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ABSTRACT

of the dissertation for the degree of Doctor of Chemical Sciences

DEVELOPMENT OF THE OXYCRACKING PROCESS OF VACUUM GASOIL IN THE PRESENCE OF HETEROGENEOUS CATALYSTS

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GENERAL CHARACTERISTICS OF THE WORK

Relevance and research of the topic. The goal of the strategic development of the world oil refining industry is to increase the share of cheap oil raw materials in petrochemical synthesis. In this case, only the availability of innovative solutions means a breakthrough and progressive development. Most of the research conducted in this direction refers to existing processes and is divided into two directions: the creation of new catalytic systems and the development of designer works[1,2]. Oxidative catalytic cracking or oxycracking (OCC), which combines these two directions, is considered to be a fundamentally new process located at the junction of two processes: catalytic cracking and partial oxidation, and it is considered catalytic cracking of heavy oil fractions with oxygen.

The analysis of modern scientific literature shows that the catalytic cracking technology, which has been on the market for almost a hundred years, has gone through several revolutions in its development. At the same time, the basic principles of its technological design have remained unchanged since the creation of the first industrial unit in 1942. In addition, in the last two decades, a trend of changing the direction of catalytic cracking towards petrochemicals has been observed in the world. Provisions are objectively made for changes in the basic technologies of catalytic cracking, as the opportunities for improvement of this dominant process today are close to saturation. Retrospective analysis shows that similar circumstances lead to substitution of technologies. An example of this is the occurrence of catalytic cracking instead of thermal cracking.

Catalytic oxycracking of vacuum gas oil (VG), based on traditional technologies, allows obtaining liquid fractions, which contain oxygenated and aromatic compounds, with a high yield of oily

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[1] Потапенко, О.В. Реакции межмолекулярного переноса водорода как ключевые стадии в процессах каталитического крекинга: достижения и перспективы / Потапенко, О.В. Доронин В.П., Сорокина Т.П. [и др.] // Успехи химии, - 2023. т. 92. №1, – С. 1-31.

[2] Adanenche, D.E. Residue fluid catalytic cracking: A review on the mitigation strategies of metal poisoning of RFCC catalyst using metal passivators/traps, / D.E. Adanenche, A. Aliyu, A.Y. Atta [et al.] // Fuel, - 2023. v. 343. 127894.

gases, which in the perspective of oxycracking products not only as fuel, but also in demand for petrochemicals. It means a significant increase in the practical importance of being used as a raw material and the expansion of the directions of use. The results obtained earlier by our research group showed that the catalytic oxycracking of VG with the presence of oxygen allows to increase the depth of conversion of raw materials and to influence the yield of targeted products[3]. However, within the framework of this work, the main fundamental important aspects have not been touched, which limits the theoretical possibilities of fundamental change in the technology of the high-tonnage process, such as catalytic cracking. It should also be noted that the process of catalytic oxycracking of VG is also important in the theoretical aspect, as it is considered a unique object for revealing specific and general regularities of catalytic processing of heavy oil fractions with oxygen.

In connection with the above, the issue of expanding the research base of catalytic oxycracking of VG is considered **actual**. First of all, this is the development of theoretical foundations, the discovery of the mechanism of the catalytic oxycracking process of VG and the selection of catalytic systems. At this time, development of the physico-chemical basis of the selection of catalysts, determination of the "composition → structure → catalytic properties" cause-and-effect relationship for them are undoubtedly the main fundamental issues. The research results in this field will lead to the development of the principles of the catalytic oxycracking process of VG and the creation of new high-efficiency catalysts for it.

The object and subject of the research. The main object of Research is the process of catalytic oxycracking of VG. The subject of the study is to determine the relationship between the composition of the catalyst and the catalytic properties they exhibit.

Taking into account the above, the purpose and issues of the research are the development of the catalytic oxycracking process of VG.

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[3] Гусейнова Э.А., Мурсалова, Л.А. Каталитический оксикрекинг вакуумного газойля / Л.А. Мурсалова, К.Ю. Аджамов // Азербайджанский химический журнал, - 2014. №3, - С.37-42.

Within the framework of achieving the set goal, the following issues were resolved:

1. Researching the catalytic activity of zeolite-containing catalyst (ZCC) in the oxycracking process of VG; Determining the impact of process parameters on the yield, quality indicators, group hydrocarbon content of VG oxycracking products with the participation of ZCC;
2. Determining the catalytic activity of metal-zeolite-containing (Me/ZCC) catalysts in the oxycracking process of VG; Determining the effect of the nature of the metal on the yield, quality indicators, group hydrocarbon content of VG oxycracking products with the participation of Me/ZCC;
3. Searching for interrelationships between the catalytic, physico-chemical and acid-base properties, composition and their activity of heterogeneous catalytic systems studied in the oxycracking process of VG;
4. Determining the area where the catalytic oxycracking process of VG takes place;
5. Determination of the factors that determine the activity and selectivity of ZCC systems in the process of catalytic oxycracking of VG; Development of recommendations on the selection of active catalytic systems for catalytic oxycracking of VG;
6. Determination of the main kinetic regularities of the catalytic oxycracking process of VG.

Research methods. A wide range of physico-chemical methods were used during the research of the quality indicators of the oxycracking products and the chemical group and individual hydrocarbon composition (GOST 3900; GOST 6258; GOST 33-2000; GOST 2177-99; GOST 19932-99; GOST 6356-75), chromium-mass-spectroscopy, gas-liquid chromatographic analysis). Determination of viscosity limits for flame propagation in gas- and steam-air mixtures was carried out in accordance with international standards (GOST 12.1.044-89 ISO 4589-84). In addition, ex situ studies of the synthesized catalysts were carried out with the help of modern analytical equipment (DTA, TQA, RFA, SEM, EDX). Mathematical statistical methods were used for the analysis of experimental evidence and the assessment of the suitability of the models of the catalytic cracking process.

The main provisions defended:

- features of the composition of products of catalytic oxycracking of VG with ZCC and Me/ZCC participation; the effect of oxidative condensation products on the activity of catalytic systems;
- causal relationship between the composition, structure, acid-base and catalytic properties of catalytic systems;
- the relationship between the composition of heterogeneous catalytic systems and the area of occurrence of the catalytic oxycracking process of VG;
- determination of the main characteristics of modifying additives affecting the activity of catalytic systems;
- kinetic, optimized parameters of catalytic oxycracking process of VG, "dynamic kinetic model".

Scientific innovation of research:

1. The concept of catalytic oxycracking of VG - a single-stage synergistic combination of catalytic cracking and partial oxidation was developed and formulated. The construction of the reaction field is scientifically based. Safe mode conditions for the process have been determined.
2. For the first time, numerous and various effects of ten oxide-modifiers: Cu, Ti, V, Cr, Fe, Co Ni, Cd, Mo and W on the catalytic properties of ZCC were determined in the oxycracking process of VG. The order of activity was established (according to the total yield of transparent fractions): Mo > Ti > Cr > Ni > Fe > W > V > Cd > Co > Cu.
3. It has been shown that increasing the acidity of the catalyst leads to an increase in the yield of target fractions: to a high degree when Lewis acidity is strengthened, to a lesser extent when Brønsted acidity is strengthened.
4. For the first time, evidence was obtained about the surface-volume stages of the catalytic oxycracking process of VG. It was concluded that the high catalytic activity of Mo-, W- and Ti/ZCC-systems is

related to the occurrence of the oxycracking process according to the heterogeneous-homogeneous mechanism.

5. Surface temperature oscillations indicating the non-stationary state of catalysts are defined and explained.
6. For the first time, the kinetic and activation parameters of the catalytic oxycracking of VG with the participation of ZCC (activation energy, rate constant, composition of reactions for the formation of oxygen-containing and oxygen-free hydrocarbons) were determined. The presence of compensation effect was determined.

The work was carried out with the support of the **EIF-KETPL-2015-1(25) Grant of the Science Development Fund under the President of the Republic of Azerbaijan "Oxidative catalytic cracking of hydrocarbon raw materials (oxycracking)"**.

Practical and theoretical importance of work:

1. The catalytic oxycracking process allows to ensure a high degree of conversion of heavy oil fractions, yield of hydrocarbon gas and diesel fractions - 71.8, 33.7 and 35%, respectively. Such catalytic systems have been developed, with their participation, the yield of diesel fractions under oxycracking conditions reaches 49.6-56.9% (Mo, Ti), and hydrocarbon gases - 26.5% (W).
2. For the first time, in the course of complex studies of the catalytic oxycracking process of VG, the effect of its parameters on the output of the target fractions and the hydrocarbon content was obtained. The possibilities of adjusting the quality and quantity of products due to the selection of technological mode parameters and composition of catalytic systems have been determined.
3. For the first time, the regularities of distribution of alkanes, oxygen-containing and ArHk in the target liquid products and gas of catalytic oxycracking of VG obtained with the participation of ZCC and Me/ZCC were determined. The study of the fractional composition and physicochemical properties of the targeted liquid hydrocarbon fractions allowed to determine the process parameters and the composition of the catalytic systems, while the resulting fractions correspond to the requirements of the GOST set for engine fuels.

4. It was determined for the first time that the oxycracking of VG with the participation of Cr/ZCC, W/ZCC and Fe/ZCC catalytic systems is considered an effective process for obtaining low-sulfur liquid products - the amount of dibenztifen and its C_1-C_3 homologues is 97.39% (relative .) decreased to
5. On the basis of kinetic laws, the concept of "dynamic kinetic model" of the operation of active centers of STL in the process of catalytic oxycracking of VG was developed. The current model had good prognostic capabilities, which proved a high degree of concordance between report and empirical evidence.

Approval and application of work. 48 articles were published on the subject of the dissertation, of which 33 were published in peer-reviewed scientific journals recommended by the RA EAC, 9 were indexed in WoS and Scopus databases, 2 patents and 1 Grant issued by the Science Development Fund under the President of the Republic of Azerbaijan was received. The main materials of the dissertation were presented and discussed at the following international conferences: VIII Всероссийской конференции с международным участием молодых ученых по химии Менделеев -2014, Санкт-Петербург; II Российском конгрессе по катализу «РОСКАТАЛИЗ», Самара, 2014; Республиканской научно-практической конференции по нефтехимическому синтезу, посвященной 100-летию академика С.Д.Мехтиева, Баку, 2014; Научно-практической конференции, «Хазарнефтятаг»-2014; Семинарах НИИ «Геотехнологические проблемы нефти, газа и химия», 2014; Республиканской научной конференции, посвященной 90-летию академика Т.Шахтахтинского, 2015; EuropaCat XII. Catalysis: Balancing the use of fossil and renewable resources. European Congress on Catalysis. Kazan, 2015; XI Всероссийской научно-технической конференции «Актуальные проблемы развития НГК России», РГУ им. И.М. Губкина, 2016 г.; IX Бакинской Международной Мамедалиевской конференции по нефтехимии, Баку, 2016; XV Международной конференции по термическому анализу и калориметрии в России (RTAC-2016), 2016; Научно-технической конференции «Нефтехимический синтез и катализ в сложных конденсированных системах», посвященной 100-летию со дня рождения академика Б.Г.Зейналова, 2017; International Turkic World Conference on Chemical Sciences and Technologies, 2017 (ITWCCST-2017); Международной научно-практической конференция «Фундаментальные и прикладные исследования в области химии и экологии-2018», 2018; Международной научной конференции «Актуальные проблемы современной химии», посвященной 90-летию Института нефтехимических процессов имени академика Ю.Х.Мамедалиева, 2019; International Conference On Actual Problems Of Chemical Engineering, Dedicate To The 100th Anniversary Of The Azerbaijan State Of Oil And Industry University, Baku, 2020; IV Российском конгрессе по катализу «РОСКАТАЛИЗ»»», Казань, 2021; V Всероссийской научной конференции с международным участием «Актуальные проблемы теории и практики гетерогенных катализаторов и адсорбентов», 2021; 6th International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface organized by Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Kraków, Poland, 2021; «Интеграция науки и образования в вузах нефтегазового профиля. Передовые технологии и современные тенденции», Уфа, 2022; Всероссийской научно-технической конференции, посвященной 75-летию ООО «ГАЗПРОМ нефтехим Салават» Наука. Технология. Производство – 2023», УГНТУ.

Place of dissertation work. Scientific-research institute "Geotechnological problems of oil, gas and chemistry" (Azerbaijan State Oil and Industry University, ASOIU), Ministry of Science and Education of the Republic of Azerbaijan.

The personal participation of the author is based on setting the goals and issues of dissertation research, choosing research objects and methods. The author freely carried out complex report-experimental work, assembled an oxycracking unit, synthesized catalysts, conducted all catalytic experiments, discussed the results, determined the kinetic characteristics of the process, and built a mathematical model. The results obtained by the author made it possible to formulate the main scientific provisions and results of the dissertation, to prepare materials in the form of articles and approvals at conferences.

Structure and scope of work. The dissertation consists of an introduction, five chapters, conclusions, and a bibliography of 231 names. The total volume of the dissertation is 447 pages and 397,444 characters. The work contains 40 tables and 118 pictures.

The introduction substantiates the relevance of the dissertation research; the purpose and main objectives of the work are formulated; describes the approach proposed by the author to solving the problems; The degree of novelty of the results obtained and their testing are characterized.

In the first chapter, the author provides data on the current state of the petrochemical industry, examines the conditions for its progressive development, and emphasizes the role of oxidation technologies. There, the author describes the results achieved by other authors and their research group in the study of the catalytic oxycracking process.

The second chapter discusses the results of a study of the oxycracking process in the presence of industrial ZCC, as a system used under the conditions of traditional catalytic cracking. This made it possible to obtain information about the differences between these two processes and the influence of the oxidizing agent. The author notes that the introduction of oxygen and the selection of process conditions makes it possible to achieve improved conversion rates and the yield of target products of appropriate quality.

The third chapter presents the results of a study of oxycracking of VG in the presence of ZCC modified with metal oxides. A comparative analysis of the nature of the modifier on the yield of target fractions and their hydrocarbon composition was carried out. The choice of the strength of the bond between surface oxygen and the surface of the transition metal oxide as a criterion for selecting active modifiers for the VG oxycracking process is justified. Activity rows are constructed. Modifiers are recommended, the introduction of which contributes to the production of deeply desulfurized liquid products.

The fourth chapter describes the results obtained by complex physical and chemical research methods: *X*-ray diffraction, thermal, dispersion analysis, scanning electron microscopy. The nature of the acid-base sites on the surface of the catalysts and their contribution to the overall activity are discussed. Possible pathways for the conversion of hydrocarbons under catalytic oxycracking conditions are considered.

The fifth chapter provides calculations of the kinetic and activation parameters of VG catalytic oxycracking.

At the conclusion of the dissertation, conclusions, a list of references and applications are provided.

MAIN CONTENTS OF THE WORK

1. RESEARCH FACILITIES

According to the purpose of the work, VG (b.st.270-b.f.500°C) obtained from the vacuum block of the ELDU-AVP-6 atmosphere-vacuum unit of H. Aliyev Refinery was selected as the research object. As a relatively more typical raw material of a catalytic cracking unit, the physico-chemical properties of VG were in accordance with ТУ 38.1011304-2004 ПС 10-2015.

The oxycracking process of VG was carried out with the participation of 13 catalytic systems: industrial cracking catalyst OMNICAT (manufactured by "Grace" company) and its 12 modified analogues. Oxides of 10 transition metals were used as modifiers: 7 *d*-elements of the IV cycle: copper (Cu), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), cobalt (Co) and nickel (Ni). ; 2 d-elements of the V period: cadmium (Cd) and molybdenum (Mo); 1d-element of the VI period: tungsten (W). The selection of cadmium (Cd), which is formally considered a non-transition metal with a filled *d*-shell, was based on empirical considerations. Modified samples were obtained by hodprum method (in the amount of 2% relative to ZCC, molybdenum - 2% and 10%) and one - by dry mechanical mixing (chromium) method according to moisture content.

2. METHODOLOGY OF THE CATALYTIC OXYCRACKING PROCESS

The development of the process of catalytic oxycracking of VG is aimed at solving two issues - determining the methodology of the process and creating the physicochemical basis for the selection of a highly selective catalyst. When working on the first issue, it arises from the need to ensure the safe implementation of partial oxidation of heavy oil fractions, which is significantly influenced by the following factors: hydrocarbon and fraction composition of raw materials; concentration of oxygen and phlegmatizer; characteristics of reaction medium design, etc.

The results of the report of density limits of explosiveness of VG and air mixture : $\varphi^{\text{M}}{}_{out} = 0.25\%, \varphi^{\text{M}}{}_{up} = 29.8\%$, showed that the lowest concentration of phlegmatizer added to the mixture of VG with air It is 36.2% (volume), this amount of mixture is not suitable for flame propagation at any ratio of raw materials and oxidizer.

The occurrence of such an explosion also depends on the dimensionless radius of the vessel ξ (a spatial coordinate equal to the ratio of the radius of the reactor to the length), which is equal to 1 for cylindrical vessels. $\xi = 0.7$ in all experimental conditions [22,39]. During the oxycracking process, a flow-type device with an immobile catalyst layer was used, the diagram of the device is shown in fig. 1.

Researches were carried out at atmospheric pressure, temperatures of 450, 500 and 550°C, volume of the catalyst - 5 cm^3, size of grains 1-2 mm, contact time (1.2-2 s), duration of the process (300-2700 s), as well as the degree of oxidation of VG (0.5-2.0%) was changed.

The received catalyst products are considered to be a mixture of target fractions and unconverted raw materials. Taking into account its complex hydrocarbon nature, it is divided into four conventional fractions based on their boiling start and end temperature intervals according to the indicators accepted in the industry: gasoline or I fraction - b.p.-195(200)°C; diesel or fraction II – 195(200)-300°C;

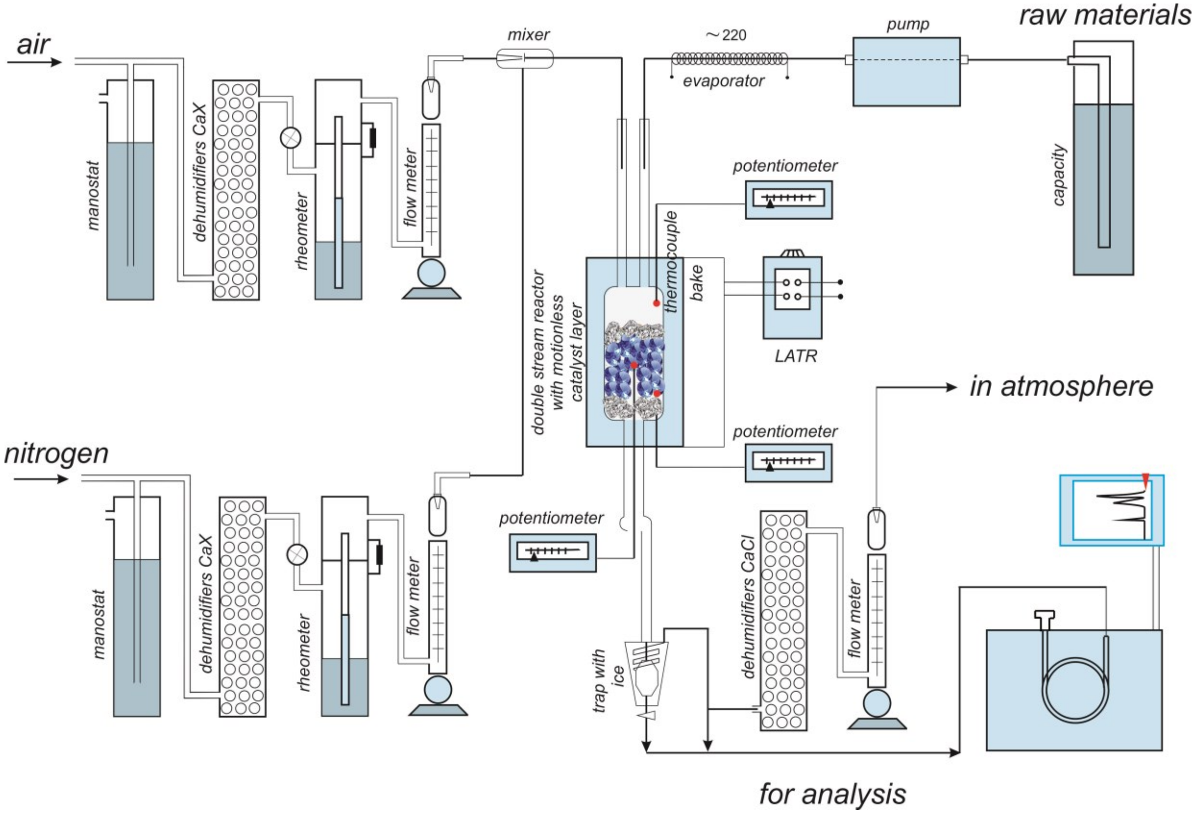


Figure 1. Scheme of the catalytic oxycracking unit of vacuum gas oil

heavy gasoil or fraction III – 300-420°C and residue or fraction IV – above 420°C. The last 2 fractions are considered unconverted raw materials due to their compatibility with the initial VG. All basic physical and physico-chemical properties for hydrocarbon raw materials and products are determined: density (GOST 3900); conditional viscosity (GOST 6258); kinematic viscosity (GOST 33-2000); fraction composition (APHC-9; GOST 2177-99); coking ability (GOST 19932-99); ignition temperature in a closed crucible (GOST 6356-75). The conversion of VG under oxycracking conditions was calculated as the total yield of gasoline fraction, light gas oil, hydrocarbon gas and coke. Clear fractions and the total release of hydrocarbon gases were taken as a measure of activity [7,8,26,34,49,53].

Catalyst samples were studied by the following methods: determination of the phase composition in the RIGAKU SC-70 X-ray diffractogram; SEM images were acquired on a JEOL JSM-6610 LV; elemental analysis evidence was obtained using an EDX-analyzer (EDS, Genesis 4000, using a Si(Li) detector); thermal analysis of samples was carried out in a NETZSCH STA 409 PC/PG device (heating rate in air 10ºC/min; corundum crucibles; temperature range 20-1000 ºC). The quantitative analysis of hydrocarbons was carried out in a complex consisting of an Agilent 6890N gas chromatograph equipped with a high-efficiency Agilent 5975 mass-selective detector. Gas chromatograph ГХ-ПИД 6890 with a flame-ionization detector from Agilent Technologies (USA) was used for the analysis of the amount of N-alkanes.

Isomerization of butene-1 was carried out in a flow-type laboratory setup. Conditions: immobile catalyst bed; temperature 300oC; atmospheric pressure. Butene-1 was obtained from the dehydration of n-C_4H_9OH over Al_2O_3. Butene-1 was given at a rate of 240 volume hr^{-1}. The isomer content of butenes was determined by the chromatographic method in the "CHROM-5" chromatograph equipped with a thermal conductivity detector. A 3 m long pipe (INZ-600 modified with 15% vaseline oil) was used.

3. VACUUM GASOIL OXYCRACKING WITH ZCC PARTICIPATION

During the study of the effect of process parameters on the oxycracking indicators of VG with the participation of S TK, the effect of temperature, process duration, degree of oxidation of raw materials and contact time was studied (Fig. 2). The degree of conversion increases with temperature and reaches the maximum value - 71.8% under oxycracking conditions at 550°C [7,8,26,34,49,50,53]. This indicator is the main contributor to the high yield of hydrocarbon gases, which indicates that the high-temperature regime equally causes an increase in the rate of both primary and secondary chemical reactions. The characteristic features of the oxycracking process at 550^{o}C are also considered to be a decrease in the amount of OCSP. The maximum amount of transparent fractions was observed at 500°C and was 38.57% (volume). In those conditions, the output of hydrocarbon gases reached 17.3% (volume).

The highest amount of hydrocarbon gases (35.1% by volume) was recorded 300 s after the start of the process, the total output of the target transparent products – after 600 s (38.5% by volume), and fraction II – by 900 s (35.6% by volume). The recorded decrease in conversion when the duration of the oxycracking process increases above 900 s is probably due to the blocking of the catalytically active centers by the increased amount of OCSP under those conditions.

In the course of studies of the influence of the amount of added oxygen, its unambiguous positive role was recorded, which means that its addition to the reaction medium leads to an additive change in the yield of reaction products: the amount of hydrocarbon gases during catalytic cracking increased from 14.1% (volume) during 2% OCC to 38.5% (volume) rises to; The yield of fraction II increased from 9% to 33.7% (volume) during 1% oxycracking. It should be noted that the presence of oxygen at a low concentration (1% OCC) leads to the formation of target liquid fractions, while an increase in oxycracking up to 2% leads to the formation of gaseous products. At this time, the

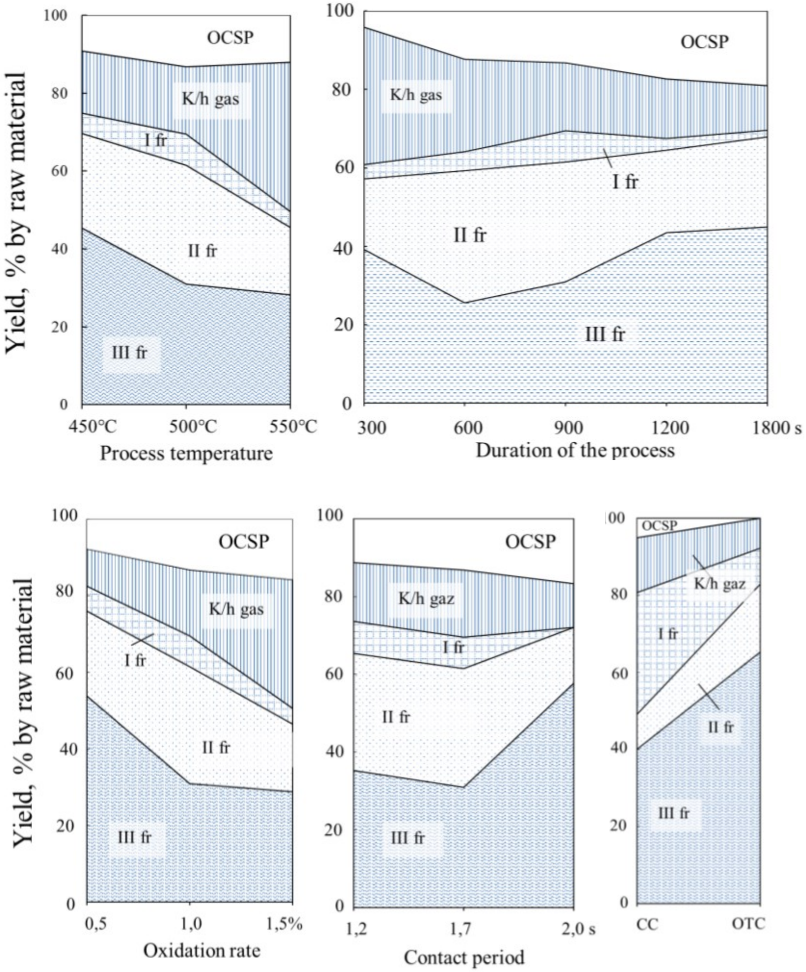


Figure 2. The effect of technological parameters on the yield of products of the oxycracking process: *a* - 900 s duration, oc. degree - 1%, contact time 1.7 s; *b* - temperature 500°C, oxygen level - 1%, contact time - 1.7 s; *c* - temperature 500°C, duration - 900 s, oxygen level - 1%.

increase in the output of fractions I and II is accompanied by a decrease in the amount of fractions III.

The output of the latter is inversely dependent on the degree of oxidation. At this time, if the amount of hydrocarbon gases and OCP increases practically exponentially, then for fractions I and II it passes the maximum at 1% oxidation degree. The total yield of clear fractions during 1% oxycracking is 38.6%, which is slightly behind the indicators of conventional CC and surpasses the corresponding indicator of 15.6% of OTC.

Changing the contact time in the range of 1.2-1.7 s significantly affects the degree of conversion of VG and the distribution of its conversion products. If the yield of transparent fractions at 1.2 and 1.7 s contact time is practically at the same level of 53-55% (volume), then the subsequent increase of the contact time to 2 s leads to a sharp increase in OCP (16.1%) against the background of its regular increase (16.1%) is accompanied by a decrease. This is due to a decrease in the conversion rate (from 69.1 to 40.8% (volume)). In these conditions, a relatively sharper decrease in the total yield of clear fractions and gas is observed, while the I fraction is not formed at all, and the yield of II fractions and hydrocarbon gases decreases more than twice. The formation of fraction IV was also recorded, which was detected only in 2 conditions during the studies: at the lowest oxidation degree of those studied (0.5% OCC; 13.0% (vol)) and at the maximum high contact time (2 s; 2.9% (vol) These evidences were obtained against the background of maximally high amount of OCP (16.1% by volume).

Thus, as a result of studies of the effect of the conditions of the oxycracking process of VG on the yield of products with the participation of ZCC, it was determined that the temperature and the degree of oxidation have a symbiotic effect on the degree of conversion of raw materials and the yield of reaction products, while the contact time has an antagonistic effect.

To monitor the role of the catalyst and oxidizing medium in the oxycracking process of VG by comparing the quantitative indicators obtained above with traditional CC and OTC evidence under the conditions of using similar raw materials, temperature (500°C), contact time (except for 1.7 s, OTC) and process duration can Thus, the addition of oxygen to the reaction medium allows the following (compared to traditional CC):

- to increase the conversion of raw materials from 61.3 to 69.4% (volume);
- to increase the output of hydrocarbon gases from 14.1 to 17.3% (volume);
- to increase the yield of II fractions from 9 to 30.6% (volume).
- conducting the process without the presence of a catalyst (OTC) is accompanied by the following compared to oxycracking:
  with a low yield of hydrocarbon gases (6.7% during OTC and 17.3% during oxycracking);
- with the overall low yield of transparent fractions (23% during OTC and 38% during oxycracking);
- with the same subtraction of fraction I.

In general, it should be noted that the presence of oxygen creates favorable conditions for the formation of a higher amount of fraction II than fraction I. This is true for both OTC and OCC.

TBP curves were constructed for the evaluation of the quality composition of liquid catalyst of oxycracking of VG (Fig. 3). The lowest boiling onset and end boiling temperatures are typical for liquid products obtained at 500°C, 900 s, 1% oxidation state, 1.7 second contact time and are 61 and 370°C, respectively. The heaviest fraction composition was recorded in the sample obtained at 500°C, for 900 s, but with 2% oxidation degree and contact time of 1.7 s: b.s. - 150°C, b.f. - 418°C. Taking into account these differences, the fractions obtained in different technological conditions of the oxycracking process have a significantly different hydrocarbon composition.

Later, fractions I and II were divided into three areas defining the light (head) (t_{10}), middle (t_{50}) and tail part (t_{90}). Only two areas, namely t_{50} and t_{90}, were considered for the characterization of II fractions.

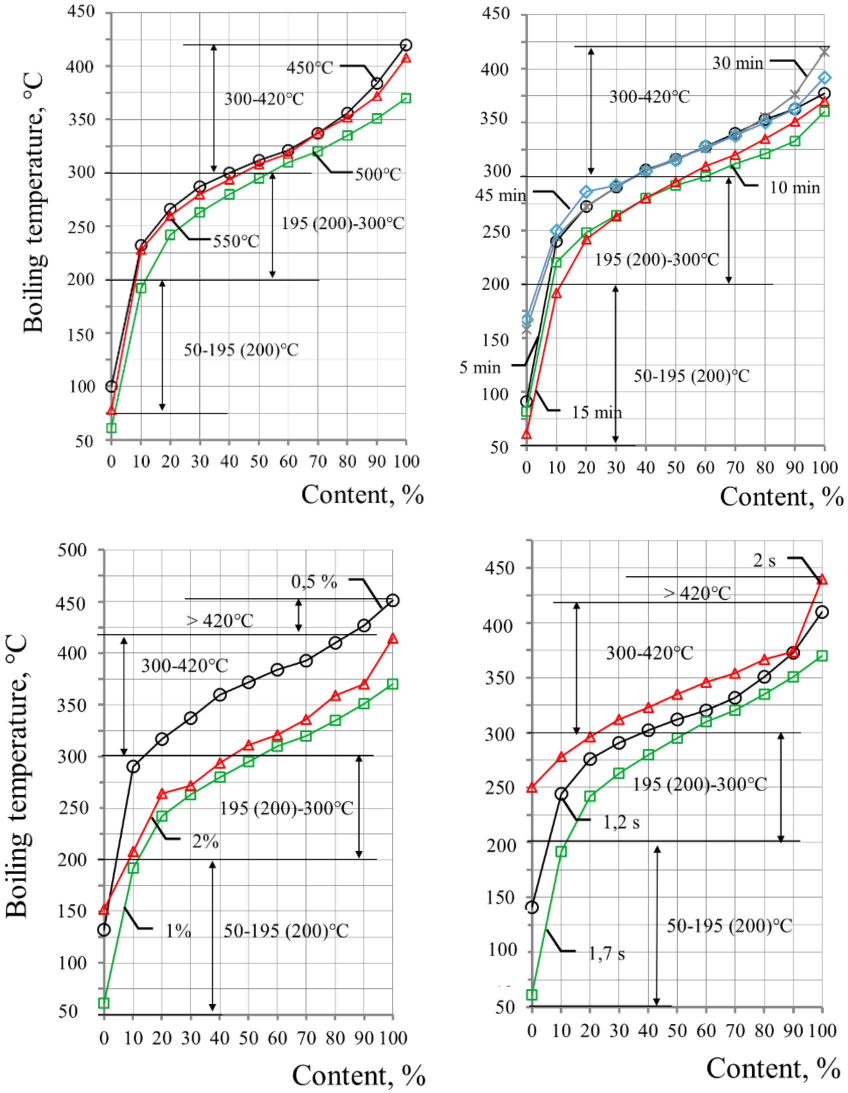


Figure 3. Dependence of the fraction composition of the liquid catalyst on the parameters of the process: *a* - duration 900 s, ox. degree - 1%, contact time - 1.7 s; *b* - temperature 500°C, oxygen level - 1%, contact time 1.7 s; *c* - temperature - 500°C, duration - 900 s, contact time - 1.7 s; *d* - temperature 500°C, duration 900 s, oxygen level - 1%.

The study of those narrow fractions was conducted in order to evaluate the possible varieties and quality of products. All graphs have the shape of increasing curves (Figure 4).

The obtained evidence allowed to determine the minimum temperature of the ambient air, in which it is still possible to start a cold engine, as well as the permissible ambient temperature in order to prevent the formation of vapor jams. It was concluded that relatively easier starting of the engine in winter will be observed when using I fractions of oxycracking obtained at a temperature of 500°C -16.5°C and 88.0°C. This fuel ensures reliable operation of a cold engine without creating "steam jams" and during the summer. Based on the presented evidence, as well as the physico-chemical properties of the liquid fractions (table 1), it can be confirmed that fraction I commodity obtained during the catalytic oxycracking process of VG at 500°C, 900 s, 1% oxidation degree, 1.7 s contact time can be used as a base component of gasoline.

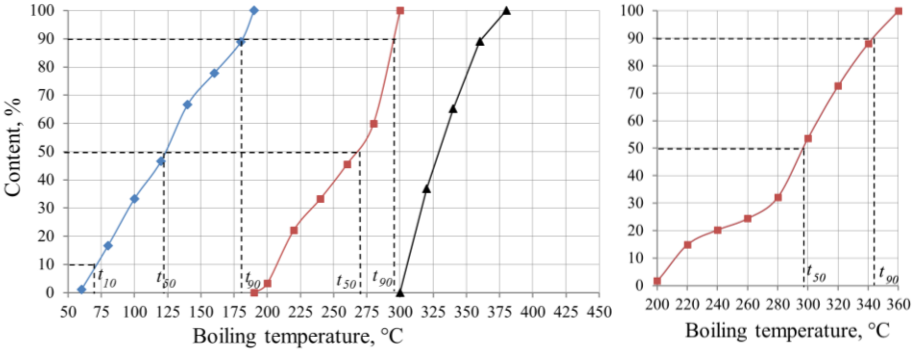


Figure 4. Distribution of boiling temperatures according to the expulsion share of fractions I-III (*a*) and II* (*b*) obtained in the oxycracking process at a temperature of 500°C

Table 1

Influence of technological conditions on the quality indicators of VG oxycracking products

Experience №	Oxycracking mode				Liquid fractions of oxycracking										
					Fraction I (50-195(200) °C			Fraction II 195(200) -300°C			Fraction III 300- 420°C				IV Fr. >420°C
	Temperature, °C	Duration, s	Oxidation state, %	Время контакта, с	Density at 15 °C, кg/м³	Reid Saturated Vapor Pressure, кPa.	Molecular weight	Density at 15 °C, кg/м³	Kinematic viscosity at 40°C, мм²/s	Flash point in closed cup , °C	Density at 15 °C, kg/м³	Kinematic viscosity at 50°C˙ мм²/с	Coking ability, %	Flash point in closed cup , °C	Density at 15 °C, kg/м³
1	450	900	1,0	1,7	788	35	110	850	4,11	59	876	6,88	2,21	112	–
2	500	900	1,0	1,7	773	41	98	840	4,05	66	869	6,80	2,36	106	–
3	550	900	1,0	1,7	780	38	106	842	4,16	57	870	6,81	2,81	108	–
4	500	300	1,0	1,7	777	44	100	837	3,91	52	870	6,79	2,77	107	–
5	500	600	1,0	1,7	775	42	99	839	4,01	55	863	6,62	2,64	104	–
$2^{/}$	500	900	1,0	1,7	773	41	98	840	4,05	66	869	6,80	2,36	106	–
6	500	1800	1,0	1,7	800	29	121	845	4,24	49	882	7,01	3,02	122	–
7	500	2700	1,0	1,7	811	26	130	851	4,63	50	891	7,09	3,15	134	–
$2^{/}$	500	900	1,0	1,7	793	32	112	842	4,12	66	890	7,09	3,11	105	923
8	500	900	1,0	1,7	773	41	98	840	4,05	51	869	6,80	2,36	106	–
9	500	900	2,0	1,7	799	30	118	834	3,87	53	871	6,82	2,84	109	–
10	500	900	1,0	1,2	780	32	111	852	4,65	61	865	6,78	2,33	101	–
$2^{/}$	500	900	1,0	1,7	773	41	98	840	4,05	66	869	6,80	2,36	106	–
11	500	900	1,0	2,0	–	–	–	869	4,98	68	893	7,13	3,24	127	930

The evidence of Figure 4 demonstrates the maximum proximity of the values of the boiling temperatures of fraction II at 50% (t_{50}) and 90% (t_{90}) – 273°C and 285°C, respectively (Figure 3, *a*). The current range of the boiling temperature value fully corresponds to the evidence for the fractional composition of diesel fuel (GOST P 52368-2005 (EH 590:2009). If we consider that the boiling point of the conventional diesel fraction is limited to 360°C in the mentioned standard, and from our side, the boiling point of fraction II the end is mArHked at 300°C, then as a possible way to expand this type of fuel resources, the possibility of "heavyening" the existing fraction (II*) to the limits allowed by the standards is considered (Figure 3, *b*). In this case, the amount of clear oil products exceeds 90% which shows the undoubted competitive advantages of the oxycracking process compared to the traditional catalytic cracking.

In general, the formation of the conventional diesel fraction (II (195(200)-300°C)) whose criteria such as density, kinematic viscosity, fractional composition correspond to the components of commodity diesel fuel is 450-550°C, 300-900 s, 1% oxidation degree, 1.7 s contact time occurs in oxycracking mode. Fractions III and IV can be used as a component of boiler fuel or as raw materials.

Group hydrocarbon composition of liquid products of oxycracking of vacuum gas oil with the presence of ZCC

The concentration of the group of hydrocarbons included in the liquid conversion products of VG under oxycracking conditions shows that the occurring complex reactions differ from both traditional CC and OTC (table 2). The group hydrocarbon composition of the liquid oxycracking catalyst is affected by the process parameters in the following way:

1. temperature: output of C_5-C_9 is the same as OCC, passing through a maximum at 500°C, while for C_{10+} this temperature is a minimum; a linear dependence is observed between temperature and yield of unsaturated compounds; with increasing temperature,

the output of naphthenes decreases regularly; an increase in temperature leads to an increase in the yield of total ArHk, especially for individual ArHk and OSP;

2. duration of the process: at 900 s from the start of the process, a relatively more significant decrease in hardness was recorded for ArHk, which is probably related to the oxidative transformations of alkyl groups, the oxidative opening of aromatic rings by the acquisition of carboxylic acid groups, or the aromatic ring carbonyl oxygen of hydrogen is exposed to an oxidative compound. It was during this period of time that an intense increase in the density of OCC was recorded; during the increase of the duration of the process above 900 s, a redistribution of group hydrocarbons was recorded - mainly high molecular unsaturated and the density of ArHk increased, which indicates the occurrence of condensation and combination reactions, the products formed during these reactions enter the condensation reactions; this evidence coincides with the results shown earlier (Figure 2) that the amount of OCP increases with the increase in the duration of the process;
3. The depth of change in the qualitative group composition of liquid oxycracking catalyst also depends on the degree of oxidation. At a low oxidation rate of 0.5%, long side chain ArHk and high molecular weight alkanes are relatively more intensively converted; with an increase in the degree of oxidation to 1%, the hardness of OCC rises past the maximum;
4. depending on the contact time, the following regularity is observed: low contact time causes a decrease in the density of high-molecular paraffin and naphthenes and an increase in aromatic hydrocarbons; The selectivity due to OCC increases during the contact time in the interval from 1.2 to 1.7 s, then it drops sharply when it increases to 2 s. The maximum concentration of unsaturated compounds was recorded under conditions of high temperature and high oxidation rate.

Table 2

Influence of oxycracking conditions on the concentration of hydrocarbon groups in liquid catalyst

Experience №	Oxycracking mode	Concentration, g/l						
		Alkanes C_5-C_9	Alkanes C_{10+}	Naphthe-nes	Unlimited	OCC	Individual ArK	2-6 ring PAU
Effect of temperature ****								
1	450°C	40	627,62	84,4	70	76,5	63,4	139,027
2	500°C	71,08	379,651	46	96,01	118,632	124	182,606
3	550°C	22	642,996	12	169	50,251	101	223,982
Effect of duration, s****								
4	300 c	35	434,74	179	38	71.021	127	181,177
5	600 c	52	586,23	112	112	79.609	96	118,74
2*	900 c	72	379,651	46	96	118.632	124	168,935
6	1800 c	31	555,25	65	218	66.116	218	195,243
7	2700 c	19	769,15	78	148	48.059	253	289,534
Effect of Oxidation state, %****								
8	0,5%	57	169,852	162	58	100,706	124	185,613
2*	1%	72	379,651	46	96	118,632	124	168,935
9	2%	104	430,815	17	312	125,018	203	129,995
Effect of contact time, s****								
10	1,2 c	106	589,311	102	204	151.021	108	182,892
2*	1,7 c	72	379,651	46	96	118.632	124	168,935
11	2 c	–	312,312	20	119	41.170	215	194,82
ВГ	–	–	542,879	196,215	–	11,402	141,666	256,646
2**	500°C	120,05	643,165	21,87	59,12	12.083	72,46	166,354
2***	500°C	18,31	312,624	126,15	254,26	76.807	98,93	346,584

VG – vacuum gas oil, raw material; 2* – oxycracking, conditions similar to sample No. 2; 2** – traditional catalytic cracking, conditions similar to sample No. 2; 2*** – oxidative thermal cracking, conditions similar to sample No. 2; ****- with the exception of a specific parameter, others are unchanged (500°C; 900 s; τ=1.7 s; 1% OCC)

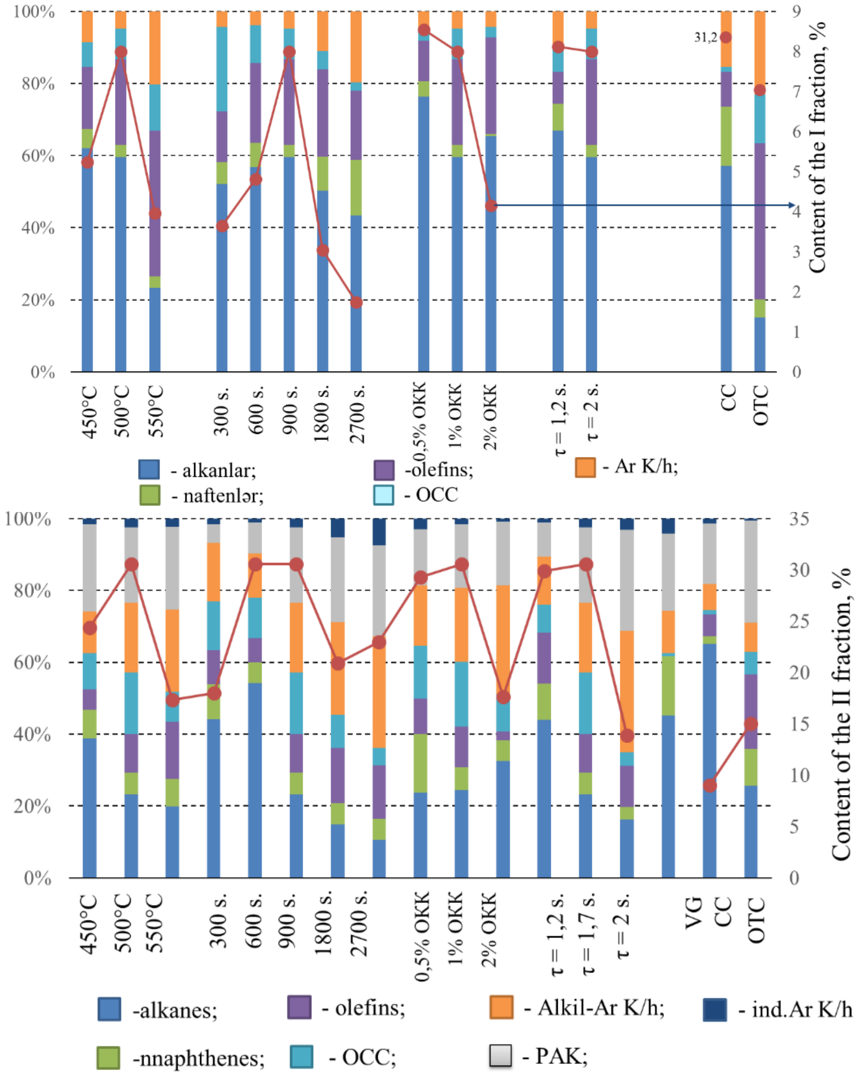


Figure 5. Distribution of group hydrocarbons in oxycracking fraction I depending on process conditions.

Note: samples was adopted according to the numbers of experiments shown in table 2; the value of subtraction of fraction I is shown on the additional ordinate axis (curved line).

Characterization of distribution of group hydrocarbons in fractions I and II of catalytic oxycracking of vacuum gas oil

Evidence for the relative distribution of different groups of hydrocarbons in fractions I and II is shown in figure 5. The results obtained for fraction I show that the moderate temperature regime and medium contact time allow obtaining a distribution of similar group of hydrocarbons with CC, while the high temperature regime – with OTC. During fraction II, the duration of the OCC process of 900 s leads to the formation of a product close to CC in terms of composition, and the high temperature regime and low oxidation rate - to the formation of a product close to OTC. In general, this means that by changing the same factors as in traditional CC - temperature and contact time, we get a change in the properties of fraction I at the outlet, which will be the same for fraction I of CC, temperature and oxidation, which are considered the main factors of oxidizing processes by changing the degree, we change the composition of II fractions, which is close to the corresponding OTC according to its composition.

Oxygen-containing compounds in liquid products of catalytic oxycracking of VG

The oxycracking process is accompanied by a high selectivity for incomplete oxidation products – the total yield of OCC reaches 19.3% (volume) in individual cases. They contain both acidic and neutral products. During the study of the characteristics of formation and distribution of OCC in the oxycracking products of VG obtained with the participation of ZCC, depending on the parameters of the process (Fig. 6,7), it was determined that:

- the low temperature of the oxycracking process is considered favorable for obtaining high molecular ethers (up to C_{27}), as the other group is formed at higher temperatures for high molecular compounds. High molecular weight acids with molecular weight C_{20} and alcohols with molecular weight C_{32} are formed under high

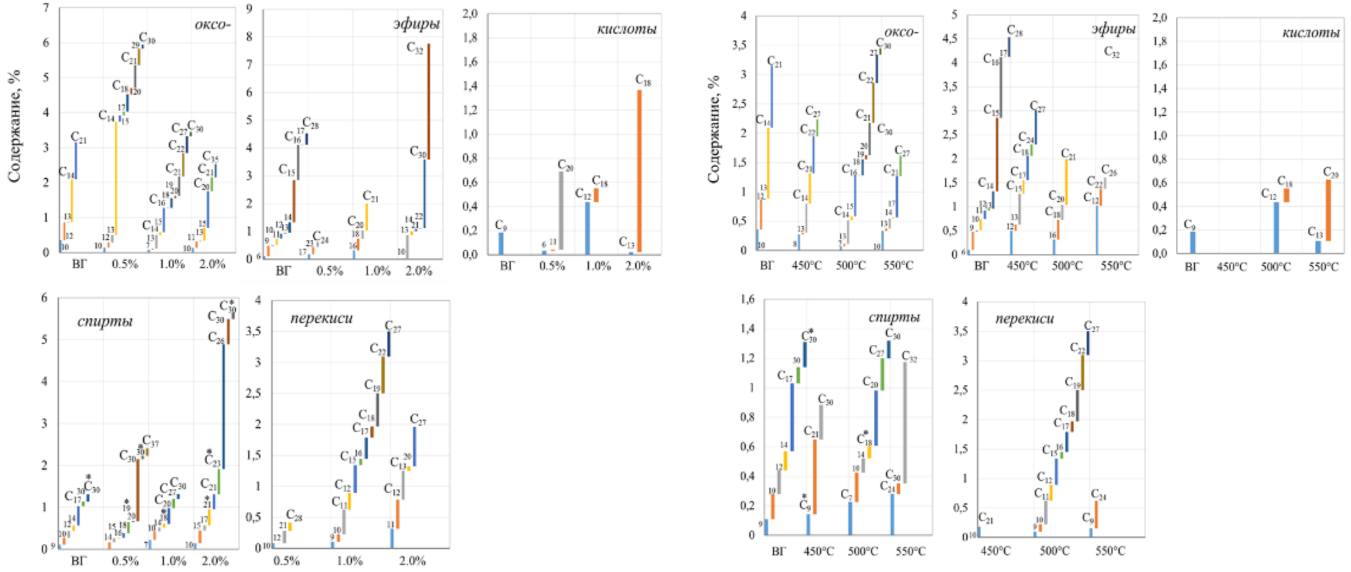


Figure 6. Effect of oxidation degree (*a*), and temperature (*b*) oxycracking process (*d*) on OCC distribution in C_{10+} oxycracking catalyst

Process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

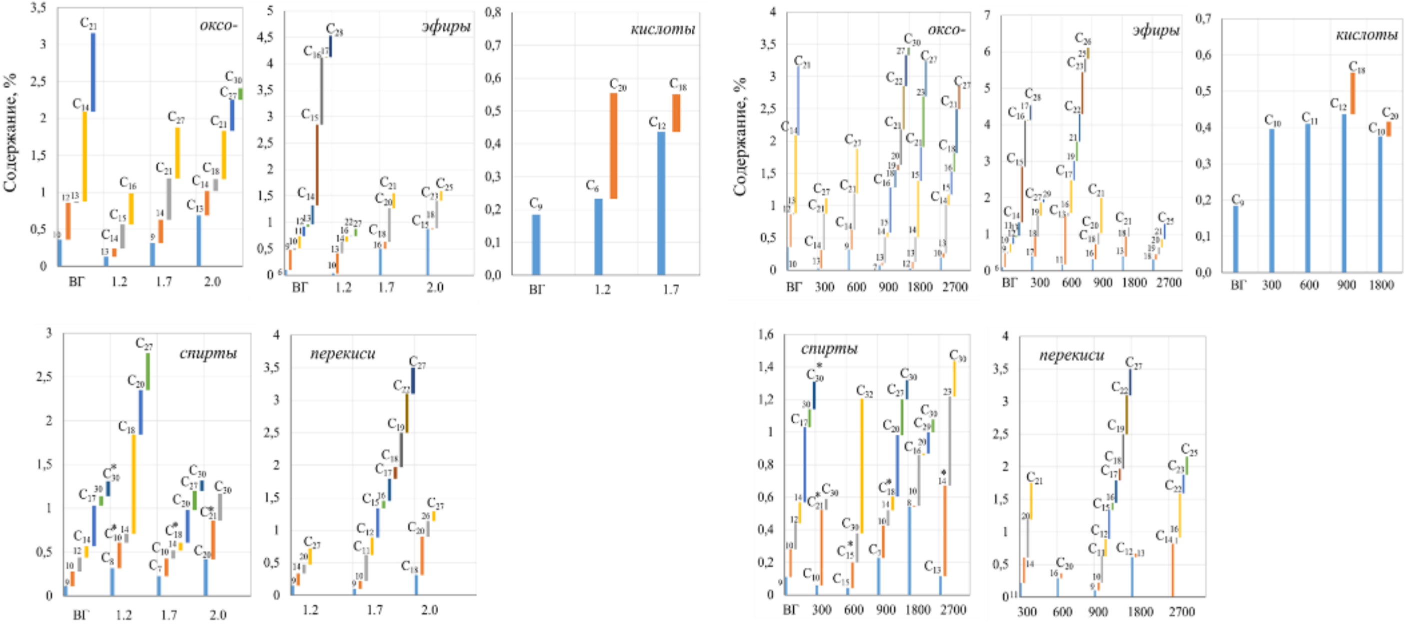


Figure 7. Effect of contact time (*a*) and duration of oxycracking process (*b*) on OCC distribution in C_{10+} oxycracking catalyst

Process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

temperature conditions. Peroxides and oxocompounds occupy an intermediate state, while the formation of relatively high-molecular compounds represented by a wide range of this group belongs to the moderate temperature regime;

- as the amount of oxygen in the reaction medium increases, the number of ethers and oxo compounds (cyclic ketones) with higher molecular weight increases, while the number of acids and alcohols, on the contrary, decreases compared to low molecular ones;
- in the oxycracking process with a low contact time (1.2 s), high molecular ethers (C_{27}) and acids (C_{20}) are formed. Unlike ethers and acids, high molecular oxo compounds (C_{30}) are formed at the highest contact time. Peroxides and alcohols occupy an intermediate position. When the contact time increases to 1.7 s, although the amount of acids remains unchanged - two (C_{12} and C_{18}), but the distribution between them changes in the diametrically opposite direction: low-molecular ones begin to dominate;
- 600 s for the formation of the maximum amount of ethers, 900 s for others is considered relatively more appropriate.

Distribution of ArHk in oxycracking products of VG

Considering the distribution of ArHk in catalysts (table 3), their relatively high amount represented by mono-, bi- and polycyclic structures (from 24.6 to 59.6% (vol) compared to 17.84% (vol) in CC) attracts attention. A relatively higher amount of ArHk is characteristic of the samples obtained under conditions of maximum temperature, oxycracking time and contact time. Unlike those parameters, the degree of oxidation does not have a significant effect on the current indicator. Almost all oxycracking patterns are dominated by polycyclic arenes. Relatively low quantitative values of the ratio of the total amount of poly-ArHk to mono-ArHk indirectly prove the intensive

Table 3

Influence of technological parameters of the oxycracking process on the content of ARH groups

Name	VG	Content in catalyst, %																	
		[1] Oxidation state, %			[2] Температура, °C			[3] Duration, s					[4] Contact time, s			[5]OTC	[6]CC
		0,5	1,0	2,0	450	*	550	300	600	*	1800	2700	1,2	*	2,0		
Aromatic hydrocarbons, incl.	35,70	30,89	27,44	27,85	24,58		35,69	36,12	28,12		45,14	59,58	30,05		42,34	46,03	17,84
mono-, alkyl-ArH	11,26	11,50	11,06	16,63	6,17		10,78	14,49	9,61		21,71	25,05	21,19		10,82	10,05	5,13
ind PAK	4,03	2,19	1,30	0,57	0,88		0,99	0,96	0,92		3,98	5,88	1,94		0,92	0,78	0,94
2-6 ring alkyl-PAHs	20,40	17,21	15,07	10,65	17,53		23,91	20,67	17,59		19,45	28,66	19,20		18,32	35,20	11,77
Σ PAHs/mono-	2,17	1,69	1,48	0,67	2,99		2,31	1,49	1,93		1,08	1,38	0,99		1,78	3,58	2,48

[1] process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

[2] process conditions: duration 900 s; oxidation degree 1%; contact time 1.7 s.

[3] process conditions: temperature 500°C; oxidation degree 1%; contact time 1.7 s.

[4] process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

[5] thermal oxidative cracking, process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

[6] traditional catalytic cracking, process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

* experimental conditions: duration 900 s; temperature 500°C; contact time 1.7 s, oxidation degree 1%.

occurrence of isomerization, hydrogen exchange, re-alkylation of aromatic hydrocarbons and cyclization reactions.

Characteristics of the hydrocarbon content of the 200°C fraction of the catalytic oxycracking of VG

The main parameter of the partial oxidation process is the amount of oxidant. For this reason, we used 0.5, 1 and 2% oxycracking catalysts to study the characteristics of the 200°C fraction and compared them with gasoline fractions of traditional CC. Figure 7 shows the dependence of the amount of hydrocarbons of different homologous series on the number of carbon atoms in the molecule. The distribution of n-paraffins in the content of conventional CC gasoline has a parabolic dependence with maxima in C_7-C_8, and in 0.5% oxycracking - C_7 is an exception, which proves the presence of high selectivity for the formation of available hydrocarbons. With an increase in the degree of oxidation up to 1%, the trend is still maintained: the highest share falls on the share of n-heptane, but already at 2% oxycracking, it gradually decreases against the background of the general drop in effect (Figure 8).

The distribution of *iso*-parafins in the 0.5% oxycracking and conventional CC gasoline fractions is practically the same and mainly falls on the share of iso-C_7, more precisely 2-methylhexane (Figure 8), which once again proves the similarity of those products not at the group level, but at the individual level. C_{10} accounts for the maximum amount of naphthenes in all samples. However, in 1 and 2% oxycracking samples, their price is 1.5-1.6 times higher than in 0.5% oxycracking and conventional CC.

The sample considered here is characterized by the general regularity of the distribution of C_{10} naphthenes in gasoline fractions: the main part belongs to 1.1-1.2 - diethylcyclohexane. The amount of ArHk in oxycracking samples also increases with the increase of oxidation degree, so it is more obvious in 1 and 2% oxycracking compared to 0.5% oxycracking and conventional CC. If the maximum

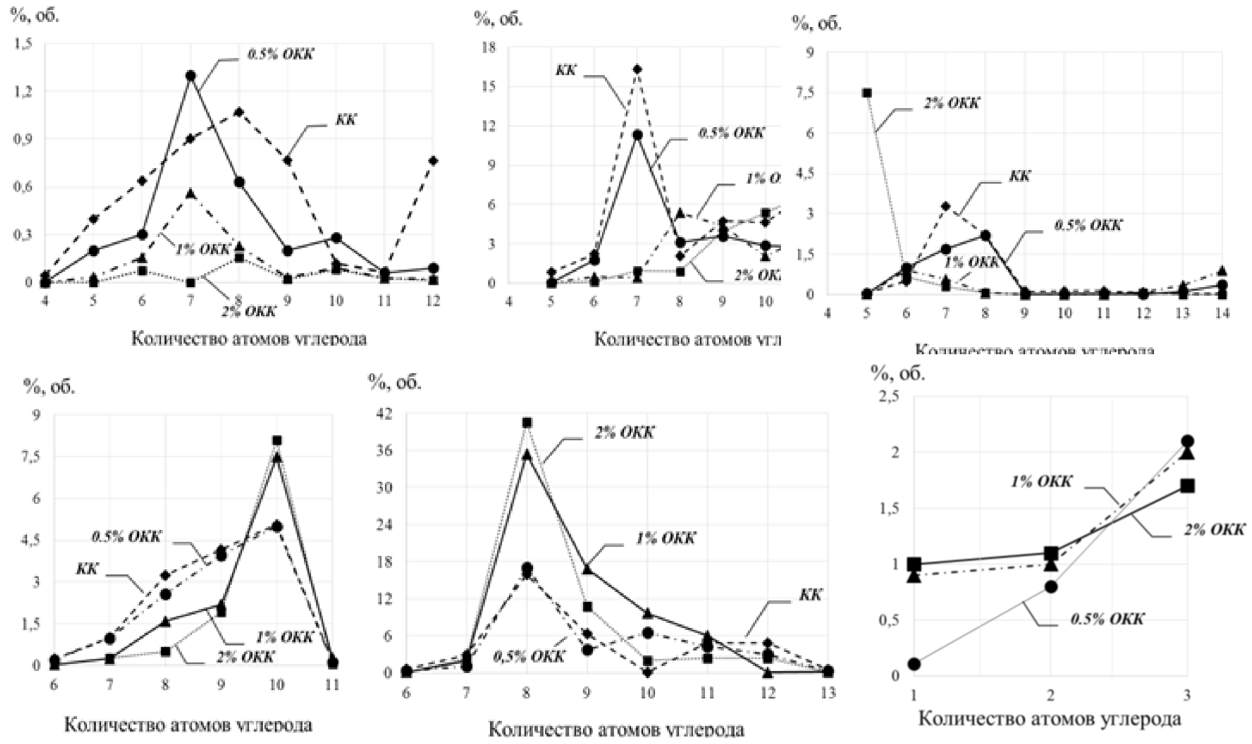


Figure 8. Dependence of the amount of hydrocarbons of different homologous series on the number of carbon atoms in the molecule: *a* – n-paraffins; *b* – *iso*-paraffins; *c* – olefins; *ç* – naphthenes; *d* – ArHk; *e* – OCC.

amount of C_8 ArHk in the latter is in the range of 16-18%, at 1 and 2% oxycracking it reaches 35 and 40.5%, respectively. The main increase of C_8 ArHk in the presence of oxygen occurs due to the increase in the share of 1,3-dimethylbenzene and a small increase for 1,2, 1,4-dimethylbenzene (Figure 9). Oxycracking conditions also increase the amount of ethylbenzene, but not as much as dimethylbenzene. An increase in the amount of xylene isomers also occurs in relation to the degree of

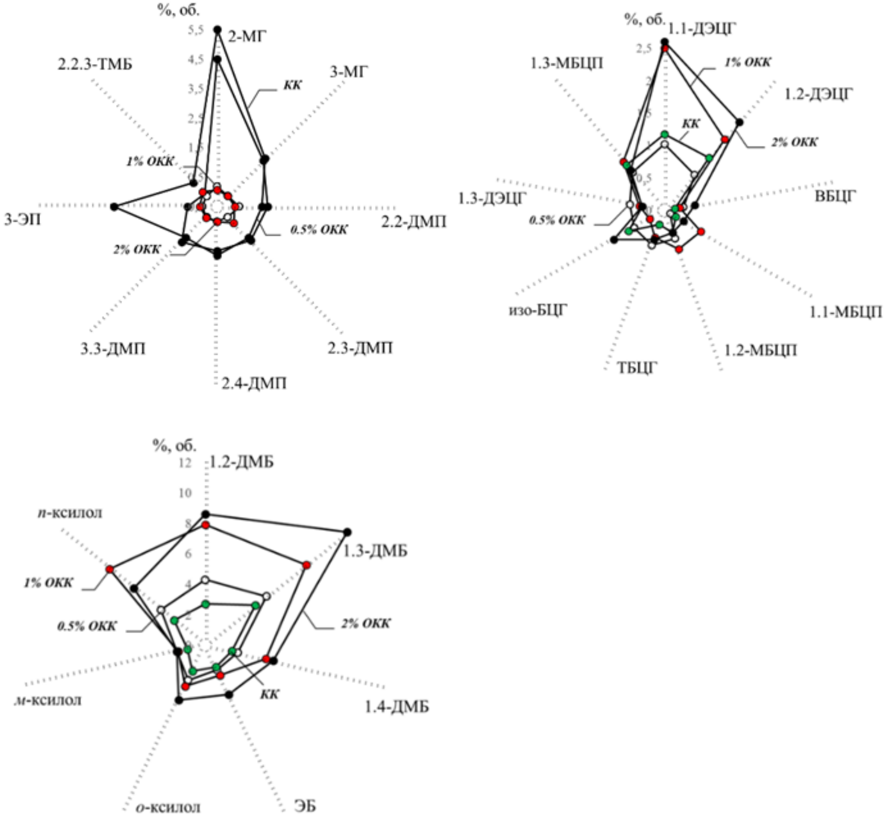


Figure 9. Distribution regularity of alkanes iso-C_7 (*a*), C_{10} naphthenes (*b*) and C_8ArHk (*c*) in gasoline fractions obtained under 0.5%, 1%, 2% oxycracking and conventional CC conditions

oxidation, with the highest selectivity being recorded for *para*-xylene. In all 4 samples, the maximum volume of the amount falls on the share of C_8, which indirectly indicates the same route of their formation - cyclization of alkenes.

The evidence on the dependence of the amount of OCC in gasoline fractions on the degree of oxidation shows the nature of their complex formation. The accumulation of low-molecular alcohols in the obtained gasoline fractions can be explained by the fact that the peroxide formed in the process of oxidation of alkanes according to the radical-chain mechanism is subjected to intense secondary decomposition reactions with the subsequent formation of the final product - alcohol. With the increase in the degree of oxidation, the share of the other growth route of the chain - fusion and stabilization increases.

In contrast to the above-considered possible accumulation routes of certain types of OCCs in gasoline fractions, along with chain development due to condensation and stabilization of high-molecular peroxides in the C_{10+} catalyst, their subsequent secondary decomposition into acids, aldehydes (in this case, the chain is broken) and alcohols (without chain breakage) is happening.

This possibility is consistent with the evidence for the distribution of OCC according to the number of carbon atoms (Figure 8). An increase in the degree of oxidation is accompanied by a sharp jump in the amount of both alcohols and acids. All this happens during an avalanche reduction of the amount of peroxide (picture 6). The presence of peroxides in the composition of oxycracking gasoline fractions was not detected.

Such a composition indicates that the conditions of oxycracking allow to obtain unique fuel compositions, which are considered to be mixtures including fossil fuels with several oxygen-containing component additives at once during one process.

4. OXYCRACKING OF VG WITH Me/ZCC PARTICIPATION

The results of the study of the effect of the nature of the modifier on the yield of all conditional fractions are shown in figure 10 (*a-e*). For a comparative analysis, oxycracking with the presence of unmodified ZCC, as well as conventional CC, non-catalytic OTC conditions, obtained corresponding evidence (Fig. 10, *j*) are shown. In general, depending on the nature of the modifier, characterizing the indicators of the conversion rate of VG, the latter can be placed in the following order according to the decrease of the conversion indicator:

A relatively higher conversion rate of VG was recorded in the oxycracking process with the sample containing 2% molybdenum (83.9%), which was higher than all other modifiers and during 1% oxycracking without modifiers, as well as during CC and OTC. was superior to those received. At this time, with the increase of the amount of molybdenum to 10%, the degree of conversion of VG decreased to 63.4%. If we compare the effect of the preparation method on the chromium sample, then the sample obtained by the impregnation method showed a higher activity than the sample obtained by the mechanical mixing method (74.5% (vol) instead of 68.7% (vol)).

It was determined on the basis of the evidence obtained about the deduction of fraction II:

- addition of modifier increases the yield of II fractions in oxycracking conditions, in non-catalytic OTC and CC conditions, respectively, by 1.8, 2.8 and 6.2 times;
- an increase in the amount of molybdenum leads to a decrease in the output of liquid oxycracking products and OCP against the background of an increase in the output of hydrocarbon gases;
- comparison of the method of addition of the modifier in the chromium sample shows that a high yield of liquid oxycracking fractions was recorded in the presence of samples obtained by the impregnation method, as mechanical mixing caused high activity in the reactions of the formation of low-molecular hydrocarbons (gases).

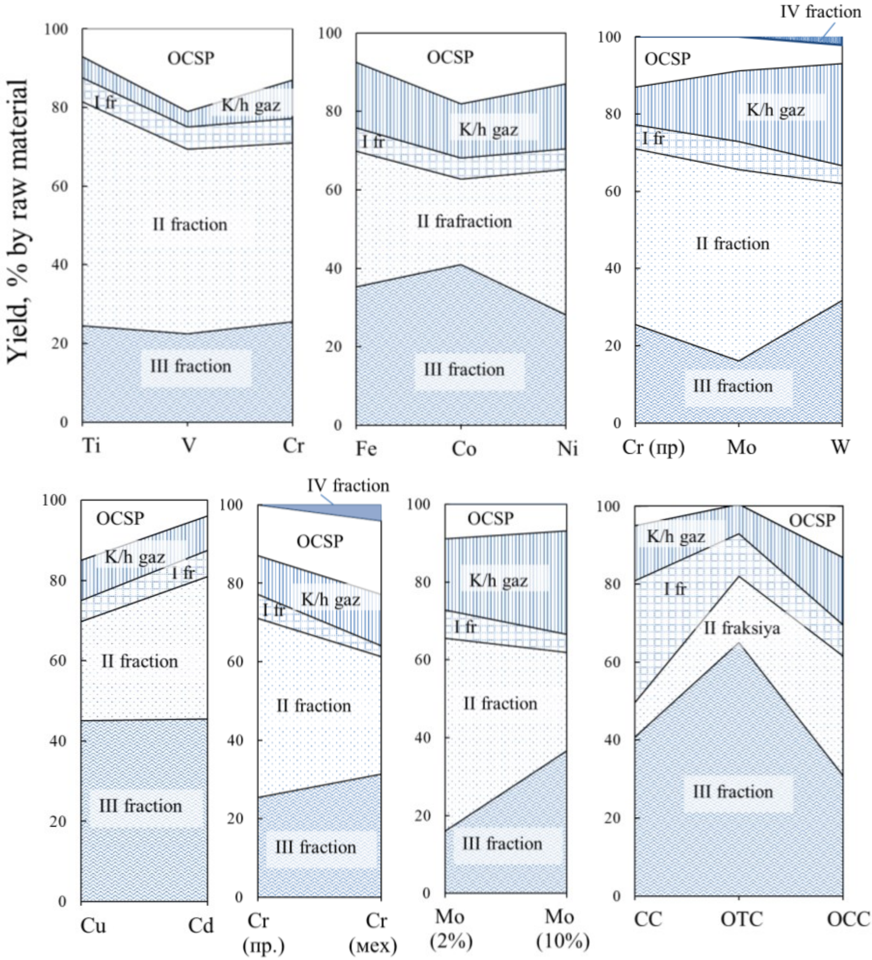


Figure 10. Influence of the nature of the modifier on the yield of products of oxycracking reactions

The maximum selectivity for the target liquid products was achieved with the presence of 84% titanium. This indicator is almost 17% higher than the price obtained with ZCC participation without modifier. However, there are such *d*-elements in the modifiers, whose effect not only affected the selectivity according to the target liquid, the catalyst, but also led to the deterioration of the indicators (Fig. 11):

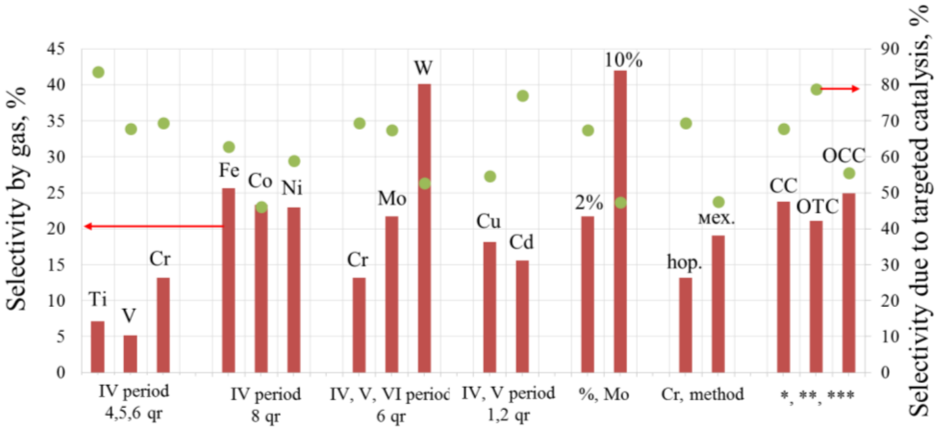


Figure 11. Effect of the nature of the modifier on the selectivity for the target catalysis (● histogram) and hydrocarbon gases (mArHker, value on the additional axis)

nickel, tungsten and copper to the first type; cobalt belongs to the second type. The comparison of the selectivity for hydrocarbon gases showed that the addition of tungsten to the composition of ZCC clearly increases this indicator compared to both unmodified and other modified samples.

It was also found that the selectivity for gases within a period is less sensitive to the nature of the modifier (for example, period IV: Fe, Co, Ni), so that it is accompanied by a large difference in transition rates from one period to another (periods IV and V: respectively, Cu and Cd). Such a conclusion can be drawn when considering the selectivity according to the target liquid catalysis: the use of a modifier located in maximally distant periods from the same period (for example, period IV: Ti, V, Cr) or neighboring periods (period IV and V: respectively, Cr and Mo) is accompanied by a rather high degree of difference in prices.

It was noted that only the 4th, 5th and 6th group elements (Ti, V and Cr, respectively), Mo and Cd of the IV period showed relatively high tendency to form mostly liquid products. The fact that the processed products, more precisely, the hydrocarbons that make up them remain genetically close to the raw materials, shows that the primary monomolecular cracking reactions are mainly realized with the participation of those modifiers, whereas the formation of hydrocarbon gases (under oxycracking conditions) is caused by elements of the same IV cycle and the same (8th) group (Fe, Co and Ni), as well as ethnic group 6 elements of the V and VI cycles (Mo and W, respectively) they are more inclined, or rather, with their participation, second- and third-order reactions prevail (re-cracking, hydrogen exchange, disproportionation of olefins, condensation of ArHk, etc.).

Attempts were made to investigate the effect of the amount of condensation products formed during the condensation and cyclization of hydrocarbons on the conversion. According to literature evidence, during CC - this is a parabola. However, in the case of modified samples, the results are ambiguous (Fig. 12, *a*). Although the conversion of VG in the presence of ZCC modified with titanium, molybdenum, chromium, vanadium and nickel is superior to unmodified samples, the amount of OCP in them varies widely: from 7 to 21% (wt.) up to.

Thus, it is generally accepted that SM is also considered as one of the components when calculating the conversion, their price gives a certain duality, for this reason, we additionally considered the conversion dependence of the target oxycracking products for each modifier (Fig. 12, *b*). The presented results show that, in contrast to vanadium, the high conversion of raw materials under oxycracking conditions in the presence of molybdenum is not due to the effect of OCP. Taking into account the known results, we assume that such a difference is related to the acid-base properties of the surface of the modified samples and the propensity to burn, as well as the possible catalytic activity of OCP itself [53].

In the course of research, the composition of the liquid catalyst fractions obtained during the catalytic heterogeneous oxycracking of VG with the use of modified ZCC containing *d*-elements was studied

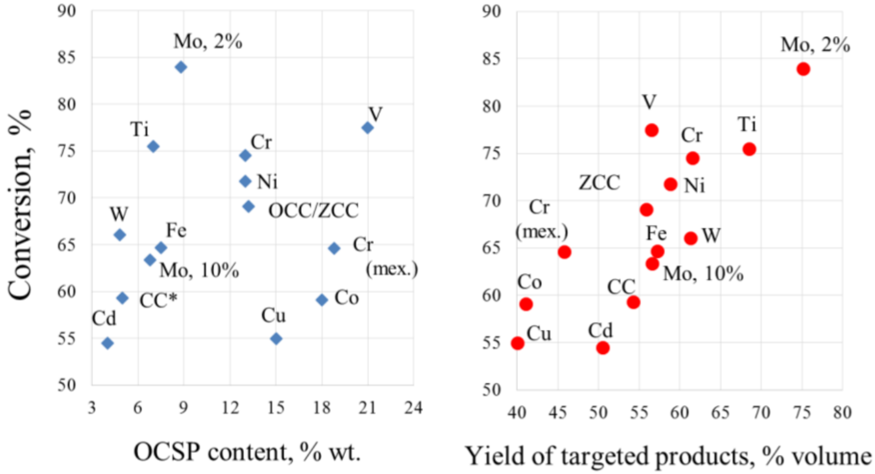


Figure 12. Dependence of vacuum gasoil conversion on the amount of OCP (*a*) and the total amount of target oxycracking products (*b*)

(Fig. 13). The results of the experiments show that the addition of transition metal oxides is accompanied by a decrease in the yield of fraction I: on average, 1.8%, 0.7% and 4 times lower than in oxycracking, OTC and CC, respectively. Among them, a relatively high yield of fraction I was observed in the presence of molybdenum, and the lowest yield was observed in the presence of tungsten. The subtraction of fraction I in descending order appears as follows:

An increase in the amount of added molybdenum leads to an increase in the yield of hydrocarbon gases and, conversely, to a decrease in the yield of fraction I. Such a trend was also observed when comparing the effect of the chromium addition method: mechanical mixing did not cause the formation of light liquid condensate.

KK	>	OTK	>	OKK		**Mo** (2%)	>	**Cd**	>	**Cr**	≈	**Ti**	≈	**Fe**	>
31.2%		9.1%		8.0%	>	7.3%		6.6%		6.2%		6.1%		6.0%	
	>	**V**	≈	**Co**	≈	**Ni**	≈	**Cu**		Mo (10%)	=	**W**	>	Cr (м)	
		5.6%		5.4%		5.3%		5.2%	>	4.6%		4.6%		2.7%	

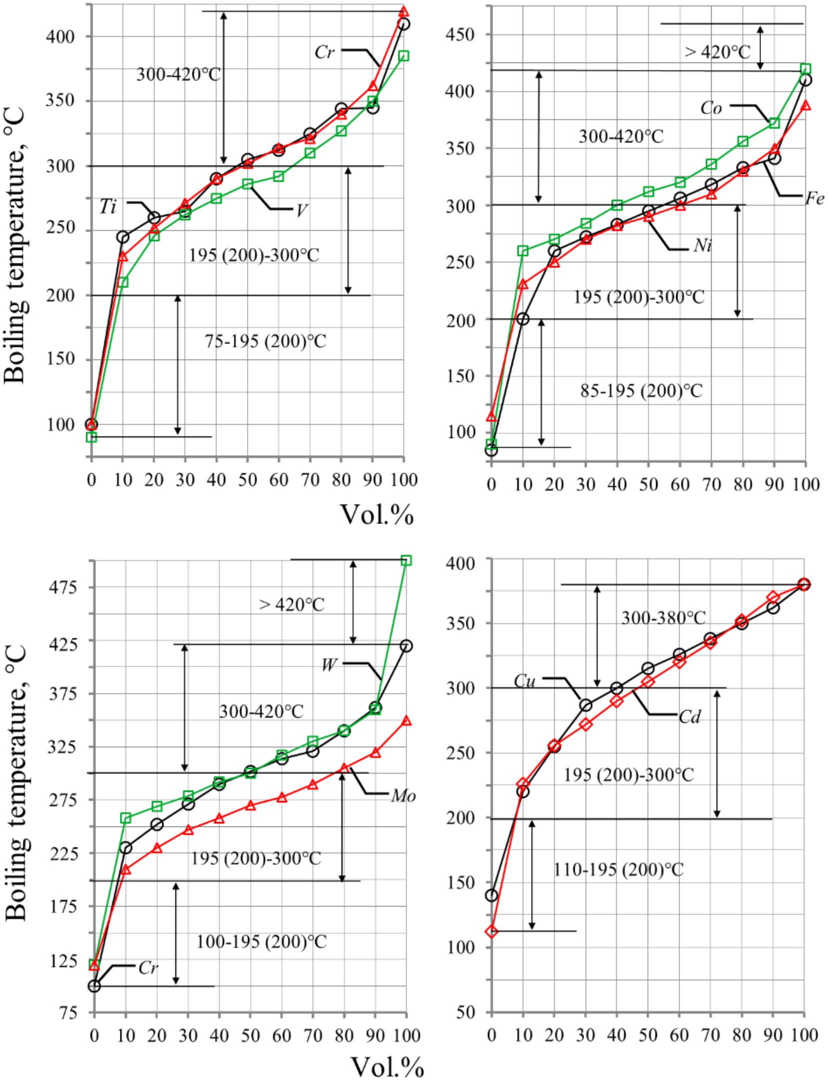


Figure 13. Correlation between the fractional composition of liquid catalyzate obtained using ZCC modified with *d*-elements.

If the yield of fraction I decreases after the addition of modifiers, then the trend has changed in the opposite direction relative to fraction II (except for copper and cobalt). The presented sequence demonstrates the obtained results:

Ti		**Mo** (2%)		**V**	>	**Cr**	>	**Ni**		**Cd**	>	**Fe**	>	**W**	>
56.9		49.6	>	46.9		45.4		37.0		35.4		34.5		31.1	
ОКК	>	Cr (м)	>	Mo (10%)	>	**Cu**	>	**Co**	>	ОТК		КК			
30.6		29.9		25.3	>	24.8		21.8		20.2		9.1			

Among all studied samples, the highest activity was recorded for molybdenum-containing ZCC, and the lowest activity was recorded for cadmium-containing and cobalt-containing ZCC (total yield of transparent products was 14% and 11% lower than unmodified ZCC). The catalyst obtained in the presence of molybdenum-containing ZCC is considered to be relatively lighter than all the tested ones. It has the lowest boiling point (350°C). In turn, the catalyst containing tungsten has the highest boiling point, which is equal to 500°C (Fig. 13).

Fraction I samples obtained with the presence of ZCC modified with V, Fe, Co and Mo meet the requirements of GOST for gasoline due to their density and saturated vapor pressure, but their compounding with light components is possible.

Indicators such as kinematic viscosity and ignition temperature in a closed crucible of fraction II are within acceptable interval limits for samples containing V, Fe, Ni. Given the practically similar nature of the fractional composition curves, it can be concluded that they have similar hydrocarbon compositions, but are relatively more homogeneous in No. 19 (Mo, 2%).

During the transition to fraction III, a sharp increase in density indicators was observed, which probably indicates a high amount of highly condensed aromatic components.

The effect of the modification on the catalytic activity of ZCC in the oxycracking process of VG was evaluated by comparing "conditional" indicators such as the yield of fractions I and II, as well as the degree of conversion of raw materials. An attempt was made to correlate the catalytic activity displayed by the location of the modifier atoms in the order of increasing *d*-electrons by analyzing the 2 maximum curves (Figures 14 and 15). It can be seen that the catalytic activity in the formation of fraction I is insignificant for the elements having electronic configurations d^0-d^1 (TiO_2, V_2O_3), $d4$ (WO_4) and d^8-d^{10} (Co_3O_4, NiO, Cu_2O). Maxima were observed for d^3 (Cr_2O_3) and d^6 (MoO_x). According to the classic works of Dauden, G.K.Boreskov and O.V.Krylov, similar two-peak dependence of the change of various properties of compounds of transition elements of the 4th period is characteristic for the lattice parameters of these metal oxides and their catalytic activity in a large number of oxidation-reduction reactions. Thus, relatively more active systems obtained during modification with molybdenum (d^6) allowed to increase the degree of conversion of raw materials by 35.3% (volume). With the presence of titanium, the amount of fraction II is more than 3 times (up to 57% (volume)), with the presence of molybdenum – 2.8 times (up to 49.6% (volume)), and the yield of fraction I is higher than unmodified ZCC – increased by 1.6 and 1.8% (volume), respectively.

It should be noted that in our experiments, the promoter effect did not always give an unambiguous positive result: See the picture for the conditions of the process the addition of cobalt and cadmium led to a certain increase in the selectivity for the gasoline fraction I; the chromium-modified sample obtained by mechanical mixing showed the lowest activity even compared to the one before modification; high content of molybdenum slightly increased the efficiency of the catalyst compared to the original sample.

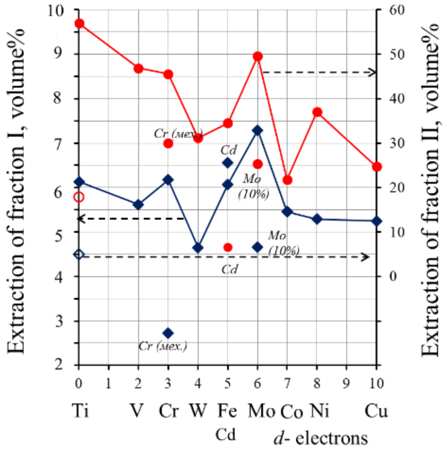


Figure 14. Change in yield of fractions I and II during oxycracking depending on the number of modifier electrons (marks without filling – in the presence of unmodified ZCC).

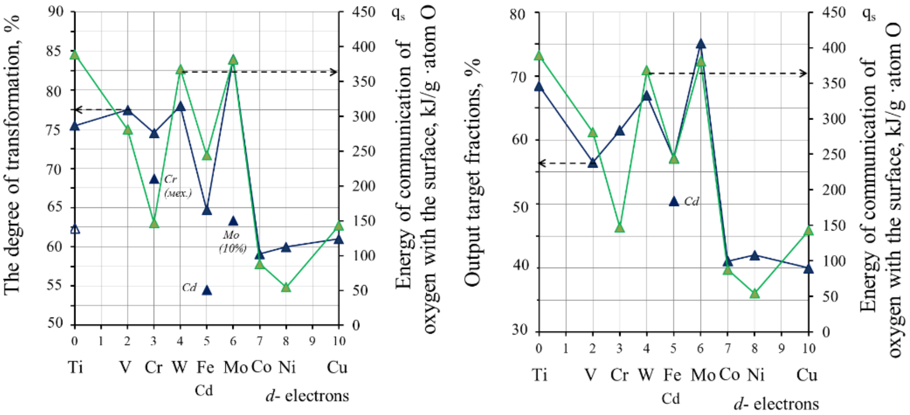


Figure 15. Relationship between the degree of conversion of vacuum gas oil (*a*), the yield of target products (*b*) and the binding energy of oxygen.

Thus, one of the main issues of the present work is the discovery of the structural structure of oxide modifiers, their physico-chemical characteristics and the properties of influence on the activity of catalytic systems, therefore, the correlation of the oxygen binding energy with the surface and the selectivity demonstrated in partial oxidation cannot be ignored. The comparison of the evidence obtained during the calorimetric studies of oxygen heteroexchange on metal oxides with the degree of conversion during oxycracking of VG and the yield of target fractions (Figure 14, 15) shows a good agreement with the classic works of G.K. Boreskov can be used as a criterion for the selection of a catalyst for the oxycracking process of VG: the demonstrated relatively high activity of vanadium, molybdenum, titanium and chromium oxides is distinguished by a rather higher bond strength of surface oxygen than others, which is selective it affects the structure of surface compounds by causing oxidation.

Hydrocarbon composition of liquid products of catalytic oxycracking of VG

Evidence of group hydrocarbon distribution of conventional fractions I and II is shown in figure 15. For the Me/ZCC catalyst, it is necessary to note the characteristic feature of fraction I - relatively high amount of naphthenes and low amount of OCC and ArHk.

A relatively higher amount of alkanes in fraction I was obtained in the presence of Ti and Co, as for ZCC (Fig. 16, *a*). In all other samples, a fairly low amount of alkanes was recorded. Also, the low content of ArHk and OCC against the background of high content of naphthenes (increasing from 5% in ZCC to 40% in Cd) is considered characteristic of modified samples. The addition of V, W and Fe led to an increase in the proportion of unsaturated hydrocarbons compared to unmodified ZCC.

Alkanes and olefins are mainly collected in II fractions, their amount increases from 13 to 75% and from 10 to 29%, respectively, while OCC, individual and polyaromatic hydrocarbons, on the contrary, are practically absent (Fig. 16, *b*). Also, in the presence of Me/ZCC, the amount of naphthenes in II fractions is higher than the initial unmodified sample.

Later, the nomenclature of each group of hydrocarbons was analyzed in detail depending on the number of carbon atoms in the molecule:

- V/ZCC due to its highest selectivity for C_{10}, C_{11}; C_{12} – Cr; V, Cd according to C_{13}, C_{14}; C_{15}- C_{20} – Cr differs;
- when using unmodified ZCC, as well as traditional CC, the current indicator is higher than the maximum determined concentration of C_{12}-C_{20} alkanes;
- the highest density of natural paraffins C_{21} – V; C_{22} – V, Co; C_{23}, C_{24} – V; C_{25} – Co; C_{26} – V; C_{27} – Cr; C_{28}, C_{29} – V; C_{30} - Cd (Cr mex); C_{31} Cd (Mo 10%); C_{32} - V, Mo (2%); C_{33} - Cd, Cr (mex); C_{34} - Mo (2%); C_{35} – Co; C_{36}-C_{40} – Recorded for Cu;
- the maximum determined concentration of C_{20}-C_{35} alkanes is higher than the current indicator obtained when using unmodified ZCC, but it was less than traditional CC; this figure is higher for C_{36}-C_{40} than similar for both ZCC and CC under oxycracking conditions;

Figure 16. Distribution of group hydrocarbons in fractions I and II oxycracking depending on the nature of modifiers (%).

Process conditions: process temperature 500oC, oxidation rate - 1%, contact time - 1.7 s, duration - 900 s.

- a comparative analysis of the price of C_{36}-C_{40} alkanes for all used metals shows that, except for vanadium and chromium added by impregnation, the presence of the remaining metals led to the formation of an additional amount of the mentioned alkanes under the conditions of the oxycracking process.

Oxygen-containing compounds in the liquid products of the oxycracking of VG obtained in the presence of Me/ZCC

OCC obtained in the presence of Me/ZCC is considered to be a mixture of oxo compounds, peroxides, alcohols and acids. The effect of modifiers can be characterized by the following regularities: in contrast to ZCC, which exhibits high selectivity towards oxo compounds, Me/ZCC are more selective in the formation of ethers and alcohols. For all modified ZCCs, the total amount of OCC is lower than that of the original catalyst. In our opinion, this is due to intensive deoxygenation, destruction of OCC with the formation of intermediate compounds that accelerate the cracking of saturated hydrocarbons. In a sense, OCC act as cracking promoters, increasing the conversion rate of raw materials.

Figure 17 shows the results obtained during the study of the effect of the nature of the modifier on the nature and distribution of OCC in the C_{10+} oxycracking catalyst. A relatively high total amount of oxo compounds was obtained in the presence of cobalt-containing samples (4.3% by volume), while the maximum was recorded for C_{19}. Among all oxo compounds, C_7 is considered to be the lowest molecular compound, and C_{33} is the highest molecular compound. The oxo compounds formed in the presence of cobalt-, cadmium- and copper/ZCC consisted of a relatively wider variety, the only difference being that lower molecular weight compounds were formed in the presence of cobalt: C_7, C_9, C_{13}, C_{14}, C_{15}, C_{19}, C_{21}, C_{28}. Fewer types of oxo compounds were formed in the presence of titanium. As the presented evidence shows, the activity of metal oxides in the formation

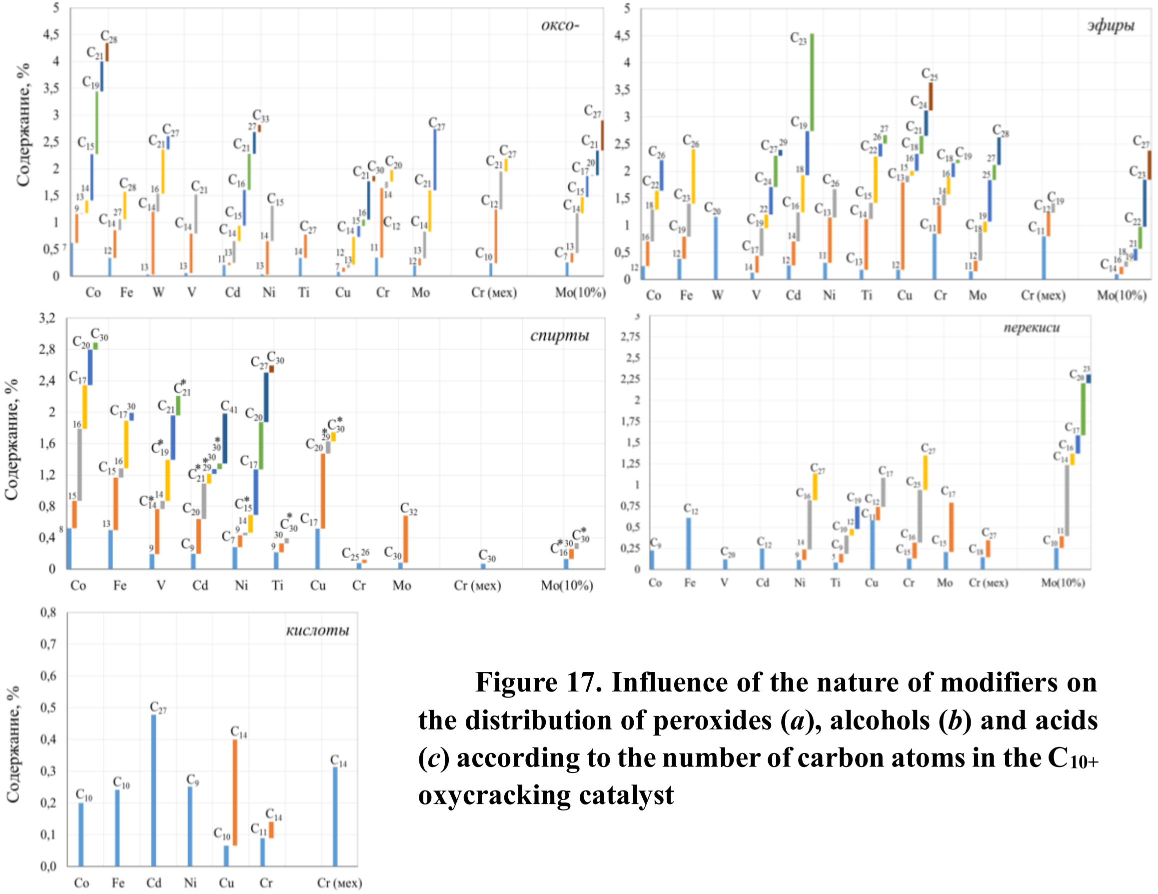


Figure 17. Influence of the nature of modifiers on the distribution of peroxides (*a*), alcohols (*b*) and acids (*c*) according to the number of carbon atoms in the C_{10+} oxycracking catalyst

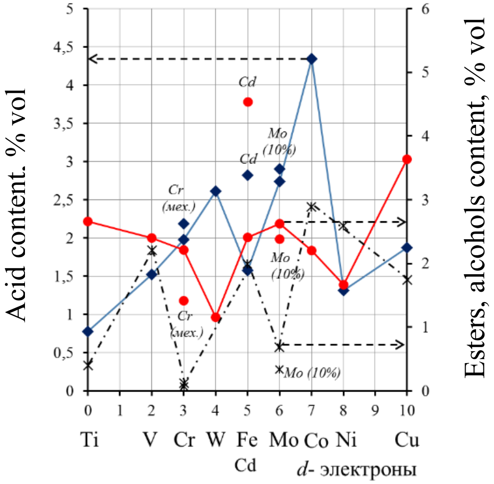


Figure 18. Dependence of the yield of acids (solid blue on the main axis), ethers (solid red on the additional axis) and alcohols (dashed-dotted on the additional axis) on the amount of *d*-electrons

of OCC also coincides with the energy of connection of oxygen with the surface (Fig. 18).

The effect of the nature of metals on the distribution and character of ArHk in liquid products of catalytic oxycracking of VG

As can be seen (table 4), iron, cobalt and molybdenum (10%) have relatively higher aromatization capacity, but it is somewhat less than unmodified ZCC under both oxycracking and CC conditions. And if the ratio of 2-3-ring PAK to mono-ArHk in traditional CC products was almost equal to 2, then under oxycracking conditions it was 1.4 (ZCC), 1.2 (Fe), 1.1 (Co) and 1.1 (Mo, 10%) would consist. The amount of mono-ArHk and individual ArHk in relatively active Co is 7.3 and 0.5% (vol), which is lower than the corresponding values of 3.7 and 0.9% (vol) obtained under oxycracking conditions with the presence of ZCC. With the exception of chromium, the value of the total amount of PAK in most modifiers is very close, but this allows us to place them in the following sequence: V > Cd > Co > Mo > Ni > Fe, W, Ti, Cu > Cr.

Deep desulfurization of products is considered an important feature of the oxycracking process of VG with the participation of Me/ZCC. Thus, the main part of sulfur-containing compounds in

Table 4

The nature of aromatic hydrocarbons in C_{10+} catalysates obtained in the process of oxycracking in the presence of [1]Me/ZCC

Name	Content in catalyst, %															
	VG	IV period 4, 5 and 6 group			IV period 8 group			V, VI period 6 group		IV, V period 4,5 group				Comparative data		
		Ti	V	Cr	Fe	Co	Ni	W	Mo 2%	Cu	Cd	Mo 10%	Cr (мех)	[2] OCC	[3]OTC	[4]CC
Oxycracking in the presence of Me/ZCC																
Aromatic hydrocarbons, incl.	35,7	11,60	14,99	12,45	15,73	16,05	13,35	14,61	14,64	13,58	12,90	16,32	13,83	27,44	46,03	17,84
mono- ArH	11,3	5,05	6,30	5,17	6,95	7,33	6,06	6,60	6,74	6,19	6,19	7,65	6,43	11,06	10,05	5,13
ind PAH	4,03	0,33	0,47	0,26	0,46	0,45	0,37	0,42	0,43	0,38	0,38	0,47	0,38	1,30	0,78	0,94
2-6 ring alkyl PAHs	20,4	6,22	8,22	7,02	8,32	8,27	6,91	7,59	7,47	7,01	7,01	8,20	7,02	15,07	35,20	11,77
ΣPAHs/mono-	2,17	1,30	1,38	1,41	1,26	1,19	1,20	1,21	1,17	1,19	1,13	1,13	1,15	1,48	3,58	2,48

[1] process conditions: oxidation degree 1%; duration 900 s; temperature 500°C; contact time 1.7 s.

[2] Oxycracking in the presence of CSA: process conditions: oxidation degree 1%; duration 900 s; temperature 500°C; contact time 1.7 s.

[3] thermal oxidative cracking, process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

[4] traditional catalytic cracking, process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

vacuum gas oil belongs to dibenzthiophene and its three C_1-C_3 homologues, which are not completely cleaned even under hydrotreating conditions (they are mainly subjected to hydrogenation, not hydrogenolysis), so the indicators of these groups were compared. The highest share of both primary VG and oxycracking products is the C_2-derivatives of chemically less active dibenzthiophene (demethyldibenzthiophene, 37 wt%), which is consistent with literature evidence. The order of activity of Me/ZCC for desulfurization according to the amount of C_2-dibenzthiophene (g/l) appears as follows (Figure 19):

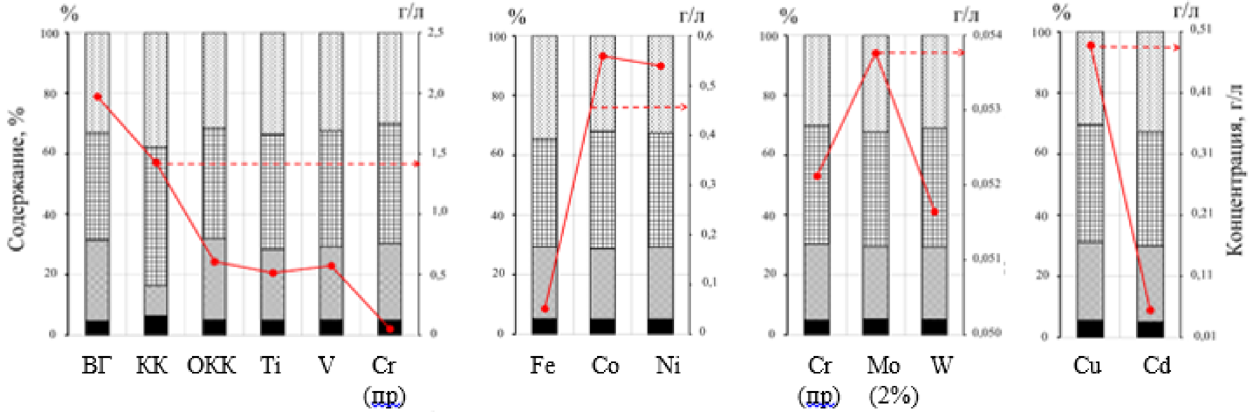
0.0186 (Fe) < 0.0205 (W) < 0.0206 (Mo) < 0.0207 (Cr, Cd) <<

<< 0.188 (Cu) < 0.197 (Ti) < 0.207 (Ni) < 0.221 (V, Co) << 0.335 < < (OTC) < 0.585613 (OKK) < 0.651545 (KK) < 0.699394 (VG)

The presented evidence shows that the use of ZCCs containing iron, tungsten, molybdenum, chromium or cadmium allows to reduce the amount of dimethyldibenzthiophene by 34-37 times compared to the original raw material and by 31-35 times compared to the traditional CC. The role of modifiers is well seen when analyzing the evidence obtained by using unmodified ZCC - the amount of dimethyldibenzthiophene decreased by 1.1 and 1.2 times compared to CC and VG. In the presence of Cr, W, Fe, Cd and Mo/ZCC, the total amount of dibenzthiophene is 0.052-0.054 g/l, which is 37.6 times less than VG and 35 times less than CC. The distribution between mononuclear dibenzthiophene and its C_1-C_3 homologues remains at the previous level.

The obtained results allow us to conclude that chromium-, tungsten-, iron-, cadmium- and molybdenum-containing catalysts exhibit high selectivity against sulfur-containing compounds under oxycracking conditions and increase the amount of dibenzthiophene and its C_1-C_3 homologues by 40 times from 1.97 to (VG) 0.05 allows to reduce to g/l.

Given that the conversion of sulfur-containing compounds is beyond the scope of the present study, we can only hypothesize that the observed desulfurization occurs due to the oxidation of thiophenes



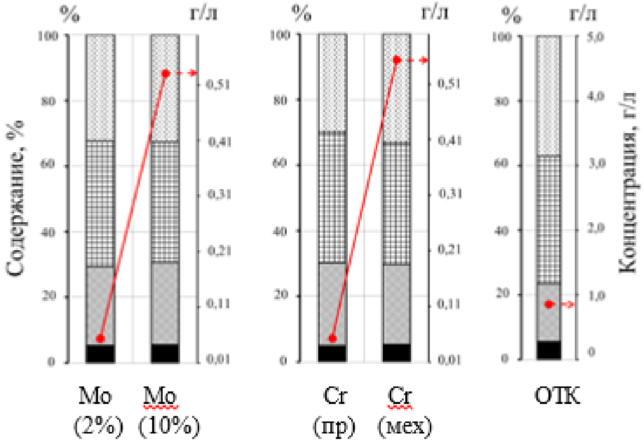


Figure 19. Effect of the nature of the modifier on the distribution of dibenzthiophene ■ and its C_1, ▨ C_2 ☒, C_3 ▦ homologues

Process conditions: oxidation rate 1%; duration 900 s; temperature 500oC; contact time 1.7 s. Example with OCC – NGO participation; OTC – thermal oxidative cracking: duration 900 s; temperature 500°C; oxidation rate 1%; CC – traditional catalytic cracking: duration 900 s; temperature 500°C; contact time 1.7 s; VG – vacuum gas oil, raw material.

to sulfides and sulfoxides, which subsequently undergo thermal destruction with the formation of sulfur gases and hydrocarbons.

Thus, the conducted studies allowed to reveal the main regularities of the oxycracking process depending on the nature of the added modifiers (Figure 20):

- the comparison of oxycracking evidence before and after the addition of modifiers clearly proved the positive effect of adding modifiers to ZCC composition to increase the yield of transparent fractions (generally 20% with molybdenum and somewhat less for vanadium and nickel);
- the catalyst obtained by using molybdenum-containing ZCC is considered the lightest, as it has the lowest boiling point, which is 350°C. At the same time, the tungsten-containing catalyst has a relatively higher end-of-boiling temperature of 500°C. Increasing the concentration of molybdenum led to aggravation of the fraction composition of the catalyst and, accordingly, to a decrease in the yield of transparent fractions;
- on the basis of the obtained evidence on the yield of the II fraction, it was determined that the addition of molybdenum and titanium in oxycracking, non-catalytic OTC and CC conditions increases the yield of the II fraction by 2-6 times, respectively, compared to unmodified ZCC;
- a relatively high yield of hydrocarbon gases among the 10 considered metals was determined in the presence of the tungsten-containing sample - 12.4% higher than in the case of traditional CC conditions, 9.3% higher than that obtained in the presence of ZCC during oxycracking and 15.5% higher than that obtained in the case of non-catalytic thermal cracking;
- low amount of ArHk and OCC against the background of high amount of naphthenes was considered characteristic for modified samples. Additions of V, W and Fe led to an increase in the ZCC; the proportion of unsaturated hydrocarbons compared to unmodified addition of metal-modifiers mainly leads to an

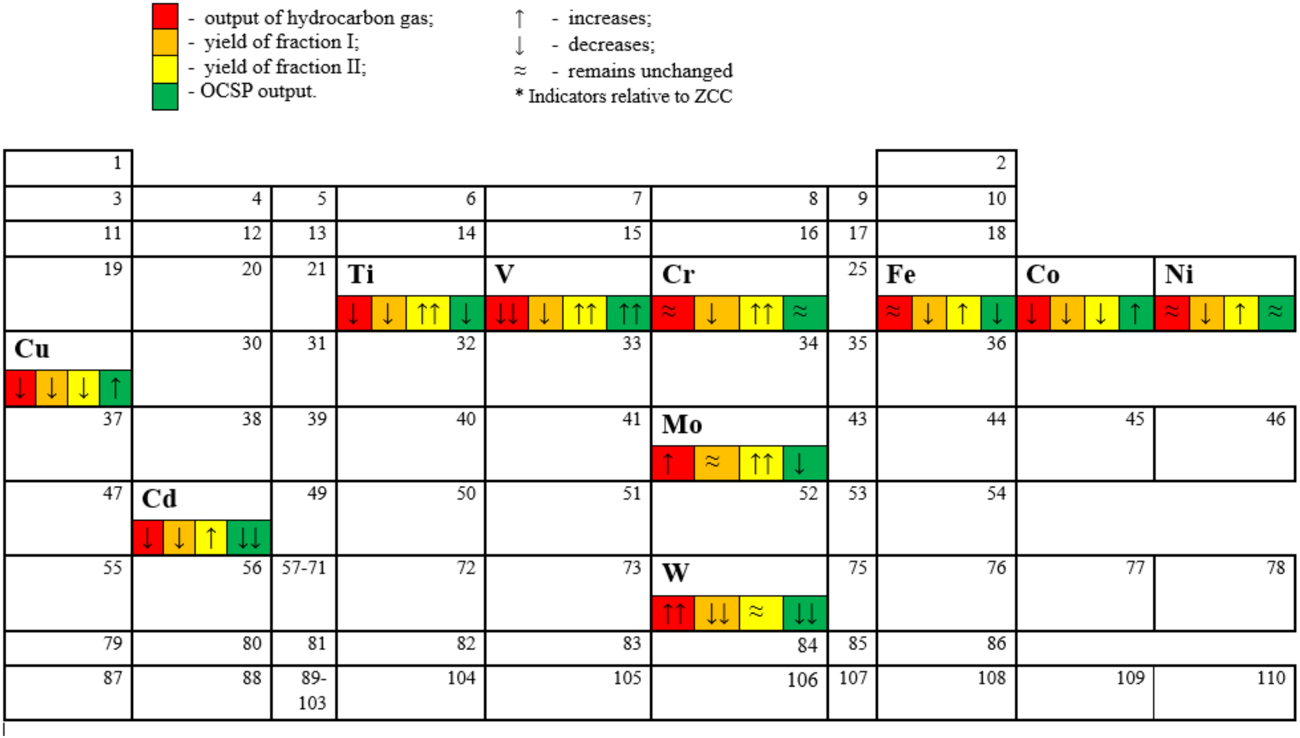


Figure 20. Influence of the nature of the modifier on the parameters of the oxycracking process of vacuum gas oil*

increase in the reactivity of alkyl-ArHk, more precisely, the share of reactions taking place with the participation of initiators increases;

- separation of molecular hydrogen occurs. This indicates that hydrogen reacts with oxygen to form water directly during dehydrogenation reactions, and this process occurs in one step rather than sequentially in two sequential reactions, as in dehydrogenation in the presence of oxygen.

The obtained results are predictive and allow to adjust the quantitative and qualitative indicators of the oxycracking process by selecting the metal.

5. PHYSICAL-CHEMICAL PROPERTIES OF ZEOLITE AND Me/ZCC

Structural properties

X-ray phase analysis confirmed that the primary catalyst belongs to the phojazite zeolite structure. Comparison of the phase diagrams of the modified Me/ZCC with the original catalyst allowed us to determine that the addition of the modifier causes the heterocharged isomorphous substitution of Si^{4+} cations in the silica-oxygen zeolite framework, which leads to the enhancement of acid-base properties. So, for all samples without exception, but after the addition of modifiers to different degrees, changes in diffraction angles were recorded in the diffractograms of zeolite samples, which indicates the transformation of the crystal lattice structure of zeolite under the influence of promoting agents, their inclusion in the zeolite framework. The degree of change of the parameters of the core depending on the nature of the modifier (calculated as the ratio of the amount of available changes of the reflex cage parameters to the total amount) is shown in figure 21. As can be seen from the above evidence, it varies symmetrically with the ionic (E^{2+}) and atomic (E^0) radii of the selected elements: from 11.8% for copper to 55.6% for titanium.

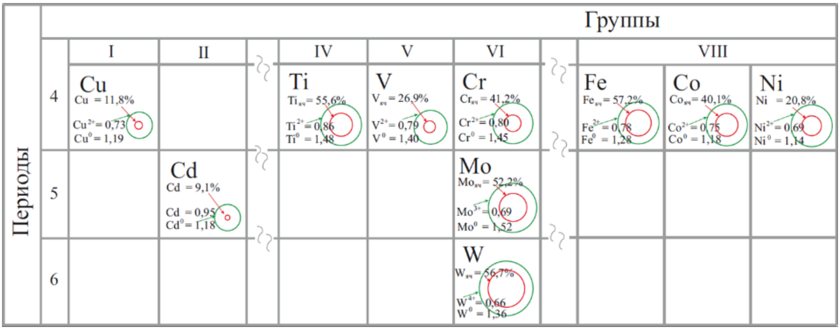


Figure 21. Influence of the nature of the modifier on the parameters of the core

The rate of change of parameters of the iron core was 57.2%, which is somewhat higher than that of titanium, which, in our opinion, is due to the predominance of 3-valent ions in the case of the latter, and 2-valent ions in iron. The lower rate of change of the parameters of the vanadium core compared to the general trend is not unexpected due to the lower ionic (E^{2+}) and atomic (E^0) radii than those of chromium and titanium.

Changes in the structure of ZCC samples under the influence of modifiers are affected by the change in the interplanar distance.

The value of the interplanar distance increases proportionally to the radius of the added elements (relative to the initial ZCC), changing according to the following sequence (as having the highest value of the integral intensity for the $2\Theta = 6.368$Å reflection):

V > Cr > Fe > W > Ni > Cd > Mo (2%) > Co = ZCC.

At the same time, a shift of the peaks to a lower angle was observed. These evidences indicate the existence of the disruption of the zeolite framework, namely the increase of the parameters of the elementary core.

In the molybdenum sample, the increase in the amount of the modifier leads to a significant decrease in the interplanar distance, which indicates a direct relationship between the hardness of the structural mixtures and the structure of Me/ZCC. According to the RFA evidence, the formation of a new compound - aluminum molybdate $Al_2(MoO_4)_3$ - was determined in the sample containing 10% molybdenum, along with faujasite, kaolin and suitable oxide-modifier phases in the modified samples. The analysis of OKP indicators made it possible to divide all samples into 3 categories: 1 – for them, OKP decreased (Ni, V, W); 2 – increased (Fe, Co, Mo, Cr); 3 – remained unchanged (Cd). On the basis of the SEM results, it can be assumed that the decrease of the OKP indicators for nickel, vanadium and tungsten is not related to the increase in the dispersion of particles, which usually leads to an increase in the active surface of the catalyst and, accordingly, to an increase in the OKP indicator, but is due to an increase in the density of defects in them. . At the same time, the increase in OKP value and the absence of practical change of this indicator in the case of cadmium indicate the geometric growth and the increase in the size of the crystals, which coincides with the SEM evidence.

Texture properties

Evidence obtained using SEM shows a change in particle size of the modified samples while maintaining a spherical shape. Using evidence of the morphological characteristics of the modified ZCC samples, we compared them with the activity exhibited by those catalytic systems (Figure 22). The presented evidence allows us to

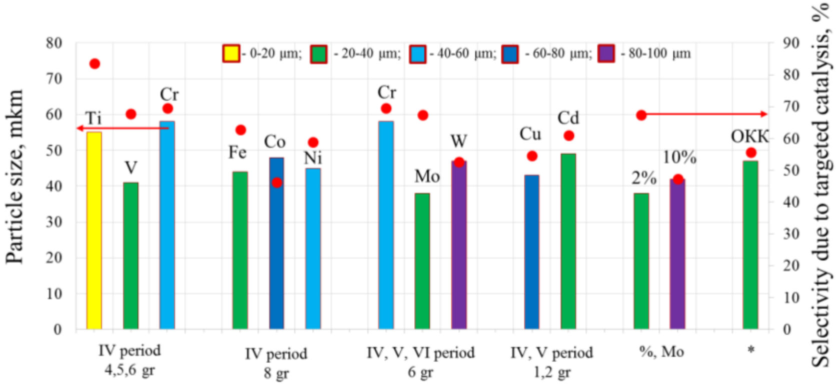


Figure 22. Selectivity to target fractions and predominant particle size as a function of the nature of the modifier

conclude that in order to exhibit high catalytic activity, the modified ZCC should consist predominantly (at least 55%) of particles up to 60 μm in size. Differences in the dispersed order of particles may be due to differences in the degree of interaction between precursor phases of modifiers and chemically similar ZCC.

Thermal properties

The presence of two areas was determined in all considered samples. The first is a well-defined symmetric endothermic peak associated with the displacement of chemically combined water. The second area is considered to be a double coated exothermic effect with maxima in the 280-690° range.

The presence of inflection points in the DTA curve between the two exo-effects indicates the presence of products on the surface of the samples, whose oxidation causes thermal effects (II *exo*- and III *exo*-) collected in a narrow temperature range and well located on the DTA curve. These two exothermic effects prove the presence of components of condensation products with different qualitative composition (oxidizing condensation products in the range of 278-600°C - OCP and condensation products without oxygen in the range of 377-831.2°C - SM). Evidence of thermal analysis of catalyst samples involved in CC, as well as the composition of condensation products determined for catalyst samples involved in the OCC process, whose component is considered oxygen, are considered the basis for a similar interpretation.

We can speculate with some degree of certainty about the KC-group character of OCP. Thus, in samples containing Cd-, Fe-, Co-, Ni-, Cu-, the temperature range of the II *exo*-effect (up to 550°C) – lactone groups, W-, V-, Ti-, Cr- , proving the presence of both lactone and anhydride groups in Mo-samples. The maximum of the existing exothermic peak also has a different value for both groups: 446-482°C for W-, V-, Ti-, Cr-, Mo-, and 482°C for Cd-, Fe-, Co-, Ni-, Cu-containing samples. -501°C. The combustion of anhydride groups in the second exothermic effect (III *exo*-) occurs at lower temperature limits than that characteristic of SM formed during CC (containing OCC), which indicates that W-, V-, Ti-, Cr-, Mo- with his participation, the latter are not actually formed. These evidences coincide with the component composition of the catalyst, in particular, the amount of OCC.

The presence of carbonate and carboxylate-type structures on the surface of oxide catalysts is considered to be the result of strong irreversible adsorption of unsaturated oxygen-containing hydrocarbons, which later become deep oxidation products. Also, subsequent re-oxidation of partially oxidized structures can contribute to the formation of oxidation products.

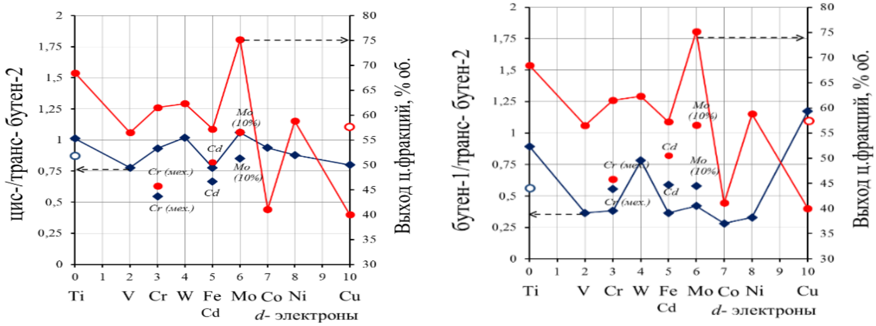
The spent ZCC involved in heterogeneous catalytic oxycracking has a relatively higher, asymmetric and strongly skewed III-exothermic effect on the temperature scale. This most likely indicates a weak occurrence of the oxidation process due to the presence of continuous oxygen of oligomer and/or polycondensed aromatic molecules in the sediments remaining on the catalyst surface. Due to this thermal effect, the mass loss of the ZCC sample is also considered to be the highest (12.0% by mass) among all considered.

Observations on the distribution of coke along the length of the catalyst layer made it possible to determine that, regardless of the nature of the modifier, coking in the oxycracking process took place along a consistent route (the increasing profile of coke deposits along the height of the reactor does not exclude the occurrence of intensive re-oxidation of OCP in the surface layer of the catalyst. From the OCC process in contrast, the distribution of coke along the height of the reactor under conventional CC conditions has a decreasing profile).

To questions about acid-base centers of oxycracking catalysts

The activity of ZCC and modified Me/ZCC in the process of isomerization of butene-1 was studied within the framework of the conducted research, and a comparative analysis of the obtained experimental evidence with the results of OCC was carried out. The nature of the dependence curve of the ratio of *cis*-/*trans*-butene-2 on the number of *d*-electrons is similar to the subtraction of target fractions (as a measure of activity) depending on the number of *d*-electrons (Fig. 23,a). Samples with a ratio of *cis*-/*trans*-butene-2 close to unity have pronounced Brønsted acidity - these are titanium, chromium, tungsten, molybdenum and cobalt.

The value of the ratio of butene-1/*trans*-butene-2 allows to obtain information about both the total isomerization activity and the Lewis acidity (Figure 23, *b*). Copper has the lowest isomerization activity. Titanium and tungsten have a pronounced Lewis acidity.



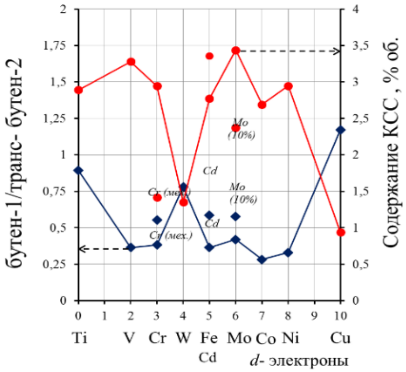


Figure 23. Dependence of the ratio of *cis*-/*trans*-butene-2 (a, c) and butene-1/*trans*-butene-2 (b) on the number of *d*-electrons (main arrow). Dependence of target fractions and OCC subtraction on the auxiliary axis on the number of *d*-electrons.

It is noteworthy that titanium and tungsten have the same positive effect on both acidity and not on a specific type of acidity, while molybdenum has a positive effect only on Brønsted acidity. At this time, the activity indicators of those three modifiers are relatively higher, and molybdenum is considered the highest. The result is that ultimately the carbonium-ion mechanism contributes significantly more to the yield of the target liquid fractions. It is possible that the presence of both types of acidity in titanium and tungsten leads to some competition, as a result of which they have a low activity index. Indirect evidence of the solvent share of Brønsted acidity is considered activity indicator of chromium (not having Lewis acidity) after titanium, tungsten and molybdenum according to the extraction of target fractions.

It was noted that catalysts with a high butene-1/*trans*- butene-2 ratio exhibit high activity in oxidation processes, which is accompanied by the formation of OCC under OCC conditions (Fig. 23,c). The obtained dependence of the yield of OCC on the number of *d*-electrons (Fig. 18) is similar to the two-peak Dauden et al. coincides well with the "scenery". In the reactions of formation of OCC, it was possible to determine the evidence of the change of activity of modifiers depending on the number of *d*-electrons, that the maximum indicator was obtained in elements with electron configuration d^2-d^3 (vanadium and chromium), d^6 (molybdenum) and d^8 (nickel); minimal activity is determined for elements located at the beginning (d^0, titanium), in the center (d^4, tungsten) and at the end (d^{10}, copper) of the series. It is the electronic structure of the modifiers that is responsible for their activity in the reactions taking place according to the oxidation-reduction mechanism. The obtained results are interpreted according to the crystal field theory and are considered to be the result of symmetry of *d*-orbitals of transition metals.

Discussion of characteristics of surface-to-volume stages and possible reaction mechanisms during catalytic oxycracking of VG

The results obtained by the free calorimetry method (Fig. 24) made it possible to determine that the OCC process takes place according to the heterogeneous-homogeneous mechanism, so that the heating of the ZCC surface occurring in the first 200 s indicates the predominance of the heterogeneous stages of the process, while after 200 s in the upper period, a practically exponential increase of Δt is observed (heating of the gas volume), which proves the increase of the share of homogeneous phases. The nature of what happens when oxygen is fed through a side-plug is similar to 1% OCC, but the difference is that the temperature difference between the reaction free volume and the catalyst bed is almost double. The nature of the curve indicates heterogeneous oxidation, but occurring with low intensity (Fig. 24,a).

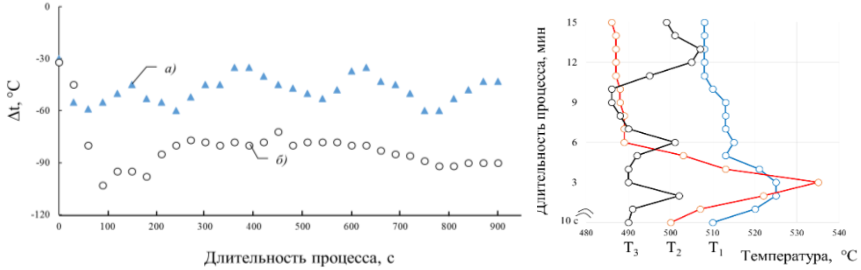


Figure 24. Variation of Δt during the OCC process of VG and depending on the place of oxygen supply (*a*) and temperature dynamics (*b*)

a – supply of oxygen from above, presence of free volume on the layer; b – supply of oxygen from the middle of the catalyst layer;

b – free volume on the catalyst layer (T_1), in the center (T_2) and in its lower part (T_3) during the OCC process of VG

In zone 3: the temperature readings taken over the catalyst layer in the free volume, in the center and in the lower part of its layer (Fig. 23, *b*) show that during the catalytic oxycracking of VG, the catalyst is in a non-stationary state – alternating deactivation is replaced by an activity cycle.

The results obtained by the free calorimetry method made it possible to determine strong differences of Δt in different catalysts (Figure 25). Thus, the heating of the surface decreased in the following order:

Ni > Co, Fe, V, Cd >> Mo > W >> Ti >> Cu, Cr
60°C 50°C 30°C 20°C 0°C (-30), (-40)°C

This allowed us to come to the conclusion that the share of heterogeneous stages during the oxycracking of VG with the presence of those catalysts is significantly different, precisely with the presence of the first 5 metals (Ni, Co, Fe, V, Cd) accompanied by the formation of OCC during oxycracking, the share of heterogeneous phases is greater than that obtained during the presence of the last 2 (Mo, W) metals. In the presence of Ti, the fraction of heterogeneous phases is most likely minimized, while it is absent at all for Cu and Cr. The addition of chromium by mechanical mixing also led to the replacement of the homogeneous phase by the heterogeneous phase. In our opinion, the amount of temperature pulsations, "hysteresis" is mainly determined by reactions between the surface of chain carriers, desorption of molecular products, change of heterogeneous breaking efficiency depending on the nature of the modifier, non-stationarity of catalyst surface properties.

The evidence established in the course of the present study allowed us to divide the studied 10 metal oxides into three groups according to the area of occurrence of reactions during oxycracking with appropriate mechanisms:

I. heterogen – with the presence of Ni-, Co-, Fe-, V- and Cd/ZCC;
II. heterogeneous-homogeneous – with the presence of Mo-, W- and Ti/ZCC, so with the presence of the latter, with the obvious advantage of homogeneous phases;
III. homogeneous – with the presence of Cu- and Cr/ZCC.

These results allowed us to assume that the "quenched" surface is probably the reason for the relatively low activity of Cu- and Cr/ZCC in the oxycracking process of VG.

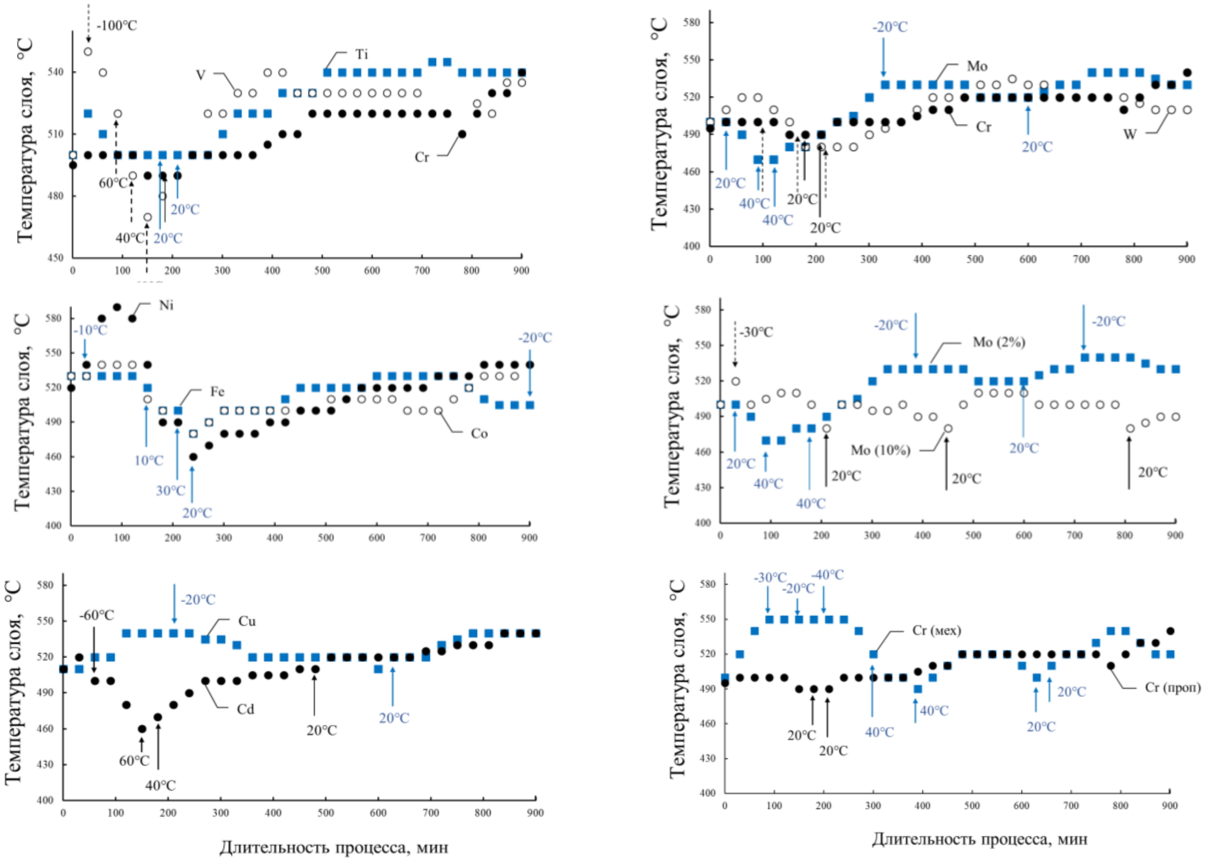


Figure 25. Temporal temperature profile of the catalyst layer depending on the nature of the modifier: a-Ti, V, Cr, b-Fe, Co, Ni, c-Cu, Cd, ч - Mo, W, Cr., d - amount of modifier - molybdenum (2 and 100%), e - method of adding modifier

5.RESEARCH OF CATALYTIC OXYCRACKING OF VG BY MATHEMATICAL STATISTICS METHOD, DEVELOPMENT OF DYNAMIC KINETIC MODEL

Taking into account the complexity of the component composition of VG and its OCC products, all hydrocarbons are divided into 8 narrow fractions according to the number of carbon atoms: C_1-C_4, C_5-C_9, C_{10}-C_{12}, C_{13}-C_{16}, C_{17}-C_{21}, C_{22}-C_{30}, C_{31} -C_{35} and C_{36}-C_{40}. Fractions C1 to C_{21} were selected as target products.

"Zeldovich curves" prove the truth of the above and exclude only the catalyst volume or only the unequivocal share of the surface, proving the homogenous-heterogeneous mechanism of the reactions. A sharp increase in the apparent activation energy when the temperature rises to 550°C shows that, more precisely, the formation of OCC in all fractions and C_{17}-C_{40} hydrocarbons occurs in the presence of radicals in a practically "quenched" catalyst, which leads to a decrease in the rate of heterogeneous stages of the process. leads to.

Based on the analysis of the activation energy values obtained and the graphs (Fig. 26, *a*), the following areas where the OCC formation process takes place can be distinguished: C_1-C_4, C_{13}-C_{16} and C_{17}-C_{21} in the intermediate area between kinetic and intra-diffusion. Formation of OCC in the range of C_5-C_9 fractions. Formation of OCC occurs in the outer transition zone between the intradiffusive and interdiffusive areas. The observed temperature dependence curve of the rate constants of OCC formation reactions in the C_{22}-C_{30} heavy raw material fraction shows that at a temperature of 500°C, the process is mainly limited in the external diffusion field by transitioning to the external-kinetic field when the temperature rises to 550°C.

The temperature dependence curves of the observed rate constants of hydrocarbon formation reactions in the target and initial fractions plotted in the Arrhenius coordinate are shown in figure 26, *b*. Let's consider how the areas of their occurrence change with the change in the conditions of the reactions:

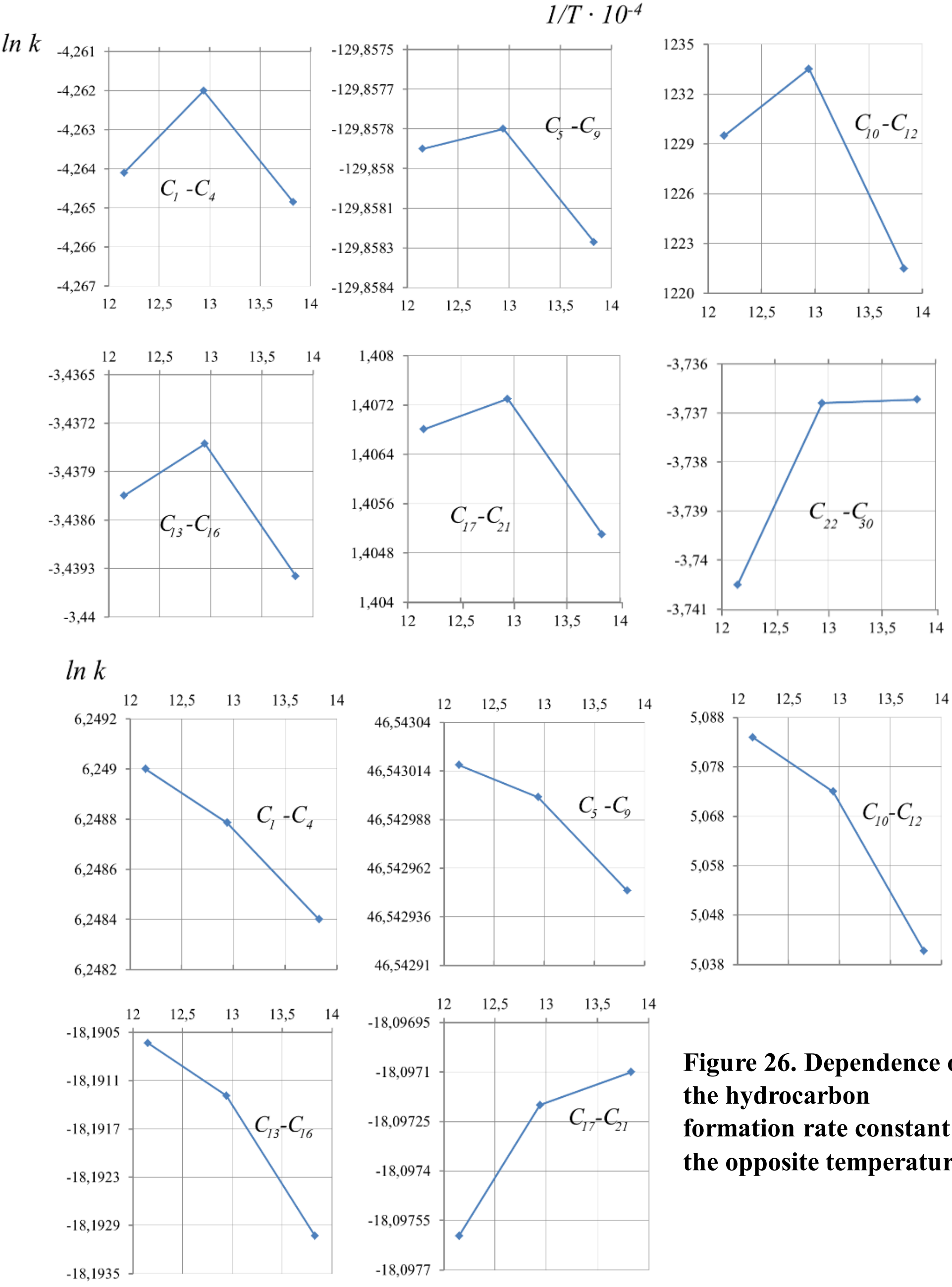
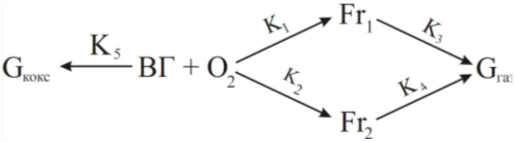


Figure 26. Dependence of the hydrocarbon formation rate constant on the opposite temperature

- curves of target fractions C_1-C_9 in the entire temperature range have a practically straight-line shape with a small bend at 500°C, based on which it is assumed that the formation of these hydrocarbons is limited by diffusion;
- temperature change does not have a significant effect - with the temperature rising to 550°C, the process begins to be inhibited by external diffusion;
- the nature of the curves of the two C_{10}-C_{16} fractions is also practically similar – at the temperature of 450-500°C, the process takes place in the kinetic field with the increase of the temperature up to 550°C, passing to the internal-transitional area, which also indicates the strengthening of the diffusion factor;
- at 450-500°C, the formation of high-molecular hydrocarbons included in fractions C_{22}-C_{30} occurs in the inner-transition zone, and C31-C40 occurs in the outer diffusion zone; with an increase in temperature, the effect of diffusion disappears, and the formation of C_{17}-C_{40} high-molecular hydrocarbons moves to the external-kinetic field.

A linear dependence between the exponential hit and the activation energy (Fig. 27) was found, which indicates the existence of a compensation effect.

Based on the kinetic compensation effect, the following dynamic kinetic model of the OCC process can be drawn up. Kinetic scheme of OCC:



$$\upsilon \cdot V_{кат} \frac{d(\alpha S_1)}{dG_{кат}} = \frac{f_1(K_{01}) e^{-\frac{f_1(E_1)}{RT}} K_1 P_1 \sqrt{K_2 P_2}}{(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5)^2}$$

$$\upsilon \cdot V_{кат} \frac{d(\alpha S_2)}{dG_{кат}} = \frac{f_2(K_{02}) e^{-\frac{f_2(E_2)}{RT}} K_1 P_1 \sqrt{K_2 P_2}}{(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5)^2}$$

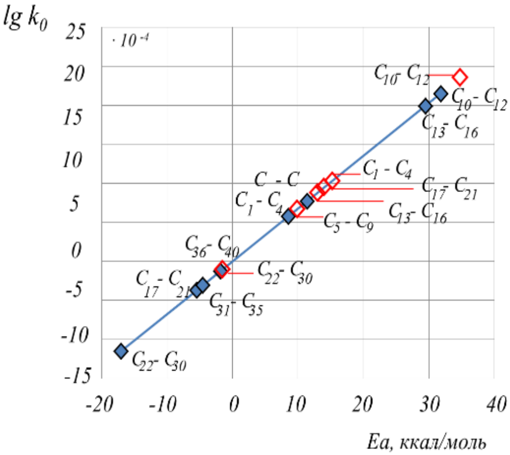


Figure 27. Compensation effect during oxycracking of vacuum gas oil on ZCC:

◆ - hydrocarbons

◇ - OCC

$$\upsilon \cdot V_{кат} \frac{d(\alpha S_3)}{dG_{кат}} = \frac{f_3(K_{03}) e^{-\frac{f_3(E_3)}{RTP_3}} + f_4(K_{04}) e^{-\frac{f_4(E_4)}{RTP_4}}}{(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5)^2}$$

where: υ – volume velocity; V_{kat} – catalyst volume; P_1 – gas oil partial pressure; Selectivity of formation of fractions Si – i = 1,...5; R – universal gas constant; T is temperature.

Based on evidence obtained in a laboratory facility and processed by mathematical statistical methods using the minimization function F_k

$$F_k = \min \sum \left\{ \left[\frac{(\alpha S_i)^Э - (\alpha S_i)^P}{(\alpha S_i)^Э} \right]^2 + \left[\frac{(\alpha S_2)^Э - (\alpha S_2)^P}{(\alpha S_2)^Э} \right]^2 \right\}$$

the following quantitative values of the constants of the kinetic model of the oxycracking process, designed by using the principles of the compensation effect in heterogeneous catalysis, were obtained:

$A_1 = 64484; B_1 = 5075; D_1 = 2165; A_2 = 63255$

$B_2 = 6590; D_2 = 2530; A_3 = 60220; B_3 = 6040$

$D_3 = 2021; A_4 = 70540; B_4 = 7565; D_1 = 3141$

$M_1 = 0{,}000589; Ф_1 = 4{,}830; M_2 = 0{,}000292; Ф_2 = 16{,}870$

$M_3 = 0{,}00064; Ф_3 = 10{,}316; M_4 = 0{,}00075; Ф_4 = 9{,}656$

$\ln K_{\upsilon c} = 25.00; E_к = 48.650$ ккал / моль.

K_i adsorption equilibrium constants:

$$K_i = K_i^0 e^{\frac{Q}{RT}}$$

$K_1^0 = -\ 6.25;\ Q_1 = 8.0$ *ккал / моль*;

$K_2^0 = -11.75;\ Q_2 = 3$ *ккал / моль*;

$K_3^0 = -8.65;\ Q_3 = 7.0$ *ккал / моль*;

$K_4^0 = -3.46;\ Q_4 = 7.0$ *ккал / моль*;

$K_5^0 = 18.5;\ Q_5 = \ 4$ *ккал / моль*.

The adequacy of the dynamic kinetic model was verified by comparing the reported and experimental evidence on the effect of technological conditions on the extraction of target fractions, as well as taking into account the cost of errors. The obtained values made it possible to draw conclusions about the adequacy of the model and the possibilities of its use during the planning of the volume and quality of the fractions received in the oxycracking process of VG, as well as during the forecasting and optimization reports of the process.

CONCLUSIONS

The scientific and methodological bases of the process of catalytic oxycracking of vacuum gas oil with the presence of heterogeneous catalysts have been developed.

1. The methodology of catalytic oxycracking of vacuum gas oil was developed: the concentration limits of hydrocarbon raw materials, oxidizer and phlegmatizer, as well as the principle of the reaction unit ensuring the safe operation of the process were determined.
2. Depending on the process parameters, the regularities of the change of the output of the products have been determined, which allows for a comprehensive assessment of the influence of those

factors. The feasibility of catalytic oxycracking of vacuum gas oil has been proven: with the presence of the industrial cracking catalyst OMNICAT (ZCC) at 550°C, for 900 s, at 1% oxidation rate, and with a contact time of 1.7 s with the catalyst, the conversion rate was 71.8% (volume). It was found that the temperature and the degree of oxidation have the same effect on the degree of conversion of vacuum gas oil and the yield of reaction products, while the temperature and the contact time have the opposite effect on each other:

- the highest yield of the 195(200)-300°C fraction (33.7%) was obtained at the process temperature of 500°C, for 600 s, at 1% oxidation rate, and for 1.7 s of contact time;
- the maximum yield of hydrocarbon gas (35.1% by volume) was recorded at the process temperature of 500oC, for 900 s, at 2% oxidation level, and for 1.7 s of contact time.

3. For the first time, 10 oxide-modifiers were screened: Cu, Ti, V, Cr, Fe, Co, Ni, Cd, Mo and W. The main differences in the effect of catalytic systems were revealed. Based on the obtained evidence, the order of activity was established (according to the total yield of transparent fractions): Mo > Ti > Cr > Ni > Fe > W > V > Cd > Co > Cu.
4. It was shown for the first time that the selection of the conditions of the oxycracking process and the composition of the catalytic systems made it possible to determine the qualitative hydrocarbon composition of the target fractions: the regularities of the distribution of alkanes, oxygen-containing and aromatic hydrocarbons in the target liquid products of the catalytic oxycracking of vacuum gas oil were determined. It was determined that the Me/ZCC sample is less active than ZCC in terms of the formation of oxygen-containing compounds.
5. It was determined for the first time that the oxycracking of VG with the participation of Cr/ZCC, W/ZCC and Fe/ZCC catalytic systems is considered an effective process for obtaining low-

sulfur liquid products - the amount of dibenzthiophene and its C_1-C_3 homologues is 97.39% (relative) has decreased.

6. The relationship between the catalytic, physical-chemical and acid-base properties of the catalytic systems was determined. It has been shown that the main factors determining the catalytic activity of modifiers are the degree of structural change of the silicon-oxygen framework, and the strength of the metal-oxygen bond of the base cation is considered.
7. According to the effect of the added modifiers on the acid-base properties of the catalytic systems and their activity, they were classified: those that lead to an increase in Lewis acidity - these are Ti and W; bransted acidity enhancer – Ti, W and Mo; which do not lead to any changes – Cr, Co, V, Ni, Fe, Cd and Cu. The addition of the first and partly the second group of modifiers had a positive effect on the activity of the catalyst in oxycracking.
8. Depending on the process conditions, the temperature profiles allowed to determine that the catalytic oxycracking of vacuum gas oil with the presence of ZCC takes place in non-stationary conditions, a temperature "window" is observed at 500°C, when the share of homogeneous and heterogeneous phases is practically similar, oxygen-containing compounds and the output is maximal. The analysis of temperature profiles during the use of various modifiers allowed to reveal that the high activity of the oxycracking process of vacuum gas oil is characteristic of such systems, where the process takes place according to the surface-volume mechanism.
9. The kinetic and activation parameters of the catalytic oxycracking process of vacuum gas oil during the use of ZCC were determined. The presence of compensation effect was determined.

The main results of the research were published in the following scientific works:

1. Abul'-Futuh, T.M. Problemy proizvodstva ekologicheski chistyh benzinov / T.M.Abul'-Futuh, E.A.Gusejnova, K.YU.Adzhamov //NANA, ZHurnal himicheskih problem, - Baku: - 2010. №3,- pp.394-405 (in Russian).
2. Abul'-Futuh, T.M. Vliyanie rezhima podgotovki katalizatora krekinga na ego ekspluatacionnye kachestvennye pokazateli / T.M.Abul'-Futuh, F.F.Mamedov, H.M.Dzhalilova, Gusejnova E.A. [i dr.]// NANA, ZHurnal himicheskih problem, - Baku: - 2011. №3, - pp.411-415 (in Russian).
3. Zeynalov, E.T. Selittərkibli katalizator üzərində heksanın çevrilməsi/ E.T.Zeynalov, F.Z.Abuzərli, E.Ə.Hüseynova, K.Y.Əcəmov //"Neftin, qazın geotexnoloji problemləri və kimya" ETİ Elmi əsərləri, - Bakı: - 2013, pp.161-163 (in Azerbaijani)
4. Mursalova, L.A. Osobennosti prevrashcheniya n-geptana v prisutstvii ceolitsoderzhashchego katalizatora / L.A.Mursalova, M.R.Salaev, Gusejnova E.A., K.YU.Adzhamov //Nauchnye trudy NII «Geotekhnologicheskie problemy nefti, gaza i himiya», - Baku: - 2013, - pp.154-160 (in Russian).
5. Mursalova, L.A. Kataliticheskij kreking ozonirovannogo syr'ya / L.A.Mursalova, M.R.Salaev, Gusejnova E.A., K.YU.Adzhamov //II Rossijskij kongress po katalizu «ROSKATALIZ», - Novosibirsk: - 2014. T.2, -pp.321 (in Russian).
6. Mursalova, L.A. Prevrashcheniya n-geksana na katalizatore krekinga / L.A.Mursalova, E.A. Gusejnova, S.YU.YUsubova, K.YU.Adzhamov // Materialy seminara uchastnikov NII «Geotekhnologicheskie problemy nefti, gaza i himiya», - Baku: - 2014, - pp.136-139 (in Russian).
7. Adzhamov, K.YU. Kataliticheskij kreking vakuumnogo gazojlya v prisutstvii kisloroda/ K.YU.Adzhamov, L.A.Mursalova, E.A.Gusejnova // Tezisy dokladov VIII Vserossijskj konferencii s mezhdunarodnym uchastiem molodyh uchenyh po himii «Mendeleev -2014», - Sankt-Peterburg: - 2014, - pp.238 (in Russian).
8. Mursalova, L.A. Kataliticheskij oksikreking vakuumnogo gazojlya/ L.A.Mursalova, Gusejnova E.A., K.YU.Adzhamov // AMEA, Azərbaycan kimya jurnalı, - Baku: - 2014. №3, - pp.37-42 (in Russian).

9. Mursalova, L.A. Prevrashcheniya n-alkanov C_6-C_7 na ceolitsoderzhashchem katalizatore krekinga / L.A.Mursalova, E.A. Gusejnova, K.YU.Adzhamov, T.M.Abul'-Futuh / NANA, ZHurnal himicheskih problem, - Baku: - 2014. №4, - pp.413-418 (in Russian).
10. Mursalova, L.A. Infrakrasnye spektry ozonirovannogo vakuumnogo gazojlya / L.A.Mursalova, Gusejnova E.A., K.YU.Adzhamov. // Akademik S.C.Mehdiyevin 100 illiyinə həsr olunmuş neft-kimya sintezi üzrə respublika elmi praktiki konfransın materialları, - Bakı: - Dekabr, 2014, - pp.75-80 (in Russian).
11. Mamedov, N.A. K voprosu o vliyanii ozona na fiziko-himicheskie svojstva vakuumnogo gazojlya/ N.A.Mamedov, SH.SH.Alekberov, U.B.Rzaeva, L.A. Mursalo [i dr.] // Xəzərneft-yataq»-2014, Elmi-təcrübi konfrans, - Bakı: - 2014, - pp.296-300 (in Russian).
12. Mursalova, L.A. Obrazovanie produktov uplotneniya v processe okislitel'nogo kataliticheskogo krekinga/ L.A. Mursalova, E.A. Gusejnova, M.R.Salaev, U.B.Rzaeva [i dr.] //NANA, Tezisy dokladov Resp.nauchnoj konferencii, posvyashchennoj 90-letnemu yubileyu akad.T.SHahtahtinskogo, - Bakı: - 2015, - P.66 (in Russian).
13. Mursalova, L.A.. Ob ozonirovanii i krekinge vakuumnogo gazojlya/ E.A. Gusejnova, K.YU. Adzhamov, Z.M. Mikail-zade [i dr.]// Nauchnye trudy NII «Geotekhnologicheskie problemy nefti, gaza i himiya», - Bakı: - 2015. Cild XVI, - pp.390-410 (in Russian).
14. Guseinova, E.A. Features of the zeolite containing catalysts of oxidative catalytic cracking by thermal analysis/ Л.А. Мурсалова, E.A.Guseinova, L.A.Mursalova, M.R.Salayev, K.Y.Adzhamov // EuropaCat XII. Absrtacts XII European Congress on Catalysis Catalysis: Balancing the use of fossil and renewable resources, Kazan: -2015, - pp.1454-1455 (in Russian).
15. Zejnalov, E.T. Vliyanie metoda aktivacii na aktivnost' nikelevogo katalizatora / E.T. Zejnalov, E.A. Gusejnova, N.N. Bagirova, K.YU. Adzhamov // Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Bakı: - 2016. T.8. №2, - pp.72-78 (in Russian).
16. Mursalova, L.A. Vliyanie ozonirovaniya na elementnyj sostav vakuumnogo gazojlya / L.A. Mursalova, M.R. Salaev, E.A., Gusejnova, K.YU. Adzhamov // Sbornik tezisov XI Vserossijskoj nauchno-tekhnicheskoj konferencii "Aktual'nye problemy razvitiya

NGK Rossii", RGU im. I.M. Gubkina, Moskva: - 2016,- P.152 (in Russian).

17. Mursalova, L.A. Vliyanie ozonirovaniya na poverhnostnye svojstva vakuumnogo gazojlya / L.A. Mursalova, E.A. Gusejnova, K.YU. Adzhamov, K.B.Rustamova // Tezisy dokladov IX Bakinskoj Mezhdunarod-noj Mamedalievskoj konferencii po neftekhimii, - Baku: - 2016, - P.132 (in Russian).
18. Mursalova, L.A. Kislotno-osnovnye svojstva ceolitsoderzhashchego katalizatora krekinga v processe izomerizacii buten-1 / L.A. Mursalova, E.A. Gusejnova, K.YU. Adzhamov // ZHurnal fizicheskoj himii, - Moskva: - 2016. T.90. №8 - pp. 1163-1169 (in Russian).
19. Adjamov, K.Y. Research seal products zeolite catalyst oxide cracking of vakuum gas oil / K.Y.Adjamov, E.A.Guseinova, L.A.Mursalova, M.R.Salayev // XV İnternational Conference on Thermal Analysis and Calorimetry in Russia (RTAC-2016),- 2016, - pp.13-15 (in Russian).
20. Mursalova, L.A. Spektroskopicheskie osobennosti ozonirovannogo vakuumnogo gazojlya / L.A. Mursalova, E.A. Gusejnova, K.YU.Adzhamov //AMEA, Gəncə Regional Elmi Mərkəzinin Xəbərlər Məcmuəsi, AMEA Gəncə Regional Elmi Mərkəzi, - Gəncə: - 2016. № 3 (65), - pp.40-46 (in Russian).
21. Mursalova, L.A. Sravnitel'nyj analiz termicheskoj i adsorbcionnoj ochistki ozonirovannogo vakuumnogo gazojlya/ L.A. Mursalova, E.A. Gusejnova, K.YU. Adzhamov// AMEA, Kimya problemleri, - Baku: - 2016, №3,- pp.277-284 (in Russian).
22. Mursalova, L.A. Raschet optimal'nyh uslovij provedeniya processa okislitel'nogo kataliticheskogo krekinga vakuumnogo gazojlya/ L.A. Mursalova, E.A. Gusejnova, K.YU. Adzhamov//PAHTEI, Azərbaycan Ali Texniki Məktəblərinin Xəbərləri, - Baku: - 2016. T.18. №3, - pp.77-84 (in Russian).
23. Mürsəlova, L.A. Ozonlaşdırılmış vakuum qazoylun katalitik krekinqi / L.A. Mürsəlova, E.Ə.Hüseynova, K.Y. Əcəmov// «Neftin, qazın geotexnoloji problemləri və kimya» ETİ-nin Elmi əsərləri, - Baku: - Dekabr 2016. Cild XVII, - S.401-406 (in Azerbaijani).
24. Mursalova, L.A..Primenenie ozonoliza dlya oblagorazhivaniya syr'ya kataliticheskogo krekinga/ L.A. Mursalova, E.A. Gusejnova, K.YU. Adzhamov // Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Baku: - 2017.Cild 9. №1, - pp.69-74 (in Russian).

25. Mürsəlova, L.A. Oksidləşdirici katalitik krekinq prosesində yaranan sixlaşma məhsullarinin xüsusiyyətləri/ L.A. Mürsəlova, E.Ə.Hüseynova, K.Y. Əcəmov// Akademik B.Q.Zeynalovun 100 illik yubileyinə həsr olunmuş "Neftkimya sintezi və mürəkkəb kondensləşmiş sistemlərdə kataliz" mövz.beyn. elmi-texniki konfrans, - Bakı: - 2017, - P.66 (in Azerbaijani).
26. Guseinova, E.A.Investigation of the catalytic cracking process in presence of oxygen and ozone / E.A.Guseinova, K.Y.Adzhamov// ITWCCST 2017, BAKU, ASOİA, Azerbaijan, - P.170.
27. Gusejnova, E.A. O prirode aktivnyh centrov biceolitnogo katalizatora v processe (okislitel'nogo kataliticheskogo) oksikrekinga vakuumnogo gazojlya/E.A.Gusejnova//Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Baku: - 2017 . T.9. №3, - pp.104-110 (in Russian).
28. Gusejnova, E.A. Predpolagaemye puti prevrashcheniya vakuumnogo gazojlya v usloviyah okislitel'nogo kataliticheskogo krekinga (oksikrekinga) / E.A.Gusejnova, L.A. Mursalova, S.A. Mamedhanova, G.CH. Dadaeva [i dr.]// AMEA, ZHurnal himicheskih problem, - Baku: - 2017 (15). 3, - pp.283-290 (in Russian).
29. 28. Gusejnova, E.A. V kn.: Poluchenie, stroenie i primenenie produktov neftekhimii i organicheskogo sinteza Glava 8. Rol' kataliticheskogo krekinga. Sostoyanie i perspektivy razvitiya. Ufa Izdatel'stvo «Neftegazovoe delo»:, - 2017, - pp.179-211 (in Russian).
30. Huseynova, E.A. Influence of ozonolysis on group hydrocarbon and elementary composition of vacuum gas oil / E.A. Huseynova, L.A.Mursalova, N.N.Bagirova, F.A.Khashimov [et al]// AMEA, Azərbaycan kimya jurnalı, - Baku: - 2017.№4, - pp.6-11.
31. Gusejnova, E.A.. Izomerizaciya n-geksana v prisutstvii nanesennyh titanoksidnyh katalizatorov / E.A Gusejnova., M.R. Salaev, N.T. Alieva, K.YU. Adzhamov // Himiya i tekhnologiya topliv i masel, - Moskva: - 2018. T.606. №2, - pp.8-13 (in Russian).
32. Gusejnova, E.A. Izomerizaciya buten-1 na sul'fatirovannom diokside titana / E.A.Gusejnova, M.R.Salaev, M.R.Al'-Battbotti, K.YU.Adzhamov [i dr.] // Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Baku: - 2018. №3, - pp.89-96 (in Russian).
33. Salaev, M.R. Osobennosti formirovaniya nanesennogo dioksida titana na osnove rentgenofazovyh issledovanij/ M.R.Salaev, E.A.

Gusejnova, K.YU.Adzhamov, S.E.YUsubova [i dr.]// Materialy mezhdunarodnoj nauchno-prakticheskoj konferenciya «Fundamental'nye i prikladnye issledovaniya v oblasti himii i ekologii-2018», - Kursk:- 2018, - pp.101-103 (in Russian).

34. Gusejnova, E.A. Vliyanie uslovij oksikrekinga vakuumnogo gazojlya na pokazateli processa// Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Baku: - 2018. T.10. №4, - pp.82-89 (in Russian).
35. Salaev, M.R. Vliyanie dobavok sul'fat-aniona na fazovyj sostav i strukturu dioksida titana / M.R. Salaev, E.A. Gusejnova, M.R.Al'-Battbotti, K.YU.Adzhamov [i dr.] //ZHurnal prikladnoj himii, - Moskva: - 2018. T.91. № 6, - pp.786-792 (in Russian).
36. Əcəmov, K.Y. IK-17-1 katalizatorun iştiraki ilə katalitik krekinq prosesinin tədqiqi / K.Y.Əcəmov, E.Ə.Hüseynova, L.A.Mürsəlova, F.A.Nurəliyeva //AMEA Gəncə Regional Elmi Mərkəzinin Xəbərlər Məcmuəsi, - Gəncə: - 2019. № 1 (75), - pp.44-51 (in Azerbaijani).
37. Salaev, M.R. IK-spektroskopicheskoe issledovanie sul'fat-anionsoderzhashchego oksida titana / M.R.Salaev, E.A. Gusejnova, S.E.YUsubova, M.R.Al'-Battbotti [i dr.]//Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Bakı: - 2019. №3, - pp.71-79 (in Russian).
38. Gusejnova, E.A. Gruppovoj sostav aromaticheskih uglevodorodov v produktah oksikrekinga vakuumnogo gazojlya / E.A. Gusejnova// Azərbaycan Mühəndislik Akademiyasının xəbərləri, - Bakı: - 2019.Cild 11. №2,- pp.70-76 (in Russian).
39. Gusejnova, E.A. Raschetnoe opredelenie uslovij provedeniya processa oksikrekinga vakuumnogo gazojlya / E.A. Gusejnova, L.A.Mursalova, N.N.Bagirova, K.YU.Adzhamov //ZHurnal «Neftekhimiya», - Moskva: - 2019, T. 59, №2, - pp. 172-177 (in Russian).
40. Adzhamov, K.Y.Termogravimetricheskij analiz katalizatorov oksikrekinga, podvergnutyh regeneracii/K.YU.Adzhamov, E.A. Gusejnova, L.A.Mursalova, S.R.Safarova // Azerbaijan Journal of Chemical News, - Baku: - 2019, №1, - pp.24-30 (in Russian).
41. Gusejnova, E.A. Termicheskij analiz katalizatora oksikrekinga,podvergnutogo okislitel'noj regeneracii / E.A. Gusejnova, S.R.Safarova, L.A.Mursalova, K.YU.Adzhamov// AMEA-nın Akademik Y.H.Məmmədəliyev adına Neft kimya prosesləri institutunun 90 illik yubileyinə həsr olunmuş “Müasir

kimyanin aktual problemləri” mövzusunda beynəlxalq elmi konfrans, - Bakı: - 2019, P.350 (in Russian).

42. Əcəmov, K.Y. Katalitik krekinq prosesində kombinəli qurğunun tətbiqi / K.Y.Əcəmov, E.Ə.Hüseynova, Z.M.Mikayıl-zadə, M.N.Əsgərova // AMEA, Gəncə bölməsi «Xəbərlər məcmuəsi», - Gəncə: - 2019. № 2 (76), - pp.69-76 (in Azerbaijani).
43. İbadova, R.C. Yüngül piroliz qətranlarının “Nikel kizelqur üzərində” katalizatorunun iştiraki ilə hidrogenləşməsi /R.C.İbadova, E.Ə.Hüseynova, K.Y. Əcəmov // “Neftin, qazın geotexnoloji problemləri və kimya” ETİ Elmi əsərləri, - Bakı: - 2019, - pp.241-247 (in Azerbaijani).
44. Əcəmov, K.Y.Katalitik krekinq prosesinin xammalının maye fazalı oksidləşdirici kükürdsüzləşmə prosesinin tədqiqi / K.Y.Əcəmov, E.Ə.Hüseynova, A.A.Teymurova, L.A.Mürsəlova // Azerbaijan Journal of Chemical News, - Bakı: - 2019, N2 s.21-26 (in Azerbaijani).
45. Safarova, S.R. Vliyanie temperatury na process regeneracii katalizatorov oksikrekinga po dannym termicheskogo analiza / S.R.Safarova, K.YU.Adzhamov, Gusejnova E.A., L.A.Mursalova //“Neftin, qazın geotexnoloji problemləri və kimya” ETİ Elmi əsərləri, - Bakı: - 2019, - pp.248-259 (in Russian).
46. Guseinova, E.A. Kinetic parameters of formation of oxygencontaining compounds in the vacuum gas oil oxycracking process / E.A.Guseinova, K.Yu.Adzhamov, S.R.Safarova // Reaction Kinetics, Mechanisms and Catalysis, - Budapest, Hungary: - Fevral, 2020. V.129, N2, - pp. 925–939 .
47. Guseinova, E.A. Formation kinetics of hydrocarbon compounds in the vacuum gas oil oxycracking process / E.A.Guseinova, K. Yu.Adzhamov, L.A. Mursalova & S.R.Safarova //Reaction Kinetics, Mechanisms and Catalysis, - Budapest, Hungary: - 2020.V. 131, N4, - pp. 57–74.
48. Gusejnova, E.A. Raschet kineticheskih parametrov obrazovaniya kislorodsoderzhashchih uglevodorodov//Azerbaijan Journal of Chemical News, - Baku: - - 2020, Vol.1, N 1, P. 60-67 (in Russian).
49. Guseinova, E.A. Influence Of Temperature On Fractional Composition Of Products Oxycracking Vacuum Gasoil / E.A.Guseinova, K.Yu. Adzhamov, S.R. Safarova, L.A. Mursalova// Book of abstracts International Conference On Actual Problems Of Chemical Engineering, Dedicate To The 100th Anniversary Of The

Azerbaijan State Of Oil And Industry University, - Baku: Azerbaijan, - 2020, - p.42.

50. Gusejnova, E.A. Vliyanie tekhnologicheskih parametrov na frakcionnyj sostav produktov oksikrekinga vakuumnogo gazojlya/E.A. Gusejnova // "Neftin, qazın geotexnoloji problemləri və kimya" ETİ Elmi əsərləri, - Bakı: - 2020, - pp.81-94 (in Russian).
51. Hüseynova, E.Ə. Katalitik krekinq prosesinə naften turşusu əlavələrinin təsirinin öyrənilməsi / E.Ə.Hüseynova, K.Y. Əcəmov, E.T. Zeynalov, İ.D. Aslanova [və b.]// "Neftin, qazın geotexnoloji problemləri və kimya" ETİ Elmi əsərləri, - Bakı: - 2020, - pp.147-155 (in Azerbaijani).
52. Adjamov, K.Y. Some Aspects Of Oxycracking Catalysts Regeneration / K.Y.Adjamov, E.A.Huseynova, L.A.Mursalova, S.R.Safarova // Azerbaijan Chemical Journal, - Baku: - - 2020. N1, - pp.77-81.
53. Gusejnova, E.A. Vliyanie prirody modifikatora na frakcionnyj sostav katalizata oksikrekinga vakuumnogo gazojlya/ E.A.Gusejnova // Nauka. Tekhnika. Tekhnologii. – Krasnodar: - 2021, № 1, - pp.246-251 (in Russian).
54. Gusejnova, E.A. Zavisimost' frakcionnogo sostava produktov oksikrekinga vakuumnogo gazojlya ot temperatury /E.A.Gusejnova //Sbornik tezisov "IV Rossijskogo kongressa po katalizu «ROSKATALIZ»", - Kazan': 2021, - pp. 698-699 (in Russian).
55. İbadova, R.C. Hydrogenation of the light pyrolysis resin via the presence of catalyst "over surface of nickel kiselgur" /R.C.İbadova, E.A.Guseinova // PAHTEI, Azərbaycan Ali Texniki Məktəblərinin Xəbərləri, - Baku: - - 2021. Cild 23, №5, - pp.16-20 (in Russian).
56. Gusejnova, E.A., Mikail-zade Z.M. Vydelenie hroma iz otrabotannogo katalizatora krekinga / E.A. Gusejnova, Z.M. Mikail-zade//Materialy V Vserossijskoj nauchnoj konferencii (s mezhdunarodnym uchastiem) «Aktual'nye problemy teorii i praktiki geterogennyh katalizatorov i adsorbentov», - Suzdal':- 2021, - s.307-309 (in Russian).
57. Guseinova, E.A. The kinetic characteristic of the vacuum gas oil`s oxycracking / E.A.Guseinova, K.Yu.Adzhamov, S.R.Safarova// Book of Abstracts 2nd İnternational Conference on Reaction Kinetics, Mechanizms and Catalysis, RKMC2021, - Budapest, Hungary, - 2021, - p.118 .

58. AR Patenti: İXTİRA Vakuum qazoylum emal üsulu, İ 2021 0076, 23.07.2021, Ramazanova, E., Adzhamov, K.YU., Gusejnova, E.A., Mursalova, L. A.
59. Guseinova, E.A. Separation Of Chromium From Used Cracking Catalyst/ E.A.Guseinova, Z. Mikayil-Zadeh //Book of Abstracts 6 th International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface. Interface, organized by Jerzy Haber Institute of Catalysis, - Kraków, Poland: - 2021, -pr.148-149 .
60. Gusejnova, E.A. Gidrostabilizaciya pirokondensata piroliza pryamogonnogo benzina v prisutstvii nikel' – hromovogo katalizatora / E.A. Gusejnova, R. A. Ismajlova, R. Dzh. Ibadova //Neftekhimiya, - Moskva: - 2022, T. 62, № 5 - pp. 659-669 (in Russian).
61. Guseinova, E.A. The Effect of Oxygen-containing Additives in Feedstock on the Perfor-mance of the Catalytic Cracking Process / E.A.Guseinova, S.R. Safarova // Catalysis Research. Special Issue: Zeolite Materials and Catalysis, 2022 67, 02024
62. Rəsulov, S.R. Ağır katalıtik krekinq qalığının bıtumda termooksidləşdirici emalı / S.R.Rəsulov, E.Ə.Hüseynova, Z.Ağakişiyeva, R.Babayev // PAHTEI, Azərbaycan Ali Texniki Məktəblərinin Xəbərləri, - Bakı: - - 2023.V. 31, I. 08, - pp.396-403 (in Azerbaijani).
63. Gusejnova, E.A., R. Dzh. Ibadova Gidrirovanie pirokondensata piroliza v prisutstvii nikel'-hromovogo katalizatora/ E.A. Gusejnova, R. Dzh. Ibadova // Materialy mezhdunarodnoj nauchnoj metodicheskoj konferencii «Integraciya nauki i obrazovaniya v vuzah neftegazovogo profilya. Peredovye tekhnologii i sovremennye tendencii», - UGNTU, Ufa: - 2022, pp.7-9 (in Russian).
64. Guseinova, E.A. Hydrocarbon composition of liquid products of catalytic oxycracking of vacuum gasoil/ E.A.Guseinova, A.A.Hasanov, and R.A. Shikhiyev// BIO Web of Conferences VVRD 2023, - 2023, 67, - 02024
65. Gusejnova, E.A. Vliyanie uslovij kataliticheskogo oksikrekinga na koncentraciyu grupp uglevodorodov v katalizate/ E.A.Gusejnova // Materialy Vserossijskoj nauchno-tekhnicheskoj konferencii, posvyashchennoj 75-letiyu OOO «GAZPROM neftekhim Salavat» Nauka. Tekhnologiya. Proizvodstvo – 2023: materialy", UGNTU, - Salavat: -2023, - pp.232-234 (in Russian).

66. Evrazijskij patent №043432 Sposob izvlecheniya lantana iz otrabotannogo katalizatora krekinga, 25 maya 2023, Gusejnova, E.A., Ismajlova, R.A., Mikail-zade, Z.M., Safarova, S. R.

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