

# Thermodynamics of phase and chemical equilibrium in the processes of biodiesel fuel synthesis in sub- and supercritical methanol

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Thermodynamic data were calculated for mono-, di- and triglycerides of fatty acids, free fatty acids and methyl esters of fatty acids, which are involved in transesterification of vegetable oils with lower alcohols. Phase diagrams of the reaction mixtures were calculated and reaction conditions providing supercritical state of the reaction mixture were selected for transesterification of triglycerides in various lower alcohols. Chemical equilibrium of simple and mixed fatty acid triglycerides transesterification reactions with methanol was studied in a wide range of temperatures, pressures and ratios of initial components, including the region of supercritical state of the reaction mixture. Calculation of the phase equilibrium and equilibrium composition of the reaction products obtained by transesterification of triglycerides with lower alcohols allowed choosing the optimal reaction conditions for practical application.

## INTRODUCTION

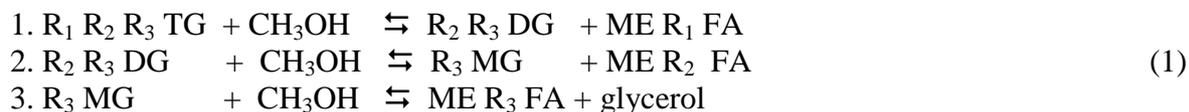
The term biodiesel refers to fatty acid esters (FAE), which are commonly obtained by transesterification of vegetable oils — triglycerides (TG) of fatty acids or esterification of free fatty acids (FFA) with lower alcohols. Natural oils produced from vegetable feedstock (oil-bearing crops) contain ca. 97% of various triglycerides — fatty acid esters, di- and monoglycerides, and FFA. Along with simple triglycerides, vegetable oil consists also of mixed triglycerides containing bases of different fatty acids.

Transesterification of triglycerides with alcohol is conventionally performed in the presence of homogeneous [1-3] and sometimes heterogeneous [4-6] acid or base catalysts; in recent years, sub- and supercritical lower alcohols are used for the purpose, both with and without heterogeneous catalyst [7-15]. In transesterification of vegetable oils catalyzed by alkalies, main disadvantage is sensitivity to water and free fatty acids present in the feedstock. As for acid catalysts in oil transesterification, they provide only a very low reaction rate [2].

Transesterification in supercritical lower alcohols is a promising new approach to the development of efficient and relatively inexpensive processes for synthesis of biodiesel from vegetable oils, animal fats, and food industry waste. Such studies are reported in the literature, for example [7-11]. Synthesis of biodiesel by this method is performed most often with methanol. The application of supercritical alcohols for transesterification of vegetable feedstock makes it possible to run the process without homogeneous catalysts and thus use a lower-grade feedstock; to attain a 90-98% conversion of the starting material at a much shorter time of contacting with the reaction mixture, which allows the use of the flow-type reactors and hence significantly raises the process productivity; to avoid waste water that

earlier resulted from washing the reaction products for removal of homogeneous alkaline or acid catalysts; all this essentially reduces the cost of biodiesel.

Transesterification of fatty acid triglycerides with lower alcohols usually proceeds in three steps via sequential substitution of one or two alkyl groups of fatty acid by hydroxyl groups to form di- and monoglycerides, which can be present in the reaction products together with FAE. In the general case, such transformations can be presented by scheme (1):



Here,  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  correspond to alkyl groups of three different fatty acids, for example, palmitic, oleic or linoleic. For  $\text{R}_1 \neq \text{R}_2 \neq \text{R}_3$ , the transformations of such mixed triglyceride by scheme (1) will include 12 reactions. For  $\text{R}_1 = \text{R}_2 \neq \text{R}_3$ , the number of reactions will reduce to 7.

Although publications on the synthesis of biodiesel via transesterification of vegetable oils in alcohols are numerous, only some works consider *the phase equilibrium* of reaction mixtures [16-21], with no studies on *the chemical equilibrium* of FFA esterification and TG transesterification. This may be related with the absence of reliable thermodynamic data for mono-, di- and triglycerides, FFA and esters of fatty acids. In this connection, aim of the present work is to calculate the thermodynamic parameters (critical parameters, formation entropy and enthalpy) for all the reactants using various methods. The found values of thermodynamic parameters will allow calculating the phase equilibrium for chosen mixtures and the chemical equilibrium for transesterification of simple and mixed TG with lower alcohols in a wide range of pressure, temperature and ratios of initial reactants. Calculation will be made to determine the reaction conditions providing a maximum yield of the target product — esters of fatty acids.

## 1. Calculation of thermodynamic and physicochemical data for individual compounds

To calculate the equilibrium constant of chemical reaction and its variation in a wide range of temperature and pressure, it is necessary to acquire thermodynamic and physicochemical data for individual compounds — reaction participants, namely: critical parameters  $T_{\text{cr}}$  and  $P_{\text{cr}}$ , boiling point  $T_{\text{boil}}$ , standard values of the formation enthalpy and entropy,  $\Delta H_f^\circ$  (298.15 K) and  $\Delta S_f^\circ$  (298.15 K), heat capacity as a function of temperature  $C_p(T)$ , and acentric factor  $\omega$ .

Table 1 lists the calculated parameters for mono-, di- and triglycerides, FFA and esters of fatty acids, which are the initial substances and products of transesterification further used to calculate the phase state and chemical equilibrium of the chosen reactions.

**Table 1.** Critical parameters, boiling point and acentric factor for compounds used in the calculation

Substance	Formula	$T_{\text{boil}}$ , K	$T_{\text{cr}}$ , K	$P_{\text{cr}}$ , atm	$\omega$
PFA	$\text{C}_{16}\text{H}_{32}\text{O}_2$	624	775	15	1.08

OFA	$C_{18}H_{34}O_2$	632	770	13.9	1.18
LFA	$C_{18}H_{32}O_2$	627	775	13.0	1.18
PFAME	$C_{17}H_{34}O_2$	599	763	16.5	0.92
OFAME	$C_{18}H_{36}O_2$	696	867	11.2	0.83
LFAME	$C_{19}H_{34}O_2$	701	875	11.6	0.82
PFATG	$C_{51}H_{98}O_6$	646	811	12.4	0.82
PFADG	$C_{35}H_{68}O_5$	618	780	13.5	0.85
PFAMG	$C_{19}H_{38}O_4$	590	760	14.65	0.73
OFATG	$C_{57}H_{104}O_6$	854	946	4.52	1.62
OFADG	$C_{39}H_{72}O_5$	757	870	8.63	1.68
OFAMG	$C_{21}H_{40}O_4$	660	800	12.75	1.02
LFATG	$C_{57}H_{98}O_6$	860	945	4.6	1.86
LFADG	$C_{39}H_{68}O_5$	756	870	8.37	1.62
LFAMG	$C_{21}H_{38}O_4$	660	800	12.14	1.19
FAPPOG	$C_{53}H_{100}O_6$	667	811	11.96	1.14
FAPPDG	$C_{35}H_{68}O_5$	646	811	10.3	0.785
FAPODG	$C_{37}H_{70}O_5$	729	855	10.2	1.523
FAOMG	$C_{21}H_{40}O_4$	663	802	12.4	1.239
FAPMG	$C_{19}H_{38}O_4$	590	760	14.6	0.736
FAOLLG	$C_{57}H_{100}O_6$	860	945	4.52	1.62
FALODG	$C_{39}H_{70}O_5$	702	813	8.9	1.569
FALLDG	$C_{39}H_{68}O_5$	751	868	9.0	1.651
FALMG	$C_{21}H_{38}O_4$	657	798	12.5	1.190
FAPOLG	$C_{55}H_{100}O_6$	831	920	4.65	1.67
Methanol	$CH_3OH$	338	513	79.9	0.56
Glycerol	$C_3H_8O_3$	562	725	66.7	1.51

Here, PFA is palmitic fatty acid; OFA – oleic fatty acid; LFA – linoleic fatty acid; PFAME – methyl ester of palmitic fatty acid; OFAME – methyl ester of oleic fatty acid; LFAME – methyl ester of linoleic fatty acid; PFATG – triglyceride of palmitic fatty acid; OFATG – triglyceride of oleic fatty acid; LFATG – triglyceride of linoleic fatty acid; FAPPOG – palmitic, palmitic, oleic glyceride of fatty acid; FAPOLG – palmitic, oleic, linoleic glyceride of fatty acid; FAOLLG – oleic, linoleic, linoleic glyceride of fatty acid; FAPPDG – palmitic, palmitic diglyceride of fatty acid; FAPODG – palmitic, oleic diglyceride of fatty acid; FAOMG – oleic monoglyceride of fatty acid; FAPMG – palmitic monoglyceride of fatty acid;

FALODG – linoleic, oleic diglyceride of fatty acid; FALLDG – linoleic, linoleic diglyceride of fatty acid; and FALMG – linoleic monoglyceride of fatty acid.

To calculate the equilibrium of any chemical reaction, it is necessary to know the values of standard (at 298 K) formation enthalpy and entropy or the Gibbs formation energy of individual substances involved in the reaction as well as their temperature dependences. Virtually for all the compounds under consideration, numerical values of these specific thermodynamic parameters are absent in the literature; thus, they should be calculated by the known methods. We chose the methods of quantum and statistical mechanics [22, 23], semiempirical method of the MINDO/3 type [24], and the group methods [25, 26], in particular, the Joback method [27]. Thus, the Joback method was used to calculate the necessary thermodynamic parameters; results of the calculation are presented in Table 2.

**Table 2.** Calculated values of standard formation enthalpy and entropy of chosen compounds. Calculated coefficients for heat capacity of the same compounds as a function of temperature

Substance	Formula	Molecular weight	$\Delta H_f$ (298) J/mol	$\Delta S_f$ (298) J/mol/K	Heat capacity coefficients		
					A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub> ×10 <sup>4</sup>
PFA	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256	-723840	-1556	218.82	1.099	-2.404
OFA	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282	-647900	-1627	246.3	1.192	-2.786
LFA	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	280	-530680	-1503	216.8	1.202	-2.943
PFATG	C <sub>51</sub> H <sub>98</sub> O <sub>6</sub>	806	-2053090	-5027	627.5	3.106	-10.55
PFADG	C <sub>35</sub> H <sub>68</sub> O <sub>5</sub>	568	-1557800	-3495	357.2	2.294	-7.908
PFAMG	C <sub>19</sub> H <sub>38</sub> O <sub>4</sub>	330	-1062510	-1964	217.4	1.314	-4.508
PFAME	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	-711490	-1656	144.2	1.164	-4.042
OFATG	C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>	884	-1825270	-5481	688.2	3.407	-12.65
OFADG	C <sub>39</sub> H <sub>72</sub> O <sub>5</sub>	620	-1405920	-3637	408.5	2.469	-8.470
OFAMG	C <sub>21</sub> H <sub>40</sub> O <sub>4</sub>	356	-986570	-2035	234.5	1.418	-4.863
OFAME	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	284	-635550	-1727	209.7	1.139	3.717
LFATG	C <sub>57</sub> H <sub>98</sub> O <sub>6</sub>	878	-1473610	-4867	683.5	3.308	-11.50
LFADG	C <sub>39</sub> H <sub>68</sub> O <sub>5</sub>	616	-1171480	-3389	405.8	2.453	-8.415
LFAMG	C <sub>21</sub> H <sub>38</sub> O <sub>4</sub>	354	-869350	-1837	233.21	1.410	-4.836
LFAME	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	294	-518330	-1602	239.7	1.021	-3.130
FAPPOG	C <sub>53</sub> H <sub>100</sub> O <sub>6</sub>	832	-1977150	-5098	647.7	3.207	-1.89
FAPPDG	C <sub>35</sub> H <sub>68</sub> O <sub>5</sub>	568	-1558	-3495	357.24	2.2937	-.791
FAPODG	C <sub>37</sub> H <sub>70</sub> O <sub>5</sub>	522	-1482	-3566	405.82	2.4528	-0.841
FAOMG	C <sub>21</sub> H <sub>40</sub> O <sub>4</sub>	320	-987	-2035	234.53	1.418	-0.486
FAPMG	C <sub>19</sub> H <sub>38</sub> O <sub>4</sub>	330	-1063	-1964	217.40	1.314	-0.451

FAOLLG	C <sub>57</sub> H <sub>100</sub> O <sub>6</sub>	880	-1590830	-4991	689.8	3.313	-1.16
FALODG	C <sub>39</sub> H <sub>70</sub> O <sub>5</sub>	618	-1289	-3513	407.14	2.461	-0.844
FALLDG	C <sub>39</sub> H <sub>68</sub> O <sub>5</sub>	616	-1250	-3389	405.82	2.453	-0.842
FALMG	C <sub>21</sub> H <sub>38</sub> O <sub>4</sub>	354	-8694	-1837	233.2	1.410	-0.484
FAPOLG	C <sub>55</sub> H <sub>100</sub> O <sub>6</sub>	856	-1783990	-5045	671.0	3.222	-1.13
Methanol	CH <sub>3</sub> OH	32	-201097	-129	23.56	0.0064	0.336
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92	-584721	-490	15.01	0.428	-3.017

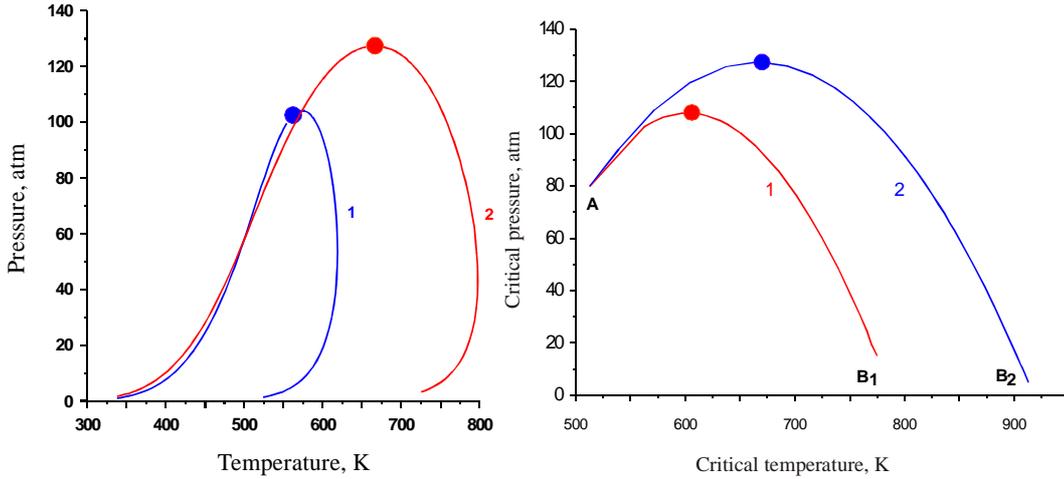
$$*C_p = A_0 + A_1 \times T + A_2 \times T^2 \text{ (J/mol/K)}$$

## 2. Phase equilibrium in transesterification of triglycerides of fatty acids with methanol

Hence, for the experiments on transesterification of triglycerides with supercritical lower alcohols, it is necessary, on the one hand, to know the temperature  $T^0$  and pressure  $P^0$  in the reactor at which the initial mixture with a fixed alcohol/oil ratio is known to be in supercritical state. As triglycerides convert during transesterification, the reaction mixture changes its composition: glycerol and esters of fatty acids are produced. Thus, on the other hand, conditions should be created at which the reaction mixture of a varying composition will be under supercritical conditions, too. To meet the above listed requirements, we calculated phase equilibrium for the mixtures containing both the initial substances (lower alcohols, triglycerides) and the reaction products (lower alcohols, triglycerides, glycerol, esters of fatty acids).

State of the mixtures is presented most comprehensively by their phase diagrams with a fixed position of the critical point. To illustrate the calculation, Fig. 1 shows in P–T coordinates the phase diagrams of two binary mixtures: mixture No. 1 (methanol – PFA) and mixture No. 2 (methanol – PFATG). The methanol content in these mixtures was set equal to 95 mol %. The chosen mixtures simulate the initial reaction mixtures in the synthesis of methyl esters of fatty acids and transesterification of fatty acid triglycerides with methanol.

Evidently, changes in the component composition of the mixture or in the quantitative content of components alter the phase boundaries, i.e., the contours of binodal lines; accordingly, this changes the coordinates of critical points. Fig. 2 shows the critical parameters (positions of the critical point) for binary mixtures Nos. 1 and 2 versus their composition (the so-called “critical curves”), the content of a component varying from 0 to 100%. The presence of a critical pressure maximum on the curves (10 mol % PFA for mixture No. 1 and 5.5 mol. % PFATG for mixture No. 2) is typical of the binary systems with a pronounced difference in critical parameters of individual components [28].



**Figure 1.** Phase diagrams on the P–T plane. Curve 1 – mixture No. 1, curve 2 – mixture No. 2. Dots correspond to critical points of the mixtures.

**Figure 2.** Critical curves for the mixtures under consideration: 1 – mixture No. 1, 2 – mixture No. 2. A – pure methanol, B<sub>1</sub> – pure palmitic acid, B<sub>2</sub> – pure triglyceride of palmitic acid. Dots on the curves correspond to the maximum values of critical pressure.

### 3. Chemical equilibrium, calculation models and methods

Calculation of chemical equilibrium of the reaction mixtures is presented as a problem of minimizing the free Gibbs energy [29]. For a mixture of components with molar numbers  $n_i$ , the total Gibbs energy  $G_{\text{mix}}$  at specified T and P in equilibrium state should take a minimum value:

$$G_{\text{mix}} = \sum_{i=1}^N n_i \mu_i \rightarrow \min \quad i = 1, 2, \dots, N \quad (2)$$

where  $N$  is the number of chemical components in the reaction mixture, and  $\mu_i$  (J/mol) is the chemical potential of the  $i$ -th component.

Chemical potential of components  $\mu_i$  is determined by a relationship

$$\mu_i \equiv \left( \frac{\partial G_{\text{mix}}}{\partial n_i} \right) = \mu_i^0(T, P=1) + RT \ln f_i(T, P, \mathbf{y}), \quad (3)$$

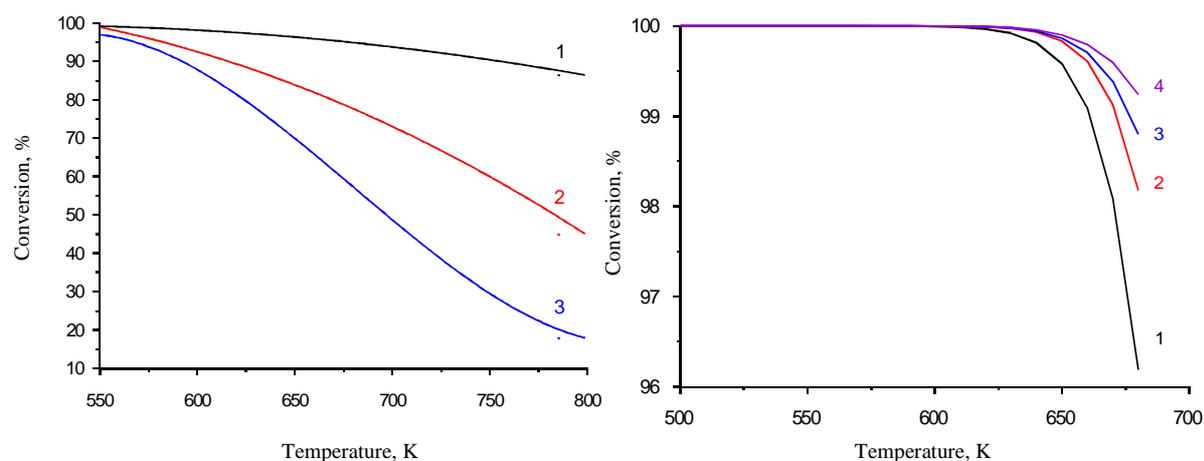
where  $\mu_i^0$  is the chemical potential of pure  $i$ -th component in its standard state, which coincides with the Gibbs energy  $G_i(T, P)$  of one mole of a pure substance calculated at the process temperature  $T$  and bearing pressure  $P = 1$  atm. These values are commonly indicated in thermochemical handbooks, but their lack for fatty acids, triglycerides and transesterification products makes it necessary to calculate enthalpy and entropy using the Joback group method [27] (see Table 2).

Fugacity of the mixture component  $f_i(T, P, \mathbf{y})$  is a function of temperature, pressure, molar composition of the mixture (vector  $\mathbf{y}$ ), critical parameters of individual components, and their acentric factors. It is calculated using the cubic Redlich–Kwong–Soave (RKS) equation of state [30].

### 3.1. Calculation of chemical equilibrium for single-step transesterification of simple triglycerides of fatty acids with methanol

Here we consider the single-step transesterification of three triglycerides of fatty acids — PFATG, OFATG and LFATG with methanol. Equilibrium conversions of the chosen triglycerides versus temperature are shown in Fig. 3. Calculation was made also for a stoichiometric composition of the initial mixture taking into account its nonideality at  $P = 130$  atm. The following examples illustrate data on the effect of methanol excess and total pressure on shifting the chemical equilibrium of a chosen reaction. The calculation was made for LFATG.

*Effect of methanol excess.* Temperature dependences of equilibrium conversion of the chosen triglyceride calculated at different ratios of methanol to initial triglyceride are shown in Fig. 4. The calculation was made at a constant pressure  $P = 130$  atm. As seen from the Figure, at the reaction temperature below 625 K, an excess of methanol in the reaction medium provides nearly a 100% conversion of triglyceride in equilibrium state. At higher temperatures, conversion starts to decline. Such behavior can be explained by methanol transformation at above 625 K into a strongly superheated vapor, the reaction mixture acquiring properties of ideal gas with the constant  $K_F \cong 1$ . However, as noted above, this temperature region has no practical value for the process under consideration. The calculation was made for LFATG.



**Figure 3.** Equilibrium conversion of triglycerides versus temperature.  $P = 130$  atm. Lines 1-3 correspond to numbering of the reactions: 1- PFATG, 2-OFATG and 3-LFATG

**Figure 4.** Effect of methanol excess on the equilibrium conversion of LFATG versus temperature. The  $\text{CH}_3\text{OH}/\text{TG}$  ratio: 1 – 10/1; 2 – 20/1; 3 – 30/1; 4 – 40/1.

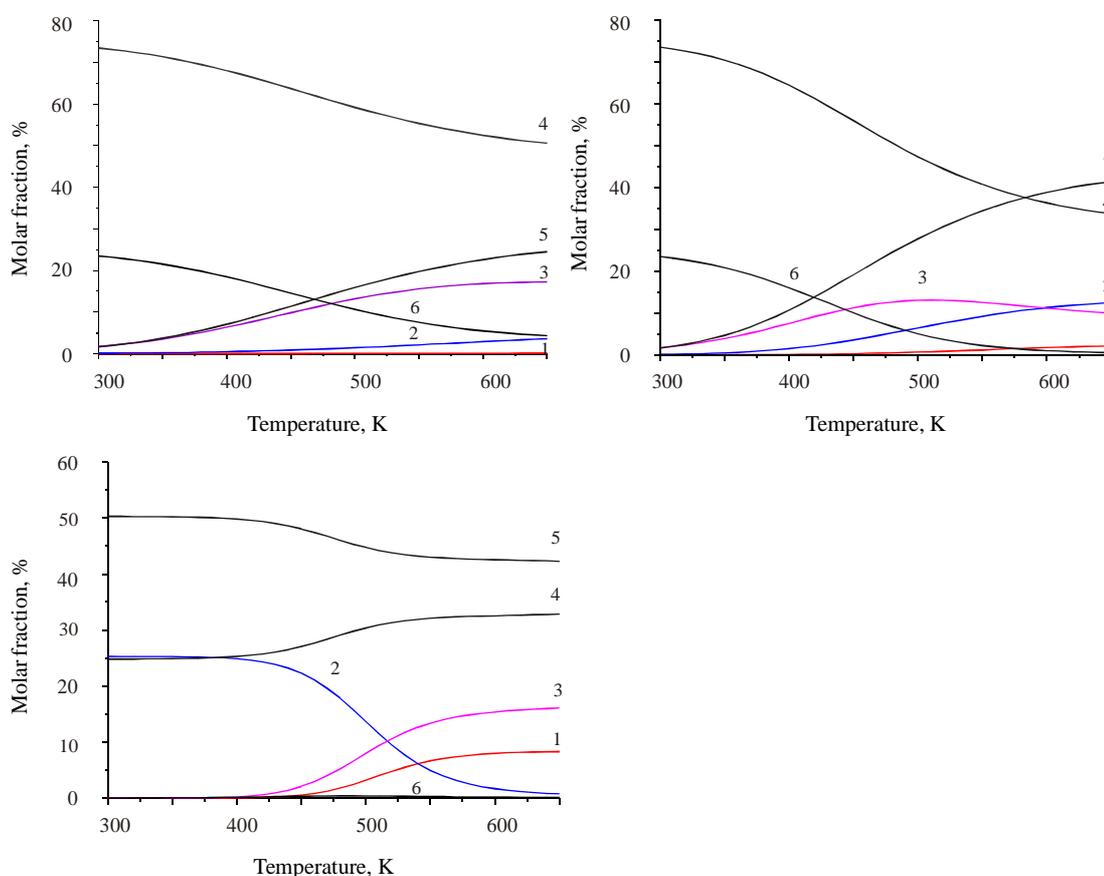
### 3.2. Calculation of chemical equilibrium for stepwise transesterification of simple triglycerides of fatty acids with methanol

As noted above, transesterification of fatty acid triglycerides with lower alcohols generally proceeds by a three-step scheme of transformations via sequential substitution of one or two alkyl groups of fatty acid by hydroxyl groups with the formation of di- and monoglycerides by scheme (1). For simple triglycerides, all alkyl groups  $R_1$ ,  $R_2$ ,  $R_3$  are

identical and correspond to one of fatty acids. This section of the work presents calculation data on the chemical equilibrium for transesterification of simple triglycerides – PFATG, OFATG and LFATG proceeding in three steps by scheme (1). Evidently, the equilibrium composition of end product will be determined by behavioral features of the equilibrium constants of individual steps versus temperature.

The equilibrium compositions for stepwise transesterification of TG were calculated by a procedure thoroughly described in above section. It should be noted that equilibrium compositions were calculated for a stoichiometric ratio of components of the initial mixture at  $y_{TG}^0 = 1$  and  $y_{methanol}^0 = 3$  in the ideal gas approximation, where the corresponding fugacity coefficients were taken equal to unity.

Figure 5a,b,c shows temperature dependences of the equilibrium compositions for stepwise transesterification of TG calculated with the obtained constants.



**Figure 5a.** *Stepwise transesterification of TG.* Equilibrium composition of the reaction products in transesterification of PFATG versus temperature. 1 – PFATG, 2 – PFADG, 3 – PFAMG, 4 – PFAME, 5 – methanol, 6 – glycerol.

**Figure 5b.** *Stepwise transesterification of TG.* Equilibrium composition of the reaction products in transesterification of OFATG versus temperature. 1 – OFATG, 2 – OFADG, 3 – OFAMG, 4 – OFAME, 5 – methanol, 6 – glycerol.

**Figure 5c.** *Stepwise transesterification of TG.* Equilibrium composition of the reaction products in transesterification of LFATG versus temperature. 1 – LFATG, 2 – LFADG, 3 – LFAMG, 4 – LFAME, 5 – methanol, 6 – glycerol.

As follows from the calculated chemical equilibrium of stepwise transesterification of TG, see Fig. 5a,b,c, at low temperatures (up to ~ 450 K) a complete conversion of all TG takes place in all cases. Intermediate products of the reaction are the corresponding mono- and diglycerides. In the case of LFATG, at low temperatures the intermediate product is represented mainly by LFADG, whereas at high temperatures there remains a substantial amount of nonconverted LFATG together with LFAMG.

It should be noted that calculation of the chemical equilibrium for stepwise transesterification of fatty acid triglycerides with supercritical methanol makes it possible to find the reaction conditions that provide a minimum yield of mono- and diglycerides and a maximum yield of the target product.

### 3.3. Calculation of chemical equilibrium for transesterification of mixed triglycerides of fatty acids with supercritical methanol

Supercritical conditions are characterized by the critical temperature, critical pressure and concentration of initial reactant in a solvent that creates a supercritical medium. In this case, solvent can be represented by methanol with the critical parameters  $T_{cr} = 512.6$  K and  $P_{cr} = 79.9$  atm. At a large excess of methanol, critical parameters of the reaction mixture should be close to the critical parameters of methanol.

To select a region of temperatures and pressures at which the reaction mixture can pass to a supercritical state, we calculated critical parameters of the initial reaction mixtures comprising FAPPOG and methanol (mixture No. 1) or FAOLLG and methanol (mixture No. 2), respectively, at different methanol concentrations in the initial mixture. The calculation was made by the method reported in our earlier work [31]. Results are presented in Table 3.

**Table 3.** Calculated critical parameters of the reaction mixtures comprising FAPPOG and methanol (mixture No. 1) or FAOLLG and methanol (mixture No. 2)

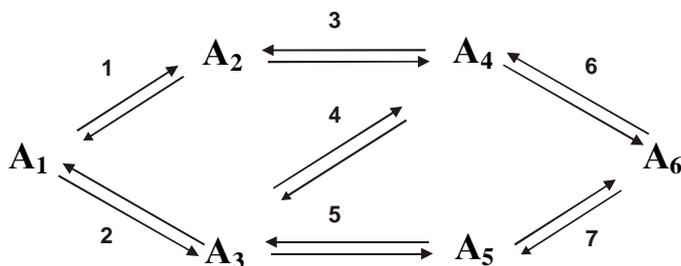
CH <sub>3</sub> OH/TG ratio, mol/mol	CH <sub>3</sub> OH concentration, mol %	Mixture No. 1		Mixture No. 2	
		T <sub>cr</sub> , K	P <sub>cr</sub> , atm	T <sub>cr</sub> , K	P <sub>cr</sub> , atm
20:1	95.2	569.9	95.0	683.3	126.0
30:1	96.8	548.4	90.2	624.8	120.6
40:1	97.6	537.7	87.1	593.4	112.9
50:1	98.0	532.5	85.4	577.4	107.7
60:1	98.4	527.4	83.7	562.1	101.8

According to Table 3, as the methanol concentration in the reaction mixture increases, its critical parameters approach those of pure methanol.

The range of operating temperatures and pressures for both mixtures were chosen at a specified methanol/triglyceride ratio equal to 50:1. For mixture No. 1,  $P = 100$  atm and  $T = 520$ - $600$  K. This corresponds to the reduced parameters  $P_{red} = P/P_{cr} = 1.17$  and  $T_{red} = T/T_{cr} = 0.98$ - $1.09$  K. Respectively, for mixture No. 2 we chose  $P = 120$  atm,  $T = 560$ - $620$  K,  $P_{red} = 1.11$ , and  $T_{red} = 0.97$ - $1.07$  K.

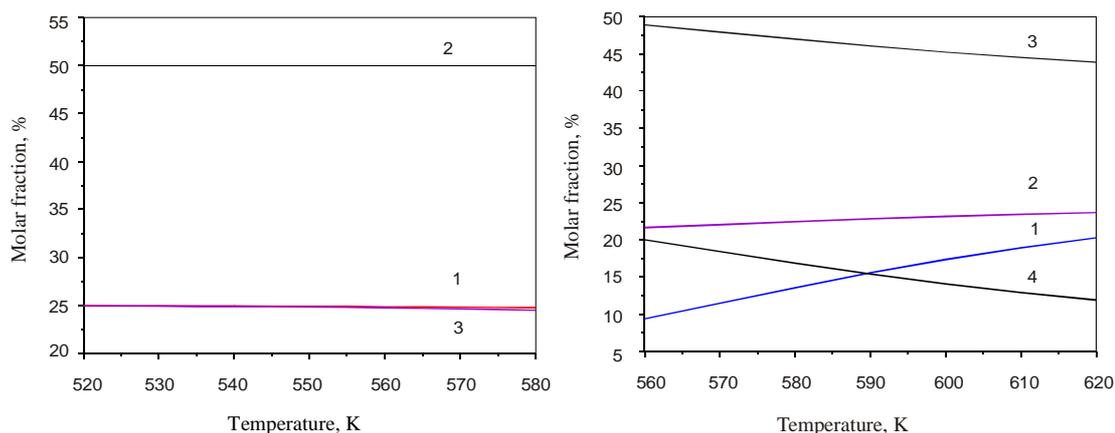
When the process is performed under supercritical conditions, one may expect a strong effect of reaction mixture nonideality on the shift of equilibrium and equilibrium distribution of the reaction products. The reaction completeness can be characterized by the yield of

glycerol. Theoretically, a maximum yield of glycerol after removal of methanol excess is equal to 25%. Such yield implies also a maximum yield of the total esters (75%) with the 2:1 ratios of PFAME to OFAME and LFAME to OFAME, respectively, for transformations of FAPPOG and FAOLLG according to scheme in Fig. 6.



**Figure 6.** A scheme of FAPPOG and FAOLLG transformations.  $A_1 - A_5$  — complex tri-, di- and monoglycerides,  $A_6$  — glycerol.

The calculation results are presented in Figs. 7 and 8, respectively, for transformations of FAPPOG and FAOLLG. Only the substances which concentrations exceeding 2% are depicted here.



**Figure 7.** Transformations of FAPPOG. Temperature dependence of the equilibrium yield of reaction products after removal of methanol excess from the products.  $P = 100$  atm. Curves: 1 – OFAME, 2 – PFAME, 3 – glycerol.

**Figure 8.** Transformations of FAOLLG. Temperature dependence of the equilibrium yield of reaction products after removal of methanol excess from the products.  $P = 120$  atm. Curves: 1 – FALMG, 2 – OFAME, 3 – LFAME, 4 – glycerol.

As seen from Fig. 7, when transformations of FAPPOG occur under supercritical conditions and in an excess of methanol, equilibrium of the reaction strongly shifts toward the end target products. The reaction runs mainly by route 1,3,6. The reaction coordinates are as follows:  $X_1 = 0.852$  and  $X_2 = 0.148$ . The yields of OFAME and PFAME are virtually equal to the maximum values, 25 and 50%, respectively. Only trace amounts of intermediate products are detected in the reaction mixture.

Transformations of FAOLLG look quite differently, Fig. 8. Similar to the previous case, here the reaction also runs mainly by route 1,3,6. The reaction coordinates are  $X_1 = 0.855$  and  $X_2 = 0.145$ . The initial substance is converted completely. However, reaction 6 remains strongly reversible, and concentration of FALMG increases with temperature. Accordingly, the yield of LFAME target product decreases.

## CONCLUSION

Investigation of phase equilibrium of the mixtures containing triglycerides and lower alcohols along with the reaction products of triglyceride transesterification — glycerol and esters of fatty acids made it possible to choose the reaction conditions for various lower alcohols providing the supercritical state of reaction mixture and complete conversion of triglycerides. Calculation of the chemical equilibrium for transesterification of fatty acid triglycerides with methanol, both in ideal approximation and taking into account nonideality of the reaction mixture, allowed us to find the reaction conditions that give a minimum yield of mono- and diglycerides and a maximum yield of biodiesel as the target product.

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