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Flow-Through Supercritical Installation for Producing Biodiesel Fuel

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Abstract**—**A flow-through installation was created and manufactured for the transesterification of triglycerides of fatty acids and production of biodiesel fuel under supercritical fluid conditions. Transesterification of rapeseed oil with ethanol was carried out according to two parameters: temperature and the ratio of alcohol/oil mixture at the constant pressure of 19 MPa. The kinetics of the yield of fatty acids ethyl esters (FAEE) was determined in the temperature range of 320-380 °C at the alcohol/oil molar ratio of 6:1-20:1. The content of the formed FAEE was determined by the method of correlation of the resulting biodiesel fuel by its kinematic viscosity. The maximum FAEE yield (about 90%) was obtained within 30 min at the ethanol/oil molar ratio of 12:1 and a temperature of 380 °C. When studying of transesterification of triglycerides, a kinetic model of an isothermal flow reactor was used. The reaction order implemented in the flow reactor has been determined. The first order of the reaction was confirmed by data on the conversion of FAEE during the reaction at different temperatures and the molar ratios of the initial reagents (ethanol/oil). Using the Arrhenius equation, the values of the effective constants of the transesterification reaction rate were calculated at different reaction temperatures. In addition, based on the experimental data, the activation energy and the pre-exponential factor of the transesterification reaction were determined.

Keywords**—**Biodiesel, fatty acid esters, supercritical fluid technology, transesterification.

I. Introduction

An important role in the economic development of the countries is their energy security. Reduction in the reserves of proven natural resources of hydrocarbons can lead to an energy crisis and a decline in industrial production. Over the past 100 years, world energy consumption has increased 18 times [1] and its demand is growing faster than the industry is able to satisfy it. By 2030, the world's energy consumption will increase by 30% [2]. This forces the industrialized countries to look for the ways to increase the productivity of depleted oil fields, as well as replacing oil with other alternative energy sources, for example: hydrogen, electricity, bioethanol, biodiesel, synthetic fuel, etc.

In addition to the reduction of hydrocarbon fuel reserves, another global problem has recently emerged - the negative environmental impact of greenhouse gas emissions to which carbon dioxide (CO_2) belongs. The main sources of significant CO_2 emissions are the fuel and energy production complex, as well as motor vehicles, which contribute one fifth of the total greenhouse gas emissions. The use of hydrocarbon fuels violates significantly the established balance of harmful and toxic substances in the biosphere, for example, nitrogen and sulfur oxides, CO_2. The huge consumption of oxygen in the combustion of hydrocarbon fuels is of great concern. At the beginning of the last century, the CO_2 content in the atmosphere was 280 mg/kg [3].

At present, the CO_2 content has increased to 396 $mg \cdot mL^{-1}$ and is annually increasing by 2 mg/kg [4], [5]. At the same time, a decrease in the oxygen content is observed. Consuming hydrocarbon fuel stored for many millions of years: coal, oil, gas, etc., there is a violation of the established balance towards the formation of CO_2 and a decrease in the oxygen content in the biosphere while one of the main conditions for the appearance of life on Earth was the reverse process - an increase in oxygen in the biosphere and a decrease in CO_2 due to the formation of hydrocarbon deposits.

One of the alternative ways to reduce greenhouse gas emissions into the atmosphere, as well as to solve the predicted problem of shortage of oil in the near future, may be the creation of production of biodiesel fuel (BD) from renewable raw materials that do not violate the established balance of substances in the biosphere. BD is considered an environmentally safe fuel, as CO_2 generated during combustion is processed by plants during their life cycle. The emissions of nitrogen oxides, soot, carbon monoxide, hydrocarbons, and polycyclic aromatic hydrocarbons are significantly reduced, CO and sulfur dioxide are almost completely absent compared to emissions from the combustion of diesel fuel derived from oil. BD is also safe for handling and storage; it is non-toxic, biologically decomposed within a month.

Currently, BD is mainly obtained by transesterification of natural oils with alcohols (methanol, ethanol) in the presence of a catalyst – alkali [6]-[8]. The transesterification of oils proceeds at atmospheric pressure in the medium of 0.5-1.0 molar excess of alcohol at a temperature of from +25 °C to +100 °C. The transesterification of oils under the above conditions is a multistage process and takes a long time, usually 6-8 hours.

The most promising way to obtain BD is the use of supercritical media [8]-[10]. Under supercritical (SC) parameters, the transesterification of oils is carried out above the critical point of methanol or ethanol (the critical point of methanol: T = 240 °C and P = 8.09 MPa; ethanol: T = 241 °C and P = 6.3 MPa). The transesterification of oils in SC-media can significantly reduce the stages of BD production, the process implementation time, and improve the technology, thus reducing capital and production, labor costs. SCFT allows

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excluding the stages of pretreatment of initial reagents, removal of soap and water formed at the final stage, as well as the use of catalysts. The BD obtained by the SC method is characterized by high purity of methyl or ethyl esters of fatty acids FAME (FAEE), respectively, as well as glycerol, which is formed as a by-product.

The aim of the study was to determine the optimal modes of transesterification of the oil with alcohol using the developed flow SC plant; to study the kinetic model of functioning of an isothermal reactor of ideal displacement during the process of oil conversion into BD; determination of effective rate constants of the transesterification reaction depending on various conditions of the reaction.

II. Experimental

The flow-through installation was designed for the transesterification process of triglycerides of fatty acids, allowing to work in SC fluid conditions. The scheme of the device is shown in Fig. 1.

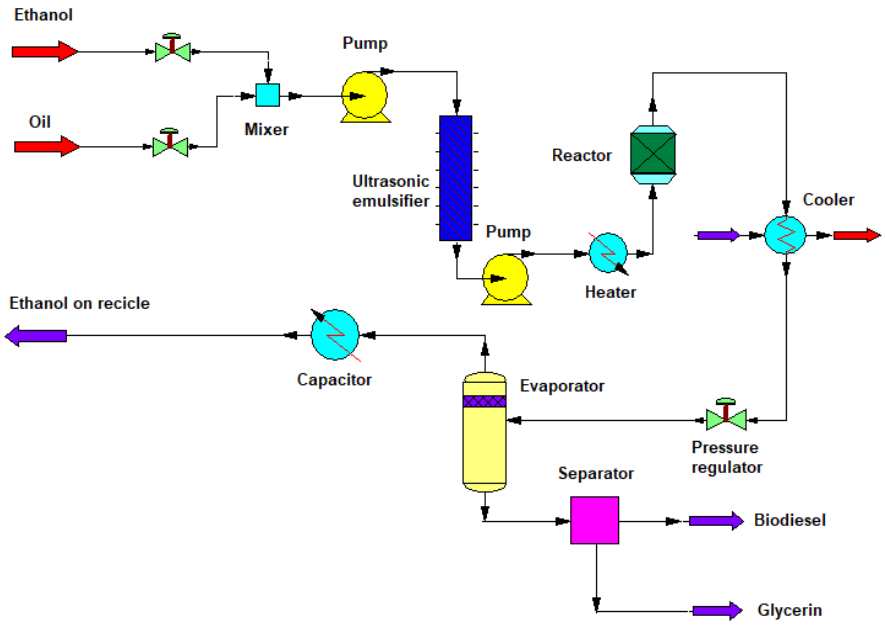


Fig. 1 Scheme of flow SC installation

The ability of the flow installation to operate is determined largely by the design of the reactor and the principles that provide thermal conditions for maintaining the transesterification process. The installation consists of a pumping and mixing unit with an ultrasonic emulsifier, a flow-through heated reactor, a cooler, pressure regulators, an evaporator and a separator for collecting liquid reaction products. In order to reduce the size of the installation, the flow section of the reactor is made of thick-walled tubes, wound in the form of coils. The use of a tubular reactor significantly reduces the metal consumption and the dimensions of the structure and ensures its high manufacturability. To reduce heat losses, direct heating is used, in which the heat source is a reactor tube connected to a step-down transformer.

According to Fig. 1, rapeseed oil and ethyl alcohol in various molar ratios are mixed and simultaneously fed into the reactor. In this study, 100% rapeseed oil produced by Aston JSC (Rostov-on-Don) GOST R53457-2009 and food grade 95% ethyl alcohol GOST R 51723-2001 were used as initial model products for the transesterification. Rational technological parameters of the transesterification of rapeseed oil were determined by changing the temperature, pressure, molar ratio of ethanol to oil in the flow reactor. A thin film evaporator is used to separate excess ethanol. For the separation of the reaction products, FAEE and glycerol (GL), the separator is provided in the design of the flow SC installation.

The determination of the FAEE content upon completion of the transesterification reaction was carried out by the method of correlation between the composition of BD and its kinematic viscosity [11]. To determine the coefficient of kinematic viscosity, a standard ВПЖ-2 viscometer with a capillary diameter of 0.56 mm GOST 10028-81 was used. The viscosity of each sample was measured five times, and the average value was calculated from the data obtained. The following formula was used to calculate the viscosity:

$$v = g \cdot T \cdot K / 9.807 \quad (1)$$

where K - viscometer constant (K = 0.01 for ВПЖ-2with a diameter of 0.56 mm); T is the flow time, sec; v is the kinematic viscosity of the fluid; g - gravitational acceleration ($m \cdot s^{-2}$).

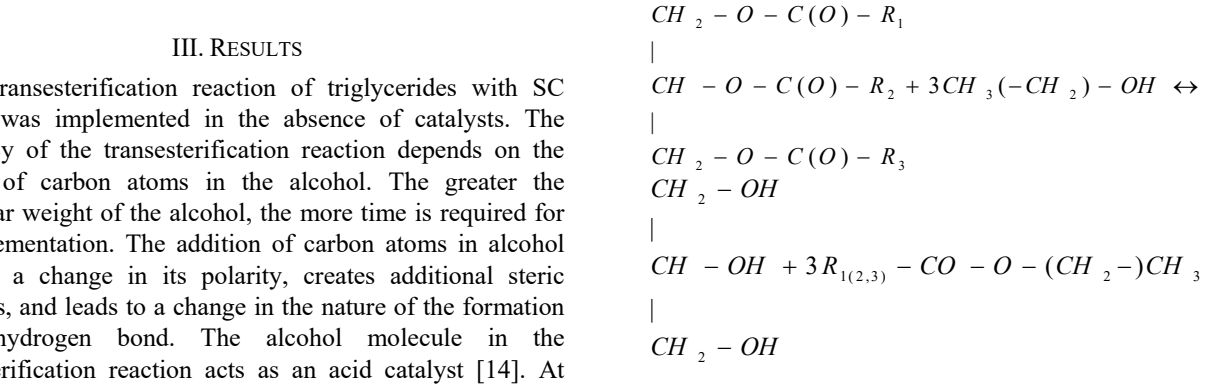
The content of FAEE, based on the results of measuring the kinematic viscosity of the samples of the product after the transesterification reaction, was determined by:

$$X_{FAEE}\,(\%) = A \cdot \ln(v) + B \qquad (2)$$

where X is the mass fraction of FAEE sample, %; v - kinematic viscosity, $mm^2 \cdot s^{-1}$; A = -51.061 and B = 174.44 are the coefficients [12], [13].

III. Results

The transesterification reaction of triglycerides with SC alcohol was implemented in the absence of catalysts. The efficiency of the transesterification reaction depends on the content of carbon atoms in the alcohol. The greater the molecular weight of the alcohol, the more time is required for its implementation. The addition of carbon atoms in alcohol leads to a change in its polarity, creates additional steric obstacles, and leads to a change in the nature of the formation of a hydrogen bond. The alcohol molecule in the transesterification reaction acts as an acid catalyst [14]. At high pressure, the alcohol attacks the carbonyl triglyceride atom and transfers a positive charge. Then, the resulting intermediate dissociates to form alkyl molecules of fatty acid, ester and diglyceride. This sequence is repeated twice more, with the formation of the glycerin molecule as the final product. Thus, the transesterification reaction of triglycerides of fatty acids includes three consecutive reversible reactions, accompanied by the sequential formation of intermediates - diglycerides and monoglycerides of fatty acids. Studies have shown that [15] the transesterification reaction with the stoichiometric molar ratio of the initial substances of the oil and alcohol does not provide a high yield of the target product – the sum of fatty acid esters. In this regard, as a rule, the transesterification reaction is carried out in an excess of alcohol. The process of transesterification of triglycerides can be described by one total irreversible reaction.



This process is significantly affected by the temperature of the process. High temperature accelerates the kinetic processes of transesterification of the oil, while an increase in the reaction rate is observed.

In this work, we studied the effect of temperature on the process of transesterification of oil under SC fluid conditions in a flow reactor in the temperature range of 320-380 °C. Based on the obtained results calculated by (2), Fig. 2 shows the kinetic data of the transesterification of the oil, at different values of the molar ratios of the initial reagents of ethanol and rapeseed oil, depending on temperature.

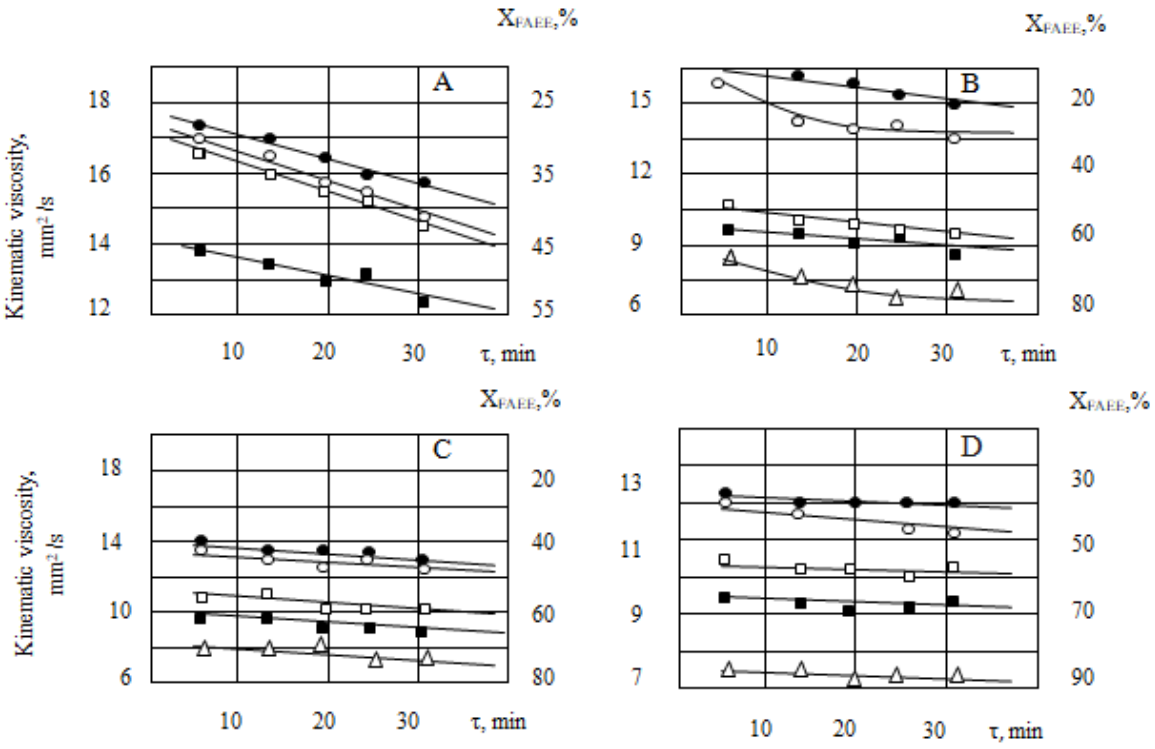


Fig. 2 Kinematic viscosity of the samples of the rapeseed oil transesterification product at different molar ratios of the initial reagents (ethanol/oil): A - 6:1; B - 8:1; C - 12:1; D - 12:1 in time, depending on the temperature of the process with the results of the FAEE yield. Curve designations: ● - 320°C; ○ - 335°C; □ - 350°C; Δ - 380°C

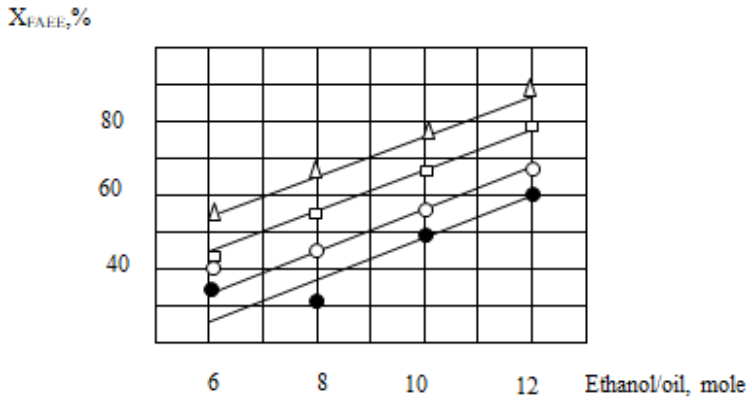


Fig. 3 Conversion of rapeseed oil to FAEE depending on the ratio of the initial reagents (ethanol/oil), the transesterification reaction time is 30 min
Curve designations: ● - 320°C; ○ - 335°C; □ - 350°C; △ - 380°C

A low FAEE yield is observed when the ratio of the components of the reaction mixture (ethyl alcohol/rapeseed oil) is 6:1. As expected, the highest yield of FAEE was obtained using a molar ratio of ethyl alcohol to oil of 12:1, within 30 minutes of the reaction time up to 90% of FAEE was obtained. Experimental data on the conversion of oil, depending on the ratio of initial reagents ethanol/oil in moles, are given in Fig. 3.

At high pressure, the ethanol density increases, which is accompanied by an increase in the rate of the reaction. A high molar ratio of ethanol to oil significantly increases the solubility of triglyceride in ethanol. It was found that the yield of the target product increases from 15% to 75% with increasing pressure from 5 MPa to 10 MPa. Increasing the pressure from 10 MPa to 25 MPa increased the yield of EEFA from 50% to 90%. A further increase in pressure above 25 MPa did not lead to a significant increase in the yield of the target product, which is also confirmed by published literature sources [9].

IV. Discussion

The mathematical model for describing the chemical kinetics in the flow was chosen based on the operating characteristics of the tubular reactor and the kinetic scheme of the chemical transesterification reaction [16]. Evaluation of the Reynolds criterion for the conditions of the experiment gave $\mathrm{Re} \approx 15000$. The value of the Peclet criterion when a fluid moves in a pipe of circular cross section can be estimated from the well-known relation: $\mathrm{Pe} = 0.76\,\mathrm{Re}^{0.125}$ which gives $\mathrm{Pe} \approx 2.5$. This value of the Peclet criterion allows concluding that the structure of the flows in the reactor was close to the model of ideal displacement (MID).

The kinetic scheme of the transesterification reaction was constructed under the assumption that the reaction is irreversible and one-step:

$$\mathrm{TG} + 3\mathrm{AL} \rightarrow 3\mathrm{BF} + \mathrm{GL}$$

where TG - rapeseed oil, AL - ethanol, BF - biodiesel, GL - glycerin. In this case, the model of chemical kinetics in the reactor will look like:

$$\frac{dC_{TG}}{d\tau} = -kC_{TG}C_{AL} \tag{3}$$

where C_{TG}, C_{AL} are volume molar concentrations [mol·L^{-1}], subscripts denote components according to the reaction scheme. Since the amount of ethanol was always in excess, it was assumed that the change in its concentration can be neglected, i.e. the reaction was considered a pseudo-first order reaction. Then, if we denote the initial molar ratio of ethanol to oil as $\frac{C_{AL}^0}{C_{TG}^0} = n$ we can get the solution of (3):

$$\ln\left(\frac{C_{TG}^0}{C_{TG}}\right) = knC_{TG}^0\tau \tag{4}$$

Here k is chemical reaction rate constant.

As a result of processing the experimental data, the time dependences of the concentration of oil in the reaction medium were obtained, the logarithmic representation of which is shown in Fig. 4. The linear nature of these dependencies can be noticed, as well as the effect on the temperature slope angle, which confirms the adequacy of the chosen mathematical model of the reactor. The effective reaction rate constant was determined for each temperature according to (4) from the linear regression equation.

The results of the calculation of the values of the effective constants of the transesterification reaction rate as a function of temperature are given in Table I.

Based on the obtained values of the effective rate constants, the parameters in the Arrhenius equation were determined [17].

$$k = Ae^{-\frac{E_a}{RT}}$$

where E_a is the activation energy; R is the universal gas

constant; A - pre-exponential factor. The values of the activation energy and the pre-exponential factors A (s^{-1}) of the SC transesterification oil obtained on the basis of experimental data are:

$$E_a = 37.785 \text{ kJ·mol}^{-1}; A = 1260.37 \text{ s}^{-1}$$

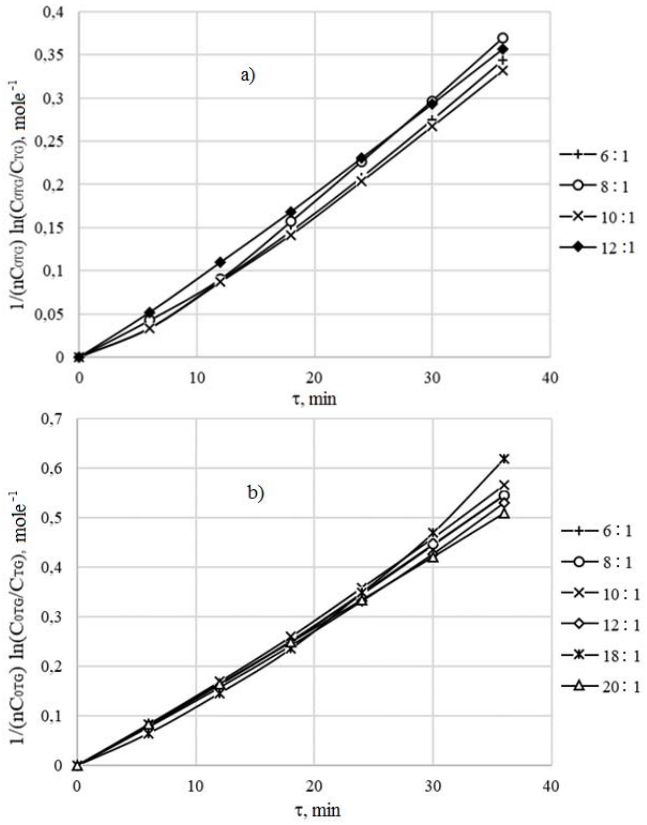


Fig. 4 Dependence of $\frac{1}{nC_{TG}^0} ln \frac{C_{TG}^0}{C_{TG}}$ on the duration of the reaction at different values of the molar ratio of the initial reagents (ethanol/oil) and temperature: (a) 320 °C; (b) 365 °C

Curve designations: + - 6:1; o - 8:1; × - 10:1; ♦-12:1; ❋ - 18:1; Δ - 20:1.

TABLE I
VALUES OF EFFECTIVE RATE CONSTANTS OF THE TRANSESTERIFICATION REACTION AS THE FUNCTION OF TEMPERATURE, AT VARIOUS MOLAR RATIOS OF ETHANOL TO OIL

Temperature, °C	Reaction rate constant k, $(mol·min)^{-1}$
320	0.009884
335	0.011014
350	0.012595
365	0.014203
380	0.01998

According to the literature, the apparent activation energy of the transesterification reaction in the SC state is 56 kJ·mol^{-1}, whereas in the subcritical region it is 11.2 kJ·mol^{-1} (below 240 °C) [18]. Several researchers [9], [14] suggested that the system should overcome the energy barrier, beyond which an increase in the reaction rate constant occurs. The reaction rate constant increased 85 times when the temperature rose from 239 °C to 350 °C [19]. It follows that high temperature is necessary to overcome the energy barrier. Further, it is noted that the change in reaction rates on Arrhenius plots was the result of an increase in the activation energy E_a, as well as a pre-exponential factor. D'Ippolito et al. suggested that a decrease in the hydrogen bond and a change in the physical properties of ethanol are the main cause of a change in the pre-exponential factor [14].

V. CONCLUSIONS

For the transesterification of fatty acid triglycerides, a flow-through plant for producing BD under SC fluid conditions was designed and manufactured, which included the pump-mixing unit, the flow-through tubular reactor, and systems for separating reaction products. The study of modes of transesterification of rapeseed oil with ethanol was carried out according to two parameters: the temperature and the ratio of the alcohol/oil reaction mixture at a constant pressure of 19 MPa. The kinetics of the yield of ethyl esters of fatty acids was determined in the temperature range 320-380 °C at a molar ratio of alcohol/oil: 6:1 - 20:1. The content of FAEE was determined by the method of correlation of the resulting BD by its kinematic viscosity. The maximum FAEE yield (about 90%) was obtained within 30 min at a molar ratio of initial reagents ethanol/oil 12:1 and a temperature of 380 °C.

When describing the processes occurring in a flow tube reactor, a kinetic model of an isothermal plug flow reactor was used. The reaction order implemented in the flow reactor was taken to be one. The first order of the reaction was confirmed by research data on the conversion of FAEE on the reaction time at various temperatures and molar ratios of the initial reagents (ethanol/oil).

The Arrhenius equation was used to calculate the values of the effective constants of the rate of transesterification reaction at different reaction temperatures. In addition, on the basis of the experimental data, the activation energy and the pre-exponential factor of the transesterification reaction were determined.

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