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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STUDY OF ALKYLATION PROCESS WITH CATALYTIC CRACKING GASES TO IMPROVE THE VISCOSITY-TEMPERATURE PROPERTIES OF LOW-INDEX OIL FRACTIONS ON MODIFIED ZEOLITES

Speciality: 3303.01 – Chemical technology and engineering

Field of science: Technical sciences

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The work was performed at the Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev of Azerbaijan Ministry of Science and Education at the «Research of petroleums and technology of oils getting» Laboratory

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GENERAL CHARACTERISTIC OF WORK

Relevance of the topic and degree of development.

The creation of environmentally friendly technological processes aimed at obtaining high-quality products using raw materials available in the republic is of great importance for the economic potential of the republic. Base oils from Azerbaijani oils are characterized by unsatisfactory viscosity-temperature properties (low viscosity index). It is known that viscosity and viscosity-temperature properties (dependence of viscosity on temperature) are important characteristics of lubricants.

Lubricants in Azerbaijan are initially produced from unique low-paraffin, low-tar oils using traditional technological processes characterized by large amounts of acid waste. The technology for obtaining these oils poses serious environmental problems, since the purification of distilled oil fractions is carried out using acid and acid-alkali contact methods. Therefore, the technology for obtaining these environmentally friendly and high viscosity-temperature oils is relevant.

The main direction for improving these properties is to use processes for their production that change their chemical composition to form hydrocarbons with a higher viscosity index.

Saturation of petroleum fractions with long side-chain isoparaffin, aromatic, and naphthenic hydrocarbons improves their viscosity-temperature and rheological properties, reduces evaporation, increases thermal-oxidative stability, and other performance indicators.

The viscosity-temperature properties of oils can be improved either by using thickening additives or by the hydrocracking process[1]. However, the use of thickening additives leads to an increase in kinematic viscosity, which is sometimes undesirable.[1]

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[1] Аббасов, В.М. Развитие производства смазочных масел в Азербайджане / В.М. Аббасов, Э.Ш. Абдуллаев, Б.М. Алиев [и др.] // Нефтегазовые технологии и аналитика, - Москва: - 2019. №2, -с.30-35.

The hydrocracking process is carried out at high temperatures and pressures, and as a result, the physicochemical properties of the extracted oil fractions change significantly[2].

An alternative method, the alkylation process, is carried out under milder conditions than hydrocracking, i.e. at lower temperatures and pressures. Various olefin feedstocks, including catalytic cracking gases, can be used as alkylating agents. This significantly reduces the cost of obtaining high-quality oils and increases their yield. Therefore, research in this area is relevant and promising.

Zeolite-based catalysts, characterized by high activity, selectivity, stability, defined microporous structure, and regeneration ability, are used for alkylation processes. Zeolites modified with noble or transition metals are mainly used.

Object and subject of work. Development of the technology and conditions of the alkylation process for the production of high-index alkylates using catalytic cracking gases in the Al+CCl_4 halloysite system and ZSM-5 zeolite modified with Zr, Fe metals of low-index T-22 and T-30 turbine distillate oil fractions.

The purpose and objectives of the research. The purpose of the work is to develop a technology and technological scheme for the alkylation process of low-index distillate oil fractions with catalytic cracking gases on modified heterogeneous catalysts. To achieve the stated goal, the following tasks were solved in the dissertation:

- The preparation and use of Zr and Fe modified zeolite-based ZSM-5 catalysts and halloysites, modified (ZSM-5-ZrO_2, ZSM 5-$FeCl_2$ and halloysite+Al+CCl_4) catalysts, which are effective for the alkylation process of low-index distillate T-22 and T-30 turbine oil fractions with catalytic cracking gases, have been studied.

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[2] Huseynova, G.A. A Study of the Products of Turbine Oil Distillate Alkylation with Catalytic Cracking Gases /Galina Huseynova, Fazila Samedova, Sanubar Rashidova [et al.] //Petroleum Chemistry, - Springer Link: - 2019. Vol.59, №11, - pp.1220-1225.

- Optimal conditions were selected for the alkylation process carried out on spent catalysts – temperature, pressure;
- Regeneration of modified ZSM-5-$ZrO_{2(reg)}$, ZSM-5-$FeCl_{2(reg)}$ catalysts used in the alkylation process and use of the regenerated catalysts in the alkylation process were carried out;
- The physicochemical properties and structure of the obtained alkylates were studied in comparison with the original oil fractions;
- The structure, phase composition, particle size, and surface state of the modified ZSM-5-ZrO_2 and ZSM-5-$FeCl_2$ catalysts are given in comparative form with the unmodified ZSM-5 zeolite and the regenerated ZSM-5-$ZrO_{2(reg)}$ and ZSM-5-$FeCl_{2(reg)}$.

Research methods. In the scientific research work, modern physicochemical analysis methods, GOST and ASTM, IR and NMR spectral methods, X-Ray X-ray phase and thermogravimetric (DTG, TG), as well as scanning electron microscopy (SEM) and dynamic light scattering (DLS) methods were used to identify and characterize oil fractions and alkylates.

The main provisions put forward for defense:

-development of the technology for the alkylation process of low-index T-22 and T-30 turbine distillate oil fractions with catalytic cracking gases;
- Preparation of Zr and Fe-modified zeolite-based ZSM-5 and halloysite-based catalysts modified in the Al+CCl_4 system for use in the alkylation process:
- selection of an effective catalyst for the alkylation process;
- the possibility of alkylation on regenerated catalysts;
- selection of optimal conditions for the alkylation process – temperature, catalysts, pressure;
- composition and properties of the initial and regenerated catalysts;
- properties of the obtained alkylates and the possibility of their compounding with the initially obtained oil fractions.

Scientific novelty of the dissertation: Firstly, the alkylation process of low-index oil fractions (T-22 and T-30 turbine oils) with olefin-based catalytic cracking gases of various compositions over metal-modified ZSM-5-ZrO_2, ZSM 5-$FeCl_2$ and halloysite-based halloysite+Al+CCl_4 catalysts was studied in order to improve their viscosity-temperature properties.

It was found that the more active and effective ZSM-5 for the alkylation process is the ZSM-5-ZrO_2 zeolite-based catalyst, which has ZrO_2 and $ZrSi_{24}O_{50}$ phases and a crystal structure.

- The incorporation of Zr and Fe metal cations into the ZSM-5 catalyst leads to the neutralization of proton centers (Brensted centers) and a change in the ratio of Lewis and Brensted acid centers. It has been found that both Brensted and Lewis acid centers participate in the alkylation process, but Lewis acid is more dominant.

-Alkylation process was carried out on regenerated ZSM-5-$ZrO_{2(reg)}$ and ZSM-5-$FeCl_{2(reg)}$ catalysts and it was determined that the catalysts annealed and regenerated in the temperature range of 530–550°C do not undergo changes in the specified temperature range and actively participate in the alkylation process. Thus, it was determined that the modified catalysts were more active than unmodified and regenerated ZSM-5.

- The phase composition (X-Ray), thermal stability (TG), average particle size and distribution pattern (DLS) in distilled water, surface topography and crystal size (SEM) of ZSM-5-ZrO_2, ZSM 5-$FeCl_2$, and regenerated ZSM-5-$ZrO_{2(reg)}$ ZSM 5-$FeCl_{2(reg)}$ catalysts were determined by analytical methods. It has been found that after regeneration and annealing, the catalysts do not undergo changes, maintaining their phase composition, particle size limits, crystal structure, and thermal stability.

- The mechanism of the alkylation reaction, which occurs by the growth and elongation of chains due to the conversion of aromatic and naphthenic hydrocarbons and their addition to side chains, is given. The alkylation process occurs by elongating side chains and forming new ones due to the addition of propylene and butylene hydrocarbons to the side chain. The improvement of the viscosity-temperature properties of oil fractions occurs due to alkylation occurring in the long side chains of aromatic hydrocarbons.

- Initially, oligomerization reactions accompanied by alkylation of olefins using catalytic cracking gases on halloysite+Al+CCl_4+Mg and ZSM-5-ZrO_2 modified catalysts were studied. It has been found that oligomerization, which occurs in a similar temperature range to the alkylation process, results in the formation of oligomers with low yields and low viscosity indices (in the range of 49-51). The oligomers formed during the alkylation process combine with the aromatic and naphthenic hydrocarbons of the oil fraction to form long side-chain molecules with a high viscosity index.

Theoretical and practical value of the work . The alkylation process of distillate fractions of low-index T-22 (viscosity index 32) and T-30 (viscosity index 49.9) turbine oils with catalytic cracking gases can be recommended for industrial application to obtain environmentally friendly, waste-free, high-quality oils. In this case, high-index oils with a viscosity index of 121.8-137 and high-index oils (viscosity index 104) can also be obtained by compounding these oils with the original oils in a 1:5 ratio.Alkylates can be compounded with other oil fractions to obtain oils with a specific viscosity level and viscosity-temperature properties.

Personal participation of the author. The author personally participated in the formulation of the issues included in the dissertation, the implementation of the research, the generalization and interpretation of the experimental results obtained, and the writing of the articles.

Approbation and application of the work . 22 scientific works have been published on the topic of the dissertation, 10 of them articles and 12-thesis.

The results of the dissertation work were presented at the following conferences: “Sustainable development strategy: Global Trends, National Experiences and New Goals” İnternational Scientific Conference (Mingachevir, 10-11 December 2021); İnternational scientific-practical Conference Machine-building and Energy: “New Consepts and Technologies” (Baku, 2-3 December 2021); XIIInternational Conference "Chemistry Oil and Gas (Russia, Томsк, 26-30 september 2022); Republican Scientific Conference on "Various Purpose Organic Substances and Compositional Materials" dedicated to the 110th anniversary of the outstanding scientist, academician Ali Musa oglu Guliyev (Bakı, 2022); The Modern

Vector Of The Development Of Science Proceedings Of The I International Scientific And Practical Conference (USA, Philadelphia, 17-18 November 2022); At the IV International Scientific Conference on “Towards Sustainable Chemistry and Chemical Engineering: Innovations for Building a Better World” dedicated to the 100th anniversary of the birth of National Leader Heydar Aliyev (Bakı, 2022); International Scientific Conference on "Actual Problems of Modern Natural and Economic Sciences" dedicated to the 100th anniversary of the birth of the National Leader Heydar Aliyev, Part II (Ganja, 05-06 may 2023); Challenges and problems of modern science, Proceedings Of The II International Scientific And Practical Conference (United Kinghdom, London, 10-11 november 2022); At the scientific conference on "Metal complex and metal-organic catalysis, synthesis and study of (so)oligomers, (so)polymers" dedicated to the 80th anniversary of the prominent Azerbaijani scientist, academician Akif Azizov(Bakı, 15 noyabr 2023); Innovative scientific research Proceedings of the IX International Scientific and Practical Conference (Canada, Toronto 14-15 march 2024); Scientific advances and innovative approaches Proceedings of the XI International Scientific and Practical Conference (Japan,Tokyo, 06-07 June 2024); XIII International Conference "Chemistry Oil and Gas » (Russia Томsк, 23-27 september 2024). dedicated to the 100th anniversary of the outstanding scientist, academician Maharram Ali Mammadyarov scientific confrans, (Baku, 26-27 september, 2024)

Name of the organization where the dissertation work was performed. The dissertation work was conducted in the “Oil Research and Oil Extraction Technology” laboratory of the Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

The total volume of the dissertation, indicating the volume of structural sections . Dissertation work is 160 pages long, consist of introduction, 5 chapters, conclusions, bibliography and appendix. The work includes 54 pictures, 30 table and 2 scheme. The structure of the dissertation – introduction 14420, the first chapter 55950, the second chapter 13210, the third chapter 31590, the fourth 49070, the fifth chapter 13075, and the results consist of 3502. The dissertation has a total volume of 180957 characters (excluding the table of contents, tables, pictures and bibliography)

In the introduction presents the main provisions of the research conducted, explains the relevance and purpose of the research, and provides information and justification about the scientific novelty, theoretical and practical significance of the work.

The first chapter discusses the current state of oil production in Azerbaijan and abroad, the use of zeolite-containing catalysts in the alkylation process, alkylation and oligomerization processes for obtaining oils with improved viscosity-temperature properties, alkylation of oil and gasoline fractions, alkylation of isobutane with olefins and olefin fractions, alkylation of benzene, and oligomerization processes of olefins and olefin fractions, and justifies the formulation of the problem.

The second chapter presents the characteristics of the initial raw materials and reagents - oil fractions, catalytic cracking gases, the composition of catalytic cracking gases, the properties of the halloysite and zeolite-based ZSM-5 catalysts used, the methodology for conducting the experiment and the scheme of the devices, and the methods for analyzing the products obtained.

In the third chapter, the selection and study of catalysts for the alkylation process, the study of catalytic systems modified based on halloysites, the development and study of the ZSM-5 zeolite-containing catalyst modified with Zr and Fe, thermogravimetric (TG, DTG), X-ray phase analysis, IR, topography of the surfaces of the modified catalysts, scanning electron microscopy (SEM) and the average size of the molecules of the obtained compounds were studied using dynamic light scattering (DLS) methods. It was concluded that the modification of halloysites and ZSM-5 catalyst allows for the production of suitable products, at the same time, their regeneration and activation after the process was carried out, and their activity in the processes was studied and confirmed by the methods given above.

In the fourth chapter, the process of alkylation of oil fractions with catalytic cracking gases in modified catalytic systems was studied. The viscosity indices of T-22 and T-30 oils increased from 32 to 84, from 49.9 to 137, and from 49.9 to 99.4, respectively, during alkylation with catalytic cracking gases at 50 °C for halloysite+Al+CCl_4, ZSM-5-ZrO_2, and ZSM-5-$FeCl_2$. The optimal conditions for the alkylation process of oil distillation fractions were determined: temperature (50°C), oil:gas volume ratio (1:1), and pressure (0.5-0.8 MPa generated by gases at a certain temperature).The catalysts were studied in the alkylation process of T-30 oil with catalytic cracking gases by regenerating them after the process and it was found that they retained their activity.

In addition, the oligomerization process on ZSM 5-ZrO_2 catalyst was carried out and studied. The particle sizes and surface morphology of the initial and regenerated catalysts were studied by dynamic light scattering (DLS) and scanning electron microscopy (SEM) methods.

In the fifth chapter, the technology and technological scheme of the alkylation process of oil fractions using catalytic cracking gases on modified zeolites are developed.The obtained alkylates can be used to obtain base-based turbine, motor, hydraulic and industrial oils.A feasibility study was conducted to obtain high viscosity index oils based on the alkylation of T-30 oil with catalytic cracking gases over a ZSM-5-ZrO_2 catalyst..

At the end of the dissertation, the results of the research conducted, a list of literature, and abbreviations are provided.

MAIN CONTENT OF THE WORK

Raw materials, reagents and equipment used in the work

The alkylation process was carried out with low-index T-22 and T-30 (AZS 445-2010) turbine oils with viscosity indices of 32 and 49.9, respectively.

Catalytic cracking gases with a volume content of 32.6; 38.4; 43.47; 56.09 and 56.35% were used as alkylating agents.

ZSM-5-ZrO_2, ZSM-5-$FeCl_2$ and halloysite-based Halloysite+Al+CCl_4, Halloysite+Al+CCl_4+Mg catalysts, which were modified by the impregnation method with zirconyl chloride ($ZrOCl_2 \cdot 6H_2O$) and ferric chloride salt ($FeCl_2$), were investigated in the alkylation process and compared with halloysite and ZSM-5 catalysts.

The alkylation process was carried out in an AMAR type stirred tank in an autoclave (Figure 1) and at the Institute's "Experimental Test Sector" (Figure 2).

Figure 1. Alkylation in autoclave

Alkylation conditions:
Temperature – 30-150 °C
Gas supply pressure – 0,3-0,9 MP
Amount of catalyst – 1,5 q
Turbine oil – 100-200 ml
Cat.cracking gases – 100-200 ml
Reaction time – 1 saat

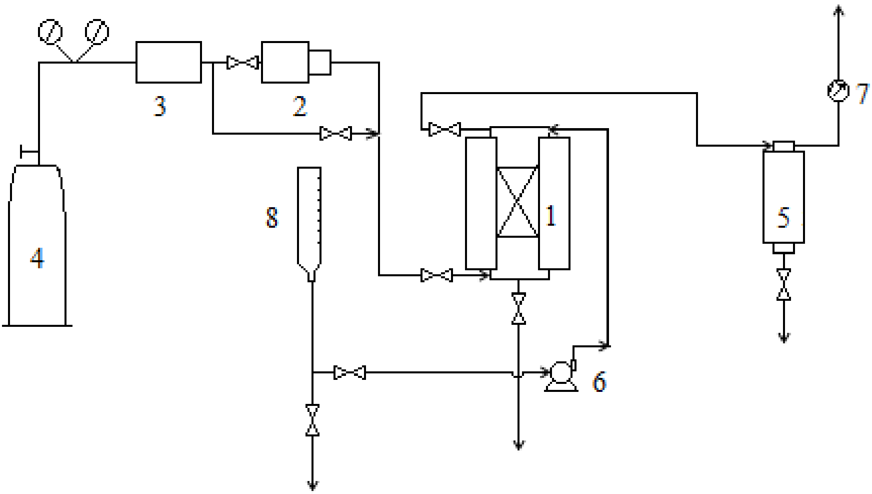


Figure 2. Periodic alkylation and oligomerization installation:
1 – Reactor filled with ZSM-5-ZrO_2 catalyst; 2 – Optos series piston pump for metering liquid delivery from Eldex, USA;
3 – filter; 4 – liquefied gas cylinder; 5 – separator; 6 – circulation pump; 7 – gas meter; 8 – measuring capacity of raw materials (oil fraction and olefins)

Study of halloysite-based modified catalytic systems in the alkylation process

The X-ray phase analysis (X-Ray) spectrum of halloysite showed that the intense maxima belong to the sample containing $Al_2Si_2(OH)_5$. As shown by the studies, the alkylation process of T 22 distillate oil fraction is more effective at low temperatures on a modified zeolite-containing halloysite+Al+CCl_4 catalyst.

The increase in viscosity index was achieved at low (50°C) temperatures, as the viscosity index of the oil increased from 32 to 84 (Table 1).

This temperature is also favorable for alkylation of the low-index fraction in modified halloysite.

Table 1.

Physicochemical properties of alkylates under different conditions and on the different catalysts

T, °C	P, MPa	Physicochemical properties				
		ρ_4^{20}, kq/m^3	n_D^{20}	Kinematic viscosity, mm^2/s 40°C	100°C	Viscosity index
Turbine oil fraction, T-22		898,4	1,4926	27,82	4,38	32
Halloysite (amount of olefins – 32,6 %)						
50	0,8	899,0	1,4932	28,56	4,66	60
100	0,8	898,8	1,4936	28,38	4,60	58
150	0,9	898,7	1,4942	28,20	4,56	55
Halloysite (amount of olefins – 38,4 %)						
50	0,8	899,1	1,4946	29,44	4,78	68
100	0,8	898,8	1,4952	29,32	4,69	61
150	0,9	898,6	1,4962	29,01	4,65	57
Halloysite+Al+CCl_4 (amount of olefins– 43,47%)						
30	0,50,6	890,0	1,4894	37,36	5,34	65
50	0,5-0,6	893,9	1,4904	40,70	5,95	84,4
80	0,5-0,6	895,3	1,4914	30,03	4,75	56

It was found that the viscosity of the alkylates was significantly higher than the viscosity of the original turbine oil fraction at all alkylation temperatures.

The alkylate obtained from the alkylation of turbine oil distillate fraction with catalytic cracking gases over halloysite+Al+CCl_4 catalysts (alkylation temperature 50°C) was studied by NMR spectrum analysis (Figure3).

As can be seen from Table 2, the alkylates of turbine oil distillate obtained on halloysite + Al + CCl_4 catalysts are characterized by an increase in aromatic hydrocarbons, since the share of protons in the aromatic structure increases.

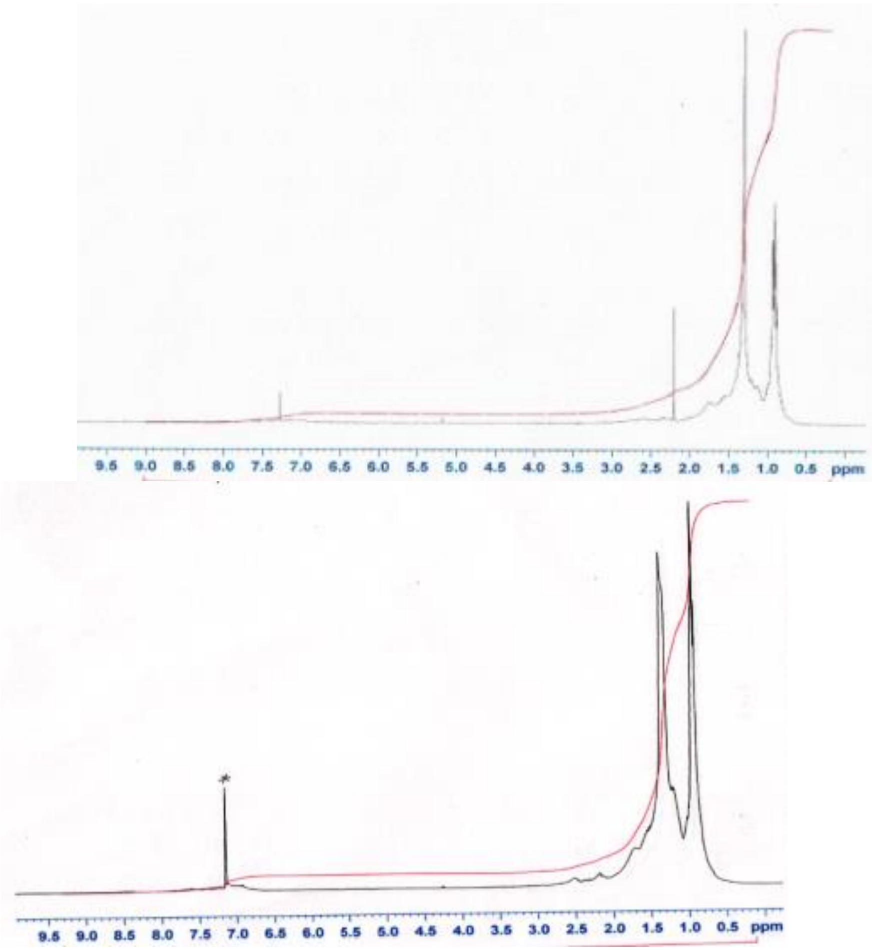


Figure 3. NMR spectrum of T-22 turbine oil distillate fraction and alkylate.

Table 2.

Structural parametres of turbine oil and alkylates

oil and alkylate	Distribution of hydrogen atoms across different structural groups, %					Degree of aromatic.	Isoparaffin index
	H_{ar}	H_{α}	H_{naf}	H_{paraf}	H_{γ}	f_{γ}	İ
Turbine oil	2,1	5,0	14,1	48,1	30,7	0,12	0,42
Alkylate (Halloysite +Al+CCl_4)	2,5	4,5	14,1	46,3	32,6	0,12	0,45

In addition, the proportion of protons (H_α) in the alkyl substituent groups CH-, CH_2-, CH_3- located in the α-position of the aromatic nucleus decreases. At the same time, the proportion of protons (H_γ) in the alkyl substituent methyl (CH_3) group located further away from the aromatic nucleus increases.

At the same time, the isoparaffin index of the initial fraction of T-22 distillate oil increases from 0.42 to 0.45. This indicates the formation of isoparaffin structures in the aromatic substituents. Chain elongation occurs when the propylene and butylene members in catalytic cracking gases combine to form a chain.

Study of the alkylation process of T-30 oil with catalytic cracking gases on Zr-modified ZSM-5 catalyst

Alkylation was carried out at a temperature of 50°C and a pressure of 0.5-0.6 MPa, created by catalytic cracking gases containing 56.09% olefins. ZSM-5-ZrO_2 catalysts were used, and annealing was carried out at temperatures of 200, 400 and 550°C (Table 3).

Table 3.

Physicochemical properties of alkylates under the given condition

Oil and alkylate	Physicochemical properties				
	ρ_4^{20}, kq/m^3	n_D^{20}	Kinematic viscosity, mm^2/s 40°C	Kinematic viscosity, mm^2/s 100°C	Viscosity index
Turbine oil, T-30	910,8,4	1,5004	49,87	6,1284	49,9
Alkylate (ZSM-5 + $ZrOCl_2$, 200°C)	896,2	1,4984	43,918	5,7816	56,5
Alkylate (ZSM-5 + $ZrOCl_2$, 400°C)	897,5	1,4994	45,565	6,2733	78,6
Alkylate (ZSM-5-ZrO_2, 550°C)	898,0	1,4954	37,986	7,0715	137
Alkylate (ZSM-5, 550°C)	897,8	1,4987	45,40	6,30	80,7

It is evident that the annealing temperature of the catalyst samples also affects their activity in the alkylation process. Therefore, further experiments were carried out after annealing the

ZSM-5-ZrO_2 catalyst at 550°C. The highest viscosity index was observed when using ZSM-5-ZrO_2 modified zeolite calcined at a temperature of 550°C. It should also be noted that Zr metal in the form of ZrO_2 significantly increases the activity of the ZSM-5 catalyst, increasing the viscosity index of the oil fraction from 80.7 to 137.

The changes in wave numbers upon replacement of the proton in the OH groups in the catalyst with Zr were determined using the IR spectroscopy method (Figure 4).

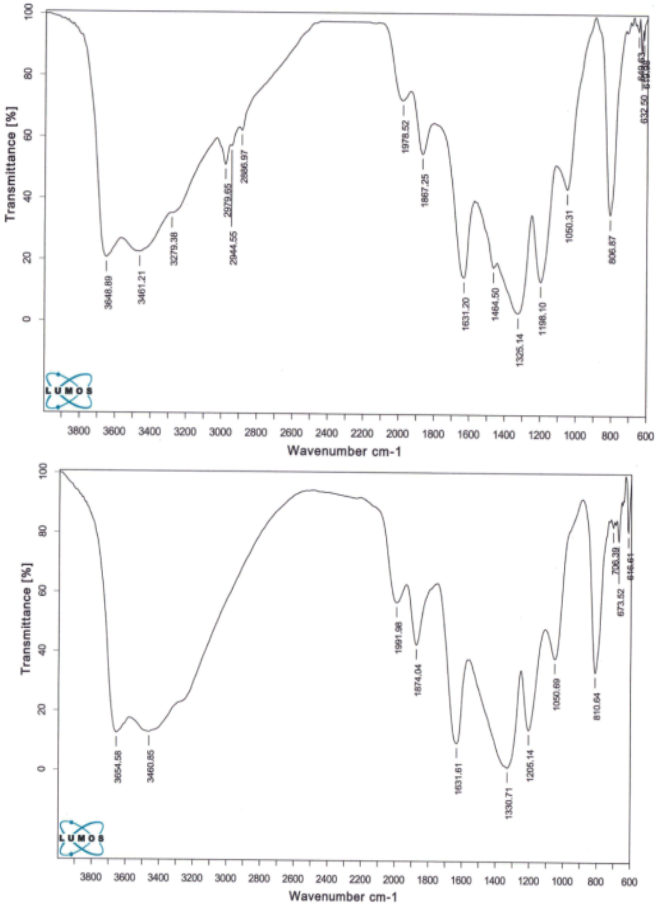


Figure 4. IR spectr of ZSM-5 and ZSM-5-ZrO_2 catalyst.

As can be seen from Figure 4, the spectra of the ZSM-5 catalyst differ from the spectra of the modified catalysts by a large number of absorption bands. Here, the previously observed absorption bands at 2979.65, 2944.55, 2886.97 cm 1 are absent (disappeared). This suggests that zirconium is bonded to oxygen instead of a proton. Moreover, given that zirconium has a valence of +4, it is bonded to four OH groups of a tetrahedron containing only silicon.

Thus, it can be said that by introducing Zr into the composition of the ZSM-5 catalyst, the ratio of Lewis and Brensted acid centers can be changed. In this case, an increase in Lewis acid centers and a decrease in Brensted acid centers occurs. Based on this, it can be assumed that both Brønsted and Lewis acid centers are involved in the alkylation process. As noted, the catalysts were prepared by calcination at various temperatures within the ranges of 200, 400, and 530–550°C. Based on the obtained research results, it can be concluded that the superior performance of the catalysts prepared at the highest temperature (550°C) is associated with the transformation of the zirconium-containing amorphous phase into a crystalline form.

X-ray phase analysis of the ZSM-5-ZrO_2 catalyst showed that the zeolite contains two phases, Zr-ZrO_2 and $ZrSi_{24}O_{50}$ (Figure 5). As can be seen, the ZrO_2 phase is formed as a result of the separation of the Zr^{4+} zirconium cation and the oxygen anion from the zeolite matrix. The resulting ZrO_2 phase is located on the outer surface of the zeolite.

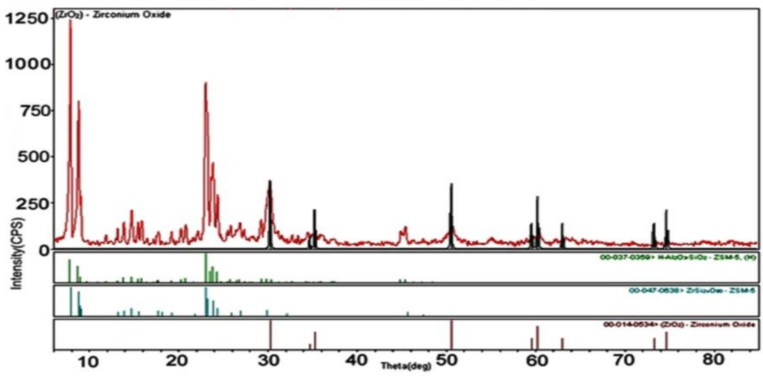


Figure 5. ZSM 5, $ZrSi_{24}O_{50}$ and ZrO_2 phases determined by X-ray diffraction in ZSM-5-ZrO_2 catalyst annealed at 530-550°C.

The ZSM-5-ZrO_2 catalyst was regenerated after the alkylation process and calcined in a muffle furnace at 530-550°C for 4-6 hours. The alkylation process was carried out with the given catalyst ZSM-5-$ZrO_{2(reg)}$ at 50°C with T-30 oil and catalytic cracking gases (56.35% olefin content). The resulting alkylate has a viscosity index of 117.8, a kinematic viscosity of 50.64 at 40°C and 6.04 mm^2/s at 100°C; a density of 906.4 kg/m^3 at 20°C, and a refractive index of 1.4992. The ZSM-5-$ZrO_{2(reg)}$ catalyst once again demonstrated its activity in the alkylation process. The viscosity-temperature characteristics of the low-index T-30 oil were improved during its alkylation complexation process to obtain base oils with a viscosity index ≥90 (Table 4). As seen from the table below, when 10% of alkylate with the highest viscosity index was added to the base T-30 oil with an initial viscosity index of 49.9, the viscosity index increased to 65, and when 50% was added, it reached 104.

Table 4.

Results of compounding with T-30 oil and amount 10 , 50% alkylates

İndicators	T-30	Alkylate	10%	50%
Kinematic viscosity, 40°C, mm^2/s	49,87	37,986	46,93	43,81
Kinematic viscosity, 100°C, mm^2/s	6,1284	7,0715	6,05	6,72
Viscosity index	49,9	137	65	104

Study of the alkylation process of T-30 oil with catalytic cracking gases over Fe-modified ZSM-5 catalyst

Alkylates obtained from the alkylation process carried out at 50°C over ZSM-5-$FeCl_2$ catalyst at 30, 50, and 80°C have the highest viscosity index (Table 5).

Table 5.

Physicochemical properties of alkylates is the given condition

T, °C	P, MPa	Physicochemical properties				
		ρ_4^{20}, kg/m^3	n_D^{20}	Kinematic viscosity, mm^2/s		Viscosity index
				40°C	100°C	
Turbine oil, T-30		910,8	1,5004	49,87	6,13	49,9
30	0,5-0,6	906,6	1,5002	49,02	6,48	74,5
50	0,7	907,9	1,4992	48,12	6,94	99,3
80	0,7	906,8	1,4987	47,38	6,5	82,5

Alkylate samples obtained at 50°C using ZSM-5-ZrO_2 and ZSM-5-$FeCl_2$ catalysts were compared with T-30 oil and studied by NMR spectroscopy (Figure 6).

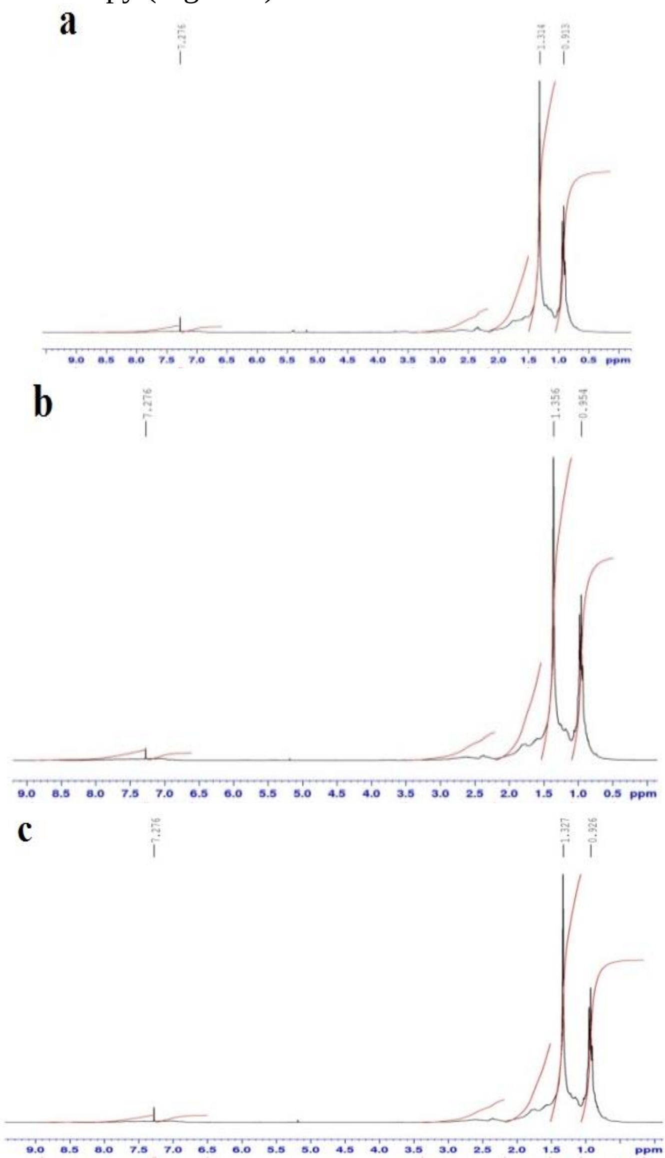


Figure 6. NMR spectrs: a) T-30; b) alkylate (ZSM-5-ZrO_2) c) alkylate (ZSM-5-$FeCl_2$).

The relative operations of protons of different structural groups cannot be combined into resonance absorption bands:

H_{ar} – unsubstituted protons in aromatic structures absorbed in the 6.6-8.1 ppm displacement region;

H_{γ} - protons of the CH_3- (2.1-2.8 ppm), CH_2- and CH- (2.8-4.5 ppm) groups in the technology of the aromatic nucleus;

H_{naft}–protons of the CH- and CH_2- groups in the naphthene cycles (1.5-2.0 ppm);

H_{paraf}–protons of the -CH_2 groups in paraffin structures and alkyl chains (1.1-1.5 ppm);

H_{α} –protons in the last -CH_3 groups (0.6-1.1 ppm).

The results of the calculation of the amount of protons, as well as the degree of aromaticity and isoparaffin index, are given in Table 6.

Table 6.

Structure parametres of Turbine oil and alkylates

T-30 and alkylate	Distribution of hydrogen atoms across different structural groups, %					Aromaticity degree	Isoparaffinic index
	H_{ar}	H_{α}	H_{naft}	H_{paraf}	H_{γ}	f_a	J
Turbin oil,T-30	2,44	4,51	14,52	47,91	30,62	7±0,5	0,43
Alkylate (ZSM-5-ZrO_2)	2,71	4,34	15,12	46,69	31,14	7 ±0,5	0,44
Alkylate (ZSM-5-$FeCl_2$)	2,76	4,36	14,97	47,12	30,79	7±0,5	0,44

Based on NMR spectra, it can be said that during the alkylation of oil fractions with catalytic cracking gases, the elongation of side chains and the formation of new ones occur due to the addition of propylene and butylene rings at the expense of propylene and butylenes. This affects the branching of hydrocarbons and, consequently, the viscosity of alkylates. Due to the decrease in the proportion of unsubstituted aromatic hydrocarbons, as well as the increase in the proportion of alkyl-substituted aromatic hydrocarbons with long side substituents, the viscosity-temperature properties of oil fractions improve, that is, the viscosity index and viscosity of alkylates increase.

ZSM-5 and Fe_2O_3 phases were identified by X-ray diffraction methods, and the corresponding peaks are shown in Figure 7. As can be seen from the studies, there are two phases, ZSM-5 and Fe_2O_3, in the Fe-containing catalyst. There is no Fe-containing phase in the zeolite structure.

As can be seen from this, Fe was not detected in the structure of the zeolite. In the case of $FeCl_2$ being used for modification, the existing iron compound is trivalent. This means that during the processing of the modified catalyst, its oxidation occurs, resulting in the transition of iron from the divalent to the trivalent state. However, iron oxide with an oxidation state of +2 was not detected.

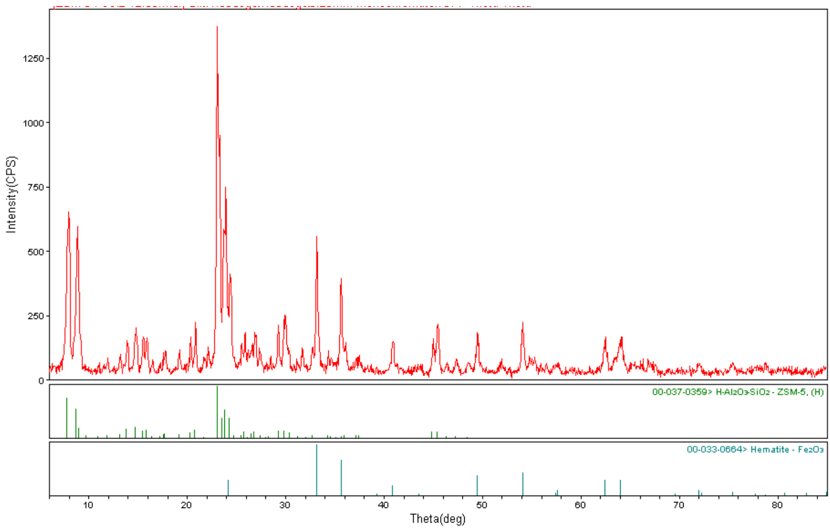


Figure 7. X-ray diffraction spectr of ZSM-5-$FeCl_2$ catalyst with ZSM-5 and Fe_2O_3 phases.

After a series of alkylation experiments, the catalyst ZSM-5-$FeCl_{2(reg)}$. was regenerated and calcined under the same conditions as the initial modified zeolite, after which the alkylation process was carried out again on it. As the study of the main physicochemical properties showed, the alkylates obtained over the spent and regenerated catalysts ZSM-5-$ZrO_{2(reg)}$ and ZSM-5-$FeCl_{2(reg)}$ also have good viscosity-temperature properties (Table 7).

Table 7.

Physicochemical properties of alkylates

Alkylate	Physicochemical properties				
	ρ_4^{20}, kg/m^3	n_D^{20}	Kinematic viscosity, mm^2/s		Viscosity index
			40 °C	100 °C	
ZSM-5-$ZrO_{2(reg)}$	906.0	1.4992	43.43	7.03	117.8
ZSM-5-$FeCl_{2(reg)}$	907.3	1.4994	48.54	6.86	94.7

The activity of the regenerated ZSM-5-$ZrO_{2(reg)}$ catalyst is higher than that of the original and regenerated Fe-containing ZSM-5-$FeCl_2$ and ZSM-5-$FeCl_{2(reg)}$ (Tables 5). This may be due to the presence of the $ZrSi_{24}O_{50}$ phase, where Zr is incorporated in the structure of the ZSM-5 zeolite.

According to the results of the TG method, it was found that the ZSM-5-$ZrO_{2(reg)}$ and ZSM-5-ZrO_2, ZSM-5-$FeCl_{2(reg)}$ and ZSM-5-$FeCl_2$ catalysts were thermally stable (Fig 8). The mass loss of the samples is presented as a percentage depending on the temperature. It can be seen from the histograms (Fig. 9) that the particles in the distilled water are homogeneous and are distributed mostly evenly for both the primary catalyst and the spent catalys ts.

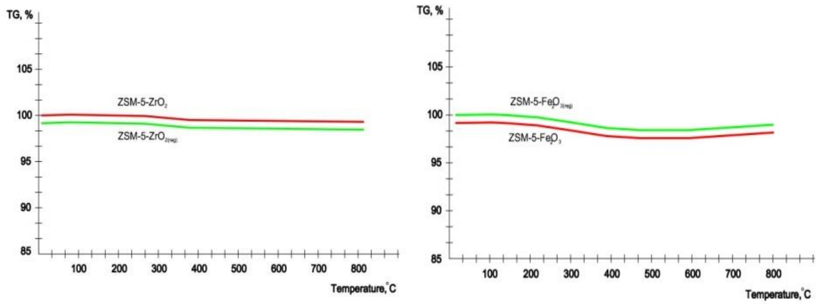


Figure 8. Thermal properties of ZSM-5-ZrO_2 və ZSM-5-$ZrO_{2(reg)}$; ZSM-5-$FeCl_2$ və ZSM-5-$FeCl_{2(reg)}$ catalysts.

It was found that the particle size of the modified catalyst after regeneration was smaller than that of the unmodified catalyst. It is possible that this metal-containing active phase changes the structure of the regenerated catalyst in the catalysts.

The evaluation of the composition of the catalysts and the structure of the catalyst surface was studied using scanning electron microscopy (SEM analysis). As can be seen, the catalyst surface consists of aggregates of different composition and different sizes.

It is clear from Figure 10 that the presence of elements constituting the catalyst at different points on the surface is different. Used and regenerated catalysts differ in the amount of Zr and Fe on their surfaces.

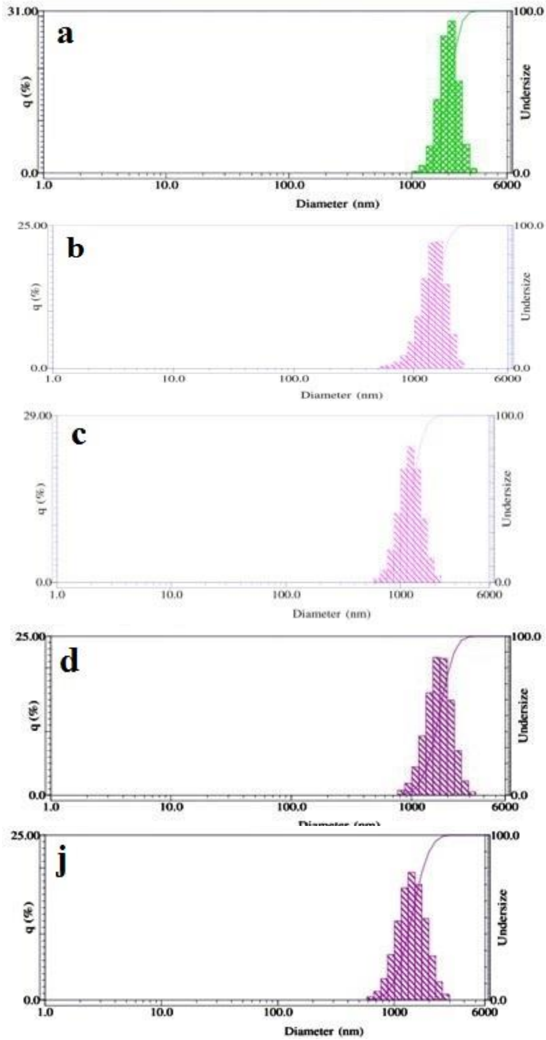
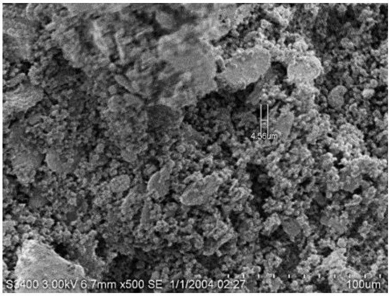
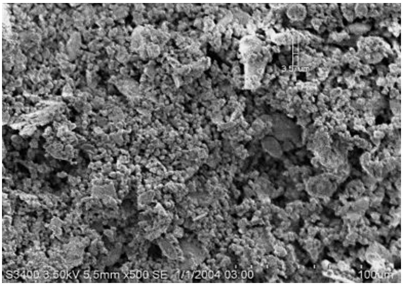


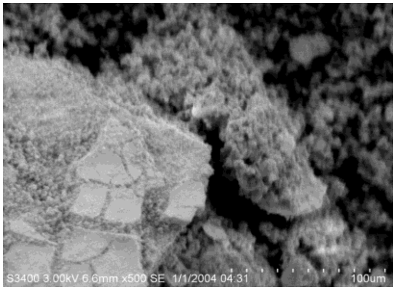
Figure 9. Partical size of) ZSM-5-ZrO_2; b) ZSM-5-ZrO_2; c)ZSM-5-$ZrO_{2(reg)}$; d) ZSM-5-$FeCl_2$; j) ZSM-5-$FeCl_{2(reg)}$ catalyst.



ZSM-5 × 500

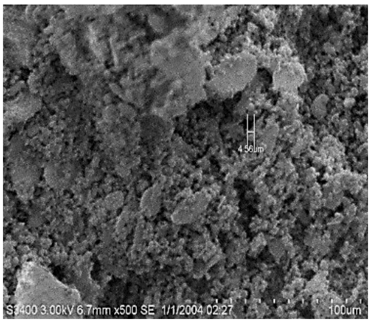


ZSM-5-ZrO_2×500



ZSM-5-$ZrO_{2(reg)}$×500

ZSM-5-$FeCl_2$×500



ZSM-5-$FeCl_{2(reg)}$×500

Figure 10. catalyst surface topography.

It is clear from Figure 11 that the presence of the elements that make up the catalyst varies at different points on the surface.

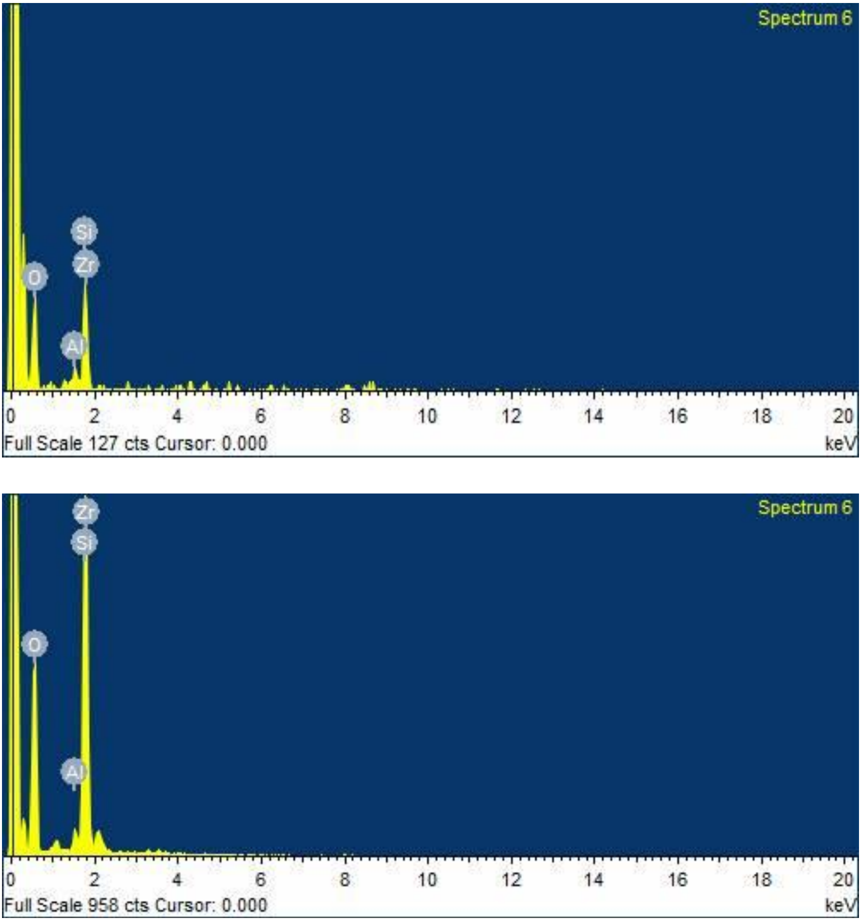


Figure 11. Atomic spectrum of ZSM 5-ZrO_2 catalyst corresponding to the Zr content of 2.10% and 6.35%.

Technology of the alkylation process of oil fractions

As a result of the study of the Zr-modified ZSM-5 zeolite, which was initially taken and regenerated after the process, it was found that it is more active in the alkylation process. 60-80 sm^3 of T-30 oil fraction and ZSM-5-ZrO_2 catalyst are loaded into reactor 1 with a volume of 250 ml and alkylation is carried out in a pilot plant (Figure 2).

The results of the studies showed that the alkylates obtained at a temperature of 50 ° C had the best viscosity index indicators. The physical and chemical properties of the alkylate are as follows: The kinematic viscosity of the alkylate was 42.3 mm^2/s at 40 ° C, 6.7 mm^2/s at 100 ° C, and the viscosity index was 111.7 units.
It has been studied that after regeneration of spent catalysts after the alkylation process and annealing at 530-550 °C, their phase composition is maintained and the catalysts are active in the alkylation process.

The main indicator of the quality of the obtained alkylate is its viscosity-temperature properties - viscosity index. The optimal temperature for the alkylation process carried out on the ZSM-5-ZrO_2 catalyst in the pilot plant and in the autoclave, respectively, is 50°C, which allows obtaining an alkylate with a viscosity index in the range of 121.8-137.0 units. The viscosity index of the alkylate obtained on the used and regenerated ZSM-5-$ZrO_{2(reg)}$ catalyst is 111.7-117.8 units.

Based on the results of the determination of the viscosity index of the ZSM-5 catalyst itself and the alkylates obtained on zeolite catalysts modified with Zr, Fe metals, it can be said that both Brensted and Lewis acid centers participate in the alkylation process. The conducted studies confirm this, that is, changes in the ratio of acid centers of zeolites occur.

The material balance of the alkylation process is given in Table 8.

Table 8.

Material balance of the alkylation process

Taken	**% (mass)**
T-30 turbine oil distillate	66,6
Catalytic cracking gases, including olefins	33,4 16,7
Total	**100,0**
Purchased	73,0
T-30 turbine oil alkylate, including olefins	25,0 8,3
Exhaust gases	2,0
Total	**100,0**

The conversion of olefin hydrocarbons is 80%, and the conversion of propylene hydrocarbons is 94-95%. As a result of the research, it was determined that the main technological parameters of the alkylation of the T-30 turbine oil fraction with catalytic cracking gases, which affect the efficiency of the process, are temperature and catalyst. These parameters were determined during the alkylation process in the autoclave and at the Institute's "Practical Test" area. Modified zirconium-containing catalyst ZSM-5-ZrO_2 was selected as an effective catalyst for the alkylation process.

Based on the research, a technological scheme for the alkylation process of low-index distillate oil fractions with catalytic cracking gases was developed (Figure 12).

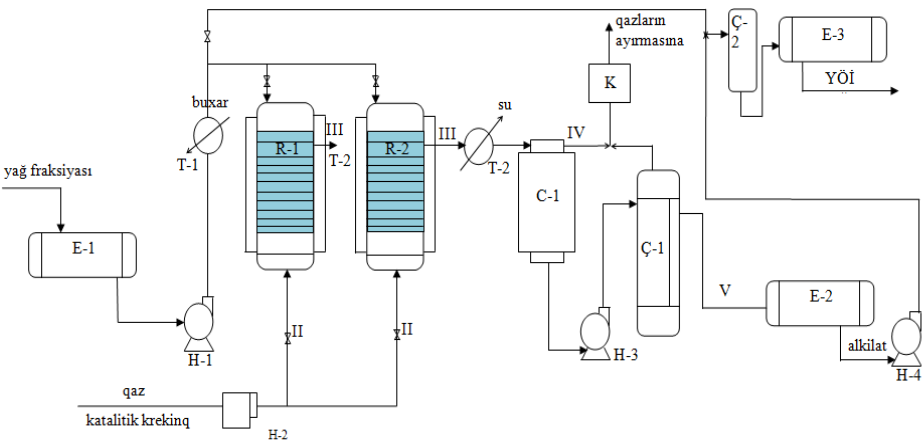


Figure 12. Technological scheme of the alkylation process of T-30 distillate oil fraction with catalytic cracking gases over ZSM-5-ZrO_2 catalyst (with compounding unit).

The technological scheme envisages 2 reactors. The diameter of the reactor is 2 m, the height is 8 m, and the volume is 25.1 m^3. The operating time of the reactor is 400 hours. The weight of the catalyst in the reactor is 8400 kg (loading volume 12 m^3, bulk density 700 kg/m^3). The oil fraction used is a distilled fraction corresponding to T-30 turbine oil with a viscosity index of 49.9.

The alkylate leaving the reactor is cooled in the T-2 heat exchanger with unreacted gases and transferred to the C-1 separator, where it is separated from the unreacted gases. The alkylate is fed to the precipitator by the H-3 pump, where it is separated from the remaining gases and collected in the E-2 tank.

The unreacted gases separated from the C-1 separator and the Ç-1 precipitator provide gas separation by means of a compressor. The exhaust gases are sent to the separator for separation, where the valuable raw material isobutane is separated, which is sent to alkylation to obtain high-octane gasoline components. The remaining gases can be sent to the EP-300 pyrolysis unit. The alkylate in the E-2 tank is fed to the Ç-2 mixer by the H-4 pump, where compounding takes place. The initial distilled part of the turbine oil is also fed there. With a 1:1 component ratio, the viscosity index of the compound is 100 units or higher. To obtain an oil with a certain viscosity index, the ratio of alkylate to the original fraction is calculated accordingly. High-index complex oil is collected in an E-3 container. By reducing the cost of high-index oil with the composition, it is possible to obtain oils at the required viscosity index level.

The productivity of the unit for the finished product is: 10,000 t/year or 1,389 kg/hour, and for raw materials - 1,267 kg/hour.

Thus, according to preliminary calculations, the production process of alkylate based on T-30 turbine oil requires costs of 1,056 thousand manats. The cost of the target product (alkylate) is formed at ~ 287.39 manat /t. Taking into account the current intra-company wholesale price of the product at 300.55 manat/t, according to preliminary calculations, it is possible to obtain a profit of ~ 58 manat from each ton of product.

The cost of 1 ton of high viscosity index oil obtained by compounding alkylate and T-30 oil distillate in a 1:1 ratio is formed at the level of 242.67 manat.

The obtained alkylates can be used for the production of high-quality base-based industrial, hydraulic and motor oils, where one of the main characteristics is “viscosity index”.

RESULTS

1. A technology and process schedule for the alkylation of the distillate fraction of low-index T-30 turbine oil (viscosity index 49.9) with catalytic cracking gases on Zr-modified ZSM-5 zeolite ($ZSM-5-ZrO_2$) has been developed, which allows the production of high-index oil (alkylate) with a viscosity index of – 137 [11,14,21,22].
2. Alkylation processes were studied in the halloysite, modified $Al+CCl_4$ system in order to improve the viscosity-temperature properties of low-index T-30 turbine oil on Zr and Fe modified ZSM-5 catalyst and T-22 distillate oil fraction (viscosity index 32). The advantages of obtaining high-index oils (viscosity index 137) on the $ZSM-5-ZrO_2$ catalyst are shown in comparison with those obtained with $ZSM-5-FeCl_2$, $Halloysite+Al+CCl_4$ and ZSM-5 catalysts (viscosity index 99.3; 84.4 and 80.7 units, respectively). The prepared catalysts were regenerated after the process and the possibility of using the obtained $ZSM-5-ZrO_{2(reg)}$ and $ZSM-5-FeCl_{2(reg)}$ catalysts was studied. As a result, alkylates with viscosity indices of 117.8 and 94.7 units, respectively, were obtained [2, 3, 5, 6, 7, 8, 9, 10, 11, 14, 15, 16, 18, 19, 20].
3. The optimal conditions for the alkylation process of distillate oil fractions were determined: the temperature (50°C), oil:gas volume ratio (1:1) and pressure (0.5-0.8 MPa, a certain temperature was created by the gases) at which the $Halloysite+Al+CCl_4$, $ZSM-5-ZrO_2$, $ZSM-5-FeCl_2$ catalysts exhibited maximum activity with catalytic cracking gases of T-22 and T-30 turbine oils [2,3,5,7,8,9,10, 11,13,14,15,16,19,22].
4. The NMR method was used to determine the structural parameters of the alkylation products of T-30 and T-22 oils with catalytic cracking gases on modified $ZSM-5-ZrO_2$ and $ZSM-5-FeCl_2$ catalysts in comparison with unmodified ZSM-5, $Halloysite+Al+CCl_4$ and Halloysite. Also, changes that occur in aromatic and naphthenic hydrocarbons of T-30 and T-22 oils due to the elongation of side chains and the formation of new ones as a result of the addition of propylene and butylene have been shown

[15,19,21,22].

5. The phase composition of ZSM-5-ZrO_2 and ZSM-5-$FeCl_2$ catalysts was studied using X-ray diffraction. It was found that the crystalline form of the ZSM-5-ZrO_2 catalyst is formed at an annealing temperature of 530-550°C and consists of three phases - $ZrSi_{24}O_{50}$, ZrO_2 and ZSM-5, which demonstrate maximum activity in the alkylation process, while the ZSM-5-$FeCl_2$ catalyst consists of two phases - Fe_2O_3 and ZSM-5 [8, 9, 11, 13, 15, 16, 19, 20, 21, 22].
6. Based on the IR-spectral analysis of ZSM-5 and ZSM-5-ZrO_2 catalysts, it was determined that the spectra of the studied zeolites contain absorption bands characteristic of ZSM-5 zeolite (1200–1205 and 2800–3800 cm-1), the presence of bands in the region characterizing the Si−O−H bond), and as a result of the introduction of Zr into the zeolite lattice, a decrease in these bands was determined in the $ZrSi_{24}O_{50}$ phase in the spectrum of ZSM-5-ZrO_2. Based on the IR-spectral analysis of ZSM-5 and ZSM-5-ZrO_2 catalysts, it was determined that the spectra of the studied zeolites contain absorption bands characteristic of ZSM-5 zeolite (1200–1205 and 2800–3800 cm^{-1}), the presence of bands in the region characterizing the Si−O−H bond), and as a result of the introduction of Zr into the zeolite lattice, a decrease in these bands was determined in the $ZrSi_{24}O_{50}$ phase in the spectrum of ZSM-5-ZrO_2 [19,22].
7. The particle sizes and surface morphology of the initial and regenerated ZSM-5-ZrO_2, ZSM-5-$FeCl_2$, ZSM-5-$ZrO_{2(reg)}$ and ZSM-5-$FeCl_{2(reg)}$ catalysts in the alkylation process were studied by dynamic light scattering (DLS) and scanning electron microscopy (SEM) methods. It has been shown that the particle size of the catalysts plays an important role in the activity of the alkylation process. It was determined by the TG thermogravimetric method that ZSM-5-ZrO_2, ZSM-5-$FeCl_2$ and ZSM-5-$ZrO_{2(reg)}$ catalysts and ZSM-5-$FeCl_{2(reg)}$ catalysts regenerated after the alkylation process are thermally stable in the temperature range of 50-800°C [15,16,18,19,20].
8. The feasibility study of the alkylation process of the low-index

fraction of T-30 turbine oil on an effective ZSM-5-ZrO_2 catalyst determined that the cost of the alkylate with a viscosity index of 137 is 287.39 manat/t. Compounding the distillation fraction of the alkylate in a 1:1 ratio allows obtaining oil with a viscosity index of 104 units, the cost of which is 242.67 manat/t.

The main content of the thesis has been published in the scientific works:

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