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Chapter

Ethanol as a Subgroup of the UNIFAC Model in the Prediction of Liquid-Liquid Equilibrium in Food and Fuel Systems

Jacqueline M. Ortega Bacicheti, Guilherme D. Machado, Fábio Nishiyama, Vladimir F. Cabral and Donato Aranda

Abstract

Ethanol has been employed as a solvent in biodiesel production and vegetable oil refining since it is more economically attractive and less toxic than methanol and hexane. Furthermore, ethanol has demonstrated easy recovery, good selectivity, and distribution coefficient for free fatty acids (FFA), which is the primary target in the refining process since high acidity oil can lead to the formation of side products. As the knowledge of phase equilibrium behavior of fatty systems is essential to design and optimize the extraction of FFA, this chapter will present two new UNIFAC subgroups for ethanol: EtOH-B, focused on biodiesel production; and EtOH-D, focused on the deacidification process. Except for ethanol and water subgroups fitted in this study, all remaining UNIFAC parameters were taken from the literature. The new EtOH-B and EtOH-D parameters provide a considerably lower mean square error (1.20% and 0.87%) than the other works available in the literature. The results show that new ethanol subgroups and the developed methodology are valuable tools in predicting liquid-liquid phase equilibrium for ethyl biodiesel and vegetable oil deacidification systems considered, resulting in reduced computational calculations and a relatively small split with the complex dataset established by the UNIFAC-LL model.

Keywords: biodiesel, deacidification, ethanol, liquid-liquid equilibrium, vegetable oil, UNIFAC

1. Introduction

Several studies have introduced ethanol as a solvent for liquid-liquid extraction, resulting in a satisfactory reduction of free fatty acid (FFA) content in oils [1–4]. High acidity level vegetable oils need to be refined either for human consumption or for fuel production. In this way, ethanol can act both as a solvent for oil deacidification by liquid-liquid extraction and as a reagent for transesterification reaction.

Considering edible vegetable oil, high levels of FFA have been associated with digestive problems for consumers, autoimmune disorders, and various types of cancer [5–8]. Besides health problems, the content of pigments, phosphatides, odoriferous molecules, and free fatty acids in edible vegetal oil is detrimental to the oil quality, oxidative stability, and consumer acceptance. Among these impurities, FFA is the most detrimental because they increase the acidity of the oil, inducing an undesirable rancid flavor [9]. In order to reduce neutral oil losses and production of undesired compounds, caused by unwanted chemical reactions [10], liquid-liquid extraction using ethanol as a solvent can replace the conventional physical and chemical refining processes.

Besides deacidification of edible vegetable oils, ethanol can be employed in biodiesel production. The conventional biodiesel production process requires the use of a feedstock with reduced acidity; however, residual oils are characterized by a high FFA content, which promotes soap production with the alkali homogeneous catalysts used in transesterification [11]. Thus, feedstock purification processes, such as oil deacidification, through solvent extraction are needed. Using residual oils for biodiesel production can provide several advantages when compared to the conventional process with refined oils, such as the minimization of environmental impacts related to the disposal of waste oils, a noncompetitive relationship with the food crops, and availability of the feedstock supply, which accounts for over 70% of the refined oil biodiesel production costs [12].

In order to correctly design, operate and optimize extraction columns and the subsequent additional purification or solvent recovery units, liquid-liquid phase equilibrium (LLE) data are necessary to determine the thermodynamic properties of the systems composed of oil, solvent, and FFA [3, 13]. In general, most of the phase equilibrium data for biodiesel systems use methanol as the reacting alcohol [14], studies regarding systems with ethanol are more recent [15]. Some advantages of using ethanol as a solvent are its high affinity for FFAs at ambient temperature, low toxicity when compared to methanol, and its easy removal under mild conditions [16, 17].

Thermodynamic modeling can be used to predict or correlate the experimental behavior of fatty acid systems described through LLE data. The approach using excess Gibbs energy models is widely applied to describe biodiesel and vegetable oil systems through thermodynamic models, such as NRTL [18–22], UNIQUAC [18, 22–24], and UNIFAC [25–28]. Although thermodynamic models, such as UNIQUAC and NRTL, are capable of accurately representing the experimental data, both are restricted to the specificity of the type of vegetable oil used, as the phase equilibrium parameters are adjusted solely for the system described in the experimental data used for the LLE data fitting. Numerous types of refined or residual feedstocks are available for biodiesel production or require deacidification to be safe for human consumption. Thus, the use of a predictive group-contribution method, such as UNIFAC, to describe the phase behavior of the variety of biodiesel reaction systems or deacidification of edible vegetable oil systems is motivated, as larger number of systems would be useful.

In the UNIFAC model, alcohols, such as methanol and propanol, used to be represented by a specific group. As stated by Magnussen et al. [29] in their work, 1-propanol ($CH_3CH_2CH_2OH$) can be represented, in principle, by the CH_3, CH_2, and OH subgroups. However, the fitting of these parameters in the UNIFAC parameter table depends on several other molecules that present these subgroups. An approach that represents molecules by a subgroup of their own, as in the case of methanol (CH_3OH), can provide more accurate property calculations.

On account of the growing tendency of substitution of environmentally damaging chemicals for less impactful compounds, added to its availability and price in the context of biofuels in Brazil and other countries, the use of ethanol as a solvent or reactant is expected to vastly increase. Therefore, the study of the possibility of using ethanol as UNIFAC subgroup must also be evaluated.

In the literature, the thermodynamic modeling of these systems focuses on the UNIQUAC and NRTL models. Reipert et al. [30] correlated the LLE experimental data of refined babassu oil, lauric acid, and hydrated ethanol using the NRTL model. The mass fraction root mean square error (RMSD) between the observed and estimated compositions was 0.85%. Gonçalves et al. [31] applied NRTL and UNIQUAC models to correlate LLE experimental data for corn oil with a hydrated ethanol solvent system at room temperature and atmospheric pressure. The RMSD of 0.89% and 0.92%, respectively. Rodrigues et al. [32] investigated the LLE of Brazil nut oil or Macadamia nut oil + commercial oleic acid + ethanol + water, at 298.2 K. They reported RMSD not higher than 1.5% using the NRTL and UNIQUAC models. Basso et al. [19] determined LLE data for glycerol + ethanol + fatty acid ethyl ester from crambe oil system and adjusted parameters for NRTL model. The RMSD between experimental and calculated values by the NRTL model was less than 0.82%. The authors verified the prediction capacity of the UNIFAC model by testing two different sets of UNIFAC binary interaction parameters and obtained a RMSD of 2.27% and 3.97%, respectively. Da Silva et al. [20] established experimental data for Jatropha curcas oil + oleic acid + ethanol + water systems at (288.15, 298.15, 308.15, and 318.15) K and correlated the experimental data by the nonrandom two-liquid (NRTL) model with temperature-dependent binary parameters. For all systems, the RMSD was lower than 0.96%. Basso et al. [33] obtained LLE experimental data of systems containing glycerol + ethanol + ethyl biodiesel from macauba pulp oil, performed thermodynamic modeling, and simulated the settling step of this biodiesel using simulation software. Binary interaction parameters were adjusted for NRTL and UNIQUAC models and the RMSD between experimental data and calculated values were 0.44%, 1.07%, 3.52%, and 2.82%, respectively, using the NRTL, UNIQUAC, UNIFAC-LLE, and UNIFAC-Dortmund models.

All the aforementioned studies indicate that the NRTL and UNIQUAC models can reproduce the experimental liquid-liquid behavior of the systems involving vegetable oil + fatty acids + ethanol + water and biodiesel + glycerol + ethanol. However, although these thermodynamic models represent satisfactorily the experimental data, the NRTL and UNIQUAC parameters obtained in these studies are specific to these systems, consequently, they are restricted to the specific vegetable oil used in the parameter correlation. Considering the numerous types of vegetable oils that need deacidification, and different triacylglycerides matrices that can be used for biodiesel production, new parameter-fitting procedures are required for other systems, and new experimental databanks are required [9, 17, 30]. However, the new parameter-fitting procedures required for new systems are not mandatory if we consider the group contribution method. UNIFAC (UNIQUAC Functional-group Activity Coefficient) model [34] is a group contribution method established by Fredenslund, Jones e Prausnitz in 1975, that can predict the liquid-liquid behavior of systems containing fatty acids using the activity coefficient calculation, which considers the interaction between the subgroups that form the molecules. Fredenslund et al. [34] proposed a group contribution method that could use experimental data available in the literature to predict the LLE of systems with no disposable experimental data.

Models based in group contribution concept estimate the properties of a mixture considering it as a solution of different functional groups that forms the molecule in the
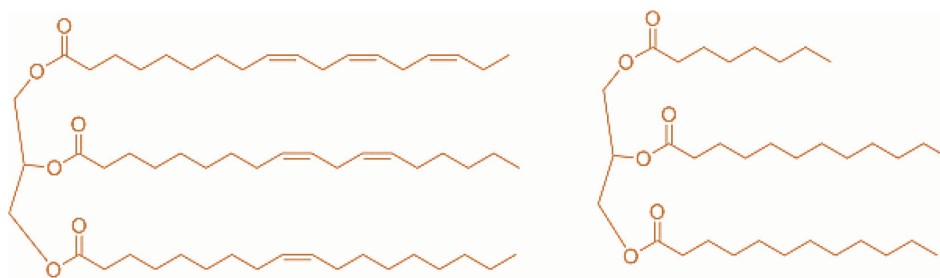
Figure 1.
Soybean oil (left) and coconut oil (right) molecular structures.

mixture. As can be seen in **Figure 1**, soybean and coconut oils are different molecules, but the same chemical compounds are encountered in these molecules. Considering these few functional groups as building blocks, a vast array of vegetable oil can be represented, as all vegetable oils present the same functional groups only differing in quantities.

This type of predictive model applicable to a larger number of systems would be useful and important in the food industry and biofuel industry, respectively, given the diversity of raw materials and the fact that most systems are multicomponent, and the variety of generated biodiesel systems.

Physical and chemical properties are considered as a sum of all contributions made by each one of the functional groups. These contributions are quantified according to the interaction parameters, adjusted by experimental data.

This model was extensively applied to study the liquid-liquid equilibrium of vegetable oils.

Batista et al. [2] applied UNIFAC and ASOG (analytical solution of groups) group contribution methods to correlate interaction parameters of triolein + oleic acid + ethanol and triolein + stearic acid + ethanol systems. The parameters were validated for canola, corn, and Spanish oil and the root mean square deviation between experimental and calculated molar fractions were 1.31% and 1.32% for the UNIFAC and ASOG models, respectively.

Bessa et al. [35] tested the predictive capability of the original UNIFAC model parameters and then modified them in terms of new readjusted binary interaction parameters. Due to inadequate results obtained by UNIFAC model without any changes in its subgroups, the authors introduced a new group ("OHgly") and two matrices of parameters were adjusted. The authors obtained good predictions and a significant improvement in the performance of this group contribution model has been achieved.

Noriega and Narvaez [28] proposed a new set of UNIFAC group interaction parameters to describe the LLE for all the systems involved in biodiesel production. The parameters presented a RMSD up to 2.07%.

In the UNIFAC model, the activity coefficient is given in terms of a combinatorial contribution taking into account entropy effects arising from differences in molecular size and shape, and a residual contribution taking into account energetic interactions between the functional groups in the mixture. To achieve a better description of the experimental data composed by the molecules presented in **Table 1**, the chosen subgroups to represent the studied fatty systems were as follows: CH_3, CH_2, CH, $CH=CH$, $COOH$, CH_2COO, OH, H_2O, and the new proposed group EtOH.

Therefore, this chapter proposes the adjustment of thermodynamic parameters of the UNIFAC model considering a new ethanol subgroup in order to predict the LLE for systems containing food or fuel. The fact that vegetable oils present different types

Molecule	Subgroups
Ethanol	1 EtOH
Water	1 H_2O
Glycerol	2 CH_2, 1 CH, 3 OH
Fatty acid	n CH_3, n CH_2, COOH
Triacylglycerol	n CH_3, n CH_2, nCH, nCH=CH, CH_2COO
Biodiesel	n CH_3, n CH_2, nCH, nCH=CH, CH_2COO

Table 1.
Chosen subgroups to represent the studied fatty systems.

of constituent fatty acids but with similarity in their structure makes it possible to use a predictive approach that represents the interactions between groups based on UNIFAC thermodynamic model in the proper representation of the LLE for industrial separation processes. Thus, this study aims to present such methodology in the prediction of food systems containing FFA to be separated as well as systems containing fuels, focusing on biodiesel produced from vegetable oils.

2. Methodology

The isofugacity criterion for phase equilibrium is conventionally used to describe a condition at which the chemical potential of each component is equal in the phases among which this component can distribute. If fugacities are expressed in terms of activity coefficients, the LLE using an excess Gibbs energy model is represented by Eq. (1) [34].

$$x_i^{AP} \gamma_i^{AP} = x_i^{OP} \gamma_i^{OP} \tag{1}$$

where x_i^{AP} and x_i^{OP} are the molar fractions of component i in the alcohol and oil phases, respectively, and γ_i^{AP} and γ_i^{OP} are the activity coefficients of component i in the alcohol and oil phases, respectively.

In this chapter, the activity coefficients are calculated through UNIFAC model [34], which considers the combinatorial and residual contributions, Eq. (2).

$$ln\,\gamma_i = ln\,\gamma_i^C + ln\,\gamma_i^R \tag{2}$$

The combinatorial contribution γ_i^C (Eq. (3)) is related to the difference in size and shape of molecules. The volume fraction $\varnothing_i$ and surface fraction θ_i of each molecule i are obtained using Eq. (5) and (6), respectively.

$$ln\,\gamma_i^C(x) = ln\,\frac{\varnothing_i}{x_i} + \frac{Z}{2}q_i\,ln\,\frac{\theta_i}{\varnothing_i} + l_i - \frac{\varnothing_i}{x_i}\sum_{j=1}^{n_c} x_j l_j, \tag{3}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); Z = 10. \tag{4}$$

$$\varnothing_i = \frac{r_i x_i}{\sum_{j=1}^{n_c} r_j x_j} \tag{5}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{n_c} q_j x_j} \tag{6}$$

where x_i is the mole fraction of component i and r_i and q_i are the measures of molecular van der Waals volumes and molecular surface areas, respectively. They are calculated as the sum of the group volume and group area parameters, R_k and Q_k.

$$r_i = \sum_{k=1}^{n_g} \nu_{ki} R_k \tag{7}$$

$$q_i = \sum_{k=1}^{n_g} \nu_{ki} Q_k \tag{8}$$

where ν_{ki} is the number of groups of type k in molecule i. Here, we use the values of R_k and Q_k reported by Magnussen *et al.* [29]. Os valores R_k e Q_k são calculados a partir do volume e área superficial dos grupos de Van der Waals (V_{wk} e A_{wk}, respectivamente), retratado por Bondi (1968):

$$R_k = \frac{V_{wk}}{15,17} \tag{9}$$

$$Q_k = \frac{A_{wk}}{2,5x10^9} \tag{10}$$

The residual contribution γ_i^R, described through Eq. (11), is due to group areas and group interaction parameters. Γ_k and $\Gamma_k^{(i)}$ are the residual activity coefficient from group k in the solution and in a solution containing only molecules of type i, respectively.

$$ln\,\gamma_i^R(T, x) = \sum_k \nu_{ki} \left(ln\,\Gamma_k - ln\,\Gamma_k^{(i)} \right) \tag{11}$$

By Eq. 12 it is possible to calculate the residual activity coefficient.

$$ln\,\Gamma_k = Q_k \left[1 - ln \left(\sum_m^k \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_{dm} \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right) \right] \tag{12}$$

where θ_m is the area fraction of group m given by:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n},\# \tag{13}$$

and X_m is the molar fraction of the group m in the mixture.

$$X_m = \frac{\sum_j^n Q_m X_m}{\sum_j \sum_n \nu_{nj} x_j} \# \tag{14}$$

The group interaction parameter ψ_{nm} between groups n and m is given by:

$$\psi_{mn} = exp\left(-\frac{a_{mn}}{T}\right), \# \tag{15}$$

where a_{mn} is an adjustable parameter of the binary interaction between groups m and n, and it has units of kelvins. Each group-group interaction possesses two parameters: a_{nm}, a_{mn}, and $a_{nm} \neq a_{mn}$. These parameters were obtained from a database using a wide range of experimental phase-equilibrium results.

The parameter fitting procedure was applied separately to fit the EtOH interaction parameters for biodiesel separation and deacidification systems. In deacidification process, the presence of water in ethanol solvent increases the polarity of the solution. This feature and the presence of glycerol in biodiesel system makes the behavior of EtOH subgroup different in deacidification systems from that in biodiesel systems, even assuming that the subgroups of both systems were similar (the CH$_3$, CH$_2$, CH, CH = CH, COOH, CH$_2$COO), and accepting that UNIFAC model is a group contribution method that can predict the liquid-liquid behavior considering the interaction between the subgroups that form the molecules.

As the ethanol parameters calculated for the biodiesel system are not adequate for deacidification process, the UNIFAC parameters for new ethanol subgroup were fitted for the biodiesel process separately from deacidification process. As result, this study will present UNIFAC interaction parameters for ethanol subgroup in biodiesel systems (EtOH-B) and in deacidification systems (EtOH-D). The UNIFAC parameters were fitted considering the phase compositions in molar fractions and binary interaction parameters in 1/K.

A data bank containing 56 systems was compiled. We used a total of 88 tie-lines from eight biodiesel types from vegetable oils with ethanol, and 246 tie-lines for the 14 types of vegetable oils with hydrated ethanol, at temperatures ranging from 288.15 to 333.15 K, all systems studied at atmospheric pressure. **Table 2** shows a summary of the equilibrium systems used in the parameter fitting and validation procedure.

For biodiesel separation fitted ethanol-related parameters, the LLE database of seven ethyl systems of vegetable oils (soybean, canola, palm, *jatropha curcas*, cottonseed, crambe, and sunflower) at different temperatures were used to fit the interaction parameters of the ethanol subgroups. The fitted ethanol-related parameters were validated against data for the macauba (*Acrocomia aculeata*) biodiesel system. Lastly, the results obtained are compared with those obtained by the UNIFAC-LL parameters [29] and parameters available from literature work [35].

For deacidification fitted ethanol-related parameters, the LLE database of 13 systems of vegetable oils (brazil nut, corn, cottonseed, garlic, grapeseed, *jatropha curcas*, palm, peanut, rice bran, sesame, soybean, and sunflower) at different temperatures were used to fit the interaction parameters of the ethanol subgroups. The validation procedure was performed using canola oil system and a total of five tie-lines at 303.15 K, and it is worth mentioning that canola oil was not included in the parameter estimation process. Lastly, the results obtained are compared with those obtained by the UNIFAC-LL parameters [29] and parameters available from literature work [26, 28, 43].

The system is composed of biodiesel, ethanol, and glycerol.

Vegetable oil source	Tie-lines	T (K)	References
Soybean	10	293.15, 323.15	[36]
Canola	5	303.15	[1]
Palm	15	298.15, 323.15	[37]
Jatropha curcas	12	303.15, 318.15, 333.15	[14]
Macauba pulp	6	298.15	[33]
Cottonseed	18	293.15, 313.15, 333.15	[38]
Crambe	18	298.15, 318.15, 338.15	[19]
Sunflower	12	298.15, 313.15	[36]

The system is composed of vegetable oil, free fatty acids (FFA), ethanol, and water.

Vegetable oil source	Tie-lines	T (K)	References
Brazil nut	6	298.15	[32]
Canola	5	303.15	[18]
Corn	21	298.15	[31]
Cottonseed	21	298.15	[4]
Garlic	21	298.15	[39]
Grapeseed	22	318.15	[39]
J. curcas	40	288.15, 298.15, 308.15, 318.15	[20]
Macadamia	15	298.15	[32]
Palm	10	318.15	[40]
Peanut	7	298.15	[9]
Rice bran	17	298.15	[41]
Sesame	14	298.15	[39]
Soybean	16	323.15	[42]
Sunflower	32	298.15	[3]

Table 2.
LLE database of the systems involved in the correlation process.

The software Microsoft Excel was used in the parameter fitting procedure coupled to XSEOS [44] and SOLVER® add-ins. The XSEOS add-in, an open-source code programmed in visual basic for applications (VBA) with several excess Gibbs energy models and equations of state, was employed to evaluate the activity coefficient of the UNIFAC model, while the SOLVER® add-in with the generalized reduced gradient (GRG) method [45] was used as the numerical calculation tool.

The parameter fitting was performed by minimizing the objective function (Eq. 16) using the generalized reduced gradient (GRG) nonlinear solving method.

$$\text{OF} = \sum_{n}^{NLa} \sum_{i}^{NCn} \left(W_{i.n}^{OPexp} - W_{i.n}^{OPcalc} \right)^2 + \left(W_{i.n}^{APexp} - W_{i,n}^{APcalc} \right)^2 \qquad (16)$$

where *NLa* and *NCn* represent the total number of tie-lines in each group and the total number of components or pseudo components in tie-line *n*, respectively. $W_{i,n}$ correspond to the mass fraction of the component or pseudo component *i* in the tie-line *n* in the oil phase (*OP*) or alcohol phase (*AP*), while the superscripts *exp* and *calc* the experimental or calculated values, respectively. During the parameter fitting procedure, the minimization of eq. (16) is constrained by the isofugacity condition expressed by Eq. (1), and the calculated mass fraction sum, which must be equal to 1.

In order to evaluate the capability of the ethanol interaction parameters [27, 43] to describe LLE in systems containing FFA accurately, the percentual mass fraction root mean square deviation between the experimental and calculated phase composition values (RMSD), Eq. (17), was compared to the results obtained using parameters available in the literature (UNIFAC-LL from Magnussen et al. [46], Bessa et al. [35], Noriega and Narváez [28], Hirata et al. [26]).

$$RMSD = 100.\sqrt{\frac{\sum_n^{Nla}\sum_i^{NCn}\left(W_{i,n}^{OPexp} - W_{i,n}^{OPcalc}\right)^2 + \left(W_{i,n}^{APexp} - W_{i,n}^{APcalc}\right)^2}{2.NLa.NCn}} \# \quad (17)$$

The subgroups chosen to represent the fatty acids systems were as follows: CH_3, CH_2, CH, CH = CH, COOH, CH_2COO, H_2O, and ethanol, EtOH. Only the binary interaction parameters corresponding to water and ethanol were estimated in this study.

In order to reduce the number of components considered in the interaction parameter estimation methodology, the pseudo-component approach can be used to characterize a complex mixture as a single component [9]. Several authors had successfully applied this approach assuming the vegetable oil as a single pseudo component with an average molar mass and average physical-chemical properties [4, 9, 17, 19, 20, 26, 28, 30–32, 35, 39–43].

Based on the results of the reported studies, it is assumed that the use of the described methodology does not cause expressive deviations in the thermodynamic modeling of deacidification and biodiesel separation systems. Therefore, each vegetable oil was replaced by a pseudo component, and the same approach was used for commercial fatty acids. The pseudo component is a thermodynamic tool applied to represent the edible oil as a single TAG and FFAs as a unique FFA. A weighted average of the vegetable oil and FFA molar masses and subgroup numbers was applied to each pseudo component, considering the fatty acid profile of each vegetable oil, [2–4, 20, 31, 32, 39–42]. The molar mass data of the components were obtained from the NIST Chemistry WebBook database.

3. Results and discussion

For biodiesel separation system, the methodology was initially applied to fit parameters for the new interaction subgroup representing the ethanol molecule (EtOH-B), while the UNIFAC-LL for the subgroups forming the other components of the system (ethyl biodiesel and glycerol) remained unchanged. The fitting process used seven ethyl biodiesel from soybean, canola, palm, *jatropha curcas*, cottonseed, crambe, and sunflower oils available in the literature. **Table 3** summarizes the UNIFAC-LL parameters [29] used and the interaction parameters fitted for the new EtOH-B subgroup proposed [43].

Subgroup	CH3	CH2	CH	CH=CH	OH	CH2COO	EtOH-B
Rk	0.90	0.67	0.45	1.12	1.00	1.68	**2.11**
Qk	0.85	0.54	0.23	0.87	1.20	1.42	**1.97**
CH3	0.00	0.00	0.00	74.54	644.60	972.40	**3582.81**
CH2	0.00	0.00	0.00	74.54	644.60	972.40	**3582.81**
CH	0.00	0.00	0.00	74.54	644.60	972.40	**3582.81**
CH=CH	292.30	292.30	292.30	0.00	724.40	−577.50	**241.75**
OH	328.20	328.20	328.20	470.70	0.00	195.60	**5299.17**
CH2COO	−320.10	−320.10	−320.10	485.60	180.60	0	**−395.51**
EtOH-B	**−53.92**	**−53.92**	**−53.92**	**−4658.24**	**−550.58**	**106.42**	**0.00**

Table 3.
UNIFAC interaction parameters for CH_3, CH_2, CH, $CH = CH$, $COOH$, CH_2COO, H_2O, *and EtOH subgroups.*

The bold numbers are the fitted one.

Figures 2 and **3** show the experimental points and calculated tie-lines obtained using the new interaction parameters summarized in **Table 3** for different types of biodiesel. For all diagrams presented in this chapter, the following classification is valid:

Δ and ▲ for experimental and calculated points, respectively;

□ and ■ for experimental and calculated overall composition, respectively;

- - - and — for experimental and calculated tie-lines;

- .. - for experimental binodal line;

The tie-lines overlapping seen in **Figures 2** and **3** suggest that the fitted UNIFAC parameters for the proposed EtOH subgroup can predict the behavior of the systems considered with high accuracy.

In order to validate these new fitted EtOH parameters, we perform a liquid-liquid equilibrium prediction for ethyl biodiesel from macauba pulp, which was not used during the parameter fitting process.
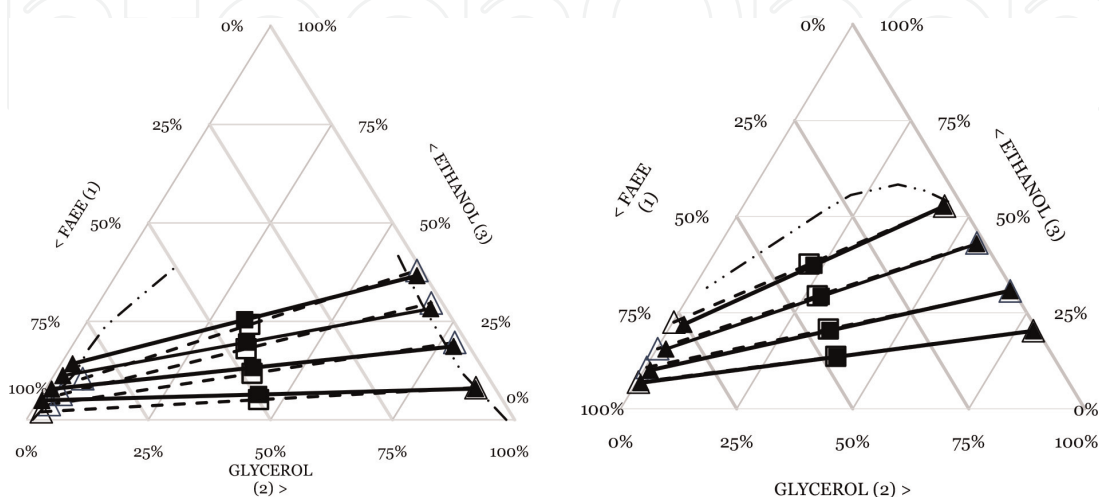
Figure 2.
Ternary LLE diagram for the ethyl biodiesel from soybean oil system at 293.15 K (left) and jatropha curcas *oil at 318.15 K (right). Experimental data from [14, 36], respectively.*
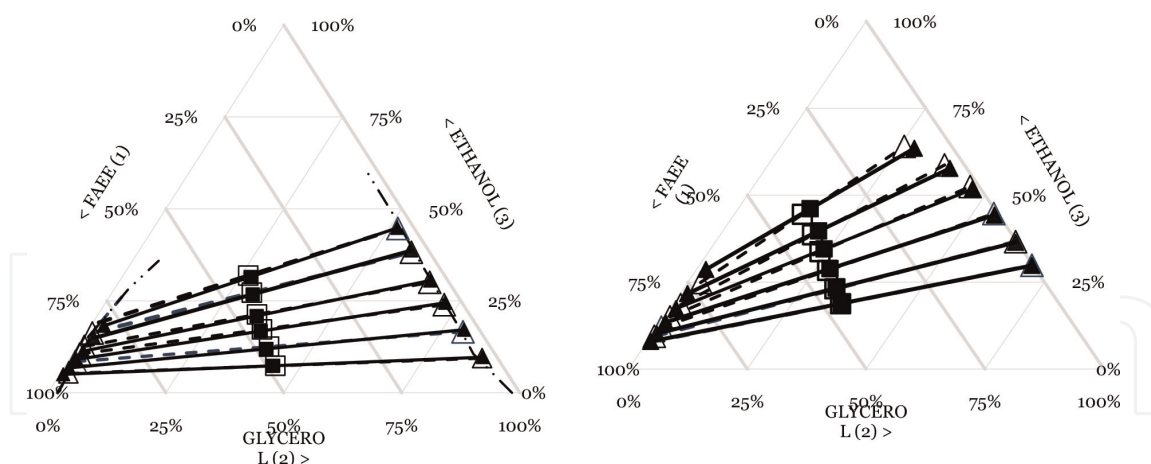
Figure 3.
Ternary LLE diagram for the ethyl biodiesel from cottonseed oil system at 333.15 K (left) and crambe oil at 298.2 K (right). Experimental data from [19, 38], respectively.

Figure 4 shows the results of this prediction in the form of a ternary diagram, which exhibit small deviations from the experimental data, thus validating the methodology used.

The results obtained in the fitting and validation processes were then compared with UNIFAC parameters proposed by Magnussen et al. [29] and Bessa et al. [35]. The UNIFAC-LL database fitted by Magnussen et al. [29] in 1981 is extensively widespread and applied to describe fatty systems equilibrium [47–49]. A more recent research by Bessa and collaborators [35] refitted all interaction parameters of the UNIFAC-LL and proposed a new OH subgroup used to represent uniquely this subgroup present in the glycerol molecule, thus having to fit 42 interaction parameters.

Table 4 shows the percentage mean square error (MSE%). The results using the parameters proposed by Machado et al. [43] are always better than those using the Magnussen et al. [29] and Bessa et al. [35] parameters.

Figure 5 shows ternary LLE diagrams for the ethyl biodiesel from macauba pulp oil system comparison with Bessa et al. [35] fitted parameters (left) and with UNIFAC-LL parameters (right).
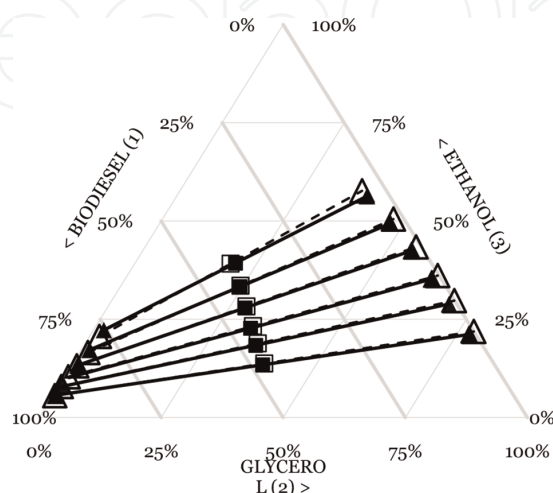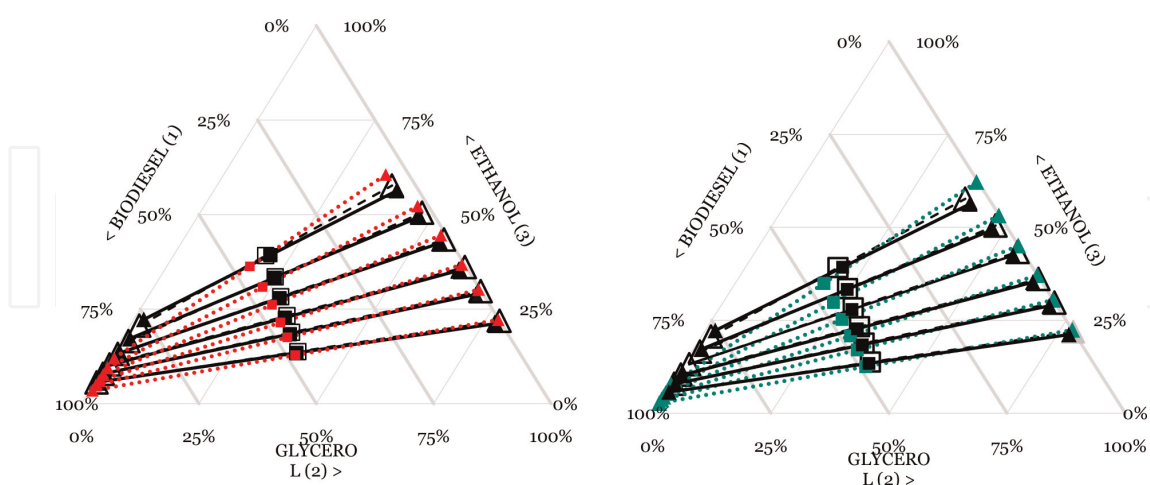

Figure 4.
Ternary LLE diagram for the ethyl biodiesel from macauba pulp oil system at 298.15 K for validation procedure. Experimental data from [33].

Biodiesel	T (K)	MSE (%)		
		UNIFAC-LL [29]	Bessa et al. [35]	Machado et al. [43]
Soybean	293.15	21.07	4.68	0.98
	323.15	30.30	2.77	2.08
Canola	303.15	4.41	2.75	2.13
Palm	298.15	4.62	3.25	0.73
	323.15	4.61	2.54	0.76
Jatropha curcas	303.15	5.62	4.04	1.34
	318.15	5.83	4.01	0.85
	333.15	15.33	5.09	1.55
Macauba pulp	298.15	5.22	3.49	0.87
Cottonseed	293.15	5.16	4.49	1.20
	313.15	5.72	4.45	0.96
	333.15	5.59	4.13	0.87
Crambe	298.15	11.00	4.76	1.50
	318.2	10.07	5.69	1.14
Sunflower	298.15	3.53	2.99	0.92
	313.15	4.17	3.54	1.23
MSE%		8.89	3.92	1.20

Table 4.
Comparative percentage mean square error (MSE%) for this study's fitting and the literature (EtOH).

Figure 5.
Ternary LLE diagram for the ethyl biodiesel from macauba pulp oil system at 298.15 K comparison with the Bessa et al. [35] (left, red tie-lines); and with the UNIFAC-LL [29] data (right, green tie-lines). Experimental data from ref. [19].

Figure 5 (right) shows that the UNIFAC-LL results have large deviations and the use of such parameters to predict equilibrium between the glycerol-rich phase and the biodiesel-rich phase for the systems considered by Machado et al. [43] is not

recommended. Although the parameters fitted by Bessa et al. [35] could better describe the LLE than the UNIFAC-LL [29] parameters, still there is considerable discrepancy between the predictions and the experimental data. Such observations corroborate the results shown in **Table 4**. **Figure 4** shows that ethanol subgroup fitting tie-lines represent considerably better the equilibrium of the biodiesel-rich phase with the glycerol-rich phase. It is worth mentioning that, only eight parameters were fitted, while Bessa et al. [35] considered 42 adjustable parameters in their study.

For deacidification system, the methodology was initially applied to fit parameters for the new interaction subgroup representing the ethanol molecule (EtOH-D) and H_2O subgroups, while the UNIFAC-LL for the subgroups forming the other components of the system (vegetable oil and free fatty acids—FFA) remained unchanged. The fitting process used experimental LLE data of 17 (Brazil nut, corn, cottonseed, garlic, grapeseed, *jatropha curcas*, macadamia, palm, peanut, rice bran, sesame, soybean, and sunflower) different vegetable oils available in the literature. **Table 5** shows the original UNIFAC-LL [29] parameters used and the interaction parameters fitted for the water (H_2O) and EtOH-D subgroups.

Figures 6 and **7** show the experimental points and calculated tie-lines obtained using the new interaction parameters summarized in **Table 5** for corn and soybean oil. Due to the systems presenting different water contents added to the ethanol solvent, ethanol and water were used as a mixed solvent to represent the pseudo-quaternary systems in a triangular diagram.

Analyzing **Figures 6** and **7** it can be noted an inversion in the tie-line slopes as water is added to the solvent. This phenomenon occurs because water decreases the solubility between oil and ethanol; hence, it increases the two-liquid phase regions [30, 32, 39, 42].

The ternary diagrams presented in **Figures 6** and **7** show that the calculated results are very close to the experimental data. Therefore, the H_2O and EtOH-D adjusted interaction parameters using the UNIFAC model correlated with the high accuracy of the LLE behavior of the considered system containing fatty acids.

Table 6 compares the RMSD from the experimental mass fraction data from the calculated data obtained by UNIFAC modeling using the parameters fitted by Bacicheti et al. [27] for EtOH-D subgroup with those obtained using parameters available in the literature (UNIFAC-LL from Magnussen et al. [29]), Noriega and Narváez [28], Hirata et al. [26]). **Table 6** still presents the RMSD between experimental and calculated data obtained using Machado et al. [43] parameter set.

Subgroup	CH$_3$, CH$_2$, CH	CH=CH	H$_2$O	COOH	CH$_2$COO	ETOH-D
CH$_3$, CH$_2$, CH	0	74.54	962.89	139.40	972.40	624.24
CH=CH	292.30	0	6337.07	1647.00	−577.50	537.49
H$_2$O	94.39	−134.08	0	363.72	−609.05	−277.75
COOH	1744.00	−48.52	−250.67	0	−117.60	−283.55
CH$_2$COO	−320.10	485.60	1716.74	1417.00	0	867.81
EtOH-D	−44.17	−61.21	8003.65	1117.01	−493.44	0

Table 5.
UNIFAC-LL [29] parameters and 18 interaction parameters fitted for H_2O and EtOH-D subgroups.
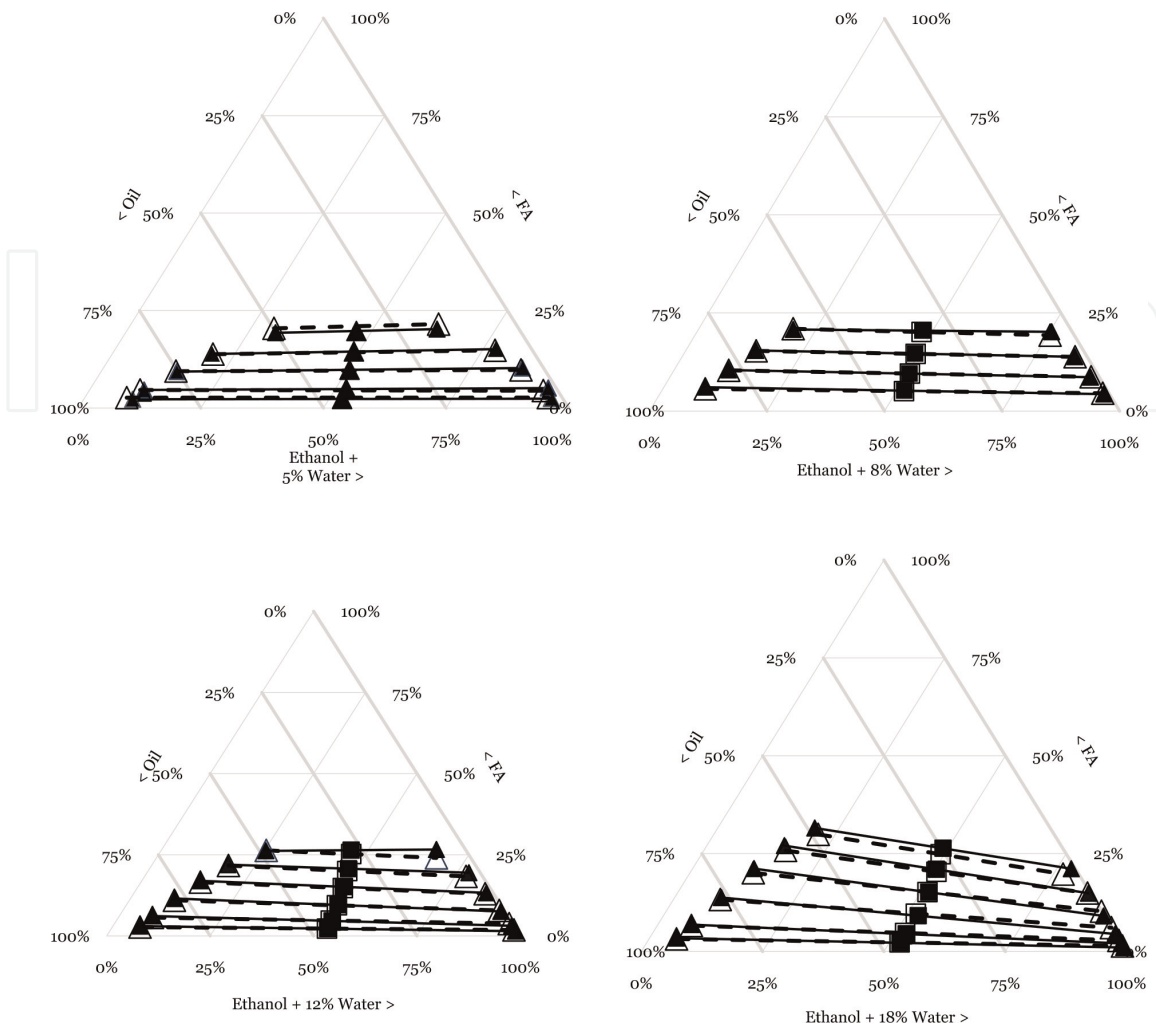
Figure 6.
LLE diagram for corn oil + commercial oleic acid 1 + and solvent (ethanol + %water) system at 298.15 K [31]. All compositions are on a mass basis.

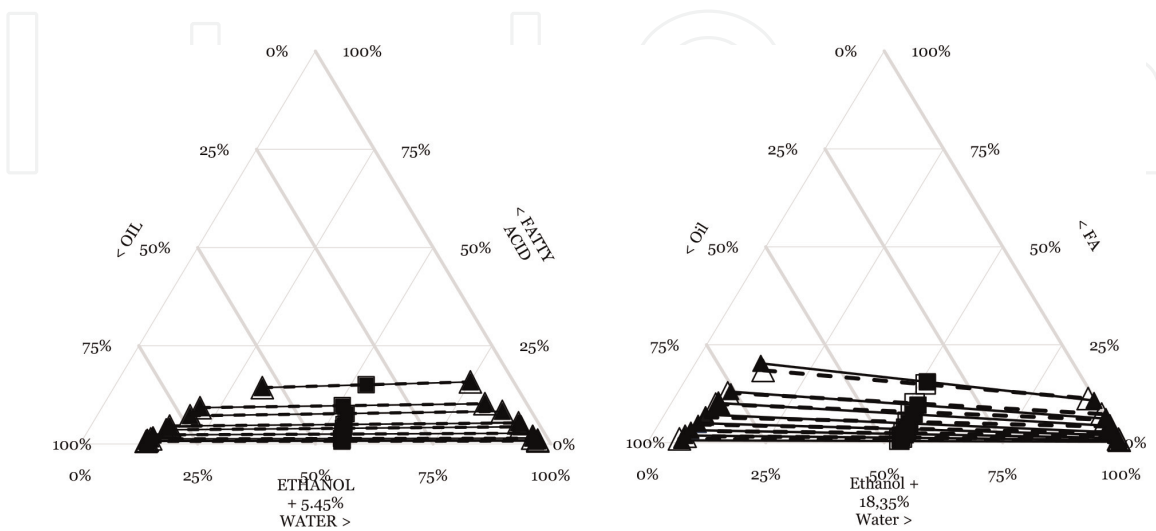**Figure 7.**
LLE diagram for soybean oil + commercial linoleic acid 1 + and solvent (ethanol + water) system at 323.15 K [42]. All compositions are on a mass basis.

Oil	T (K)	RMSD (by mass)				
		UNIFAC-LL [29]	Noriega and Narváez [28]	Hirata et al. [26]	Machado et al. [43]	Bacicheti et al. [27]
Brazil nut	298.15	5.95	11.49	0.72	10.90	0.52
Corn	303.15	10.11	14.25	0.93	9.94	0.78
Cottonseed	298.15	9.59	13.63	2.59	12.13	0.90
Garlic	298.15	11.81	12.98	0.63	11.32	0.58
Grapeseed	318.15	7.75	11.90	1.85	12.58	0.77
Jatropha	288.15	9.37	11.05	0.73	11.46	0.89
	298.15	11.99	16.02	0.67	10.31	0.76
	308.15	13.91	16.83	0.64	9.27	0.86
	318.15	15.19	11.49	0.75	8.90	0.59
Macadamia	298.15	5.28	12.11	1.97	10.06	1.77
Palm	318.15	3.74	15.45	0.46	7.19	1.63
Peanut	298.15	11.15	14.04	1.15	11.36	0.72
Rice bran	298.15	10.56	16.46	1.12	11.43	0.59
Sesame	298.15	8.57	12.23	1.42	11.62	0.75
Soybean	323.15	4.74	18.73	1.34	10.18	0.60
Sunflower (O)	298.15	5.53	10.27	2.29	12.27	0.97
Sunflower (L)	298.15	11.63	9.35	2.13	12.72	1.01
Global RMSD%		9.24	13.43	1.27	10.81	0.87

Table 6.
*Root mean square deviation (*RMSD *for fittings in this chapter and the literature.*

As commented previously, Noriega and Narvaez [28] fitted 30 UNIFAC parameters of the subgroups related to pseudo-ternary and pseudo-quaternary systems of biodiesel + alcohol + glycerol and oil + fatty acid + alcohol + water. Hirata et al. [26] used plenty of pseudo-quaternary data available in the literature to fit all the 30 UNIFAC interaction parameters of interest for fatty systems. The present study adjusted only 16 interaction parameters for pseudo-ternary biodiesel systems and adjusted only 18 interaction parameters for pseudo-quaternary deacidification systems.

The global RMSD displayed in **Table 6** shows that the parameters set proposed by UNIFAC-LL [29] and Noriega and Narváez [28] are not suitable to describe the liquid-liquid equilibrium of deacidification and biodiesel-related systems. The global RMSD using UNIFAC-LL and Noriega and Narváez [28] were 9.24 and 13.43, respectively, while using the parameters fitted by Bacicheti et al. [27] resulted in a global RSMD of 0.87.

The considerable difference in RMSD between experimental and calculated data applying Machado et al. [43] parameter set (10.81%) and Bacicheti et al. [27] parameter set (0.87%) subgroup parameters emphasize the difference in ethanol subgroup in biodiesel separation and deacidification systems due to water and glycerol molecules in the system.

It was expected that Noriega and Narváez [28] parameters and Machado et al. [43] parameter set resulted in slightly high deviations (**Table 6**) since they were adjusted to biodiesel systems. But we were expecting that the other UNIFAC subgroups (CH$_3$, CH$_2$, CH, CH = CH, COOH, CH$_2$COO) would be able to represent the liquid-liquid equilibrium behavior, giving a fair and enough performance of UNIFAC model. However, the presence of water is too sharp, turning the hole systems distinct and the deviations significant, despite having similar UNIFAC subgroups.

In contrast to results obtained by the other UNIFAC parameter matrices, the RMSD obtained by using Hirata et al. [26] proposed parameters were closer to this study's parameters performance. It is worthy to quote that, although using a similar databank, this chapter ensues in lower RMSD between experimental and calculated data and, moreover, it has the upgrade of adjusting only 18 interaction parameters, resulting in a considerable faster procedure and relatively lower computational calculations than Hirata et al. [26] that fitted 30 interaction parameters.

The validation procedure of the parameters was taken for canola oil system, which was not used in the parameter fitting process. **Table 7** lists the RMSD between the experimental and calculated molar fractions using Bacicheti et al. [27] parameter set with those obtained using UNIFAC-LL from Magnussen et al. [29]), Noriega and Narváez [28], and Hirata et al. [26]). As previously stated, canola oil [18] data did not take part in this study's parameter fitting, but it was used by Hirata et al. [26] in their parameter fitting procedure, resulting in alike RMSD.

According to **Table 7**, the Bacicheti et al. [27] parameter set exhibits lower RMSD values than those obtained by applying the parameter matrix from the previously cited authors; hence the EtOH-D subgroup can successfully describe the deacidification systems of vegetable oils.

Figure 8 exhibits the ternary diagrams for the validation with canola oil data. Bacicheti et al. [27] parameter set exhibited small deviations from the experimental data than the other parameter matrices. In contrast, the results using the Machado et al. [43] parameter set and the parameters of Noriega and Narváez [28] have a considerable deviation from the experimental data, and thus, they are not recommended for quantitatively predicting the equilibrium of deacidification of vegetable oils.

As shown in **Figure 8**, Machado et al. [43] and Noriega and Narváez [28] parameter set, and UNIFAC-LL [29] present the highest average deviation from the experimental points. The average deviation values between the experimental and calculated data obtained using the interaction parameters from Hirata et al. [26] were close to

Oil	T(K)	RMSD% (by mass)				
		UNIFAC-LL [29]	Noriega and Narváez [28]	Hirata et al. [26]	Machado et al. [43]	Bacicheti et al. [27]
Canola	303.15	8.92	11.16	0.46	9.86	0.40

Table 7.
RMSD between experimental and calculated data mass fraction for the validation system composed of canola oil + commercial oleic acid 3 + ethanol + water at 303.15 K.
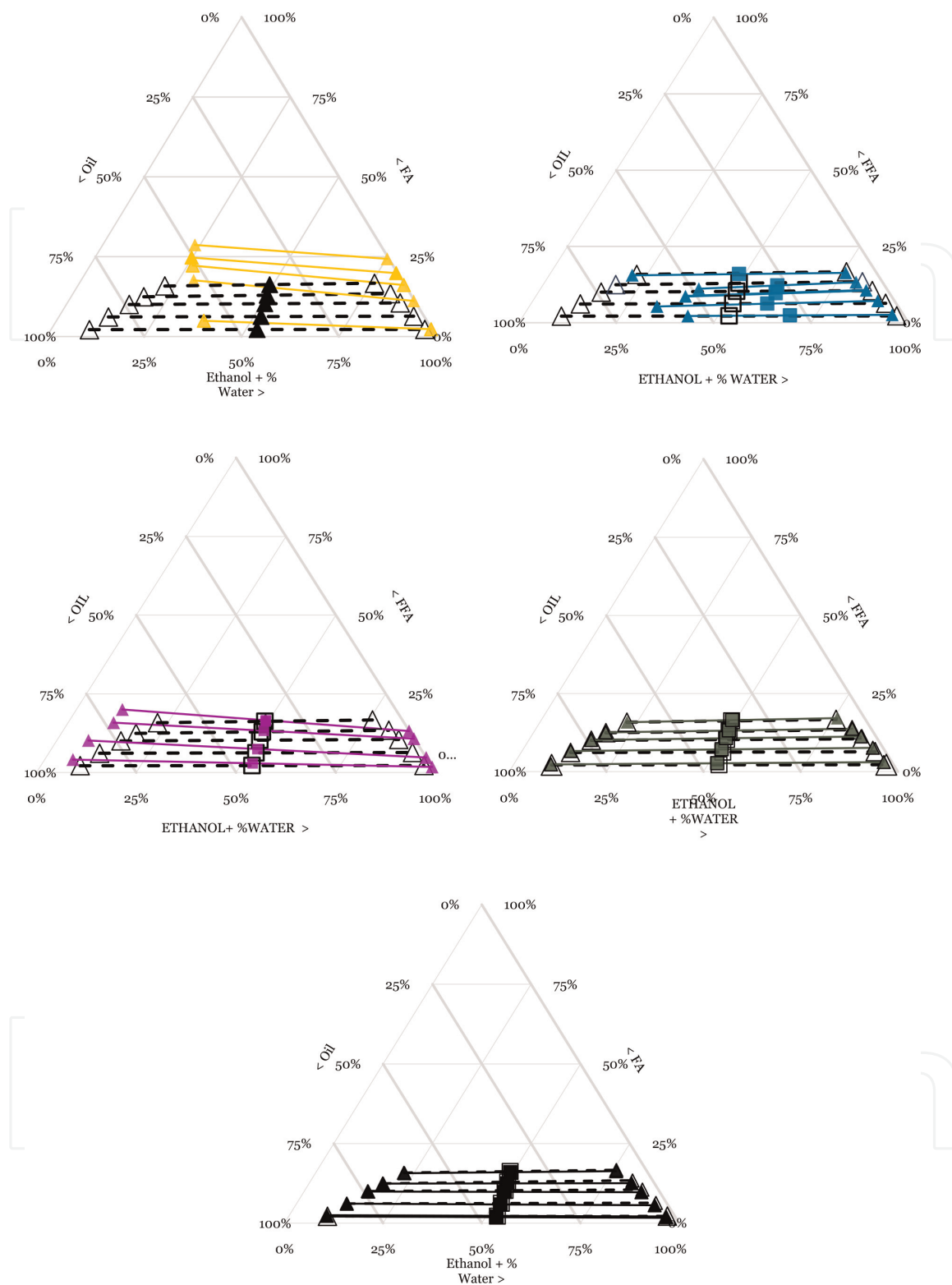
Figure 8.
LLE diagram for validation procedure with canola oil system [18]. Comparison between literature data (traced line) with predictions using parameters from Bacicheti et al. [27] (black lines), Noriega and Narváez [28] (yellow lines), Machado et al. [43] (blue lines), UNIFAC-LL [29] (purple lines), and Hirata et al. [26] (green lines). All compositions are on a mass basis.

those obtained by Bacicheti et al. [27]. However, Bacicheti et al. [27] only refitted 18 parameters, taking fewer computational calculations than those required by Hirata et al. [26], who readjusted all of them.

4. Conclusions

The new ethanol subgroups for the UNIFAC model presented in this chapter could correctly and accurately describe the liquid-liquid phase equilibrium of deacidification and biodiesel systems. The ethanol binary interaction parameters were fitted using a data bank of LLE available in the literature for biodiesel vegetable oil systems.

Using relatively few computational calculations and aiming to result in a relatively small split with the complex data set established by the UNIFAC-LL model, Bacicheti et al. [27] maintain CH_3, CH_2, CH, $CH = CH$, $COOH$ and CH_2COO subgroups parameters, and refitted just water and ethanol UNIFAC interaction parameters. Ethanol-fitted parameters were then validated with very small deviations in the prediction of macauba pulp oil biodiesel for EtOH-B and canola oil for EtOH-D. The overall deviation calculated in the validation of these new UNIFAC parameters was 1.20% for biodiesel systems and 0.87% for deacidification systems.

When compared to prediction results for biodiesel systems using UNIFAC-LL parameters and those fitted by Bessa et al. [35], Machado et al. [43] had better results for the tie-lines, despite the small number of parameters fitted. The same results were obtained considering deacidification systems of vegetable oils, which ethanol interaction parameters proposed by Bacicheti et al. [27] exhibited small deviations from the experimental data and lower deviations than Noriega and Narváez [28], UNIFAC-LL [29], and Hirata et al. [26].

The method applied can contribute to a better description of the phase behavior of fatty systems involved in the deacidification of vegetable oil using liquid-liquid extraction and biodiesel separation process, as this biofuel is subject to strict composition and purity regulations. Moreover, taking into account the lower root mean square deviation between the experimental and calculated molar fractions obtained here and the relatively low computational calculations for the parameter fitting procedure, this chapter presents an easier and faster alternative approach instead to refitting all UNIFAC parameters.

The results show that the methodology employed is consistent and may be useful in predicting equilibrium when experimental equilibrium data are not available.

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