International Journal of Thermodynamics (IJoT)
ISSN 1301-9724 / e-ISSN 2146-1511
https://dergipark.org.tr/en/pub/ijot

Vol. 27 (No. 2), pp. 019-026, 2024
doi: 10.5541/ijot.1372558

Research Article

Evaluation of the Effect of Ethyl Alcohol Content In A Ternary Ethanol/Biodiesel/Diesel System

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Received 10 October 2023, Revised 13 December 2023, Accepted 15 January 2024

Abstract

Increasing concern about climate change and the need to reduce dependence on fossil fuels have driven the search for more sustainable energy alternatives. One way to reduce emissions is by adding oxygenated compounds such as biodiesel and alcohols to diesel fuel. However, this can lead to phase separation between the fuels and have serious consequences for engine performance. In this context, the present study aimed to evaluate the effect of ethanol content on the miscibility of components in mixtures containing ethanol + biodiesel + diesel through the study of liquid-liquid equilibrium. The results from ternary phase diagrams revealed that the amount of water present in ethanol has a significant effect on the miscibility of the mixture components, with larger biphasic regions observed in systems with lower ethanol content. For the 95% ethanol diagram, the reliability of experimental data on equilibrium lines was assessed through the Othmer-Tobias and Hand correlations, which showed correlation coefficients (R^2) of 0.996 and 0.995, respectively. The results obtained from the NRTL and UNIQUAC thermodynamic models demonstrated excellent agreement with the experimental data, with a deviation of only 1.78 and 0.78% for the NRTL and UNIQUAC models.

Keywords: *Liquid-liquid equilibrium; ethanol; biodiesel; UNIQUAC; NRTL; othmer-tobias correlation.*

1. Introduction

Growing energy demands and the harm caused by fossil fuels have been an increasing concern in recent years. Although fossil fuels constitute a large part of energy consumption worldwide, they exhibit several disadvantages, such as environmental pollution and greenhouse gas emissions responsible for global warming. In this respect, numerous scientific studies have focused on promoting biofuels, considered sustainable and with a smaller carbon footprint [1], [2], [3].

In this category, biodiesel is a promising alternative to mitigate the damage caused by diesel fuel used in road transport. This biofuel can be produced from several renewable sources and has similar characteristics to oil-derived diesel. In addition, biodiesel combustion in diesel engines produces fewer greenhouse gases, such as carbon dioxide, carbon monoxide and hydrocarbons, thereby reducing atmospheric emissions from non-renewable fuels [4], [5]. Adding oxygenated compounds, such as ethanol, to diesel oil has also proved to be an interesting alternative since it has renewable origins, strengthens combustion and consequently engine performance [6], [7], [8].

In this respect, partial substitution of fossil diesel by biodiesel has been investigated, demonstrating good perspectives due to its technical and environmental capacity [9]. In addition to these advantages, ethanol also increases the octane rating of gasoline and withstands a higher compression rate. On the other hand, the limitations of these biofuels must be respected when added to fossil diesel, such as mixture immiscibility as a function of composition and temperature [10], [11].

A liquid-liquid equilibrium (LLE) study is essential to understanding how components interact and are distributed between the liquid phases present in the mixture. Thermodynamic modeling using models such as UNIQUAC and NRTL (which apply the local composition theory) is a valuable tool in predicting and understanding phase behavior in complex multicomponent systems [12], [13]. A thorough understanding is crucial to developing optimized mixtures capable of ensuring the stability and performance inherent to fuels [14].

In this respect, the present study aimed at assessing the effect of ethyl alcohol content in a ternary system consisting of Ethanol + Biodiesel + Diesel, including a liquid-liquid

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equilibrium study to assess mixture miscibility and fuel stability when using different ethanol contents.

2. Materials and Methods

2.1 Raw Material

In the LLE, were used biodiesel produced according to the methodology of Bezerra et al.[15]. pure diesel (Nordeste Logística from Guamaré, Brazil) and ethyl alcohol (Dinâmica Química Contemporânea, 99.5%) were diluted at concentrations of 98.5, 97.5, 96.5 and 95.5%. Table 1 shows the the materials used in this study.

2.2 Isothermal Phase Diagram

Binodal curves were determined using the cloud point method, similar to mass titration, widely applied for these determinations [16], [17]. Titrations were performed in a glass cell, where the temperature was kept constant by water circulation supplied by a thermostatic bath (Figure 1). This method involves slowly adding a component to a monophasic mixture containing known amounts of each component up to the cloud point, where a second phase is visually detected. In order to determine the uncertain pattern of a binodal curve, in terms of molar fraction (x), the binodal compositions were assessed in duplicate and the u deviation values (x) for each system are presented in the footnotes of each table. The experimental data obtained for binodal curves provide useful information to select compositions in the biphasic region to be used as global composition for tie-line measurements.

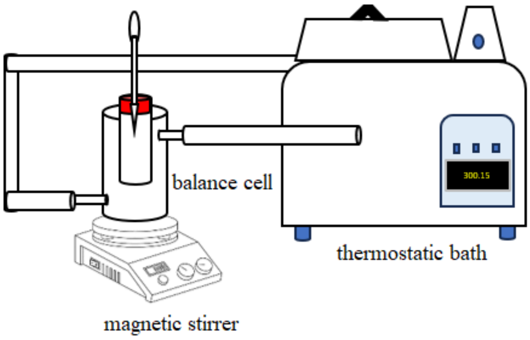

Figure 1. Schematic drawing of the system.

2.3 Tie-lines compositions

Because of the extensive area of the curve, tie-line compositions were assessed for the 95.5% diagram. Samples were prepared by weighing 30 mL of each component and the mixture was submitted to constant agitation in a magnetic agitator for three hours. Samples of each phase were collected with a syringe and their densities measured in an automatic densimeter (Anton Paar DMA 4500M). Tie-line construction required the addition of a known amount of one of the components present in the mixture in order to guarantee that the samples remained in a single phase (homogeneous mixture).

The LLE data of the ternary systems were plotted using the Origin Pro 2018 program. Based on the equilibrium lines, the distribution (β) and selectivity (S) coefficients were calculated to determine the efficiency of the solvent in extraction. The values of these parameters were obtained using Equations (1), (2) and (3), where β_2 represents the distribution coefficient of biodiesel, β_3 the distribution coefficient of diesel, S the selectivity coefficient; w_{21} the mass fraction of biodiesel in the ethanol-rich phase; w_{23} the mass fraction of biodiesel in the B12 diesel-rich phase; w_{33} the mass fraction of diesel in the diesel-rich phase and w_{31} the mass fraction of diesel in the ethanol-rich phase.

$$\beta_2 = \frac{w_{21}}{w_{23}} \tag{1}$$

$$\beta_3 = \frac{w_{31}}{w_{33}} \tag{2}$$

$$S = \frac{\beta_2}{\beta_3} \tag{3}$$

2.4 Thermodynamic Models

The thermodynamic consistency of experimental LLE data was assessed using Othmer-Tobias [18] and Hand correlations [19]. These correlations consider the mass fractions of components present in the ethanol and diesel-rich phases to reproduce the equilibrium lines and ensure data reliability. The fractions were calculated using Equations (4) and (5), where w_{11} is the mass fraction of ethanol in the ethanol-rich phase, w_{33} the mass fraction of diesel in the diesel-rich phase, w_{21} the mass fraction of biodiesel in the ethanol-rich phase and w_{23} the mass fraction of biodiesel in the diesel-rich phase.

Table 1. Materials used in this study.

Chemical Name	IUPAC Name	Source	Mass fraction	Analysis method
Biodiesel	Biodiesel	[15]	>0.98	GC[a]
Ethyl alcohol	Ethanol	Dinâmica Química Contemporânea	>0.99	GC[a]
Diesel[b]	Diesel	Nordeste Logística	>0.99	-

[a] Gas chromatography purities were provided by the manufacturers and the chemicals used without any additional treatment.

[b] Diesel sample (see supplementary materials).

$$ln\left(\frac{1-w_{33}}{w_{33}}\right) = a + b\left(\frac{1-w_{11}}{w_{11}}\right) \quad (4)$$

$$ln\left(\frac{w_{23}}{w_{33}}\right) = a + b\left(\frac{w_{21}}{w_{11}}\right) \quad (5)$$

In addition, thermodynamic modeling was assessed using the NRTL and UNIQUAC models based on excess Gibbs energy. Experimental data reliability was attested by the binary interaction parameters of the ternary systems composed of ethanol, biodiesel and diesel. The regression parameters of the NRTL and UNIQUAC models were determined using an objective function, according to Equation (6), which compares experimental mass compositions calculated from the different phases and equilibrium lines, where j, i, and k indicate the phase, the component and equilibrium line, respectively; M the number of equilibrium lines; w^{exp} the experimental mass composition and w^{cal} the calculated mass composition. The TML computational tool was used to determine the binary interactions of the parameters [20].

$$OF = \sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\left[\left(w_{ijk}^{exp} - w_{ijk}^{cal}\right)^2\right] \quad (6)$$

To evaluate the accuracy of the two models, the root-mean-square deviation (RMSD) was calculated by Equation (7), where k, j, i, w^{exp} and w^{cal} are the same as expressed in Equation (6).

$$RMSD(\%) = 100x\left[\sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\frac{\left(w_{ijk}^{exp} - w_{ijk}^{cal}\right)^2}{6M}\right]^{\frac{1}{2}} \quad (7)$$

The UNIQUAC model uses van der Waals® molecular volume parameters and surface area (q) for each component of the mixture. These parameters are calculated by adding the individual terms of each subgroup present in the molecules of the components, as defined by Equations (8) and (9) [21], where i is the component of the system; k, group identification; $v_k^{(i)}$, the number of k subgroups of component i; R_k, the UNIFAC volume and Q_k, the UNIFAC surface parameter. For biodiesel, the parameters were determined considering a weighted mean that considers the composition of the main esters present.

$$r_i = \sum_k v_k^{(i)} R_k \quad (8)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (9)$$

Table 2. Experimental (Liquid-Liquid) Equilibrium Data from the Binodal Curve of the Systems: Ethanol (1) + Biodiesel (2) + Diesel (3) for Mass Fractions (w) at a Temperature 300.15 K and 101.3 kPa.

ethanol 99.5% (system 1)			ethanol 98.5% (system 2)			ethanol 97.5% (system 3)			ethanol 96.5% (system 4)			ethanol 95.5% (system 5)		
w1	w2	w3	w1	w2	w3	w1	w2	w3	w1	w2	w3	w1	w2	w3
0.813	0.006	0.181	0.894	0.006	0.100	0.888	0.013	0.099	0.048	0.429	0.523	0.091	0.856	0.053
0.676	0.034	0.290	0.739	0.075	0.186	0.740	0.075	0.185	0.090	0.362	0.548	0.016	0.886	0.098
0.549	0.084	0.367	0.621	0.113	0.266	0.596	0.148	0.256	0.142	0.332	0.526	0.014	0.788	0.198
0.415	0.171	0.414	0.528	0.118	0.354	0.509	0.151	0.340	0.210	0.314	0.476	0.014	0.690	0.296
0.322	0.194	0.484	0.420	0.160	0.420	0.408	0.184	0.408	0.288	0.289	0.423	0.014	0.591	0.395
0.245	0.185	0.570	0.332	0.171	0.497	0.317	0.208	0.475	0.357	0.239	0.405	0.014	0.493	0.493
0.167	0.166	0.667	0.253	0.157	0.590	0.227	0.244	0.529	0.474	0.203	0.323	0.014	0.395	0.591
0.089	0.116	0.795	0.158	0.212	0.630	0.150	0.250	0.600	0.631	0.158	0.211	0.014	0.296	0.690
0.050	0.0	0.950	0.085	0.155	0.760	0.079	0.216	0.705	0.766	0.086	0.148	0.014	0.200	0.786
			0.043	0.143	0.814	0.035	0.049	0.916	0.856	0.045	0.099	0.014	0.099	0.887
			0.026	0.049	0.925	0.043	0.096	0.861	0.012	0.395	0.593	0.047	0.893	0.060
						0.072	0.187	0.741	0.024	0.293	0.683	0.075	0.831	0.094
									0.016	0.198	0.786	0.083	0.753	0.164
									0.022	0.097	0.881	0.161	0.641	0.198
									0.028	0.049	0.923	0.238	0.557	0.205
												0.318	0.478	0.204
												0.395	0.396	0.209
												0.484	0.322	0.194
												0.590	0.255	0.155
												0.701	0.182	0.117
												0.824	0.094	0.082
												0.895	0.047	0.058

3. Results and Discussion

3.1 Ternary Diagram Fuel Blends

The experimental miscibility curves of the ternary system [Ethanol (1) + Biodiesel (2) + Diesel (3)], at ethanol concentrations of 99.5% (system 1), 98.5% (system 2), 97.5% (system 3), 96.5% (system 4) and 95.5% (system 5), constructed at a temperature of 300.15 K, are presented in Tables 1 and 2 and plotted on the ternary diagrams of Figure 2. Ternary diagrams are generally used for extraction or purification, and to observe stable and relevant regions in fuel formulation studies [22].

The appearance of the phase diagrams plotted in Figure 2 demonstrates that the reciprocal solubility of the constituents of the mixture defines the size of the monophasic and biphasic regions. The ternary diagrams show that as ethanol content declines, there is a significant increase in the biphasic region. This behavior is associated with the rise in the amount of water present and consequent increase in ethanol molecule polarity, thereby reducing miscibility of the constituents [23], [24].

This shows the importance of a larger ethanol content when using it as an additive in fuel formulations aimed at optimizing miscibility and minimizing phase separation problems, which directly influence engine performance and efficiency [22].

Of the ternary systems studied, system 5 (ethanol 95.5%) contained an extensive biphasic region (Figure 2e), especially due to the hydrophilic and polar nature of water, present in larger amounts (5%wt), exhibiting unequal electron density distribution. Despite dissolving very well in nonpolar compounds such as gasoline, the polar extremity of ethanol molecules is characterized by the presence of a hydroxyl group (-OH). Adding water strengthens ethanol polarity due to the strong dipole-dipole interactions between them [11]. On the other hand, diesel is a mixture of nonpolar hydrocarbons composed primarily of hydrophobic alkanes. The presence of water in ethanol is even more incompatible with diesel, given that the polar nature of ethanol is intensified. Phase separation compromises fuel quality [25].

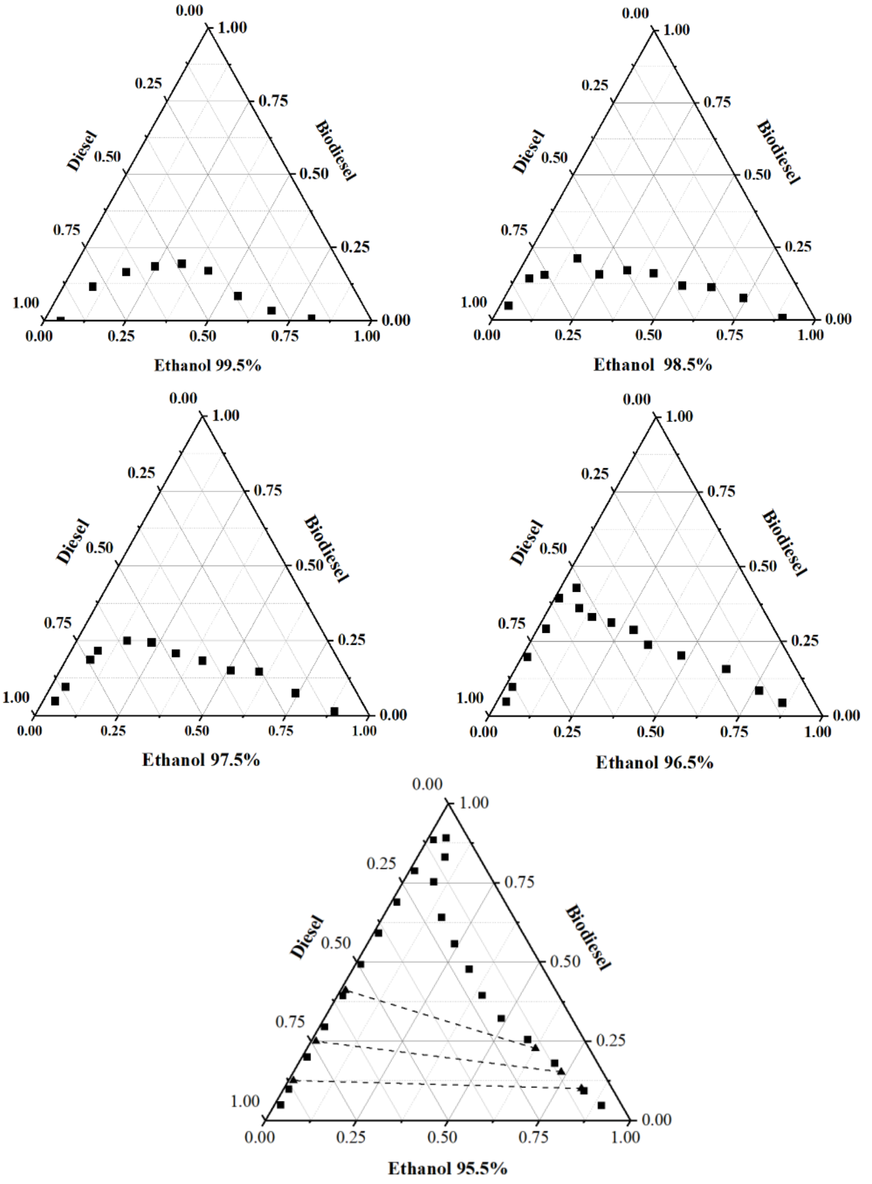

Figure 2. Ternary diagrams for LLE of different systems with Ethanol (1) + Biodiesel (2) + Diesel (3) solubility (■) and tie lines point in system 5 (▲---▲) for a mass fraction (w) at 300.15 K and 101.3 kPa.

3.2 Distribution Coefficients and Selectivity

The distribution and selectivity coefficients were performed only for system 5 (Ethanol 95.5%) because of the large biphasic region. The compositions of the equilibrium lines in the diesel and ethanol-rich phases are presented in Table 3. Greater affinity between biodiesel and diesel when compared with ethanol is evident in the slope of the equilibrium lines, indicating that the amount of biodiesel present in the diesel-rich phase is higher than in the ethanol-rich phase. The different component distribution between the phases shows a preference for a greater proportion of biodiesel to mix and solubilize in diesel when compared to ethanol [26].

The miscibility behavior of the constituents was assessed using the distribution coefficients (Figure 3), which are parameters capable of describing the distribution of a component between the two immiscible liquid phases, and selectivity coefficient (Figure 4), which quantifies the solvent extraction power of the system components [27]. The values obtained exhibited a biodiesel distribution coefficient less than 1 ($\beta_2 < 1$), which means that a larger amount of biodiesel is distributed in the diesel-rich phase, corroborating the equilibrium line results. Selectivity exhibited values above 1, underscoring diesel's preference for biodiesel and its extraction capacity, and in agreement with the other results presented. Bezerra et al. [16], obtained distribution coefficient values less than 1 and selectivity greater than 1 for systems containing biodiesel + glycerol + methanol and methyl palmitate + glycerol + methanol. Bezerra et al. [15] assessed the use of biodiesel as an additive to stabilize alcohol mixtures in diesel, proposing new formulations based on LLE studies between methanol/ethanol/butanol + biodiesel + diesel, obtaining distribution coefficient values less than 1 and selectivity greater than 1.

Table 3. Phase Equilibrium Composition of the constituents: Ethanol 95.5% (1) + Biodiesel (2) + Diesel (3) for Mass Fractions (w) at 300.15 K and 101.3 kPa.

diesel rich-phase				ethanol rich-phase			
w_1	w_2	w_3	densities ($g.cm^{-3}$)	w_1	w_2	w_3	densities ($g.cm^{-3}$)
0.014	0.411	0.575	0.841	0.626	0.223	0.151	0.820
0.014	0.250	0.736	0.834	0.733	0.153	0.114	0.815
0.014	0.126	0.860	0.829	0.815	0.101	0.084	0.811

[a]Standard uncertainties *u* are $u(T) = 0.5$ K, $u(P) = 1$ kPa, and $u(w) = 0.003$.

3.3 Thermodynamic Models

3.3.1 Hand and Othmer-Tobias Correlations

The reliability and consistency of the data obtained from the equilibrium lines were assessed using Othmer-Tobias and Hand correlations. The linearity of these correlations indicates the degree of consistency of the experimental data [28]. The correlation coefficients (R^2) for both equations were close to 1 (greater than 0.99), as shown in Table 4, which demonstrates the thermodynamic consistency of the experimental data. Linear behavior is also evident in the graphs presented in Figure 5. Similar results were reported by Toledo et al. [29] when studying the system (Peanut Biodiesel + Glycerol + Ethanol).

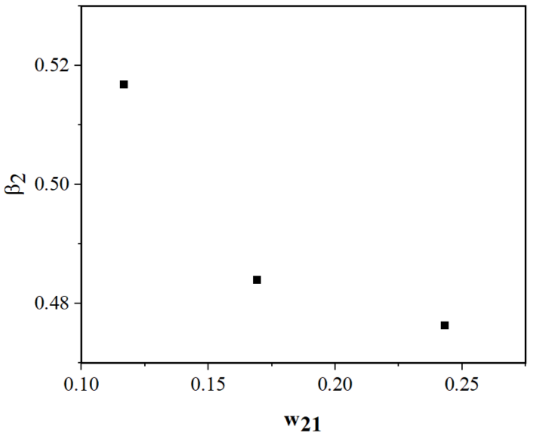

Figure 3. Experimental solute distribution coefficient (β_2) as a function of ethanol 95.5% mass fraction for system 5 at 300.15 K and 101.3 kPa.

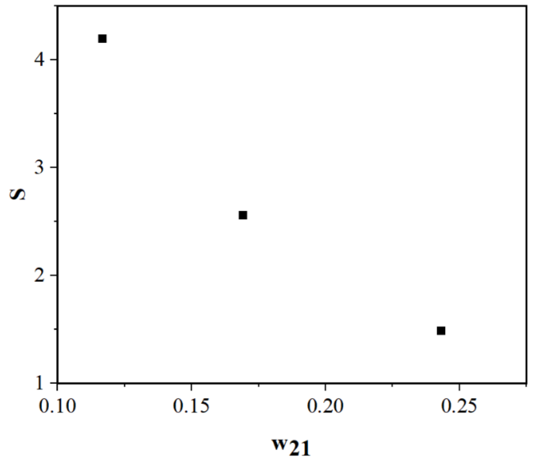

Figure 4. Experimental selectivity value (S) as a function of ethanol mass fraction for system 5 at 300.15 K and 101.3 kPa.

Table 4. Othmer-Tobias and Hand Equation coefficients and the linear coefficient (R^2) for system 5.

Correlation	a	b	R^2
Othmer-Tobias	0.688	1.397	1
Hand	1.238	1.283	0.999

3.3.2 NRTL and UNIQUAC Models

Liquid-liquid equilibrium data predictability was established using the NTRL and UNIQUAC thermodynamic models. These models can predict the molar fractions of the components in each phase, considering the intermolecular forces and molecular characteristics of each substance [21]. The values of structural parameters r and q used in the UNIQUAC model are presented in Table 5. These parameters can estimate the contributions of the groups present in the individual components, and their values are influenced by the molecular structure of each component [21]. The binary parameters Aij, Aji and aij of the UNIQUAC and NRTL correlations were estimated and are shown in Table 6.

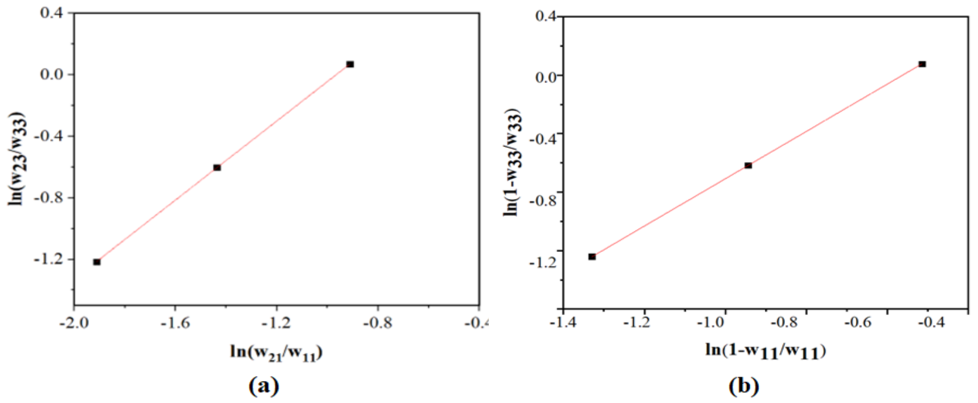

Figure 5. Thermodynamic consistency [(a) Hand and (b) Othmer-Tobias] of the experimental data for system 5 with ethanol 95.5%.

Table 5. UNIQUAC Structural Parameters (r and q) for Pure Components.

Component	r	q
Ethanol	2.575	2.588
Biodiesel	13.073	10.760
Diesel	9.677	8.004

Figure 6 shows that the experimental data were satisfactorily fit to the UNIQUAC and NRTL models, confirmed by the low root mean square deviations of 0.78 and 1.78%, respectively. These results indicate that the UNIQUAC model better fit the experimental data, demonstrating more accurate agreement between the model predictions and real observations. Santos et al.[26] reported that the experimental data of the ternary system (methyl oleate + methanol + water) fit the UNIQUAC and NRTL models satisfactorily and the former resulted in better data predictions when compared to NRTL. Evangelista Neto *et al.* [17] correlated the experimental equilibrium data of the ternary system (Chicken Fat biodiesel + Methanol + Glycerol) with the UNIQUAC model and obtained low RMSD values of 0.78 and 0.89%, respectively. These results corroborated the data obtained in the present study. Machado *et al.*, [30] assessed the estimated parameters of the UNIFAC subgroup for ethanol in predicting the LLE of the biodiesel systems, exhibiting an RMSD of 1.2%. Bezerra *et al.*[15], assessed the stimated parameters of UNIQUAC and NRTL for ternary phase diagrams for LLE of (a) methanol (1) + biodiesel (2) + diesel (3) (system 1) and (b) ethanol (1) + biodiesel (2) + diesel (3) (system 2) at 300.15 K and the results corroborated the data obtained in the present study.

Table 6. Binary parameters and Root-Mean-Square Deviation (RMSD) of system 5 [Ethanol 95.5% (1) + Biodiesel (2) + Diesel (3)].

Model	i-j	Aij	Aji	aij	RMSD (%)
UNIQUAC	1-2	-288.57	2994.5		0.77
	1-3	294.01	168.22		
	2-3	-54.89	122.99		
NRTL	1-2	149.12	337.41	0.429	1.78
	1-3	177.33	1879.5	0.2	
	2-3	2174.6	-48.15	0.47	

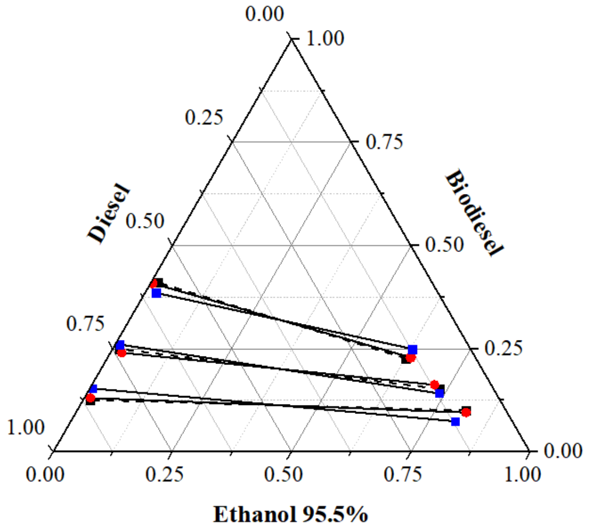

Figure 6. Ternary phase diagram for LLE of Ethanol 95.5% (1) + Biodiesel (2) + Diesel (3) at 300.15 K. Experimental tie line points for system 5 (–■–), NRTL model (–■–) and UNIQUAC model (–●–).

4. Conclusion

LLE analysis in the systems containing ethanol, biodiesel and diesel revealed that ethanol content plays a crucial role in the miscibility of components. Adding ethanol with higher concentrations of water resulted in a large phase separation region in the mixture, indicating lower miscibility among the constituents, due to the polar and hydrophilic nature of water. On the other hand, adding ethanol with higher purity grades promoted better miscibility, evidenced by smaller phase separation regions. The consistency of equilibrium data was assessed for system 1 using Othmer-Tobias and Hand correlations, whose correlation coefficients were higher than 0.99, demonstrating the reliability of the data. For system 5, the experimental equilibrium data and the results obtained using the NRTL and UNIQUAC thermodynamic models were compared. Both models were able to suitably represent the experimental data, with a slight advantage for the UNIQUAC model, with an average deviation of 0.78%, and 1.78% for the NRTL. These results underscore the significant influence of ethanol content on the solubilization capacity of the components and provide valuable information for the development of more stable, efficient, and sustainable fuel formulations, contribute to reducing the damage caused by fossil fuels to the environment. And, the experimental data measured in this study for the biodiesel system may be useful in building a database for researchers involved in biodiesel process development and optimization.

Acknowledgments:

The authors are grateful to CAPES and the PPGEQ/DEQ/UFRN for their financial support.

Nomenclature:

Symble	***Variable***
β	*distribution coefficient*
S	*selectivity coefficient*
w^{exp}	*experimental mass composition*
w^{cal}	*mass composition*
$r[cm^3.g^{-1}]$	*van der Waals molecular volume*
$q[m^2.g^{-1}]$	*molecular surface area*
v_k,	*the number of k subgroups*
R_k,	*UNIFAC group volume parameter*
Q_k,	*UNIFAC surface parameter.*

Subscripts

1	*Ethanol*
2	*Biodiesel*
3	*Diesel*
j	*phase*
i	*component*
k	*tie lines*
M	*number of tie lines*

Abbrevations

LLE	*Liquid-Liquid Equilibrium*
GC	*Gas Chromatography*
OF	*Objective Function*
RMSD	*Root-mean-square deviation*
R^2	*Regression coefficient*

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