

Catalytic transesterification of rapeseed oil under supercritical fluid conditions and physical properties of the reaction product

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Abstract

This research examines the transesterification reaction of rapesed oil with ethanol in the presence of heterogeneous catalysts - Al₂O₃ and CaO/Al₂O₃ with 2% mass impregnation of CaO. The experiments were carried out at a molar ratio of ethanol: rapeseed oil of 18:1 (volume ratio \approx 1:1) at temperatures of 608, 623 K, and a pressure of 20 MPa for up to 30 minutes in a flow-type unit. The state's selected pressure and temperature parameters correspond to the supercritical fluid conditions. The results are presented for kinematic viscosity (T=313 K, P=0.1 MPa), density (T=288÷323 K, P=0.1 MPa), refractive index (T=298 K, P=0.1 MPa) of the transesterification reaction product. A quantitative assessment of the target product was carried out using chromatographic analysis. We have established the influence of temperature and duration of the reaction process on its efficiency. We present the strength characteristics of the catalysts used before and after the experiments. During attrition, the initial Al₂O₃ catalyst lost weight by 0.4 ± 0.1%. The mechanical crushing strength along the generatrix was 7.1 ± 0.3 N/mm. The strength of catalysts after carrying out the transesterification reaction under supercritical fluid conditions decreases, on average, by 24-28%. The use of heterogeneous catalysts Al₂O₃ and CaO/Al₂O₃ with 2% wt. impregnation of CaO showed an increase in the fatty acid ethyl esters concentration in the transesterification reaction product compared to the reaction carried out without the use of catalysts.

Keywords: Biodiesel fuel, Ethanol, Heterogeneous catalysis, Rapeseed oil, Supercritical fluid conditions.

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1. Introduction

In recent years, the global scientific community has been paying great attention to the activities of chemical production, trying, if possible, to place emphasis on the so-called "green chemistry," not forgetting about energy savings, energy efficiency, and environmental friendliness of the technologies being developed. One of the common proofs of this thesis is the increase in atmospheric pollution with greenhouse gases, a significant part of which is caused by waste products of various vehicles. As we all know, the vast majority of vehicles use petroleum fuel in their engines, a non-renewable source of energy, prompting us to explore new fuel types, primarily derived from renewable sources. Recently, biodiesel has attracted increased attention as an alternative, non-toxic, biodegradable, and renewable fuel produced from vegetable oils or animal fats [1]. Biodiesel is made from agricultural inputs that are produced through photosynthetic carbon fixation [2]. Burning biodiesel doesn't add any net CO2 to the atmosphere because it cuts down on total unburned and polycyclic aromatic hydrocarbons by 93 and 80%, respectively [3]. Biodiesel fuel contains almost no sulfur and has high lubricating properties, making it capable of burning completely in existing diesel engines, which simplifies the introduction of biofuels into industry [4]. Despite all the advantages of the fuel, there are also limitations associated with its commercialization. In particular, the cost of fuel is slightly higher than the cost of petroleum diesel fuel, which is primarily due to the fact that:

- The use of vegetable oils to produce biodiesel, many of which are used for human food, affects the human food chain and increases food prices. As a result, the question of finding suitable crops during the raw material production stage arises;
- The fatty acid esters obtained during transesterification have larger molecules compared to conventional diesel fuel, their viscosity will be higher, and this will especially affect the pump and injection system, affecting engine performance. This aspect makes the use of this fuel impractical at low temperatures, leads to low power consumption, oxidation instability, and the formation of deposits in engine combustion chambers, leading to corrosion and inefficient operation [5].

Thus, when producing biodiesel fuel, you need to pay attention to its viscosity. Kinematic viscosity according to the American Society for Testing and Materials (ASTM) D6751 is 1.9–6 mm²/s [6] and according to the European standard EN 14214, 3.5–5 mm²/s at 313 K and atmospheric pressure [7].

There are various methods for producing biodiesel, such as the microemulsion process, thermal cracking, and the most traditional and industrially used method, the transesterification process [8]. In industry, this reaction is carried out using methanol at atmospheric pressure, temperatures of 60-70 °C, with some excess alcohol corresponding to a methanol-oil molar ratio of 6:1. In this case, we use homogenous catalysts, primarily sodium or potassium hydroxide, to accelerate the reaction. The convenience of the state parameters is offset by disadvantages, which include the excessive duration of the process (1-20 hours), the formation of undesirable saponification products, the need to purify the reaction product from the catalyst and by-products (glycerol), as well as the cumbersomeness of the equipment used. The primary cause of the noted disadvantages is the two-phase "liquid-liquid" region in which the reaction occurs, resulting in poor miscibility of the starting reagents and, consequently, a low rate of chemical reaction. To neutralize the alkali formed during the reaction and purify the product, a large amount of water is consumed and, accordingly, significant volumes of wastewater are generated, which puts a significant burden on meeting various environmental requirements and, as a result, has an extremely negative impact on the energy of the process as a whole and the cost of the resulting fuel.

The disadvantages of the traditional process became the basis for research aimed at studying new approaches and developing more efficient technologies for producing biodiesel fuel. One of these basically involves the implementation of the transesterification reaction in sub- (SbKF) or supercritical fluid (SCF) conditions [9-12] which makes it possible to solve a significant part of the above-mentioned problems. But this technology also has disadvantages, and, in particular, these are high state parameters (P>25 MPa, T>513 K) and high values of the molar ratio of the starting reagents (40:1 and higher) [13, 14], which do not contribute to achieving the desired profitability of industrial sales.

One of the ways to reduce the state parameters and the molar ratio of alcohol to oil is to carry out the reaction in the presence of heterogeneous catalysts. These heterogeneous catalysts are reusable, do not require catalyst removal from the reaction product, and do not form saponification products, unlike homogenous catalysts.

For heterogeneously catalyzed transesterification, the attention of many researchers has been paid to alkaline earth metal oxides due to their lower solubility and lower corrosiveness compared to other basic catalysts [15, 16]. Calcium-based catalysts are attractive because they are inexpensive and least toxic [17]. CaO has the disadvantage of unwanted formation of Ca(OCH₃)₂ on the surface of CaO as a result of reaction with fatty acid triglycerides. To increase the catalytic activity and stability of the catalyst, it is advisable to use CaO on various oxide supports (for example, MgO, SiO₂, Al₂O₃) [18, 19]. Thus, the authors conducted experiments with ethanol and palm oil at a molar ratio of 30:1, T = 558 K and P = 20 MPa using catalysts Al₂O₃, ZnO/Al₂O₃, CaO/Al₂O₃, Al₂O₃/Al₂O₃ catalysts had the greatest effect on the conversion of oil into biofuels. The La₂O₃/Al₂O₃ catalyst had slightly higher initial activity and has potentially greater strength than CaO/Al₂O₃, but the price of La₂O₃ is significantly higher (up to 800 times) than CaO.

The goal of this work is to carry out the transesterification reaction using rapeseed oil as example and an ethanol under supercritical conditions. The challenge lies in conducting the reaction in supercritical fluid environment with a realitively low molar ratio of ethanol to rapeseed oil (18:1). The experiments are carried out in a flow-type experimental setup with preliminary ultrasonic emulsification of the reaction mixture and using a catalytic reactor with a fixed catalyst bed. The main objective of the work also includes assessing the composition and physical properties of the resulting product, such as

kinematic viscosity, density, and refractive index. This is necessary in order to comply with international standards for the properties and content of fatty acid ethyl esters (FAEE) in the reaction product.

2. Materials and Methods

2.1. Initial Raw Materials

The raw materials for transesterification reaction were: refined deodorized rapeseed oil of the highest grade, hot pressed "P" brand Oily, Republic of Belarus, as well as 96% ethanol (n_D^{298} =1.36242, ρ^{25} =797.1 kg/m³). We subjected the oil to chromatographic analysis. Table 1 provides the composition of rapeseed oil by fatty acid content.

Table 1.

Fatty acid composition of rapeseed oil.	
Fatty acid name	Mass fraction of fatty acid (% of total fatty acids)
Tetradecanoic (Myristic)	0.02
Pentadecanoic (Pentadecylic)	0.01
Hexadecanic (Palmitic)	6.46
Hexadecene (Palmitoleic)	0.17
Octadecanic (Stearic)	3.12
Octadecene (Oleic)	67.67
Octadecadiene (Linoleic)	21.69
Eicosanoic (Arachidic)	0.22
Eicosene (Gondoic)	0.59
Docosane (Behenic)	0.03
Docosene (Erucic)	0.02
Tetracosane (Lignoceric)	< 0.01
Tetracosanoic (Nervonic)	< 0.01
Total amount	100±0.01

The catalyst carrier was aluminum oxide (a mixture of gamma and chi oxides [20]. A CaO/Al₂O₃ catalyst of 2 wt% was obtained by impregnating Al₂O₃ granules with an aqueous solution of calcium nitrate salt [21].

The textural characteristics of the original and synthesized catalysts were studied using the method of nitrogen thermal desorption using an installation for rapid analysis of surface area and pore size for two samples called NOVA 2200e from the Quantachrom Company, USA. The Brunauer-Emmett-Teller method was used to analyze the specific surface area of the catalysts, and the Barrett-Joyner-Halenda method on a desorption isotherm was used to estimate the volume and pore size distribution. Table 2 presents the obtained results.

Table 2.

Texture characteristics of catalysts.

Catalyst	S _{уд} ,	\overline{d} ,	V _{mesopores} , sm ³ /g	Distribution of pore volume mesopore region, %		blume in the n, %
	m-∕g	nm	_	$2 \div 5 \text{ nm}$	5 ÷ 10 nm	10 ÷ 50 nm
Al ₂ O ₃	153 ± 10	7.7	0.3066	26.6	56.5	16.9
CaO/Al ₂ O ₃ (2 %)	149 ± 10	7.8	0.2958	25.2	55.5	19.3

The original and synthesized catalysts show the presence of mesopores with a polymodal pore volume distribution with a predominance of pores characterized by a diameter in the range of 5-10 nm.

Element-by-element analysis of the amount of catalyst deposited on the surface of the support was assessed by X-ray fluorescence analysis on the universal X-ray SUR-02 "Renom FV" device and showed the amount of Ca in the amount of 1.95 ± 0.2 wt%.

2.2. Equipment and Experimental Methodology

To obtain biodiesel fuel under supercritical fluid conditions in the reaction mixture, a continuous (circulation) process was used [22]. Figure 1 displays the diagram of the experimental unit. To ensure intensive mixing of difficult-to-mix reagents under atmospheric conditions and increase the phase contact area, probe-type ultrasonic apparatus for laboratory testing and industrial liquid processing "UIP1000HD" from Hielscher (Germany) (item 6) was added to the process flow diagram in order to optimize the process. We also introduced a catalytic fixed-bed reactor (position 11) into the plant. We calculate the volume of the catalytic reactor to be up to 5% by weight of the total mass of the loaded reacting mixture. The amount of catalyst used in the experiments did not exceed 2% of the weight of the feedstock. To completely fill the catalytic reactor, as well as to increase the contact area and further intensify the process, the catalyst is loaded alternately with ceramic hollow cylinders.



Figure 1.

Schematic diagram of a continuous installation with a flow-type reactor for producing biodiesel fuel under supercritical fluid conditions of the reaction mixture: 1 - Tank for alcohol; 2 – Oil reservoir; 3, 7, 15 – Shut-off and control valves; 4 - Mechanical mixer; 5 - Gear pump; 6 – Ultrasonic emulsifier from Hielscher; 8 - Dosing pump; 9 - Insulator; 10 - Continuous reactor; 11 – Catalytic reactor with a fixed catalyst bed; 12 – Power supply; 13 - Refrigerators; 14 - Film evaporator.

We used chromatography on a DFS (Distributed File System) device from Thermo Electron Corporation (Germany) to evaluate the transesterification reaction product. A capillary column of the ID-BP5X brand with a length of 50 m and a diameter of 0.32 mm was used in the work. The chemical composition of the phase includes 5% biphenyl and 95% dimethylpolysiloxane, the thickness of the phase layer is 0.25 microns, the carrier gas is helium.

We set the following conditions for obtaining the chromatogram: injector temperature -250 °C, flow division -1:10; The column was heated by software: initial temperature -120 °C (1 min); heating rate 20 °C/min to 280 °C (10 min); carrier gas flow through the column -2 ml/min; temperature of the communication device with the mass spectrometer -250 °C; the sample volume was 0.1 µl.

We used standard glass viscometers SLV-2 (suspended liquid viscometers) with capillaries with a diameter of 0.73 mm for transesterification reaction samples and 0.99 mm for rapeseed oil to measure kinematic viscosity. Each sample was subjected to measurements to determine viscosity five times.

Viscosity measurements were carried out at 313 K and P=0.1 MPa to ensure compliance with international standards EN 14214 and ASTM D6751. We maintained the water temperature in the viscometer at 313k using a thermostat (Huber, Germany) with an accuracy of 10 mK. The water temperature was measured with a pRT100 thermometer on the ITS-90 scale with an accuracy of 0.03 K.

The kinematic viscosity of rapeseed oil and the resulting transesterification reaction products were determined by the formula:

$$v = \mathbf{K} \cdot g \cdot \tau / 9.807 \tag{1}$$

Where: v - kinematic viscosity of the liquid (mm²/s); K is the constant of the viscometer (K=0.03307 for SLV-2 with a diameter of 0.73 mm; K= 0.092326 for SLV-2 with a diameter of 0.99 mm); g - free fall acceleration at the place of measurements (m/s²); τ - fluid outflow time (s); 9.807 - free fall acceleration at the instrument calibration site (m/s²).

Density was measured by the gravimetric method using a glass pycnometer GP 2-10 KSh 7/16 (GOST (State standard of the Russian Federation) 22524-77). Weighing was carried out on analytical balances model BLA-200 (Balances laboratory analytical) and electronic balances "Metter PM 600". Density at T=288 K and atmospheric pressure according to the European standard EN 14214 is 0.86÷0.9 g/cm³.

The refractive index was measured using an IRF-23 refractometer. The device and method for determining the refractive index are described in detail in [23]. The calculation formula for determining the refractive index at 20 °C (T=293 K) has the form:

$$N_D^{20} = \sqrt{N_\lambda^2 - \sin^2\varphi},$$

Where N_D^{20} is the refractive index of the test sample; N_λ is the refractive index of the measuring prism; ϕ is the limiting beam exit angle measured on the instrument.

Recalculation of refractive indices for t=25 °C (T=298 K) is made from:

$$N_D^t = N_D^{20} + (t - 20) \cdot 0,00035.$$
 (3)

Determination of the strength of the catalysts used before and after the experiments was carried out on a Lintel PK-21 device, designed for testing catalysts for mechanical strength under static conditions using the compression method. The static relative error in measuring the tensile strength is 1%, the rate of lowering of the rod during compression of the catalyst is 4.4 N/s. The calculation of the arithmetic mean strength value is made according to the equation:

$$P_{op} = \frac{1}{N} \sum_{l=1}^{N} \frac{x_{l}}{s}, (4)$$

Where N is the number of tests; S is the average cross-sectional area of the granules specified before the series of tests, cm^2 , X_i is the value of the tensile strength during testing, N.

3. Results and Discussion

3.1. Kinematic Viscosity

The experimental study was carried out at temperatures of 608 and 623 K, at a pressure of 20 MPa, a molar ratio of "ethanol: rapeseed oil" of 18:1 (volume ratio \approx 1:1), and a reaction duration of 0÷30 min. The authors of the article chose these conditions based on the successful outcomes of their previous work, which used different catalysts [12, 21]. After reaching a steady state during heating, samples were taken every 6 minutes and up to 30 minutes of the reaction.

Figure 2 and 3 show the nature of the change in the kinematic viscosity of the transesterification reaction product samples, measured at T = 313 K, P = 0.1 MPa, depending on the reaction duration and process temperature.



Figure 2.

Kinetics of changes in kinematic viscosity of transesterification reaction product samples obtained at T=608 K.



Kinetics of changes in kinematic viscosity of transesterification reaction product samples obtained at T=623 K.

The kinematic viscosity of the transesterification reaction product samples decreases from approximately 10 to 6 mm^2/s (Figure 2, 3), which is significantly lower than the measured value of the rapeseed oil kinematic viscosity at T = 313 K, P = 0.1 MPa, equal to 35.7 mm²/s. The graphs (Figure 2, 3) show that with increasing reaction duration, the kinematic viscosity of the product decreases. There is also a decrease in kinematic viscosity values with increasing process temperatures. This is explained by the fact that with increasing temperature, the kinetic energy of molecules increases faster than the potential energy of their interaction.

3.2. Chromatographic Analysis

The samples have the lowest viscosity values after 30 min of reaction. These samples were used for chromatographic analysis to determine the quantitative composition.

The results of chromatographic analysis of some samples are presented in Figure 4 and in Table 3.



Figure 4.

Table 3.

Chromatogram of the transesterification reaction product samples, carried out under supercritical fluid conditions at the end of the reaction: T=623 K, the molar ratio "ethanol/rapeseed oil" 18:1; P=20 MPa. (RT - Reaction time).

	FAEE amount. wt %.					FAEE amount		
	Temperature Palmitic		Stearic	Oleic	Linoleic	Arachidic	Gondoic	in the reaction
Catalyst	(1, K)	acid	acid	acid	acid	acid	acid	product
Without	608	9.09	3.12	68.31	5.43	1.08	0.48	87.51
catalyst	623	8.87	3.03	75.24	2.89	1.32	1.13	92.48
A1 O	608	8.83	2.68	73.43	3.99	1.37	0.61	90.91
AI ₂ O ₃	623	8.39	2.62	75.93	3.02	1.85	1.62	93.43
CaO/Al ₂ O ₃	608	9.02	2.56	75.59	4.30	1.12	1.25	93.84
(2% wt)	623	10.38	2.43	76.14	2.89	2.32	1.23	95.39

From Table 3, it is clear that the main content of the ester structure is given to oleic acid ethyl esters, as the fatty acid represents the largest amount of the original rapeseed oil (see Table 1). At the same time, under current temperature conditions, there is a significant decrease in linoleic acid ethyl esters, which is due to the thermal decomposition of unsaturated fatty acid esters under supercritical conditions of the transesterification reaction at temperatures above 573-598 K, which is also confirmed by the results of studies by other authors [24, 25]. In this work, in addition to FAEE, compounds of 1-hexadecene, 2-butyl-1-octanol, pentadecane, and 2,6,10,14-tetramethylheptadecane were found in amounts varying from 4 to 11 wt%. We observed no decomposition of oleic acid ethyl esters in the studied temperature range. The decomposition of these esters is possible at higher process temperatures, which is reflected in works [21, 26]. It is also important to note that thermal decomposition is not observed in saturated fatty acids (palmitic, stearic, arachidic) ethyl esters, due to even higher decomposition temperatures for these esters. Thus, the resulting increase in the concentration of fatty acid ethyl esters in the reaction product, compared to the initial fatty acid composition, is explained by their concentration in the total content of esters in the reaction product (see Table 3) [26].

From the presented data (Table 3), it is clear that heterogeneous catalysis increases the concentration of fatty acid ethyl esters in the reaction product by up to 5.92% when using the Al₂O₃ catalyst and up to 6.33% when using the CaO/Al₂O₃ catalyst.

The maximum content of the FAEE in the reaction product is achieved at T = 623 K after 30 min of reaction using the CaO/Al₂O₃ catalyst. However, none of the samples meets the EN 14214 standard [7] for the level of fatty acid esters in the reaction product.

3.3. Density

Figure 5 shows how the density of some transesterification reaction product samples, measured in the temperature range T=298÷323 K, P=0.1 MPa, changes depending on temperature. This is demonstrated by the example of samples obtained at T=608 K, P=20 MPa with reaction durations of 0, 18, and 30 minutes. The density values obtained at T=288 K, P=0.1 MPa for comparison with the EN 14214 standard were approximated and extrapolated based on the available experimental data at T=298÷323 K (Figure 5).



Figure 5. Density of the transesterification reaction product depending on temperature, for the reaction carried out at T=608 K, P=20 MPa for the following conditions: $1 - \tau = 0$ min, without catalyst; $2 - \tau = 18$ min, without catalyst; $3 - \tau = 30$ min, without catalyst; $4 - \tau = 0$ min, with Al₂O₃; $5 - \tau = 18$ min, without catalyst; $3 - \tau = 30$ min, without catalyst; $4 - \tau = 0$ min, with Al₂O₃; $5 - \tau = 18$ min, with CaO/Al₂O₃; $8 - \tau = 18$ min, with CaO/Al₂O₃; $9 - \tau = 30$ min, with CaO/Al₂O

The measured values of the reaction product density (Figure 5) are similar to each other within the measurement error. As temperature increases, the density of biodiesel decreases. The results of extrapolation of density values at T=288 K lie

in the range of 0.884 to 0.898 g/cm³, which corresponds to the European standard EN 14214. Density data obtained at the experimental temperature T=623 K are of a similar nature.

3.4. Refractive Index

Refractive indices were measured at T=298 K, P=0.1 MPa for rapeseed oil and for biodiesel fuel samples obtained at T=608 K, P=20 MPa (Table 4).

Table 4.

Refractive indices of rapeseed oil and FAEE samples.

Sample	τ, minutes	N _D ²⁹⁸
Rapeseed oil	-	1.472
FAEE	0	1.458
without catalyst	18	1.458
	30	1.456
FAEE with	0	1.459
catalyst Al ₂ O ₃	18	1.458
	30	1.457
FAEE with	0	1.455
catalyst CaO/Al ₂ O ₃	18	1.457
	30	1.458

We assessed the refractive index value using the additivity rule for the main compounds in the oil and transesterification reaction product. Due to the high concentration of these substances in both the original oil and the biodiesel fuel, oleic acid esters in the reaction production contribute the most to obtained values.

3.5. Strength of Catalysts

Since the transesterification process in SCF conditions takes place at high temperatures and pressures, the mechanical strength of the original and spent catalysts was also analyzed. As a quantitative characteristic of the mechanical strength of catalysts, "mechanical attrition strength" (ASTM D 4058-92, Standard Test Method for Attrition Strength of Catalysts and Supports) and "mechanical crushing strength" (ASTM D 4179, Standard Method for Determining Crushing Strength for (Moulded Catalyst Grains). The weight loss of the original Al₂O₃ catalyst during attrition was $0.4 \pm 0.1\%$. The mechanical crushing strength along the generatrix was 7.1 ± 0.3 N/mm.

The mean strength values of the catalysts, calculated by formula (4) for 12 test samples of each catalyst, are presented in Table 5.

Table 5.

Table 5.	
Mean strength of catalysts, N/cm ² .	
Al ₂ O ₃	
Before experiment	After experiment
1042,534	795,5204
CaO/Al ₂ O ₃	
Before experiment	After experiment
878,5068	626,1991

The measurement results (Table 5) show a significant deterioration in the strength of the catalysts after a single experiment (after 30 minutes of reaction).

4. Conclusions

An experimental study of the transesterification reaction of rapeseed oil in ethanol in supercritical fluid conditions was carried out at temperatures T = 608; 623 K, pressure 20 MPa; and a molar ratio of "ethanol: rapeseed oil" of 18:1 in the presence of heterogeneous catalysts - Al₂O₃, CaO/Al₂O₃. The maximum conversion of rapeseed oil into biodiesel fuel, equal to 95.39%, is achieved at a temperature of T = 623 K, with a reaction duration of 30 minutes in the presence of a CaO/Al₂O₃ catalyst. None of the presented samples meets the requirements of the standards for kinematic viscosity of fuel. We recommended using the resulting fuel as an additive to petroleum diesel fuel.

Abbreviations:

ASTM American Society for Testing and Materials RT reaction time SURspectrometer universal X-ray DFS Distributed File System SLV Suspended liquid viscometers GOST State standard of the Russian Federation BLABalances laboratory analytical T. K Temperature, Kelvin mm²/s square millimeter per second. SCFsupercritical fluid. SbKF subcritical fluid. FAEE fatty acids ethyl esters. Al₂O₃ Aluminum oxide. CaOCalcium oxide. ⁰C Degree Celsius. KDegree Kelvin. MPa Megapascal. min minutes.

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