

Theoretical and Experimental Study of Reaction of Transesterification of Vegetable Oils in an Alcohol Environment in the SbCF and SCF Conditions with the Ultrasonic Emulsification of Reaction Mixture and the Use of Heterogeneous Catalysts

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Abstract

A quantum-chemical study of the mechanism of transesterification reaction carried out in the traditional and supercritical fluid (SCF) conditions has been performed. Samples of biodiesel fuel have been derived from rapeseed oil in the environment of supercritical ethanol using a flow type unit, both in the absence and in the presence of heterogeneous catalysts-metal oxides. Experimental studies of kinematic viscosity of a large array of samples of derived biodiesel have been performed. The viscous correlation allowing determining the content of the desired product-fatty acid ethyl esters (FAEE)—in biodiesel samples, has been made based on the obtained experimental data on the kinematic viscosity of biodiesel samples. The influence of change of the dielectric permittivity of working environments on the rate of reaction of transesterification in the supercritical fluid conditions has been revealed.

Keywords

Supercritical Fluids, Biodiesel Fuel, Thermophysical Properties, the Dielectric Permittivity, Reaction Kinetics, Quantum-Chemical Calculations, Heterogeneous Catalysts

1. Introduction

The modern possibilities of mathematical modelling and software allow simpli-

ifying the process of study of the regularities that take place in chemical reactors in the conditions of intensive heat and mass transfer. It is possible to refer safely to such conditions the chemical transformations observed in supercritical fluid environments as well. The acceleration of reaction in the SCF conditions caused, among other things, by the low viscosity of environment and the high diffusion of components, allowing reducing significantly the duration of the process, is extremely important for industrial implementations. During the design of processing facilities, these conditions make it possible to replace static closed reactors by that of the flow type, along with this, by that of smaller geometric dimensions, which, finally, reduces the cost of both operating and capital costs. The use of supercritical fluid condition of reaction mixture during the synthesis of biodiesel fuel determines several undeniable technological and ecological advantages [1] [2] [3]. These advantages are just the ones that are supposed to be converted into the reduction of prime cost of biodiesel fuel, which is still 10% - 20% higher than that of oil diesel fuel, for the traditional homogeneous catalytic process [4].

One of important conditions of creation of economically efficient SCF-technology and, among other things, of derivation of biodiesel fuel, is the search of optimum conditions for carrying out a chemical reaction, which is extremely difficult in the absence of the mathematical model based on the results of experimental studies, including thermophysical ones.

2. Materials and Methods

The bulk of quantum-chemical studies [5] [6] has been formed in the Linux operating system using the program "Priroda, version 4.11" (Laikov D. N., Moscow, Russia), which implements the density functional theory (DFT) method with the PBE(Perdew-Burke-Ernzerhof) density functional and a basis set of effective potentials 3z basis set. The results, by key elementary act, have been confirmed by quantum-chemical calculations using the Becke 3-Parameter (Exchange), Lee, Yang and Parr (B3LYP) method with the 6-311++g (*df*, *p*) basis set within the use of *Gaussian09* (Gaussian, Inc., Pittsburg, USA) programs.

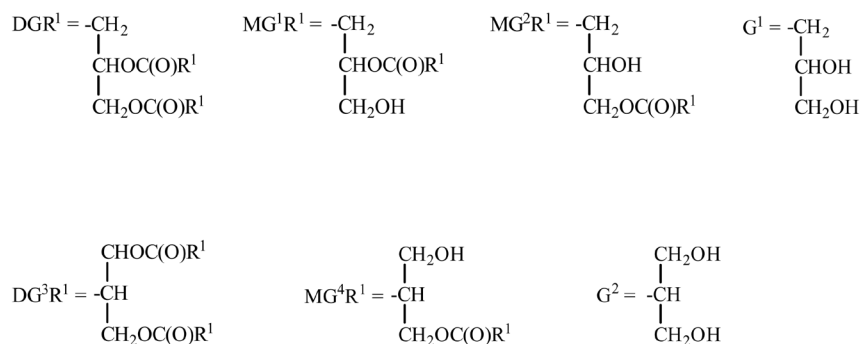
Figures and tables of article are shows the activation energy of the forward (E^{\ddagger}) and reverse (E^{\ddagger}) directions of the reaction and the heat of reaction (Q) in the level of PBE/3z approximation. In addition, given also the thermodynamic characteristics to 298.15 K temperature for the forward direction and reverse direction of the elementary act, respectively: the enthalpy of activation (ΔH^{\ddagger} , ΔH^{\ddagger}_{-}), the activation energy of Gibbs (ΔG^{\ddagger} , ΔG^{\ddagger}_{-}) and entropy of activation (ΔS^{\ddagger} , ΔS^{\ddagger}_{-}), as well as the reaction enthalpy ($\Delta\Delta H$). Mutual conversion of thermodynamic parameters was carried out according to the formula $\Delta G = \Delta H - T\Delta S$.

Transition states are indicated by the abbreviation TS. In the reaction schemes the dotted line highlighted the distance between the atoms of interest for discussion and orientation communication, exceeding a length of 2.6 Å, that is, conditional maximum length of the emerging or breaking hydrogen bond in the transition state. In the reaction schemes in bold are highlighted atoms, which form

new connections between them or broke old connections.

Translation Hartree units in kcal/mol was carried out by the ratio: 1 H_a = 627.5095 kcal/mol, 1 calorie = 4.184 joules.

For schemes and tables the following notation are adopted: R = Alcohol or substructure of diglyceride (DG), monoglyceride (MG) with hydrocarbon substituent R^1 (DGR^1 и MG^1R^1 , MG^2R^1 respectively) and glycerol (G) with the appropriate binding C-O structure in the secondary carbon centre or substructure of diglyceride (DG^3), monoglyceride (MG^4) with hydrocarbon substituent R^1 (DG^3R^1 и MG^4R^1 respectively) and glycerol (G^2) with the corresponding C-O bonding structure at the centre of the tertiary carbon; R^1 = hydrocarbon residue of fatty acids and their analogues; R^2 , R^3 = Me (methanolysis reaction), H (hydrolysis reaction). Hydrocarbon residue of oleic acid is abbreviated-Ole. Structural interpretation of the received specific designations substituents R, R^1 ; R^2 , R^3 :



The transesterification reaction was carried out using the experimental setup shown in **Figure 1**. Raw materials (ethanol (“Ecopharm”, Kazan, Russia, GOST R 51723-2001) and rapeseed oil (“Aston”, Rostov-on-Don, Russia, GOST R 53457-2009)) from tanks (1) and (2) are introduced into a mechanical mixer (4).

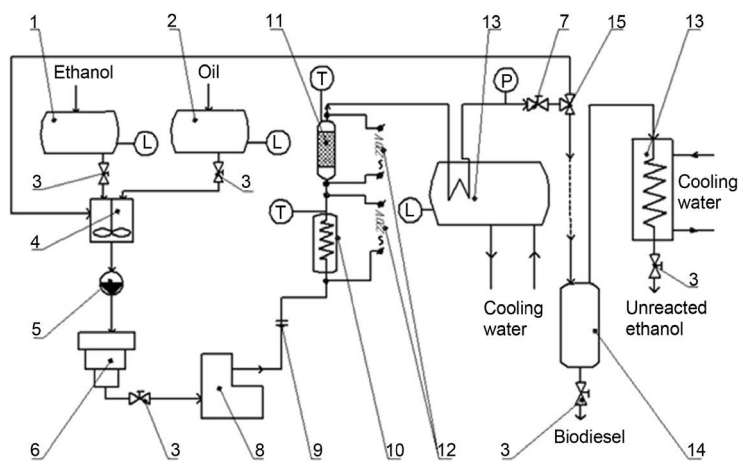


Figure 1. Experimental plant for carrying out a catalytic reaction in the SbCF and SCF conditions: 1-alcohol tank; 2-oil tank; 3, 7 and 15-valves; 4-mixer; 5-pump; 6-emulsifier; 8-dosing pump; 9-insulator; 10-reactor; 11-catalyst section of the reactor; 12-power supply unit; 13-refrigerators; 14-evaporator.

A gear pump (5) allows the mixture to pass through an ultrasonic emulsifier (UIP 1000HD Hielscher (Hielscher Ultrasonics GmbH, Oderstr. 53 D-14513 Teltow, Germany)) (6) pressurized at 0.4 MPa; this pressure is chosen to ensure the maximum mixing efficiency and to obtain a homogeneous and stable emulsion. Then the initial mixture (ethyl alcohol-rape seed oil) in different molar ratios determined with the metering pump (8), at the split-off film evaporator (13), is circulated continuously through the reactor (10), and the catalyst section of the reactor (11), before reaching the predetermined temperature. The processing time varies from 25 to 35 minutes, depending on the reaction conditions. After reaching the predetermined temperature and outputting a steady state within 30 min, the resulting reaction product is fed to the film evaporator (13), by locking the control valves (14), for complete removal of excess alcohol presents in the reaction product after sampling [7].

All experiments were performed under a pressure of 30 MPa. The effects of ethanol to oil molar ratio (12:1, 18:1 and 20:1), the reaction temperature (623 K and 653 K), and the amount and type of catalysts on the conversion ratio of the triglycerides to FAEE were investigated.

The ethyl ester content of the transesterification product was analyzed by gas chromatography-mass spectrometry (GC-MS) using a DFS device from Thermo Electron Corporation (Waltham, Massachusetts, USA). It was equipped with a 5% diphenyl/95% dimethyl polysiloxane stationary phase of a capillary column (Australian company SGE (Scientific Glass Engineering) ID-BP5H (analogue DB-5MS)), using helium as the carrier gas. The dimensions of the column were (50 m × 0.32 mm I.D., and the film thickness 0.25 μm).

After separation in the column, the ionization method was used to quantify the compounds in the stream. The energy of the ionizing electrons was 70 eV and the temperature of the ion source was 553 K.

The requirements to obtain chromatograms are the following: injector temperature of 573 K, split ratio of 1:10; the carrier gas flow through a column of 2 ml/min; the delay time is 50 minutes; the temperatures of the communication device

- 1) Initial temperature: 393 K (1 min);
- 2) The heating rate 20/min up to 573 K.

Sample volume of 0.1 μl is dissolved in ethanol in a ratio of 1: 100. The quantitative analysis was also performed by the method of internal normalization. The processing of mass spectral data is carried out using the program “Xcalibur” (Thermo Electron Corporation (Waltham, Massachusetts, USA)).

3. Discussion

3.1. Quantum-Chemical Study of Transesterification Reaction in the Traditional and Supercritical Fluid Conditions

Due to the presence of water in the initial mixture of reagents when carrying out a transesterification reaction, a competitive reaction of hydrolysis is considered along with the main reaction. **Figure 2** presents the chemistry of reactions.

There are one or two elementary acts of reaction, depending on the participating alkoxy-carbonyl group (**Figure 3** and **Figure 4**). The traditional reaction under atmospheric pressure without the use of catalysts is impossible to be carried out due to the high-energy barrier $E_a = 33.66$ kcal/mol (**Table 1**).

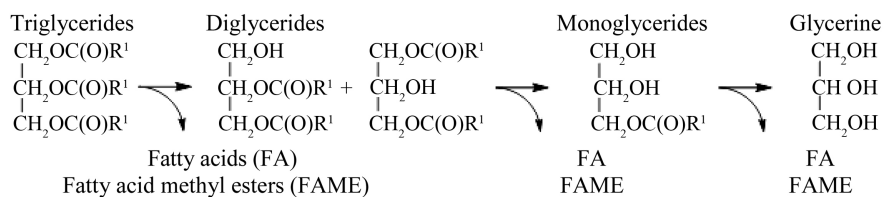


Figure 2. Stages of reformation of triglycerides during methanolysis and hydrolysis with the consecutive intermediate formation of diglycerides, monoglycerides and the final formation of glycerine, FA or FAME; R^1 is a hydrocarbon residue of fatty acids and their analogues.

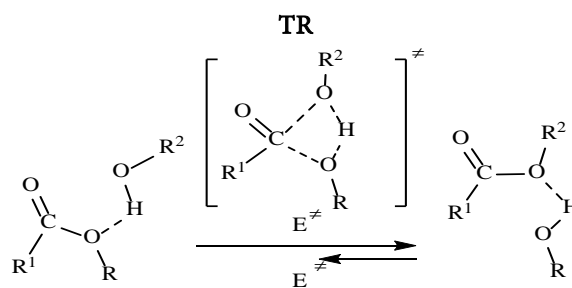


Figure 3. Elementary acts of single-stage transesterification and hydrolysis of triglycerides with the participation of alkoxy-carbonyl group and monomeric form of methanol.

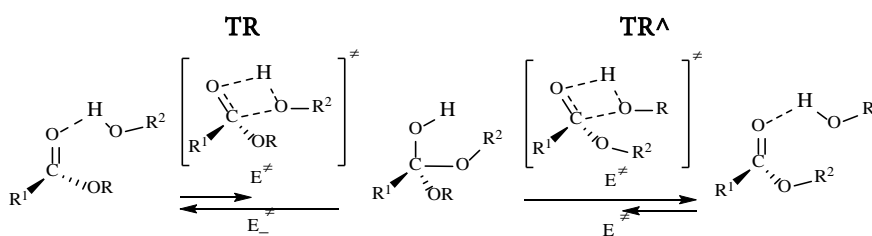


Figure 4. Elementary acts of two-stage transesterification and hydrolysis of triglycerides and its analogues with the participation of alkoxy-carbonyl group and monomeric form of methanol.

The participation of dimeric associate of methanol in the reaction (**Figure 5**) is energetically more effective (**Table 2**) than the participation of trimeric associate (**Figure 6**) (27.47 and 31.78 kcal/mol, respectively). The presence of glycerine in the initial mixture only slightly affects the energy of the process. The presence of several percent of water in alcohol provides that there is a relatively large potential trap (10.33 kcal/mol) for products of forward reaction (**Table 2**) for the glycerine-water associate pair when interacting with a triglyceride alkoxy-carbonyl bond. Because of hydrolysis reaction, fatty acids that act as catalysts are

Table 1. Calculated energy and thermodynamic characteristics (in kcal/mol, ΔS^\ddagger in cal/mol·K) of reaction systems under normal conditions ($P = 1$ atm, $t = 25^\circ\text{C}$) (corresponding to **Figure 3** and **Figure 4**) in the approximation of the PBE/3z and B3LYP/6-311++G (*df, p*) methods.

Substituting groups			Density functional	Forward reaction				Reverse reaction				Heat effect and enthalpy of reaction	
R	R ¹	R ²		E^\ddagger	ΔH^\ddagger	ΔG^\ddagger	ΔS^\ddagger	E^\ddagger_{-}	ΔH^\ddagger_{-}	ΔG^\ddagger_{-}	ΔS^\ddagger_{-}	Q	$\Delta\Delta H$
Figure 2													
Me	Me	Me	PBE	33.66	30.33	35.45	-17.17	33.66	30.33	35.51	-17.38	0.00	0.00
Me	Me	Me	B3LYP	46.50	41.45	46.53	-70.88	46.50	41.45	46.53	-70.90		0.00
DGMe	Me	Me	PBE	33.31	30.10	36.12	-20.20	35.12	31.86	37.15	-17.74	1.80	-1.76
Figure 3													
Me	Me	Me	PBE	36.79	33.36	38.22	-16.31	25.16	21.70	21.15	1.85	11.63	-11.66
Me	Me	Me	B3LYP	46.18	41.12	46.22	-71.06	26.64	27.38	26.63	10.43		-13.74
Me	Me	Me	PBE	25.16	21.70	21.15	1.85	36.79	33.36	38.22	-16.31	11.63	-11.66

Table 2. Calculated energy and thermodynamic parameters (in kcal/mol, ΔS^\ddagger in cal/mol·K) of reaction systems under normal conditions ($P = 1$ atm, $T = 25^\circ\text{C}$) (corresponding to **Figure 5** and **Figure 6**) in the approximation of DFT methods with the PBE/3z and B3LYP/6-311++G (*df, p*) density functional.

Substituting groups				Density functional	Forward reaction				Reverse reaction				Heat effect and enthalpy of reaction	
R	R ¹	R ²	R ³		E^\ddagger	ΔH^\ddagger	ΔG^\ddagger	ΔS^\ddagger	E^\ddagger_{-}	ΔH^\ddagger_{-}	ΔG^\ddagger_{-}	ΔS^\ddagger_{-}	Q	ΔH
Me	Me	Me	Me	PBE	28.37	23.88	30.27	-21.32	28.37	23.88	30.27	-21.41	0.0	0.0
Me	Me	Me	Me	B3LYP	42.01	36.06	42.04	-83.47	42.01	36.06	42.04	-83.47		0.0
DGMe	Me	Me	Me	PBE	27.47	23.22	30.14	-23.22	30.75	26.27	32.38	-20.48	3.3	-3.0
DGMe	Me	Me	Me	B3LYP	32.03	30.53	36.33	-59.93	36.26	32.58	40.33	-56.83		-4.2
DGMe	Me	DGMe	Me	PBE	28.67	24.24	30.14	-19.79	29.77	25.43	31.60	-20.69	1.1	-1.2
DGMe	Me	Me	DGMe	PBE	30.80	26.26	31.40	-17.23	32.52	27.87	32.35	-14.99	1.7	-1.6
DGMe	Me	G ¹	Me	PBE	28.83	25.03	29.19	-13.93	29.74	25.18	30.60	-18.21	0.9	-0.1
DGMe	Me	Me	G ¹	PBE	27.83	23.48	29.93	-21.64	30.98	26.35	31.92	-18.69	3.1	-2.9
DG ³ Me	Me	Me	G ²	PBE	27.64	23.11	30.33	-24.22	30.68	26.00	32.84	-24.22	3.0	-2.9
DG ³ Me	Me	H	G ¹	PBE	28.96	25.51	31.88	-21.36	39.30	35.81	42.06	-20.94	10.3	-10.3
DG ³ Me	Me	H	G ¹	B3LYP	35.70	33.42	39.28	-49.93	44.56	42.91	47.98	-47.64		-8.9
DGMe	Me	H	Me	PBE	33.08	29.44	33.62	-14.00	40.55	37.41	39.22	-6.06	7.4	-7.9
DGMe	Me	H	Me	B3LYP	35.89	38.52	36.76	-26.76	48.62	46.81	45.45	-13.61		-6.9
DGMe	Me	Me	H	PBE	28.58	25.44	30.96	-18.50	34.33	31.05	35.06	-13.45	5.8	-5.6
DGMe	Me	Me	H	B3LYP	35.60	40.00	35.69	-12.96	40.62	44.18	40.95	-14.69		-5.0
Me	Me	Me	H	PBE	31.02	26.82	32.19	-17.99	28.77	24.82	28.98	-13.97	-2.3	2.0
Me	Me	Me	H	B3LYP	36.16	39.92	37.57	-22.57	38.84	32.22	37.17	-17.17		2.7

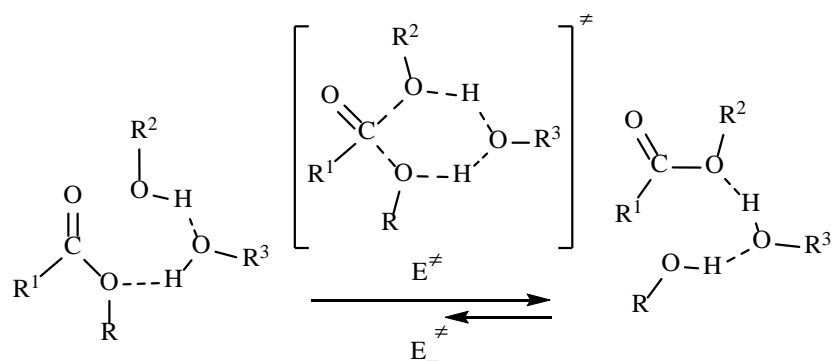


Figure 5. Elementary acts of single-stage transesterification and hydrolysis of triglycerides with the participation of triglyceride alkoxy-carbonyl group of the dimeric associate of methanol and its substitution analogues.

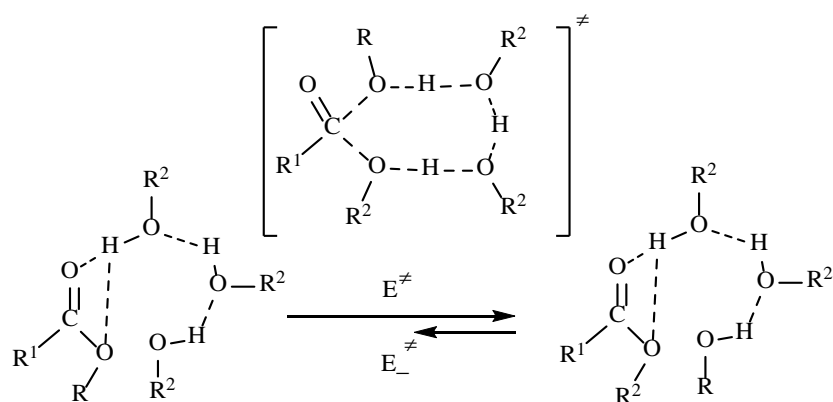


Figure 6. Elementary act of single-stage transesterification of methyl acetate (the analogue of triglycerides) with the participation of alkoxy-carbonyl group and trimeric associate of methanol.

formed making the process autocatalytic.

Table 3 gives the results of quantum-chemical calculations of the transesterification reaction carried out in the SCF conditions. The constant of reaction rate calculated using the formula (1) sharply increases with an increase in temperature, which indicates the high rate of reaction in the SCF conditions (**Figure 7** and **Figure 8**) [8].

The formula for calculating the rate constants of the pseudo-first order reaction is:

$$K = k \cdot T \cdot h^{-1} e^{-\Delta G^{\ddagger}/RT} \quad (1)$$

where $k = 1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ (Boltzmann constant), T is temperature in kelvins, $h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$, $R = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$ (the universal gas constant), $e = 2.71828$, ΔG^{\ddagger} is Gibbs energy of activation.

According to the rule of Semenchenko, the most preferable solvent is the one with dielectric permittivity, the closest to substance dissolved, under dissolution conditions. From this point of view, it seems quite logical that the area of sharp increase in the reaction rate in **Figure 8** accrues to the range of close values of dielectric permittivity of oil and alcohol (**Figure 9**).

Table 3. Calculated energy and thermodynamic characteristics (in kcal/mol) of reaction systems within the temperature range of 300 - 623 K ($P = 30$ MPa) in the approximation of the B3LYP method with the 6-311++g (*df, p*) basis.

T (K)	$\Delta\Delta H$ (kcal/mol) fwd	$\Delta\Delta H$ (kcal/mol) rev	Q (kcal/mol)	$\Delta\Delta G$ (kcal/mol) fwd	$\Delta\Delta G$ (kcal/mol) rev
First stage of elementary act					
300	30.91	16.33	14.58	34.49	17.08
400	30.64	16.21	14.43	35.73	17.36
500	30.45	16.07	14.38	37.02	17.66
600	31.1	11.3	19.8	38.35	17.99
623	30.29	15.94	14.35	38.66	18.07
First stage of elementary act					
300	11.78	31.65	-19.87	12.58	35.69
400	11.62	31.42	-19.8	12.87	37.07
500	11.45	31.23	-19.78	13.2	38.5
600	11.3	31.1	-19.8	13.57	39.97
623	11.27	31.07	-19.8	13.65	40.31

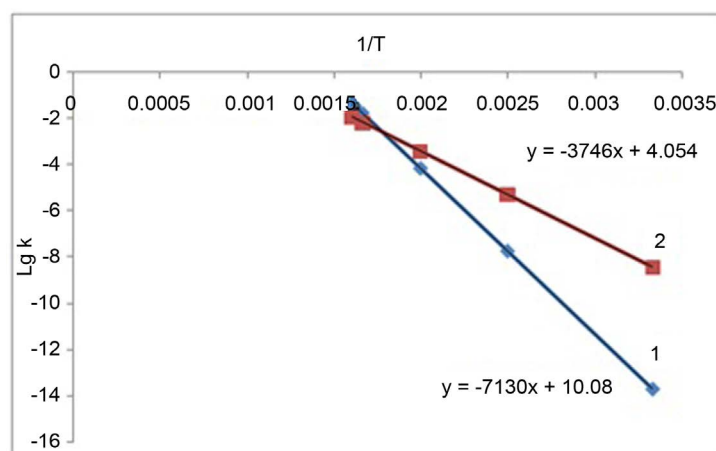


Figure 7. Dependences of $LgK - 1/T$ for the *forward* single-stage reaction (1) and the *forward direction* of the first stage of two-stage reaction (2) of methanolysis of elementary analogue of triglyceride-triacetin.

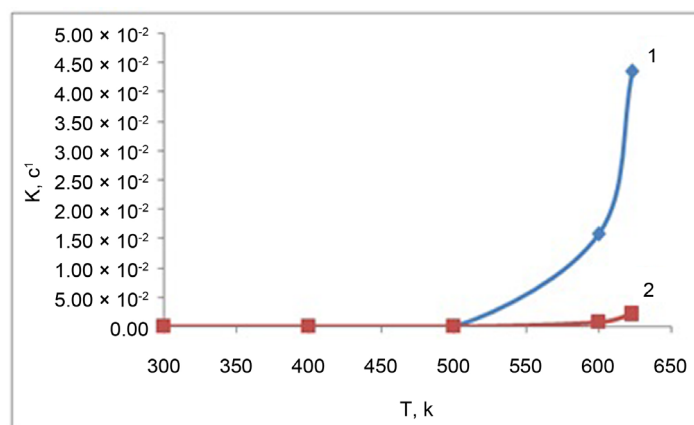


Figure 8. Dependences of constants of rates of single-stage methanolysis of elementary analogue of triglyceride-triacetin on temperature (1-the forward elementary act, 2-the reverse elementary act).

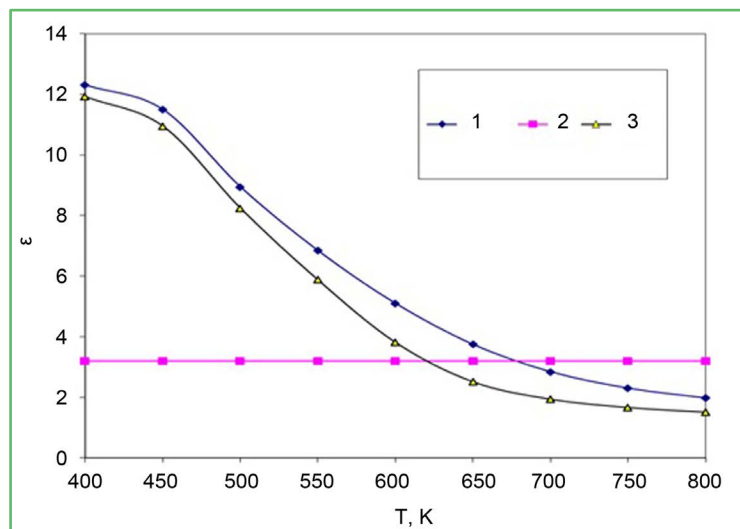


Figure 9. Dielectric permittivity of ethyl alcohol and rapeseed oil (1—ethyl alcohol under the pressure of 20 MPa, 2—rapeseed oil, 3—ethyl alcohol under the pressure of 30 MPa).

3.2. Transesterification of Vegetable Oils in an Alcohol Environment in the SbcF and SCF Conditions with the Ultrasonic Emulsification of Reaction Mixture and the Use of Heterogeneous Catalysts of Various Chemical Nature

The low miscibility of vegetable oils with alcohols under normal and often other conditions determines a relatively small surface of contact of phases which, eventually, reduces the completeness of transesterification reaction. The use of ultrasonic emulsifier allows increasing significantly the area of contact of phases, and, respectively, the rate of chemical reaction.

According to many articles, to accelerate the transesterification reaction in supercritical conditions heterogeneous catalysts are used [9] [10] [11] [12] [13]. The granulated Al_2O_3 carrier/catalyst and the samples of catalysts $\text{ZnO}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Al}_2\text{O}_3$ and $\text{SrO}/\text{Al}_2\text{O}_3$ derived using the impregnation method are characterized by polymodal pore distribution with the prevalence of pores in diameters of 5 - 10 nm. The texture of synthesized samples of catalysts is slightly different from the texture of the initial aluminum oxide, except for an insignificant, within 10%, decrease in the volume of mesopores in the sample containing 5% of active component of the total weight of catalyst. Studies of the problem of regeneration of heterogeneous catalysts and, first of all, active aluminum oxide have been conducted [14] [15] [16] [17].

Figure 10 and **Figure 11** provide the characteristics of non-catalytic and catalytic reactions of transesterification of rapeseed oil in the environment of ethanol carried out in the temperature range of 623 - 653 K under the pressure of 30 MPa and the ethanol-rapeseed oil molar ratios of 12:1 and 18:1 with the use of heterogeneous catalysts Al_2O_3 , $\text{ZnO}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Al}_2\text{O}_3$, $\text{SrO}/\text{Al}_2\text{O}_3$ with various degrees of impregnation (1% - 5%) of the carrier [7].

The use of ultrasonic emulsification of initial reaction mixture and heterogeneous catalysis has allowed to intensify the reaction and to receive high values of

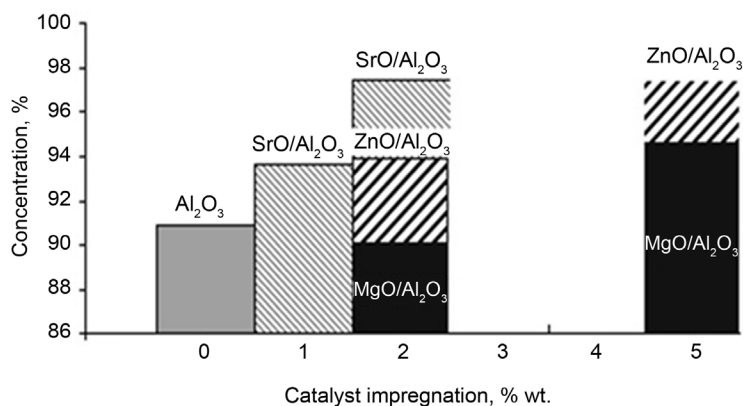


Figure 10. Concentration of FAEE in the reaction product in case of the use of catalysts with various degrees of impregnation: T = 623 K, P = 30 MPa, the mole ratio is 12:1.

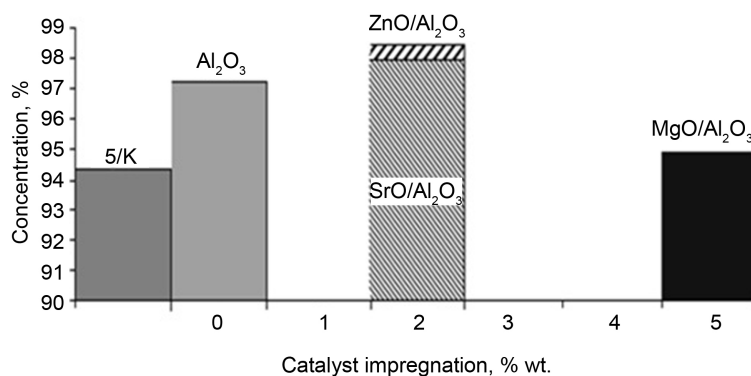


Figure 11. Concentration of FAEE in the reaction product in case of the use of catalysts with various degrees of impregnation: T = 638 K, P = 30 MPa, the mole ratio is 18:1.

conversion with rather low values of the alcohol/oil molar ratio (18:1 and even lower). In case of the reaction carried out with T = 623 K and the molar ratio of 12:1 with the use of heterogeneous catalyst an evident growth (up to 20%) of concentration of FAEE in the reaction product in comparison to the non-catalytic variant of reaction has been established. At the same time, in case of the catalytic reaction carried out with T = 653 K and the molar ratio of 18:1 the similar growth of concentration of FAEE was only about 4%. The catalytic properties of Al₂O₃ were the least preferable among the studied catalysts. The catalysts with the impregnation of the carrier (ZnO/Al₂O₃ and MgO/Al₂O₃) of 5% for the reaction carried out with T = 623 K and the molar ratio of 12:1 are more effective than the catalysts with the impregnation of 2%. SrO/Al₂O₃ together with MgO/Al₂O₃ and ZnO/Al₂O₃ is most preferable among the catalysts with the impregnation of 2%. The increase in the temperature of reaction within the range of T = 638 - 653 K is followed by a decrease in the concentration of FAEE in the reaction product because of the thermal decomposition of esters of unsaturated fatty acids with the formation of ortho-esters of carbon acids. Glycerine decomposes in this case as well, with the formation of ethyl esters of glycerine, water

and FAEE with a lower molecular weight changing within the range of C8-C14 which provides that the mechanism of the reaction carried out in the SCF conditions slightly differs from the reaction mechanism within the traditional method of receiving biodiesel fuel and has the following form:



The correlation dependence of the content of FAEE in the product of reaction of transesterification of vegetable oils in the alcohol environment carried out in the SCF-conditions from the value of kinematic viscosity coefficient of reaction product (“viscosity correlation”) (2) implemented by means of measurements of kinematic viscosity coefficient of samples of biodiesel fuel, numerous and various in reaction conditions, has been studied. The kinematic viscosity of the biodiesel fuel samples was measured with commercial capillary viscometer VPZ-2 (Labtex Com., Moscow). All samples were measured at least 7 - 10 times. The estimated combined expanded uncertainty (standard uncertainty multiplied by the factor of k) of the kinematic viscosity measurements at the 95% confidence level with a coverage factor of $k = 2$ is to be 0.35% (the standards uncertainty is 0.18%, stating the expanded uncertainty). The repeatability of viscosity measurements is 0.1% [18]. According to this study the kinematic viscosity coefficient of samples of biodiesel fuel decreases with an increase in temperature, duration of reaction and value of molar ratio of the “ethanol/rape oil” initial mixture (Figures 12-15).

The use of catalyst increases the reaction rate and the yield of the desired product (FAEE) the viscosity of which concedes in value to the viscosity of vegetable oil which, thus, determines an additional decrease in the viscosity of reaction product (Figures 12-15).

The “viscosity correlation” (2) of content of FAEE in the samples of biodiesel fuel received in the SCF conditions is based on the IR-spectrometric analysis of compositions of samples of biodiesel fuel and has the following quantitative

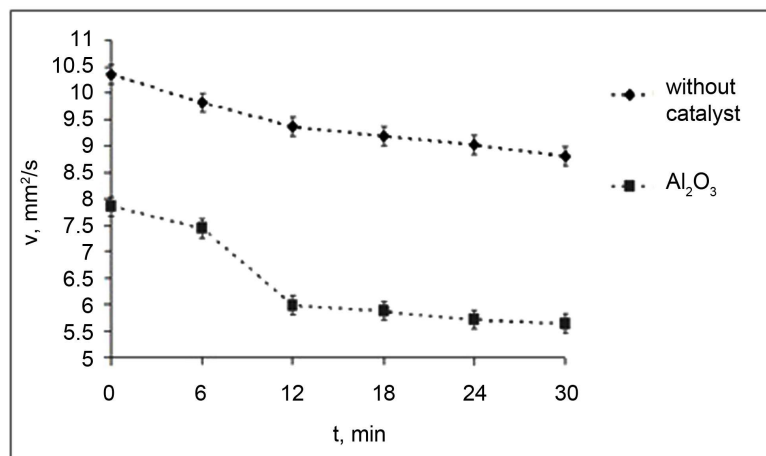


Figure 12. Kinetics of change of kinematic viscosity coefficient of samples within the reaction with (Al_2O_3) and without a catalyst (a flow type plant, the molar ratio is 12:1, $T = 623 \text{ K}$).

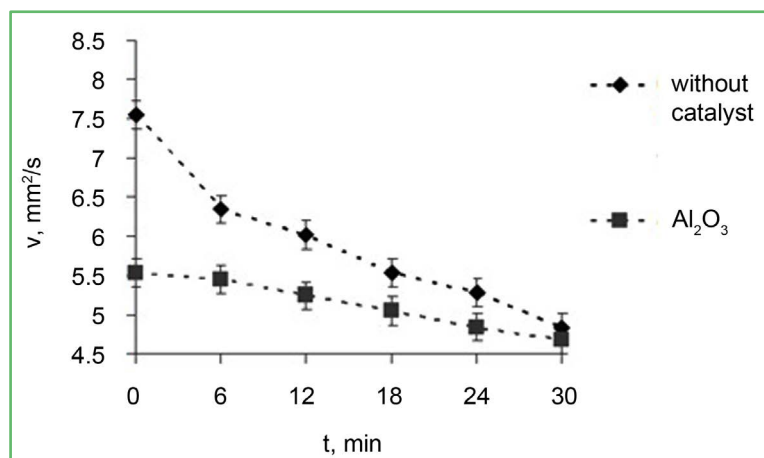


Figure 13. Kinetics of change of kinematic viscosity coefficient of samples within the reaction with (Al_2O_3) and without a catalyst (a flow type plant, the molar ratio is 18:1, $T = 653 \text{ K}$).

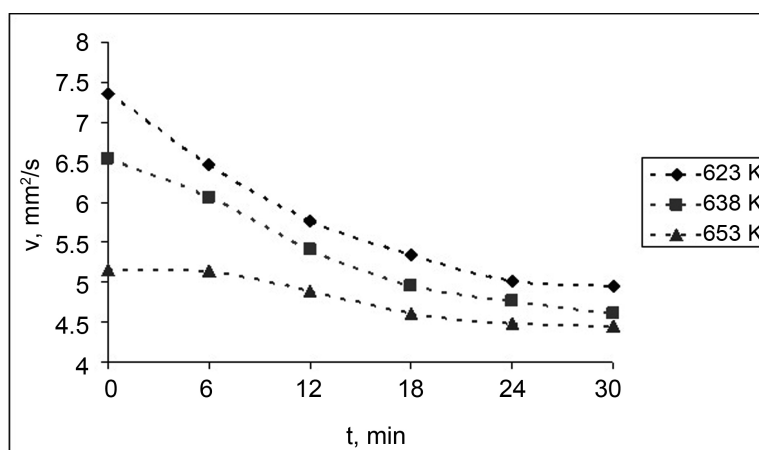


Figure 14. Kinetics of change of kinematic viscosity coefficient of samples within the reaction with (Al_2O_3) (a flow type plant, the molar ratio is 20:1, $T = 623 - 653 \text{ K}$).

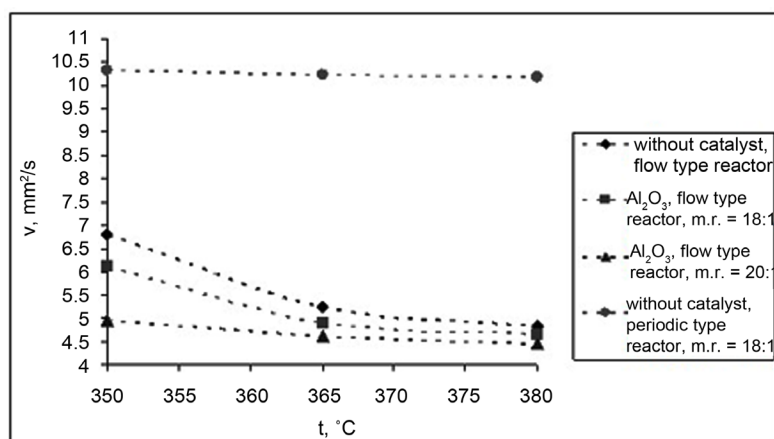


Figure 15. Dependence of kinematic viscosity coefficient of samples within the reaction with the Al_2O_3 catalyst and without a catalyst on temperature (the molar ratio is = 18:1 and 20:1).

characteristics:

$$W = A \ln(\nu) + B; \quad \nu = \exp(W/A - C) \quad (2)$$

where W is the concentration of FAEE in the sample of biodiesel fuel, % wt.; ν is kinematic viscosity, $\text{mm}^2 \cdot \text{s}^{-1}$; A , B and C are empirical parameters ($A = -49.392473$; $C = -3.513642$; $C = B/A$). The ratio (2) sufficiently describes the samples of biodiesel fuel received both in the absence (Table 5) and in the presence of heterogeneous catalysts (Table 6). Several selected biodiesel fuel samples obtained with different molar ratio ethanol: rapeseed oil for different temperatures (623 K, 638 K, and 653 K) were also analyzed with a GC-MS (Figure 16, Table 4) to confirm the viscosity analyses results. The last column of Table 5, Table 6 contains the values of FAEEs concentration obtained using GC-MS analyses. The agreement between the viscosity correlation and GC-MS analyses is good enough.

4. Conclusion

As a result of quantum-chemical study of the mechanism of reaction of transesterification of triglycerides of fatty acids and their analogues in the supercritical

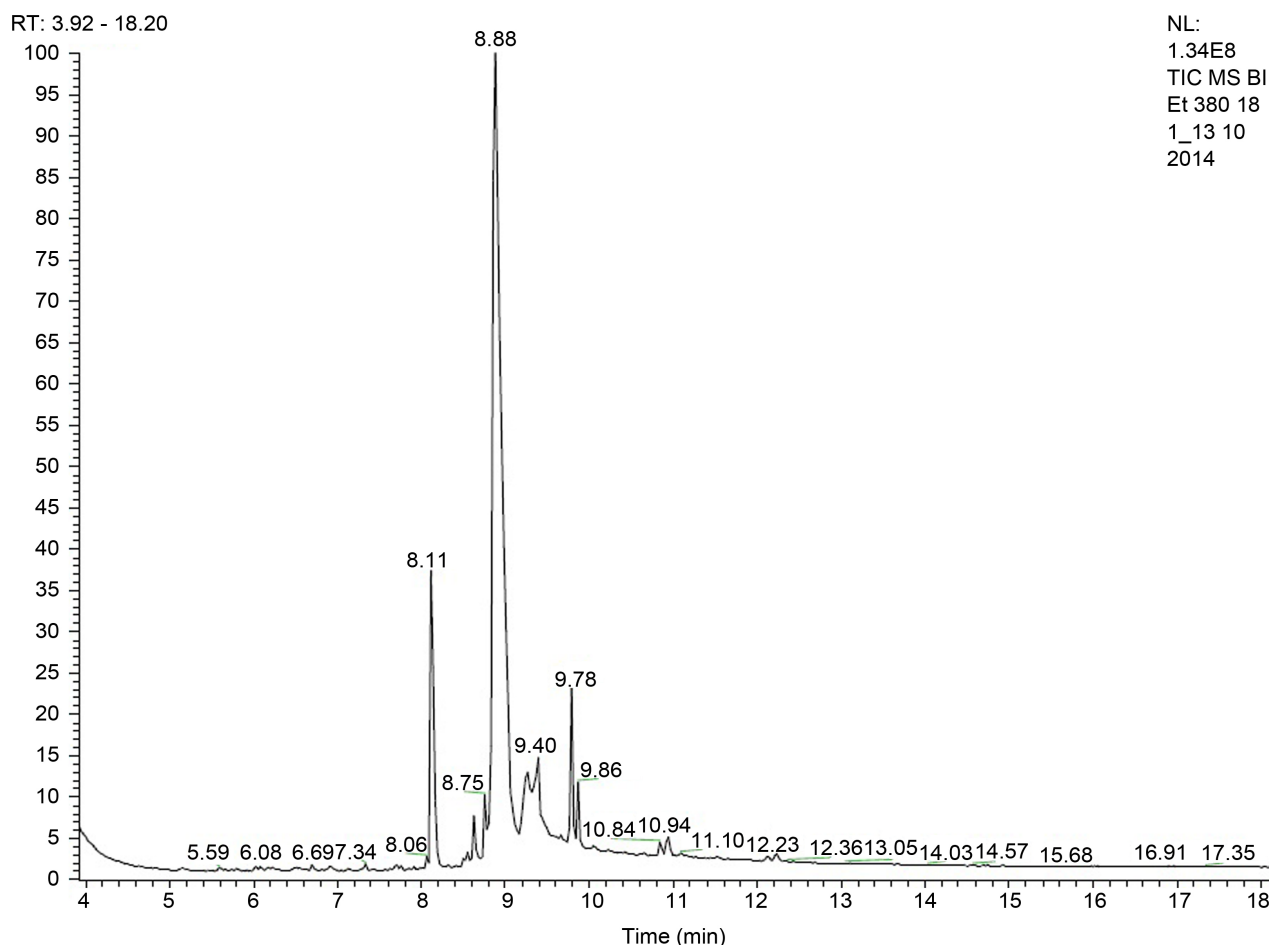


Figure 16. Chromatogram of obtained biodiesel fuel sample using a catalyst $\text{ZnO}/\text{Al}_2\text{O}_3$ ($T = 653 \text{ K}$, molar ratio “ethanol: rapeseed oil”-18:1).

Table 4. Principal GC-MS peaks data of biodiesel fuel samples from rapeseed oil after supercritical fluid transesterification.

Retention time (min)	Component	Chemical formula	Peak area (mm ²)	Concentration (wt %)
8.11	Ethyl esters (EE) of palmitin acid	C ₁₈ H ₃₆ O ₂	1.45 × 10 ⁸	11.9
8.88	EE of oleate acid	C ₂₀ H ₃₈ O ₂	9.17 × 10 ⁸	75.24
9.24	EE of linolenate acid	C ₂₀ H ₃₄ O ₂	3.51 × 10 ⁷	2.89
9.86	EE of arachidonic acid	C ₂₂ H ₄₄ O ₂	1.61 × 10 ⁷	1.32
10.84	EE of hypogeic acid	C ₁₈ H ₃₄ O ₂	2.99 × 10 ⁶	0.25
10.94	EE of behenic acid	C ₂₄ H ₄₈ O ₂	8.65 × 10 ⁶	0.71

Table 5. Content of FAEE (% wt.) in the samples of product of transesterification reaction carried out in the SCF conditions with the preliminary ultrasonic emulsification of reaction mixture according to the results of GS-MS and within “viscosity correlation”.

Molar ratio of initial reagents	Temperature of reaction mixture, K	Viscosity, mm ² /s	Content of FAEE, % in the samples by viscosity correlation (2)	Content of FAEE, % in the samples according to the data of GC-MS
6:1	623	14.466	41.58	42.41
	638	14.412	41.76	49.87
	653	12.444	49.01	50.26
8:1	623	9.444	62.64	63.21
	638	8.844	65.88	65.12
	653	6.828	78.66	80.11
10:1	638	8.394	68.46	68.34
	653	6.636	80.07	80.54
	608	9.882	60.40	60.39
12:1	623	8.802	66.12	66.50
	638	7.578	73.51	72.77
	653	6.036	84.75	81.92
16:1	653	4.986	94.19	92.08
	623	5.302	91.15	92.25
18:1	638	5.040	93.65	93.66
	653	4.830	95.76	94.56
	608	8.002	70.82	71.12
20:1	623	6.054	84.60	85.41

fluid conditions, it has been established that alcohol dimers participate in the reaction. The reaction is autocatalytic due to the presence of several percent of water in the initial mixture and the formation of carbonic acids. The rate of reaction of transesterification sharply increases in the SCF conditions. The use of

Table 6. Content of FAEE (% wt.) in the samples of product of the transesterification reaction carried out in the SCF conditions with the preliminary ultrasonic emulsification of reaction mixture and the use of heterogeneous catalysts.

Catalysts used for the transesterification reaction	Temperature of reaction and molar ratio of the initial reagents	Content of FAEE, % in the samples by viscosity correlation (2)	Content of FAEE, % in the samples according to the data of GC-MS
Non-catalytic reaction	623 K (12:1)	66.11	64.21
	653 K (18:1)	95.76	94.25
Al ₂ O ₃	623 K (12:1)	88.15	87.1
	653 K (18:1)	97.36	96.0
ZnO/ Al ₂ O ₃	623 K (12:1)	86.48	85.2
	653 K (18:1)	91.32	92.2
MgO/ Al ₂ O ₃	623 K (12:1)	84.11	84.11
	653 K (18:1)	89.30	90.5
SrO/ Al ₂ O ₃	623 K (12:1)	80.92	82.0
	653 K (18:1)	94.37	94.1

heterogeneous metal oxide catalysts allows to reduce the temperature of process and the molar ratio of the initial alcohol and oil reagents.

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