



Liquid–liquid equilibrium data and thermodynamic modeling, at $T/K = 298.2$, in the washing step of ethyl biodiesel production from crambe, fodder radish and macauba pulp oils



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HIGHLIGHTS

- LLE data of systems containing water + ethanol + ethyl biodiesels were presented.
- NRTL, UNIQUAC, UNIFAC-LLE and UNIFAC-Dortmund were compared.
- Description of the LLE among the systems was different.
- NRTL and UNIQUAC properly described the LLE of the systems.
- The use of UNIFAC derived models results in deviations higher than 1.9%.

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ABSTRACT

In this work, pseudo-ternary liquid–liquid equilibrium data were obtained for three systems composed for water + ethanol + ethyl biodiesel from crambe, fodder radish and macauba pulp oils, at $T/K = 298.2$. Ethanol, which distributes in both phases, had greater affinity for the water-rich phase. Biodiesels and water showed almost complete immiscibility. Modeling with the NRTL and UNIQUAC thermodynamic models was performed, resulting in average deviations ranging from 0.49% to 1.29%. UNIFAC-LLE and UNIFAC-Dortmund were used in prediction of the liquid–liquid equilibrium of these systems, resulting in average deviations ranging from 1.91% to 2.27% for the systems containing biodiesel from crambe and fodder radish oils, and ranging from 3.17% to 3.28% for biodiesel from macauba oil.

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1. Introduction

Biodiesel, defined as mono-alkyl esters of fatty acid from vegetable oils or animal fats, is an environmentally attractive alternative to conventional petroleum diesel fuel. In transesterification, the reaction by which biodiesel is produced, the stoichiometric relationship between alcohol and oil is 3:1, however an excess of alcohol is typically employed to improve conversion towards the desired product. Biodiesel presents many important technical advantages over petroleum diesel including low toxicity, derivation from renewable feedstocks, superior biodegradability, negligible sulfur content, higher flash point and fewer exhaust emissions [1]. The biodiesel produced with oils from crambe

(*Crambe abyssinica*) seeds, fodder radish (*Raphanus sativus*) seeds and macauba (*Acrocomia aculeata*) pulp is technically interesting due to the properly fatty acid composition of these oils, the high oil content and the favorable agricultural characteristics of these plants, and the advantageous physical properties of the biofuel [2–8].

Although commercial processes use vegetable oils and methanol in the transesterification reaction, the use of ethanol in biodiesel synthesis is appealing because it is produced from biorenewable sources, resulting in a completely agricultural-based fuel obtained by ethanolysis [9,10].

After the transesterification reaction, glycerol is separated by settling or centrifuging to form two distinct phases, an ester-rich phase and a glycerol-rich phase. Considering a typical alkaline catalysis where 3 moles in excess of ethanol are used in the reaction, and an ideal settling, the ester-rich phase has a very

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low glycerol content, about 0.7% [8,11], due to the low solubility between glycerol and ethyl esters. Following this separation step, the ester-rich phase is purified before being used as a biofuel [12,13].

Water washing is very effective in removing contaminants from biodiesel in purification steps due to the high solubility of a set of compounds in this solvent. This process can reduce methanol and residual free glycerol levels down to biodiesel standard quality requirements and can be efficiently carried out at ambient temperature, because this is the most economical condition for biodiesel purification [12,13]. In this step of the biodiesel production process, two immiscible phases are formed, one rich in esters and one rich in water, where methanol distributes in both phases.

The study of liquid–liquid equilibrium (LLE) for water washing in ethyl biodiesel production is important because this step determine the final biodiesel purity according to the biodiesel standard quality requirements and allows for evaluating possible ester losses to the water-rich phase. In addition, knowledge on the LLE of systems containing biodiesel + water + ethanol is crucial for optimization of this purification step, which can allow for reducing the large amount of water used in this process.

Despite of the relevance of this knowledge, there is little experimental data related to the LLE behavior of systems composed of water + alcohol + pure methyl esters [14], pure ethyl esters [15] and methyl and ethyl biodiesels [16,17]. Additionally, only one of these works [14] compared different g^E and activity coefficient thermodynamic models when describing the LLE of these systems with similar components. None of these studies compared LLE behavior of these systems as a function of different fatty ester profiles of the biodiesels.

The objectives of this work are to present LLE data, at 298.2 K, for three systems containing water + ethanol + ethyl biodiesel from crambe, macauba pulp and fodder radish oils, whose ester profiles are significantly different; adjust parameters of the NRTL and UNIQUAC models and compare these molecular models with two group contribution activity coefficient models, UNIFAC-LLE and UNIFAC-Dortmund (UNIFAC-DRTM), in relation to prediction of LLE in these systems.

2. Experimental procedure

2.1. Material

Crude crambe oil and crude macauba pulp oil were respectively supplied by Foundation MS (Maracaju, MS, Brazil) and Paradigma Óleos Vegetais Ltda (Jaboticatubas, MG, Brazil).

Fodder radish seeds were supplied by Sementes Pirai (Piracicaba, SP, Brazil). Crude fodder radish oil was extracted, using a pilot expeller, and filtered for removal of the fibers from the seeds.

Crude oils were neutralized with a sodium hydroxide solution prior to biodiesel production.

Anhydrous ethanol (Merck, >0.9999), anhydrous sodium hydroxide (Carlo Erba, >0.9700), glacial acetic acid (Ecibra, >0.9970) Hydranal Composite 5 (Fluka Analytical), Hydranal Coulumat CG (Fluka Analytical) and deionized water were used in several steps of this work, without further purification.

2.2. Biodiesels

Crambe, fodder radish and macauba pulp oils were used for ethyl biodiesel (fatty acid ethyl esters – FAEE) production, as reported in detail by Basso et al. [11].

The biodiesel ethyl ester profiles were obtained as described by Basso et al. [11]. Ethyl ester biodiesel compositions are presented in mass percentage in Table 1.

2.3. LLE experiments

Each system was prepared by the adding of deionized water, ethanol and a different ethyl biodiesel in a sealed headspace glass tubes (20 mL) (Perkin Elmer).

In the LLE determination of the systems, each component was transferred to the headspace tubes and weighted on an analytical balance Adam Equipment, model AAA160L (± 0.0001 g). The tubes were vigorously stirred using a vortex Phoenix, model AP56 and then centrifuged in a Centrifuge Jouan, model BR4i for 300 s at 4000 rpm. All systems were left at rest for a minimum of 36 h at constant temperature in a thermostatic bath Paar Physica, model Physica VT2 ($T/K \pm 0.2$). Two clear layers and a well defined interface were formed when the systems reached the equilibrium state.

2.4. Analytical methodology

Weighing of the analysis was performed on an analytical balance Precisa, model XT 220 A (± 0.0001 g).

Water content in the water-rich phase was determined using a Karl Fisher Titration system (701 KF Titrimo, Methron) at least in triplicate. Since the Karl Fisher Coulometer has high precision for low water content, the water in ester-rich phase was quantified using a Karl Fisher Coulometer (831 KF Coulometer, Metrohm).

Samples of each phase from the headspace tubes were weighed and transferred, in triplicate, to previously weighed Petri plates. The plates were then taken to an oven with forced air circulation where they were maintained for at least 20 h, at $T/K = 353.2$ and atmospheric pressure, until complete evaporation of ethanol and water from the samples. The biodiesel mass fraction was determined from the plate weighing after complete evaporation of water and ethanol.

Ethanol mass fraction in each phase was determined from the difference between the mass fraction obtained from the mass evaporated (water + ethanol) and the water mass fraction obtained by Karl Fisher analysis.

A similar procedure was performed by Ansolin et al. [18] when studying the LLE of fatty systems with an emphasis on the distribution of tocopherols and tocotrienols in vegetable oils.

With the intention of testing the experimental methodology used for these systems, three synthetic systems containing known contents of water, ethanol and biodiesel were analyzed. Three different levels of water and FAEE from fodder radish oil were tested. The system containing low water content (0.66/71.33/28.01; water/ethanol /FAEE, in mass percentage) was analyzed using the Karl Fisher coulometer; the system containing high water content (17.33/81.72/0.95; water/ethanol /FAEE, in mass percentage) was analyzed using the Karl Fisher titration and, the system with intermediate water content (5.43/89.33/5.24; water/ethanol /FAEE, in mass percentage) was analyzed using both equipment. The biodiesel from fodder radish oil was used to represent the three biodiesels because it has significant contents of the main ethyl esters (ethyl ester from palmitic acid, oleic acid, linoleic acid, linolenic acid, eicosenoic acid and erucic acid) present in the studied biodiesels.

3. Calculation approach

3.1. Combined absolute deviation in experimental methodology

The combined absolute deviation of the analytical methodology was obtained from the difference between true values, by weighting of components used for synthetic systems, and analyzed values

Table 1

Ethyl ester composition of FAEE from crambe, fodder radish and macauba pulp oil in mass percentage.

Fatty acid group in ethyl ester	Molecular formula	Common name	M/(g mol ⁻¹)	FAEE		
				CRAMBE (100w ^a)	Fodder radish (100w ^a)	Macauba (100w ^a)
c16:0	C ₁₈ H ₃₆ O ₂	ethyl palmitate	284.48	2.07	5.11	21.8
c16:1	C ₁₈ H ₃₄ O ₂	ethyl palmitoleate	282.46	–	–	4.08
c18:0	C ₂₀ H ₄₀ O ₂	ethyl stearate	312.53	1.03	2.36	2.76
c18:1	C ₂₀ H ₃₈ O ₂	ethyl oleate	310.51	19.38	39.47	58.97
c18:2	C ₂₀ H ₃₆ O ₂	ethyl linoleate	308.50	8.33	16.69	11.64
c18:3	C ₂₀ H ₃₄ O ₂	ethyl linolenate	306.48	4.53	12.19	0.75
c20:0	C ₂₂ H ₄₄ O ₂	ethyl arachidate	340.58	1.22	0.87	–
c20:1	C ₂₂ H ₄₂ O ₂	eicosenoic acid ethyl ester	338.57	4.04	10.04	–
c22:0	C ₂₄ H ₄₈ O ₂	ethyl behenate	368.64	1.99	0.36	–
c22:1	C ₂₄ H ₄₆ O ₂	ethyl erucate	366.62	56.39	11.71	–
c22:2	C ₂₄ H ₄₄ O ₂	docosadienoic acid ethyl ester	364.60	0.49	–	–
c24:0	C ₂₆ H ₅₂ O ₂	ethyl lignocerate	394.67	0.53	0.30	–
c24:1	C ₂₆ H ₅₀ O ₂	ethyl nervonate	394.67	–	0.90	–

^a Mass fraction of ethyl ester.

obtained from analytical methodology, calculated according to Eq. (1).

$$d_{am}(\%) = 100 \cdot \left[\sum_i (w_i^a - w_i^t)^2 \right]^{1/2} \quad (1)$$

where w is the mass fraction of the component, or pseudo-component, a is the analyzed value using the described methodology, t is the true value obtained by weighing and i is the component, or pseudo-component, of the systems.

3.2. Calculation of deviations in mass balance of the phases

Validity of the LLE experimental data was evaluated according to the procedure developed by Marcilla et al. [19] and applied by Rodrigues et al. [20]. In this procedure, the sum of the calculated mass in both phases is compared with the actual value for total mass used in the experiment. According to Marcilla et al. [19], overall mass balance deviations less than 0.5% ensure good quality of experimental data. The mass balance of each component can be calculated according to Eq. (2).

$$M^{OC} w_i^{OC} = M^{WP} w_i^{WP} + M^{EP} w_i^{EP} \quad (2)$$

where i represents each component, or pseudo-component (biodiesel), of the system; M^{OC} is the mass of the overall composition; M^{WP} and M^{EP} are the total masses of the water-rich and ester-rich phases, respectively; w_i^{OC} is the mass fraction of component, or pseudo-component, i in the initial mixture; and, w_i^{WP} and w_i^{EP} are the mass fractions of component, or pseudo-component, i , respectively, in the water-rich and ester-rich phases.

When applying K equations related to K balances, the values of M^{WP} and M^{EP} can be calculated from the experimental mass fraction of component i in both phases w_i^{WP} and w_i^{EP} by least square fitting. Considering M as the matrix formed by the values of w_i^{OC} , B as the transformation matrix formed by w_i^{WP} and w_i^{EP} , and P as the matrix formed by the masses of the phases M^{WP} and M^{EP} , the system can be mathematically described as:

$$M = B \cdot P \quad (3)$$

Eq. (3) can be transformed into the expression below:

$$P = (B^T B)^{-1} B^T M \quad (4)$$

where B^T is the transposed matrix of B and $(B^T B)^{-1}$ is the inverse matrix of $(B^T B)$.

Thus, values of M^{WP} and M^{EP} for the systems can be obtained, and the sum of M^{WP} and M^{EP} can be compared to M^{OC} to calculate the overall mass balance deviation by:

$$\delta(\%) = 100 \cdot \frac{|(M^{WP} + M^{EP}) - M^{OC}|}{M^{OC}} \quad (5)$$

The relative average deviation for mass balance of each component i in each system is given by:

$$\delta_i(\%) = \frac{1}{N} \sum_n \left[100 \cdot \frac{|(w_{i,n}^{GP} M^{GP} + w_{i,n}^{EP} M^{EP}) - w_{i,n}^{OC} M^{OC}|}{w_{i,n}^{OC} M^{OC}} \right] \quad (6)$$

where n is the tie line number and N is the total number of tie lines for each system.

The maximum combined deviation of experimental data for each system was calculated from the highest value obtained by the sum of the deviations in mass balance for each component in the same tie line of each system using Eq. (7):

$$d_{cd}(\%) = \left(\sum_i \delta_i^2 \right)^{1/2} \quad (7)$$

3.3. NRTL and UNIQUAC thermodynamic modeling

The experimental data measured for the systems were used to adjust the binary interaction parameters for the NRTL and UNIQUAC models. Mixtures of fatty acid ethyl esters which comprise the three biodiesels were treated as a single ethyl ester with the average molar mass of the ester mixture, denoted as FAEE. This approach assumes that the mixture of different fatty acid ethyl esters behaves similarly in the systems under study. Therefore, the mixture of ethyl esters was replaced by a pseudo-component with the corresponding average physical-chemical properties. Basso et al. [11] validated this approach when studying the LLE of systems containing glycerol + ethanol + ethyl biodiesel from crambe oil at different temperatures. Thus, adjustments to the NRTL and UNIQUAC parameters were made, considering the systems as pseudo-ternary. All parameters were adjusted to the experimental data.

The mass fraction was used as composition unit due the difference in molar masses of the components in the systems; this same approach was presented by Oishi and Prausnitz [21] and used by other authors studying the LLE of systems containing vegetable oils + ethanol + free fatty acids [22], and studying the LLE of systems containing glycerol + ethanol + ethyl biodiesel [11]. Thus,

the isoactivity criterion of LLE developed on a molar fraction basis can be expressed on a mass fraction basis as:

$$(\gamma_i x_i)^{WP} = (\gamma_i x_i)^{EP} \quad (8)$$

$$(\gamma_i^w w_i)^{WP} = (\gamma_i^w w_i)^{EP} \quad (9)$$

where:

$$\gamma_i^w = \frac{\gamma_i}{M_i \sum_j (W_j/M_j)} \quad (10)$$

Estimation of the NRTL and UNIQUAC parameters was obtained using an algorithm developed in the FORTRAN programming language. This algorithm uses the modified simplex method to estimate thermodynamic parameters by minimizing the objective function of the composition (Eq. (11)). The procedure for calculation of the parameters involves flash calculations for the midpoint composition of the experimental tie lines, according to the procedure developed by Stragevitch and d'Avila [23].

$$OF_w = \sum_m^D \sum_n^K \sum_i^{K-1} \left[\left(\frac{w_{i,n,m}^{WP,exp} - w_{i,n,m}^{WP,calc}}{\sigma_{w_{i,n,m}^{WP}}} \right)^2 + \left(\frac{w_{i,n,m}^{BP,exp} - w_{i,n,m}^{BP,calc}}{\sigma_{w_{i,n,m}^{BP}}} \right)^2 \right] \quad (11)$$

where D is the total number of data groups; N is the total number of tie lines; K is the total number of components in the data group; w is the mass fraction; subscripts i , n and m are the component, tie line and group numbers, respectively; exp and $calc$ represent, respectively, the experimental and calculated compositions; and σ is the standard deviation observed for the composition of each phase.

3.4. UNIFAC-LLE and UNIFAC-DRTM

UNIFAC-LLE and UNIFAC-DRTM were used to test the LLE prediction capability for the systems. The model denoted as UNIFAC-LLE was presented by Fredenslund et al. [24], and its binary interaction parameters for LLE were updated by Magnussen et al. [25]. The model denoted as UNIFAC-DRTM was presented by Weidlich and Gmehling [26], and its LLE binary interaction parameters were updated by Gmehling et al. [27]. Structural

molecular groups selected to represent the studied systems were “CH₃”, “CH₂”, “CH”, “CH=CH”, “CH₂COO”, “OH” and “H₂O”.

All individual fatty acid ethyl esters (FAEE) were considered for UNIFAC-LLE and UNIFAC-DRTM modeling. Thus, the systems were represented by water, ethanol and all fatty acid ethyl esters of each biodiesel. However, in ternary diagram representations the esters were grouped by the addition of each individual ester mass fraction, and the systems were graphically represented as pseudo-ternary systems containing water (1) + ethanol (2) + FAEE (3).

The predictive capability of the UNIFAC-LLE and UNIFAC-DRTM models was tested using the commercial simulator software Aspen Plus (Aspen Technology). A thermodynamic flash was performed for the overall composition of all tie lines of each system. Thus, compositions of the water-rich and ester-rich phases were obtained and compared to the experimental data.

3.5. Deviations in description of LLE

Average deviations between the experimental and calculated compositions, for all models and in both phases, were determined according to Eq. (12), similar to that used by other researchers [28].

$$\Delta w = 100 \cdot \left\{ \frac{\left[\sum_n^K \sum_i^{K-1} \left(w_{i,n}^{WP,exp} - w_{i,n}^{WP,calc} \right)^2 + \left(w_{i,n}^{BP,exp} - w_{i,n}^{BP,calc} \right)^2 \right]}{2NK} \right\}^{1/2} \quad (12)$$

4. Results and discussions

The fatty acid ethyl ester compositions of the three biodiesels were very different according to Table 1. The FAEE from crambe oil presents ethyl erucate, a long chain ethyl ester with 24 carbon atoms in the molecule, and ethyl oleate as the main esters, totalizing more than 75% of its composition. The FAEE from macauba pulp oil presents ethyl oleate and ethyl palmitate as the major ethyl esters, representing more than 80% of the biodiesel composition, where saturated ethyl esters (ethyl palmitate and ethyl stearate) make up almost 25% of its components. On the other hand, FAEE from fodder radish oil presents ethyl oleate as the mainly ester

Table 2

Experimental liquid–liquid equilibrium data, in mass fraction (w), for the pseudo-ternary systems water (1) + ethanol (2) + FAEE (3/4/5) at $T/K = 298.2$.

	Overall composition			Water-rich phase			Ester-rich phase			δ (%)
	100w ₁	100w ₂	100w _x	100w ₁	100w ₂	100w _x	100w ₁	100w ₂	100w _x	
FAEE from crambe oil ($x = 3$) ^a	50.09	0.00	49.91	99.99	0.00	0.01	0.19	0.00	99.81	0.00
	32.92	19.59	47.49	63.69	36.22	0.09	0.45	2.74	96.81	0.11
	29.80	30.31	39.89	50.05	49.94	0.01	0.43	3.99	95.58	0.03
	26.19	36.05	37.76	43.06	56.81	0.13	0.48	6.26	93.26	0.11
	16.11	42.10	41.79	28.28	70.31	1.41	0.70	7.21	92.09	0.10
	10.76	49.76	39.48	17.91	79.00	3.09	1.05	12.52	86.43	0.20
FAEE from fodder radish oil ($x = 4$) ^b	49.86	0.00	50.14	99.99	0.00	0.01	0.22	0.00	99.78	0.00
	39.07	10.54	50.39	78.97	21.03	0.00	0.29	0.91	98.80	0.20
	36.30	20.36	43.34	66.66	33.32	0.02	0.48	3.24	96.28	0.32
	34.85	30.02	35.13	57.53	42.46	0.01	0.50	6.10	93.40	0.28
	30.19	39.94	29.87	44.83	55.05	0.12	0.62	6.48	92.90	0.10
	17.18	48.06	34.76	26.94	71.18	1.88	1.01	9.57	89.42	0.00
FAEE from macauba pulp oil ($x = 5$) ^c	46.78	0.00	53.22	99.97	0.00	0.03	0.29	0.00	99.71	0.00
	45.56	8.93	45.51	87.80	12.19	0.01	0.29	4.81	94.90	0.25
	37.94	19.35	42.71	69.70	30.29	0.01	0.47	5.34	94.19	0.23
	34.55	32.74	32.71	52.24	47.68	0.08	0.64	8.38	90.98	0.00
	18.23	39.85	41.92	33.63	65.51	0.86	1.06	13.00	85.94	0.21

^{a,b,c}The maximum combined deviation, calculated by Eq. (7) for the systems containing components (3), (4) and (5) are, respectively, 2.28%, 5.48% and 3.49%.

and large amounts of four other esters, ethyl linoleate, ethyl linolenate, eicosenoic acid ethyl ester and ethyl erucate. The molar mass of the pseudo-component, calculated from these ethyl ester profiles, were 342.26, 317.80 and 303.03 g mol⁻¹, respectively, for FAEE from crambe oil, fodder radish oil and macauba pulp oil.

The combined absolute deviation of the experimental methodology for the system containing low water content, high water content and intermediate water content were, respectively 0.71%, 0.50%, and 0.77% (using both Karl Fisher devices). Thus, the maximum deviation indicates the proper representation of the analyzed systems.

Table 2 shows that the deviations per tie line for overall mass balance, calculated according to the Eq. (5), were less than 0.32%, considering the three systems. This maximum deviation indicates good quality of the experimental data. The relative deviations in mass balance of each component, calculated according to Eq. (6), ranged from 0.00% to 3.49%, 0.01% to 4.62% and 0.00% to 2.27%, respectively, for the system containing FAEE from macauba pulp oil, fodder radish oil and crambe oil.

According to Fig. 1 and Table 2, FAEE and water are almost mutually immiscible. The bottoms of the diagrams show that for low ethanol content in overall compositions, the mass fractions of FAEE and water are very low in the water-rich and ester-rich phases, respectively. Ethanol distributes between the both phases, and according to the slopes of tie lines, it has greater affinity for the water-rich phase. Increase of the ethanol mass fraction in the

overall composition causes a greater increase in FAEE mass fraction in the water-rich phase than elevation of the water mass fraction in the ester-rich phase.

There was phase inversion when the water-rich phase made up the upper phase and the ester-rich phase is in the lower phase, with the tie lines containing mass fractions of 41.79% and 39.48% of FAEE from crambe oil and 34.76% of FAEE from fodder radish oil in overall composition. This behavior occurs at high ethanol content in the overall composition, because ethanol has lower density in relation to all components in the systems. The high affinity of ethanol to the water-rich phase causes the decrease in density of this phase.

Table 3 presents the adjusted parameters for the NRTL and UNIQUAC models of the three systems under study. Both molecular models were able to properly describe the LLE of the systems, where average deviations between experimental data and calculated values (Eq. (12)) were on average lower when using the NRTL model than the UNIQUAC model, as showed in Table 4.

In the system containing FAEE from crambe oil, all tie lines calculated by both models almost overlap the experimental data, indicating a good representation of the LLE by the molecular models of the system for the full studied composition range. The tie line with high ethanol content in the system containing FAEE from fodder radish oil, had its ethanol content slightly underestimated in the water-rich phase and overestimated in the ester-rich phase by the two models. In the system containing FAEE from macauba pulp

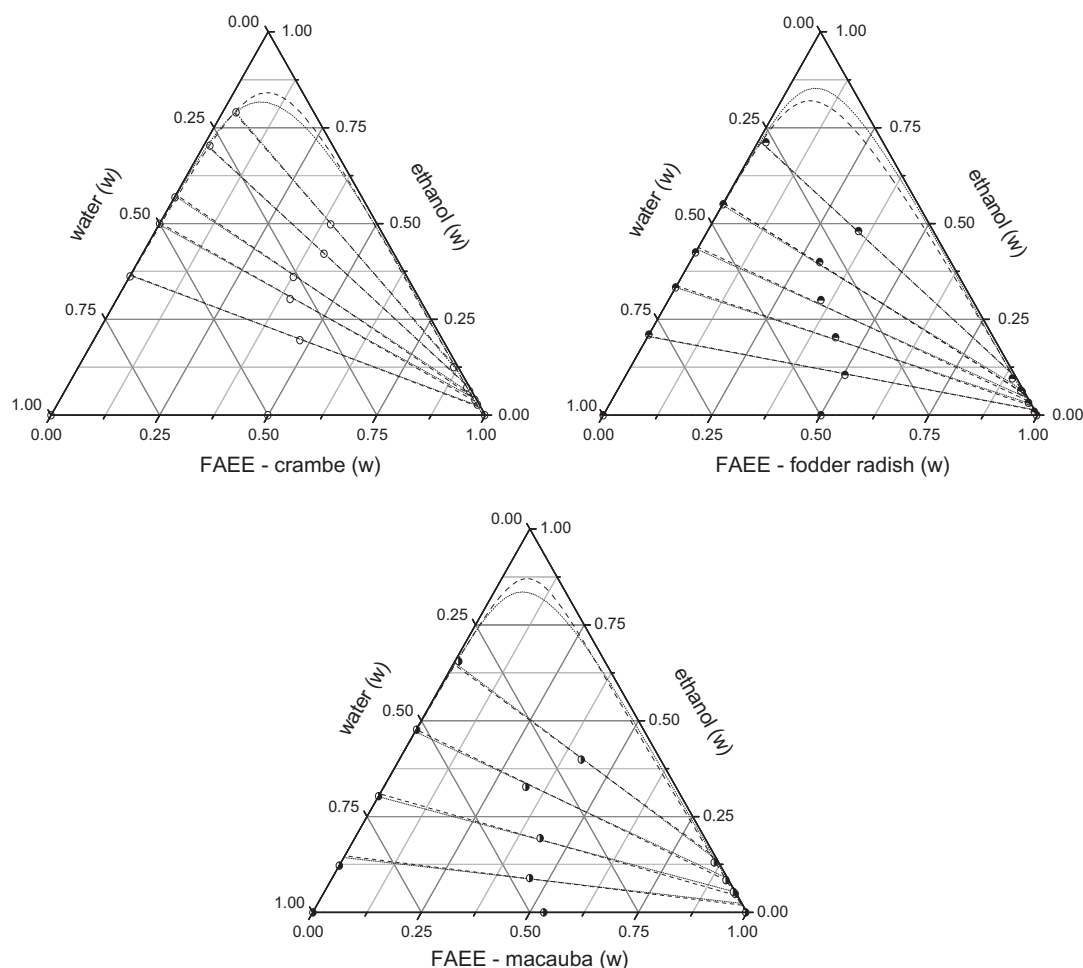


Fig. 1. Liquid-liquid equilibrium diagram of systems composed of water (1) + ethanol (2) + FAEE from crambe oil (3)/FAEE from fodder radish oil (4)/FAEE from macauba oil (5) at $T/K = 298.2$: (w) mass fraction; (○), (●), (■) experimental data; (---) NRTL model; (—) UNIQUAC model.

Table 3
UNIQUAC and NRTL model binary parameters.

Pair ij ^a	UNIQUAC		NRTL		
	A(0) _{ij} /K	A(0) _{ji} /K	A(0) _{ij} /K	A(0) _{ji} /K	$\alpha(0)_{ij} = \alpha(0)_{ji}$
12	−251.9600	297.7500	54.4570	279.6700	0.1010
13	−39.0850	768.8600	4057.1000	297.4500	0.1443
23	31.8680	75.0600	812.7000	2224.7000	0.4732
14	60.9410	755.6100	3914.7000	9442.4000	0.1462
24	7.9797	65.4150	812.6800	1340.8000	0.5700
15	−3.9697	874.5500	3076.9000	615.9800	0.1618
25	370.4300	−217.1800	782.0400	−144.4800	0.5700

^a Components: water (1), ethanol (2), FAEE from crambe oil (3), FAEE from fodder radish oil (4), FAEE from macauba pulp oil (5).

Table 4
Average global deviations (Δw) between experimental data and calculated mass fractions.

Model	Δw (%) (system 1 + 2 + 3) ^a	Δw (%) (system 1 + 2 + 4) ^a	Δw (%) (system 1 + 2 + 5) ^a
NRTL	0.51	0.66	0.97
UNIQUAC	0.49	0.86	1.29
UNIFAC-LLE	2.27	2.10	3.28
UNIFAC-DRTM	2.25	1.91	3.17

^a Water (1), ethanol (2), FAEE from: crambe oil (3), fodder radish (4), macauba pulp oil (5).

oil, the tie line with 45.51% of this component presented an over-estimated ethanol mass fraction in the water-rich phase and underestimated fraction in the ester-rich phase; the tie line with 41.92% of FAEE had its ethanol content underestimated in the water-rich phase and overestimated in the ester-rich phase.

The binodal curves calculate by the NRTL and UNIQUAC models showed significant differences in description of the LLE behavior in the region with high ethanol mass fraction, at the top of diagrams, for all the three systems. In the water-rich phase region the binodal curves overlap each other, indicating the same description of the LLE by both models for all studied systems. The LLE behavior of the systems containing FAEE from crambe and macauba pulp oil were represented similarly by the binodal calculated by both models in the ester-rich phase region, but on the other hand, the NRTL model showed a slightly broader region of phase separation than the UNIQUAC model in this region for the system containing FAEE from fodder radish oil.

The differences between the deviations obtained by the UNIFAC-LLE and UNIFAC-DRTM models for description of the LLE of each system were lower than 0.25%, indicating a similar prediction capability for LLE behavior for these systems by both models. The LLE of the systems containing FAEE from crambe oil and FAEE from fodder radish oil had similar average global deviations between experimental data and predicted values, as observed in Table 4. On the other hand, these deviations were substantially higher for the system containing FAEE from macauba pulp oil. All deviations

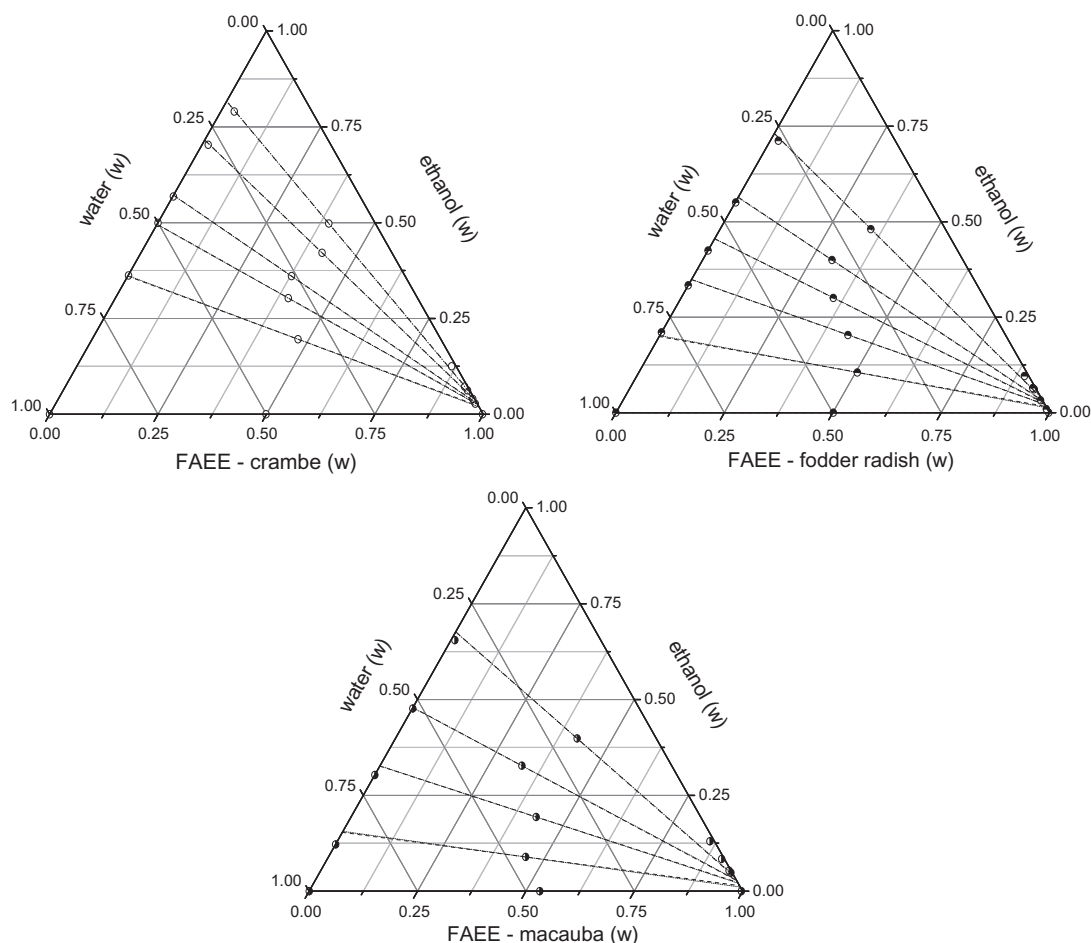


Fig. 2. Liquid–liquid equilibrium diagram of systems composed of water (1) + ethanol (2) + FAEE from crambe oil (3)/FAEE from fodder radish oil (4)/FAEE from macauba oil (5) $T/K = 298.2$: (w) mass fraction; (○), (●), (◐) experimental data; (---) UNIFAC-DRTM model; (—) UNIFAC-LLE model.

were higher than 1.9%, indicating that these models were generally not able to properly predict the LLE of these systems.

Both UNIFAC models underestimated the ethanol mass fraction in the ester-rich phase, and this behavior was more significant in the systems containing biodiesel from macauba pulp oil and fodder radish oil, as showed in Fig. 2. The predictive models also underestimated the FAEE mass fraction in the water-rich phase. Except for the system containing FAEE from crambe oil, the predictive models also overestimated ethanol content in the water-rich phase. The group contribution model could not predict properly the region of phase separation, overestimating it for the three systems.

Different capabilities for predicting the LLE of systems related to biodiesel production, by UNIFAC derived models, considering different alkyl ester compositions, were obtained by other authors. Lee et al. [14], using the UNIFAC-LLE and UNIFAC-DRTM models for predicting the LLE of systems composed of water + methanol + methyl esters, obtained average deviations of about five times higher for system containing methyl oleate in comparison to the systems containing methyl linoleate. Basso et al. [11] and Basso et al. [8] tested the prediction of LLE for systems containing glycerol + ethanol + ethyl biodiesel by UNIFAC-LLE models, and obtained average deviations of 2.72% and 3.52%, respectively, for biodiesel from crambe oil and from macauba pulp oil at $T/K = 298.2$.

Thus, the LLE prediction capability for systems containing alkyl esters by UNIFAC derived models is probably directly related to the ester composition of these systems. The number and/or presence of specific structural molecular groups in ester molecules that comprise the biodiesel may have different effects on the LLE prediction capability of this type of system.

Despite of the great availability of group interaction parameters and their constant updates, the generation of derived models and the practicality in the use, because they are previously programmed in many simulation softwares, the utilization of UNIFAC models in design analysis and process simulation in the biodiesel production process must be done judiciously due to the deviations in prediction of LLE for this type of system.

5. Conclusions

In the study of LLE for the three different systems composed of water + ethanol + FAEE (from crambe, fodder radish and macauba pulp oils), FAEE and water were almost immiscible and ethanol was distributed in both phases, but it presented greater affinity for the water-rich phase. The NRTL and UNIQUAC thermodynamic models properly described the LLE of these systems resulting in average deviation ranging from 0.49% to 1.29%. Although the UNIFAC-LLE and UNIFAC-DRTM models similarly predicted the LLE of these systems, these models could not properly describe it, with average deviations ranging from 1.91% to 3.28%.

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Appendix A

Activity coefficient γ_i^w of the NRTL model using the mass fraction as concentration unity.

$$\ln \gamma_i = \frac{\sum_{j=1}^K \tau_{ji} G_{ji} w_j / \bar{M}_j}{\sum_{j=1}^K G_{ji} w_j / \bar{M}_j} + \sum_{j=1}^K \left[\frac{w_j G_{ij}}{M_j \sum_{l=1}^n G_{lj} w_l / \bar{M}_l} \times \left(\tau_{ij} - \frac{\sum_{l=1}^k \tau_{lj} G_{lj} w_l / \bar{M}_l}{\sum_{l=1}^k G_{lj} w_l / \bar{M}_l} \right) \right] \quad (A1)$$

$$G_{ji} = \exp(-\alpha_{ij} \tau_{ij}) \quad (A2)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \quad (A3)$$

$$\alpha_{ij} = \alpha_{ji} \quad (A4)$$

$$\tau_{ii} = 0; G_{ii} = 0 \quad (A5)$$

Activity coefficient γ_i^w of the UNIQUAC model using the mass fraction as concentration unity.

$$\ln \gamma_i = \ln \gamma_i^{\text{Comb}} + \ln \gamma_i^{\text{Res}} \quad (A6)$$

$$\ln \gamma_i^{\text{Comb}} = \frac{\ln \theta_i}{\ln (W_i / \zeta \bar{M}_i)} + 1 - \frac{\zeta \bar{M}_i \theta_i}{W_i} + \frac{z}{2} \bar{M}_i q'_i \ln \frac{\phi'_i}{\theta'_i} - \frac{z}{2} \bar{M}_i q'_i \left(1 - \frac{\phi'_i}{\theta'_i} \right) \quad (A7)$$

$$\zeta = \sum_{j=1}^K \frac{w_j}{\bar{M}_j} \quad (A8)$$

$$\theta'_i = \frac{q'_i w_i}{\sum_{j=1}^K q'_j w_j}; \phi'_i = \frac{r'_i w_i}{\sum_{j=1}^K r'_j w_j} \quad (A9)$$

$$\ln \gamma_i^{\text{Res}} = \bar{M}_i q'_i \left[1 - \ln \left(\sum_{j=1}^K \theta'_j \tau_{ji} \right) - \sum_{j=1}^K \left(\frac{\theta'_i \tau_{ij}}{\sum_{k=1}^K \theta'_k \tau_{kj}} \right) \right] \quad (A10)$$

$$\tau_{ij} = \exp \left(-\frac{A_{ij}}{T} \right) \quad (A11)$$

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