

# LIQUID–LIQUID EQUILIBRIUM FOR TERNARY SYSTEMS CONTAINING ETHYLIC BIODIESEL + ANHYDROUS ETHANOL + REFINED VEGETABLE OIL (SUNFLOWER OIL, CANOLA OIL AND PALM OIL): EXPERIMENTAL DATA AND THERMODYNAMIC MODELING

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**Abstract** - Phase equilibria of the reaction components are essential data for the design and process operations of biodiesel production. Despite their importance for the production of ethylic biodiesel, the reaction mixture, reactant (oil and ethanol) and the product (fatty acid ethyl esters) up to now have received less attention than the corresponding systems formed during the separation and purification phases of biodiesel production using ethanol. In this work, new experimental measurements were performed for the liquid–liquid equilibrium (LLE) of the system containing vegetable oil (sunflower oil and canola oil) + ethylic biodiesel of refined vegetable oil + anhydrous ethanol at 303.15 and at 323.15 K and the system containing refined palm oil + ethylic biodiesel of refined palm oil + ethanol at 318.15 K. The experimental data were successfully correlated by the nonrandom two–liquid (NRTL) model; the average deviations between calculated and experimental data were smaller than 1.00%.

**Keywords:** Ethylic biodiesel; Liquid–liquid equilibrium; Sunflower oil; Canola oil; Palm oil; Ethanol; NRTL model.

## INTRODUCTION

Biodiesel, a clean renewable, biodegradable, and nontoxic fuel, has recently been considered as the best candidate for diesel fuel substitution because it can be used in any compression ignition engine without the need of modification. Ethylic biodiesel pro-

duced from some vegetable oils and ethanol is entirely based on renewable agricultural sources. In relation to methanol, ethanol has a superior dissolving capability, lower toxicity, higher heat content, higher cetane index and lower cloud and pour points and it is produced in large quantities from sugar cane in Brazil. Although there is an emphasis on produc-

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tion of biofuel made of soybean oil, the other vegetable oils such as sunflower, canola and palm have the potential to produce biodiesel (Porte *et al.*, 2010; Stamenkovic *et al.*, 2011).

Biodiesel is a mixture of fatty acid esters that is industrially produced through the transesterification reaction of a vegetable oil or a fat with an alcohol, usually using a basic catalyst (Issariyakul and Dalai, 2014).

The phase equilibria of the reaction components are very important for ethylic biodiesel production. The transesterification shows a complex phase behavior, forming two phases initially due to the fact that the reactants (ethanol and vegetable oil) are partially miscible, as demonstrated by Follegatti-Romero *et al.* (2010b). In the presence of a catalyst, the reaction mixture changes slowly into a fatty acid ethyl ester (biodiesel)–ethanol–vegetable oil–glycerol mixture, forming a partially miscible system.

The solubility of ethanol in the vegetable oil and fatty acid ethyl ester (FAEE) can greatly influence the reaction rate during the production of biodiesel. Consequently, the composition and the prediction of the reactant distributions between the immiscible phases in several conditions are required to design and to operate chemical reactors destined for ethylic biodiesel production.

Liquid–liquid equilibrium (LLE) data for systems containing fatty acid ethyl esters, vegetable oils and ethanol have recently been the focus of several research works. Liu *et al.* (2008) determined experimentally the LLE data for fatty acid ethyl esters + ethanol + soybean oil from 300.15 to 343.15 K. Mesquita *et al.* (2011) measured the LLE of biodiesel (from soybean or sunflower oils) + glycerol + ethanol at different temperatures and compared the experimental data with the ones calculated from the NRTL model. Finally, Follegatti-Romero *et al.* (2010b) measured the mutual solubility of soybean oil, sunflower oil, rice bran oil, cottonseed oil, palm olein and palm oil with anhydrous ethanol from 298.15 K to 333.15 K. Silva *et al.* (2010) measured the mutual solubility of canola oil, corn oil, macauba oil and *Jatropha curcas* oil with ethanol and water at different temperatures. However, the data for the ternary system containing a mixture of ethylic biodiesel, ethanol and vegetable oil is still scarce in literature.

The objective of this work was to increase the available liquid–liquid equilibrium data for systems containing fatty acid ethyl esters, ethanol and refined vegetable oils of interest for the production of ethylic biodiesel, in particular the equilibrium data for systems containing refined vegetable oil (sunflower oil and canola oil) + ethylic biodiesel of vegetable oil +

anhydrous ethanol at 303.15 and at 323.15 K and a system containing refined palm oil + ethylic biodiesel of palm oil + ethanol at 318.15 K.

## EXPERIMENTAL SECTION

### Materials

Anhydrous ethanol and the glacial acetic acid were purchased from Merck (Germany), with purities of 99.5% and 99.0%, respectively. Tetrahydrofuran (THF) was purchased from Tedia (USA), with a purity of 99.8% and sodium ethoxide, from Sigma Aldrich (USA), with a purity of 99%.

Refined sunflower and canola oils were purchased from Bunge (São Paulo/SP, Brazil) and palm oil was provided by Agropalma (Belém/PA, Brazil). The fatty acid compositions of the vegetable oils studied in this work are presented in Table 1. These compositions were determined by gas chromatography of the fatty acid methyl esters using the official AOCS method (1–62) (Aocs, 1988). Prior to the chromatographic analysis, the fatty acids of the samples were transformed into the respective fatty acid methyl esters using the method of Hartman and Lago (1973). From the fatty acid compositions, the probable triacylglycerol compositions of the vegetable oil were calculated using the algorithm suggested by Antoniosi Filho *et al.* (1995). In order to calculate the probable triacylglycerol compositions, the quantities of *trans* isomers (see Table 1) were computed with their respective *cis* isomers. In Table 1, the main triacylglycerol represents the component with the greatest composition in the isomer set with *x* carbons and *y* double bonds. The results shown allow the calculation of the average molar masses of the sunflower oil, canola oil and palm oil. The values obtained were 877.61 g mol<sup>-1</sup>, 881.77 g mol<sup>-1</sup>, and 851.81 g mol<sup>-1</sup>, respectively.

Fatty acid ethyl ester compositions of biodiesels were determined in triplicate using the official AOCS method (1–62) (Aocs, 1988). In Table 2, the compositions of biodiesel studied in this work are presented. From these compositions (Table 2), the average molar masses of biodiesels from sunflower oil, from canola oil and from palm oil were calculated and the values found were 307.24, 309.26 and 299.10 g mol<sup>-1</sup>, respectively.

For the fitting process of the thermodynamic model, the vegetable oils and biodiesels were treated as a respective single triacylglycerol and a single fatty acid ethyl ester (FAEE) with the calculated average molar masses.

**Table 1: Fatty acid compositions of the vegetable oils.**

Fatty acid	Symbol	Cx:y <sup>a</sup>	M <sup>c</sup> g.mol <sup>-1</sup>	Sunflower oil	Canola oil	Palm oil
				100w <sup>d</sup>		
Dodecanoic acid	L	C12:0 <sup>a</sup>	200.32	0.06	0.00	0.72
Tetradecanoic acid	M	C14:0	228.38	0.02	0.05	0.02
Hexadecanoic acid	P	C16:0	256.43	6.30	4.43	40.94
Cis-9 hexadecenoic acid	Po	C16:1	254.42	0.12	0.12	0.08
Trans-9 hexadecenoic acid		C16:1t <sup>b</sup>	254.42	0.03	0.00	0.01
Heptadecanoic acid	Ma	C17:0	270.45	0.03	0.00	0.02
Cis-9 Heptadecenoic acid	Mg	C17:1	268.45	0.04	0.00	0.07
Octadecanoic acid	S	C18:0	284.49	3.30	2.41	4.51
Cis-9 Octadecenoic acid	O	C18:1	282.47	35.95	62.33	44.68
Cis-9, Cis-12 Octadecadienoic acid	Li	C18:2	280.45	52.75	22.45	8.32
Trans-9, Trans-12 Octadecadienoic acid		C18:2t <sup>b</sup>	280.45	0.11	0.28	0.02
Cis-9, Cis-12, Cis-15 Octadecatrienoic acid	Le	C18:3	278.44	0.77	6.13	0.13
Eicosanoic acid	A	C20:0	312.54	0.30	0.56	0.34
Cis-11 Eicosenoic acid	Ga	C20:1	310.52	0.22	0.85	0.14
Docosanoic acid	Be	C22:0	340.59	0.00	0.36	0.00
Tetracosanoic acid	Lg	C24:0	368.65	0.00	0.03	0.00

<sup>a</sup> Cx:y, x = number of carbons and y = number of double bonds; <sup>b</sup> Trans isomers; <sup>c</sup> Molar mass; <sup>d</sup> Mass fraction**Table 2: Fatty acid ethyl ester compositions of biodiesels.**

Fatty Acid Ethyl Ester	Cx:y	M <sup>c</sup> g. gmol <sup>-1</sup>	Sunflower oil	Canola oil	Palm oil
			100.w <sup>d</sup>		
Dodecanoic acid ethyl ester	C12:0 <sup>a</sup>	228.32	0.08	0.00	0.92
Tetradecanoic acid ethyl ester	C14:0	256.38	0.03	0.07	0.03
Hexadecanoic acid ethyl ester	C16:0	284.43	6.92	4.38	40.64
Cis-9 hexadecenoic acid ethyl ester	C16:1	282.42	0.10	0.11	0.07
Trans-9 hexadecenoic acid ethyl ester	C16:1t <sup>b</sup>	282.42	0.01	0.00	0.02
Heptadecanoic acid ethyl ester	C17:0	298.45	0.03	0.00	0.04
Cis-9 Heptadecenoic acid ethyl ester	C17:1	296.48	0.03	0.00	0.05
Octadecanoic acid ethyl ester	C18:0	312.49	3.26	2.45	4.91
Cis-9 Octadecenoic acid ethyl ester	C18:1	310.47	35.00	62.68	44.29
Cis-9, Cis-12 Octadecadienoic acid ethyl ester	C18:2	308.45	53.09	22.10	8.40
Trans-9, Trans-12 Octadecenoic acid ethyl ester	C18:2t <sup>b</sup>	308.45	0.11	0.27	0.01
Cis-9, Cis-12, Cis-15 Octadecatrienoic acid ethyl ester	C18:3	306.44	0.87	6.13	0.13
Eicosanoic acid ethyl ester	C20:0	340.54	0.27	0.56	0.36
Cis-11 Eicosenoic acid ethyl ester	C20:1	338.52	0.20	0.87	0.13
Docosanoic acid ethyl ester	C22:0	368.59	0.00	0.36	0.00
Tetracosanoic acid ethyl ester	C24:0	396.65	0.00	0.03	0.00

<sup>a</sup> In Cx:y, x = number of carbons and y = number of double bonds; <sup>b</sup> Trans isomers; <sup>c</sup> Molar mass; <sup>d</sup> mass fraction

## Apparatus and Procedures

The liquid-liquid equilibrium data for the systems containing vegetable oils (sunflower oil and canola oil) + ethylic biodiesels of the vegetable oil + anhydrous ethanol were determined at 303.15 and at 323.15 K and the system containing refined palm oil + ethylic biodiesel of the palm oil + ethanol was determined at 318.15 K.

Tie lines were determined using sealed headspace glass tubes (20 mL) (Perkin Elmer) by the same pro-

cedure described by Basso *et al.* (2012). After addition of the compounds into the vial, this was sealed and vigorously stirred (Phoenix, model AP 56, Araquara, Brazil) and conditioned in a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA) for temperature control. After approximately 24 hours, two clean and transparent phases with a well defined interface are formed. Sample of the two phases, a phase rich in vegetable oil and a phase rich in ethanol, were collected with the help of syringes and diluted in tetrahydrofuran immediately after the collec-

tion, as described by Follegatti-Romero *et al.* (2012a).

Samples of the two phases were analyzed by High Pressure Size Exclusion Chromatography (HPSEC) using the same procedure described by Follegatti-Romero *et al.* (2012a).

The reliability of the tie lines obtained from the experimental data was checked according to the procedure proposed by Marcilla *et al.* (1995), recently used by Follegatti-Romero *et al.* (2012b), Basso *et al.* (2012) and Ansolin *et al.* (2013). According to Marcilla *et al.* (1995), global mass balance deviations less than 0.5% ensure the good quality of the experimental data.

### Thermodynamic Modeling

The experimental data determined were used to adjust the parameters of the NRTL model. The model in terms of mass fractions was used in the objective function instead of mole fractions due to the large difference in molar masses between vegetable oils and ethanol. This approach was also applied by Follegatti-Romero *et al.* (2010) and Lanza *et al.* (2008). In this case, the NRTL-model is expressed as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^C \frac{\tau_{ji} G_{ji} w_j}{\bar{M}_j}}{\sum_{j=1}^C \frac{G_{ji} w_j}{\bar{M}_j}} + \sum_{j=1}^C \left[ \frac{w_j G_{ij}}{\bar{M}_j \sum_{k=1}^C \frac{G_{kj} w_k}{\bar{M}_k}} \left( \tau_{ij} - \frac{\sum_{k=1}^C \frac{\tau_{kj} G_{kj} w_k}{\bar{M}_k}}{\sum_{k=1}^C \frac{G_{kj} w_k}{\bar{M}_k}} \right) \right] \quad (1)$$

where:

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (2)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \quad (3)$$

$$\alpha_{ij} = \alpha_{ji} \quad (4)$$

$A_{ij}$ ,  $A_{ji}$  and  $\alpha_{ij}$  are the adjustable interaction parameters between the pair of components  $i$  and  $j$ ,  $C$  is the number of components and  $T$  is the absolute temperature.

The estimation of the interaction parameters was performed by using a flash liquid-liquid calculation implemented in Fortran code TML-LLE 2.0 following the same procedure utilized by Stragevitch & d'Ávila (1997).

The average deviations ( $\delta$ ) between the experimental compositions and those estimated by the NRTL model were calculated according to Eq. (5).

$$\delta(\%) = 100 \sqrt{\frac{\sum_n^N \sum_i^C \left[ \left( w_{i,n}^{\text{OP,exptl}} - w_{i,n}^{\text{OP,calcd}} \right)^2 + \left( w_{i,n}^{\text{EP,exptl}} - w_{i,n}^{\text{EP,calcd}} \right)^2 \right]}{2NC}} \quad (5)$$

$N$  is the total number of tie lines of the corresponding system,  $C$  is the total number of components ( $C=3$ ), the superscripts OP and EP represent the oil rich phase and ethanol rich phase, respectively. The subscript  $i$  is the component and  $n$  stands for the tie line number and the superscripts exptl and calcd refer to the experimental and calculated compositions, respectively.

### RESULTS AND DISCUSSION

Liquid-liquid equilibrium data at  $9.42 \cdot 10^5$  Pa approximately for refined vegetable oil (sunflower oil or canola oil) + ethylic biodiesel of the refined vegetable oil + anhydrous ethanol systems were measured at 303.15 and at 323.15 K. The system containing refined palm oil + ethylic biodiesel of the palm oil + ethanol was studied at 318.15 K.

Tables 3, 4 and 5 present the overall compositions and the corresponding tie lines for the pseudoternary systems composed of refined sunflower oil (1) + ethylic biodiesel of the refined sunflower oil (4) + anhydrous ethanol (7); refined canola oil (2) + ethylic biodiesel of the refined canola oil (5) + anhydrous ethanol (7); and refined palm oil (3) + ethylic biodiesel of the refined palm oil (6) + anhydrous ethanol (7).

The deviations of the global mass balance for all systems studied were less than 0.5%, ensuring the quality of the experimental data.

Figure 1 shows the ternary diagrams of systems composed of refined sunflower oil (1) + biodiesel of the refined sunflower oil (4) + ethanol (7), refined canola oil (2) + biodiesel of the refined canola oil (5) + anhydrous ethanol (7) at 303.15 K and 323.15 K and the systems composed of refined palm oil (3) + biodiesel of the refined palm oil (6) + ethanol (7) at the 318.15 K,

**Table 3: Experimental liquid-liquid equilibrium data for the pseudoternary system containing refined sunflower oil (1) + ethylic biodiesel of the refined sunflower oil (4) + anhydrous ethanol (7) at 303.15 K and 323.15 K.**

T (K)	Overall composition			Oil-rich phase			Ethanol-rich phase		
	100.w <sub>1</sub>	100.w <sub>4</sub>	100.w <sub>7</sub>	100.w <sub>1</sub>	100.w <sub>4</sub>	100.w <sub>7</sub>	100.w <sub>1</sub>	100.w <sub>4</sub>	100.w <sub>7</sub>
303.15	48.47	0.00	51.53	84.97	0.00	15.03	7.13	0.00	92.87
	48.96	2.24	48.80	81.25	2.51	16.25	7.22	3.18	89.61
	47.80	4.47	47.73	78.63	4.30	17.07	7.35	5.01	87.64
	46.92	6.81	46.27	73.79	6.84	19.37	8.02	7.06	84.92
	45.52	10.91	43.57	67.29	10.88	21.83	8.66	10.87	80.48
	42.88	14.39	42.73	59.36	14.71	25.93	10.26	14.43	75.31
	41.55	16.82	41.63	54.83	16.57	28.59	12.64	16.59	70.77
323.15	49.50	0.00	50.50	73.67	0.00	26.33	12.03	0.00	87.97
	49.22	2.19	48.59	68.97	2.24	28.79	12.28	3.18	84.55
	48.01	4.39	47.60	64.70	4.46	30.84	13.52	4.65	81.84
	46.66	6.77	46.56	60.60	6.84	32.57	14.06	7.02	78.93
	45.73	8.31	45.96	57.29	8.44	34.26	15.53	8.28	76.19
	45.65	10.17	44.18	53.43	10.36	36.22	17.82	10.26	71.93
	44.85	11.26	43.90	49.32	11.17	39.50	23.09	11.51	65.41

**Table 4: Experimental liquid-liquid equilibrium data for the pseudoternary system containing refined canola oil (2) + ethylic biodiesel of the refined canola oil (5) + anhydrous ethanol (7) at 303.15 K and 323.15 K.**

T(K)	Overall composition			Oil-rich phase			Ethanol-rich phase		
	100.w <sub>2</sub>	100.w <sub>5</sub>	100.w <sub>7</sub>	100.w <sub>2</sub>	100.w <sub>5</sub>	100.w <sub>7</sub>	100.w <sub>2</sub>	100.w <sub>5</sub>	100.w <sub>7</sub>
303.15	50.09	0.00	49.91	85.55	0.00	14.45	4.92	0.00	95.08
	48.90	2.24	48.86	80.50	2.36	17.14	4.71	2.51	92.78
	48.43	4.59	46.98	76.56	5.13	18.31	5.13	4.64	90.23
	46.80	6.90	46.30	71.91	6.99	21.10	5.24	6.44	88.32
	44.41	8.97	46.62	67.97	9.09	22.94	6.50	7.91	85.59
	44.30	11.38	44.32	63.71	11.87	24.42	6.69	10.02	83.29
	42.93	14.30	42.78	58.73	14.45	26.82	7.52	12.68	79.80
	41.44	16.60	41.96	54.69	17.02	28.29	8.99	15.05	75.96
323.15	50.02	0.00	49.98	74.80	0.00	25.20	10.21	0.00	89.79
	49.01	2.33	48.65	70.82	2.58	26.60	10.36	2.33	87.31
	47.58	4.41	48.01	67.22	4.78	28.00	11.54	4.02	84.44
	46.45	6.78	46.77	62.44	6.99	30.57	12.15	6.84	81.01
	45.57	8.60	45.83	59.95	8.60	31.45	13.87	8.74	77.39
	46.28	9.93	43.80	57.63	10.18	32.19	14.62	9.69	75.69
	44.39	11.20	44.40	53.33	11.75	34.92	15.67	11.26	73.07
	43.57	12.83	43.60	50.63	13.33	36.04	16.45	12.01	71.54

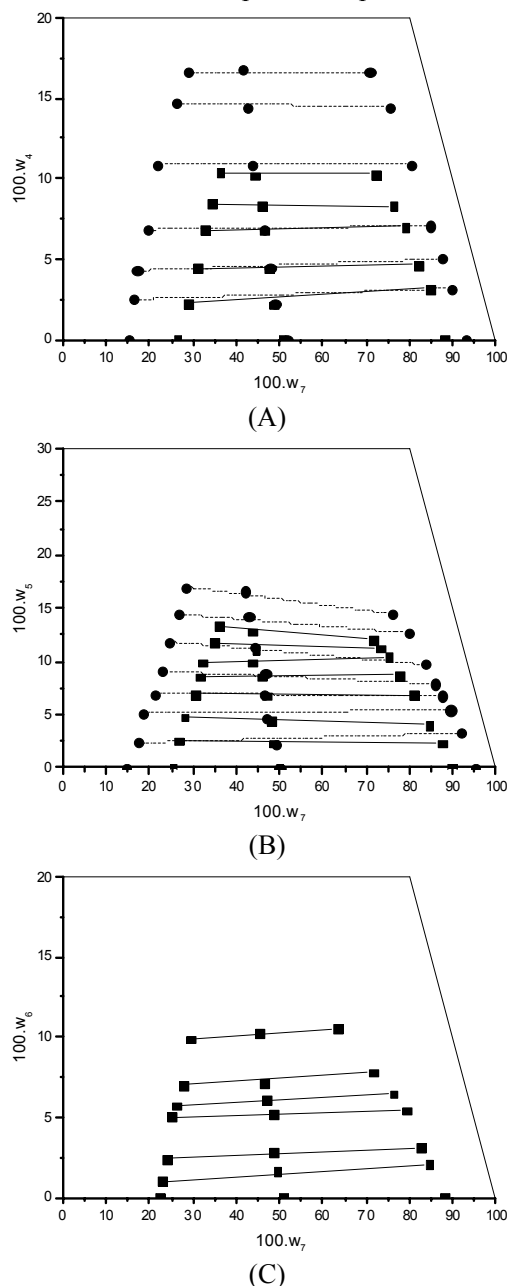
**Table 5: Experimental liquid-liquid equilibrium data for the pseudoternary system containing refined palm oil (4) + ethylic biodiesels of the refined palm oil (6) + anhydrous ethanol (7) at 318.15 K.**

T(K)	Overall composition			Oil-rich phase			Ethanol-rich phase		
	100.w <sub>3</sub>	100.w <sub>6</sub>	100.w <sub>7</sub>	100.w <sub>3</sub>	100.w <sub>6</sub>	100.w <sub>7</sub>	100.w <sub>3</sub>	100.w <sub>6</sub>	100.w <sub>7</sub>
318.15	49.36	0.00	50.64	77.87	0.00	22.13	12.18	0.00	87.82
	49.00	1.63	49.37	76.13	1.04	22.83	13.48	2.09	84.43
	48.75	2.83	48.42	73.84	2.39	23.77	14.16	3.14	82.70
	46.16	5.27	48.57	70.13	4.47	25.40	15.51	5.43	79.06
	46.88	6.11	47.02	68.28	5.75	25.97	17.25	6.49	76.26
	46.36	7.14	46.50	65.43	7.00	27.57	20.61	7.80	71.59
	44.58	10.31	45.11	60.73	9.89	29.38	26.18	10.60	63.22

The solubility of the oil-rich phase and the ethanol-rich phase was enhanced by the increase of the temperature in the systems studied at different temperatures. In Figure 1 (A) and 1 (B), it can be noted that, with the increase in temperature, the solubility

between both phases increases and the heterogeneous area decreases. Figure 1 (B) shows that biodiesel of canola oil has a slight preference for the oil-rich phase. The opposite behavior can be observed in Figure 1 (A) and 1 (C), where the ethylic biodiesel of

sunflower oil and ethylic biodiesel of palm oil, respectively, have a slight preference for the ethanol-rich phase. From this figure, a good alignment can also be observed in the experimental data, relative to the overall and to the two phase compositions.



**Figure 1:** Liquid-liquid equilibrium for the system containing (A) refined sunflower oil (1) + ethylic biodiesel of the refined sunflower oil (4) + ethanol (7) at 303.15 K (---●---) and at 323.15 K (—■—); (B) refined canola oil (2) + ethylic biodiesel of the refined canola oil (5) + ethanol (7) at 303.15 K (---●---) and at 323.15 K (—■—) and (C) refined palm oil (3) + biodiesel of the refined palm oil (6) + ethanol (7) at 318.15 K (—■—).

Table 6 shows the binary interaction parameters adjusted for the NRTL model for the systems composed of refined sunflower oil (1) + ethylic biodiesel of the sunflower oil (4) + anhydrous ethanol (7), refined canola oil (2) + ethylic biodiesel of the canola oil (5) + anhydrous ethanol (7) at 303.15 K and at 323.15 K and refined palm oil (3) + ethylic biodiesel of the palm oil (6) + anhydrous ethanol (7) at 318.15 K. The average deviations between the experimental and calculated composition for these systems are shown in Table 7.

**Table 6:** Parameters of the NRTL model for the systems composed of refined sunflower oil (1) + ethylic biodiesel of the sunflower oil (4) + anhydrous ethanol (7), refined canola oil (2) + ethylic biodiesel of the canola oil (5) + anhydrous ethanol (7) at 303.15 K and at 323.15 K and refined palm oil (3) + ethylic biodiesel of the palm oil (6) + anhydrous ethanol (7) at 318.15 K.

Temperature (K)	Pair (ij)	$A_{ij}$ (K)	$A_{ji}$ (K)	$\alpha_{ij}$
303.15	14	-40.000	250.00	0.40500
	17	650.00	1390.0	0.53000
	47	5100.0	735.00	0.62000
	25	105.00	200.50	0.51880
	27	-343.99	1855.50	0.35960
	57	-350.68	1144.30	0.48053
323.15	14	-37.000	240.000	0.41000
	17	690.00	1230.00	0.59600
	47	5000.0	720.000	0.64500
	25	115.00	277.460	0.53880
	27	-419.89	1749.50	0.42193
	57	-380.25	1300.00	0.38990
318.15	36	400.45	325.41	0.13310
	37	30000.	1305.9	0.59008
	67	2018.1	1099.5	0.31369

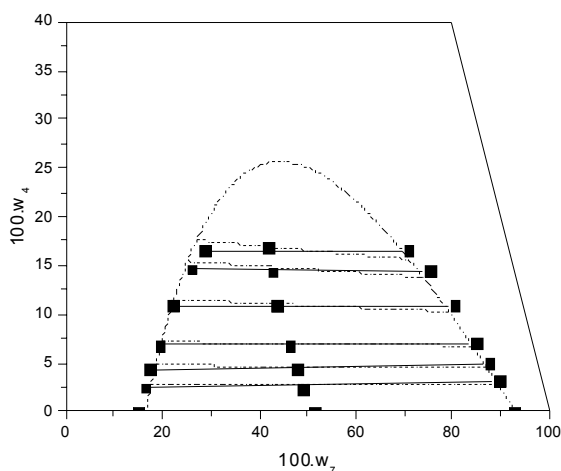
**Table 7:** Average deviations between the experimental and calculated phase compositions of the systems.

Systems	$\delta$ (%)
Sunflower oil +biodiesel of the sunflower oil + ethanol at 303.15 K	0.84
Sunflower oil +biodiesel of the sunflower oil + ethanol at 323.15 K	0.93
Canola oil +biodiesel of the canola oil + ethanol at 303.15 K	0.99
Canola oil +biodiesel of the canola oil + ethanol at 323.15 K	0.57
Palm oil +biodiesel of the palm oil + ethanol at 318.15 K	0.82

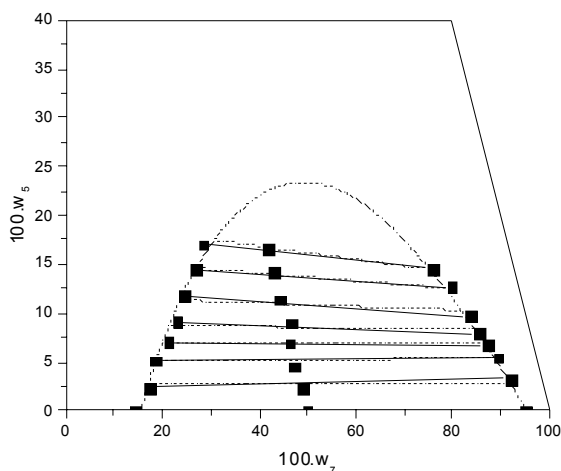
According to the values of the average deviations between experimental and calculated phase composition of the systems presented in Table 7, the thermo-

dynamic model was able to accurately describe the phase compositions of the systems studied in this work. Follegatti-Romero *et al.* (2010a) and Silva *et al.* (2010) found values for deviations between experimental and calculated liquid-liquid equilibrium data similar to those found in this work.

The good adjustment of the parameters of the NRTL model can be viewed in the ternary diagram shown in Figure 2. This figure represents the good agreement between experimental and calculated data.



(A)



(B)

**Figure 2:** NRTL model correlations and experimental data for the systems composed of: (A) refined sunflower oil (1) + ethylic biodiesel of the refined sunflower oil (4) + anhydrous ethanol (7) at 303.15 K; (B) refined canola oil (2) + ethylic biodiesel of the refined canola oil (5) + anhydrous ethanol (7) at 303.15 K: (—■—) experimental data; (----) NRTL model.

## CONCLUSIONS

Liquid-liquid equilibrium data for the pseudoternary systems containing vegetable oil + ethylic biodiesel of the vegetable oil + anhydrous ethanol were obtained at different temperatures. From the results obtained, it was found that the solubilities of the systems were affected by temperature and concentration of biodiesels.

The average deviations between the experimental data and the compositions calculated by NRTL presented values between 0.55% and 1.00%, representing a good description in LLE of these systems.

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