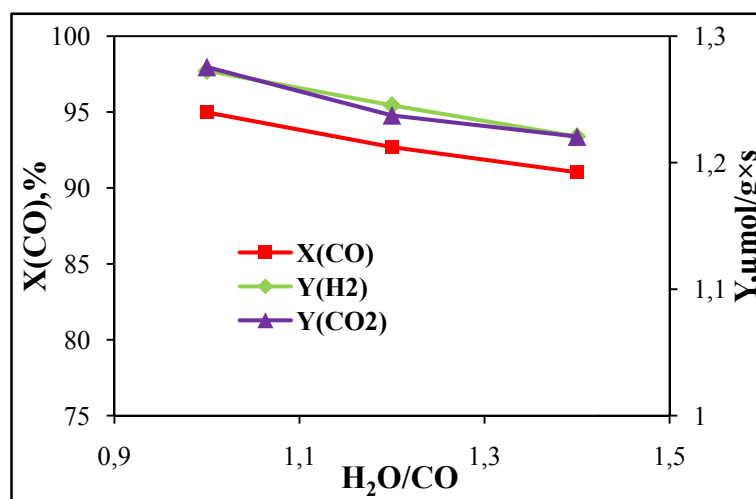


Figure 3 – Effect of H<sub>2</sub>O/CO ratio on WGSR process parameters over 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, P=1 atm, t=310°C, GHSV=1000 h<sup>-1</sup>

The iron-cobalt catalyst is less sensitive to the effect of steam excess in comparison with the Fe-Cu. Nevertheless, the observed insignificant extremal dependence of carbon monoxide conversion and

products yields on H<sub>2</sub>O/CO ratio indicates a negative impact of steam excess for this catalyst too (Fig. 4). The optimal ratio H<sub>2</sub>O/CO=1.2 at temperature of 320°C when degree of CO conversion is 95.2% and yields of hydrogen and carbon dioxide are equal to 1.31 μmol/(g·s) each.

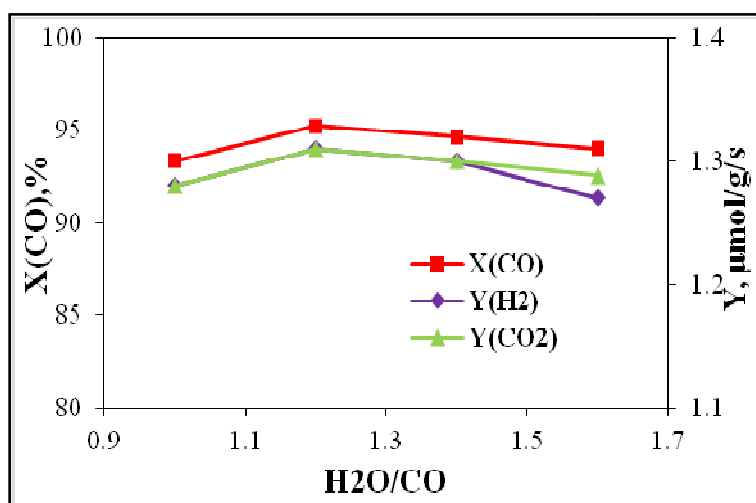


Figure 4 – Effect of H<sub>2</sub>O/CO ratio on WGS process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, P=1 atm, t=320°C, GHSV = 1000 h<sup>-1</sup>

The effect of gas hourly space velocity on WGS process parameters was studied over the 10%Fe-Co(1:1)-0.25%M/Al<sub>2</sub>O<sub>3</sub> catalyst. The optimal value of GHSV in terms of products yields is 1000 h<sup>-1</sup>, when the carbon monoxide conversion is 91.0% that is slightly lower than 93.6% at GHSV=500 h<sup>-1</sup>. The yields of hydrogen and carbon dioxide are equal to 1.2 μmol/g·s, that is twice higher in comparison with GHSV=500 h<sup>-1</sup> (Table 1). Increase in GHSV to 1500 h<sup>-1</sup> is accompanied with decrease in both carbon monoxide conversion and products yields (Table 1).

Table 1 – Effect of space velocity on WGS process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at H<sub>2</sub>O/CO=1/1, P=1 atm, t=310°C

GHSV, h <sup>-1</sup>	X(CO), %	Yield of products, μmole/(g·s)	
		Y(H <sub>2</sub> )	Y(CO <sub>2</sub> )
500	93.6	0.5	0.6
1000	91.0	1.2	1.2
1500	60.4	0.8	0.81

Thus, the testing of 10%Fe-M(1:1)/Al<sub>2</sub>O<sub>3</sub> catalysts, where M is Co or Cu, demonstrate their high activity in water-gas shift reaction. The comparison of catalysts under the following conditions: H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV = 1000 h<sup>-1</sup>, is given in Table 2. It needs to note that the cobalt-containing catalyst has lower but quite sufficient activity. The catalyst has not a tendency to significant decrease in activity with increasing temperature.

Table 2 – Comparative characteristics of the catalysts in WGS process at H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

Catalyst	X(CO) <sub>max</sub> , %	t, °C	Yield of products, μmole/g·s	
			Y(H <sub>2</sub> )	Y(CO <sub>2</sub> )
10%Fe-Cu(1:1)- 0.25%M/Al <sub>2</sub> O <sub>3</sub>	96.4	290	1.33	1.30
10%Fe-Co(1:1)-0.25%M/Al <sub>2</sub> O <sub>3</sub>	94.6	315	1.29	1.29



Both catalysts worked without loss of stability for 20 hours of their exploitation. The values of specific surface area and pore volume of the fresh and spent catalyst are given in Table 3. Insignificant decreasing of both parameters is occurred, that can be explained by blocking of surface by reaction products, which were not removed from the surface after reaction running for 20 hours.

Table 3 – Specific surface area (BET) and pore volume of catalyst samples

Catalyst	Specific surface area, m <sup>2</sup> /g		Pore volume, ml/g	
	Fresh	Spent	Fresh	Spent
10%Fe-Cu(1:1)- 0.25%M/Al <sub>2</sub> O <sub>3</sub>	132.2	123.9	n/d	n/d
10%Fe-Co(1:1)-0.25%M/Al <sub>2</sub> O <sub>3</sub>	156.2	141.9	146.1	126.6

## CONCLUSIONS

On the base of data obtained the following can be concluded.

The both iron-containing catalysts studied perform the high activity in water gas shift reaction with production of hydrogen. Conversion degree of carbon monoxide reaches 94.6 and 96.4% in maximum for Fe-Co and Fe-Cu catalysts respectively. The copper containing catalyst exhibit somewhat higher activity: higher carbon monoxide conversion (96.4% versus 94.6%) is achieved at lower temperature (290°C versus 315°C).

The both catalysts can be assigned as the middle temperature ones. The optimal temperatures of WGSR are within the temperature region of 290-320°C depending on the second metal nature – Cu or Co.

Further studies of catalysts are planned in particular to scale the water gas shift process - WGSR over the developed catalysts.

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## ПОЛИМЕТАЛДЫ Fe-ҚҰРАМДЫ ҚОНДЫРЫЛҒАН КАТАЛИЗАТОРЛАРДА СУДЫҢ КЕРІ ЫҒЫСУ РЕАКЦИЯСЫ

**Аннотация.** Бұл жұмыста ауыспалы металдар қоспасымен модифицирленген және алюминий тотығына қондырылған полиметалды темірқұрамды катализаторларда судың кері ығысу реакциясы зерттелді. Көміртек тотығымен судың әрекеттесуі процесінде темірқұрамды катализаторлар сипатына процесс температурасы мен қоспа (Со немесе Си) табиғатының әсері, сонымен қатар H<sub>2</sub>/CO қатынасы мен көлемдік жылдамдық әсері қарастырылған болатын. Кобальт немесе мыс қоспасымен модифицирленген, сондай-ақ үшінші компонент ретінде 8-ші топ элементінің ауыспалы металын құрайтын және алюминий тотығына қондырылған темір негізіндегі синтезделген катализаторлар судың кері ығысу реакциясында сутегі бойынша жоғары белсенділік пен талғамдылықты көрсетті. Синтезделген катализаторларда судың кері ығысу жолымен сутегі алудың тиімді жағдайы анықталды.

**Түйін сөздері:** Судың Кері Ығысу Реакциясы, Fe-Құрамды Қондырылған Катализатор, Сутегі, Көміртек Тотығы

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## РЕАКЦИЯ ВОДЯНОГО СДВИГА НА ПОЛИМЕТАЛЛИЧЕСКИХ Fe-СОДЕРЖАЩИХ НАНЕСЕННЫХ КАТАЛИЗАТОРАХ

**Аннотация:** В данной работе была изучена реакция водяного сдвига на полиметаллических нанесенных на оксид алюминия железосодержащих катализаторах, модифицированных добавками переходных металлов. Было рассмотрено влияние температуры процесса и природы добавок (Co или Cu) на поведение железо-содержащих катализаторов в процессе взаимодействия воды с оксидом углерода. Показано, что синтезированные катализаторы на основе железа, модифицированные добавками меди или кобальта, а также содержащие в качестве третьего компонента – переходной металл из 8-ой группы элементов, нанесенные на оксид алюминия, обладают высокой активностью и селективностью по водороду в реакции водяного сдвига. Определены оптимальные условия получения водорода путем реакции водяного сдвига на синтезированных катализаторах.

**Ключевые слова:** Реакция Водяного Сдвига, Fe-содержащий Нанесенный Катализатор, Водород, Оксиды Углерода.

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## STUDY OF VITAMINS CONTENT OF MICROALGAE

**Abstract.** The efficiency of using microalgae biomass for practical purposes is determined by their physiological and biochemical features. The growth and development of algae are closely interrelated with external factors, under the influence of which the structural, functional and biochemical characteristics of the cell change. Selection of new highly active microalgae-producers of essential compounds in the natural conditions would expand the area of their practical application. The present work shows a comparative study of the amount of vitamins — provitamin A, vitamin C, vitamin E in the ten types and strains of green and *Euglena* microalgae, isolated from the local flora that grown in semi-industrial terms and under the open atmospheric conditions: *Chlorella pyrenoidosa* ChickYA-1-1; *Scenedesmus obliquus* YA-2-6; *Ankistrodesmus angustus* YA-3-1; *Ankistrodesmus braunii*; *Chlamydomonas reinhardtii* YA-5-16; *Chlamydomonas reinhardtii* 449; *Euglena gracillis* YA-4-17; *Euglena* YA-4-19; *Dunaliella salina*; *Dunaliella minuta* UA-5-10. It is shown that the vitamins content depends on the type of algae strain and the seasons, the duration of cultivation and the type of mixing. The developed biomass with a high content of vitamins allow to increase the biotechnological potential of microalgae that will provide an opportunity for the problems solving related to the provision of various sectors of the national economics by algae-rich raw materials: animal husbandry, poultry farming, fish farming, as well as food and pharmaceutical industries.

**Keywords:** biosynthesis, cultivation technology, microalgae, strain, vitamins.

## INTRODUCTION

Currently, in the field of algal biotechnology, the studies are based on the isolation of new species and strains of microalgae [4, 16]. Mostly, the studies of their physiological, biochemical and environmental features that enhance productivity and the synthesis of biologically active substances are applied [6]. The demand for food having beneficial effects on human health is also increasing in Kazakhstan [10].

As known, vitamins play an important function in normal metabolism and vital activity of organisms. They are essential for human nutrition, animals and other organisms, but unlike proteins, fats and carbohydrates, the quantitative needs of the body for vitamins are negligible. Vitamins often ensure the functioning of biological catalysts. For the catalytic activity of many enzymes, certain non-protein cofactors are required, the function of which can be performed by vitamins [5].

Microbiological synthesis is most suitable for the production of vitamins for livestock and crop production, and it became as basis of their industrial production for these purposes [2].

Algal biomass is rich in various vitamins, including those typical for plants. However, their content varies in different algae. For example, the content of provitamin A or Carotene is the most promising for *Dunaliella* (1100 mg %), the content of which exceeds all known vegetable foods. The amount of Carotene in *Chlorella* reaches 140-200 mg % that is 3 times more than in grass meal [15].

Algae are rich in vitamin C or Ascorbic acid, the content of which is as much as in lemon and 100 times more than milk. Algae contain in significant amounts of Tocopherol, Riboflavin, Nicotinic acid and other biologically active compounds. Algae contain Thiamine and Pyridoxine as much as corn, barley and oats 5.6 & 5.3 (µg/g), respectively. Vitamin B12 and D are found in significant amounts of green algae biomass. For instance, 100 g of dry *Dunaliella* biomass consists in 7.5 µg/g of vitamin B12, and 100 mg of vitamin D in *Chlorella* 100 mg of green algae are currently found [16].

Along with chemotrophic microorganisms, phototrophic microorganisms, in particular microalgae can also be a source of a complex of various groups of vitamins [11].

One of the essential compounds is vitamin C (Ascorbic acid) that is involved in a number of redox reactions and provides vital processes in the human body. Presently, in assessing the mechanism of action of Ascorbic acid, great importance is attached for its possible participation in the prevention of oxidation of active sulfonate hydroxyl groups, including proteins with biocatalytic activity. This function is performed by the reduced form of Ascorbic acid [13].

Recently, more attention of researchers acquires vitamin E (Tocopherol) due to its influence on the function of the sex glands in reproduction. It is also known that it takes part in the regulation of a number of vital processes in living organisms. Therefore, it is often used as a vitamin supplement to feed [8].

Tocopherol can input to the body only by food. Its absence in the organism leads to the disruption of the activity of not only the reproductive system, but also of many other organs and tissues. By preventing the oxidation of saturated fatty acids, the most important component of cell membranes and organelles, Tocopherol thereby maintains a structural integrity of the cells and consequently of the whole living organism [7].

Therefore, in the production of food based on microalgae, the main requirement is a high content of vitamins in them.

**Purpose of the study:** the purpose of this work was a comparative study of the content of three important vitamins from biomass of 10 species and strains of microalgae isolated from the local nature and producers of the above mentioned compounds with the determination of the change in the amount of these vitamins depending on the season of the year and the duration of cultivation.

## OBJECTS AND METHODS

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 [9].

The objects of the study were 10 types and strains of microalgae: *Chlorella pyrenoidosa* ChickYA-1-1, *Scenedesmus obliquus* YA-2-6, *Ankistrodesmus angustus* YA-3-1, *Ankistrodesmus braunii*; *Chlamydomonas reinhardtii* YA-5-16; *Ch.reinhardtii* 449; *Euglena gracillis* YA-4-17; *Euglena proxima*YA-4-19; *Dunaliella salina*, *Dunaliella minuta* UA-5-10.

For the cultivation, phytoplanktons of the Shardara reservoir (Turkestan region, Kazakhstan) were used as a source material in the laboratory studies [12]. Under the open atmospheric conditions, algae were cultivated in a horizontal installation of a tray type with a volume of 1000 liters. For the growing microalgae, the following standard mineral nutrient media were used - 04, (for the cultivation of *Chlorella*) Tamiya, (*Scenedesmus*) Yaguzhensky, (*Ankistrodesmus*) Gromov, (*Chlamydomonas*) Artari (*Dunaliella*), UzA (*Euglena*) that are optimal for the cultivation of these algae and determined in laboratory studies. The growth and morphological state of the cells was checked under observation and counting in the Goryaev chamber by using the MBI-3 microscope. The productivity of algae was determined on a dry mass by the gravimetric method [11].

Carotene content in fresh pasta of microalgae was determined by the method of Murri. Tocopherol was determined by the iron-dipyridyl method in the modifications of Devyatina and Solunina [3]. Ascorbic acid was determined by titration of the extract with 2,6-dichlorophenolindophenol [8].

## RESULTS AND DISCUSSION

Studies shown that the content of vitamins, depending on the type and strain of microalgae, varies widely: Carotene - 90.6÷1100 mg%, Ascorbic acid - 62.2÷182.7 mg%, Tocopherol - 25.2 ÷123.4 mg% of dry weight. The high contents of Carotene, Ascorbic acid, Tocopherol are related with *Dunaliella* species, where its amount reached 1100 mg%. In the intensive culture and in conditions without stirring the suspension under the open atmospheric conditions, in the accumulations of carotene *D.salina* exceeds *D.minuta* (Table 1).

As seen Table 1, the highest amounts of Ascorbic acid and Tocopherol were for *E.proxima* and *D.salina* that respectively: 108.7 & 123.4 (mg%). The minimum amount of these vitamins was observed in *Chlorella* and *Scenedesmus*: 68.5 &77.3 (mg%) for Ascorbic acid and 25.2&48.0 (mg%) for Tocopherol. Comparison of microalgae of the Tocopherol content with various known objects showed following: soybean oil - 114.0 mg%, cotton oil – 99 mg%, sunflower oil - 67.0 mg%, olive oil - 13.0 mg%, hazelnut - 25.5 mg%, walnut-23.0 mg%, corn - 31.9 mg%, green dried lucerne 1<sup>st</sup> crop - 12.5 mg%,

reeds flour - 12.5 mg%, barley - 2.0 mg%. Consequently, microalgae are rich in vitamin E than the above mentioned objects.

Table 1 - Efficiency and vitamin content in microalgae that grown under the conditions of open mass cultivation (of absolute dried mass)

Culture	Productivity g/m <sup>2</sup> per day	Carotene, mg%	Ascorbic acid, mg%	Tocopherol, mg%
<i>Chlorella pyrenoidosa</i> YA-1-1	22,0	220,3	68,5	25,2
<i>Scenedesmus obliquus</i> YA-2-6	17,2	90,6	77,3	48,0
<i>Ankistrodesmus angustus</i> YA-3-1	15,0	160,4	80,2	58,5
<i>Ankistrodesmus braunii</i>	14,9	140,7	74,6	55,0
<i>Chlamydomonas reihardii</i> 449	23,6	125,0	66,4	52,0
<i>Chlamydomonas reinhardii</i> YA-5-16	18,5	152,0	62,2	46,5
<i>Euglena graulis</i> YA-4-17	18,0	137,0	182,7	67,8
<i>Euglena Proxima</i> YA-4-19	16,0	120,3	108,7	60,0
<i>Dunaliella minuta</i>	20,0	1100,0	100,5	103,8
<i>Dunaliella salina</i>	21,0	815,7	120,0	123,4

In addition, *Dunaliella* species outnumber the three vitamins from other tested forms of algae. Therefore, the changes in the amount of these vitamins in *Dunaliella* were investigated further depending on the seasons, the cultivation and the type of mixing.

In order to introduce them into industrial cultivation in the Turkestan region of Kazakhstan, the development of the open-air cultivation of the halophilic alga *Dunaliella minuta* has begun, in a wooden tray installation of 50 l and 500 l with 1-5(m<sup>2</sup>) illuminated surface without mixing and with suspension mixing (circulating, bubbling) on *Arthari* culture medium containing different concentrations of NaCl.

Studies shown that the amount of vitamins in *D.minuta* depends both on the season of the year and on the temperature and light intensity (Table 2).

Carotene content in *D.minuta* biomass grown in open-air conditions from February till September varied in the range of 171-672.9 (mg%). The most favorable for the development of this seaweed were the April-May and August-September months. The accumulation of Carotene in these months in biomass reached 405-599.0 (mg %), and in *D.minuta* cells grown in June-July, it increased by 15% or 654-672 (mg %). Perhaps this is due to the fact that, with an increased intensity of light, a grow in the biosynthesis of Carotene is due to its participation in the protection of chlorophyll against oxidation at high light intensities. Therefore, to obtain a *D.minuta* biomass with a high content of Carotene, the culture should be grown in summer in open-type plants at high light intensity. Similar data were obtained for *D.salina* [6].

In the biomass of *D.minuta* grown in April, May and August, the increasing in the amount of Ascorbic acid and Tocopherol occurs at the same time. Synthesis of Ascorbic acid correlated with changes in temperature and light intensity. In May, it was two times more in *Dunaliella* biomass than in cells that grew in March (48 mg % versus 92.4 mg %). Moreover, at high temperature (T=34<sup>0</sup>C) and light intensity, suppression of the synthesis of Ascorbic acid was observed.

Thus, the maximum accumulation of valuable substances over the seasons of the year (vitamins et al) in the holofilous algae *D.minuta* when it is cultivated in the open plants conditions of the Turkestan region has scientific and practical importance.

Table 2 - Influence of the seasons on the vitamins content in *Dunaliella minuta* biomass (of absolute dried mass)

Months	Temperature, °C	Illumination, kilolux	Carotene, mg%	Ascorbic acid, mg%	Tocopherol, mg%
February	8-14	40-60	171±8,1	35,6±0,95	30,5±1,00
March	10-16	60-80	202,9±10,2	48,0±1,12	60,4±1,27
April	14-24	70-90	405,1±16,4	75,3±1,42	80,8±1,40
May	16-26	80-100	444,6±15,0	92,4±2,0	103,8±1,90
June	24-34	100-140	672,9±20,3	63,8±1,10	50,4±1,31
July	22-30	100-130	654,0±22,4	80,2±1,67	62,3±1,05
August	19-28	90-120	599,0±16,1	71,5±1,00	41,5±1,10
September	15-24	70-100	450,5±17,3	85,2±1,72	95,0±1,42

The study of the dynamics of the accumulation of vitamins in *Dunaliella* with open-air mass cultivation showed (Table 3) that at the cultivating under conditions without moving in the first 10 days of cultivation, the amount of vitamins gradually increases, and starting from 12 days the content of Ascorbic acid increases by 25% or 102 mg% compare with 9 days or 75 mg%. During the same periods (on the 12th day) of cultivation, the dry matter (1.7 g/l) and Tocopherol (60.2 mg %) accumulate to the maximum. This is apparently due to the fact that at the beginning of the life cycle of algae, the directionality of their synthetic processes changes from structural to the middle and end of the life cycle towards the synthesis of reserve substances. The greatest amount of Carotene was noted on the 15th day and can reach 410 mg%.

Table 3 - Effect of cultivation duration on dry matter and vitamins in *Dunaliella minuta* at the open air conditions (of absolute dried mass)

Duration of cultivation	Dry matter, g/l	Carotene, mg%	Ascorbic acid, mg%	Tocopherol, mg%
without mixing				
The beginning of the experiment	-	-	-	-
3 <sup>d</sup> day	0,45±0,01	213,5±8,1	43,7±0,55	26,4±0,15
6 <sup>th</sup> day	0,80±0,02	247,0±6,2	63,7±0,72	37,3±0,25
9 <sup>th</sup> day	1,08±0,05	273,5±5,0	75,0±0,94	50,0±0,85
12 <sup>th</sup> day	1,70±0,12	325,0±9,0	102,0±0,85	60,2±0,93
15 <sup>th</sup> day	1,52±0,10	410,0±9,5	72,5±0,78	55,0±0,72
18 <sup>th</sup> day	1,00±0,09	370,5±9,3	48,2±0,42	43,1±0,48
with mixing (bubbling)				
The beginning of the experiment	0,88±0,02	250,7±5,3	72,3±0,85	-
2 <sup>d</sup> day	1,20±0,05	258,1±8,4	100,4±0,92	35,7±0,32
4 <sup>th</sup> day	1,42±0,09	375,5±9,2	118,8±0,97	42,4±0,82
6 <sup>th</sup> day	1,73±0,12	580,0±10,0	135,4±0,80	60,5±0,65
8 <sup>th</sup> day	2,65±0,15	935,2±12,1	142,0±0,94	75,0±0,96
10 <sup>th</sup> day	3,00±0,18	1100,0±22,6	129,2±0,72	78,5±0,90
12 <sup>th</sup> day	2,75±0,12	1015,4±19,2	-	65,6±0,77

Therefore, under conditions without mixing of the suspension in the middle of 12-15 days of cultivation, *Dunaliella* cells are in the most active state. At the bubbling method of cultivation of *Dunaliella*, the periods of culture transition to the active state reduced, and the maximum content of vitamins is observed in the cells on the 10<sup>th</sup> day of cultivation (3.0 g/l of dry matter, 1100 mg% Carotene and 78.5 mg% Tocopherol). The maximum accumulation of Ascorbic acid was noted for two days earlier. After 10 days of growth, the amount of dry matter of Carotene and Tocopherol in *Dunaliella* decreases and amounts to 2.75 g/l, 1015 mg% and 65.6 mg%, respectively.

Thus, during the cultivation of *Dunaliella* by bubbling mixing in biomass, the vitamins content is optimized after 8-10 days of cultivation. Similar data for the optimal cultivation were obtained by other authors regarding the biosynthesis of Eicosapentaenoic acid from other algae [1].

## CONCLUSION

Thus, the study results showed that the microalgae consist in irregular amount of vitamins and depending on the type and strains. The high content of provitamins A (Carotene) is characteristic for species of the genus *Dunaliella* 935.2÷1100.0 (mg%), of absolute dry weight. The greatest amount of vitamin C (Ascorbic acid) and vitamin E (Tocopherol) was in the species *Euglena* 182.7 & 67.8 (mg%) and *Dunaliella* 120.0 & 123.4 (mg%), respectively. In terms of productivity, it is also not inferior to *Chlamydomonas*. The minimum amount of these vitamins was observed in the *Chlorella* species or 68.5 & 25.2 (mg%) and *Chlamydomonas* or 62.2 and 46.5 (mg%), respectively. As can be seen, by the number of studied vitamins, *Dunaliella* and *Euglena* species are more promising producers of these compounds and can serve as sources of vitamin A, vitamin C and vitamin E. Following contents are discovered: provitamin A - 90.6÷1100 (mg%); vitamin C - 62.2÷120 (mg%); vitamin E - 25.2÷123 (mg%) of dry mass. The productivity and content of the three vitamins in *Dunaliella* depends on the season of the year, the duration of cultivation and the type of mixing. The highest productivity and the maximum amount of vitamins were observed during cultivation in May-June, at 8-10 days of cultivation by the bubbling cultivation method. The developed biomass with a high content of vitamins allow to increase the

biotechnological potential of microalgae that will provide an opportunity for the problems solving related to the provision of various sectors of the national economics by algae-rich raw materials: animal husbandry, poultry farming, fish farming, as well as food and pharmaceutical industries. In this regard, the need for the expanding of number and range of cultivated algae by searching for and isolating their local forms, especially promising species, as well as identifying sensitiveness and resistance to wide ecological ranges have a significant value.

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### МИКРОБАЛДЫРЛАРДЫҢ ДӘРУМЕНДІК ҚҰРАМЫНЫ ЗЕРТТЕУ

**Аннотация.** Микробалдырлардың биомассасын тәжірибелік мақсатта пайдалану тиімділігі олардың физиологиялық және биохимиялық ерекшеліктерімен анықталады. Балдырлардың өсуі мен дамуы сыртқы факторлармен тығыз байланысты, олардың әсерінен жасушаның құрылымдық, функционалдық және биохимиялық сипаттамалары өзгереді. Табиғи жағдайларда жаңа жоғары белсенді микробалдырлар алмастырылмайтын қосылыстардың продуценттерін іріктеу олардың тәжірибелік қолдану саласын кеңейтуге мүмкіндік береді. Осы жұмыста жергілікті флорадан бөлінген жасыл және *Euglena* микробалдырлардың он түрі мен штамдарында С дәруменінің, Е дәруменінің А продәруменінің санын салыстырмалы зерттеу көрсетілген, олар жартылай өнеркәсіптік режимдерде және ашық атмосферада өсірілген: *Chlorella pyrenoidosa* ChickYA-1-1; *Scenedesmus obliquus* YA-2-6; *Ankistrodesmus braunii*; *Chlamydomonas reinhardii* YA-5-16; *Chlamydomonas reinhardii* 449; *Euglena gracillis* YA-4-17; *Euglena* YA-4-19; *Dunaliella salina*; *Dunaliella minuta* UA-5-10. Дәрумендердің құрамы балдырлар штаммының түріне және жыл уақытына, өсіру ұзақтығына және араластыру түріне байланысты екендігі көрсетілді. Өзірленген дәрумендік құрамы жоғары биомасса микробалдырлардың биотехнологиялық әлеуетін арттыруға мүмкіндік береді, бұл мал шаруашылығы, құс шаруашылығы, балық шаруашылығы, сондай-ақ тамақ және фармацевтика өнеркәсібін халық шаруашылығының әртүрлі салаларын шикізатпен қамтамасыз етуге байланысты міндеттерді шешуге мүмкіндік береді.

**Түйін сөздер:** биосинтез, өсіру технологиясы, микробалдырлар, штамм, дәрумендер

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### ИССЛЕДОВАНИЕ ВИТАМИННОГО СОСТАВА МИКРОВОДОРΟΣЛЕЙ

**Аннотация.** Эффективность использования биомассы микроводорослей в практических целях определяется их физиологическими и биохимическими особенностями. Рост и развитие водорослей тесно связаны с внешними факторами, под влиянием которых меняются структурные, функциональные и биохимические характеристики клетки. Отбор новых высокоактивных микроводорослей-продуцентов незаменимых соединений в естественных условиях позволит расширить область их практического применения. В настоящей работе показано сравнительное исследование количества витаминов - провитамина А, витамина С, витамина Е в десяти типах и штаммах зеленых и *Euglena* микроводорослей, выделенных из местной флоры, выращенных в полупромышленных режимах и в условиях открытой атмосферы: *Chlorella pyrenoidosa* ChickYA-1-1; *Scenedesmus obliquus* YA-2-6; *Ankistrodesmus braunii*; *Chlamydomonas reinhardii* YA-5-16; *Chlamydomonas reinhardii* 449; *Euglena gracillis* YA-4-17; *Euglena* YA-4-19; *Dunaliella salina*; *Dunaliella minuta* UA-5-10. Показано, что содержание витаминов зависит от типа штамма водорослей и времени года,



продолжительности выращивания и типа смешивания. Разработанная биомасса с высоким содержанием витаминов позволит повысить биотехнологический потенциал микроводорослей, что даст возможность для решения задач, связанных с обеспечением различных отраслей народного хозяйства богатым водорослями сырьем: животноводство, птицеводство, рыбоводство, а также пищевая и фармацевтическая промышленности.

**Ключевые слова:** биосинтез, технология культивирования, микроводоросли, штамм, витамины

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## SYNTHESIS, STRUCTURE AND ANTI-RADICAL ACTIVITY OF 6-METHYL-4-OXO-4H-CHROMEN-3-ACYLHYDRAZONES

**Abstract.** This paper demonstrates data on synthesis of 6-methyl-4-oxo-4H-chromen-3-acylhydrazones with condensation of substituted 3-formylchromones and acylhydrazides. It is testified to the fact that 4-oxo-4H-chromen-3-carboxaldehyde with hydrazides of isonicotinic and *o*- and *n*-hydroxybenzoic acids in isopropanol at boiling a reaction mixture for 2 h lead to the relevant chromen-containing hydrazones. Structures of the synthesized compounds were investigated with methods of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and data on two-dimensional (<sup>1</sup>H-<sup>1</sup>H) COSY and (<sup>1</sup>H-<sup>13</sup>C) HMQC spectra. Values of the chemical shifts, multiplicity and integrated intensity of <sup>1</sup>H and <sup>13</sup>C signals in one-dimensional NMR spectra were defined. Homo- and heteronuclear interactions confirming structure of the investigated compounds were determined with (<sup>1</sup>H-<sup>1</sup>H) COSY and (<sup>1</sup>H-<sup>13</sup>C) HMQC spectra. Data on an antiradical activity of synthesized 6-methyl-4-oxo-4H-chromen-3-acylhydrazones were showed. It was shown that the above compounds in the final concentration of 50 μM reduce the optical density of the initial solution of the DPPG radical by 27.5%, 25.2% and 8.8%, respectively, therefore, do not show pronounced antiradical activity under the conditions of this test system.

**Key words:** acylhydrazides, condensation, 4-oxo-4H-chromen-3-carboxaldehyde, <sup>1</sup>H and <sup>13</sup>C NMR spectra, two-dimensional (<sup>1</sup>H-<sup>1</sup>H) COSY and (<sup>1</sup>H-<sup>13</sup>C) HMQC spectra, antiradical activity.

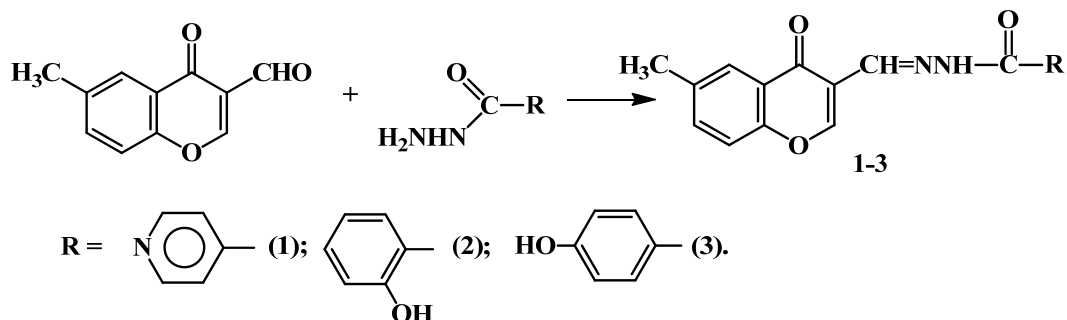
### Introduction

Chromone (4H-1-benzopyran-4-one) is a parent of the class of oxygen-containing heterocyclic compounds – flavonoids widespread in flora. The flavonoids and chromone derivatives isolated from plants and fungi possess various types of the biological activity such as antitumoral, antifungal, antioxidant, P-vitamin, etc. [1-5]. Chromone cyclic system takes an important position among oxygen-containing heterocyclic systems. Some of the synthetic chromone products show a wide range of the biological activities such as antifungal, anticancer, antimicrobial and inhibit human immunodeficiency virus and mushroom tyrosinase virus [6-8]. It is natural that the chromen-containing derivatives are the valuable intermediate products in synthesis of new biologically active compounds including the pharmaceutical products. It should be noted that a chromone system is a part of flavonoids (quercetin, dihydroquercetin, etc.) belonging to group of antioxidant substances [1]. By reason of low toxicity for mammals and essential solubility, a chromone fragment is one of the exclusive structural blocks to develop the pharmacological important substances [9-20].

### Experimental part

Referring to a large scientific interest to flavonoid compounds and their prospects in the applied relation and search the new antioxidant products, the synthesis of 6-methyl-4-oxo-4H-chromen-3-acylhydrazones (**1-3**) was performed by correlation of 6-methyl-4-oxo-4H-chromen-3-carboxaldehyde with hydrazides of isonicotinic and *o*- and *p*-hydroxybenzoic acids. It is demonstrated that at boiling in

isopropanol for 2 h the reaction proceeds smoothly and leads to the corresponding chromen-containing hydrazones with high yields.

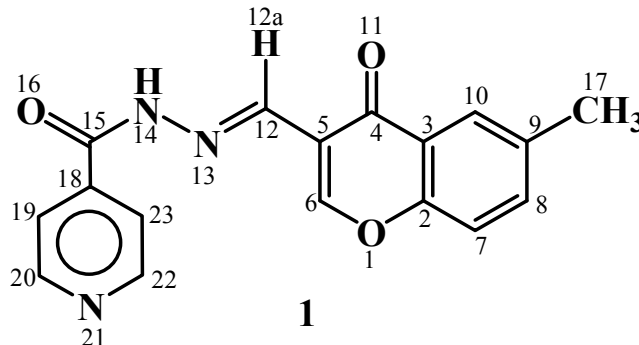


Reaction products of **1-3** are the light yellow powders soluble in many organic solvents, and a yield of compounds makes 63-98%.

### Results and discussion

The structure of compounds **1-3** was confirmed with data of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and two-dimensional ( $^1\text{H}$ - $^1\text{H}$ ) COSY and ( $^1\text{H}$ - $^{13}\text{C}$ ) HMQC spectra.

NMR spectrum of compound **1** was studied in detail.  $^1\text{H}$  NMR spectrum of compound **1** is characterized with strong pole area at 2:41 ppm of a singlet signal with intensity 3H belonging to protons  $\text{H}^{17}$  of a methyl substituting group. A multiplet signal with intensity 6H belonging to two symmetric protons  $\text{H}^{8,10}$  of a methyl substituting group of an aromatic system, to proton  $\text{H}^7$  of this aromatic nucleus, two symmetric protons  $\text{H}^{19,23}$  of a pyridine cycle, and to proton  $\text{H}^{12}$  at  $\text{sp}^2$ -hybridized carbon atom were observed in aromatic area of a spectrum at 7.61-7.88 ppm. The unscreened protons  $\text{H}^{20,22}$  of a pyridine cycle and protons  $\text{H}^6$  close by oxygen atom were shown as a multiplet at 8-48-9.80 ppm with integrated intensity 3H. Protons  $\text{H}^{14}$  of a hydrazine fragment of a molecule were observed as a broadened singlet with integrated intensity 1H in the lowest pole area of spectrum at 142.11 ppm.



In  $^{13}\text{C}$  NMR spectrum of the compound **1** the methyl carbon signals were found at 20.97 ( $\text{C}^{17}$ ) ppm. Carbon signals of an aromatic nucleus were shown at 118.37 ( $\text{C}^3$ ), 119.02 ( $\text{C}^7$ ), 124.93 ( $\text{C}^{10}$ ), 136.25 ( $\text{C}^9$ ), 136.34 ( $\text{C}^8$ ) and 154.56 ( $\text{C}^2$ ) ppm. Carbon atom  $\text{C}^5$  condensed with an aromatic nucleus of the heterocyclic oxygen-containing cycle not connected with oxygen atoms was observed at 123.48 ppm. Because of the shift of electronic density on carbon atoms as a result of correlation with electronegative oxygen the signals of  $\text{C}^6$  and  $\text{C}^4$  atoms passed into a low pole area of spectrum and were at 155.18 and 175.43 ppm respectively. Equivalent couple of atoms of pyridine fragment  $\text{C}^{19,23}$  with low shift of the electronic density on carbon nucleus was found at 122.02 ppm. Whereas other couple of pyridine carbons  $\text{C}^{22,22}$  with low screening of carbon nucleus was observed in lowest pole area at 150.26 ppm. Carbon atom  $\text{C}^{18}$  of pyridine nucleus resonated at 140.67 ppm. The signal with a chemical shift at 142.32 ppm belongs to a carbon atom connected with double bond with nitrogen atom. In low pole area at 161.86 ppm the signal of carbonyl atom  $\text{C}^{15}$  was observed.

The structure of compound **1** was confirmed with methods of two-dimensional NMR spectroscopy, ( $^1\text{H}$ - $^1\text{H}$ ) COSY and ( $^1\text{H}$ - $^{13}\text{C}$ ) HMQC to establish the homo- and heteronuclear spin-spin interactions (Fig. 1 and 2).

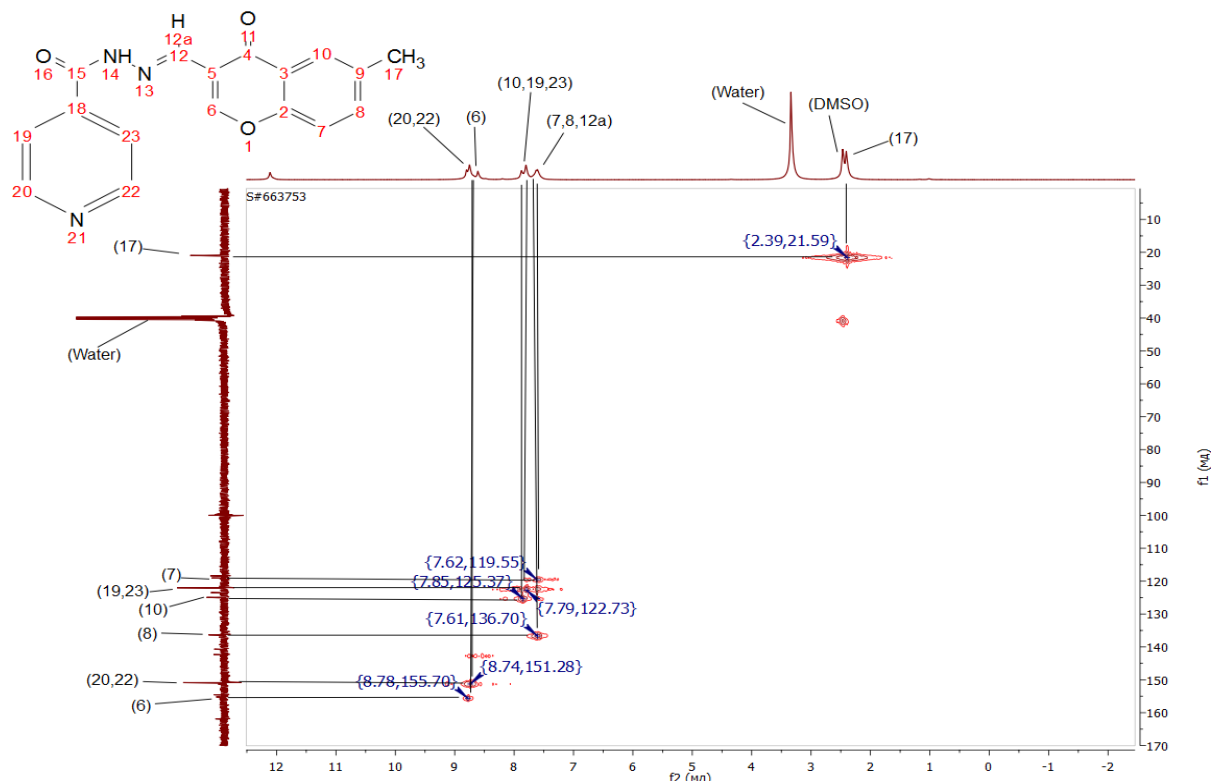


Figure 1 – Recording of HMQC spectrum of compound 1

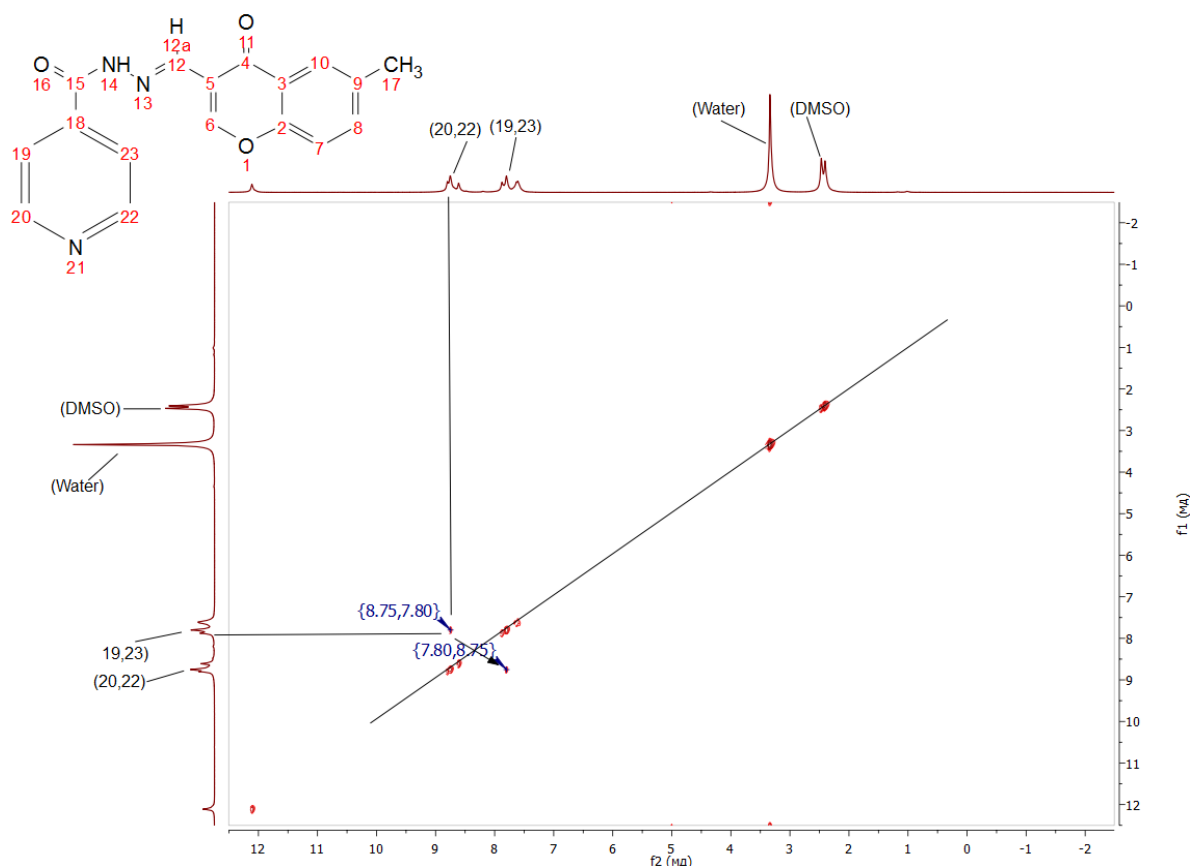


Figure 2 – Recording of COSY spectrum of compound 1

The observed correlations in a molecule are presented on the scheme. Spectra of  $^1\text{H}$ - $^1\text{H}$  COSY of compound demonstrate the spin-spin correlations through three proton bonds of next methine groups  $\text{H}^{19,23}$ - $\text{H}^{20,22}$  of a pyridine ring with cross-peaks at 8.75, 7.80 and 7.78, 8.75.

The heteronuclear interactions of protons with carbon atoms through one bond were determined with  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectroscopy for all couples of compounds:  $\text{H}^{17}$ - $\text{C}^{17}$  (2.39, 21.59),  $\text{H}^7$ - $\text{C}^7$  (7.62, 19.55),  $\text{H}^8$ - $\text{C}^8$  (7.61, 136.70),  $\text{H}^{12}$ - $\text{C}^{12}$  (7.62, 142.30),  $\text{H}^{19,23}$ - $\text{C}^{19,23}$  (7.79, 122.73),  $\text{H}^{10}$ - $\text{C}^{10}$  (7.85, 125.37),  $\text{H}^{20,22}$ - $\text{C}^{20,22}$  (8.74, 151.28) and  $\text{H}^6$ - $\text{C}^6$  (8.78, 155.70).

One- and two-dimensional NMR spectra of molecule **2** – isomer of compound **3** in size of the chemical shifts  $^1\text{H}$  and  $^{13}\text{C}$  NMR have big analogy. However change of a hydroxyl group position in an aromatic ring from the symmetric position in the asymmetrical corresponding to compound **2** slightly changed the size of the electronic density on the studied nucleus  $^1\text{H}$ . As a result of it some signals of NMR protons, earlier presented as doublet, passed into areas of other spectra and were as multiplets. So,  $^1\text{H}$  NMR spectrum of compound **2**,  $\delta$ , ppm: 2.34 s (3H,  $\text{H}^{17}$ ), 6.74-7.92 m (8H,  $\text{H}^{7,8,10,12,20-23}$ ), 8.48-8.80 m (3H,  $\text{H}^{6,20,22}$ ), 8.58 s (1H,  $\text{H}^6$ ), 11.84 s (1H, NH).  $^{13}\text{C}$  NMR spectra of the studied isomers were very identical. This result was predicted. So, the studied molecules have two aromatic cycles which signals of protons are very similar and thus there is a high probability of their superposition at each other. The general integrated intensity of protons of the studied isomers did not change.

Possibility to identify isomers on position of a hydroxyl group in an aromatic nucleus was shown with a homonuclear correlation of COSY ( $^1\text{H}$ - $^1\text{H}$ ) NMR spectroscopy. The spin-spin correlations through three proton bonds of next methine groups  $\text{H}^{20}$ - $\text{H}^{21}$  (7.39, 6.90; 6.91, 7.37) and  $\text{H}^{22}$ - $\text{H}^{23}$  (7.83, 6.87; 6.88, 7.81) were observed in isomer **2** in an aromatic fragment (Fig. 3). Such homonuclear correlation of NMR spectroscopy corresponds to isomer compound **2**.

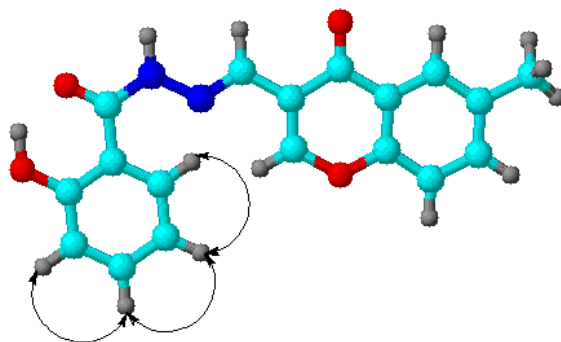


Figure 3 – Correlation scheme in COSY spectra of compound **2**

In order to investigate the pharmacological activity of the synthesized compounds **1-3** the screening of antiradical activity based on interaction of compounds with stable chromogen-radical 2,2- diphenyl-1-picrylhydrazil (DPPH) was performed. The methanol solution DPPH (100  $\mu\text{M}$ ) was used to evaluate primary the antiradical activity of the studied samples in test with the DPPH –radical. In order to select substances with the antiradical activity, 2 ml of the DPPH methanol solution (100  $\mu\text{M}$ ) was mixed with 20  $\mu\text{L}$  of the studied object dissolved in DMSO in concentration 5 mM. Thus, the final concentration of the studied substance in reactionary mixture made 50  $\mu\text{M}$ . The reduction in optical density at 515 nm was measured in 10 min after addition of the studied substance solution to the DPPH radical solution. The substances, which are able to reduce optical density more 30%, were tested for interaction with the DPPH radical in the final concentration of the studied substances (100, 75, 50, 25, 20, 10 and 5  $\mu\text{M}$ ). Then concentration of the studied substance reducing an optical density by 50% -  $\text{IC}_{50}(\text{DPPH})$  was determined. In control 20 $\mu\text{L}$  solvent (DMSO) was added in 100  $\mu\text{M}$  DPPH solution. Research results of biological activity of compounds **1-3** are presented in the table.

This table demonstrates that compounds **1**, **2** and **3** in final concentration 50  $\mu\text{M}$  reduce the optical density of the initial DPPH radical solution by 27.5%, 25.2% and 8.8%, respectively. Thus they do not show the expressed antiradical activity in the conditions of this test system.

Table – The optical density values of the DPPH radical solution (100 µM) after 10 min incubation with the studied substance in final concentration 50 µM

Comp.No.	Name of compound	Optical density	Value of decrease in optical density of initial solution DPPH-radical, in % from control
1	N'-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)isonicotinohydrazide	0.814	27.5
2	2-hydroxy-N'-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)benzohydrazide	0.839	25.2
3	4-hydroxy-N'-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)benzohydrazide	1.023	8.8
4	Control (DPPH solution without the studied substance)	1.122	-

### Experimental part

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JNM-ECA Jeol 400 spectrometer (frequency 399.78 and 100.53 MHz respectively) with using of DMSO-d<sub>6</sub> solvent. The chemical shifts were measured concerning signals of residual protons or carbon atoms of dimethyl sulfoxide-d<sub>6</sub>. The control of the reaction and purity of the received compounds was performed by Thin Layer Chromatography method on Silufol UV-254 plates in isopropyl alcohol-benzene-ammonia system (10:5:2). Plates were processed with iodine vapour.

**N'-((6-Methyl-4-oxo-4H-chromen-3-yl)methylene) isonicotinohydrazide (1).** To 0.5 g (0.0027 mol) of 6-methyl-4-oxo-4H-chromen-3-carboxaldehyde in 10 ml of ethanol at stirring was added 0.36 g (0.0027 mol) of hydrazide of isonicotinic acid in 5 ml of ethanol (hot). The reaction mixture was boiled for 1 h. The yellow residue dropped out, was cooled, filtered and recrystallized from ethanol. The yield of the product was 0.8 g (96% from theor.), m.p. 210-211°C. <sup>1</sup>H NMR spectrum, δ, ppm: 2.41 s (3H, H<sup>17</sup>), 7.61-7.88 m (6H, H<sup>7,8,10,12,19,23</sup>), 8.48-8.80 m (3H, H<sup>6,20,22</sup>), 12.11 s (1H, NH). <sup>13</sup>C NMR spectrum, δ, ppm: 20.97 (C<sup>17</sup>), 118.37 (C<sup>3</sup>), 119.02 (C<sup>7</sup>), 122.02 (C<sup>19,23</sup>), 124.93 (C<sup>10</sup>), 136.25 (C<sup>9</sup>), 140.67 (C<sup>18</sup>), 142.32 (C<sup>12</sup>), 150.86 (C<sup>20,22</sup>), 155.18 (C<sup>6</sup>), 161.86 (C<sup>15</sup>), 175.43 (C<sup>4</sup>).

**2-hydroxy-N'-((6-methyl-4-oxo-4H-chromen-3-yl)methylene) benzohydrazide (2)** was received similarly to compound **1**. The yield of the product **2** was 77%, m.p. 206-207°C. <sup>1</sup>H NMR spectrum, δ, ppm: 2.34 s (3H, H<sup>17</sup>), 6.74-7.92 m (8H, H<sup>7,8,10,12,20-23</sup>), 8.48-8.80 m (3H, H<sup>6,20,22</sup>), 8.58 s (1H, H<sup>6</sup>), 11.84 s (1H, NH).

**4-hydroxy-N'-((6-methyl-4-oxo-4H-chromen-3-yl)methylene) benzohydrazide (3)** was received similarly to compound **1**. The yield of the product **3** was 83%, m.p. >350°C. <sup>1</sup>H NMR spectrum, δ, ppm (J, Hz): 2.39 s (3H, H<sup>17</sup>), 6.80 d (2H, H<sup>20,22</sup>, <sup>3</sup>J 5.5), 7.59 d (1H, H<sup>7,8</sup>, <sup>3</sup>J 10.4 Hz), 7.77 d (2H, H<sup>19,23</sup>, <sup>3</sup>J 6.0 Hz), 7.86 s (1H, H<sup>10</sup>), 8.55 s (1H, H<sup>12</sup>), 8.72 s (1H, H<sup>6</sup>), 10.10 s (1H, OH), 11.69 s (1H, NH). <sup>13</sup>C NMR spectrum, δ, ppm: 21.00 (C<sup>17</sup>), 115.54 (C<sup>20,22</sup>), 118.83 (C<sup>3</sup>), 119.04 (C<sup>7</sup>), 123.54 (C<sup>5</sup>), 124.12 (C<sup>18</sup>), 124.96 (C<sup>10</sup>), 130.23 (C<sup>19,23</sup>), 136.21 (C<sup>9</sup>), 136.25 (C<sup>8</sup>), 136.94 (C<sup>12</sup>), 154.64 (C<sup>6</sup>), 161.26 (C<sup>2,21</sup>), 163.06 (C<sup>15</sup>) and 175.56 (C<sup>4</sup>).

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### 6-МЕТИЛ-4-ОКСО-4Н-ХРОМЕН-3-АЦИЛГИДРАЗОНДАРДЫҢ СИНТЕЗІ, ҚҰРЫЛЫСЫ МЕН РАДИКАЛДАРҒА ҚАРСЫ БЕЛСЕНДІЛІГІ

**Аннотация.** Жұмыста 6-метил-4-оксо-4Н-хромен-3-ацилгидразондарды функционалды ауысқан 3-формилхромендер мен ацилгидразидтердің конденсациясы арқылы синтездеу нәтижелері келтірілген. 6-метил-4-оксо-4Н-хромен-3-карбоксальдегидінің изоникотин және *o*- мен *n*-гидроксibenзой гидразидтерімен

реакциялық қоспасын изопропанол еріткішінде 2 сағат бойы қайнату олардың сәйкес хроменқұрамды гидразондарының түзілуіне әкелетіні көрсетілген. Синтезделініп алынған заттардың құрылыстары ЯМР  $^1\text{H}$  пен  $^{13}\text{C}$  спектроскопия, сондай-ақ COSY ( $^1\text{H}$ - $^1\text{H}$ ) және НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ )-дың екі өлшемді спектрлерімен зерттелген. ЯМР бірөлшемді спектрлеріндегі  $^1\text{H}$  және  $^{13}\text{C}$  атомдарының химиялық жылжымаларының, мультиплеттілік және интегралды сигналдарының мәндері анықталған. COSY ( $^1\text{H}$ - $^1\text{H}$ ) және НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ ) форматындағы спектрлер бойынша зерттелуші заттардың құрылысын дәлелдейтін гомо- мен гетероядролық әрекеттесулер анықталған. Синтезделініп алынған 6-метил-4-оксо-4Н-хромен-3-ацилгидразондардың радикалдарға қарсы белсенділіктері туралы деректер келтірілген. Осы жоғарыда айтылған заттар 50  $\mu\text{M}$  ең төмен концентрациясында бастапқы ДФПГ-радикалының ерітіндісінің оптикалық тығыздығын 27,5%, 25,2% және 8,8%-ға төмендетеді, сол себепті, олар осы тестік жүйе жағдайында айқын радикалдарға қарсы белсенділіктерді көрсетпейді.

**Түйін сөздер:** ацилгидразидтер, конденсация, 4-оксо-4Н-хромен-3-карбоксальдегид, ЯМР  $^1\text{H}$ - пен  $^{13}\text{C}$ -спектрлер, екіөлшемді COSY ( $^1\text{H}$ - $^1\text{H}$ ) мен НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ ) спектрлері, радикалдарға қарсы белсенділіктер.

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### СИНТЕЗ, СТРОЕНИЕ И АНТИРАДИКАЛЬНАЯ АКТИВНОСТЬ 6-МЕТИЛ-4-ОКСО-4Н-ХРОМЕН-3-АЦИЛГИДРАЗОНОВ

**Аннотация.** В работе приведены данные по синтезу 6-метил-4-оксо-4Н-хромен-3-ацилгидразонов конденсацией функционально замещенных 3-формилхромонов и ацилгидразидов. Показано, что реакции 4-оксо-4Н-хромен-3-карбоксальдегида с гидразидами изоникотиновой и *o*- и *n*-гидроксибензойной кислотами в изопропанол при кипячении реакционной смеси в течение 2 ч приводит к образованию соответствующих хроменосодержащих гидразонов. Исследованы строения синтезированных соединений методами ЯМР  $^1\text{H}$  и  $^{13}\text{C}$  спектроскопии, а также данными двумерных спектров COSY ( $^1\text{H}$ - $^1\text{H}$ ) и НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ ). Определены значения химических сдвигов, мультиплетность и интегральная интенсивность сигналов  $^1\text{H}$  и  $^{13}\text{C}$  в одномерных спектрах ЯМР. С помощью спектров в форматах COSY ( $^1\text{H}$ - $^1\text{H}$ ) и НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ ) установлены гомо- и гетероядерные взаимодействия, подтверждающие структуру исследуемых соединений. Приведены данные по антирадикальной активности синтезированных 6-метил-4-оксо-4Н-хромен-3-ацилгидразонов. Показано, что вышеуказанные соединения в финальной концентрации 50  $\mu\text{M}$  снижают оптическую плотность исходного раствора ДФПГ-радикала на 27,5%, 25,2% и 8,8%, соответственно, следовательно, не проявляют выраженной антирадикальной активности в условиях данной тест-системы.

**Ключевые слова:** ацилгидразиды, конденсация, 4-оксо-4Н-хромен-3-карбоксальдегид, ЯМР  $^1\text{H}$ - и  $^{13}\text{C}$ -спектры, двумерные спектры COSY ( $^1\text{H}$ - $^1\text{H}$ ) и НМҚС ( $^1\text{H}$ - $^{13}\text{C}$ ), антирадикальная активность.

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**ESTABLISHMENT OF OIL DISPERSED SYSTEMS BY  
THE PARAMAGNETIC PROBE AND FREE RADICALS**

**Abstract.** We managed to establish experimentally existence of disperse particles of resinous asphaltene substance (RAS) in crude oil. The EPR spectra of nitroxyl in the oils of the Caspian region were studied, and as it can be seen, the component  $m_z=-1$  splits into two lines. Heating up to 100 °C leads to disappearance extreme components which after cooling of a sample to room temperature appears only after long upholding (not less than 2 h). This phenomenon is connected with heterogeneity of oil, that is with existence in it of considerable number the asphaltene particles. This phenomenon is associated with the heterogeneity of oil, that is, with the presence in it of a significant number of resin-asphaltene particles. At low concentrations of RAS in oil, they are molecularly dispersed and the molecules of the dissolved RAS freely move in the oil independently of each other. With a significant content of RAS in the oil micelles are formed. Particles of nitroxyl radicals are adsorbed on RAS micelles. Non-adsorbed particles of nitroxyl radicals chaotically move in the dispersive environment of oil. Two such different conditions of the nitroxyl radical in oil are in thermodynamic balance.

In low viscosity oils (Tengiz) where RAS is molecularly dispersed, particles of dissolved nitroxyl radicals move freely, and in the EPR spectrum we can observe three lines of them with the same intensities.

**Keywords:** paramagnetic probe, oil heterogeneity, free radical, disperse systems, adsorption.

As it is known from the literature data [1,2], resinous-asphaltene substances (RAS) of oil are dispersed particles. They are an element of the structure of mainly spherical shape, capable of independent existence in these conditions. The inner region (core) and the solvate shell surrounding the core are distinguished in the composition of the dispersed particle. The inner region of RAS is represented by a supramolecular structure consisting of molecules most prone to the association process. It can be asphaltene. In turn, asphaltene is the main source of the so-called "coal" (free) radical, which is fixed in the EPR spectrum of the viscous oil field Zhubantam (pic. 16) between the lines of nitroxyl  $m_z=0$  и  $m_z=-1$ .

Nasirov R. N. applied the method of paramagnetic probe [3] to assess the viscosity of the Caspian region oils [4].

There is a connection between the rotational mobility of stable nitroxyl radicals and viscosity, which is determined by the Stokes-Einstein equation:

$$\tau_c = (4\pi/3kT)\alpha^3\eta \quad (1)$$

where  $\tau_c$  - the correlation time of rotational mobility;  $\eta$  - dynamic viscosity of the medium;  $\alpha$  - effective hydrodynamic radius of the radical;  $k$  - Boltzmann constant;  $T$  - temperature.

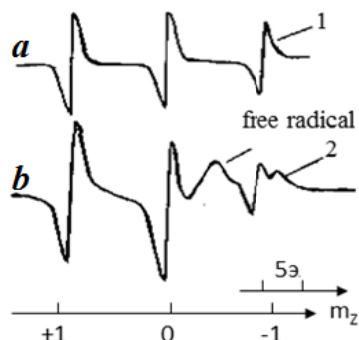
Value  $\tau_c$  determined from the ratio

$$\tau_c = 6,65\Delta H_{+1}(\sqrt{I_{+1}/I_{-1}}-1)10^{-10} \quad (2)$$

where  $I_{+1}$  - is the intensity of the components of the hyperfine structure (HFS), the corresponding value of the projection of the mechanical moment of the nucleus in the direction of the external magnetic field



$m_z=+1$ ;  $I_1$ - the intensity of the STS component corresponding to the value of  $m_z=-1$ ;  $\Delta H$ - line width corresponding to  $m_z=+1$ . Picture 1 shows the EPR spectra of nitroxyl (2,2,6,6-tetrametil-4-oxopiperidine-1-oxyl) in oil fields Kotyrtas and Zhubantam. Nitroxyl was injected into the oil in dry form and dissolved with prolonged stirring (nitroxyl concentration -  $10^{-3}$  mole/l).

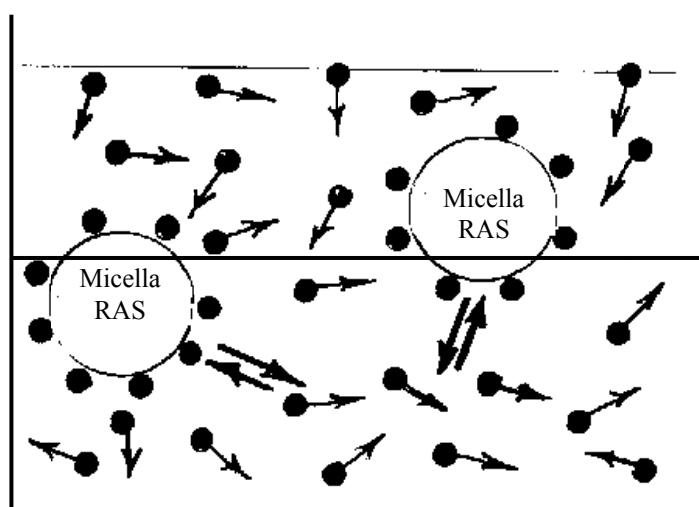


Picture 1- The EPR spectra of nitroxide at a temperature of 25°C in oils:  
a – from Kotyrtas, b – from Zhubantam

As can be seen from the EPR spectra (pic. 1), relation  $I_{+1}/I_1$  varies dramatically depending on the field, due to the different viscosity of these oils.

In this paper, the colloidal structure of oil disperse systems is established using a paramagnetic probe and free radicals.

As can be seen from pic.1b, component  $m_z=-1$  is split into two lines. Heating up to 100°C leads to the disappearance of the extreme component, which appears only after a long settling (at least 2H), through the cooling of the sample to room temperature. This phenomenon is due to the heterogeneity of oil, that is the presence of a significant number of RAS particles in it. At low RAS concentrations in oil, they are dispersed and the dissolved RAS molecules move freely in the oil independently. With a significant content of RAS comes formation of micelles (pic. 2). On the surface of RAS micelles goes the adsorption of nitroxyl radicals particles. Unadsorbed particles of nitroxyl radicals randomly move in the dispersion medium of oil. Two such different states of nitroxyl radical in oil are in thermodynamic equilibrium. In low-viscosity oils (Tengiz, well 38 and Chingiz, well 12), where RAS are molecularly dispersed, the particles of dissolved nitroxyl radicals move freely, and we observe three lines with the same intensities (isotropic spectrum) in the EPR spectrum. Adsorption of nitroxyl on these dispersed RAS particles leads to the change of g-factor and  $\alpha_N$  nitroxyl. When heated, the adsorption layer is destroyed, and then slowly restored.



Picture 2- Colloidal structure of oil, which is established by the method of paramagnetic probe: ● - nitroxyl particles adsorbed on the surface of RAS oil micelles; ●→ - dissolved nitroxyl particles in oil dispersion medium

Thus, the EPR method was able to experimentally establish the presence of RAS dispersed particles in crude oils of Kazakhstan with the help of a paramagnetic probe and FR, and the dynamics of the structure of their models was also confirmed.

Table 1 shows the content of asphaltenes, resins, FR and the value of the radical rotation correlation time of  $\tau_c$  obtained by formula (2) in crude oils of Western Kazakhstan. The region of the slow rotation of nitroxyl  $1,0 \cdot 10^{-8} - 1,4 \cdot 10^{-8}$  is observed in oils with a high content of RAS and FR, constituting the dispersed phase, and the region of fast rotations of nitroxyl  $\tau_c < 2 \cdot 10^{-11}$  (Chingiz oil) corresponds to the low content of resins and asphaltenes ( $< 0,2\%$ ). In low-viscosity oils (Tengiz), where RAS are molecularly dispersed, the particles of dissolved nitroxyl radicals move freely, and we observe three lines with the same intensities (isotropic spectrum) in the EPR spectrum. In the latter case, crude oils approach to become true solutions.

Table 1 - The content of the RAS, FR and the value of  $\tau_c$  in some crude oils of Western Kazakhstan

Field, well number	Content, %		$\tau_c \cdot 10^{10}, c$	CP $\cdot 10^{-17}, \text{spin/g}$
	silica resin	asphaltenes		
Karazhanbas, 850	17,4	6,40	14,5	31
Zhubantam, 14	15,2	3,40	13,0	13,3
Uzen, 5118	20,1	0,70	5,5	15,9
Zaburun, 11	8,8	0,30	4,9	6,3
South-East Kamishitov, 4	8,7	0,20	2,3	4,9
South-West Kamishitov, 118	2,5	следы	1,0	0,2
Kotyrtas, 28	7,2	0,28	1,8	3,3
Tengiz, 38	2,3	0,18	0,3	1,5
Chingiz, 12	следы	0,2	0,2	0,4

## EXPERIMENTAL PART

EPR spectra of oil samples were taken on the E-12 spectrometer of "Varian" at room temperature [5]. Oil samples before the analysis were purified from associated water and mechanical impurities by centrifugation (centrifuge T-22) at a speed of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length. We have found EPR signals from both vanadium and FR ions in the oils of the studied fields. To determine the concentration, the most intense hyperfine structure (HFS) line from the complexes of tetravalent vanadium and a single line from FR were used. Urichtausk oil (from well 8) with known vanadium ( $27,6 \text{ г/т}$ ) and FR ( $7,8 \cdot 10^{17} \text{ spin/sm}^3$ ) content was taken as the concentration standard. Nitroxyl was injected into the oil in dry form and dissolved with prolonged stirring.

## CONCLUSIONS

Thus, the method of paramagnetic probe and free radicals was able to experimentally determine the presence of dispersed particles of RAS in crude oils. Free radical in oils does not affect the accuracy of determination  $\tau_c$ , since it is fixed in the EPR spectrum of nitroxyl between the lines  $m_z=0$  and  $m_z=-1$

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### ПАРАМАГНИТТИ ЗОНДЫ ӘДІСІМЕН ЖӘНЕ БОС РАДИКАЛ КӨМЕГІМЕН МҰНАЙДЫҢ ДИСПЕРСТІ ҚҰРЫЛЫМЫН АНЫҚТАУ

**Аннотация.** Біз шикі мұнайдағы ШАЗ дисперсті бөлшектерінің болуын эксперименталды түрде анықтадық. Каспий маңы аймағындағы мұнайлардағы нитроксил радикалының  $m_z = -1$  сызығы екі сызыққа

ыдырайды. Бұл сызықтар 100°C дейін қыздырғанда, бір сызыққа бірігеді, ал одан кейін бөлме температура-сында екі сағат шамасында екі сызыққа бөлінеді. Бұның себебі мұнайдың құрамындағы шайыр асфальтен затына ғана байланысты. Шайыр асфальтен заттарының едәуір дәрежесінде ШАЗ мицеллі түзіледі. ШАЗ мицеллінде нитроксил радикалдары адсорбцияланады. Адсорбцияланбаған бөлігі мұнайдың дисперсті ортасында хаосты қозғалады. Осындай нитроксил радикалдың екі күйі бір-бірімен термодинамикалық тепе-тендікте болады.

Тұтқыр емес мұнайларда (Теңіз) ШАЗ молекулаулары дисперсті болады. Сондықтан да нитроксил радикалдары еркін қозғалыста болады. Соның нәтижесінде біз ЭПР спектрінде үш бірдей сызықтан тұратынын көреміз.

**Түйін сөздер:** парамагнитті зонд, мұнайдың гетерогендігі, бос радикал, дисперсті жүйелер, адсорбция.

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### УСТАНОВЛЕНИЕ НЕФТЯНЫХ ДИСПЕРСНЫХ СИСТЕМ С ПОМОЩЬЮ ПАРАМАГНИТНОГО ЗОНДА И СВОБОДНЫХ РАДИКАЛОВ

**Аннотация.** Нам удалось экспериментально установить наличие дисперсных частиц смолисто-асфальтовых веществ (САВ) в сырых нефтях. Изучены ЭПР спектры нитроксила в нефтях Прикаспийского региона, и как видно компонента  $m_z = -1$  расщеплена на две линии. Подогрев до 100°C приводит к исчезновению крайней компоненты, которая после охлаждения образца до комнатной температуры появляется лишь после длительного оттаивания (не менее 2ч). Это явление связано с гетерогенностью нефти, то есть с наличием в ней значительного числа смолисто-асфальтовых частиц. При малых концентрациях САВ в нефти они молекулярно дисперсны и молекулы растворенного САВ свободно перемещаются в нефти независимо друг от друга. При значительном содержании САВ в нефтях образуются мицеллы. На мицеллах САВ адсорбируются частицы нитроксильных радикалов. Неадсорбированные частицы нитроксильных радикалов хаотично движутся в дисперсионной среде нефти. Два таких разных состояния нитроксильного радикала в нефти находятся в термодинамическом равновесии.

В маловязких нефтях (Тенгиз) где САВ молекулярно дисперсны, частицы растворенных нитроксильных радикалов свободно перемещаются, и в спектре ЭПР мы наблюдаем от них три линии с одинаковыми интенсивностями.

**Ключевые слова:** парамагнитный зонд, гетерогенность нефти, свободный радикал, дисперсные системы, адсорбция.

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## **MODELING PROCESS OF SYNTHETIC LIQUID HYDROCARBONS FUEL PRODUCTION BY COMBINED STEAM-DRY REFORMING OF METHANE OVER Co-CONTAINING MULTICOMPONENT CATALYST**

**Abstract.** The paper is devoted to modeling the stages of a two-step technology proposed by authors for synthetic liquid hydrocarbons (SLH) production from syngas produced by bireforming of methane – combined steam and dry reforming of methane over own developed catalyst. In both processes: bireforming of methane and Fischer – Tropsch synthesis, the samples of the same catalyst containing cobalt, modified by additives of the transition metals of Groups IV<sup>th</sup> and VIII<sup>th</sup> of the Periodic Table and supported on alumina – 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> have been long-term tested (> 100 hours in each process). The obtained experimental results were used as the basis for calculations at modeling the technological circuit for both processes. As software, Aspen HYSYS was used. In the paper, the modeled technological circuits of syngas production by bireforming of methane and production of synthetic liquid hydrocarbons from syngas over the developed catalyst are presented; the material and heat balances obtained at modeling technology are included too.

**Keywords:** Modeling; Catalyst; Combined Steam-Dry Reforming of Methane; Syngas; Synthetic Liquid Hydrocarbons.

### **1 INTRODUCTION**

Due to the growth of Earth's population and economic development, the demand for energy sources is significantly increasing. That requires searching the new and that is more important the clean energy sources to reduce the negative impact on the environment. Thanks to the larger amount, availability, versatility and less environmental impact, natural gas is becoming the most desirable type of raw material compared to other fossil fuels [1]. Thus, International Energetic Agency (IEA) made forecast that global production of natural gas can be increased by 55% from 2010 to 2035 year [2]. At present time, increasing of global reserves of natural gas/methane occurs, that caused by high rate of exploration and particularly by contribution of shale gas. However, a significant amount of the world's natural gas reserves remain difficult to recover or are located in remote places. Monetization of such reserves is an important task for gas producers and demands for major investments into organization of industry and export/transportation infrastructure [4].

Transportation of energy raw materials in liquid form by oil tankers, rail and road transport is an economical way. However, the large amount of natural gas remaining after compression, even under high pressure, makes it difficult to store and transport over long distances. One of the ways to solve this problem is the GTL technology. GTL is the chemical transformation of gas (methane) into heavier hydrocarbons, which are in a liquid state under atmospheric pressure and can be easily transported [5, 6].

Over the past three decades, GTL technologies have been further developed and allow to the gas producers to expand and diversify their markets through various types of high-quality liquid motor fuels [7], in particular, diesel and jet fuels. The diesel fuel produced by the GTL process has a significantly higher quality than that produced during the processing of crude oil. So, its cetane number is at least 70 compared to 45-55 for most conventional fuels, low sulfur content (less than 5 ppm) and aromatic hydrocarbons (less than 1%) [8]. The global demand for diesel fuel tends to grow and is projected to increase from 25 million to 37 million barrels per day from 2011 to 2035 [9]. Technology of GTL can contribute in meeting this demand.

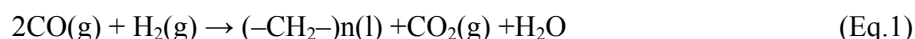
As a rule, the GTL technologies include three main stages [10]:

1. Production of syngas by catalytic interaction of methane with oxygen containing agent (processes of partial oxidation of methane or steam and bireforming of methane). Ratio of hydrogen to carbon monoxide in syngas produced is varied depending on feed composition;

2. Catalytic Fischer–Tropsch synthesis (FTS) – syngas conversion in FTS reactors of various construction into a wide range of aliphatic hydrocarbons (synthetic oil);

3. Cracking – transformation of the heavy hydrocarbon obtained into high-quality products: naphtha, diesel fuel, lubricants.

Fischer–Tropsch synthesis occurs accordingly to the following reaction (Eq.1):



FTS is highly exothermic process ( $140\text{--}160 \text{ kJ/mol}^{-1}$  of converted CO) and is accompanied by the formation of some amount of carbon dioxide and water along with the production of liquid hydrocarbons [11]). The main FTS reactions compete with methanation (Equation 2) and reactions leading to the formation of propane and butane (LPG), which are very exothermic:



In order to ensure the preferential running of the FT reaction, the synthesis is carried out at low temperatures:  $220\text{--}350^\circ\text{C}$ ; pressure:  $2\text{--}3 \text{ MPa}$  over the carefully selected catalysts (usually cobalt or iron) in reactors that promotes the growth of long-chain hydrocarbons. Nowadays, only Sasol and Shell have constructed the large-scale industrial plants – Oryx and Pearl, respectively.

There are two main categories of FTS technologies – high and low temperature synthesis, which differ in type of applied catalyst – Fe and Co respectively, composition and distribution of the products [12–14]. Commonly the yield of diesel fuel at FTS plants is about 70% that is much higher than for processing crude oil – about 40% [15]. A great advantage of FTS technologies is their focus exclusively on producing the high-value light and medium distillates, in contrast to traditional oil refining, where a significant amount of low-value fuel oil is formed. The proportion of middle distillates in the products composition is about a third higher than for conventional refining [16].

The main ways of syngas producing are partial oxidation, auto thermal reforming, and combined steam-dry reforming of methane [17–20]. Disadvantage of first two processes is high dilution by nitrogen both of the inlet gas stream and the final reforming products, when air is used as an oxidant; in case of pure oxygen use, the need of its extraction from the air and storage is appeared. It is economically unprofitable and technically unsafe. As for the processes of dry and steam reforming, the  $\text{H}_2/\text{CO}$  ratio in the resulting synthesis gas is lower ( $<2$ ) or higher ( $>3$ ) respectively than the optimum ratio for FTS.

One of the ways for production of syngas with required composition is combination of steam and dry reforming, the so-called bireforming of methane. Its main disadvantage is strong endothermicity and, as a result, high energy intensity of process as a whole. That can be compensated by integration of energy streams of natural gas reforming reactor (endothermic process) and of Fischer–Tropsch reactor (exothermic process). In general, bireforming process has the following essential advantages:

- 1)  $\text{H}_2/\text{CO}$  ratio of obtained syngas can be optimized for the specific catalyst;
- 2) carbon dioxide and water formed in Fischer–Tropsch process can be recycled to the process of syngas production;
- 3) opportunity to utilize the alternative sources of carbon, like biogas.

Currently, to solve the issue of the appropriateness of the use of various technological processes and schemes, the various software products developed by companies or researchers for their own and/or commercial needs are widely used [21]. The Aspen HYSYS and Aspen Plus packages are the most common used software. These software products are used to scale the processes studied in the laboratory as well as to determine the feasibility of their commercialization, and to find ways to optimize existing technological processes.

The present work deals with simulation of technology for two stages of GTL process: production of syngas by bireforming of methane and production of synthetic liquid hydrocarbons by Fischer–Tropsch synthesis over the developed Co-containing catalyst using software package Aspen HYSYS.

## 2 EXPERIMENTAL

To simulate both the syngas production by bireforming of methane and the production of synthetic liquid hydrocarbons by conversion of syngas formed at the first step over the developed Co-containing catalyst, the software package ASPEN HYSYS was used. It includes five modes for modeling of chemical reactions proceeding (so called types of reaction), which are differed by type of incoming data:

- **conversion reaction** – for this type of reaction, the stoichiometry of reaction and conversion degree of base component on reactor's outlet are specified;

- **equilibrium reaction** – equilibrium constant is specified as temperature function either as formula or as table;

- **kinetic reaction**, including three options – the parameters are kinetic data (the reaction orders by reactants, the constants of direct and reverse reactions, the appropriate activation energies and pre-exponential factors).

Due to absence of data on kinetic parameters of processes studied to simulate both bireforming and Fischer–Tropsch synthesis the first type of reaction was chosen – *Conversion reaction*. In process of modeling, a number of assumptions were made: all reagents are chemically pure and carbon deposition is absent. The last assumption based on the fact that catalyst studied in dry reforming of methane (more active process towards carbon deposition compared to other type of methane conversion) did not demonstrate decrease in its activity during continuous long-term testing for more than 100 hours.

For modeling, the data obtained during testing the 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by impregnation method in both processes – the bireforming of methane and Fischer–Tropsch synthesis were used. Bireforming was carried out under the following conditions: CH<sub>4</sub>/CO<sub>2</sub> ratio on inlet of reactor was 1:1, steam amount – 25 vol.%, GHSV=1250 h<sup>-1</sup>, pressure – 1 atm, t = 700°C. The degrees of methane and carbon dioxide conversion are 94.8% and 61.7% respectively. FTS process was carried out under pressure of 1.0 MPa, temperature – 233°C, ratio of H<sub>2</sub>:CO=2:1, GHSV=4000 h<sup>-1</sup> over the fresh sample of the same catalyst.

## 3 RESULTS AND DISCUSSION

### 3.1 Technological scheme for combined steam-dry reforming of methane

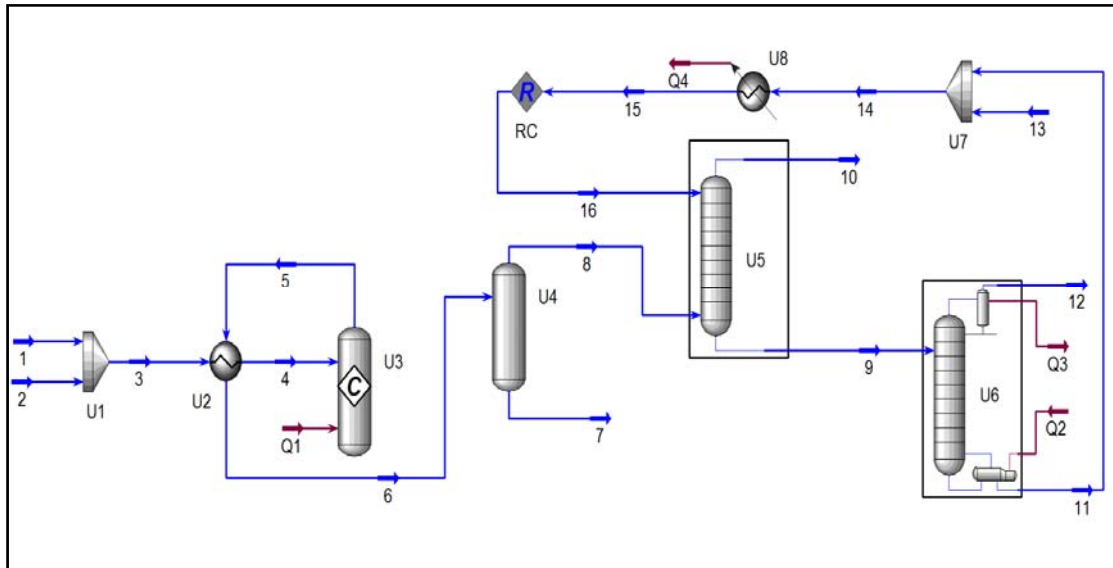
The technology of production and processing of synthesis gas has been modeled using Aspen HYSYS software and based on the general principles for calculations of the mass and energy balances of technological schemes. The software includes a set of auxiliary subsystems to provide the solutions for chemical-technological processes.

To make a model for combined steam-dry reforming of methane (bireforming of methane), the technological parameters corresponding to the experimental data obtained during the long-term testing of the 5% Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> catalyst for 100 hours were used. Also, the reactor-converter was used to simulate the technology.

In Figure 1, the technological scheme of synthesis gas production by bireforming of methane is presented. A model includes the following streams of products and energy described below.

Carbon dioxide and methane (1) enter the mixer U1 to be mixed with steam, part of which is returnable due to contribution of both unreacted water after the bireforming of methane as well as water formed after Fischer-Tropsch synthesis. Then, the mixture of gases (3) passes through the heat exchanger U2, where heat exchange takes place between the streams of the initial products (inlet) and the products after the reactor (outlet flow with temperature is about 700 ° C). After the heat exchanger U2, the heated mixture (4) enters an isothermal reactor U3 filled with the fixed bed catalyst – 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> heated by external energy flow Q1 to maintain the process temperature is about 700°C. Then, the hot gases (5) including reaction products – hydrogen and carbon monoxide as well as unreacted water, methane, and carbon dioxide are directed to the heat exchanger U2, where they are cooled and then stream (6) is sent to separator U4 for separation of unreacted water (7). The mix of gases (8) – hydrogen, methane, and carbon oxides are passed through the absorber U5 irrigated with a solution of monoethanolamine to absorb unreacted carbon dioxide and release synthesis gas with residues of unreacted methane (10), which is sent to the FTS reactor. The carbon dioxide enriched monoethanolamine solution (9) is sent to the regenerator U6, where it is separated into carbon dioxide (12) and the

monoethanolamine solution, then the latter is diluted with makeup water (13) to the desired concentration in the mixer U7, is cooled in the refrigerator U8, and is sent to the recycling RC to be reused in the absorber U5.



1 – methane and carbon dioxide; 2 – steam; 3 – steam-gas mixture; 4 – heated gas mixture;  
 5 – reaction products + unreacted raw materials; 6 – cooled products; 7 – condensate,  
 8 – raw synthesis gas, 9 – monoethanolamine saturated with carbon dioxide;  
 10 – synthesis gas purified from CO<sub>2</sub>; 11 – regenerated monoethanolamine; 12 – carbon dioxide; 13 – feed water; 14 –  
 monoethanolamine for recycling; 15 – cooled monoethanolamine; U1 – mixer, U2 – heat exchanger,  
 U3 – conversion reactor; U4 – separator; U5 – absorber; U6 – monoethanolamine regenerator; U7 – mixer;  
 U8 – refrigerator; Q1, Q2, Q3, Q4 – energy flows; RC – recycling

Figure 1 – Technological scheme for synthesis gas production by bireforming of methane

A summary mass balance for the synthesis gas production technology is given in Table 1.

Table 1 – Summary mass balance of technology for the synthesis gas production by bireforming of methane over the 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> catalyst

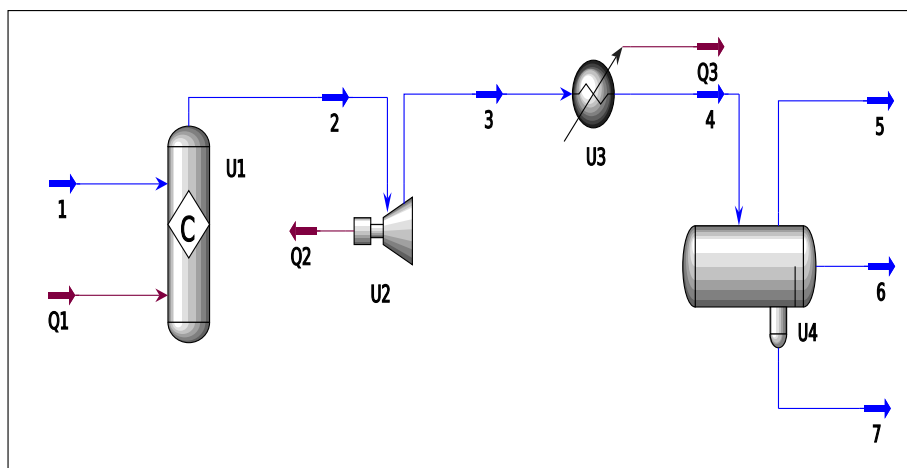
Input, Mass IN	Kg/h	Output, Mass OUT	kg/h
CO <sub>2</sub>	110.0243	CO <sub>2</sub>	0.4777
H <sub>2</sub> O	18.0151	H <sub>2</sub> O	0.1083
CH <sub>4</sub>	40.1073	CH <sub>4</sub>	2.0710
H <sub>2</sub> O(feed)	1.8015	H <sub>2</sub>	11.2978
		CO	107.9750
		Losses	48.0180
TOTAL	169.9482	TOTAL	169.9478
	100%		100%

### 3.2 Technological scheme for synthetic liquid hydrocarbon production by FTS

The synthesis gas (1) produced at the previous stage by the combined steam-dry conversion of methane enters the isothermal reactor U1 for Fischer-Tropsch synthesis. The mix of reaction products and unreacted reagents (2) pass through the expander U2, where the pressure is reduced to atmospheric one. After expander, the partially cooled mix of products (3) enters the refrigerator U3, then the cooled products (4) are sent to a three-phase separator U4, where the products are divided into three phases: gas (5), organic (6) and water (7) (Fig.2).

The main products of the Fischer-Tropsch synthesis are the C<sub>5+</sub> fraction – synthetic liquid hydrocarbons (SLH) mainly composed of n-alkanes. The selectivity of their formation is about 80%. Also, methane, water, C<sub>2</sub>-C<sub>4</sub> hydrocarbons, and carbon dioxide formed during FTS and unreacted hydrogen and carbon monoxide are presented in product flow after reactor.

The mass balance of the FTS reactor, where the process occurs over the 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> catalyst is presented in Table 2.



1 – synthesis gas produced at the previous stage; 2 – reaction products and unreacted substances; 3 – products under atmospheric pressure; 4 – cooled products; 5 – mix of hydrocarbons, unreacted synthesis gas, and CO<sub>2</sub>; 6 – C<sub>5+</sub> hydrocarbons, 7 – water; U1 – FTS reactor; U2 – expander; U3 – refrigerator, U4 – three-phase separator; Q1, Q2, Q3 – energy flows

Figure 2 – Technological scheme for Fischer-Tropsch synthesis

Table 2 – Mass balance of reactor for FTS over 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> catalyst

Input	Amount, Kg/h	Output	Amount, Kg/h
Hydrogen	13.4400	Hydrogen	1.7898
Carbon monoxide	93.3697	Carbon monoxide	18.6737
		Carbon dioxide	0.9699
		Methane	2.6855
		Water	47.2464
		ΣC <sub>2</sub> -C <sub>4</sub>	2.7634
		ΣC <sub>5+</sub>	32.6786
TOTAL	106.8097	TOTAL	106.8073

In Table 3, the energy balance of the Fischer-Tropsch synthesis reactor is given.

Table 3 – Energy balance of reactor for FTS over 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub>

Input	MJ/h	%	Output	MJ/h	%
H <sub>2</sub> +CO	312.2398	33.82	Gases	118.9012	12.88
Q <sub>1</sub>	442.5103	47.92	SLH	60.7977	6.58
Q <sub>2</sub>	31.3409	3.39	Water	743.6607	80.54
Q <sub>3</sub>	137.2686	14.87			
TOTAL	923.3597	100	TOTAL	923.3597	100

Thus, the simulation of the two main stages of the GTL process – the production of synthesis gas and its processing including calculations of mass and energy balances confirms the high efficiency of the proposed technology for the production of synthetic liquid hydrocarbons over the developed – 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub>.



## CONCLUSION

Earlier by means of Aspen HYSYS software, the authors have simulated the process of methane bireforming over the 5%Co-M(9:1)/Al<sub>2</sub>O<sub>3</sub>-5%REE-1 catalyst performed the high degrees of methane and carbon dioxide conversion [22]. In present work, bireforming was modeled using another Co-containing catalyst showed lower conversion both of methane and carbon dioxide – 94.8% and 61.7% respectively at 700°C. In addition, Fischer–Tropsch synthesis over the same catalyst was modeled.

As a first approximation, the simulated technology for the two-stage production of synthetic liquid hydrocarbons from syngas obtained by bireforming of methane using developed catalyst – 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> demonstrates its viability. Such technology is applicable in remote areas of gas production. Liquid hydrocarbons formed consist mainly of n-alkanes. The fraction corresponding to diesel fuel is a final commercial product. The resulting liquid products can be easily transported to places where they can be further refined.

In the future, it is planned to combine the two stages – production of syngas and its conversion by FTS into one integrated technological scheme including the step of compression of the syngas obtained at first stage up to pressures required to perform FTS over the developed catalyst/catalysts.

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### СО ҚҰРАМДЫ КӨПКОМПОНЕНТТІ КАТАЛИЗАТОРДА МЕТАННЫҢ БУЛЫ КӨМІРҚЫШҚЫЛДЫ РИФОРМИНГІМЕН ЖҮРЕТІН ССК ӨНДІРІС ТЕХНОЛОГИЯСЫН МОДЕЛДЕУ

**Аннотация.** Бұл жұмыс авторлармен ұсынылған жеке катализаторлардың қолданылуымен метанның біріктірілген – булы көмірқышқылды және булы риформингі жолымен алынатын синтез-газдан синтетикалық сұйық көмірсутектерді (ССК) өндіру технологиясының екі сатысының әрқайсын моделдеуге арналған. Екі процесте де (метанның көмірқышқылды конверсиясы және Фишер-Тропш синтезі) алюминий тотығына қондырылған және периодтық жүйенің 4 және 8-ші топ ауыспалы металдар қоспасымен модифицирленген кобальт негізіндегі жалғыз катализатор 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub> ұзақ және үздіксіз (әрбірі 100 сағаттан артық) тестілеуден өтті. Алынған тәжірибелік нәтижелер әрбір процестерге арналған технологиялық сұлбаны моделдеу кезінде есептеулердің негізіне енгізді. Бағдарламалық қамтамасыз ету ретінде Aspen HYSYS өнімі қолданылған болатын. Жұмыста жасалған катализаторда метанның булы көмірқышқылды риформингі жолымен синтез-газды өндірудің және синтез-газдан синтетикалық сұйық көмірсутектерді алудың технологиялық сұлбасы келтірілген, моделдеу барысында алынған материалдық және жылулық баланс есептелген.

**Түйін сөздер:** Моделдеу; Катализатор; Метанның Булы көмірқышқылды Конверсиясы; Синтез-газ; Синтетикалық Сұйық Көмірсутектер.

УДК .001.57; 665.644.4; 547.211; 546.264-31

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### МОДЕЛИРОВАНИЕ ТЕХНОЛОГИИ ПРОИЗВОДСТВА СЖУ ПУТЕМ ПАРОУГЛЕКИСЛОТНОГО РИФОРМИНГА МЕТАНА НА СО-СОДЕРЖАЩЕМ МНОГОКОМПОНЕНТНОМ КАТАЛИЗАТОРЕ

**Аннотация.** Работа посвящена моделированию стадий предлагаемой авторами двухстадийной технологии производства синтетических жидких углеводородов (СЖУ) из синтез-газа, получаемого путем пароуглекислотного риформинга метана – комбинированный углекислотный и паровой риформинг метана, с применением собственных катализаторов. В обоих процессах: пароуглекислотная конверсия метана и синтез Фишера-Тропша, длительно и непрерывно (более 100 часов в каждом процессе) тестировались образцы одного и того же катализатора на основе кобальта, модифицированного добавками переходных металлов 4-ой и 8-ой групп Периодической системы, нанесенного на оксид алюминия – 5%Co-M1-M2/Al<sub>2</sub>O<sub>3</sub>. Полученные экспериментальные данные легли в основу расчетов при моделировании технологической

схемы каждого процесса. В качестве программного обеспечения был использован продукт Aspen HYSYS. В работе приведены технологические схемы производства синтез-газа путем пароуглекислотного риформинга метана и получения синтетических жидких углеводородов из синтез-газа на разработанном катализаторе, рассчитаны материальные и тепловые балансы, полученные в ходе моделирования.

**Ключевые слова:** Моделирование; Катализатор; Пароуглекислотная Конверсия Метана; Синтез-Газ; Синтетические Жидкие Углеводороды.

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## NEWS

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## SYNTHESIS AND MICROBIOLOGICAL EVALUATION OF ACETYLENIC AMINO ALCOHOLS N-PHENYL CARBAMATE DERIVATIVES

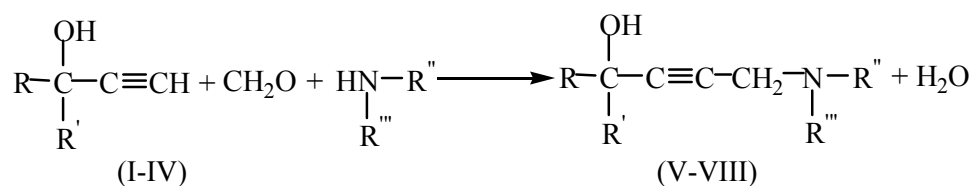
**Abstract.** The paper presents the results of synthesizing of acetylenic amino alcohols N-phenyl carbamate derivatives and the microbiological evaluation of the latter has been studied. The following microorganisms were considered as objects of microbiological research: *Bacillus subtilis*, *Botrytis cinerea*, *Echerchia coli*, *Ervinia caratovororum*, *Candida albicans*, *Fusarium solani* u *Helminthosporium*. There were researched physicochemical and bactericidal properties of acetylenic amino alcohols N-phenyl carbamate derivatives. The output of carbamates depends on the content and structure of acetylenic amino alcohols and is 68-88%. The purity, identification and structure of the compounds obtained been has determined by thin-layer and gas-liquid chromatography, elemental analysis, IR (Infrared) and PMR (Proton Magnetic Resonance) spectroscopy. It established that these compounds exhibit high antimicrobial activity against the causative agents of certain animal and plant diseases. The relatively high microbiological activity of the phenylcarbamates studied is associated with the presence of various functional groups in the composition of the molecules.

**Key words:** carbamates, acetylene amino alcohols, bactericidal properties, microorganisms, microbiological activity.

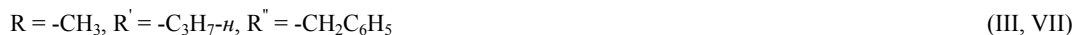
**Introduction.** Obviously, the search for biologically active compounds is an actual problem of organic chemistry, biological chemistry and pharmacology. Because the efficiency and environmental safety of currently used compounds do not fully meet modern requirements [1-3].

Continuing our work in this direction [4,5], we synthesized a number of acetylenic amino alcohols, obtained N-phenyl carbamate derivatives and studied the antimicrobial activity of the latter.

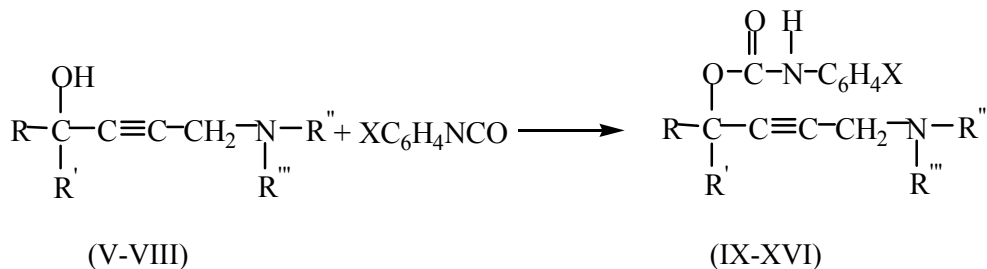
**Methods.** Acetylenic alcohols were synthesized by the well-known Favorsky reaction [6] and obtained a series of amino acids by aminomethylation with dibenzylamine under the reaction conditions of Mannich [7] in the presence of formaldehyde:



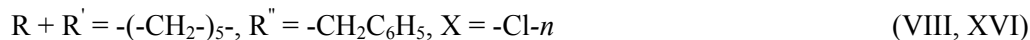
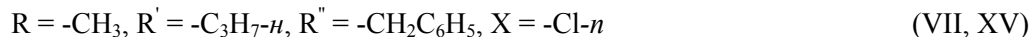
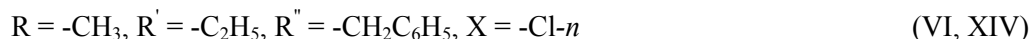
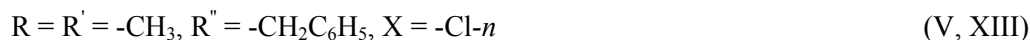
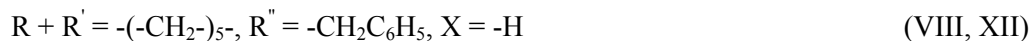
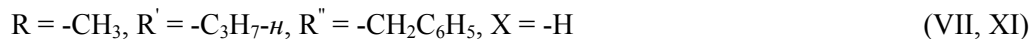
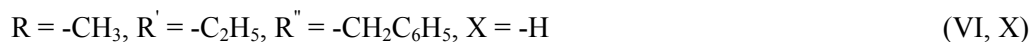
where:



The obtained amino acids reacted with phenyl and p-chlorophenyl isocyanate for 3-5 hours in an environment of benzene (between 70-80°C) or in an environment of acetone (boiling point). The reaction proceeds as follows:



where:



The yield of carbamates varied from 68 to 88%, depending on the structure and composition of acetylene amino alcohols. The purity, individuality and structure of the obtained compounds were determined by thin layer and gas chromatography, as well as by elemental analysis using IR and PMR spectra [8,9]. Synthesized carbamates are white needle-like crystals that dissolve in polar organic solvents.

**Results and discussions.** The main lines and physicochemical characteristics of the IR and PMR spectra of new carbamates are given in Tables 1 and 2.

As can be seen from Table 1, acetylenic amino acids are not absorbed by the hydroxyl group in the IR spectra (in the range of ~ 3600 cm<sup>-1</sup>), but in the carbonyl group (in the range of 1730 cm<sup>-1</sup>) and absorption bands on the aromatic rings.

Also, acetylenic amino acids are clearly visible in the absorption bands (IR spectra) and chemical shift lines (PMR spectra) characteristic of functional groups and compounds that determine the composition of carbamates.

White or light yellow crystals, dissolved in many organic solvents, have a weak characteristic of these compounds (Tables 2,3). It is known that the presence of several functional groups in a molecule can give the molecule exceptional properties and increase its biological activity. From this point of view, it was particularly interesting to determine the microbiological activity of carbamates from acetylenic amino alcohols, taking into account the biological, in particular, testing ease and low cost.

To detect microbiological activity, we investigated a number of new carbamates and thiocarbamates using certain methods [10-12]. From the results it can be seen that almost all investigated compounds showed a certain degree of microbiological activity.

For example, were obtained the result of the antimicrobial activity of 1-cyclohexyl-3-diethylaminoprop-3-yl-1-yl ester is given under the name AA-008 - N-phenylcarbamic acid and -2-methyl-5-dibenzylaminopent-3-yl-2-phenylcarbamate, conditionally called AA-007 - N-phenylcarbamic acid.

For conducting microbiological tests, the obtained 1% solution of AA-007 and AA-008 preparations in ethyl alcohol (1:1 ratio of ethyl alcohol and water) were used, using serial dilution of solutions of 0.05% to 0.0001%.

Table 1 - IR and PMR spectra of carbamates from acetylenic amino alcohols

Number of compounds	IR spectra (KBr), $\nu$ , $\text{cm}^{-1}$	PMR spectra, ( $\text{CDCl}_3$ ), $\delta$ , ppm
(IX)	2190 ( $\text{C}\equiv\text{C}$ ); 3300 ( $\text{N-H}$ ); 1180 ( $\text{C-O-C}$ ); 1755 ( $\text{C=O}$ ); 2920 ( $-\text{CH}_2-$ ); 1580 ( $-\text{C}_6\text{H}_5$ )	0,91 t 3H( $\text{CH}_3$ ); 1,21 t 3H( $\text{CH}_3$ ); 1,37 m 2H( $\text{CH}_2$ ); 2,57 t ( $\text{C-N}$ ); 2,60-2,71 m (cycle H); 3,52 t ( $\text{C-O}$ )
(X)	2195 ( $\text{C}\equiv\text{C}$ ); 3310 ( $\text{N-H}$ ); 1170 ( $\text{C-O-C}$ ); 1745 ( $\text{C=O}$ ); 2930 ( $-\text{CH}_2-$ ); 1585 ( $-\text{C}_6\text{H}_5$ )	0,93 t 3H( $\text{CH}_3$ ); 1,20 t 3H( $\text{CH}_3$ ); 1,37 m 2H( $\text{CH}_2$ ); 2,58 t ( $\text{C-N}$ ); 2,60-2,71 m (cycle H); 3,53 t ( $\text{C-O}$ )
(XI)	2195 ( $\text{C}\equiv\text{C}$ ); 3320 ( $\text{N-H}$ ); 1190 ( $\text{C-O-C}$ ); 1750 ( $\text{C=O}$ ); 2940 ( $-\text{CH}_2-$ ); 1583 ( $-\text{C}_6\text{H}_5$ )	0,90 t 3H( $\text{CH}_3$ ); 1,19 t 3H( $\text{CH}_3$ ); 1,35 m 2H( $\text{CH}_2$ ); 2,59 t ( $\text{C-N}$ ); 2,60-2,70 m (cycle H); 3,55 t ( $\text{C-O}$ )
(XII)	2198 ( $\text{C}\equiv\text{C}$ ); 3315 ( $\text{N-H}$ ); 1180 ( $\text{C-O-C}$ ); 1753 ( $\text{C=O}$ ); 2880 ( $-\text{CH}_2-$ ); 1575 ( $-\text{C}_6\text{H}_5$ )	0,92 t 3H( $\text{CH}_3$ ); 1,22 t 3H( $\text{CH}_3$ ); 1,38 m 2H( $\text{CH}_2$ ); 2,58 t ( $\text{C-N}$ ); 2,61-2,71 t (cycle H); 3,55 t ( $\text{C-O}$ )
(XIII)	2200 ( $\text{C}\equiv\text{C}$ ); 3310 ( $\text{N-H}$ ); 1185 ( $\text{C-O-C}$ ); 1745 ( $\text{C=O}$ ); 2890 ( $-\text{CH}_2-$ ); 1580 ( $-\text{C}_6\text{H}_5$ )	0,93 t 3H( $\text{CH}_3$ ); 1,19 t 3H( $\text{CH}_3$ ); 1,37 m 2H( $\text{CH}_2$ ); 2,60 t ( $\text{C-N}$ ); 2,61-2,72 m (cycle H); 3,49 t ( $\text{C-O}$ )
(XIV)	2195 ( $\text{C}\equiv\text{C}$ ); 3313 ( $\text{N-H}$ ); 1190 ( $\text{C-O-C}$ ); 1740 ( $\text{C=O}$ ); 2890 ( $-\text{CH}_2-$ ); 1575 ( $-\text{C}_6\text{H}_5$ )	0,91 t 3H( $\text{CH}_3$ ); 1,21 t 3H( $\text{CH}_3$ ); 1,38 m 2H( $\text{CH}_2$ ); 2,59 t ( $\text{C-N}$ ); 2,60-2,71 m (cycle H); 3,54 t ( $\text{C-O}$ )
(XV)	2205 ( $\text{C}\equiv\text{C}$ ); 3315 ( $\text{N-H}$ ); 1195 ( $\text{C-O-C}$ ); 1742 ( $\text{C=O}$ ); 2910 ( $-\text{CH}_2-$ ); 1570 ( $-\text{C}_6\text{H}_5$ )	0,92 t 3H( $\text{CH}_3$ ); 1,21 t 3H( $\text{CH}_3$ ); 1,36 m 2H( $\text{CH}_2$ ); 2,56 t ( $\text{C-N}$ ); 2,60-2,70 t (cycle H); 3,55 t ( $\text{C-O}$ )
(XVI)	2201 ( $\text{C}\equiv\text{C}$ ); 3320 ( $\text{N-H}$ ); 1185 ( $\text{C-O-C}$ ); 1740 ( $\text{C=O}$ ); 2905 ( $-\text{CH}_2-$ ); 1570 ( $-\text{C}_6\text{H}_5$ )	0,91 t 3H( $\text{CH}_3$ ); 1,20 t 3H( $\text{CH}_3$ ); 1,38 m 2H( $\text{CH}_2$ ); 2,57 t ( $\text{C-N}$ ); 2,60-2,71 m (cycle H); 3,53 t ( $\text{C-O}$ )

Table 2 - Some physicochemical characteristics of carbamates from acetylenic amino alcohols

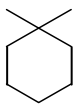

Number of compounds	Formula	Yield, %	$t^{\circ}_{\text{melting}}$ , $^{\circ}\text{C}$	$R_f$
IX	$\text{QCONHC}_6\text{H}_5$ $(\text{CH}_3)_2\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	61	101-102	0,63
X	$\text{QCONHC}_6\text{H}_5$ $\text{C}_2\text{H}_5(\text{CH}_3)\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	64	107-108	0,54
XI	$\text{QCONHC}_6\text{H}_5$ $\text{N}_3\text{H}_7(\text{CH}_3)\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	58	123-124	0,51
XII	$\text{H}_5\text{C}_6\text{NHOCO}$  $\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	52	135-136	0,39
XIII	$\text{QCONHC}_6\text{H}_4\text{Cl-}n$ $(\text{CH}_3)_2\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	53	156-157	0,43
XIV	$\text{QCONHC}_6\text{H}_4\text{Cl-}n$ $\text{C}_2\text{H}_5(\text{CH}_3)\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	49	163-164	0,38
XV	$\text{QCONHC}_6\text{H}_4\text{Cl-}n$ $\text{N}_3\text{H}_7(\text{CH}_3)\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	47	175-176	0,33
XVI	$n\text{-ClH}_4\text{C}_6\text{NHOCO}$  $\text{C}\equiv\text{C}-\text{CH}_2-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$	43	201-202	0,26

Table 3 - Elemental analysis of carbamates from acetylenic amino alcohols

Number of compounds	discovered, %			Gross formulas	calculated, %		
	C	H	N		C	H	N
IX	78,60	7,03	6,81	C <sub>27</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub>	78,64	6,79	6,79
X	78,94	7,12	6,68	C <sub>28</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub>	78,87	7,04	6,57
XI	79,31	7,37	6,49	C <sub>29</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub>	79,09	7,27	6,36
XII	79,76	7,21	6,30	C <sub>30</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub>	79,65	7,08	6,19
XIII	76,08	6,46	6,71	C <sub>27</sub> H <sub>27</sub> N <sub>2</sub> O <sub>2</sub> Cl	75,97	6,33	6,56
XIV	72,98	6,37	6,26	C <sub>28</sub> H <sub>29</sub> N <sub>2</sub> O <sub>2</sub> Cl	72,96	6,29	6,08
XV	73,40	6,58	6,08	C <sub>29</sub> H <sub>31</sub> N <sub>2</sub> O <sub>2</sub> Cl	73,34	6,53	5,90
XVI	74,09	6,42	5,86	C <sub>30</sub> H <sub>31</sub> N <sub>2</sub> O <sub>2</sub> Cl	73,99	6,37	5,75

The objects of the microbiological test are microorganisms *Bacillus subtilis*; *Botrytis cinerea*, *Echerchia coli*, *Ervinia caratovorom*, *Candida albicans*, *Fusarum solani* и *Helminthosporium*.

The test results showed that all studied compounds have a certain antimicrobial activity, which inhibits or even aggravates their growth. The results of microbiological testing of drugs AA-007, AA-008 are presented in Table 4.

Table 4 - Results of microbiological testing of synthesized carbamates

A drug	Test microorganisms	Drug concentration % (mass.)*				
		0,0001	0,001	0,005	0,01	0,05
AA-007	<i>Bacillus subtilis</i>	-	-	±	+	++
	<i>Botrytis cinerea</i>	-	-	+	+	++
	<i>Candida albicans</i>	-	±	+	+	++
	<i>Echerchia coli</i>	-	-	+	+	++
	<i>Ervinia caratovorom</i>	-	±	+	+	++
	<i>Fusarum solani</i>	±	±	+	+	++
	<i>Helminthosporium</i>	±	+	+	++	++
AA-008	<i>Bacillus subtilis</i>	-	-	±	+	++
	<i>Botrytis cinerea</i>	±	+	+	++	++
	<i>Candida albicans</i>	±	+	+	+	++
	<i>Echerchia coli</i>	±	+	+	+	++
	<i>Ervinia caratovorom</i>	±	±	+	+	++
	<i>Fusarum solani</i>	±	+	+	++	++
	<i>Helminthosporium</i>	±	+	+	++	++

\* - (-) – in this case, do not show biological activity; (±) - the zone for the removal of microorganisms does not exceed 5 mm; (+) - zone for the removal of microorganisms above 5 mm; (++) - zone for the removal of microorganisms above 10 mm

As can be seen from table 4, any of the phenylcarbates exhibits significant bactericidal activity against microorganisms at significantly lower concentrations.

At the same time, it is clear that the antimicrobial properties of these compounds definitely depend on their composition. For example, the bactericidal activity of the drug AA-008 is significantly higher than AAA-007.

In our opinion, this difference is due to the fact that the drug molecule AA-008 contains an alcohol fragment containing a ring group as a hexyl radical, since the other components of both drugs are the same.

**Conclusion.** The relatively high microbiological activity of the phenylcarbamate molecules under study may be due to the presence of a set of active functional groups, for example, if the interrelated chemical bonds with using unused electron pairs in outer electron shells ( $-C\equiv C-$ )  $\pi$ -electrons and several

heteroatoms (E, N, Cl) tend to donor-acceptor and chemical-coordinate bonds, methyl groups and carbocycles can enhance these properties and improve their interaction with receptors of microorganisms.

Compared with the current bactericidal activity, in most cases the priority of bactericidal activity of new compounds is observed.

The advantage of new bactericides is that they are obtained without any difficulties on the basis of the compounds obtained in the volume of production, the high bactericidal activity of their highly diluted solutions and the simplicity of their use.

In the case of using new compounds, the socio-economic benefits are as follows:

- well - completed seed stock in agriculture;
- protection against root diseases during the cultivation and development of crops;
- cost reduction during storage of agricultural products;
- reduce the cost of sanitizing the building, warehouses, various premises, securities, and so on, because solutions with a very low concentration are used due to the high bactericidal activity of AA-007 and AA-008;
- possibility of use as a solvent in technical waters of different hardness.

Thus, thanks to the aforementioned benefits, AA-007 and AA-008 and other drugs of the same type can be used in agriculture, medicine and sanitation.

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#### **АЦЕТИЛЕН АМИНСПИРТТЕРІ N-ФЕНИЛКАРБАМАТТАР ТУЫНДЫЛАРЫНЫҢ СИНТЕЗІ ЖӘНЕ МИКРОБИОЛОГИЯЛЫҚ БАҒАЛАУ**

**Аннотация.** Жұмыста бірқатар ацетилен аминспирттері синтезделіп, олардың N-фенилкарбаматтары алынды және соңғыларының микробтарға қарсы әрекеті зерттелді. Микробиологиялық сынақ объектілері ретінде *Bacillus subtilis*; *Botrytis cinerea*, *Echerchia coli*, *Ervinia caratovorom*, *Candida albicans*, *Fusarum solani* және *Helminthosporium* сынды микроорганизмдер қарастырылды. Ацетилен қатары аминспирттерінің N-фенилкарбаматтарының физика-химиялық және бактерицидтік қасиеттері зерттелген. Карбаматтардың шығымы ацетилен аминспирттерінің құрамы мен құрылысына байланысты 68-ден 88% аралығында болды. Алынған қосылыстардың тазалығы, даралығы, құрылысы жұқа қабатты және газсұйық хроматографиялық әдістері бойынша бақыланып, элементтік сараптау және ИҚ мен ПМР спектрлерін түсіру арқылы анықталды. Аталмыш қосылыстардың жануарлар мен өсімдіктер ауруларын қоздыратын микроағзаларға қарсы пәрменділігінің жоғары екендігі көрсетілген. Зерттелген фенилкарбаматтардың салыстырмалы түрде микробиологиялық белсенділіктерінің жоғары болуы молекулалары құрамында функционалдық белсенді топтардың болуына байланысты екендігі анықталды.

**Түйін сөздер:** карбаматтар, ацетилен аминспирттері, бактерицидтік қасиеттері, микроорганизмдер, микробиологиялық белсенділік.

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#### **СИНТЕЗ И МИКРОБИОЛОГИЧЕСКАЯ ОЦЕНКА ПРОИЗВОДНЫХ АЦЕТИЛЕНОВЫХ АМИНОСПИРТОВ N-ФЕНИЛКАРБАМАТОВ**

**Аннотация.** В работе представлены результаты синтеза производных ацетиленовых аминок спиртов N-фенилкарбаматов и дана микробиологическая оценка. В качестве объектов микробиологических исследований были рассмотрены микроорганизмы: *Bacillus subtilis*; *Botrytis cinerea*, *Echerchia coli*, *Ervinia caratovorom*, *Candida albicans*, *Fusarum solani* и *Helminthosporium*. Исследованы физико-химические и бактерицидные свойства N-фенилкарбаматов аминок спиртов ацетиленового спирта. Выход карбаматов зависит от содержания и строения ацетиленовых аминок спиртов и составляет 68-88%. Чистота, идентификация и строение полученных соединений определены тонкослойной и газожидкостной хроматографией, методами элементного анализа, ИК- и ПМР- спектроскопии. Установлено, что

указанные соединения проявляют высокую антимикробную активность против возбудителей некоторых болезней животных и растений. Относительно высокая микробиологическая активность исследованных фенолкарбаматов связана с наличием в составе молекул различных функциональных групп.

**Ключевые слова:** карбаматы, ацетиленовые аминоспирты, бактерицидные свойства, микроорганизмы, микробиологическая активность.

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## **FEATURES OF DISTRIBUTION OF THE PARAMAGNETIC CENTERS ON THE AREA OF THE EMBA REGION OIL DEPOSITS**

**Abstract.** In the oils of the studied deposits, we detected EPR signals both from vanadium ions and free radicals (FR). To determine their concentration, the most intense hyperfine structure (HFS) line was used among the complexes of tetravalent vanadium and a single line from the FR.

There are no noticeable changes in the density of oil and the content of vanadium (IV) in the studied wells from the area of the Jurassic deposits of the Kyrykmylytk field. It means that on the area, vanadium content in oil does not change, there is a good hydrodynamic communication between production wells, and the Kyrykmylytk field belongs to low-vanadium oils.

Uniform distribution of vanadium, is also established on the area of the Aptian, Albian and Cenomanian horizons of the Kara-Arna deposit and it characterizes the conditioned content of vanadium. Between the producing wells of each horizon there is observed a good hydrodynamic connection.

**Keywords:** complex of tetravalent vanadium, free radical, electronic paramagnetic resonance, hydrodynamic communication, conditioned content.

During the work [1], we found that in the Kalamkas field in the context of productive layers there is a clear distinction between two independent deposits by paramagnetic features and vanadium distribution (in the upper – 200g/t, in the lower -140g/t). This gave rise to the authors argue that the vanadium content is a reliable correlation feature that can be used in monitoring the development of oil reservoirs [2].

The study of the relationship between the content of stable free radicals and vanadium (IV) in oils with their physical and chemical characteristics in the area of deposits was carried out at the fields of the Emba region.

The interdependence between the content of vanadium (IV), FR and physico-chemical characteristics of the oils were studied on the area of the oil horizon for deposits Kyrykmylytk, Kara-Arna, Karsak and Iskene. Table 1 shows the results of the determination of vanadium (IV) in oils with different densities. Table 1 shows that the relationship between oil density and vanadium (IV) content is quite clear.

The analysis of paramagnetic features of the oils of Permo-Triassic deposits of the Iskene field showed that the oils of the southern and northern fields differ sharply in vanadium (IV) content. The industrial content of vanadium was found in the oils of the southern field (table 1). These oils are also characterized by high density and high sulfur content ( $S \geq 1$  %) in contrast to lighter and low-sulfur ( $S \geq 0,2$  %) oils of the northern field. This indicates various hypergenic changes in the oils of the southern and northern fields.

IV Albian horizon deposits of Karsak – the most significant in size, thickness and oil reserves. IV Albian horizon quality oil is divided into two types: west field - low-sulphur, resinous, paraffinic; east field - low-sulphur, low-resinous, high-paraffinic, oily. As can be seen from table 1, the average vanadium (IV) content in the oils of the IV Albian horizon of the western field is 3 times higher than in the oils of the IV Albian horizon of the eastern field. Such a difference in the area of this productive horizon oil

seems to be explained either by the losses of light oil fractions of the western field, or by their migration towards the eastern field.

Table 1 – Results of the study of correlations between density and vanadium (IV) content

Field	The number of the studied wells	Oil extraction interval, m	Horizon	Change interval	
				Density, g/cm <sup>3</sup>	Vanadium content, g/t of oil
Kyrykmylytk	8	911 – 943	Jurassic	0,8867 – 0,8919	2,38 – 3,38
Kara-Arna	11	1047- 1074	Aptian	0,9153	110,1
Iskene:					
south field	2	659-948	Permo-Trias	0,9294-0,9397	167,7-190,8
north field	6	704-773	Permo-Trias	0,7974-0,8144	0,7-1,3
Karsak:					
west field	2	472-782	IV albian	0,9051	9,2
east field	3	481-484	IV albian	0,8612	2,9

For the oil fields Kyrykmylytk, the relationship between FR and vanadium (IV) content, as well as physico–chemical characteristics (table 2) also established. As can be seen from table 2, the content of sulfur, resins, asphaltenes, as well as the density and viscosity of oils increases with the content of FR and vanadium (IV). There is an inversely proportional relationship between the content of FR and vanadium (IV) in oils and the yield of gasoline fractions. From the results of the analysis of the data given in table 1, it is also seen that with the increase in the depth and age of the oil, the vanadium (IV) and FR content naturally decreases. The highest content of vanadium (28 g/t) and FR falls on the Cretaceous oil horizon (table 2). Vanadium content is much higher in the lower Cretaceous deposits than in the Jurassic deposits. A similar change is characteristic of the FR. In Cretaceous sediment oils the concentration of FR is higher than in Jurassic sediments.

Table 2 - The interdependence between the content of vanadium (IV), FR and physico-chemical characteristics of low-vanadium oil from Kyrykmylytk field

Well number	Depth, m	Age	Vanadium content, g/t	FR·10 <sup>-17</sup> , spin/g	Density, g/cm <sup>3</sup>	Content, %			Fraction output up to 300 <sup>0</sup> C, %
						Sulfur	Resin	Asphaltenes	
11	389...396	Cret	23,2	9,2	0,927	0,35	20,0	2,56	24,1
15	930...931	J <sub>2</sub>	2,6	2,5	0,888	0,25	8,46	0,76	28,8
11	883...891	J <sub>2</sub>	3,3	3,6	0,887	0,39	9,01	0,29	32,3
16	469...477	Cret	17,9	5,9	0,914	0,38	14,1	1,19	15,2

At the studied wells on the area of Jurassic deposits of the field Kyrykmylytk, there are no noticeable changes in density of oil and the content of vanadium (IV) (table.1).

The uniform distribution of vanadium (IV) is also established on the area of the Aptian horizon of the Kara-Arna field with the help of oil samples obtained from 11 producing wells (wells 23, 25, 53, 57, 66, 68, 82, 86, 87, 90, 94) (table 1). For illustration, figure 1 shows the central parts of EPR spectra of oil samples of the Aptian horizon of the Kara-Arna field (wells 82, 57, 90, 53), taken at -196<sup>0</sup> C, containing one of the components of the hyperfine vanadium (IV) structure and the singlet from FR.

Table 3 – Change of paramagnetic properties of Kara-Arna oil field

The number of the studied wells	Oil extraction interval, m	Age	The average content of vanadium, g/t	FR·10 <sup>-17</sup> , spin/g
3	510-555	Cenomanian	60,08	8,36
4	967-983	Early Albian	93,83	10,95
11	1047-1074	Aptian	102,44	11,99

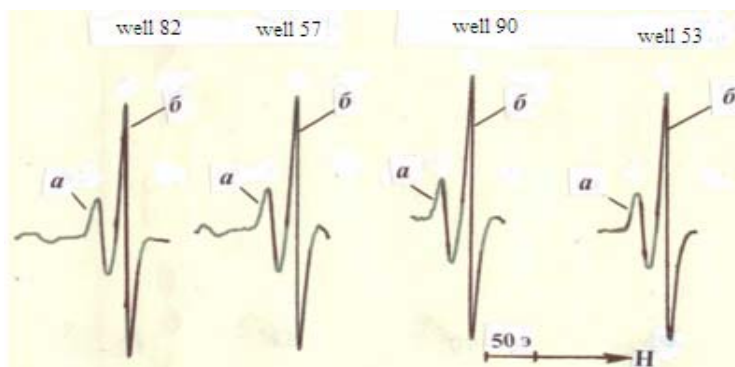


Figure 1- The Central part of EPR spectra of oils on the area of the Aptian horizon of the Kara-Arna field (wells 82, 57, 90, 53) in  $-196^{\circ}\text{C}$ : *a* – central line of HFS from vanadium (IV); *б* – signal from FR.

As can be seen from figure 1, the intensity of both lines of the spectrum of oil samples for the studied wells is the same. This suggests that the area content of vanadium (IV) and FR in oil does not change and between producing wells, there is a good hydrodynamic connection. It should be noted that the Aptian horizon is also characterized by the conditioned content of vanadium (IV), so the industrial significance of the Kara-Arna deposit as a raw material source of vanadium is of practical interest.

Vanadium content in the oils of Emba district ranges from 60 to 126 g/t. Its increased concentration is characterized mainly by oil fields in the area, located on the South Emba uplift. Oils also belong to the category of high viscosity with a high content of resin, asphaltene and low – light fractions [3-5]. The work [6,7] discusses the patterns of distribution of vanadium in low-vanadium oils ( $<10\text{g/t}$ ) from East Moldabek, North Kotyrtas, Kemerkol, South Kozha, South Tagan and Kyrykmylyk fields, located in the South-Emba oil and gas province, united by the interdependence between the vanadium content and the physical-chemical parameters of these oils.

### EXPERIMENTAL PART

EPR spectra were recorded on the E-12 spectrometer of “Varian” company. We have found EPR signals from FR and vanadium ions in the oils of the studied fields. For the determination of concentrations used the most intense line hyperfine structure (HFS) of complexes of tetravalent vanadium [5,7]. The standard concentrations were the oil from Urichtau field (from well 8) with known vanadium content (27,6 g/t) and FR (7,8-1017 spin/cm<sup>3</sup>). Samples of oil before the analysis was subjected to purification from associated water and solids by centrifugation (centrifuge T-22) when the rotation frequency of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length.

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

### CONCLUSIONS

Evaluation of the composition and properties of oils based on the study of their paramagnetic features is proposed as a necessary step for the selection of rational ways of oil development.

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### ЕМЫ МҰНАЙ КЕНІШТЕРІНДЕ ПАРАМАГНИТТІ ОРТАЛЫҚТАРДЫҢ ҚАБАТТАРЫ БОЙЫНША ТАРАЛУ ЕРЕКШЕЛІКТЕРІ

**Аннотация.** Біз зерттеген кен орындардағы мұнайларда ванадий ионымен бос радикалдардың ЭПР сигналдары анықталды. Концентрациясын анықтау үшін төрт валентті ванадий кешенінің және бір сызықтан тұратын бос радикалдың аса жіңішке құрылымын (АЖҚ) пайдаландық.

Қырықмылтық кенорнының юра шөгіндісінің ауданы бойынша мұнай тығыздығының және ванадийдің (IV) мөлшерінің зерттелген ұңғымалар бойынша өзгерісі байқалған жоқ. Бұл дегеніміз аудан бойынша ванадий мөлшерінің өзгермейтінін, яғни зерттелген ұңғымалар арасында жақсы гидродинамикалық байланыс бар екендігін сонымен қатар Қырықмылтық кеншінің мұнай құрамы төмен ванадийлі мұнайға жататынын көрсетеді.

Қара Арна мұнай кеншінің барлық зерттелген қабаттары бойынша ванадий (IV) және бос радикалдардың тұрақты болатынын және олардың жоғарғы ванадийлі топқа жататынын көрсетеді.

**Түйін сөздер:** төрт валентті ванадий кешені, бос радикал, электронды парамагниттік резонанс, гидродинамикалық байланыс, өндірістік мөлшер.

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### ОСОБЕННОСТИ РАСПРЕДЕЛЕНИЯ ПАРАМАГНИТНЫХ ЦЕНТРОВ ПО ПЛОЩАДИ В НЕФТЯХ МЕСТОРОЖДЕНИЙ ЭМБИНСКОГО РЕГИОНА

**Аннотация.** В нефтях изученных месторождений нами обнаружены сигналы ЭПР как от ионов ванадия, так и от свободных радикалов (СР). Для определения их концентрации использовалась наиболее интенсивная линия сверхтонкой структуры (СТС) среди комплексов четырех валентного ванадия и одиночная линия от СР.

По площади юрских отложений месторождения Кырыкмылтык заметные изменения плотности нефти и содержания ванадия (IV) по изученным скважинам не проявляются. Это говорит о том, что по площади содержание ванадия в нефтях не изменяется, между добывающими скважинами имеется хорошая гидродинамическая связь, а само месторождение Кырыкмылтык относится к низкованадиевым нефтям.

Равномерное распределение ванадия, так же установлено по площади аптского, альбского и сенманского горизонтов месторождения Кара-Арна и оно характеризует кондиционное содержание ванадия. Между добывающими скважинами каждого горизонта наблюдается хорошая гидродинамическая связь.

**Ключевые слова:** комплекс четырехвалентного ванадия, свободный радикал, электронный парамагнитный резонанс, гидродинамическая связь, кондиционное содержание.

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**R.A. Aubakirova<sup>1</sup>, Zh.K. Shomanova<sup>2</sup>, R.Z. Safarov<sup>3</sup>, E. Atasoy<sup>4</sup>**<sup>1</sup>Sarsen Amanzholov East Kazakhstan State University, Ust-Kamenogorsk, Kazakhstan;<sup>2</sup>Pavlodar State Pedagogical University, Pavlodar, Kazakhstan;<sup>3</sup>L.N. Gumilyov Eurasian National University, Astana, Kazakhstan;<sup>4</sup>Uludag University, Bursa, Turkey[roza.aubakirova@bk.ru](mailto:roza.aubakirova@bk.ru)**ATOMIC EMISSION METHOD WITH INDUCTIVELY COUPLED PLASMA FOR DETERMINING OF NOBLE METALS (Au, Ag) IN SAMPLES OF INDUSTRIAL BLISTER COPPER**

**Abstract.** In the article we are presenting the results of investigation of AES ISP method for Au and Ag determination in samples of industrial blister copper. The developed method allows determining Au in the range 28-56 g/ton, Ag – 2000-3000 g/ton. Control of precision was conducted using control analytical method (assay-gravimetric) as well as using measurement of state standard sample of copper content with attested values of impurities. The developed method is not inferior in metrological characteristics to control analytical method. Optimal spectral lines for Au – 242,795 nm and for Ag – 328,068 nm were selected because they have the most sensitivity and do not have spectral noises. Statistical processing of calibration characteristics for AES ISP determination of Ag and Au was conducted in accordance to RIS 54-2002. As a result, values of average standard relative deviations, the ratio of the average squared deviations and quantile of distribution were obtained. Parameters of precision, correctness, repeatability, reproducibility of the method were calculated according to RIS 61-2013.

**Keywords:** blister copper, noble metals, melting, gold, silver, atomic emission, inductively coupled plasma.

**Introduction**

Kazakhstan copper, as well as aluminum, nickel and ferrous metals, is one of the main export goods. Copper presents on market as copper concentrate, refined copper and copper wire rod.

Blister copper contains impurities, which deteriorate quality of copper (sulfur, oxygen et al.), and therefore to be removed, as well as impurities non-affecting the quality of copper, but extracted because of their value (silver and gold) [1-4].

In present time for determination of gold and silver content in samples of blister copper of copper production assay-gravimetric method of analysis is widely used [5-9]. Related to bulk up of copper production necessary of using more express method of analysis emerges not giving up by accuracy to assay-gravimetric method. Thus, the development and implementation of appropriate methods of blister copper analysis is an important issue.

**Methods and materials**

Development of the method of determination of noble metals (Au, Ag) in industrial blister copper samples includes following stages [10-13]:

- 1) investigation of influence of sample preparing stage and measuring on the analysis result;
- 1) making of calibration characteristics and their statistical processing;
- 2) description of the AES ICP method of impurities content determining in samples of copper production;
- 3) metrological substantiation of the developed measurement procedure.

### Results and Discussion

The calibration characteristics for determination of noble metals impurities content by the atomic emission method were built using certified mixtures prepared from pure metals in accordance with the method of measures performing [10, 11].

From scientific literature it is known that for determination of Au and Ag analytical spectral lines are used, which bands lengths are represented in Table 1.

Table 1 - Analytical spectral lines for determination of Au and Ag content using AES ICP method

Determined element	Band width
Au	242,795/267,595 nm
Ag	328,068/338,289 nm

We have selected the most optimal spectral lines for building of calibration characteristics for gold – 242,795 nm, and for silver – 328,068 nm. These lines are the most sensitive and do not have spectral interferences.

The initial data necessary for building of calibration characteristics are represented in Table 2.

Table 2 - The results of AES ICP determination of Au and Ag in calibration solutions

$C_{Me}$ , mg/l	$I_{imp/sec}$	
	Ag (328,068 nm)	Au (242,795 nm)
Blank	22042,9	5038,77
PC-1	681869	16094,4
PC-2	1217090	25561,5
PC-3	2345950	44945,3

where  $I$  – the average value of intensity of analytical signal of the metal, imp/sec  
 $C_{Me}$  – content of the metal in calibration solution, mg/l (Table 3)

Table 3 - Concentrations of comparative solution

Comparative solution	Concentration, mg/l	
	Ag	Au
PC-1	10,0	0,5
PC-2	20,0	1,0
PC-3	40,0	2,0

Intensity of analytical signal (number of impulses per second) was measured triple for each element and for each calibration solution. Using obtained values calibration characteristics have been built. The characteristics represent dependence of analytical signal intensity on analyte content in calibration solutions (mg/l). Calibration characteristics are represented on Figures 1 and 2.

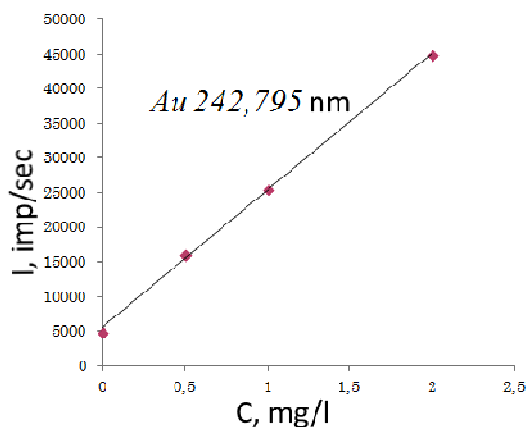


Figure 1 - Dependence of analytical signal intensity on Au concentration

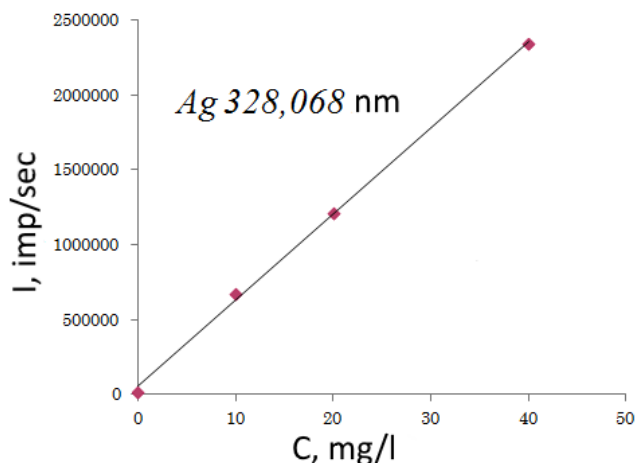


Figure 2 - Dependence of analytical signal intensity on Ag concentration

According to the Recommendations on interstate standardization 54-2002 «Calibration characteristics of means of measurement of composition and properties of substances and materials. Measurement procedure with the use of reference materials» (RIS 54-2002) statistical calculation of built calibration characteristics has been performed. As a result of statistical calculations of calibration characteristics for determination of Ag and Au values of average standard relative deviation, standard deviations of coefficients  $a$  and  $b$ , relation of average squares of the deviation and quantile of distribution were obtained. The results are represented in Table 4. Statistical processing of the results of calibration characteristics were conducted using the least squares method as far as arithmetic mean value of relative standard deviations  $\bar{\gamma} \leq 0,4$  [14].

Table 4 - Results of statistical processing of calibration characteristic for AES ICP determination of Au and Ag

Analyte	$\gamma$	$a$	$S_a$	$b$	$S_b$	$V_y$	$F(V_1, V_2)$
Ag	0,011	2,20	8,35	6,31	1,36	4,22	4,77
Au	0,002	5,04	2,59	2,08	2,69	4,31	

$\gamma$  – average value of relative standard deviation;  $a$  and  $b$  – coefficients in equation  $\gamma = a + bx$ ;  $S_a$ ,  $S_b$  – standard deviations of coefficients  $a$  and  $b$ ;  $V_y$  – relation of average squares of deviations;  $F$  – quantile of distribution.

Table 5 - Published data of the calibration standard sample (VSM 1.3) content

Element	Index of Standard sample									
	VSM1.3-1	VSM1.3-2	VSM1.3-3	VSM1.3-4	VSM1.3-5	VSM1.3-6	VSM1.3-7	VSM1.3-8	VSM1.3-9	VSM1.3-10
Mass fraction of elements, %										
Ag	0,094±0,005	0,293±0,005	0,00270±0,0002	0,0474±0,0023	0,0257±0,0009	0,00164±0,00015	0,00204±0,00021	0,0108±0,0008	0,105±0,008	0,0244±0,0027

Obtained value  $V_y$  is compared with the value of quantile of distribution  $F$  [14] with the degree of freedom  $V_1 = N - 2$  and  $V_2 = N(I - 1)$ .

As a result of mathematical processing we have obtained  $V_y \leq F(V_1, V_2)$  ( $V_y=4,22$  (Ag),  $V_y=4,31$  (Au),  $F(V_1, V_2) = 4,77$ ), which justifies the hypothesis about linearity of calibration characteristic.

For calibration of spectral equipment, we used state standard samples of blister copper with the content VSM 1.3 as represented in the Table 5.

We have determined content of Ag impurity in calibration standard sample of VSM1.3-2 set in order to define opportunities for using of the developed method for analytical control of blister copper in copper industry. The obtained results in comparison with attested values for each element are represented in Table 6.

Table 6 - The results of AES ISP determination of Au and Ag content in samples of industrial blister copper and calibration standard sample of substance content set VSM1.3 (n – results number, n=3, C – an average of analysis results mg/l,  $S_r$  – relative standard deviation of analysis results,  $t_p$  – Student coefficient,  $t_p=0,95$ )

Sample index	Element	Attested analyt content, g/ton	Concentration of analyte, g/ton	$S_r$ , %	$\delta = \pm \frac{S_r t_p}{\sqrt{n}}$ , %
A-1	Ag	-	2330,2	0,008	0,021
A-2		-	2330,2	0,005	0,012
A-3		-	2923	0,004	0,011
VSM 1.3 -2		2930 ±0,005	2929,06	0,0034	0,0085
A-1	Au	-	37,25	0,002	0,0057
A-2		-	29,95	0,0017	0,0041
A-3		-	55,45	0,019	0,048

Accuracy control was performed using the control method of analysis (assay-gravimetric). The results are presented in table 7. The developed technique is not inferior in its metrological characteristics to the control method of analysis.

Table 7 - Comparison of analysis results obtained with AES ISP and assay-gravimetric methods

Sample index	Metal content, g/ton			
	AES ISP		Assay-gravimetric method	
	Au	Ag	Au	Ag
A-1	37,25	2330,20	41,30	2681,40
A-2	29,95	2330,20	30,00	2335,00
A-3	55,45	2923,00	56,60	2962,70

Ranges and subranges of determined element concentrations are presented in Table 8.

Table 8 - Determined concentration ranges of Au and Ag in samples of blister copper

	Au, g/ton	Ag, g/ton
Determined concentration ranges	28-60	2000-3000
Determined concentration subranges	28-36	2000-2300
	37-46	2301-2600
	47-60	2601-3000

Processing of accuracy characteristics of results was conducted in accordance with requirements of the Recommendations on interstate standardization 61-2003 «State system for ensuring the uniformity of measurements. Accuracy, trueness and precision measures of the procedures for quantitative chemical analysis. Methods of determination» (RIS 61-2003) [15].

For estimation of repeatability of parallel determinations of control analysis values of mean square deviations -  $S_{rm}$  and repeatability limit -  $r_m$  of corresponding subranges of components have been obtained (Table 9).



Table 9 - Parameters of repeatability for AES ISP method of determination of Ag, Au content in industrial blister copper

Element	Subranges of determined concentration, g/ton	$S_{rm}$	$\dots_{rm}$	$r_m$
Au	28-36	0,2997	0,2997	0,8302
	37-46	0,3723	0,3723	1,0315
	47-60	0,5576	0,5576	1,5447
Ag	2000-2300	23,3751	23,3751	64,7491
	2301-2600	23,3987	23,3987	64,8146
	2601-3000	29,2317	29,2317	80,9718

For estimation of analysis method reproducibility for parallel determination of control analyses values  $S_{ml}^2$ ,  $S_{Rm}$ ,  $G_{m(max)}$ ,  $\dots_{Rm}$ ,  $R_m$  for corresponding subranges of determined components have been obtained (Table 10).

Table 10 - Parameters of reproducibility for AES ISP method of determination of Ag, Au content in industrial blister copper

Element	Subranges of determined concentration, g/ton	$S_{Rm}$	$G_{m(max)}$	$\dots_{Rm}$	$R_m$	$S_{ml}^2 \cdot 10^{-4}$
Au	28-36	0,1237	0,4716	0,1237	0,3428	0,089
	37-46	0,1537	0,4752	0,1537	0,4258	0,014
	47-60	0,2300	0,4856	0,2300	0,6372	0,031
Ag	2000-2300	9,6465	0,4762	9,6465	26,7208	0,055
	2301-2600	9,6525	0,4819	9,6525	26,7374	0,054
	2601-3000	12,055	0,4864	12,055	33,3916	0,085

Estimation of correctness has been conducted using check method of analysis (assay-gravimetric) and through measuring of state standard sample of copper content with attested amounts of impurities.

Values of precision parameters are presented in Table 11.

Table 11 - Precision parameters for AES ISP method of determination of Ag and Au content in blister copper

Element	Subranges of determined concentration, g/ton	Repeatability (Standard sample of concentration) $\sigma_r$	Reproducibility (Standard sample of concentration) $\sigma_R$	Correctness (limits of non-excluded systematic error) $\pm \Delta c$	Precision (limit of the absolute error) $\pm \Delta$
Au	28-36	0,2997	0,123755	0,33956	0,242559
	37-46	0,3723	0,153718	0,33958	0,301288
	47-60	0,5576	0,230036	0,33958	0,450871
Ag	2000-2300	23,3751	9,646498	0,48749	18,90714
	2301-2600	23,3987	9,652491	0,57398	18,91888
	2601-3000	29,2317	12,05473	0,42777	23,62727

## Conclusions

Thus, possibility of determination of Au and Ag content in samples of blister copper using AES ISP method has been revealed based on analysis of scientific and regulatory literature.

Advantages of the method are high stability of discharge radiation, high measurement speed, calibration simplicity, possibility of simultaneous multielemental determination of macro- and micro-components. Weak matrix noise caused rapid introduction this method of analysis in the workflow of many research and industrial laboratories.

At the present time assay-gravimetric method is the most used method for determination of gold and silver content in samples of blister copper in copper production. Because of increasing of copper production necessity of more express, not inferior in accuracy to assay-gravimetric analytical method is occurring.

The developed AES ISP method for Au and Ag determination in samples of industrial blister copper allows determining Au in the range 28-56 g/ton, Ag – 2000-3000 g/ton. Control of precision was conducted using control analytical method (assay-gravimetric) as well as using measurement of state

standard sample of copper content with attested values of impurities. The developed method is not inferior in metrological characteristics to control analytical method.

In the course of this research work scanning electron microscopy was used for confirmation of presence of micro- and macro-quantities of Au and Ag in the samples of blister copper.

Optimal spectral lines for Au – 242,795 nm and for Ag – 328,068 nm were selected because they have the most sensitivity and do not have spectral noises.

Statistical processing of calibration characteristics for AES ISP determination of Ag and Au was conducted in accordance to RIS 54-2002. As a result, values of average standard relative deviations, standard deviations of a and b coefficients, the ratio of the average squared deviations and quantile of distribution were obtained.

Parameters of precision, correctness, repeatability, reproducibility of the method were calculated according to RIS 61-2013.

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#### **ИНДУКТИВТІ-БАЙЛАНЫСҚАН ПЛАЗМАМЕН АТОМДЫҚ-ЭМИССИЯЛЫҚ ӘДІСІМЕН МЫС ӨНДІРІСІНІҢ ҚАРА МЫС ҮЛГІЛЕРІНДЕ АСЫЛ МЕТАЛДАРДЫ (Au, Ag) АНЫҚТАУ**

**Аннотация.** Бұл мақалада мыс өндірісінің қара мыс үлгілерінде алтын мен күмісті анықтау үшін индуктивті-байланысқан плазмамен атомдық-эмиссиялық әдістің зерттеу нәтижелері берілген. Әзірленген әдіс 28-56 г/т, күміс – 2000-3000 г/т диапазондарында алтынды анықтауға мүмкіндік береді. Дәлдікті бақылау талдаудың бақылау әдісі (сынамалы-гравиметриялық) және қоспалардың аттестацияланған мәндері бар мыс құрамының мемлекеттік стандартты үлгісін өлшеу арқылы жүргізілді. Әзірленген әдістеме өзінің метрологиялық сипаттамалары бойынша талдаудың бақылау әдісінен кем емес. Алтынға-242, 795 нм, күміске-328,068 нм үшін оңтайлы спектралды сызықтар таңдалды, олар өте сезімтал, спектралды кедергілері жоқ. РМГ 54-2002 сәйкес Ag, Au анықтау АЭС-ИСП градуирлеу сипаттамаларына статистикалық өңдеу жүргізілді, нәтижесінде орташа стандартты салыстырмалы ауытқулардың, а және b коэффициенттерінің стандартты ауытқуларының мәндері, ауытқулардың орташа квадраттарының қатынасы және бөлу квантилі алынды. РМГ 61-2013 сәйкес әзірленген әдістеменің дәлдігі, дұрыстығы, қайталануы, қайта орындалу көрсеткіштері есептелген.

**Түйін сөздер:** қара мыс, асыл металдар, балқыту, алтын, күміс, атомдық эмиссия, индуктивті-байланысқан плазма.

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#### **АТОМНО-ЭМИССИОННЫЙ С ИНДУКТИВНО-СВЯЗАННОЙ ПЛАЗМОЙ МЕТОД ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ (Au, Ag) В ОБРАЗЦАХ ЧЕРНОВОЙ МЕДИ МЕДНОГО ПРОИЗВОДСТВА**

**Аннотация:** В данной статье представлены результаты исследования атомно-эмиссионного метода с индуктивно-связанной плазмой для определения золота и серебра в образцах черновой меди медного производства. Разработанный метод позволяет определять золото в диапазонах 28-56 г/т, серебро – 2000-3000 г/т. Контроль точности производился с помощью контрольного метода анализа (пробирно-гравиметрический) и с помощью измерения государственного стандартного образца состава меди с аттестованными

значениями примесей. Разработанная методика не уступает по своим метрологическим характеристикам контрольному методу анализа. Были подобраны оптимальные спектральные линии для золота – 242, 795 нм, серебра – 328,068 нм, которые обладают наибольшей чувствительностью, не имеют спектральных помех. Проведена статистическая обработка градуировочных характеристик АЭС-ИСП определения Ag, Au согласно РМГ 54-2002, в результате были получены значения средних стандартных относительных отклонений, стандартных отклонений коэффициентов  $a$  и  $b$ , отношение средних квадратов отклонений и квантиль распределения. Рассчитаны показатели точности, правильности, повторяемости, воспроизводимости разработанной методики согласно РМГ 61-2013.

**Ключевые слова:** черновая медь, благородные металлы, плавление, золото, серебро, атомная эмиссия, индуктивно-связанная плазма.

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## **ANALYSIS OF COPPER-CONTAINING PRODUCTS FOR THE CONTENT OF NOBLE METALS**

**Abstract:** In the article we are presenting the results of electron microscopy study of the samples of blister copper taken from copper production. It was shown significant amount of noble metals – silver and gold. As a result, silver was found in the range of 0.29-0.59%, gold – up to 0.66%. The method of assay-gravimetric detection of gold and silver in samples of blister copper is described.

**Keywords:** copper, noble metals, melting, gold, silver, electron microscopy, impurity.

### **Introduction**

Kazakhstan is one of the largest producers of copper in the world meanwhile more than half of produced refined copper is exported. That is why copper as well as aluminum, nickel and ferrous metals are ones of the key export products. Exported copper is represented by copper concentrate, refined copper and copper wire rod.

Blister copper contains impurities, which deteriorate quality of copper (sulfur, oxygen et al.), and therefore to be removed, as well as impurities non-affecting the quality of copper, but extracted because of their value (silver and gold) [1-4].

In present time for determination of gold and silver content in samples of blister copper of copper production assay-gravimetric method of analysis is widely used [5-9]. Related to bulk up of copper production necessary of using more express method of analysis emerges not giving up by accuracy to assay-gravimetric method. Thus, the development and implementation of appropriate methods of blister copper analysis is an important issue.

### **Methods and materials**

Normally used methods of assay-gravimetric detection of gold and silver in samples of blister copper are described, for example, in standards [10, 11].

The method is based on melting of blister copper samples with furnace charge containing lead (as a collector of noble metals) and borax as a flux at temperature of 1000±50°C. A lead bullion (werkblei, lead alloy containing silver and gold) and slug are obtained after sherber melting. Lead is separated from gold and silver by cupellation of alloy on cupel in muffle furnace at temperature of 950±50°C with obtaining of gold-silver regulus. Gold is separated from silver by solvation of silver in nitric acid. Mass of silver is calculated as difference between mass of gold-silver regulus and mass of the gold.

The method is designed for identification of mass fraction of gold from 20 to 400 g./ton and silver from 500 to 12000 g./ton.

The sample of blister copper (5.00 g.) is weighed on precision (technical) scales, placed in a borax glazed sherber. Above the sample components of furnace charge are poured. The components are weighed on electronic scales, they contain 80 g. of granulated lead and 8 g. of borax.

Sherbering is carried on in the muffle furnace at a temperature of  $1000 \pm 50^\circ\text{C}$ . During sherbering oven door is slightly opened up for access of air oxygen. In the presence of oxygen, melt is oxidized and after interaction with borax it gives a slug, in which base-metal oxides move. The slug is shifted to sherber periphery, and melted lead forms center or «eye» of the melt. When lead «eye» will be covered with slug, the sherber stays in the muffle from five to 8 minutes and then melt is poured into a mould. Cooled lead alloy is separated from the slug, forged as a cube and cupelled.

Cupelling is carried on in the muffle furnace at a temperature of  $950 \pm 50^\circ\text{C}$ . Werkblei is placed in the muffle furnace onto a cupel with diameter from 35 to 42 mm. Preliminary heated muffle furnace stays with closed door from 2 to 3 minutes until complete melting of the werkblei. After disposal of last remains of lead that can be signed with fulguration, following darkening and solidification of reguluses, cupels are taken off from the furnace, cooled; reguluses are got off from the cupels using forceps, cleaned from adhered particles of cupel mass, flatten out on stithy obtaining thin plates and weighed on microscales. Obtained mass represents total mass of gold and silver. Golden-silver reguluses are parted.

Parting of reguluses is carried on on the electric stove. Solution of nitric acid ( $\rho = 1.06 \text{ g/cm}^3$ ) is poured into the porcelain crucible filling it to three-quarters of volume. Then, crucibles are set on the stove and heated until emergence of bubbles. Flattened reguluses are placed into crucibles and solved until full solvation of silver not bringing the solution to a boil. After solvation, solution is drained into reservoir for collection of silver nitrate and hot solution of nitric acid ( $\rho = 1.21 \text{ g/cm}^3$ ) is poured into the crucibles up to two thirds by volume. Crucibles are stood on the stove until full discontinuation of nitrogen oxides releasing. Then, the solution is also drained into a reservoir for collection of silver nitrate and gold beads are washed triple with hot water by decantation. Crucibles with gold beads are carefully dried on the stove and annealed in the muffle oven at a temperature of  $550 \pm 50^\circ\text{C}$  for 5 minutes. After cooling gold bead is weighed on microscales. The difference between mass of golden-silver regulus and mass of gold bead is the mass of silver.

If the mass fraction of silver in the samples of blister copper is 600 g/ton or more, check sample is prepared from silver with mass corresponding to it's mass fraction in the sample for taking into account silver loss after cupelling. For that samples of silver are placed into pockets of lead foil, compressed tightly and placed in the muffle oven on the cupels preliminary heated up to a temperature of  $950 \pm 50^\circ\text{C}$ . In the cupel along with the pocket the granulated lead is placed granulated in the amount at which total mass of lead with a mass of leaden pocket would correspond to mass of sample of werkblei obtained after sherber melting, and then it is cupelled.

Cupelling of check samples is carried on straight after analysis of the samples in the same muffle under the same conditions.

The values of metrological characteristics and standards for determining the mass fraction of gold must not exceed the values given in tables 1 and 2, respectively.

Table 1 - Numerical values of the limits of the absolute error of silver content (g/ton)

Mass fraction of silver	Standard deviation of repeatability $\sigma_r$	Repeat limit at $n = 3$ $r_3$	Standard deviation of reproducibility $\sigma_R$	Reproducibility limit at $t = 2$ $R$	Limits of absolute error $\pm\Delta$
500 « 1000	10,6	35,0	15,2	42,0	30,0
1000 « 2000	21,1	70,0	30,0	83,0	59,0
2000 « 3000	30,2	100,0	43,3	120,0	85,0
3000 « 4000	45,3	150,0	65,0	180,0	128,0
4000 « 6000	60,4	200,0	86,6	240,0	170,0
6000 « 8000	75,5	250,0	108,3	300,0	213,0
8000 « 10000	90,6	300,0	130,0	360,0	256,0
10000 « 12000	105,7	350,0	151,6	420,0	298,0

Table 2 - Numerical values of the limits of the absolute error of gold content (g/ton)

Mass fraction of gold	Standard deviation of repeatability $\sigma_r$	Repeat limit at $n = 3$ $r_3$	Standard deviation of reproducibility $\sigma_R$	Reproducibility limit at $t = 2$ $R$	Limits of absolute error $\pm\Delta$
20 « 30	0,91	3,0	1,30	3,6	2,6
30 « 45	1,21	4,0	1,73	4,8	3,4
45 « 70	1,36	4,5	1,95	5,4	3,8
70 « 100	1,51	5,0	2,17	6,0	4,3
100 « 150	1,81	6,0	2,56	7,1	5,0
150 « 250	2,11	7,0	3,00	8,3	5,9
250 « 400	2,42	8,0	3,43	9,5	6,7

### Results and discussion

The method of scanning electron microscopy is intended primarily for the study of the surface structure.

Scanning electron microscopes have  $10^3$  times greater depth of field than optical instruments, which provides a much higher image quality and allows you to successfully apply the technique of obtaining stereo pairs. The resulting images allow you to recreate a three-dimensional picture of the surface of the sample.

The scanning method allows for sequential analysis and element-by-element scanning of multiple sites in automatic mode and processing of data in relation to the corresponding observation points [12, 13].

We have applied the SEM method to prove the presence of micro-and macro-quantities of gold and silver, respectively, in the samples of blister copper of copper production.

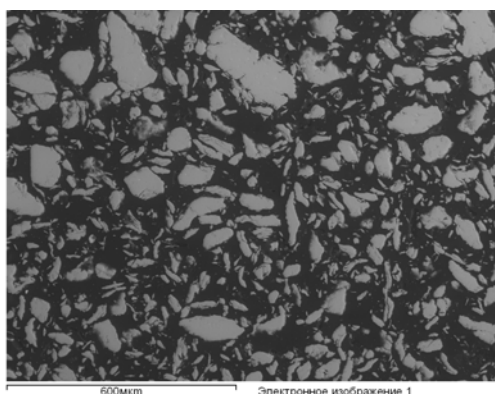


Figure 1. An electronic image of the surface structure of the sample of blister copper

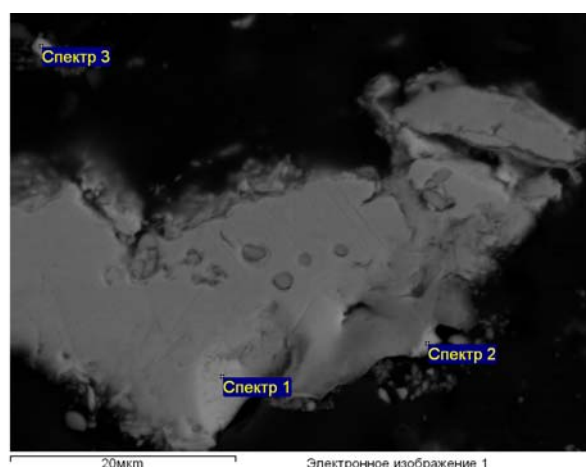


Figure 2. Fragment of SEM image of the surface structure of the sample of blister copper on the impurity content (C, O, Al, Si, Au, Sn, Fe)

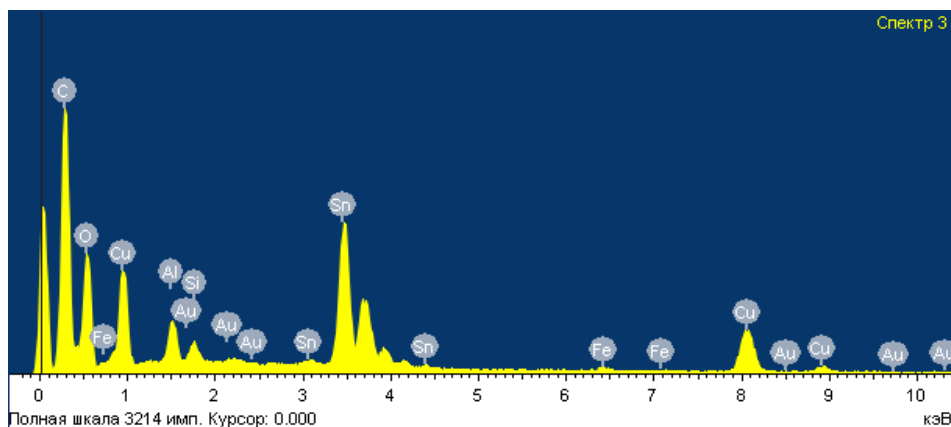


Figure 3 - Spectrum of the analysis site (site №1)

Table 3. Processing parameters of the site №1 for the analysis of all elements (all results in weight %)

Spectrum	O	Al	Si	Fe	Cu	Ag	Sn	Au	Total
Spectrum 1	4.37				95.63				100.00
Spectrum 2	3.85				95.56	0.59			100.00
Spectrum 3	44.29	3.48	1.25	0.74	17.12		32.44	0.66	100.00
Max.	44.29	3.48	1.25	0.74	95.63	0.59	32.44	0.66	
Min.	3.85	3.48	1.25	0.74	17.12	0.59	32.44	0.66	

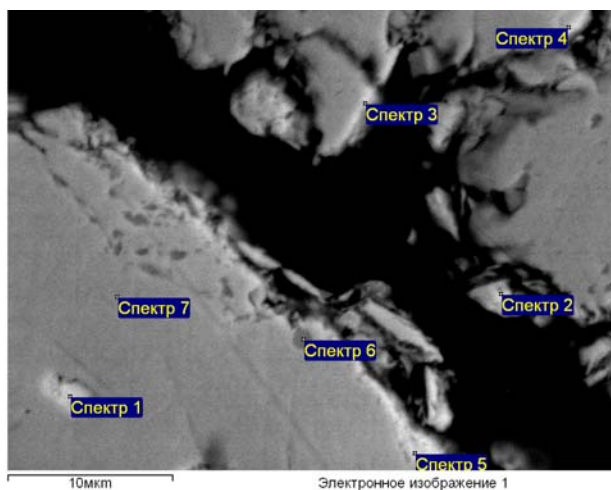


Figure 4 - Fragment of SEM image of the surface structure of the sample of blister copper on the impurity content (C, O, As, Pb, Ag, Sb)

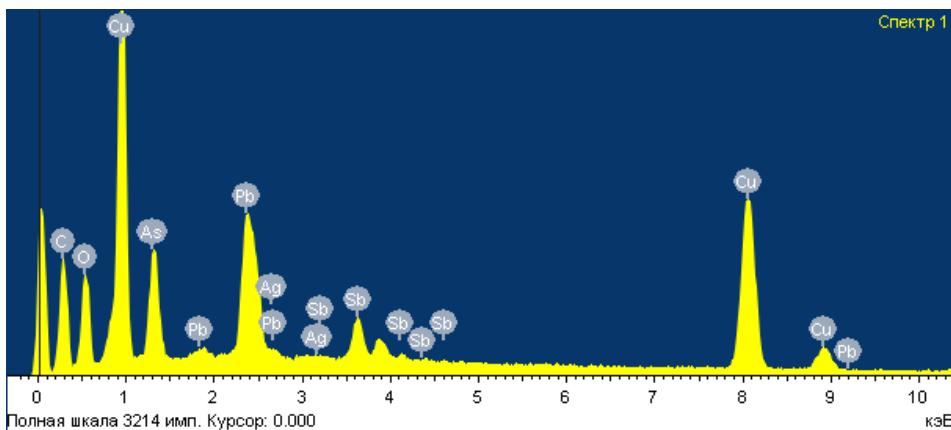


Figure 5 - Spectrum of the analysis site (site №2)

Table 4 - Processing parameters of the site №2 for the analysis of all elements (all results in weight %)

Spectrum	O	Si	Cu	As	Ag	Sb	Pb	Total
Spectrum 1	15.00		41.71	13.94	0.29	7.40	21.67	100.0
Spectrum 2	7.96	0.57	91.47					100.0
Spectrum 3	5.60	1.33	93.06					100.0
Spectrum 4	12.73		62.99	11.92		4.19	8.17	100.0
Max.	15.00	1.33	93.06	13.94	0.29	7.40	21.67	
Min.	5.60	0.57	41.71	11.92	0.29	4.19	8.17	



Ag La1

Figure 6 - A fragment of the SEM image of silver on the surface of the sample of blister copper

### Conclusion

Thus, studying of structure surface of samples using SEM we have revealed presence of impurities (C, O, As, Pb, Ag, Sb, Al, Si, Au, Sn, Fe) in blister copper of copper production. Herewith, there was a significant presence of precious metals. So, silver was found in the range of 0.29-0.59%, gold – up to 0.66%.

ӘОК 549:622.775

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### ҚҰРАМЫНДА МЫС БАР ӨНІМДЕРДІ АСЫЛ МЕТАЛДАРҒА ТАЛДАУ

**Аннотация:** Бұл мақалада мыс өндірісінің бастапқы кара мыс үлгілерін электронды-микроскопиялық зерттеу нәтижелері берілген. Асыл металдар – күміс пен алтынның елеулі мөлшері көрсетілген. Нәтижесінде 0.29-0.59% шамасында күміс, 0.66% – ға дейін алтын табылды. Кара мыс үлгілерінде алтын мен күмісті анықтаудың сынамалы-гравиметриялық әдісі сипатталған.

**Түйін сөздер:** мыс, асыл металдар, балқыту, алтын, күміс, электронды микроскопия, қоспалар.



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Усть-Каменогорск, Казахстан;<sup>2</sup>Павлодарский государственный педагогический университет, Павлодар, Казахстан;<sup>3</sup>Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан;<sup>4</sup>Университет Улудаг, Бурса, Турция**АНАЛИЗ МЕДЬ-СОДЕРЖАЩИХ ПРОДУКТОВ  
НА СОДЕРЖАНИЕ БЛАГОРОДНЫХ МЕТАЛЛОВ**

**Аннотация:** В данной статье представлены результаты электронно-микроскопического исследования образцов черновой меди медного производства. Показано значимое количество благородных металлов – серебра и золота. В результате серебро было обнаружено в пределах 0.29-0.59%, золото – до 0.66%. Описан пробирно-гравиметрический метод обнаружения золота и серебра в образцах черновой меди.

**Ключевые слова:** медь, благородные металлы, плавление, золото, серебро, электронная микроскопия, примеси.

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## **HYDROGENATION OF PALM OIL ON Pt-CONTAINING CATALYSTS**

**Abstract.** The article is devoted to the study of the catalytic hydrogenation of palm oil to obtain a high yield of fat without double bonds and trans-isomers. The catalysts used were platinum supported on various carriers - alumina, ball aluminosilicate, synthetic HY zeolite and activated carbon, among which ball aluminosilicate was the most active. The effect of process temperature and hydrogen pressure on the content of double bonds and trans-isomers of fatty acids was studied. In the temperature range of 80–200°C and pressures of 0.3–1.5 MPa, the content of C = C bonds decreases from 54 g I<sub>2</sub>/100g, and the content of trans fats from 22 to 0%. On the Pt/aluminosilicate catalyst at 200°C and 1.5 MPa, double bonds and trans-isomers of fatty acids are completely absent in the reaction products. Using the BET, porometry and EM methods, a uniform formation of zero-valence metal particles on the catalyst surface was established, and nanoscale particles of Pt were determined.

**Keywords:** palm oil, catalyst, hydrogenation, platinum, aluminosilicate.

### **Introduction**

More than 60-70% of the oil and fat industry in the world is based on hydrogenated oils. Unhydrogenated fats are rancid, get oxidized due to double bonds, they have an unpleasant smell and taste. Hydrogenation slows down these processes and, in addition, allows from cheap oils to produce more valuable solid fats, which is the basis for the production of food margarines and technical hydrogenated fats.

Since the 2000s, the world has introduced a ban on trans fats, called "fat-killers". The following negative consequences of eating trans fats have been established: weakened immunity, reduced resistance to stress, the risk of depression, the birth of children with pathologically low weight, the risk of developing diabetes, a negative effect on the joints and connective tissue, the enzyme cytochrome oxidase, neutralizing carcinogens, they lead to atherosclerosis, ischemic heart disease, cancer, obesity, visual impairment, etc. [1-2].

In this regard, the content of trans-isomers in oil-fat products got stringent prohibition. In developed countries, their content in products is minimized or completely banned. As early as 2003, WHO recommended that the content of trans-fats in the caloric content of the diet should not exceed 1%. Legislative limitations of trans fat content of no more than 1-2% in products are introduced in the USA, Canada and all European countries. The FDA agency (USA) legally permits the content of trans fats below 0.5 g per 100 g of product [3-4].

According to the requirements of the Technical Regulations of the Customs Union (CU) "Technical regulations for fat and oil products" (TR CU 024/2011), the content of the isomers of fatty acids from 01.01.2018 for hard, soft and liquid margarines, spreads and mixtures should not exceed 2% [5]. In Kazakhstan, currently in widely consumed oil-fat products, the content of trans fats is up to 40-50%. Therefore, reduction of trans-isomers in edible oil-fat products is an actual and urgent problem in our country, since from 2018 onwards it would be necessary to produce products in accordance with the Technical Regulations of the Customs Union. The urgency of the problem of developing new catalysts for the hydrogenation of vegetable oils is also determined by the fact that the demand for hydrogenated fats is

high, and the existing catalysts do not meet the requirements of modern technology in a number of parameters.

The problem of hydrogenation of fats is covered in many studies of scientists and technologists. Such studies are conducted in the developed countries of Europe, America and Asia [6-7]. In general, all studies are devoted to the partial hydrogenation of various vegetable oils and cetylated fatty acid esters, which makes it possible to form trans-isomers as more stable, and to reduce the degree of isomerization in order to reduce the content of trans isomers. The most studied and effectively used in developed countries are nickel catalysts and catalysts based on platinum metals.

When hydrogenating sunflower oil on a Ni/SiO<sub>2</sub> catalyst using 3 texturally different silica gel materials, the authors achieved the optimal fat composition [8]. It is shown that the high activity of the catalyst results in a greater number of reaction routes and side chemical reactions.

Hydrogenation of sunflower oil in cis-C18:1 was tested on heterogeneous catalysts - palladium and platinum deposited on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> [9]. It was found that Pd-catalysts are much more active than the industrial Ni-catalyst and the lowest yields of trans fats were obtained. Pt-catalysts were also applied to carriers of different nature: ZSM-5 with platinum nanoparticles [10], diatomite from the Mugodzhar deposit of Kazakhstan [11], Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, MgO, BaSO<sub>4</sub> and MoO<sub>3</sub> [12].

The reduction of the Pd-B/γ-Al<sub>2</sub>O<sub>3</sub> catalyst with potassium borohydride (KBH<sub>4</sub>) affects the structure of the catalyst, which leads to high conversion and reduces the selectivity for trans-isomerization compared to the unreduced catalyst [13].

The effect of the nature of the precursor of platinum on the activity of catalysts has been studied [14]. The catalyst prepared from Pt(AcAc)<sub>2</sub> is more active than H<sub>2</sub>PtCl<sub>6</sub>. The effect of a change in the Pt content (0.7-4.6% wt) on a new mesoporous SiO<sub>2</sub> for the hydrogenation of sunflower oil was studied. It is shown that the smaller the platinum, the lower the content of trans-isomers, which is due to the smaller catalyst particles.

Modification of catalysts also leads to a decrease in the formation of trans-isomers. Silver-modified Mg-Ni/diatomite catalysts have shown a decrease in trans-isomerization during the hydrogenation of soybean oil [15]. Partial hydrogenation of sunflower oil on Pd/γ-Al<sub>2</sub>O<sub>3</sub>, modified with magnesium glycine revealed a minimal formation of trans-isomers.

Studies show that on catalysts based on noble metals with the hydrogenation of vegetable oils the yields of trans fatty acids are lower than those from nickel catalysts. Ni-catalysts are not very active below 120°C, and platinum ones are active at temperatures up to 70°C. Pt, Pd and Ru are the most active catalysts for the hydrogenation of vegetable oils, but on Pt-catalysts there're the minimum amount of trans fatty acids.

Monolithic catalysts based on anodized aluminum Pd/Al<sub>2</sub>O<sub>3</sub>/Al showed high activity when hydrogenating sunflower oil with 50% conversion C=C [16]. These structured catalysts may be a good alternative in the partial hydrogenation reaction.

In addition to conventional catalytic methods for carrying out hydrogenation processes, new ones are proposed, such as electrocatalytic hydrogenation, hydrogenation in supercritical conditions, hydrogenation using membranes and cold plasma, which have shown promising results in reducing trans fatty acids. But these alternative methods are not brought to the introduction for industrial production of fats without trans-isomers yet.

Hydrogenation of sunflower oil in supercritical propane and dimethyl ether 2% Pd/C showed the best profile of hydrogenated products, supercritical conditions significantly affect the melting characteristics compared to conventional hydrogenation [17].

A significant decrease in the content of trans fatty acids in soybean oil is demonstrated by a low-temperature electrochemical process [18]. Compared to the commercial process of hydrogen gas hydrogenation, the application of this method leads to a decrease in trans fatty acid by 80%.

Membrane reactors are proposed in [19], which address the drawbacks of the process of conventional three-phase hydrogenation, such as the insufficient provision of the catalyst with hydrogen, the slow diffusion mass transfer of reactants from the gas phase through the liquid to the active sites of the catalyst.

High-voltage atmospheric cold plasma (HVACP) was studied to produce partially hydrogenated soybean oil without the formation of trans fatty acids [19]. This study is the first study demonstrating an alternative technology to conventional catalytic hydrogenation.

Despite a large number of studies in this field, industries of almost all the countries of the world, including in Kazakhstan, use the method of classical hydrogenation on nickel catalysts, in which the double bonds do not completely hydrogenate and a sufficient number of trans isomers is brewed. In particular, Johnson Matthey company's catalysts PRICAT 9910 and 9920 (nickel catalyst based on silicon dioxide with a content of 22% wt) are used in Kazakhstan.

Disadvantages of industrial processes and catalysts are a short service life (one-time catalyst), a laborious filtration stage for separating the catalyst from the target product and significant losses of fat and active catalyst phase. But the main disadvantage of these catalysts is that nickel is partially present in the hydrogenated fat, which is harmful to the human body. Therefore, harmless hydrogenation catalysts, such as platinum-containing catalysts, are needed.

Usually, hydrogenation of double bonds of vegetable oils on metal catalysts leads to the formation of trans-isomers, as the most stable substances. It is generally accepted that platinum catalysts produce the least amount of trans-fatty acids upon hydrogenation.

The aim of this work is to develop active selective palm-oil hydrogenation catalysts for the production of fat-free high-yield grease without double bonds and trans-isomers.

### **Experimental part**

At preparation of catalysts was used  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  of "chemically pure" mark. Solutions of this compound was applied by the adsorption method on the prepared carriers: alumina, ball aluminosilicate, synthetic HY zeolite and activated carbon. 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 hydrogenation process was carried out by Amar Equipment Ltd autoclave in the isobaric-isothermal regime in the temperature range of 80-200°C and hydrogen pressure of 0.3-1.5 MPa. The analysis of the reaction products was carried out for the content of the double bond (method of iodine number) and content of trans-fats by gas chromatography on Crystal-5000 chromatograph.

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**

The influence of the nature of the support on the content of double bonds in the salomas (Table 1) was studied during the hydrogenation of palm oil on Pt-catalysts. ShAS - ball aluminosilicate carrier brand ShAS-2, alumina, activated carbon and HY zeolite were used as supports.

When hydrogenating palm oil on platinum catalysts on the listed supports at 1.5 MPa and 200°C, the content of double bonds varies depending on the type of support and decreases from 54% in the original palm oil to 0%. The content of trans-isomers also varies depending on the support - from 21 to 0%. The most active catalyst is Pt/ShAC, on which the content of C = C bonds and trans-isomers is 0.

The effect of temperature and pressure of hydrogen on the double bond content in the lard (Tables 2 and 3) was studied during the hydrogenation of palm oil on the most active catalyst - Pt/ShAS. With an increase in temperature from 80 to 200°C, the content of C = C bonds decreases from 46 to 0 g I<sub>2</sub>/100g. The content of trans-isomers of fatty acids with increasing temperature increases from 1% in the initial oil to 22%, with a further increase in temperature to 200°C, the trans-isomers completely disappear as all double bonds (Table 1).

Table 1 - The content of double bonds and trans-isomers of fatty acids at hydrogenation of palm oil on the Pt/support catalysts at 200°C and 1.5MPa

Catalyst	Content of double bonds, g I <sub>2</sub> /100g	Content of trans-isomers, %
Initial oil before treatment	54	1
Pt/C	47	21
Pt/Al <sub>2</sub> O <sub>3</sub>	5	3
Pt/HY	21	10
Pt/ShAC	0	0

Table 2 - The content of double bonds and trans-isomers of fatty acids at hydrogenation of palm oil on the Pt / ShAC catalyst at 0.3 MPa and different temperatures

Temperature, °C	Content of double bonds, g I <sub>2</sub> / 100g	Content of trans-isomers, %
Initial oil before treatment	54	1
80	46	15
120	28	22
150	5	3
200	0	0

Table 3 - The content of double bonds and trans-isomers of fatty acids at hydrogenation of palm oil on a Pt /ShAC catalyst at 120°C and various hydrogen pressures

Pressure, MPa	Content of double bonds, g I <sub>2</sub> / 100g	Content of trans-isomers, %
Initial oil before treatment	54	1
0,3	28	22
0,5	21	15
1,0	15	11
1,5	8	3

Similar to the effect of temperature, as the pressure rises, the content of double bonds decreases in catalyzate from 54 in the initial palm oil mode to 8g I<sub>2</sub>/100g at 1.5 MPa. The content of trans-isomers first increases to 22%, while at 1.5 MPa it decreases to 3% (Table 3). This is due to the complete hydrogenation of the double bonds of palm oil.

When the hydrogen pressure is changed from 0.3 to 1.5 MPa, the time of the catalytic treatment of palm oil decreases from 65 to 32 minutes (figure 1). The absence of C=C bonds in this case after the experiment was observed at 1.5 MPa. The content of trans-isomers is also equals 0.

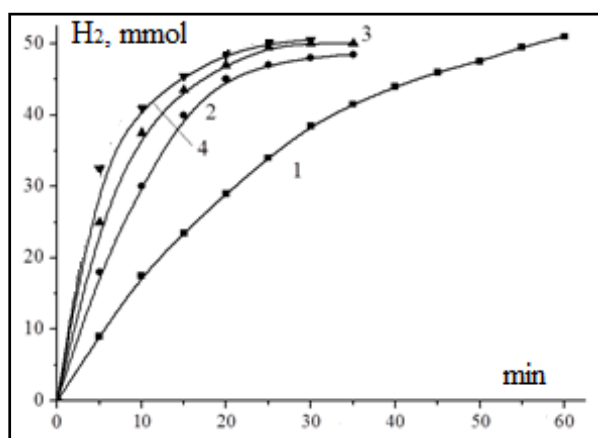


Figure 1 - Hydrogenation of palm oil at different hydrogen pressures on Pt/ShAS catalyst at 50°C. a - 1 – 0.3; 2 - 0.5; 3 - 1.0; 4 - 1.5 MPa

An increase in temperature from 80 to 200°C increases the rate of hydrogenation of palm oil (Figure 2, b) and the apparent activation energy is 40.8 KJ/mol.

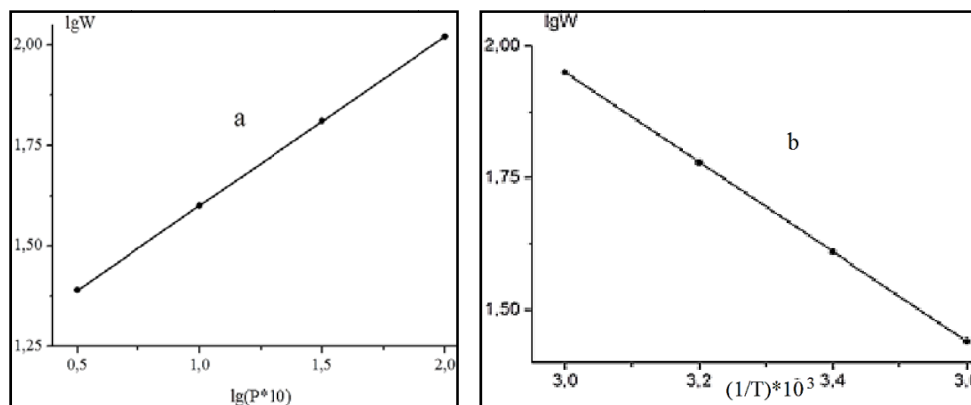


Figure 2 - Hydrogenation of palm on Pt/ShAS at 1.0 MPa. a - bilogarithmic dependence of rate from pressure; b - dependence of the logarithm of rate from reciprocal temperature

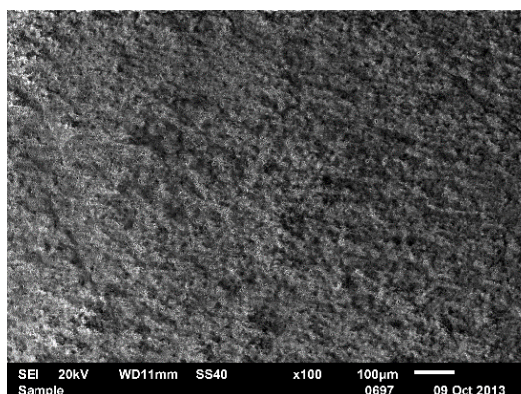
Thus, according to the results of Tables 2-3 and figures 1-2 on the Pt /ShAC catalyst, the optimal temperature and pressure are 200°C and 1.5 MPa, at which the double bonds and trans-isomers of fatty acids are completely absent in the reaction product.

The catalysts were studied by physicochemical methods of analysis by BET and EM. In table 4 the characteristics of used 4 catalysts are presented. Pt/ShAC has the largest surface 201 m<sup>2</sup>/g and pore size 15-20 Å.

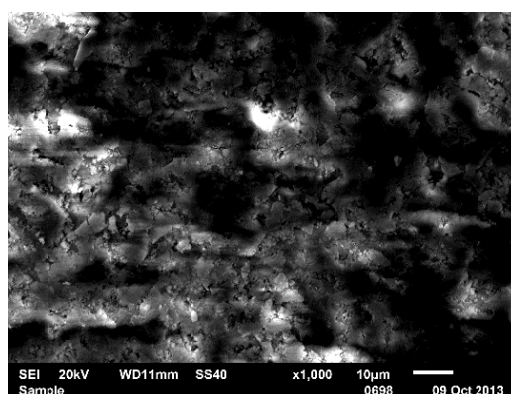
Table 4 - Surface area and pore size of the prepared supported catalysts

Catalyst	S*, m <sup>2</sup> /g	d*, Å
Pt/C	175	12-25
Pt/Al <sub>2</sub> O <sub>3</sub>	164	4-14
Pt/HY	185	5-18
Pt/ShAC	201	15-20

The surface of catalysts was studied by scanning electron microscopy. In figure 3 of different increase of the Pt/ShAC catalyst is shown the uniform surface of the carrier, on which agglomerates of active metals are viewed.

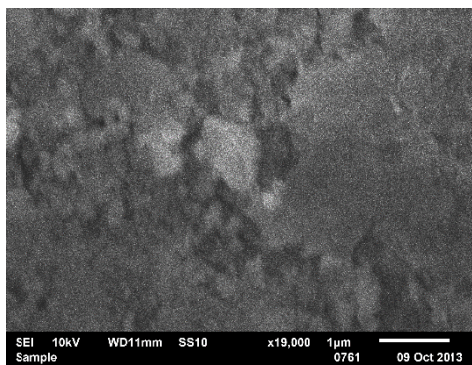


1



2





3

Figure 3 - EM images of Rh-Pt (9:1)/Al<sub>2</sub>O<sub>3</sub>

The most active catalyst Pt/ShAC was investigated by transmission electron microscopy (TEM). On figure 4 Pt/ShAC-catalyst was presented by fine particles 2-2.5 nm in size and a small amount of more dense and large particles of 50 nm. Microdiffraction patterns of particles are represented by diffuse rings, corresponding to metals Pt<sup>0</sup> which are most active in hydrogenation of double bonds of fatty acids of palm oil. Apparently, high catalyst activity is due to the uniform distribution of nanoscale particles on the surface of catalyst.

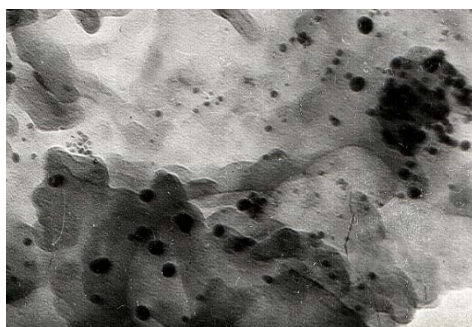


Figure 4 - TEM image of catalyst Pt/ShAC (increase 160,000)

A distinctive feature of the used catalysts and technology from the nickel catalysts widely used on an industrial scale is the complete hydrogenation of double bonds of fatty acids to 100% removal of trans-isomers [20]. In addition, the further application of the process of trans-esterification of hydrogenated fats with liquid vegetable oils that do not initially contain trans-isomers leads to optimum margarines, spreads and milk fat substitutes that are in accordance with the norms of the Technical Regulations of the Customs Union.

### Conclusions

Platinum supported on various carriers - alumina, ball aluminosilicate, synthetic HY zeolite and activated carbon were prepared. Among carriers ball aluminosilicate was the most active.

The effect of process temperature and hydrogen pressure on the content of double bonds and trans-isomers of fatty acids was studied. In the temperature range of 80–200°C and pressures of 0.3–1.5 MPa, the content of C = C bonds decreases from 54 g I<sub>2</sub>/100g, and the content of trans fats from 22 to 0%. For Pt/aluminosilicate catalyst optimal parameters were selected: 200°C and 1.5 MPa double bonds and trans-isomers of fatty acids are completely absent in the reaction products. Apparent activation energy for hydrogenation of palm oil is 40.8 KJ/mol.

Using the BET, porometry and EM methods, a uniform formation of zero-valence metal particles on the catalyst surface was established, and nanoscale particles of Pt were determined.

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### **ҚҰРАМЫНДА Pt БАР КАТАЛИЗАТОРЛАРДЫ ПАЛЬМА МАЙЫНДА ГИДРЛЕУ**

**Аннотация.** Мақала саломастың қос байланыссыз және транс-изомерлерсіз жоғары өнімділігін алу үшін пальма майының каталитикалық гидриленуін зерттеуге арналған. Катализаторлар ретінде әртүрлі тасымалдағыштар қолданылды – алюминий оксиді, шарикті алюмосиликат, синтетикалық цеолит НҮ және белсендірілген көмір қолданылған, олардың арасында ең белсенді шарикті алюмосиликат болды. Үрдіс температурасы мен сутегі қысымы май қышқылдарының қос байланыстары мен транс-изомерлерінің құрамына әсері зерттелді. С=C құрамы 80-200°C температуралық интервал мен 0,3-1.5 МПа қысымда 54 г-нан I<sub>2</sub>/100 г дейін, ал транс-майлардың мөлшері 22-ден 0% - ға дейін азаяды. Pt/алюмосиликат катализаторында 200°C және 1,5 МПа кезінде реакция өнімінде май қышқылдарының қос байланысы және транс-изомерлері болмайды. БЭТ, порометрия және ЭМ әдістерімен металл бөлшектері катализаторлардың беттік қабатына валенттіліктің нөлдік деңгейінде біркелкі орнатылған және Pt нано өлшемді бөлшектері анықталды.

**Түйін сөздер:** пальма майы, катализатор, гидрлеу, платина, алюмосиликат.

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### **ГИДРИРОВАНИЕ ПАЛЬМОВОГО МАСЛА НА Pt-СОДЕРЖАЩИХ КАТАЛИЗАТОРАХ**

**Аннотация:** Статья посвящена исследованию каталитического гидрирования пальмового масла для получения с высоким выходом саломаса без двойных связей и транс-изомеров. В качестве катализаторов использовались платиновые, нанесенные на различные носители – оксид алюминия, шариковый алюмосиликат, синтетический цеолит НҮ и активированный уголь, среди которых наиболее активным оказался шариковый алюмосиликат. Исследовалось влияние температуры процесса и давления водорода на содержание двойных связей и транс-изомеров жирных кислот. В температурном интервале 80-200°C и давлений 0,3-1.5 МПа содержание С=C связей уменьшается с 54 г I<sub>2</sub>/100г, а содержание транс-жиров с 22 до 0 %. На катализаторе Pt/алюмосиликат при 200°C и 1,5 МПа в продукте реакции полностью отсутствуют двойные связи и транс-изомеры жирных кислот. Методами БЭТ, порометрии и ЭМ установлено равномерное образование на поверхности катализаторов частиц металлов в нулевой степени валентности, определены наноразмерные частицы Pt.

**Ключевые слова:** пальмовое масло, катализатор, гидрирование, платина, алюмосиликат.

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## **CATALYTIC TECHNOLOGY FOR REDUCING THE CONTENT OF AROMATIC HYDROCARBONS IN MOTOR FUELS**

**Abstract.** The aim of the work was to study the process of hydrodearomatization of diesel fractions for the production of environmentally friendly fuels with a low content of aromatic hydrocarbons. The hydrogenation of two diesel fractions 180-350°C and 230-360°C of PKOP LLP (PetroKazakhstanOilProducts, Shymkent) has been studied. Rh-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were used in the work. The influence of the technological parameters of the process of hydrodearomatization (hydrogen pressure 2-6 MPa, temperature 100-220°C) on the reaction rate, conversion and aromatic hydrocarbon content at the "aniline point" was investigated. To increase stability and resistance to poisoning with sulfur-containing compounds of petroleum fractions, the carrier was modified with chromium oxide and synthetic zeolite ZSM-5, which led to an increase in the reaction rate and conversion of aromatic hydrocarbons. Optimal conditions have been selected (temperatures 200-220°C, hydrogen pressure 4-6 MPa, solvent - ethanol, propanol, isopropanol) for hydrogenation of diesel fractions 180-350°C and 230-360°C on Pt-Rh-catalysts supported on alumina and mixed carriers. The content of aromatic hydrocarbons was reduced by 10-20%. Some operational properties of diesel fuel (kinematic viscosity at 20°C, pour point and cloud point and density at 20°C) of the initial diesel fractions and after catalytic treatment were determined, the effect of temperature and pressure on the change in these characteristics was investigated.

**Keywords:** catalyst, hydrogenation, hydrodearomatization, aromatic hydrocarbons, diesel fraction.

### **Introduction**

The constantly deteriorating of environmental situation in the world dictates the need for use of clean and quality fuel. Harmful compounds (carcinogens, in particular benzyrene) are formed upon incomplete combustion of benzene and aromatic hydrocarbons. Aromatic hydrocarbons promote coking in the engine combustion system, which increases the NO<sub>x</sub> content in exhaust gases. For diesel fuels, the high content of polycyclic aromatic hydrocarbons reduces their cetane index; a lot of soot (black smoke) is contained in exhausts at combustion. The limiting value of aromatic hydrocarbons content according to the new EURO-5.6 specifications is less than 30%, benzene is less than 0.1%. One of the methods for improving the composition of fuels is their hydrodearomatization; olefins also hydrogenate at the same time, which reduce the stability of fuel as a result of their polymerization [1-6].

Development and introduction of the technology of hydrodearomatization of fuels and fuel fractions are relevant for the Republic, taking into account the high content of benzene (up to 5-7%) and aromatic hydrocarbons (up to 40-50%) in gasolines and diesel fuels, as the environmental situation in some regions raises concerns. The technological line for the proposed project is simple and the process can be carried out on the lines of oil hydrotreating at any refinery in Kazakhstan. The process technology is one-step and low-waste. Hydrodearomatization of fuels will help improve the performance properties of domestic gasolines, diesel fuels and will allow in a short time to cover the need for fuels with improved performance characteristics.

Many countries: Russia, United States, Great Britain, France, Germany, Japan, China, Poland, etc. are engaged in the problem of hydrodearomatizing of fuels [7-19]. Major trends in this field consist in

reducing the cost of catalyst (reduction of the noble metal content, selection of carriers and modifiers), increase stability and resistance to sulfur-containing compounds. In industry catalysts based on noble metals and sulfides are used, but in the latter, the process is carried out under more stringent conditions.

Recently Pt-Pd-catalysts have been intensively used for hydrotreatment of petroleum products, especially for reducing the content of benzene in gasolines and aromatics in diesel fuels, therefore, close attention of researchers has been riveted on them. The addition of Pd to Pt/Al<sub>2</sub>O<sub>3</sub> leads to an increase in not only the activity, but also the stability in the hydrogenation of benzene. By varying the nature of the carrier and modifier the Pd catalysts with the addition of a second metal such as Cu, Ru or Pt a uniform distribution of metals in the pores, optimal acidity and stability against sulfur-containing compounds were achieved. Thus, in the literature of recent years on catalysis there has been considerable interest to the process of hydrogenation of aromatics, which is largely due to the practical use in the production of environmentally friendly fuels.

At present, Kazakhstan's refineries produce rather low-quality motor fuels, which are far from international standards. In addition to harmful emissions into the atmosphere, rapid deterioration of the details of equipment occurs due to the deposition of carbon during the combustion of such fuels. The service life of equipment is reduced by 30%.

In previous works [15-20] we investigated the catalytic hydrogenation of aromatic hydrocarbons and developed catalysts and technological regimes for the process of hydrodearomatization (removal of benzene and reduction of polyaromatic hydrocarbons) of gasoline fractions of ANPZ LLP (Atyrau Oil Refinery). Advantages of these catalysts are a high conversion of benzene 99.5%, reduction of aromatic hydrocarbons content to 25%, high stability to poisoning with sulfur-containing compounds. The purpose of this work is the catalytic hydrogenation of polyaromatic hydrocarbons in diesel fractions of PKOP LLP (PetroKazakhstanOilProducts, Shymkent).

### Experimental part

Bimetallic modified catalysts based on Group 8 metals (Pt and Rh) on aluminum oxide were prepared for hydrodearomatization of diesel fractions of PKOP LLP (Shymkent) - 180-350°C and 230-360°C with aromatics content of 30 and 39%, respectively.

At preparation of catalysts RhCl<sub>3</sub>·3H<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O of "chemically pure" mark were used. Solutions of these compounds were applied by the adsorption method on the prepared carrier Al<sub>2</sub>O<sub>3</sub>. A mixture of aqueous solutions of two metals was applied at preparation of bimetallic catalysts. The catalyst samples were filtered off and dried at 100-110°C to constant weight. The reduction of supported catalysts was carried out in a quartz tube with electrical heating in a hydrogen stream at 200°C for 4 hours, then the catalysts were cooled in a hydrogen stream until room temperature.

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

The "aniline point" method was used to determine the total content of aromatic hydrocarbons.

### Results and discussion

Hydrodearomatization of diesel fractions of 180-350°C and 230-360°C was carried out on the prepared catalysts and the technological parameters (temperature and hydrogen pressure) were tested. The effect of temperature in the range of 100-200°C on the rate, duration of hydrogenation, and the content of aromatic hydrocarbons was studied.

Table 1 shows the data on the hydrogenation of the diesel fraction of oil 180-350°C. With increasing of temperature, the rate increases from 8.2 to 12.3 ml/min, the duration of the process decreases from 180 to 130 minutes. The aniline point increases from approximately <44 to <54. This indicates a decrease in the content of aromatic hydrocarbons by approximately 18% (the initial content of aromatic hydrocarbons is approximately 30%).

The effect of hydrogen pressure was studied in the range of 2.0-4.0 MPa. The change in reaction rate and duration at these pressure values is similar to the effect of temperature: the reaction rate increases from 8.2 to 10.1 ml/min, and the duration of the process decreases from 180 to 150 minutes (Table 1). The content of aromatic hydrocarbons is reduced by 15% as measured by the aniline point, which increases from <44 to <53.

Table 1 - Hydrogenation of the diesel oil fraction: 180-350°C on Pt-Rh/Al<sub>2</sub>O<sub>3</sub> catalyst

Conditions	Rate, ml/min	Duration, min	Aniline point	
			before	after
100°C	8.2	180	<44	<51
120°C	9.0	169	<44	<52
140°C	9.8	156	<44	<53
160°C	10.2	149	<44	<54
180°C	11.0	139	<44	<54
200°C	12.3	130	<44	<55
2 MPa	8.2	180	<44	<51
3 MPa	9.1	165	<44	<52
4 MPa	10.1	150	<44	<53
ethanol	8.6	170	<44	<54
propanol	7.8	195	<44	<51
isopropanol	8.2	180	<44	<51

Ethanol, propanol, and isopropanol were used as solvents. According to the reaction rate and duration of the process, ethanol is the best solvent. These solvents by reaction rate are arranged in a row: ethanol > isopropanol > propanol.

And accordingly the speed values in this row are reduced from 8.6 to 7.8 ml/min, and the duration of the process is antipate increased from 170 to 195 minutes (Table 1). For all values of temperature, hydrogen pressure and solvent type, the rate of hydrogenation of the diesel fraction 180-350°C is greater than the fraction 230-360°C.

Pt-Rh/Al<sub>2</sub>O<sub>3</sub> catalyst showed low activity for diesel fractions, which is associated with poisoning with sulfur-containing compounds (0.02%) contained in the fuel. Therefore, to increase its activity, the catalyst was modified in two ways: by introducing chromium oxide and zeolite ZSM-5. Chromium oxide increases resistance to poisoning by sulfur, and zeolite affects the formation of active surface phases, providing a sufficiently high concentration of strong proton donor and electron acceptor centers, thereby increasing the catalytic activity.

When hydrogenating diesel fuel with an aromatic content of 30-39% on catalysts modified by chromium oxide and zeolite, the reaction rate is higher than on an unmodified catalyst, the duration of the process is reduced. Conversion increases and is 10-13% (table 2). The content of aromatic hydrocarbons was determined by measuring aniline point. On modified catalysts, the aniline point after the reaction is <55, which indicates a decrease in the aromatic content. By all indications, a catalyst modified with zeolite is more active than unmodified and modified chromium oxide.

Table 2 - Hydrogenation of two diesel fractions on various catalysts

Catalyst	Type of fraction	Content of aromatics, %	Rate, ml/min	Conversion, %	Duration, min	Aniline point	
						before	after
Pt-Rh/Al <sub>2</sub> O <sub>3</sub>	Diesel fraction 180-350°C	30	0.01	9	> 360	<44	<54
	Diesel fraction 230-360°C	39	0.01	8	> 480	<42	<53
Pt-Rh/Al <sub>2</sub> O <sub>3</sub> +Cr <sub>2</sub> O <sub>3</sub>	Diesel fraction 180-350°C	30	0.05	10	280	<44	<55
	Diesel fraction 230-360°C	39	0.06	10	270	<42	<55
Pt-Rh/Al <sub>2</sub> O <sub>3</sub> +ZSM-5	Diesel fraction 180-350°C	30	0.07	13	210	<44	<56
	Diesel fraction 230-360°C	39	0.08	12	200	<42	<56

For the same process the parameters of the regime (temperature and hydrogen pressure) were tested for some performance properties of diesel fuel, such as viscosity at 20°C, pour point and cloud point, and density at 20°C (Table 3). Table 3 shows the sample data for the Pt-Rh/Al<sub>2</sub>O<sub>3</sub> catalyst.

In Table 3 the data of the initial diesel fuel before and after the catalytic treatment with the change of hydrogen pressure from 2 to 6 MPa and temperature from 180-220°C are presented. The characteristics presented are important operational parameters and are measured under laboratory conditions. The kinematic viscosity of the resulting product decreases from 3.15 to 2.86 mm<sup>2</sup>/s compared to the original fuel. Density is also reduced from 0.833 to 0.823 g/cm<sup>3</sup>. The cloud point decreases from -19 to -27°C, and the pour point from -22 to -29°C.

Table 3 - Effect of hydrogen pressure and temperature on the properties of diesel fuel

Conditions	Density at 20°C, g/cm <sup>3</sup>	cloud point, °C	pour point, °C	Kinematic viscosity at 20°C, mm <sup>2</sup> /s
Before treatment	0.833	-19	-22	3.15
2 MPa	0.830	-21	-25	3.00
4 MPa	0.829	-24	-27	2.98
6 MPa	0.823	-25	-28	2.86
180°C	0.830	-21	-25	3.00
200°C	0.828	-25	-27	2.72
220°C	0.825	-27	-29	2.70

Table 4 shows some of the performance properties (physico-chemical indicators) of diesel fuel in the process of hydrogenation on three catalysts: Pt-Rh/Al<sub>2</sub>O<sub>3</sub>, Pt-Rh/Al<sub>2</sub>O<sub>3</sub>+Cr<sub>2</sub>O<sub>3</sub> и Pt-Rh/Al<sub>2</sub>O<sub>3</sub>+ZSM-5.

Table 4 – Physico-chemical indicators of diesel fuel in the process of hydrogenation

Conditions	Density at 20°C, g/cm <sup>3</sup>	cloud point, °C	pour point, °C	Kinematic viscosity at 20°C, mm <sup>2</sup> /s	Aniline point
Before treatment	0.833	-19	-22	3.15	<44
Pt-Rh/ Al <sub>2</sub> O <sub>3</sub>	0.830	-21	-25	3.00	<54
Pt-Rh/Al <sub>2</sub> O <sub>3</sub> +Cr <sub>2</sub> O <sub>3</sub>	0.829	-24	-27	2.98	<55
Pt-Rh/Al <sub>2</sub> O <sub>3</sub> +ZSM-5	0.823	-25	-28	2.86	<56

After treatment on developed catalysts, the fuel density decreases from 0.833 to 0.823. The cloud point and pour point are reduced, respectively, from -19 to -25 and from -22 to -28°C. Viscosity also decreases from 3.15 to 2.86 mm<sup>2</sup>/s. The content of aromatic hydrocarbons, measured by the aniline point method, decreases from <44 to <56. The best results were shown by the Pt-Rh/Al<sub>2</sub>O<sub>3</sub> + ZSM-5 catalyst, which had the lowest cloud point -28°C, pour point -28°C, viscosity 2.86 mm<sup>2</sup>/s, as well as the content of aromatic hydrocarbons - aniline point <56.

Thus, the advantage of the prepared catalysts is in reduction the concentration of polycyclic aromatic hydrocarbons (PAHs) by 10–20% in diesel oil fractions. Diesel fuels obtained after hydrodearomatization have a lower cloud point and pour temperature, as well as kinematic viscosity. The catalysts have a high stability to poisoning with sulfur-containing compounds, which is especially important for diesel fuels in Kazakhstan.

The technology of hydrodearomatization of diesel fuels is applicable to the production of environmentally friendly fuels with a low content of aromatic hydrocarbons, has low energy consumption and high environmental friendliness. Reducing the amount of aromatic hydrocarbons in automotive fuels will reduce the amount of gaseous emissions and extend the service life of cars by 1/3, which will also bring an economic effect.

### Conclusions

The process of hydrodearomatization of two diesel fractions of PKOP LLP (PetroKazakhstanOilProducts, Shymkent) of 180-350°C and 230-360°C on the prepared Rh-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts was investigated. The influence of the technological parameters of the process of hydrodearomatization (hydrogen pressure 2-6 MPa, temperature 100-220°C) on the reaction rate, conversion and aromatic hydrocarbon content at the “aniline point” was investigated.

To increase stability and resistance to poisoning with sulfur-containing compounds of petroleum fractions, the carrier was modified with chromium oxide and synthetic zeolite ZSM-5, which led to an increase in the reaction rate and conversion of aromatic hydrocarbons.

Optimum conditions have been selected (temperatures 200-220°C, hydrogen pressure 4-6 MPa, solvent - ethanol, propanol, isopropanol) for hydrogenation of diesel fractions: 180-350°C and 230-360°C on Pt-Rh-catalysts supported on alumina and mixed carriers. Some operational properties of diesel fuel (kinematic viscosity at 20°C, pour point and cloud point and density at 20°C) of the initial diesel fractions and after catalytic treatment were determined, the effect of temperature and pressure on the change in these characteristics was investigated.

In the presence of developed catalysts, the fuel density decreases from 0.833 to 0.823, cloud point and pour point decrease, respectively, from -19 to -25 and from -22 to -28°C, viscosity also decreases from 3.15 to 2.86 mm<sup>2</sup>/s. The content of aromatic hydrocarbons is reduced by 10-20%. The best results were shown by the Pt-Rh/Al<sub>2</sub>O<sub>3</sub>+ZSM-5 catalyst, which had the lowest cloud point of -28°C, solidification of -28°C, viscosity 2.86 mm<sup>2</sup>/s, as well as the content of aromatic hydrocarbons - aniline point <56.

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### **МОТОР ЖАНАРМАЙЛАРЫНДА АРОМАТТЫ КӨМІРСУТЕКТЕРДІҢ ҚҰРАМЫН АЗАЙТУДЫҢ КАТАЛИЗДІК ТЕХНОЛОГИЯСЫ**

**Аннотация.** Жұмыстың мақсаты ароматты көмірсутектердің аз мөлшері бар экологиялық таза жанармайды өндіруге арналған дизель фракцияларын гидродеароматизациялау процесін зерттеу болып табылады. «ПКОП» ЖШС-нің (PetroKazakhstanOil Products, Шымкент) екі дизельдік фракциясының гидрогенизациясы 180-350°C және 230-360°C-та зерттелген. Жұмыста Rh-Pt/Al<sub>2</sub>O<sub>3</sub> катализаторы қолданылды. Реакция жылдамдығына, гидрероматизация процесінің технологиялық параметрлері (қысым 2-6 МПа, температура 100-220°C), «анилин нүктесінде» конверсия және ароматты көмірсутектердің құрамының әсері зерттелді. Мұнай фракцияларының құрамында күкірті бар қосындылармен улануы тұрақтылығы мен жалпы тұрақтылығын арттыру үшін тасымалдағыш хром оксидімен және ZSM-5 синтетикалық цеолитімен модификацияланды, бұл ароматты көмірсутектердің реакциясы мен конверсиясының жылдамдығын арттыруға әкелді. Алюминий оксидіне және аралас тасымалдағыштарға отырғызылған Pt-Rh-катализаторларында дизельді фракцияларды гидрирлеу үшін оңтайлы жағдайлар (температурасы 200-220°C, сутегі қысымы 4-6 МПа, еріткіш - этанол, пропанол, изoproпанол) іріктелді. Ароматты көмірсутектердің құрамы 10-20% төмендейді. Дизель отынының кейбір пайдалану қасиеттері анықталды (20°C кезіндегі кинематикалық тұтқырлығы, қату және тұндыру температурасы және 20°C кезіндегі тығыздығы) және катализдік өндеуден кейін, температура мен қысымның осы сипаттамалардың өзгеруіне әсері зерттелді.

**Түйін сөздер:** катализатор, гидрирлеу, гидродеароматизация, ароматты көмірсутектер, дизельді фракция.



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### **КАТАЛИТИЧЕСКАЯ ТЕХНОЛОГИЯ СНИЖЕНИЯ СОДЕРЖАНИЯ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ В МОТОРНЫХ ТОПЛИВАХ**

**Аннотация.** Целью работы являлось изучение процесса гидродеароматизации дизельных фракций для производства экологически чистых топлив низким содержанием ароматических углеводородов. Изучено гидрирование двух дизельных фракций ТОО ПКООП («ПетроКазахстанОйлПродактс», г. Шымкент) 180-350°C и 230-360°C. В работе использовался Rh-Pt/Al<sub>2</sub>O<sub>3</sub> катализатор. Исследовалось влияние технологических параметров процесса гидродеароматизации (давление 2-6 МПа, температура 100-220°C) на скорость реакции, конверсию и содержание ароматических углеводородов по «анилиновой точке». Для повышения стабильности и устойчивости к отравлению серусодержащими соединениями нефтяных фракций носитель модифицировали оксидом хрома и синтетическим цеолитом ZSM-5, что привело к повышению скорости реакции и конверсии ароматических углеводородов. Осуществлен подбор оптимальных условий (температура 200-220°C, давление водорода 4-6 МПа, растворитель - этанол, пропанол, изопропанол) для гидрирования дизельных фракций: 180-350°C и 230-360°C на катализаторах Pt-Rh, нанесенных на оксид алюминия и смешанные носители. Содержание ароматических углеводородов снижается на 10-20%. Определены некоторые эксплуатационные свойства дизельного топлива (кинематическая вязкость при 20°C, температуры застывания и помутнения и плотность при 20°C) исходных дизельных фракций и после каталитической обработки, исследовано влияние температуры и давления на изменение этих характеристик.

**Ключевые слова:** катализатор, гидрирование, гидродеароматизация, ароматические углеводороды, дизельная фракция.

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