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RESEARCH PAPER

Liquid-Liquid Equilibrium for Ternary Systems Containing Biodiesel + Glycerol + Alcohol (Ethanol or Methanol): Thermodynamic Modeling

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Abstract

Biodiesel is a substitute for fossil fuels which is produced through a transesterification reaction between vegetable oils or animal fats and light alcohols such as methanol or ethanol. In this reaction, along with the production of biodiesel, glycerol as a byproduct and non-reacted alcohol that reduces biodiesel quality is produced. Hence, many studies have been carried out on liquid-liquid equilibrium (LLE) for ternary systems containing biodiesel + glycerol + alcohol. Two phases are formed as 1-rich in biodiesel and 2-rich in glycerol; moreover, alcohol is distributed between these two phases. In this work, based on previous experimental data, the UNIQUAC and NRTL thermodynamic models were used to forecast the composition of the phases. The intermolecular interaction term for each of the models was considered as a linear function of the reverse temperature. In both models, there was no difference between the amount of biodiesel produced from different oils and obtained from the general interaction parameters. Based on the results, the percentage of absolute average deviation for NRTL and UNIQUAC models for biodiesel + glycerol + ethanol system were 1.24% and 2.13%, respectively, and for biodiesel + glycerol + methanol system was 1.13% and 1.71%, respectively.

Keywords:
Biodiesel,
Ethanol or Methanol,
Glycerol,
LLE,
NRTL,
UNIQUAC

Introduction

Today, the largest source of energy consumption is crude oil, and the reduction in crude oil resources is of general anxiety. The use of fossil fuels not only increases greenhouse gas emissions but also restricts their limited resources. As a result, in the last years, many works have focused on biodiesel as an alternative source of energy [1]. Biodiesel has many advantages over petroleum fuels, most notably lower greenhouse gas emissions, favorable combustion profiles, easier storage, ease of transport, biodegradation, and non-toxicity [2-5].

When vegetable oils react with alcohol (ethanol or methanol) in the presence of a catalyst, it results in the production of fatty acid ethyl methyl or esters (FAME or FAEE), which is biodiesel. Biodiesel production reaction ends with an excess of alcohol. In this reaction, the final yield is contaminated with other impurities, such as glycerol as a byproduct and non-reacted alcohol [6]. These impurities affect the performance of biodiesel as a fuel. Glycerol is deposited in engines or stored at the ends of reservoirs. Alcohol can reduce the biodiesel flashpoint [7].

The production of high-quality biodiesel depends on the purification of products obtained from a transesterification reaction. The separation of these products is facilitated by the

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formation of two non-miscible liquid phases. The heavier phase mainly contains glycerol. On the other hand, the lighter phase mainly consists of biodiesel. Extra alcohol is distributed between the two phases [6,8]. As a result, many researchers have studied different ternary systems (containing fatty acid methyl esters + glycerol + methanol and fatty acid ethyl esters + glycerol + ethanol) to understand LLE.

To forecast the final equilibrium composition of the phases, UNIFAC, UNIQUAC, Wilson, and NRTL models have been used in various studies [9-15]. In this study, using experimental data obtained from previous studies, UNIQUAC and NRTL thermodynamic models were used to forecast component equilibrium for ternary systems containing biodiesel + glycerol + ethanol or methanol [8,11,17,20,25-28]. In order to increase the accuracy of the models as well as the general ones, different oils, such as castor oil [16,17,27], coconut oil [12], cottonseed oil [18], crambe oil [19], Jatropha oil curcas [20], Macauba pulp oil [21], palm oil [22], soybean oil [14,15,23-25], sunflower oil [8,11,14], Brazil nut oil [26], canola oil [8,11], and waste fish oil [28] were used for biodiesel (FAEE or FAME) production. The number of collected data on biodiesel + ethanol + glycerol system was 176, and the temperature range was from 293.15 to 343.15 K. Moreover, the number of data on biodiesel + methanol + glycerol system was 142, and the temperature ranged from 293.15 to 333.15 K.

Thermodynamics Modelling

This study used UNIQUAC (UNIversal QUAsi Chemical) [29] and NRTL (Non-Random Two-Liquid) [30] models to calculate γ_i. In the following sections the equations of each model are presented.

UNIQUAC model

Eqs. 1 to 4 have been used to calculate the activity coefficient of the UNIQUAC model:

$$\ln\gamma_i = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j - q_i'\left(1 + \ln\left(\sum_j \theta_j'\tau_{ji}\right) - \sum_j \frac{\theta_j'\tau_{ij}}{\sum_j \theta_k'\tau_{kj}}\right) \quad (1)$$

$$\tau_{ij} = \mathrm{e}^{-\frac{a_{ij}}{R}} = e^{A_{ij}+\frac{B_{ij}}{T}} \qquad (\tau_{ij} \neq \tau_{ji} \text{ and } \tau_{ii} = 0) \quad (2)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad (3)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}, \qquad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \qquad \theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \quad (4)$$

where i, j, and k represent each component; γ is the activity coefficient; τ_{ij} and τ_{ji} are interaction energies between the molecules i and j; x is the mole fraction; A_{ij} and B_{ij} are the binary interaction parameters, and T is the absolute temperature. Also, ϕ_i is the volume fraction of i component, θ_i is the surface fraction of i component, θ_i' is the interaction surface fraction of i component, r_i is the i molecule volume, q_i is the i molecule surface, q_i' is the i molecule interaction surface (fluids other than water or lower alcohols style $q_i = q_i'$), and z is the coordination number (set at 10) [29]. Table 1 presents r_i, q_i, and q_i' values of ethanol, methanol, glycerol, FAEE, and FAME. According to the data at different temperatures, temperature dependence is intended for model interaction parameters.

NRTL model

Eqs. 5 to 7 were used for calculating NRTL activity coefficient model.

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_l x_l G_{li}} + \sum_j \frac{x_j G_{ij}}{\sum_l x_l G_{li}} \left[\tau_{ij} - \frac{\sum_r x_r \tau_{rj} G_{rj}}{\sum_l x_l G_{li}} \right] \quad (5)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} = A_{ij} + \frac{B_{ij}}{T} \qquad \left(\tau_{ij} \neq \tau_{ji} \text{ and } \tau_{ii} = 0\right) \quad (6)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad (\alpha_{ij} = \alpha_{ji} \text{ and } \alpha_{ii} = 0) \quad (7)$$

where i, j, and k represent each component; γ is the activity coefficient; τ_{ij} and τ_{ji} are the interaction energies between the molecules i and j; x is the mole fraction; A_{ij} and B_{ij} are the binary interaction parameters, and T is the absolute temperature. α_{ij} is non-random parameter which is set at 0.2 [31].

Table 1. Parameters r_i, q_i and q_i' for the focused systems

Component	r_i	q_i	q_i'	Ref.
Biodiesel (ethyl ester)	13.72	11.28	11.28	[25]
Biodiesel (methyl ester)	13.17	10.78	10.78	[25]
Ethanol	2.11	1.97	0.92	[30]
Methanol	1.43	1.43	0.96	[30]
Glycerin	4.8	4.91	4.91	[11]

Liquid-Liquid Equilibrium Phase Calculations and Parameters Estimation

Binary interaction parameters of the UNIQUAC and NRTL models are obtained by minimizing the difference between measured and calculated mass fractions. The objective function is presented in the following equation:

$$\text{OF} = 100 \times \frac{1}{D.M.N} \sum_{k=1}^{D} \sum_{j=1}^{M} \sum_{i=1}^{N} \left(\left(w_{ijk}^{\text{B,exp.}} - w_{ijk}^{\text{B,calc.}} \right)^2 + \left(w_{ijk}^{\text{G,exp.}} - w_{ijk}^{\text{G,calc.}} \right)^2 \right) \quad (8)$$

where D is the total number of references in the database; M is the total number of tie lines in reference k; N is the total number of components in the data group; i, j, and k are the components, tie lines, and groups number, respectively; exp. and calc. are the measured and calculated values. Moreover, B and G are biodiesel-rich phase and glycerol-rich phase, respectively.

In this study, the absolute average deviation (AAD %) was used to compare the accuracy of the proposed models, which is presented in the following equation:

$$\text{AAD \%} = 100 \times \frac{1}{D.M.N} \sum_{k=1}^{D} \sum_{j=1}^{M} \sum_{i=1}^{N} \left(\left| w_{ijk}^{\text{B,exp.}} - w_{ijk}^{\text{B,calc.}} \right| + \left| w_{ijk}^{\text{G,exp.}} - w_{ijk}^{\text{G,calc.}} \right| \right) \quad (9)$$

Calculation Algorithm

The equilibrium relations for different components in the biodiesel-rich phase and glycerol-rich phase are presented below:

$$w_i^{\text{B}} \gamma_i^{\text{B}} (w_1^{\text{B}}, w_2^{\text{B}}, w_3^{\text{B}}) = w_i^{\text{G}} \gamma_i^{\text{G}} \left(w_1^{\text{G}}, w_2^{\text{G}}, w_3^{\text{G}} \right) \quad ; i = 1, 2, 3 \quad (10)$$

$$K_i = \frac{\gamma_i^{\text{B}}}{\gamma_i^{\text{G}}} = \frac{w_i^{\text{G}}}{w_i^{\text{B}}} \quad ; i = 1, 2, 3 \quad (11)$$

where K_i is the constant of equilibrium between the two phases for i component. Mass balance for the system is presented as follows:

$$F = B + G = 1 \quad (12)$$
$$Z_i F = w_i^{\mathrm{B}} B + w_i^{\mathrm{G}} G \;\; ; i = 1, 2, 3 \quad (13)$$

where F, B, and G are feed mass, biodiesel-rich phase mass, and glycerol-rich phase mass, respectively. Also, Z_i is the mass fraction of component i in the feed. With merging Eqs. 11, 12, and 13, the following equations are obtained.

$$w_i^{\mathrm{B}} = \frac{Z_i}{1 + (K_i - 1)G} \;\; ; i = 1, 2, 3 \quad (14)$$
$$w_i^{\mathrm{G}} = \frac{K_i Z_i}{1 + (K_i - 1)G} \;\; ; i = 1, 2, 3 \quad (15)$$

Sum of the mass fraction of all components in biodiesel-rich phase and glycerol-rich phase are equal to 1, so $\sum w_i^{\mathrm{B}} - \sum w_i^{\mathrm{G}} = 0$, and:

$$\sum_{i=1}^{3} \frac{Z_i (K_i - 1)}{1 + (K_i - 1)G} = 0 \quad (16)$$

The equilibrium calculation algorithm is as follows:

1. Input the components mass fraction (Z_i) and temperature (T).
2. Guess values of the interaction parameters between different molecules (A_{ij} and B_{ij}).
3. Guess initial values for the components mass fraction of biodiesel-rich phase (w_i^{B}) and glycerol-rich phase (w_i^{G}).
4. Calculate the activity coefficients of components in different phases.
5. Calculate K_i values for different components using Eq. 11.
6. Solve Eq. 16 using the Newton - Raphson method and determine G.
7. Solve w_i^{B} and w_i^{G} values using Eqs. 14 and 15.
8. Check the objective function; if OF $< \varepsilon$ go to the end, otherwise go to step 2.

Results and Discussion

Intermolecular Interaction Parameters

Of all the experimental data described in the materials and methods section (section 2), 70% was used to determine the intermolecular interaction parameters of the presented models. Using the aforementioned algorithm, we obtained the intermolecular interaction parameters of the UNIQUAC and NRTL models. Table 2 presents the values of interaction parameters between molecules of biodiesel + glycerol + ethanol (A_{ij} and B_{ij}) for different thermodynamic models. Moreover, Table 3 presents the same items for the biodiesel+ glycerol+ methanol ternary system. The value of the objective function (Eq. 8) for biodiesel+ glycerol+ ethanol system obtained using UNIQUAC and NRTL models were 0.088 and 0.037, respectively. Moreover, this value for biodiesel+ glycerol+ methanol systems was 0.087 and 0.052, respectively (for two ternary systems the accuracy of NRTL > UNIQUAC).

Comparison of Different Models

Using the thermodynamic models presented in this study on all databases were obtained to be of good thermodynamic models. Tables 4 and 5 show the average absolute deviation (AAD%) of models for each reference separately (Table 4 for equilibrium systems of biodiesel + glycerol + ethanol and Table 5 for equilibrium systems of biodiesel + glycerol + methanol). As shown

in these tables, it is clear that the NRTL model has minimum errors, and the UNIQUAC model has maximum errors.

Table 2. UNIQUAC and NRTL interaction parameters between biodiesel, glycerol, and ethanol obtained from global temperature fit

Pair ij	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)
UNIQUAC				
Biodiesel-Ethanol	-0.113	1.375	9.669	0.403
Biodiesel-Glycerol	-0.800	1.015	-3.506	-4.284
Ethanol-Glycerol	0.980	1.523	0.191	-5.778
NRTL				
Biodiesel-Ethanol	-0.863	-1.711	-12.063	5.979
Biodiesel-Glycerol	-2.218	-1.756	-1.077	10.065
Ethanol-Glycerol	-0.891	0.326	6.124	-0.841

Table 3. UNIQUAC and NRTL interaction parameters between biodiesel, glycerol, and methanol obtained from global temperature fit

Pair ij	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)
UNIQUAC				
Biodiesel-Methanol	-1.142	1.142	5.745	-3.958
Biodiesel-Glycerol	-3.389	3.680	-2.926	8.125
Methanol-Glycerol	-2.299	0.281	0.423	0.868
NRTL				
Biodiesel-Methanol	-0.089	-2.260	-26.430	-5.172
Biodiesel-Glycerol	-2.250	-1.892	-12.718	11.725
Methanol-Glycerol	0.326	0.726	14.770	-18.257

Fig. 1 shows the predicted ethanol mass fraction values by models in biodiesel-rich phase and glycerin-rich phase and compares them with their counterpart experimental values. Moreover, Fig. 2 shows these values for methanol in biodiesel-rich and glycerol-rich phases. As shown in these two figures (Figs. 1 and 2) it is clear that both models accurately predicted the amount of ethanol and methanol in the glycerol-rich phase which was higher than the biodiesel-rich phase. This can be due to the same biodiesel consideration despite using different oils.

Table 4. LLE data of the systems of biodiesel + glycerol + ethanol and accuracy of the UNIQUAC and NRTL models

No.	System	T (K)	NDP	AAD %		Ref.
				UNIQUAC	NRTL	
1	Castor oil biodiesel+ Glycerol+ Ethanol	298.15	6	3.13	1.26	[16]
2		303.15	5	2.14	1.18	[17]
3		318.15	5	1.65	0.68	[17]
4		333.15	5	2.09	1.00	[17]
5		333.15	7	3.27	1.56	[16]
6	Coconut oil biodiesel+ Glycerol+ Ethanol	293.15	6	1.61	1.42	[12]
7		323.15	5	2.11	1.78	[12]
8	Cottonseed oil biodiesel+ Glycerol+ Ethanol	293.15	6	1.04	0.67	[18]
9		313.15	6	0.98	0.58	[18]
10		333.15	6	1.61	1.24	[18]
11	Crambe oil biodiesel+ Glycerol+ Ethanol	298.15	6	2.36	1.09	[19]
12		318.15	6	2.34	0.92	[19]
13		338.15	6	2.40	0.85	[19]
14	Jatropha curcas oil biodiesel+ Glycerol+ Ethanol	303.15	4	1.66	1.23	[20]
15		318.15	4	1.75	1.38	[20]
16		333.15	4	1.71	1.49	[20]
17	Macauba pulp oil biodiesel+ Glycerol+ Ethanol	298.15	6	5.78	6.37	[21]
18	Palm oil biodiesel+ Glycerol+ Ethanol	298.15	7	1.64	0.85	[22]

Table 4. Continued

19		323.15	8	1.83	0.71	[22]
20	Soybean oil biodiesel+ Glycerol+ Ethanol	293.15	5	1.11	0.40	[14]
21		298.15	4	1.19	0.84	[15]
22		298.15	6	2.38	1.04	[23]
23		300.15	5	2.17	1.30	[24]
24		303.15	6	3.37	1.24	[25]
25		318.15	4	2.41	1.06	[25]
26		323.15	5	1.37	1.11	[24]
27		323.15	5	2.44	1.59	[14]
28		333.15	6	1.30	1.14	[25]
29		333.15	5	3.03	0.95	[15]
30		343.15	5	2.36	1.10	[24]
31	Sunflower oil biodiesel+ Glycerol+ Ethanol	298.15	6	1.47	1.10	[14]
32		313.15	6	1.49	0.56	[14]

Table 5. LLE data of the systems of biodiesel + glycerol + methanol and accuracy of the UNIQUAC and NRTL models

No.	System	*T* (K)	NDP	AAD %		Ref.
				UNIQUAC	NRTL	
1	Brazil nut oil biodiesel+ Glycerol+ Methanol	303.15	5	2.75	1.14	[26]
2		323.15	5	2.28	1.10	[26]
3	Canola oil biodiesel+ Glycerol+ Methanol	293.15	5	0.79	1.02	[11]
4		303.15	4	1.38	1.02	[8]
5		303.15	5	1.12	0.60	[11]
6		313.15	4	0.92	1.00	[8]
7		313.15	5	1.05	0.62	[11]
8		323.15	4	1.07	1.17	[8]
9	Castor oil biodiesel+ Glycerol+ Methanol	298.15	7	3.90	3.49	[27]
10		303.15	5	2.13	1.27	[17]
11		318.15	5	2.82	1.61	[17]
12		333.15	5	2.06	1.59	[17]
13	Jatropha curcas oil biodiesel+ Glycerol+ Methanol	303.15	6	1.48	1.01	[20]
14		318.15	6	1.90	0.97	[20]
15		333.15	5	1.56	1.32	[20]
16	Soybean oil biodiesel+ Glycerol+ Methanol	303.15	7	1.24	0.55	[25]
17		318.15	6	1.57	0.51	[25]
18		333.15	6	3.52	2.90	[25]
19	Sunflower oil biodiesel+ Glycerol+ Methanol	293.15	5	0.80	0.75	[11]
20		303.15	4	0.89	1.07	[8]
21		303.15	5	0.92	0.71	[11]
22		313.15	4	1.39	1.00	[8]
23		313.15	5	0.86	0.59	[11]
24		323.15	4	1.10	0.96	[8]
25	Waste fish oil biodiesel+ Glycerol+ Methanol	298.15	6	1.52	0.98	[28]
26		313.15	7	1.92	1.24	[28]
27		328.15	7	1.28	0.72	[28]

Furthermore, Figs. 3 and 4 present the accuracy of the UNIQUAC and NRTL thermodynamic models for predicting systems composition (Fig. 3 for equilibrium system of biodiesel + glycerol + ethanol and Fig. 4 for equilibrium system of biodiesel + glycerol + methanol). In these figures, it is clear that both models had the highest AAD% for predicting Macauba pulp oil biodiesel + Glycerol + Ethanol system composition. In this study, the differences between biodiesels produced from different oils have not been considered for determining interaction parameters. Therefore, the thermodynamic models have less adaptation with experimental data when the biodiesel compositions are more different from the others.

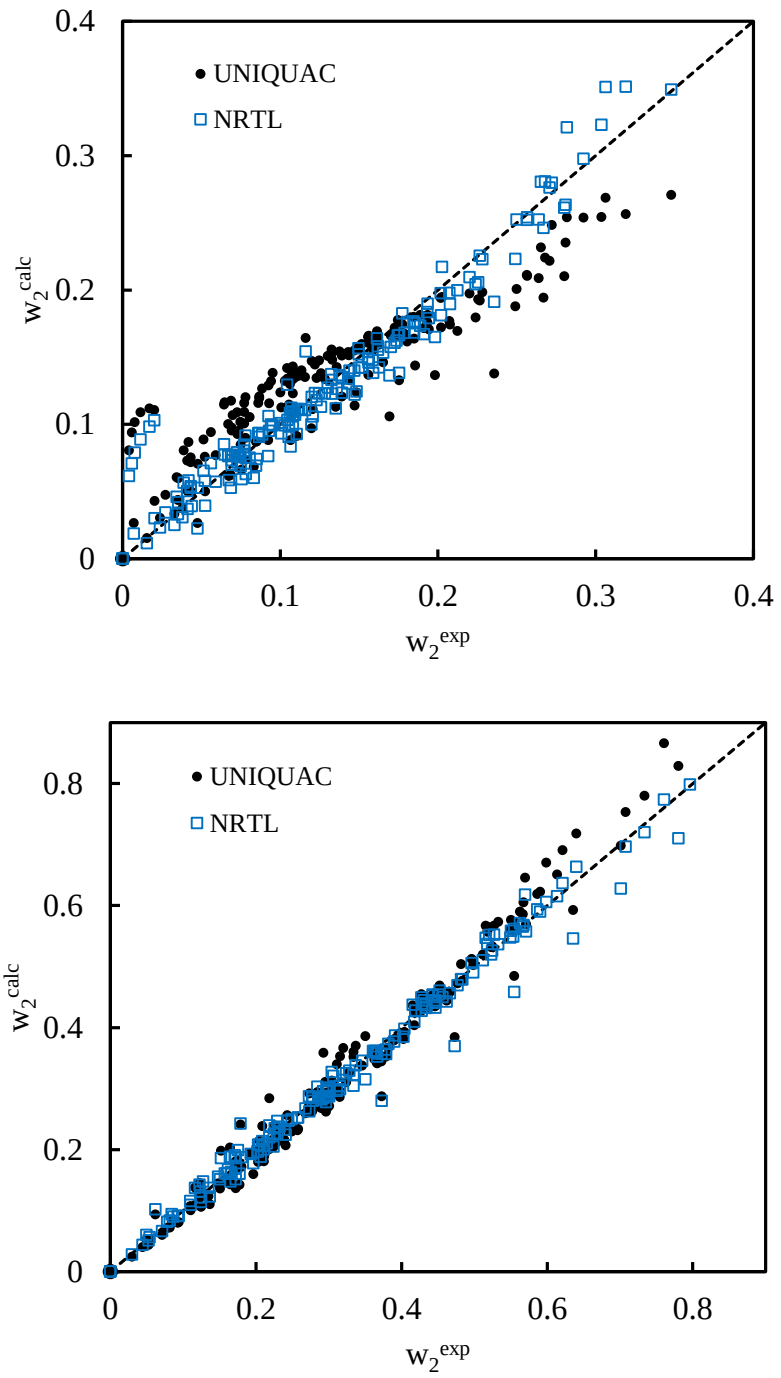

Fig. 1. Adjustment of the calculated and experimental ethanol mass fraction (w_2) for the LLE a) biodiesel-rich phase; b) glycerol-rich phase

Besides, the accuracy of each model is generally shown in Figs. 3 and 4. AAD% of the UNIQUAC and NRTL models for biodiesel + glycerol + ethanol system was 2.13% and 1.24%, respectively, and for biodiesel + glycerol + methanol system was 1.71% and 1.17%, respectively. The accuracy of different models is as follows: NRTL>UNIQUAC. The accuracy of the UNIQUAC model was lower than the other model which might be due to taking average values for r_i, q_i, and q_i' for the biodiesel produced from different oils.

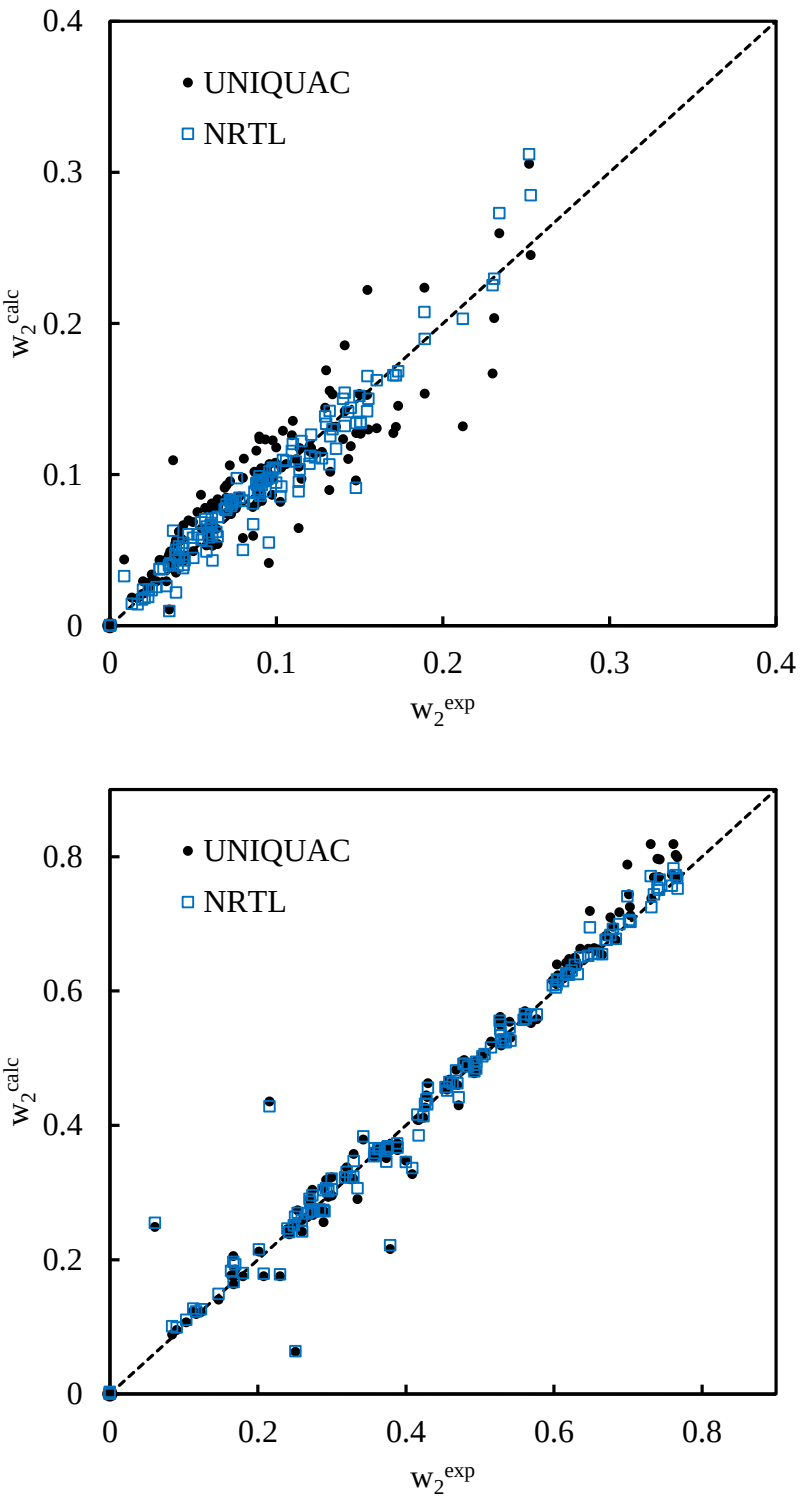

Fig. 2. Adjustment of the calculated and experimental methanol mass fraction (w_2) for the LLE. a) biodiesel-rich phase; b) glycerol-rich phase

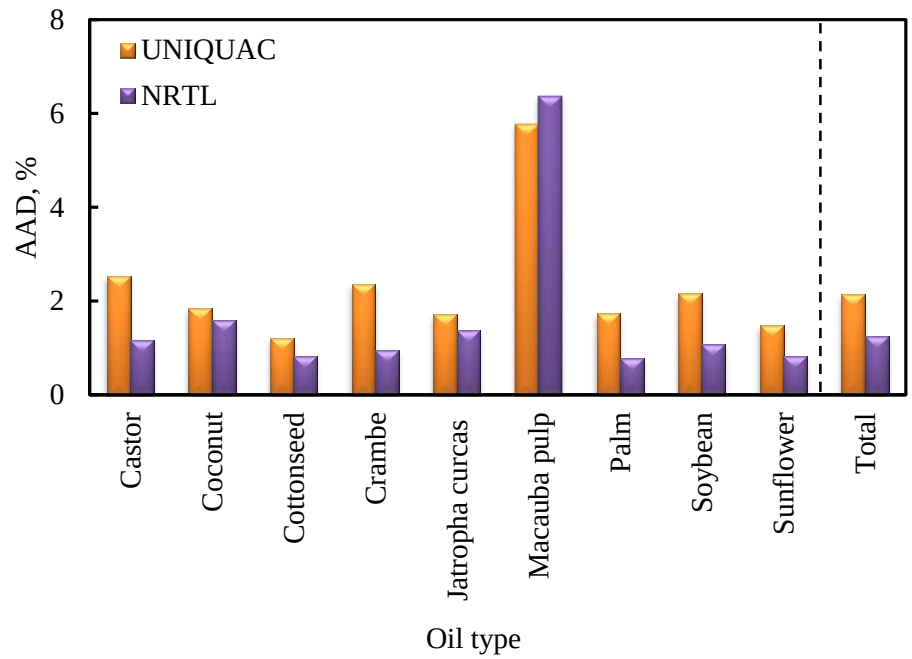

Fig. 3. Adjustment of the accuracy of thermodynamic models for calculating the composition of the components of biodiesel + glycerol + ethanol ternary systems

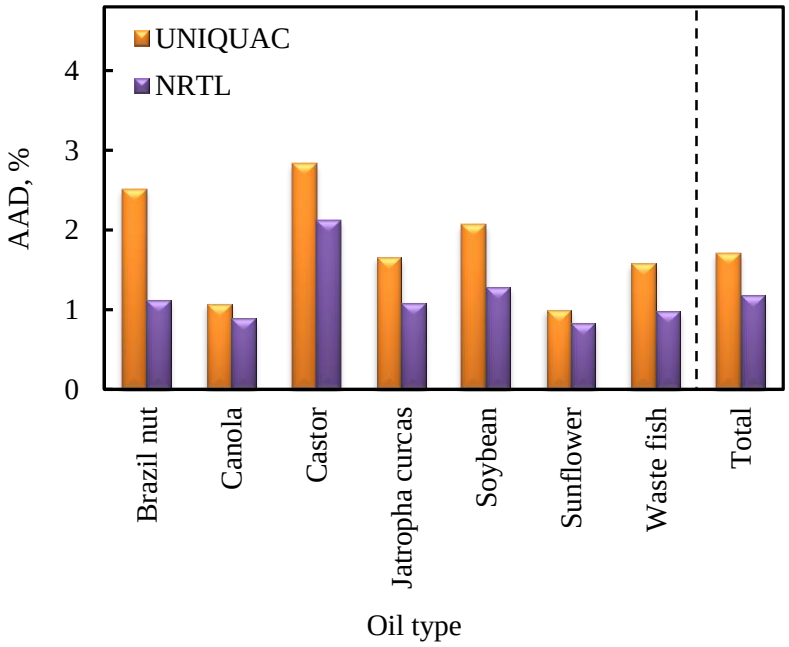

Fig. 4. Adjustment the accuracy of thermodynamic models for calculating the composition of the components of biodiesel + glycerol + methanol ternary systems

Conclusion

The LLE for ternary systems containing biodiesel (FAEE or FAME) + glycerol + alcohol (ethanol or methanol) was studied to examine two thermodynamic models (UNIQUAC and NRTL). In these models, the intermolecular interaction parameters for all biodiesels produced (regardless of the type of oil used for producing biodiesel) were considered the same. These parameters were considered as a two-term function of the inverse temperature. The outcomes showed the high accuracy of the two models.

The results also showed that the NRTL model was more accurate than the UNIQUAC model for predicting the composition of the liquid-liquid equilibrium of biodiesel + glycerol + alcohol system.

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