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SUPERCRITICAL FLUID TECHNOLOGY

FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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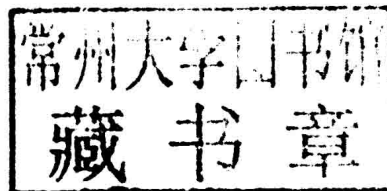
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Contents

Synthesis of Biodiesel Fuel in Supercritical Lower Alcohols with and without Heterogeneous Catalysts (Thermodynamics, Phase and Chemical Equilibriums, Experimental Studies)

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OUTLINE

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1.1 INTRODUCTION

The technology of motor fuel synthesis from vegetable oils or animal fats was developed quite a long time ago. Such fuels are classified as a synthetic fuel called biodiesel (BD). In contrast to diesel fuel produced from petroleum, BD is virtually free of aromatic and sulfur-containing compounds, which decreases the content of hazardous substances in combustion products. The main advantages of BD fuel as compared to similar fuels produced from petroleum are well known [1−3] and require no special discussion here.

The term "biodiesel" refers to fatty acid esters (FAEs), which are commonly obtained by transesterification of vegetable oils—triglycerides (TGs) of fatty acids (1) or esterification of free fatty acids (FFAs) (2) with lower alcohols. Natural oils produced from vegetable feedstock (oil-bearing crops) contain approximately 97% of various triglycerides—FAEs, di- and monoglycerides, and FFAs. Along with simple triglycerides, vegetable oil consists also of mixed triglycerides containing bases of different fatty acids [4]:

$$PFATG + 3CH_3OH \rightleftarrows 3PFAME + glycerol \quad (1.1)$$

$$PFA + CH_3OH \rightleftarrows PFAME + H_2O \quad (1.2)$$

where PFATG is triglyceride of palmitic fatty acid, PFAME is methyl ester of palmitic fatty acid, and PFA is palmitic fatty acid.

Transesterification of triglycerides with alcohol is conventionally performed in the presence of homogeneous [1,5,6] and sometimes heterogeneous [7−9] acid or base catalysts; in recent years, sub- and supercritical lower alcohols have been used for that purpose, both with and without heterogeneous catalyst [10−18,19−22].

Homogeneous catalysis in transesterification reactions: Alkali-catalyzed reactions. The chemical reactions of transesterification and esterification of vegetable oils and animal fat with the participation of lower alcohols are (in the best known processes) catalyzed by alkalis, acids, or enzymes.

In the case of the alkali-catalyzed reactions, the initial raw material and alcohol should contain no water because water directs the reaction toward saponification. The soap that forms reduces the yield of fatty acid esters and leads to problems with separating the FAEs and glycerol from the soapy water. The soap that is created also helps to form an emulsion when washing the products with water, which also makes separation of the target products more difficult [2]. In addition, the initial raw material to be catalyzed by alkali should have a low content of FFAs [6,23,24]; these react with the alkali catalysts to generate soap, which suppresses the formation of FAEs [25]. Unfortunately, many types of vegetable and animal raw material contain large amount of FFAs. Only when the content of FFAs in vegetable oil is no more than 5% can transesterification reactions still occur in the presence of an alkali homogeneous catalyst, provided that an additional amount of oil is introduced into the reactor to compensate for its consumption in saponification.

For synthesized biodiesel to meet the main international standards (e.g., American ASTM D6751 [26]), the ester and glycerol must first be separated; then, the ester must be washed and dried. Ester washing and drying are required to neutralize any residues of the homogeneous catalyst and to remove any soap that has formed. Ester drying is also needed to remove the water used in washing.

Acid-catalyzed transesterification. One of the drawbacks of transesterification reactions catalyzed by alkalis is their sensitivity to the purity of raw material (reactants), especially to water and to FFAs. Because of this, a process for the transesterification of vegetable raw material with an FFA content of more than 1% catalyzed by homogeneous acid catalysts has been proposed. The process is less sensitive to the presence of FFAs in the raw material. The transesterification reaction of vegetable oils with the use of sulfuric and hydrochloric acids (1−5%) occurs in the temperature range of 25−60 °C, at an oil/solvent (alcohol) molar ratio of 1:4 to 1:30, a water content of 0.1−5%, an FFA content of 0−33%, and a contact time of 48−96 h. It has been shown that under such conditions for the reaction, the conversion of >90% oils was not achieved when the raw material contained approximately 5% FFAs or 0.5 wt% of water. A high alcohol content increases the degree of oil conversion but reduces the productivity of the process. Comparisons also showed that sulfuric acid is superior to hydrochloric acid as a catalyst. The main

disadvantage of using a homogeneous acid catalyst for the transesterification of oils is an extremely low rate of reaction.

Acid- and alkali-catalyzed two-stage transesterification. As shown above, acid and alkali catalysts have both advantages and disadvantages in the transesterification of vegetable oils. In light of this, we propose using both types of catalysts for the synthesis of biodiesel. In such cases, an acid catalyst is initially used to transform FFAs into esters and to reduce the FFA levels in the raw material to 1%. In the second stage, the transesterification of oils can finally be conducted with the use of an alkali catalyst. It has thus been shown that:

1. Two-stage acid-alkali transesterification improves the productivity (yield) of fatty acid methyl esters.
2. The reaction rate rises along with the concentration of homogeneous catalyst.
3. When ethyl alcohol is used as a solvent, the rate at which the FFA concentration is reduced is higher than with methanol.

The conventional methods now used for the large-scale production of biodiesel fuel from vegetable raw material (i.e., oils) using homogeneous catalysts thus have serious drawbacks: the process is multistage; specific requirements are imposed on the initial raw material; it is necessary to separate homogeneous catalyst from the reaction products; large quantities of byproducts are produced; and the contact time of the reaction mixture is quite long. These disadvantages currently make the production of biodiesel noncompetitive when compared to diesel fuel obtainable from petroleum.

Heterogeneous catalysis in transesterification reactions. Solid catalyst with the same acidic or alkali properties as homogeneous liquid catalyst eliminates the problem of reactor material corrosion, does not require the separation of products and acid, and makes it possible to perform the process in the continuous mode. At the same time, some poisoning of the heterogeneous catalyst is to be expected, along with a reduction in its activity and the emergence of pore diffusion resistance, resulting in a low rate of reaction.

The surface of the heterogeneous catalyst used in the transesterification of triglycerides must have hydrophobic properties in order to limit glycerol and water adsorption on the active centers of the catalyst, as such adsorption results in a loss of its activity. The properties and nature of heterogeneous catalyst being used determine to a large extent the conditions for conducting the reaction and the method of product separation. Heterogeneous catalysts with acid [5,27] or basic [28,29] properties are used in triglyceride transesterification reactions, as in the case of homogeneous catalysts.

Heterogeneous catalysts with basic properties. As such catalysts, we investigated oxides and hydroxides of alkali metals: CaO, ZnO, SrO, MgO/Al_2O_3, zeolites, and the like.

Zeolites with basic properties. Synthetic zeolites, as a rule, have uniform pore structure and identical pore size. Zeolite with various basic or acidic properties can be developed and modified to change the hydrophobic properties of its surface. According to the literature data [30,31], NaX, KX, and CsX zeolites exhibit low activity in transesterification reactions of soybean oil (after 24 h of reaction, the yield of esters was no more than 10.3%). Titanium and lithium containing zeolites of the ETS-4 and ETS-10 types, however, exhibited high activity in the investigated reactions (after 3 h of reaction, the yield of esters was ~92%) [30,32]. The use of alkali metal oxides or salts on zeolites considerably raises their activity in transesterification [33].

Catalysts based on alkali metal oxides. Alkali metal oxides are the main catalysts for the reactions of triglyceride transesterification. The activity of oxides of group II metals changes in the order Mg > Ca > Sr > Ba. Bases containing Ca are considered to be the most promising catalysts due to their low cost, low toxicity, and poor solubility in lower alcohols [11,34], despite their relatively low catalytic activity in reactions of triglyceride transesterification (after 25 min of reaction, oil conversion is a mere 2.5%). Adding small amounts of Li (0.23 and 1.23 wt%), however, raises the initial raw material's degree of conversion from 83% to 100% [35,36].

Alkali metal salts on porous supports. The reactions of fatty acid esterification and triglyceride transesterification with lower alcohols also occur on catalysts obtained by using alkali metal salts on different porous supports [29,37]. Plain supports (e.g., aluminum oxide) do not, as a rule, exhibit any noticeable catalytic activity. The use of salts such as K_2CO_3, KF, $LiNO_3$, and NaOH results in a high degree of conversion of vegetable oil triglycerides [38]. Another promising catalyst for the transesterification of vegetable oil triglycerides is KF supported on ZnO [39]. The use of 15 wt% of KF on ZnO and subsequent calcining at 873 K for 5 h was shown to produce a catalyst with strong basic properties, ensuring its activity in reactions.

Heterogeneous catalysts with acid properties. Some heterogeneous catalysts with acid properties showed high activity in reactions of fatty acid esterification and triglyceride transesterification. Among these were zeolites [40,41]; modified oxides of zirconium (TiO_2/ZrO_2, WO_3/ZrO_2, K_2O/ZrO_2) [5,37,42,43] and titanium [41]; sulfides of zirconium oxides (SO_4/ZrO_2) [41] and of tin [44,45]; ion-exchange resins [41,46,47] and other materials [1,6,48–50]. To achieve high degrees of conversion of the initial oil, the reaction temperature for the majority of these catalysts must be considerably higher than

that for the basic catalysts [42]. However, the increase in the reaction temperature serves to lower their activity, especially in the case of resins [43].
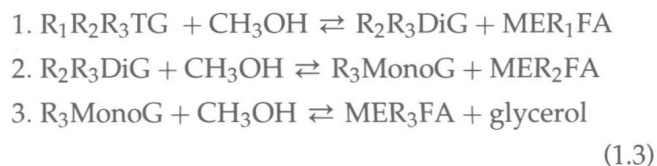
Synthesis of biodiesel in supercritical lower alcohols. Transesterification in supercritical lower alcohols is a promising new approach for the development of efficient and relatively inexpensive processes for the synthesis of biodiesel from vegetable oils, animal fats, and food industry waste. Such studies have been reported in the literature [10−14,51]. 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, 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), and avoid wastewater that earlier resulted from washing the reaction products for removal of homogeneous alkaline or acid catalysts; all of this essentially reduces the cost of biodiesel. It should be noted that transesterification of triglycerides in supercritical alcohols, in contrast to a similar reaction with participation of homogeneous catalysts, proceeds selectively to yield glycerol and esters of fatty acids and gives only a small amount of side products.

Heterogeneous catalysts for the reaction of oil transesterification in supercritical alcohols. Despite obvious advantages of noncatalytic synthesis of biodiesel in supercritical lower alcohols over respective synthesis in subcritical alcohols catalyzed by homogeneous systems, the studies of these reactions in the presence of heterogeneous catalysts are of great interest as well [15,18]. This interest stems from an opportunity to decrease the reaction temperature that makes the process more energy efficient, as well as to reach the required selectivity regardless of the feedstock type.

The end product of transesterification reaction, biodiesel, must comply with the requirements to diesel fuel; in this connection, it is necessary to separate methyl esters from methanol (which is taken in excess) and glycerol, and to perform washing and drying of esters, which leads to a large amount of waste [1]. A general problem in the synthesis of biodiesel under conventional and supercritical conditions is related to the large amount of glycerol produced by the reaction; it cannot be used in pure form and should be converted into useful products. In addition, under supercritical conditions of biodiesel synthesis, esterification of FFAs (a low-percentage component of vegetable oil) yields water, which should be removed from biodiesel fuel.

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 represented by Scheme (1.3):

$$
\begin{aligned}
&1.\ R_1R_2R_3TG + CH_3OH \rightleftarrows R_2R_3DiG + MER_1FA \\
&2.\ R_2R_3DiG + CH_3OH \rightleftarrows R_3MonoG + MER_2FA \\
&3.\ R_3MonoG + CH_3OH \rightleftarrows MER_3FA + glycerol
\end{aligned}
$$

$$(1.3)$$

Here, R_1, R_2, R_3 correspond to alkyl groups of three different fatty acids, such as palmitic, oleic, or linoleic. For $R_1 \neq R_2 \neq R_3$, the transformations of such a mixed triglyceride by Scheme (1.3) will include 12 reactions. For $R_1 = R_2 \neq R_3$, the number of reactions will reduce to 7. A comparison of reaction Scheme (1.1) with Scheme (1.3) gives grounds to conclude, for example, that equilibrium compositions for the reaction calculated by the single- or three-step schemes may strongly differ.

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 [52−60], 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, FFAs, 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, compare the data obtained, and select the most correct data by comparing with available results of experiments. 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 TGs with lower alcohols in a wide range of pressures, temperatures, and ratios of initial reactants. Calculations will be made to determine the reaction conditions, providing a maximum yield of the target product—esters of fatty acids.

1.2 CALCULATION OF THERMODYNAMIC AND PHYSICOCHEMICAL DATA FOR INDIVIDUAL COMPOUNDS

To calculate the equilibrium constant of a chemical reaction and its variation in a wide range of temperatures and pressures, it is necessary to acquire thermodynamic and physicochemical data for individual compounds and reaction participants, namely the critical parameters T_{cr} and P_{cr}, boiling point T_{boil}, standard values of the formation enthalpy and entropy, ΔH_f^o

(298.15 K) and ΔS_f^o (298.15 K), heat capacity as a function of temperature $C_p(T)$, and acentric factor ω. For some simple compounds, such data can be found in reference books; however, for the majority of complex organic compounds, thermodynamic parameters are calculated using appropriate semiempirical and empirical methods.

1.2.1 Determination of Critical Parameters for Individual Substances

By now, numerous group methods have been suggested for determination of critical parameters of individual substances and their boiling points. In the present work, we compare data on critical parameters and boiling points of triglycerides, fatty acids, and esters of fatty acids that were calculated using different group methods developed by A.L. Lydersen, G. Thodos and L. Riedel [61], K.G. Joback [62], and a method reported in [63]. For the majority of compounds under consideration, it is impossible to determine the indicated parameters in experiments due to thermal instability of the compounds (at temperatures above 250 °C, virtually all fats decompose to form glycerol, acrolein, etc.). Some Internet sources provide experimental values of the boiling points for one or two triglycerides, but these values were obtained at low pressures (about 10 Torr). Thermodynamic parameters calculated by different methods were compared with the available literature data (e.g., [55,60]).

Knowing the critical temperature of a compound, it is possible to calculate its boiling point by the following relationship:

$$T_{boil} = \Theta T_{cr}, \tag{1.4}$$

where Θ depends on the structure of the molecule, polarity, and dipole moment, among others. L. Riedel, A.L. Lydersen, and A. Jadoul [61] suggested some dependences for calculation of Θ from the fractions of atoms and groups of atoms. On the other hand, H.P. Meissner [61] proposed a formula for determination of the boiling point without knowing the critical temperature of a compound:

$$T_{boil} = \frac{637 R_D^{1.47} + B}{P_{ch}}, \tag{1.5}$$

where B is the constant, R_D is the molar refraction, and P_{ch} is the parachor, for which the value can also be found by the methods of F.Z. Eisenlohr, A. Vogel, S. Soegden [61], and others.

As an example calculation, Table 1.1 lists the values of T_{cr}, P_{cr}, and T_{boil} for oleic fatty acid triglyceride (OFATG) obtained using three different methods; a comparison with the recent literature data is presented. One may

TABLE 1.1 Critical Temperature, Pressure, and Boiling Point for OFATG Calculated by Different Methods

Parameter	Method			Literature Data
	Ref. [63]	Riedel [61]	Thodos [61]	
T_{boil}, K	854	743.5	—	827.4 [60]
T_{cr}, K	1038	1245	945.6	947 [55], 977.9 [60]
P_{cr}, MPa	0.47	0.46	—	0.48 [55], 0.33 [60]

see that three methods give virtually identical values of critical pressure. Riedel's method [61] uses a simple calculation procedure, so it was chosen for determination of P_{cr}.

As seen from Table 1.1, different methods used for calculation of critical temperature give a considerable spread of values. In the literature [55,60], we found only the critical parameters and standard enthalpy formation for OFATG, which allowed us to estimate the calculation deviation. According to Table 1.1, the closest calculated value is obtained by the Thodos's method; therefore this method was taken as the most accurate one and was used to calculate the critical temperature for all the chosen substances. However, being applied to the calculation of T_{boil}, this method introduces an essential error.

With the known values of intensive thermodynamic parameters, the acentric factor can be calculated using the formula suggested in [64]:

$$\omega = \frac{3}{7} \lg\left(P_{kp}\right) \frac{\Theta}{1 - \Theta} - 1, \quad \text{where } \Theta = T_{boil}/T_{cr}. \tag{1.6}$$

The calculated parameters T_{cr}, P_{cr}, T_{boil}, and ω for mono-, di-, and triglycerides, FFAs, 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 are presented in Table 1.2.

1.2.2 Calculation of Standard Values of the Formation Enthalpy, Gibbs Energy, and Entropy

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 [65,66], semiempirical method of the MINDO/3 type [67], and the group methods [61,63], in particular, the Joback method [62].

TABLE 1.2 Critical Parameters, Boiling Points, and Acentric Factors for Compounds Used in the Calculation

Substance	Formula	T_{boil}, K	T_{cr}, K	P_{cr}, atm	ω
PFA	$C_{16}H_{32}O_2$	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
PFADiG	$C_{35}H_{68}O_5$	618	780	13.5	0.85
PFAMonoG	$C_{19}H_{38}O_4$	590	760	14.65	0.73
OFATG	$C_{57}H_{104}O_6$	854	946	4.52	1.62
OFADiG	$C_{39}H_{72}O_5$	757	870	8.63	1.68
OFAMonoG	$C_{21}H_{40}O_4$	660	800	12.75	1.02
LFATG	$C_{57}H_{98}O_6$	860	945	4.6	1.86
LFADiG	$C_{39}H_{68}O_5$	756	870	8.37	1.62
LFAMonoG	$C_{21}H_{38}O_4$	660	800	12.14	1.19
PPOFAG	$C_{53}H_{100}O_6$	667	811	11.96	1.14
PPFADiG	$C_{35}H_{68}O_5$	646	811	10.3	0.785
POFADiG	$C_{37}H_{70}O_5$	729	855	10.2	1.523
OFAMonoG	$C_{21}H_{40}O_4$	663	802	12.4	1.239
PFAMonoG	$C_{19}H_{38}O_4$	590	760	14.6	0.736
OLLFAG	$C_{57}H_{100}O_6$	860	945	4.52	1.62
LOFADiG	$C_{39}H_{70}O_5$	702	813	8.9	1.569
LLFADiG	$C_{39}H_{68}O_5$	751	868	9.0	1.651
LFAMonoG	$C_{21}H_{38}O_4$	657	798	12.5	1.190
POLFAG	$C_{55}H_{100}O_6$	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

PFA, 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; PPOFAG, palmitic, palmitic, oleic glyceride of fatty acid; POLFAG, palmitic, oleic, linoleic glyceride of fatty acid; OLLFAG, oleic, linoleic, linoleic glyceride of fatty acid; PPFADiG, palmitic, palmitic diglyceride of fatty acid; POFADiG, palmitic, oleic diglyceride of fatty acid; OFAMonoG, oleic monoglyceride of fatty acid; PFAMonoG, palmitic monoglyceride of fatty acid; LOFADiG, linoleic, oleic diglyceride of fatty acid; LLFADiG, linoleic, linoleic diglyceride of fatty acid; LFAMonoG, linoleic monoglyceride of fatty acid.

Triglycerides of fatty acids, FFAs, and their esters are organic compounds of a complicated geometrical structure; therefore, calculation of thermodynamic parameters by the methods of quantum and statistical mechanics is highly time-consuming (the computing

time may reach a few tens of hours). Moreover, for molecules of FFAs and their esters that have a relatively simple geometry, data obtained by quantum mechanical calculations are comparable with the available literature data, whereas for triglycerides we failed to acquire probable and sound data. Thus, the Joback method was used to calculate the necessary thermodynamic parameters (standard formation enthalpy and entropy, coefficients for heat capacity as a function of temperature). Results of the calculation are presented in Table 1.3.

1.3 PHASE EQUILIBRIUM IN TRANSESTERIFICATION OF TRIGLYCERIDES OF FATTY ACIDS WITH METHANOL

Under normal conditions (temperature 10−30 °C, atmospheric pressure), it is very difficult to dissolve triglycerides of fatty acids, products of their transesterification, and fatty acids in lower alcohols (in particular, methanol) [58,68]. Only at elevated pressure and temperature can these immiscible liquids form homogeneous single-phase mixtures with properties close to those of compressed liquids. Such conditions generally correspond to the supercritical state of the mixture. Advantages of such a state of the reaction mixture for chemical transformations manifest themselves mainly when the reaction runs entirely in a supercritical region near the critical point of reaction mixture. 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).

1.3.1 Calculation of Phase Diagrams

Table 1.4 lists the calculated values of critical temperature and pressure for OFATG mixtures of different compositions with three lower alcohols. It is seen that the same increase in the mole fraction of alcohol causes

TABLE 1.3 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	ΔH_f (298) J/mol	ΔS_f (298) J/mol/K	Heat Capacity Coefficients[1]		
					A_0	A_1	$A_2 \times 10^4$
PFA	$C_{16}H_{32}O_2$	256	−723,840	−1556	218.82	1.099	−2.404
OFA	$C_{18}H_{34}O_2$	282	−647,900	−1627	246.3	1.192	−2.786
LFA	$C_{18}H_{32}O_2$	280	−530,680	−1503	216.8	1.202	−2.943
PFATG	$C_{51}H_{98}O_6$	806	−2,053,090	−5027	627.5	3.106	−10.55
PFADiG	$C_{35}H_{68}O_5$	568	−1,557,800	−3495	357.2	2.294	−7.908
PFAMonoG	$C_{19}H_{38}O_4$	330	−1,062,510	−1964	217.4	1.314	−4.508
PFAME	$C_{17}H_{34}O_2$	270	−711,490	−1656	144.2	1.164	−4.042
OFATG	$C_{57}H_{104}O_6$	884	−1,825,270	−5481	688.2	3.407	−12.65
OFADiG	$C_{39}H_{72}O_5$	620	−1,405,920	−3637	408.5	2.469	−8.470
OFAMonoG	$C_{21}H_{40}O_4$	356	−986,570	−2035	234.5	1.418	−4.863
OFAME	$C_{19}H_{36}O_2$	284	−635,550	−1727	209.7	1.139	3.717
LFATG	$C_{57}H_{98}O_6$	878	−1,473,610	−4867	683.5	3.308	−11.50
LFADiG	$C_{39}H_{68}O_5$	616	−1,171,480	−3389	405.8	2.453	−8.415
LFAMonoG	$C_{21}H_{38}O_4$	354	−869,350	−1837	233.21	1.410	−4.836
LFAME	$C_{19}H_{34}O_2$	294	−518,330	−1602	239.7	1.021	−3.130
PPOFAG	$C_{53}H_{100}O_6$	832	−1,977,150	−5098	647.7	3.207	−1.89
PPFADiG	$C_{35}H_{68}O_5$	568	−1558	−3495	357.24	2.2937	−.791
POFADiG	$C_{37}H_{70}O_5$	522	−1482	−3566	405.82	2.4528	−0.841
OFAMonoG	$C_{21}H_{40}O_4$	320	−987	−2035	234.53	1.418	−0.486
PFAMonoG	$C_{19}H_{38}O_4$	330	−1063	−1964	217.40	1.314	−0.451
OLLFAG	$C_{57}H_{100}O_6$	880	−1,590,830	−4991	689.8	3.313	−1.16
LOFADiG	$C_{39}H_{70}O_5$	618	−1289	−3513	407.14	2.461	−0.844
LLFADiG	$C_{39}H_{68}O_5$	616	−1250	−3389	405.82	2.453	−0.842
LFAMonoG	$C_{21}H_{38}O_4$	354	−8694	−1837	233.2	1.410	−.484
POLFAG	$C_{55}H_{100}O_6$	856	−1,783,990	−5045	671.0	3.222	−1.13
Methanol	CH_3OH	32	−201,097	−129	23.56	0.0064	0.336
Glycerol	$C_3H_8O_3$	92	−584,721	−490	15.01	0.428	−3.017

[1]$C_p = A_0 + A_1 \times T + A_2 \times T^2$ (J/mol/K).
PFA, 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; PPOFAG, palmitic, palmitic, oleic glyceride of fatty acid; POLFAG, palmitic, oleic, linoleic glyceride of fatty acid; OLLFAG, oleic, linoleic, linoleic glyceride of fatty acid; PPFADiG, palmitic, palmitic diglyceride of fatty acid; POFADiG, palmitic, oleic diglyceride of fatty acid; OFAMonoG, oleic monoglyceride of fatty acid; PFAMonoG, palmitic monoglyceride of fatty acid; LOFADiG, linoleic, oleic diglyceride of fatty acid; LLFADiG, linoleic, linoleic diglyceride of fatty acid; LFAMonoG, linoleic monoglyceride of fatty acid.

a more pronounced decrease in the critical temperature for the system methyl alcohol—OFATG.

The state of the mixtures is presented most comprehensively by their phase diagrams with a fixed position of the critical point. To illustrate the calculation, Figure 1.1 shows in P—T coordinates the phase diagrams of two binary mixtures: mixture 1 (methanol—PFA) and mixture 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. The calculation was made using the earlier developed multifunctional program *Phasediagram* [69]. Calculation

TABLE 1.4   Critical Parameters of OFATG Mixtures in Various Alcohols

Alcohol	Mole Fraction of Alcohol	T_{cr}, K	P_{cr}, MPa
Methyl	0.96	657.6	12.94
	0.98	581.0	11.15
	0.99	553.1	10.06
	0.99	540.1	9.55
Ethyl	0.94	690.6	11.59
	0.97	605.7	10.34
	0.98	574.6	9.22
	0.99	557.6	8.58
Isopropyl	0.93	714.5	10.38
	0.96	621.5	9.51
	0.98	582.6	8.40
	0.98	564.9	7.64

methods and algorithms were described also in our other articles [70–73].

Lines 1 and 2 in Figure 1.1 are called the binodal lines. Dots on the curves indicate the critical points for mixtures 1 and 2 of a specified composition. Outside the region bounded by binodal lines, there are single-phase mixtures: to the left of the critical point is a compressed liquid, whereas to the right is vapor/gas. Within the region bounded by binodal lines, the mixture is
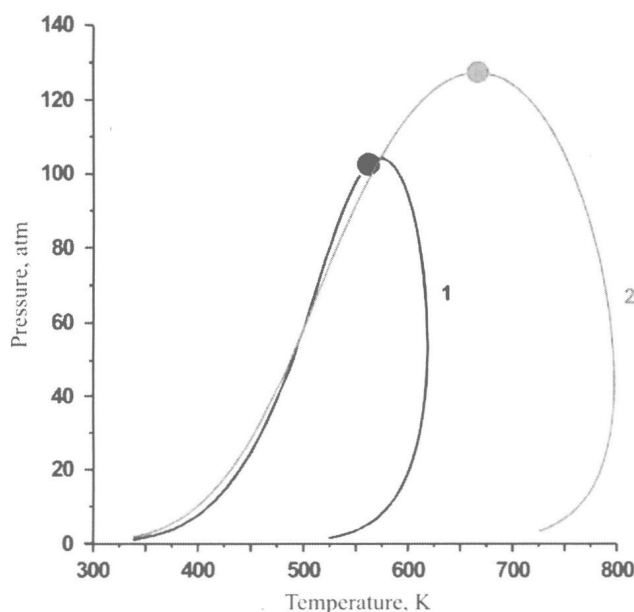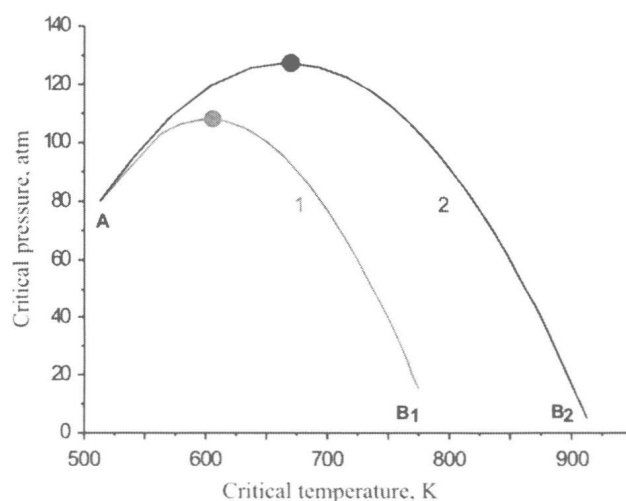
separated into two phases. Noteworthy is the difference in the extent of two-phase regions for mixtures 1 and 2, which is naturally caused by different properties of the mixtures being compared. For these mixtures, the liquid-phase lines virtually coincide, whereas positions of the gas-phase lines differ considerably. Coordinates of critical points for the chosen mixtures are as follows:

Mixture 1: $T_{cr} = 562.3$ K, $P_{cr} = 10.4$ MPa

Mixture 2: $T_{cr} = 666.6$ K, $P_{cr} = 12.9$ MPa

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. Figure 1.2 shows the critical parameters (positions of the critical point) for binary mixtures 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 1 and 5.5 mol% PFATG for mixture 2) is typical of the binary systems with a pronounced difference in critical parameters of individual components [74].

Due to chemical transformations of triglyceride during transesterification with alcohol, its concentration decreases, and reaction products (glycerol and esters of fatty acids) are produced. Quantitative and qualitative changes in the reaction mixture composition are reflected both in the parameters of critical point and in the shape of phase diagram. Calculation was made for two mixtures with the composition corresponding to 50% and 100% conversion of triglyceride in methanol. According to the calculation, during the transformation

FIGURE 1.1   Phase diagrams on the P–T plane. Curve 1: mixture 1; curve 2: mixture 2. Dots correspond to critical points of the mixtures. (For color version of this figure, the reader is referred to the online version of this book.)

FIGURE 1.2   Critical curves for the mixtures under consideration: 1: mixture 1; 2: mixture 2; A: pure methanol; B_1: pure palmitic acid; B_2: pure triglyceride of palmitic acid. Dots on the curves correspond to the maximum values of critical pressure. (For color version of this figure, the reader is referred to the online version of this book.)