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Technological Features of Producing High-Index Oils in the Alkylation Process

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Abstract

This article presents the results of studies on key technological parameters—namely temperature and the use of modified ZSM-5 catalysts with Zr and Fe—in the alkylation process aimed at producing high-viscosity-index oils. The development of novel modified catalyst compositions exhibiting high activity in alkylation, to enhance oil viscosity indices to meet global standards, holds significant scientific and practical importance. Modified catalysts based on ZSM-5 zeolite incorporating ZrO₂ and Fe₂O₃ (ZSM-5-ZrO₂ and ZSM-5-Fe₂O₃), along with their regenerated forms after use in alkylation, were evaluated in both autoclave and pilot-scale alkylation processes. Catalyst characterization was performed using X-ray phase analysis, thermogravimetric analysis (TG), and dynamic light scattering (DLS). Alkylation of the low-viscosity-index fraction of turbine oil T-30 (initial viscosity index of 49.9) was conducted at 50 °C using catalytic cracking gases containing 56.35% olefins. The ZSM-5-ZrO₂ catalyst produced alkylates with viscosity indices of 137.0 and 121.8 in the autoclave and pilot plant, respectively. The regenerated ZSM-5-ZrO₂ catalyst yielded viscosity indices of 117.8 (autoclave) and 111.7 (pilot plant). Alkylates obtained with ZSM-5-Fe₂O₃ and its regenerated counterpart showed viscosity indices of 99.3 and 94.7, respectively. The feasibility of reusing spent and regenerated catalysts in the alkylation process was confirmed. Among the catalysts tested, ZSM-5-ZrO₂ demonstrated the highest activity and is recommended for alkylating low-viscosity-index oil fractions with catalytic cracking gases at 50 °C.

1. Introduction

Developing environmentally friendly technological processes to produce high-quality products from locally available raw materials is crucial for enhancing the economic potential of the republic. The adoption of technologies that ensure safe process management and minimize environmental impact is increasingly significant and relevant. Recently, Azerbaijan successfully hosted the 29th session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP29), underscoring the country's commitment to regional security and environmental protection in the South Caucasus. The decisions made at COP29 are

of exceptional importance for the future of humanity and further highlighted Azerbaijan's leadership and international standing. Given this, developing waste-free, eco-friendly processes is vital for environmental preservation.

Azerbaijani base oils typically exhibit unsatisfactory viscosity-temperature properties, characterized by a low viscosity index. Producing low-freezing oils with a high viscosity index from Azerbaijani crude requires restructuring the hydrocarbon composition. The primary approach to improving these properties involves processes that enhance the formation of hydrocarbons with a higher viscosity index. Saturating oil fractions with isoparaffin hydrocarbons improves rheological properties, reduces evaporation, increases thermal-oxidative stability, and enhances several performance characteristics.

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Historically, lubricating oils in Azerbaijan were produced from low-paraffin, low-gum oils using traditional technologies that generated large quantities of acidic waste. These processes, which relied on acid and acid-base purification methods, posed significant environmental challenges. Therefore, it is essential to replace these outdated technologies with eco-friendly methods that produce oils with superior viscosity-temperature properties while protecting the environment.

The viscosity-temperature properties of oils can be improved either by using thickening additives or through hydrocracking. However, thickening additives can increase kinematic viscosity, which is sometimes undesirable. Hydrocracking, on the other hand, requires high temperatures and pressures, significantly altering the physical and chemical properties of the original oil fractions.

An alternative approach is the alkylation process, which operates under milder conditions – lower temperatures and pressures compared to hydrocracking. This reduces production costs and increases the yield of high-quality oils, making research in this area highly relevant and promising. During alkylation, mono- and polyaromatic hydrocarbons can be converted into aromatic hydrocarbons with long side chains, and normal paraffins into isoparaffins, producing oils that meet modern performance standards. Saturation of oil fractions with isoparaffin and long-chain aromatic hydrocarbons, as well as reducing polycyclic aromatic hydrocarbons, improves viscosity-temperature properties.

Alkylation has become a key area of innovation in oil refining, with numerous new technologies emerging in recent years [1]. Global research focuses on developing environmentally friendly, low-waste technologies using efficient heterogeneous catalysts [2, 3]. Alkylation of isobutene [4-6], aromatic compounds [7-9], and gasoline fractions [10, 11] with olefins on various zeolite catalysts is widely practiced to produce high-octane gasoline fractions. In these reactions, isobutane and butylenes combine to form iso-octanes with high octane numbers.

In world literature, there are practically no sources on the alkylation of oil fractions with olefins for the purpose of increasing the viscosity index of low-index oils. This process was used by scientists in our republic specifically to improve the viscosity-temperature properties of oils from Azerbaijani oils.

Research on the alkylation of oil fractions with olefins has primarily used homogeneous AlCl_3 -based systems. Studies indicate that when oil fraction hydrocarbons react with ethylene in the presence of

AlCl_3 , the resulting alkylates yield oils with a viscosity index of 95–101 and a 65% product yield. However, this process also produces acid tar at a yield of 33.3%, which is environmentally and economically undesirable.

For alkylation processes, zeolite-containing catalysts are employed due to their high activity, selectivity, stability, defined microporous structure, and regenerability. Typically, zeolites modified with noble or transition metals are used.

The Institute of Petrochemical Processes previously studied industrial samples of zeolite-containing catalysts – Seokar 2, Seokar 600, and Omnicat 210 P during the alkylation of various distillate oil fractions [12]. The alkylation was performed using liquefied gases derived from catalytic cracking. Distillates with kinematic viscosities of 9.8, 27.8, and 76.4 mm^2/s at 40 °C, corresponding to viscosity indices of 79, 32, and 55, were used as feedstocks.

Using the Seokar-600 catalyst at 50 °C, 0.6 MPa pressure, and an oil-to-gas ratio of 1:1, the viscosity index of the turbine oil distillate fraction increased from 32 to 75. In comparison, other zeolites yielded alkylates with viscosity indices ranging between 35 and 45. When alkylating a distillate fraction with a kinematic viscosity of 76.4 mm^2/s at 40 °C, the viscosity index increased from 55 to 70 with Seokar-600, whereas other zeolites only achieved up to 60 [12]. Research indicates that alkylation efficiency decreases as the viscosity of oil fractions increases. While zeolite-containing catalysts can enhance the viscosity index of low-index oil fractions, achieving a viscosity index of 90 or higher remains unattainable with these catalysts. It appears that the compositions of Seokar and Omnicat catalysts, which contain Pt and oxides of metals like Ni, Co, Ti, and Zn, are not optimal for alkylation with catalytic cracking gases. Therefore, more effective zeolite-containing catalysts with alternative metal modifiers are required for this purpose. To achieve various reactions with high selectivity for target products, modified zeolite ZSM-5 compositions are employed. A key advantage of ZSM-5 is its ability to regenerate and retain its catalytic properties.

Zeolite-containing catalysts based on ZSM-5, known for their high selectivity, generally exhibit activity at elevated temperatures. For example, during the conversion of propane into liquid hydrocarbons within the temperature range of 350–550 °C on a $\text{PtZn}/\text{SiO}_2 + \text{ZSM-5}$ catalyst, multiple sequential and parallel reactions occur, including dehydrogenation, oligomerization, cracking, and aromatization [13, 14]. The conversion of olefins to aromatic

compounds using bifunctional Ga- or Zn-ZSM-5 catalysts is significantly higher compared to unmodified ZSM-5 [13]. Modifying ZSM-5 with metals such as Pt, Zn, and Ga enhances its activity for these reactions within the 200–550 °C range. In addition to aromatic hydrocarbons, products such as methane, ethane, ethylene, propylene, butenes, and C_5 + olefins are obtained. Studies [13-15] suggest that aromatic hydrocarbons form predominantly on modified Pt, Zn, and Ga ZSM-5 catalysts, while oligomerization reactions occur on ZSM-5 [16].

For various reactions, many researchers use ZSM-5 zeolite modified with metals (Fe, Zr, Ga, Ti, Co, Zn, Ni, and others) [17-20]. The incorporation of metals, including transition metals such as Fe, into the ZSM-5 zeolite promotes the oligomerization of ethylene into C_5 +hydrocarbons, facilitates the dehydrogenation of paraffins into olefins, and the conversion of naphthenes into aromatic hydrocarbons [17, 18].

As a result of ZSM-5 zeolite modification with Zr [19, 20], during ethanol conversion reactions, an increase in the acidity of Lewis acid sites (L-sites) was observed, along with enhanced thermal stability up to 923 K and an increased yield of C_3 + hydrocarbons compared to the unmodified zeolite. Aromatic hydrocarbons are formed through the dehydrocyclization of intermediate olefins. The catalytic stability of ZSM-5 was improved through zirconium modification. Surface acidity and the presence of metal ions play a crucial role in propylene production. Zirconium oxide is widely used as a base for industrial isomerization catalysts.

In the alkylation of oil fractions with catalytic cracking gases, various reactions – such as oligomerization, isomerization, alkylation, hydrogen redistribution, and cracking-can occur. The catalyst plays a crucial role in ensuring that the desired reactions proceed effectively. To obtain alkylates with higher viscosity indices, an efficient zeolite-containing catalyst is essential. Additionally, temperature is another critical parameter influencing the success of the alkylation process. The aim of this study is to determine the key technological parameters-temperature and catalyst type-for the alkylation process of a low-viscosity index oil fraction in order to obtain alkylates with a high viscosity index.

2. Materials and methods of research

Zeolite ZSM-5 with a medium pore size (0.4–0.6 nm) and a silicate modulus of 60 was modified with zirconium (Zr) and iron (Fe) to enhance its activity in the alkylation process. The modification was performed by impregnating the zeolite with solutions of

zirconyl chloride ($ZrOCl_2 \cdot 2H_2O$) and ferrous chloride ($FeCl_2$) at a temperature of 50–60 °C for 18 hours. Water was then evaporated at 100–105 °C, followed by drying at 110 °C for 4 hours. The modified zeolites, Zr/ZSM-5 and Fe/ZSM-5, were calcined in a muffle furnace at 200 °C, 400 °C, and 550 °C for 4 hours. Key parameters for ensuring the stable operation of these catalysts include thermal stability, particle size, composition.

X-ray phase analysis was carried out at room temperature on a TD-3500 diffractometer (made in China) at an angle of 5-90° using a $CuK\alpha$ X-ray source ($\alpha = 1.54184\text{\AA}$) and a Ni filter.

The thermal stability (TG) of the modified Zr/ZSM-5 and Fe/ZSM-5 catalysts, both before and after the alkylation process, was evaluated using a synchronous thermal analyzer (STA-449 Jupiter F3, NETZSCH, Germany). The analysis was conducted in a nitrogen (N_2) atmosphere in a dynamic temperature-programmed mode ranging from 23 °C to 800 °C, with a heating rate of 10 °C/min and a nitrogen flow rate of 20 ml/min. The sample weight used for the study was 9.4 mg.

Particle size and distribution were analyzed using the DLS method with an LB 550 analyzer (Horiba, Japan) [21]. Measurements were conducted at room temperature with a radiation source power of 5 mW, a wavelength of 650 nm, and corresponding software. The DLS method determines particle size by analyzing fluctuations in the intensity of scattered light from particles in a solvent. The particle size is calculated using the diffusion coefficient and the liquid's viscosity based on the Stokes-Einstein equation.

Analysis of the initial and exhaust gases was carried out on a Perkin Elmer AutoSystem XL gas chromatograph using helium carrier gas, a flame ionization detector, and a 10×2.5 m capillary column, injector temperature -250 °C, detector temperature – 280 °C. The carrier gas flow rate is helium 1 ml per minute.

The fraction corresponding to turbine oil T-30, with a viscosity index of 49.9, was used as the oil fraction. Catalytic cracking gases, with olefin contents of 56.35%, served as the alkylating agent.

Alkylation of the T-30 oil distillate fraction with catalytic cracking gases was carried out on modified Zr/ZSM-5 and Fe/ZSM-5 catalysts, in comparison with unmodified ZSM-5. The process was conducted in an autoclave (volume 1 l) with a stirrer, over a temperature range of 30–100 °C and a pressure range of 0.5–0.9 MPa (generated by the gases), using an oil-to-gas ratio of 1:1 and a catalyst quantity of 1.5 g. The reaction time was 1 hour.

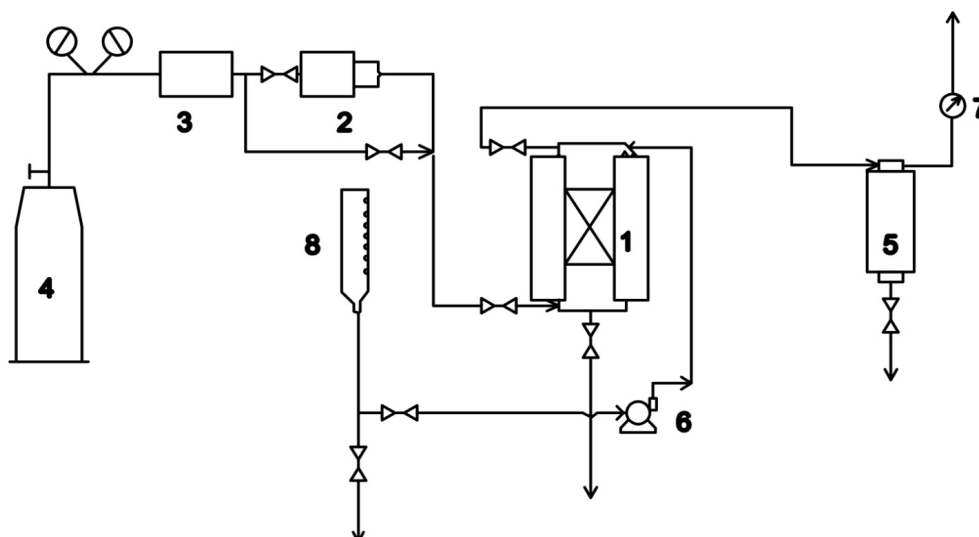


Fig. 1. Scheme of the pilot installation for the alkylation process: 1 – reactor; 2 – piston dosing liquid pump of the Optos series from the American company Eldex; 3 – filter; 4 – gas cylinder; 5 – separator; 6 – circulation pump; 7 – gas meter; 8 – measuring container of raw materials (oil fraction).

Kinematic viscosity and viscosity index values are determined according to ASTM D445. The alkylation reaction was tested on a pilot installation with a 250 ml reactor, as illustrated in Fig. 1.

The catalyst was activated directly on the unit at a temperature of 550 °C for 4 h under a nitrogen flow. The oil fraction was loaded into reactor 1 from measuring tank 8 using pump 6. Catalytic cracking gases from cylinder 4 were introduced through filter 3 by pump 2 to the bottom of reactor 1. Unreacted gases from the separator were removed from the unit via a gas meter into a gas collector. After the reaction was complete, the alkylate was discharged from separator 5. Circulation of the fed components and reaction products was also performed using pump 6.

The gases were supplied by a piston liquid pump, allowing the gas flow rate to be regulated based on their ratio to the oil fraction. Alkylation was carried out in the temperature range of 30 to 80 °C, with a gas supply pressure of 0.25–0.70 MPa, and a volume ratio of oil fraction to liquefied gases of 1:1.

3. Results and discussion

Table 1 presents the main physicochemical properties of alkylates obtained using Zr/ZSM-5 and Fe/ZSM-5 catalysts in the temperature range of 30–100 °C during the alkylation of T-30 oil with catalytic cracking gases.

Table 1. Main properties alkylates

T, °C	P, MPa	Physicochemical properties alkylates				
		ρ_4^{20} , kg/m ³	n_D^{20}	Kinematic viscosity, mm ² /s, at		
				40 °C	100 °C	Viscosity index
Zr/ZSM-5						
30	0.5-0.6	890.8	1.4992	45.80	6.70	76.1
50	0.7	898.0	1.4954	37.99	7.07	137.0
100	0.8	897.5	1.4968	43.21	6.91	117.6
Fe/ZSM-5						
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

Table 2. Main properties of T-30 oil fraction and alkylates

Name	Physicochemical properties of T-30 and alkylates				
	ρ_4^{20} , kg/m ³	n_D^{20}	Kinematic viscosity, mm ² /s, at		Viscosity index
			40 °C	100 °C	
T-30 oil fraction	910.8	1.5004	49.87	6.13	49.9
Alkylate Zr/ZSM-5	898.0	1.4954	37.99	7.07	137.0
Alkylate Zr/ZSM-5 _(reg)	906.0	1.4992	43.43	7.03	117.8
Alkylate Fe/ZSM-5	906.4	1.4992	48.12	6.94	99.3
Alkylate Fe/ZSM-5 _(reg)	907.3	1.4994	48.54	6.86	94.7
Alkylate ZSM-5	897.8	1.4987	45.40	6.30	80.7

The optimum alkylation temperature, where the maximum viscosity index values for alkylates were observed, was found to be 50 °C. The data on the main physicochemical properties of alkylates obtained at this temperature, compared to T-30 oil, on modified catalysts Zr/ZSM-5 and Fe/ZSM-5, and on unmodified ZSM-5, are provided in Table 2. Alkylation was conducted in an autoclave.

Additionally, the catalysts spent in the alkylation process were re-tested to assess their performance for developing alkylation technology for oil fractions with catalytic cracking gases on modified zeolites. After the alkylation process, the catalysts Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg) were regenerated and calcined at temperatures of 530–550 °C for 4 hours. After each experiment in the autoclave, the alkylates were filtered, and the Zr/ZSM-5 and Fe/ZSM-5 catalysts were collected separately. The collected catalysts were then regenerated in a muffle furnace for 10–12 h with a gradual temperature increase from room temperature to 500 °C, followed by calcination.

The results showed that the alkylates obtained from the spent and regenerated Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg) catalysts also exhibited good viscosity-temperature properties, with viscosity indices slightly lower than those of alkylates from freshly prepared modified catalysts. However, the viscosity indices of alkylates from both initial and spent modified catalysts were significantly higher than those from the unmodified ZSM-5 catalyst. This suggests that the catalysts are active through different active centers. The comparison of acidic and catalytic properties of modified zeolite catalysts is also confirmed by the authors [22–24], who determined that the activity of the catalytic system is influenced by the acidic properties of the zeolite combined with the distribution of modifying elements and their interaction with the acidic centers of the zeolite.

Based on the studies of the initial and spent catalysts and their activity in the alkylation process, preference was given to the ZSM-5 zeolite modified with Zr. Alkylation of the T-30 oil fraction was carried out on a pilot installation with 60–80 cm³ of the modified Zr/ZSM-5 zeolite loaded into reactor 1, which has a volume of 250 ml (Fig. 1).

As the results of the studies showed, the best viscosity index values were obtained for alkylates at a temperature of 50 °C. The alkylate had the following physical and chemical properties: kinematic viscosity (mm²/s) at 40 °C 38.81, at 100 °C 6.6, viscosity index 121.8 units, density at 20 °C 908.6 kg/m³, refractive index 1.4992. At the pilot plant, the catalyst operated in the alkylation process for a total of about 20 hours. After the alkylation process, the catalyst was regenerated directly in the reactor and alkylation was carried out again. Regeneration was carried out for 24 h, calcination for 4 h at a temperature of 550 °C.

After the alkylation process, the catalyst was regenerated directly in the reactor, and alkylation was carried out again. The regenerated alkylate had a kinematic viscosity of 42.3 mm²/s at 40 °C, 6.7 mm²/s at 100 °C, and a viscosity index of 111.7 units. Table 3 shows the compositions of the initial catalytic cracking gases before and after alkylation (on the original catalyst Zr/ZSM-5 and on the regenerated catalyst Zr/ZSM-5_(reg)).

As shown by the composition of the gas before and after alkylation, propylene, butene-1, and butene-2 participate in the process, with propylene being the most reactive olefin hydrocarbon. The conversion of olefin hydrocarbons from catalytic cracking gases is 78–80%. Following the alkylation process, significant amounts of isobutane are produced, which is recommended to be collected in gas tanks for subsequent use as a raw material in further alkylation with olefins to produce high-octane

Table 3. Composition of catalytic cracking gases before and after alkylation

Hydrocarbons	Gas composition, % vol.		
	Original	After alkylation on catalysts	
		Zr/ZSM-5	Zr/ZSM-5 _(reg)
Ethane-ethylene	0.06	0.04	0.03
Propylene	28.63	1.64	1.09
Propane	8.12	12.02	8.89
iso-butane	26.30	58.43	62.14
Butene-1	14.07	3.43	5.15
n-butane	7.80	13.98	13.64
trans-butene-2	7.70	3.71	2.86
sis-butene-2	5.45	2.41	3.32
3-methylbutene-1	0.24	0.01	0.01
iso-pentane	1.37	4.30	2.86
2-methylbutene-1	0.14	0.02	0.01
Pentene-1	0.06	0.01	-
n-pentane	0.01	-	-
trans-pentene-2	0.01	-	-
sis-pentene-2	0.01	-	-
2-methylbutene-2	0.01	-	-
Σ olefinic hydrocarbons	56.35	11.32	12.68

gasoline components. Moreover, a greater amount of isobutane is formed when using the regenerated Zr/ZSM-5_(reg) catalyst. The use of spent gases as feedstock for other processes demonstrates the advantage of the developed technology, which operates without waste.

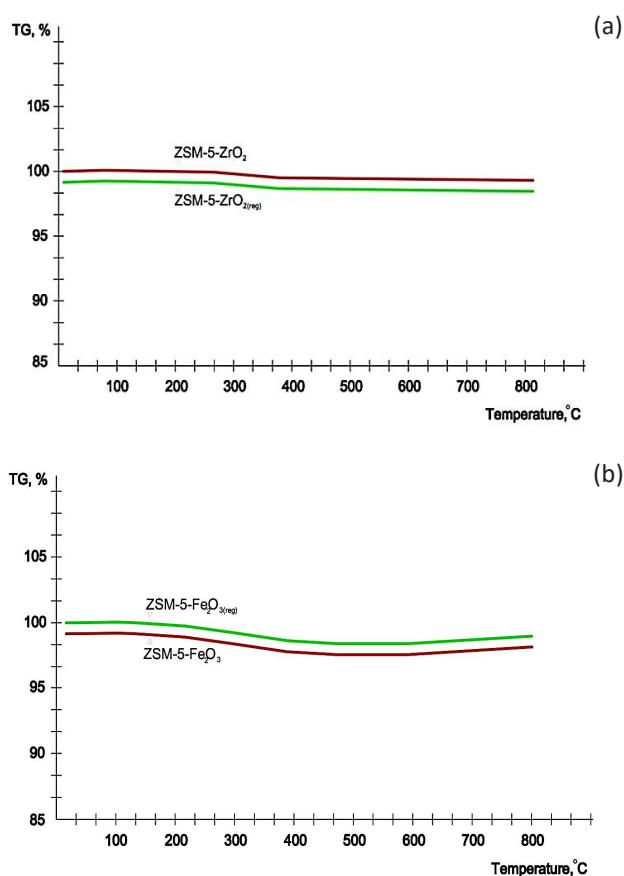
The study of the composition and properties of catalysts before and after the alkylation process is crucial for the development of the technology and the selection of an active catalyst. Studies on the phase composition, using X-ray diffraction (XRD), established that the crystalline phase of the modified zeolite Zr/ZSM-5 forms at a calcination temperature of 530–550 °C and consists of three phases: ZrSi₂₄O₅₀, ZrO₂, and ZSM-5 [25]. The Fe/ZSM-5 catalyst form calcined at a temperature of 530–550 °C consists of two phases – Fe₂O₃ and ZSM-5. No introduction of Fe into the structure of zeolite ZSM-5 is observed. Therefore, the activity of the Fe-containing catalyst in the alkylation process is lower than that of the Zr-containing catalyst (Table 1). Studies by the authors [22–24] have also established that modified zeolite-containing catalysts possess multifunctional properties. The acidic centers may include metals in various ox-

idation states, which are anchored both inside the zeolite cavities and on their external surfaces.

Apparently, the presence of Zr in the crystal structure of zeolite ZSM-5 in the form of the ZrSi₂₄O₅₀ phase contributes to an increase in the activity of the modified catalyst Zr/ZSM-5.

The catalysts Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg), after being used in the alkylation process, were studied by thermogravimetry (TG) and dynamic light scattering (DLS). After regeneration and calcination at 530–550 °C, the phase composition of the catalysts remains unchanged, and they retain their activity in the alkylation process.

Figure 2 presents the thermograms of spent Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg) catalysts, compared with the initial Zr/ZSM-5 and Fe/ZSM-5 catalysts. Regeneration of the spent samples was carried out in a muffle furnace in an air flow, then all samples were calcined at a temperature of 530–550 °C for 4 hours. Based on the thermograms, it can be concluded that the regenerated catalysts, calcined in a flow of purified air at temperatures between 530–550 °C for 4 h, do not differ from the catalysts in their original state. They are fully restored after regeneration.

**Fig. 2.** Thermogram of the original and regenerated modified catalysts: (a) – Zr/ZSM-5 and Zr/ZSM-5_(reg); (b) – Fe/ZSM-5 and Fe/ZSM-5_(reg).

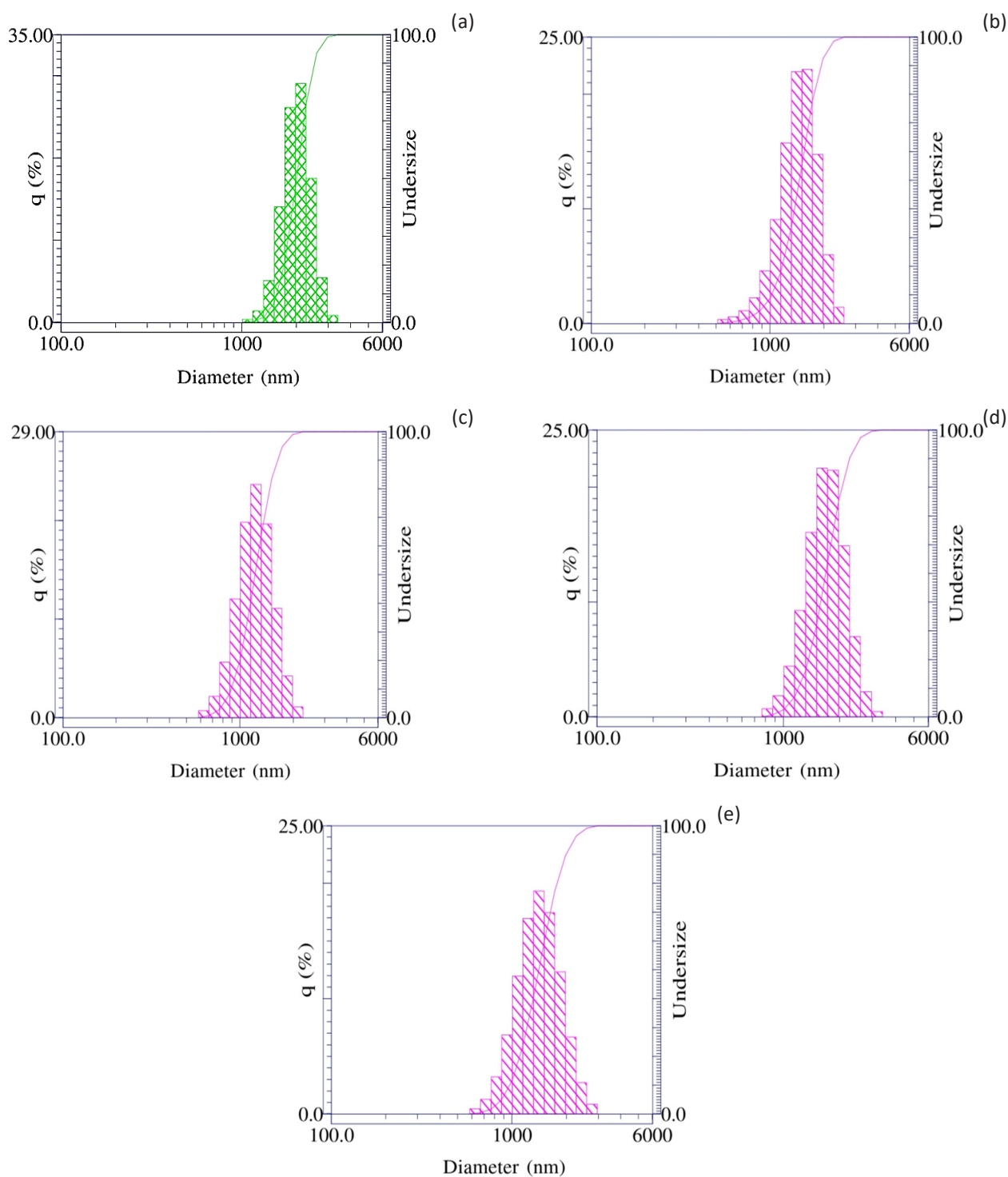


Fig. 3. Particle sizes and distribution parameters for catalysts: (a) – ZSM-5; (b) – Zr/ZSM-5; (c) – Zr/ZSM-5_(reg); (d) – Fe/ZSM-5; (e) – Fe/ZSM-5_(reg).

The results indicate that both the initial and spent catalysts maintain stability within the studied temperature range.

It is important to study the change in catalyst particle size before and after the alkylation process. The DLS analysis of particle sizes and their distribution is shown in Fig. 3. The diffusion coefficients were calculated using the Stokes-Einstein formula according to the presented data and are given in Table 4.

From the histograms, the particles in distilled water are homogeneous and predominantly evenly distributed for both the initial and spent catalysts in the alkylation process [21]. As seen from the data in Table 4, the lower limit of the particle sizes of the modified initial and regenerated spent catalysts is less than the lower limit of the particle size of the unmodified ZSM-5 catalyst. In addition, the average particle sizes of the regenerated modified catalysts

Table 4. Catalyst particle sizes and diffusion coefficients

Catalyst	Dynamic Light Scattering (DLS) Parameters					
	Diameter of particles in liquid phase, mkm					Diffusion coefficient, E ⁻¹³ m ² /sec
	Lower limit	Upper limit	Mean	Mode	Medium	
Zr/ZSM-5	0.62	3.20	1.43	1.58	1.46	1.2479
Zr/ZSM-5 _(reg)	0.60	0.09	1.24	1.23	1.22	1.4931
Fe/ZSM-5	0.88	3.41	1.67	1.64	1.69	1.0775
Fe/ZSM-5 _(reg)	0.67	2.27	1.40	1.41	1.41	1.2918
ZSM-5	1.15	3.41	1.99	2.08	2.01	1.2866

Where: mean – the average numerical value of the sizes of all observed particles; mode – the largest value of the observed particle size; medium – the value is equal to the arithmetic mean size of 50% of the particles.

Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg) are smaller than the particle sizes of the original catalysts Zr/ZSM-5 and Fe/ZSM-5. According to the authors [20], an increase in the crystal size of ZSM-5 leads to a slight decrease in the surface area and acidity of the external surface of the supports. However, they exhibit higher activity in the conversion of hydrocarbon FCC fractions in aromatization reactions.

The diffusion coefficients of spent and regenerated catalysts are higher than those of the original samples. An increase in the number of smaller particles characterizes these samples.

The results show that the modified catalysts have smaller particle sizes compared to the unmodified ZSM-5 zeolite. This suggests that particle size influences the alkylation reaction; smaller particles appear to enhance the efficiency of the process. The particle size of the spent modified catalysts is even smaller than that of the unmodified catalyst, indicating that the structure and redistribution of active components, such as the metal phases (Zr and Fe), may change in the spent and regenerated catalysts. Therefore, during alkylation, the modified initial catalysts exhibit the greatest activity compared to regenerated and unmodified ZSM-5. Therefore, the efficiency of the alkylation process is influenced by both the phase composition and the crystal size of the catalysts.

When studying the phase composition of the spent catalysts Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg) after the alkylation process, it was determined that the same phases were retained as in the original catalysts.

4. Conclusion

As a result of the research, it was determined that the main technological parameters influencing

the efficiency of the alkylation process of turbine oil T-30 with catalytic cracking gases are temperature and catalyst type. These parameters were evaluated both in the alkylation process conducted in an autoclave and on an experimental pilot installation. A modified zirconium-containing catalyst, Zr/ZSM-5, was selected as the most effective catalyst for the alkylation process.

The primary indicator of the quality of the obtained alkylate is its viscosity-temperature properties, specifically the viscosity index. The optimal alkylation temperature was found to be 50 °C, which produces an alkylate with a viscosity index ranging from 121.8 to 137.0 units on the Zr/ZSM-5 catalyst. The viscosity index of the alkylate produced on the spent and regenerated Zr/ZSM-5_(reg) catalyst ranges from 117.8 to 111.7 units.

A study of the gas composition before and after the alkylation process showed that propylene, butene-1, and butenes-2 participate in the reaction. Isobutane does not take part in the alkylation reaction and is instead concentrated in the exhaust gases, which are recommended for subsequent alkylation reactions to produce high-octane gasoline components.

The results of thermal stability studies showed that both the initial catalysts Zr/ZSM-5 and Fe/ZSM-5, as well as the spent catalysts Zr/ZSM-5_(reg) and Fe/ZSM-5_(reg), remain stable within the studied temperature range. The regenerated and calcined catalysts do not undergo any significant changes within the temperature range of 530–550 °C and remain active in the alkylation process.

Particle size studies using the DLS method revealed that the modified catalysts have smaller particle sizes compared to the unmodified ZSM-5 zeolite. Furthermore, the spent catalysts exhibit even smaller particle sizes than the original ones.

The phase composition of the catalyst, which contains a modifier not only on the surface but also exerts the main influence in the alkylation process included in the structure of the ZSM-5 zeolite. Therefore, the Zr/ZSM-5 catalyst, containing the $\text{ZrSi}_{24}\text{O}_{50}$ phase, has a higher activity compared to Fe/ZSM-5.

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