

DFT Study of Transesterification and Hydrolysis of the Fatty Acid Triglycerides, Carried Out under Supercritical Fluid Conditions. Analysis of Thermochemistry and Kinetics

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Abstract: By quantum-chemical simulation using DFT method with B3LYP density functional and basis 6-311++g(df, p) in the implementation of the program Gaussian16 and subsequent comparison with calculations data, obtained by using density functional wB97XD/6-311++g(df, p), mechanism of reactions of transesterification and hydrolysis of fatty acid triglycerides, carried out under supercritical fluid conditions has been investigated. The energy characteristics of the elementary acts of potential steps for Supercritical Fluid (SCF) conditions has been calculated, their thermochemical analysis has been given, the rate constants of elementary acts for the temperature range 300-623 K has been investigated. It is shown that under supercritical fluid conditions, transesterification and hydrolysis of fatty acid triglycerides with dimer and trimer associates of alcohol and water in various combinations can proceed by one-step and two-step mechanism.

Key words: Kinetics, quantum-chemical simulation, fatty acid triglycerides, supercritical fluid state, transesterification, hydrolysis

INTRODUCTION

The depletion of non-renewable energy resources causes the search for alternative renewable energy sources. An alternative to petroleum diesel fuel can be biodiesel fuel which is a product of the transesterification reaction of vegetable oils and fats in alcohol medium (more often methanol or ethanol). One of the ways to produce biodiesel is to carry out a transesterification reaction in Supercritical Fluid (SCF) conditions ($T = 573-673$ K, $P = 20-30$ MPa), thereby increasing the reaction rate, there is no need for a catalyst and therefore, its isolation and saponification products from of the reaction product, so, the process becomes less staged (Mazanov *et al.*, 2016). By Dos Santos *et al.* (2011), three ways of reaction were considered and it was concluded that according to the values of the activation energy obtained by the Electrostatic Potential distribution (ESP) method, the transesterification of the central ester bond is more preferable than the peripheral etheral bonds. Due to the presence of water in alcohol, a hydrolysis reaction occurs in parallel with the alcoholysis reaction. Alkyl-catalyzed alcoholysis of monoglycerides has been investigated by a number of researchers (Dos Santos *et al.*, 2011; Asakuma *et al.*, 2009) and alkaline hydrolysis of esters in the gas phase has been theoretically studied by the ab initio method, the reaction pathway has been described and energy barriers have been obtained (Yates, 1971; Lopez *et al.*, 2005, 2007; Papageorgiou *et al.*, 1996). The basic knowledge of

methanolysis and its competing reaction of triglyceride hydrolysis at the molecular level are of great importance for the development of biodiesel production. A DFT/B3LYP study of glycerol triacetate or triacetin as a model triglyceride compound was conducted in the presence of a sulfated zirconia catalyst and they were detected by the adsorption of triacetin and an alcohol solvent which caused the exchange H of alcohol with the group of triacetin which then causes the transesterification process to produce the experimentally observed methyl acetate (Muniz *et al.*, 2016; Delesma *et al.*, 2017).

We made a DFT study of the effects of various chemical reactions on the production of the second generation biodiesel fuel, carried out by transesterification of fatty acids triglycerides in an alcoholic medium, performed under supercritical fluid conditions and also use triacetin as a model compound. The reaction of fatty acids triglycerides transesterification, excluding catalytic specificity, may flow through a two-step (Fig. 1) and one-step mechanism (Fig. 2). In this case, the second reactant is dimer associate of methyl or ethyl alcohols and their substitutional analogs. The validity of study of the dimer associates reactivity follows from (Yamaguchi *et al.*, 2000) in which by the method of pulsed neutron diffraction with isotopic substitution of the hydroxyl hydrogens, the methanol structures in two relating to supercritical fluid (623, 117.7 and 623 K, 14.3 MPa) and a subcritical fluid (500 K, 73.7 MPa) conditions has been studied. It is shown that large clusters of methanol in SCF conditions are broken down into

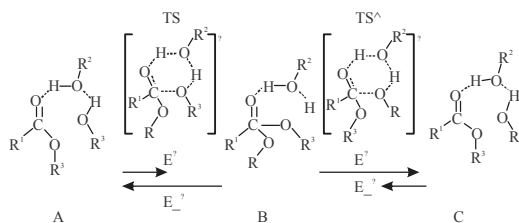


Fig. 1: Elementary acts of a two-step transesterification and hydrolysis of triglycerides with the carbonyl group of triglyceride and dimer associate of methanol and its substitution analogs or homologs

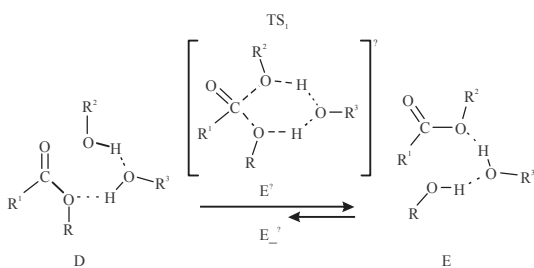


Fig. 2: Elementary acts of the one-step transesterification and hydrolysis of triglycerides with an alkoxy carbonyl group of triglyceride and dimer associate of methanol and its substitution analogs

monomers or small oligomers, resulting in the average number of hydrogen bonds per molecule drops to 1.0 ± 0.1 and the corresponding length of the chain is reduced to 1.8 ± 0.2 in the molecular basis. Thermodynamic conditions in the framework of this simulation correspond to the above, it proves the legitimacy of operating it with methanol dimers. The latter is determined by the fact that the activation energy in the interaction of fatty acid triglycerides analogues with the monomeric form of alcohol are less preferred (average of 5 kcal mol^{-1}) than in case of interaction with the dimer of alcohol analogues (Table 1).

On the other hand, the dimer of alcohol and its substitution analogs forms hydrogen associates with fatty acids triglycerides of unshared electron pairs of their carboxyl and alkoxy oxygen atoms. These hydrogen associates is extremely easy to break and re-form due to metabolic processes. The activation energy in this case is estimated in the range of $1\text{-}3 \text{ kcal mol}^{-1}$. Dimer of the alcohol is always present in an amount, sufficient for transformation of fatty acid triglycerides.

Before turning to a discussion of the results of quantum-chemical calculations, it is important to understand how gas-phase quantum-chemical approach is applicable to reactions in supercritical fluid conditions.

The first noticeable change in the activation characteristics of the reaction systems according to experimental studies observed only at pressures close to

Table 1: The calculated energy and thermodynamic parameters (in kcal mol^{-1}) of the reaction system under normal conditions ($P = 0.1 \text{ MPa}$, $T = 298 \text{ K}$) (corresponding to Fig. 1, 2) in the DFT approach with the density functionals wB97XD/6-311++G(df, p) and B3LYP/6-311++G(df, p)

Transition state	Substitutes				Functional of density	Forward reaction direction			Reverse reaction direction			Thermal effect and reaction enthalpy	
	R	R ¹	R ²	R ³		E ⁺	ΔH^+	ΔG^+	E ⁻	ΔH^-	ΔG^-	Q	ΔH
TS	DGMe	Me	Me	Me	wB97XD	27.99	27.37	31.05	14.21	13.59	14.11	-13.78	13.78
TS [^]	DGMe	Me	Me	Me	wB97XD	10.75	10.13	10.82	28.98	28.36	32.49	18.23	-18.23
TS	DGMe	Me	Me	Me	B3LYP	29.75	29.13	34.44	17.13	16.51	17.63	-12.62	12.62
TS [^]	DGMe	Me	Me	Me	B3LYP	12.75	12.13	13.01	32.46	31.84	34.17	19.71	-19.71
TS	DGEt	Et	H	H	B3LYP	33.97	33.35	38.49	18.21	17.59	19.22	-15.76	15.76
TS [^]	DGEt	Et	H	H	B3LYP	17.48	16.86	18.41	33.04	32.42	37.37	15.56	-15.56
TS	DGEt	Et	H	Me	wB97XD	29.96	29.34	32.52	14.94	14.32	16.42	-15.02	15.02
TS [^]	DGEt	Et	H	Me	wB97XD	13.76	13.14	13.21	29.56	28.94	31.41	15.80	-15.80
TS	DGEt	Et	H	Me	B3LYP	30.85	30.23	34.95	17.53	16.91	17.87	-13.32	13.32
TS [^]	DGEt	Et	H	Me	B3LYP	16.27	15.65	16.56	30.15	29.53	33.42	13.88	-13.88
TS	DGMe	Me	G ¹	H	wB97XD	24.88	24.26	29.06	9.33	8.71	10.38	-15.55	15.55
TS [^]	DGMe	Me	G ¹	H	wB97XD	11.07	10.44	10.43	26.59	25.97	29.38	15.52	-15.52
TS	DGMe	Me	G ¹	H	B3LYP	29.29	28.67	34.12	10.68	10.06	13.07	-18.61	18.61
TS [^]	DGMe	Me	G ¹	H	B3LYP	15.44	14.82	14.91	28.31	27.69	31.88	12.87	-12.87
TS	DGMe	Me	Me	H	wB97XD	24.22	23.60	28.45	9.53	8.91	10.83	-14.69	14.69
TS [^]	DGMe	Me	Me	H	wB97XD	10.97	10.35	11.54	24.85	24.23	30.48	13.88	-13.88
TS	DGMe	Me	Me	H	B3LYP	29.03	28.41	34.02	11.11	10.49	13.47	-17.92	17.92
TS [^]	DGMe	Me	Me	H	B3LYP	15.00	14.38	14.83	28.46	27.84	31.99	13.46	-13.46
TS	DGMe	Me	H	Me	B3LYP	29.41	28.79	34.11	11.44	10.82	13.77	-17.97	17.97
TS [^]	DGMe	Me	H	Me	B3LYP	15.34	14.72	14.58	28.27	27.65	31.92	12.93	-12.93
TS	DG ³ Me	Me	H	Me	B3LYP	29.49	28.87	34.48	11.60	10.98	13.86	-17.89	17.89
TS [^]	DG ³ Me	Me	H	Me	B3LYP	15.51	14.89	14.67	28.46	27.84	32.07	12.95	-12.95
TS	DG ³ Me	Me	G ¹	H	wB97XD	25.99	25.37	29.46	9.56	8.94	10.96	-16.43	16.43
TS [^]	DG ³ Me	Me	G ¹	H	wB97XD	11.48	10.86	12.67	29.54	28.92	34.69	18.06	-18.06
TS	DG ³ Me	Me	G ¹	H	B3LYP	29.67	29.05	34.92	11.90	11.28	14.38	-17.77	17.77

Table 1: Conitnue

Transition state	Substitutes				Functional of density	Forward reaction direction			Reverse reaction direction			Thermal effect and reaction enthalpy	
	R	R ¹	R ²	R ³		E [*]	ΔH [*]	ΔG [*]	E [*]	ΔH [*]	ΔG [*]	Q	ΔH
TS [^]	DG ³ Me	Me	G ¹	H	B3LYP	15.98	15.36	15.68	28.80	28.18	33.09	12.82	-12.82
TS	Me	Me	Me	H	wB97XD	25.96	25.34	29.03	10.86	10.24	11.86	-15.10	15.10
TS [^]	Me	Me	Me	H	wB97XD	9.96	9.34	11.63	22.19	21.57	22.58	12.23	-12.23
TS	Me	Me	Me	H	B3LYP	30.04	29.42	33.06	13.80	13.18	14.58	-16.24	16.24
TS [^]	Me	Me	Me	H	B3LYP	13.56	12.94	14.25	27.46	26.84	27.42	13.90	-13.90
TS ₁	Me	Me	Me	Me	wB97XD	34.36	33.74	38.27	34.36	33.74	38.27	0.0	0.0
TS ₁	Me	Me	Me	Me	B3LYP	36.68	36.06	42.04	36.68	36.06	42.04	0.0	0.0
TS ₁	DGMe	Me	Me	Me	wB97XD	27.05	26.43	33.55	30.35	29.73	37.69	3.30	-3.30
TS ₁	DGMe	Me	Me	Me	B3LYP	31.15	30.53	36.33	33.20	32.58	40.33	2.05	-2.05
TS ₁	DGMe	Me	G ¹	Me	wB97XD	32.06	31.44	37.03	33.36	32.74	37.84	1.30	-1.30
TS ₁	DGMe	Me	G ¹	Me	B3LYP	34.63	34.01	39.13	35.29	34.67	39.52	0.66	-0.66
TS ₁	DG ³ Me	Me	H	G ¹	wB97XD	32.45	31.83	37.21	40.95	40.33	45.62	8.50	-8.50
TS ₁	DG ³ Me	Me	H	G ¹	B3LYP	34.04	33.42	39.28	43.53	42.91	47.98	9.49	-9.49
TS ₁	DGMe	Me	H	Me	wB97XD	33.00	32.38	34.77	44.41	43.79	44.97	11.41	-11.41
TS ₁	DGMe	Me	H	Me	B3LYP	34.14	33.52	36.76	47.43	46.81	45.45	13.29	-13.29
TS ₁	DGMe	Me	Me	H	wB97XD	39.29	38.67	33.49	31.70	31.08	37.48	7.59	-7.59
TS ₁	DGMe	Me	Me	H	B3LYP	39.62	39.00	35.69	34.80	34.18	40.95	4.82	-4.82
TS ₁	Me	Me	Me	H	wB97XD	34.40	33.78	34.97	36.31	35.69	36.95	1.91	-1.91
TS ₁	Me	Me	Me	H	B3LYP	36.54	35.92	37.57	36.84	36.22	37.17	0.30	-0.30

100 MPa (Shtyrilin *et al.*, 1996) which is markedly superior to the traditional conditions and the pressure in the processes, implemented in SCF conditions. As a consequence, it can be assumed that the gas-phase approach to the prevalence of SCF conditions.

Secondly, the permittivity of water and methanol at transition from ambient conditions to the supercritical fluid state substantially reduced (from 78.4-2.0) (Katritzky *et al.*, 1996) for the water and from 31.9-3.0 (for methanol). As a consequence, the influence of solvation environment that was considered by Da Silva *et al.* (2014), on the energy of the process in this case is actually reduced to zero and it seems logical to conclude that the SCF-conditions, from the point of view of the quantum-chemical simulation, again correspond to gas-phase approximation.

Comparison of the calculated and experimental data, apparently can give a definitive answer to the above question of the applicability of the gas-phase approach for the analysis of the processes, occurring in SCF conditions. However, the experimental data on the kinetics of the fatty acid triglycerides transesterification reaction under supercritical fluid conditions, obtained by various researchers have quite significant differences (Permsuwan *et al.*, 2011). The problem is compounded by the fact that in all the studies ignored the possibility of a catalytic effect of the presence of water in the reaction mixture (a catalytically active fatty acids) and other catalytic agents. In the experimental research (Kusdiana and Saka, 2004), it was proved that water promotes the transesterification reaction of fatty acids triglycerides that is catalyzes it. Permsuwan *et al.* (2011) shows the activation energy values for SbCF and SCF conditions, varying in the range of 2.7-25.2 kcalmol⁻¹. This is likely only possible, if under the supercritical fluid

conditions formed some catalytic agents which reduce the activation energy of the true uncatalyzed steps to values typical for the catalyzed steps. And if so, it raises the question of the legality of the kinetic experiments without taking into account this factor, since, for kinetic experiments in view of the catalytic factor should be applied fundamentally different methodology for experiments, devoted to the first place the control over the formation and equilibrium disappearance of catalysts-authentic acids triglycerides. On the basis of the formed concept, we implemented quantum chemical calculation of the energy of the elementary acts of transesterification and hydrolysis of the fatty acids triglycerides, occurring without inauthentic catalysts (catalytic reagents are not identical acid triglycerides) as well as the elementary acts of catalytic transesterification and hydrolysis of the triglycerides that occurring involving thermodynamic equilibrium and catalysts, authentic to acids triglycerides which however, may also be present in the reaction mixture initially.

According to this study, the catalytic agent in the transesterification reaction of fatty acid triglycerides are associated form of fatty acids, formed during hydrolysis of triglycerides. The total energy of their formation indicates the preference of the thermodynamic shift in the direction of their fatty esters but even in this case, their kinetic impact will be inevitable due to reversibility. It should also be noted that an increase in alcohol concentration will displace the equilibrium towards the products of triglycerides transesterification according to Le Chatelier's principle.

Thus, the calculated values of the activation energy of non-catalytic transesterification of fatty acids triglycerides based on the results of this study are changed

in the range of 32.0-34.4 kcalmol⁻¹ and the catalyst within 20.3-29.4 kcalmol⁻¹. It is evident that the experimental latching the activation energy should be a cross which coincides with the upper limit of the activation energy values, given in the review (Permsuwan *et al.*, 2011).

MATERIALS AND METHODS

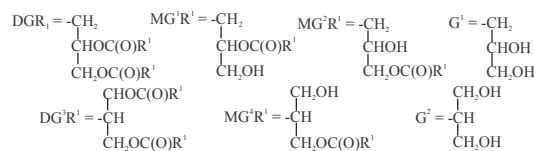
The quantum-chemical studies made in the Linux operating system using the program Gaussian16 implementing the DFT method with the B3LYP density functional and basis 6-311++g(df, p) in the implementation and subsequent comparison with calculations data, obtained by using density functional wB97XD/6-311++g(df, p). These methods are well suited for simulation the supercritical fluid state, according to (Zhang *et al.*, 2013, 2016). The difference in energy characteristics when using the density functional wB97XD and B3LYP is 2-5 kcalmol⁻¹ which agrees with the work of other researchers (De Castro *et al.*, 2014).

Figures and tables of article are shows the activation energy of the forward (E^{*}) and reverse (E^{*_}) directions of the reaction and the heat of reaction (Q) in the level of B3LYP/6-311++g(df, p) and wB97XD/6-311++g(df, p) approximation. In addition, given also the thermodynamic characteristics to 298.15 K temperature for the forward direction of the elementary act and reverse directions, respectively: the enthalpy of activation (ΔH^{*}, ΔH^{*_}), the activation energy of Gibbs (ΔG^{*}, ΔG^{*_}) as well as the reaction enthalpy (ΔΔH). Mutual conversion of thermodynamic parameters was carried out according to the formula ΔG = ΔH-TΔS.

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 highlighted the atoms that form new connections or between them old connections are broken.

Translation Hartree units in kcalmol⁻¹ was carried out by the ratio: 1 Hartree = 627.5095 kcalmol⁻¹, 1 calorie = 4.184 J. For schemes and tables the following notation are adopted: R = Diglyceride (DG), Monoglyceride (MG) with hydrocarbon substituent R¹ (DGR¹ и MG¹R¹, MG²R¹, respectively) and Glycerol (G) with the appropriate binding C-O structure in the secondary carbon center or substructure of Diglyceride (DG³), Monoglyceride (MG⁴) with hydrocarbon substituent R¹ (DG³R¹ и MG⁴R¹, respectively) and Glycerol (G²) with the corresponding C-O bonding structure at the center of the tertiary carbon; R¹ = hydrocarbon residue of fatty acids and their analogues;

R², R³ = CH₃ (methanolysis reaction), H (hydrolysis reaction). Hydrocarbon residue of oleic acid is abbreviated-Ole. Structural interpretation of the received specific designations substituents R, R¹; R², R³:



RESULTS AND DISCUSSION

Study of the elementary acts: The fundamental point for further discussion is the fact that substitution nature in triglycerides has a negligible impact on the overall energy of reactions, so, replacing of hydrocarbon residue of oleic acid to methyl substituent makes the difference in the activation energies of rate-controlling first step of two-step methanolysis reaction in approximation of B3LYP method no more than 0.37 kcalmol⁻¹. It allows you to transfer energy of simplified reaction systems for real fatty acids triglycerides, containing in its composition a variety of fatty acid residues. In this regard as the optimum model analog of fatty acid triglycerides triacetin molecule has been considered which is the simplest analog of triglycerides.

To obtain the additional characteristic information, thermochemical calculations for reaction systems which corresponds to the transition states TS, TS[^] (for a two-step reaction) and transition states TS (for the one-step reaction) has been conducted. Namely, the activation and thermodynamic characteristics has been counted in a series of temperatures of 300, 400, 500, 600 and 623 K. The pressure in the thermochemical calculations was 0.1 MPa because the value of this parameter up to 30 MPa (which correspond to the experimental conditions) is not provided any changes-or even hundredths of the calculated values which confirms the idea that the effect of pressure on energy reactions should be expected only at pressures above 100 MPa (Shtyrlin *et al.*, 1996) (Fig. 3 and 4).

The thermochemical analysis of the elementary acts:

In all the studied stages the associated intermolecular nature pre-reaction complex are formed that allows us to consider all the elementary acts as a first-order reaction. In our case it is appropriate to call such reactions are pseudo-first order reactions because can be formally considered elementary acts of the formation of such complexes but for processes in SCF conditions they are energetically negligible. That is why the reaction rate constants were calculated according to the formula of the theory of absolute reaction rates:

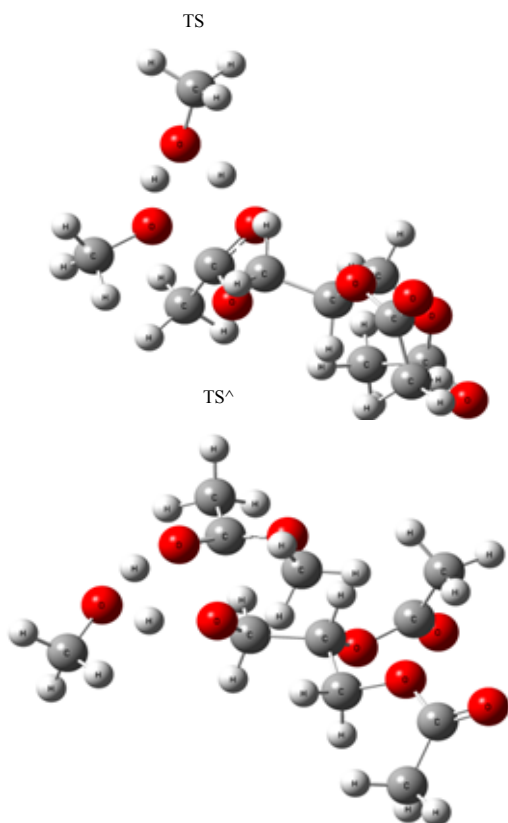


Fig. 3: Transition states (TS, TS[^]) of a two-step transesterification and hydrolysis of triglycerides with the carbonyl group of triglyceride and dimer associate of methanol (Table 1)

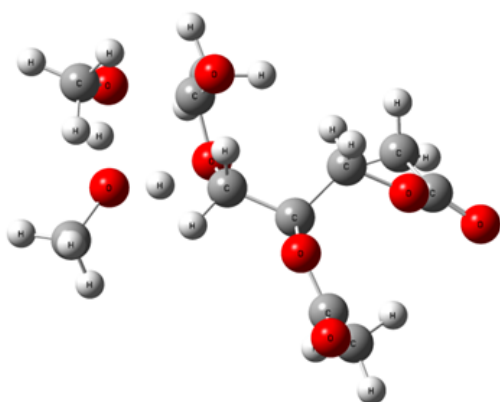


Fig. 4: Transition state of the one-step transesterification and hydrolysis of triglycerides with an alkoxycarbonyl group of triglyceride and dimer associate of methanol (Table 1)

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

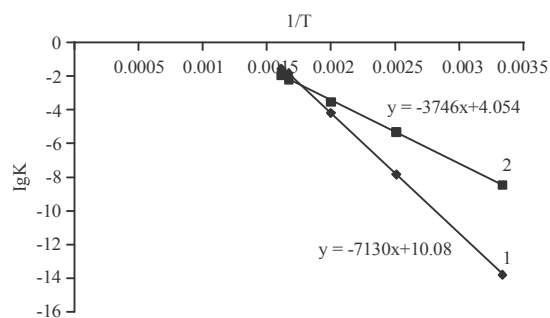


Fig. 5: Dependences LgK^{-1}/T (in the graph, these parameters correspond to the ordinate y and abscissa x, respectively) for the forward direction of a one-step reaction and the forward direction of the first step of a two-step methanolysis reaction of a simple triglyceride's analog-triacetin

There $k = 1.38 \cdot 10^{-23} \text{ JK}^{-1}$ (Boltzmann's constant), T-temperature, K, $h = 6.6261 \cdot 10^{-34} \text{ J}\cdot\text{s}$, $R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (universal gas constant), $e = 2.71828$, ΔG^\ddagger —Gibbs activation energy.

The rate constant of the limiting first-stage of the reaction at $T = 623 \text{ K}$ calculated by Eq. 1 is 0.0110 sec^{-1} , it is close to the value obtained by Kusdiana and Saka (2001) 0.0178 sec^{-1} at the same temperature which indicates the reliability of this method of calculation.

As seen from Table 1, the activation energy of the forward direction of the first step of a two-step reaction and a direct one-step reaction differ by $0.61 \text{ kcalmol}^{-1}$ energy of preference in favor of a two-step reaction. It was important to understand whether the changes trend at constant data of reactions in a temperature range other than room temperature, it is convenient to follow when rendering them Arrhenius straight lines, i.e., LgK^{-1}/T (Fig. 5). It can be seen that the Arrhenius straight lines intersect at a temperature close to 555 K . The intersection point that is the point at which the constants of these reactions are the same. The subsequent rise in temperature up to 623 K reverses the energy preference in favor of the one-step reaction. However, the absolute values of the rate constants vary symbolically which suggests that both reactionary direction of methanolysis of fatty acid triglyceride under supercritical fluid conditions, close to the point of intersection are equal among themselves and competitive on the other equal conditions.

For two-step transformation of fatty acids triglycerides is important to compare the rate constants for the reverse direction of the elementary act of the first step of a two-step methanolysis and the forward direction of the second step. Figure 6 shows the dependence of the constants on the temperature.

From Fig. 6, it can be seen that the magnitude of the rate constants of elementary act of reverse direction of the

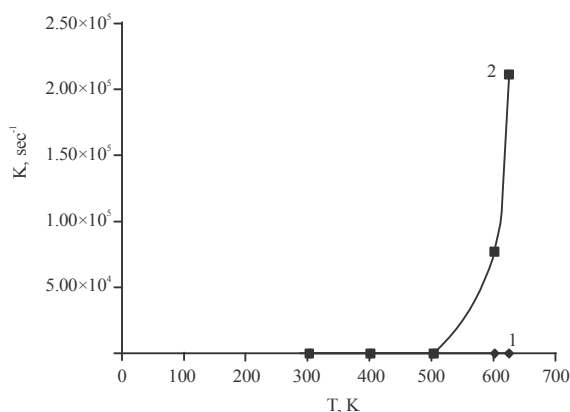


Fig. 6: The dependence of the constants of the elementary act of the reverse direction of the first step of a two-step methanolysis of triacetin 1 and the forward direction of the second step 2 on the temperature

first-step and the forward direction of the second step of two-step methanolysis in the absence of catalyst in temperature range 300-500 K is very small and constants comparable in magnitude. However, if the magnitude of the rate constant for the reverse direction in the temperature range 500-623 K doesn't change substantially, the rate constant of the forward direction for a second step exponential dependence abrupt change is observed in the direction of its explosive increase at the temperature 623 K, this constant becomes 1.2×10^4 time (on the four order) more than constant of the reverse direction of the first step. This clearly indicates that if the initial reaction complex A (Fig. 1) has been reported enough energy to overcome the activation barrier to the forward direction of the first step and the formation of an intermediate complex B, the supercritical fluid conditions of thermodynamic equilibrium $A \rightarrow B$ doesn't occur and the reaction was irreversible rolls a potential target product in a pit of a negative reaction enthalpy $-7.09 \text{ kcalmol}^{-1}$. Importantly, the rate constants for the forward direction of the elementary act of the first step of triacetin's methanolysis also characterized by a sharply exponentially increase since the temperature of 500 K (Fig. 7).

As noted above, based on the existence of the point of intersection for the forward direction of the two-step and one-step mechanism of methanolysis of triacetin, both reactionary trends in supercritical fluid conditions are equal in this regard, it is also important to consider the dependence of the forward and reverse rate constants of one-step methanolysis of the simple triglyceride analog-triacetin on temperature. As can be seen from Fig. 8, a reverse direction of the reaction rate constant until the temperature of 600 K virtually unchanged and has an extremely low value and only in the temperature range 600-623 K is increased slightly which is of minor

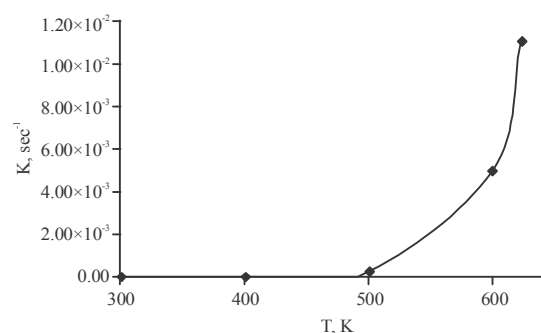


Fig. 7: Changes in the rate constants of the elementary act of forward direction of the first step of a two-step triacetin's methanolysis on temperature

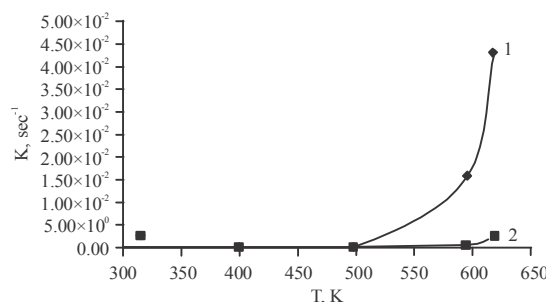


Fig. 8: Dependence of the rate constants of one-step methanolysis of the simple triglyceride's analog-triacetin on temperature 1-a forward direction of the elementary act, 2-the reverse direction of the elementary act

importance, since, the value of the constant of forward direction of the one-step triacetin's methanolysis, starting from a temperature of 500 K sharply increases exponentially and at a temperature of 623 K becomes 5.20 times greater than the rate constant of the reverse direction. This as in the case of two-step directions, resulting in a significant shift of the thermodynamic equilibrium between the original complex D and the target reaction product-complex E (Fig. 2) and the irreversible formation of the latter in view of the availability of the potential well with a negative enthalpy of reaction $-4.23 \text{ kcalmol}^{-1}$.

As part of a well-known practice of interpretation of kinetic experiments, it is known that low-barrier reaction at high temperatures giving way to high-barrier reactions that determine the specifics of interactions. However, before our investigations such analysis with respect to SCF-process wasn't conducted. The obtained results are fixed the unique effect of reagents reactivity changing directly during the transition from the subcritical to the supercritical region in particular, for the reaction of transesterification of fatty acids triglycerides and alcohols.

Figure 7 visually recorded a sharp increase in the reaction rate constants of the targeted reactions since the temperature of 500 K.

Our arguments relate to only one type of reaction, i.e., the hydrolysis and transesterification of fatty acid triglycerides and we have to figure out whether this is a general rule for most supercritical processes or the effect is only a special case. The answer to this question will be obtained in subsequent studies.

CONCLUSION

The rate constants of the various elementary acts taking place in the transesterification of fatty acids triglycerides in an alcoholic medium, flowing in supercritical fluid conditions has been calculated using quantum-chemical methods.

As a result of quantum-chemical simulation shows that under normal conditions and in the absence of catalysts, the reaction of transesterification of triglycerides and alcohols isn't proceeds due to the high activation energy values. Transesterification reaction is possible only in those physical conditions which will ensure the overcoming of the activation barrier in the 32.0-34.9 kcalmol⁻¹. Supercritical fluid conditions satisfy these requirements.

One-step and two-step mechanisms of fatty acids triglycerides transesterification are insensitive to the nature of the alkyl substituents and the rate controlling step is the forward direction of the one-step reaction or the first step of a two-step reaction and as a model of triglyceride is convenient to consider the simplest of its representative-triacetin.

Analysis of the calculated Arrhenius lines in coordinates LgK⁻¹/T of rate control directions of the one-step and two-step mechanisms of fatty acids triglycerides transesterification showed that the point of intersection is observed for Arrhenius lines data for about 555 K. However, at 623 K the absolute values of the rate constants vary symbolically which suggests that both reactionary direction of methanolysis of triglycerides in the supercritical fluid conditions are equal and competitive when other conditions being equal.

Graphic review of the quantum-chemically calculated thermochemical dependencies clearly show the nature of rate constants changes of different directions of the elementary acts that occur during the process of alcoholysis and hydrolysis of the triglycerides in the supercritical fluid conditions and identify the new law, lies in the fact that for the vast majority considered elementary acts, characterized by a sharp exponential increase in the absolute values of the reaction rate constants ranging from 500 K.

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REFERENCES

- Asakuma, Y., K. Maeda, H. Kuramochi and K. Fukui, 2009. Theoretical study of the transesterification of triglycerides to biodiesel fuel. *Fuel*, 88: 786-791.
- Da Silva, A.C.H., E.L. Dall'Oglio, P.T. de Sousa Jr, S.C. da Silva and C.A. Kuhnen, 2014. DFT study of the acid-catalyzed ethanolysis of butyric acid monoglyceride: Solvent effects. *Fuel*, 119: 1-5.
- Delesma, C., R. Castillo, P.Y. Sevilla-Camacho, P.J. Sebastian and J. Muniz, 2017. Density functional study on the transesterification of triacetin assisted by cooperative weak interactions via a gold heterogeneous catalyst: Insights into biodiesel production mechanisms. *Fuel*, 202: 98-108.
- Dos Santos, V.M.L., J.A.B. Da Silva, L. Stragevitch and R.L. Longo, 2011. Thermochemistry of biodiesel oxidation reactions: A DFT study. *Fuel*, 90: 811-817.
- Franck, E.U. and R. Deul, 1978. Dielectric behaviour of methanol and related polar fluids at high pressures and temperatures. *Faraday Discuss. Chem. Soc.*, 66: 191-198.
- Katritzky, A.R., S.M. Allin and M. Siskin, 1996. Aquathermolysis: Reactions of organic compounds with superheated water. *Acc. Chem. Res.*, 29: 399-406.
- Kusdiana, D. and S. Saka, 2001. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel*, 80: 693-698.
- Kusdiana, D. and S. Saka, 2004. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresour. Technol.*, 91: 289-295.
- Lopez, D.E., J.G. Goodwin Jr. and D.A. Bruce, 2007. Transesterification of triacetin with methanol on Nafion® acid resins. *J. Catal.*, 245: 381-391.
- Lopez, D.E., J.G. Goodwin Junior, D.A. Bruce and E. Lotero, 2005. Transesterification of triacetin with methanol on solid acid and base catalysts. *Applied Catal. A: Gen.*, 295: 97-105.
- Mazanov, S.V., A.R. Gabitova, R.A. Usmanov, F.M. Gumerov and S. Labidi *et al.*, 2016. Continuous production of biodiesel from rapeseed oil by ultrasonic assist transesterification in supercritical ethanol. *J. Supercrit. Fluids*, 118: 107-118.

- Muniz, J., R. Castillo, J.B. Robles and E. Sansores, 2016. Density functional theory study of the reactivity and electronic structure of the transesterification of triacetin in biodiesel production via a sulfated zirconia heterogeneous catalysis. *Intl. J. Quantum Chem.*, 116: 988-999.
- Papageorgiou, D.G., I.N. Demetropoulos, I.E. Lagaris and P.T. Papadimitriou, 1996. How many conformers of the 1, 2, 3-propanetriol triacetate are present in gas phase and in aqueous solution?. *Tetrahedron*, 52: 677-686.
- Permsuwan, A., N. Tippayawong, T. Kiatsiriroat, C. Thararux and S. Wangkarn, 2011. Reaction kinetics of transesterification between palm oil and methanol under subcritical conditions. *Energy Sci. Technol.*, 2: 35-42.
- Shtyrlin Y.G., V.Y. Fedorenko, G. Iskhakov, V.D. Kiselev and A.I. Konovalov, 1996. The influence of external and internal pressure on the reaction rate of the Diels-Alder reaction of 9,10-dimethylantracene acrylonitrile. *J. Org. Chem.*, 3: 499-501.
- Yamaguchi, T., C.J. Benmore and A.K. Soper, 2000. The structure of subcritical and supercritical methanol by neutron diffraction, empirical potential structure refinement and spherical harmonic analysis. *J. Chem. Phys.*, 112: 8976-8987.
- Yates, K., 1971. Kinetics of ester hydrolysis in concentrated acid. *Acc. Chem. Res.*, 4: 136-144.
- Zhang, J., X. Weng, Y. Han, W. Li and J. Cheng *et al.*, 2013. The effect of supercritical water on coal pyrolysis and hydrogen production: A combined ReaxFF and DFT study. *Fuel*, 108: 682-690.
- Zhang, Y., C. Liu and X. Chen, 2016. Mechanism of glucose conversion in supercritical water by DFT study. *J. Anal. Appl. Pyrolysis*, 119: 199-207.
- de Castro, E.A.S., D.A.B. de Oliveira, S.A.S. Farias, R. Gargano and J.B.L. Martins, 2014. Structure and electronic properties of azadirachtin. *J. Mol. Model.*, 20: 1-7.