Liquid−Liquid Equilibrium Data for Systems Containing *Jatropha curcas* Oil + Oleic Acid + Anhydrous Ethanol + Water at (288.15 to 318.15) K

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This work presents liquid−liquid equilibrium data for systems of interest in biodiesel production, composed of *Jatropha curcas* oil (1) + oleic acid (2) + ethanol (3) + water (4), at temperatures ranging from (288.15 to 318.15) K and with water mass fractions in the solvent (ethanol + water) of (0.00, 2.00, and 4.00) %. The experimental data were correlated using the nonrandom two-liquid (NRTL) model, and for all systems, the global deviations between calculated and experimental data were lower than 0.96 %, showing the good descriptive quality of the NRTL model. To verify the effect of temperature (T), the water mass fraction of the solvent (w_{4s}), and the fatty acid mass fraction in the oil phase (w_2^{OP}) on the distribution coefficient of the oleic acid (k_2), a complete second-order model was fitted with a determination coefficient value higher than 0.9. The results showed that the oleic acid distribution coefficient was more affected by water content in the solvent than by temperature. Moreover, as a result of the reductions in temperature and water mass fraction in the alcoholic solvent, greater oleic acid distribution coefficients were found.

Introduction

Biodiesel is defined as fatty acid alkyl esters produced from vegetable oils, animal fats, or recycled cooking oils by transesterification with short-chain alcohols. The reaction begins with separate oil and alcohol phases, and at the end of this reaction, the mixture, if allowed to settle, is comprised mainly of an upper ester-rich layer and a lower glycerol-rich layer.[1] Rapeseed oil, soybean oil, sunflower oil, palm oil, and even corn oil are currently the most common vegetable oils employed in biodiesel production. Among the short-chain alcohols, methanol is preferred over others due to its low cost. However, ethanol presents low toxicity and can be produced from agricultural renewable sources, allowing biodiesel to be exclusively produced from renewable raw materials.[2]

Because of the reversibility of the transesterification reaction, an excess of alcohol is usually needed to force the equilibrium to the product side; moreover, to obtain reasonable conversion rates, the reaction requires the presence of a catalyst. Although many new catalysts have been reported in literature, most of the biodiesel plants nowadays operate with alkaline catalysts.[3] These catalysts require anhydrous conditions and, principally, highly refined vegetable oils, whose price can account for (60 to 75) % of the final biodiesel costs.[4]

Most of vegetable oils used for biodiesel production are also used in the food industry. This fact creates a market conflict between biodiesel and edible oils, leading to even greater biodiesel costs.[5] Great attempts have been made for producing biodiesel with nonedible oils such as *Jatropha curcas* oil. Because of the presence of phorbol esters in its composition, *Jatropha curcas* oil is unsuitable for food and feed applications.[6] Thus, interest in using *Jatropha curcas* oil as a feedstock for biodiesel production has rapidly grown in recent years.[7−15] Crude *Jatropha curcas* oil usually presents free fatty acid (FFA) mass fractions ranging from (2.0 to 7.5) %,[11] which are fairly greater than those recommended for biodiesel production using alkaline catalysts, that is, lower than 0.5 %.[4]

Solutions for biodiesel production using nonedible vegetable oils were studied, and a multistep process, commonly called the integrated process, has being increasingly applied to produce biodiesel with good results.[4,7,12,15] Despite the added cost of production, this process allows the use of feedstock with high FFA concentrations by first carrying out the acid-catalyzed pre-esterification of the FFAs prior to the base-catalyzed triacylglycerol transesterification.[4,16,17]

In this way, it is important to study other processes capable of reducing the FFA of crude vegetable oil, lowering production costs. An alternative refining process, performed under more mild conditions, is the deacidification by liquid−liquid extraction (LLE). Since this process is generally carried out at room temperature and atmospheric pressure, less energy is consumed; it also avoids the formation of waste products such as soaps and minimizes the loss of neutral oils.[18,19] The LLE for oil refining is based on the difference in solubilities of FFA and neutral triacylglycerols in an appropriate solvent.[20,21] Several works have suggested that ethanol is more appropriate for the deacidification of vegetable oils when compared to other short chain alcohols and various selective solvents such as acetone, furfural, ethyl acetate, and ethyl methyl ketone;[21−27] besides, ethanol showed good values of selectivity and FFA distribution coefficients.[25,28]

Once the same solvent can be used for the deacidification and transesterification processes, it is possible to combine the steps of both processes. However, knowledge of phase equilibrium data in these systems is essential for a better understanding of the process and improvement of reaction rates.[29] In our previous work, we measured the mutual solubility of *Jatropha curcas* oil + anhydrous ethanol + water, at temperatures ranging from (298.15 to 333.15) K.[30] In this respect, information on the effect of water content in the solvent and temperature, when

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Table 1. Fatty Acid Compositions of *Jatropha curcas* Oil and Oleic Acid

			M[a]	*Jatropha curcas* oil		oleic acid	
fatty acid	symbol	Cx:y[b]	g·mol^{-1}	100 x	100 w	100 x	100 w
decanoic	C	C10:0	172.26			0.37	0.23
dodecanoic	L	C12:0	200.32			3.22	2.33
tetradecanoic	M	C14:0	228.38	0.07	0.06	0.89	0.73
hexadecanoic	P	C16:0	256.43	14.45	13.34	7.00	6.48
cis-hexadec-9-enoic	Po	C16:1	254.42	0.97	0.89	0.07	0.06
heptadecanoic	Ma	C17:0	270.45	0.13	0.13	0.04	0.04
cis-heptadec-9-enoic	Mg	C17:1	268.43	0.05	0.05	0.04	0.04
octadecanoic	S	C18:0	284.49	6.15	6.30	2.21	2.27
cis-octadec-9-enoic	O	C18:1	282.47	41.02	41.68	71.05	72.45
trans-9-octadecenoic		C18:1T[c]	282.47			0.91	0.93
cis,*cis*-octadeca-9,12-dienoic	Li	C18:2	280.45	36.66	37.00	12.83	12.99
trans,*trans*-octadeca-9,12-dienoic	Le	C18:2T[c]	278.44			0.65	0.65
all-*cis*-octadeca-9,12,15-trienoic		C18:3	278.44	0.21	0.21	0.11	0.11
all-*trans*-octadeca-9,12,15-trienoic		C18:3T[c]	278.44			0.10	0.10
icosanoic	A	C20:0	312.54	0.18	0.20	0.13	0.15
cis-icos-9-enoic	Ga	C20:1	310.52	0.06	0.07	0.30	0.34
docosanoic	Be	C22:0	340.59	0.02	0.03	0.04	0.05
tetracosanoic	Lg	C24:0	368.65	0.03	0.04	0.04	0.05

[a] M = molar mass. [b] Cx:y, x = number of carbon and y = number of double bonds. [c] Trans isomers.

Table 2. Probable Triacylglycerol Composition of *Jatropha curcas* Oil

main		M[a]	composition	
TAG[b]	group	g·mol^{-1}	100 x	100 w
POP	50:1[c]	833.37	2.46	2.35
PLiP	50:2	831.35	2.51	2.39
POS	52:1	861.42	2.21	2.19
POO	52:2	859.41	9.39	9.25
POLi	52:3	857.39	13.60	13.36
PLiLi	52:4	855.38	6.71	6.58
SOS	54:1	889.48	0.57	0.59
SOO	54:2	887.46	3.87	3.93
OOO	54:3	885.45	13.32	13.52
OOLi	54:4	883.43	22.34	22.60
OLiLi	54:5	881.41	17.63	17.81
LiLiLi	54:6	879.40	5.39	5.43

[a] M = molar mass. [b] Groups with a total triacylglycerol (TAG) composition lower than 0.5 % were ignored. [c] x:y, x = number of carbons (except carbons of glycerol); y = number of double bonds.

aiming to reduce the loss of neutral oil without a significant reduction of the solvent capacity for extracting FFA, was not evaluated. Thus, this work presents experimental data of systems composed of *Jatropha curcas* oil + oleic acid + ethanol + water at (288.15, 298.15, 308.15, and 318.15) K. The experimental data were correlated by the nonrandom two-liquid (NRTL) model with temperature-dependent binary parameters. For a better understanding of the effect of process variables (water mass fraction of the solvent and temperature) on the FFA distribution coefficients, a complete second-order model was adjusted to the experimental data. The adjusted equation can also be used as an alternative to the NRTL model, providing an easier way to quote FFA distribution coefficients at different conditions.

Experimental Section

Materials. Crude *Jatropha curcas* oil was kindly supplied by Bionasa Combustível Natural S. A. (Porangatu/GO, Brazil). The crude oil was submitted to a prior deacidification treatment and was qualified as semiprocessed oil. Commercial oleic acid was purchased from Merck, with a purity of about 73.0 %.

All fatty reagents used in this work were analyzed by gas chromatography for the quantification of fatty acid methyl esters, according to the official method (1-62) of the American Oil Chemists' Society (AOCS).[31] Prior to chromatographic analysis, the fatty samples were prepared in the form of methyl esters, according to the method of Hartman and Lago.[32] The chromatographic analyses were carried out using a capillary gas chromatography system under the same experimental conditions shown in previous works of our research group.[30,33]

The fatty acid compositions of the vegetable oil and oleic acid are presented in Table 1, from which the probable triacylglycerol composition of the *Jatropha curcas* oil could be determined (Table 2) using the algorithm suggested by Antoniosi Filho et al.[34] To calculate the probable triacylglycerol composition, the quantities of trans isomers were added with their respective cis isomers. In Table 2, the main triacylglycerol represents the component with the greatest composition in the isomer set with x carbons and y double bonds. Using the results shown in Table 2, the average molar mass of the *Jatropha curcas* oil was calculated, obtaining a value of 872.6 g·mol^{-1}. The average molar mass of the oleic acid was estimated from the fatty acid composition shown also in Table 1. The obtained value for the average molar mass of the oleic acid was 277.0 g·mol^{-1}.

Anhydrous ethanol was purchased from Merck (Germany), with a purity greater than 99.9 %. The hydrated ethanol solvents with water mass fractions of (2.00 and 4.00) % were then prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol. The Karl Fischer reagent was also purchased from Merck (Germany).

The FFA mass fraction of the *Jatropha curcas* oil was used in the calculation of the overall composition of all tie lines, and the water mass fraction was considered in data involving hydrated ethanol.

Apparatus and Procedures. Determination of Liquid−Liquid Equilibrium Data. Glass equilibrium cells, those described by Silva et al.,[35] were used for the experiments. The components were weighed on an analytic balance (Precisa, model XT220A, Sweden), accurate to ± 0.0001 g. The mixtures were prepared inside the cell and then vigorously agitated for 15 min with a magnetic stirrer (Ika Werke, model RH-KT/C, Staufen, Germany); temperature was controlled with a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA), accurate to ± 0.01 K. After a clear and well-defined interface was formed (approximately 12 h later),

Table 3. Liquid−Liquid Equilibrium Data for Systems of *Jatropha curcas* Oil (1) + Oleic Acid (2) + Ethanol (3) + Water (4) at Temperatures Ranging from (288.15 to 318.15) K

	overall composition				alcoholic phase				oil phase			
100 w_{4s}[a]	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
					T = 288.15 K							
0.00	49.98	0.02	50.00		3.88	0.02	96.10		88.90	0.02	11.08	
	47.98	2.02	50.00		5.20	2.39	92.41		85.24	1.72	13.04	
	45.94	4.01	50.05		6.15	4.54	89.31		81.93	3.33	14.74	
	43.97	6.01	50.02		8.26	6.73	85.01		78.27	5.05	16.68	
	41.99	8.00	50.01		10.35	8.81	80.84		73.82	6.75	19.43	
2.00	48.74	0.02	50.19	1.05	3.10	0.02	94.70	2.18	90.20	0.02	9.67	0.11
	47.54	2.48	48.96	1.02	4.00	2.73	91.17	2.10	86.30	2.06	11.50	0.14
	44.89	4.99	49.10	1.02	4.87	5.50	87.55	2.08	82.42	4.21	13.20	0.17
	42.06	7.41	49.50	1.03	6.29	8.09	83.72	1.90	78.22	6.34	15.23	0.21
	39.96	10.00	49.02	1.02	7.57	11.18	79.42	1.83	72.79	9.19	17.75	0.27
4.00	49.86	0.02	48.11	2.01	2.05	0.02	93.67	4.26	91.81	0.02	8.00	0.17
	47.01	2.98	48.01	2.00	2.56	3.18	90.19	4.07	87.26	2.73	9.77	0.24
	43.90	5.96	48.13	2.01	3.35	6.22	86.53	3.90	83.01	5.35	11.34	0.30
	41.02	8.98	48.00	2.00	4.74	9.49	82.09	3.68	77.72	8.03	13.87	0.38
	37.70	11.88	48.40	2.02	4.80	12.86	78.88	3.46	71.98	11.19	16.31	0.52
					T = 298.15 K							
0.00	49.98	0.02	50.00		6.86	0.02	93.12		84.90	0.02	15.08	
	47.99	2.01	50.00		7.64	2.30	90.06		81.90	1.69	16.41	
	46.00	4.00	50.00		9.14	4.55	86.31		77.68	3.39	18.93	
	44.00	6.00	50.00		12.09	6.68	81.23		72.36	5.18	22.46	
	42.00	8.00	50.00		16.12	8.64	75.24		66.40	6.97	26.63	
2.00	49.97	0.02	49.00	1.02	4.00	0.02	93.83	2.15	88.06	0.02	11.77	0.15
	47.03	2.45	49.49	1.03	4.86	2.87	90.19	2.08	84.07	2.17	13.57	0.19
	44.19	4.90	49.87	1.04	6.00	5.59	86.42	1.99	79.81	4.30	15.67	0.22
	42.50	7.48	48.99	1.02	7.94	8.40	81.72	1.94	74.71	6.67	18.34	0.28
	39.94	10.03	49.01	1.02	10.16	11.38	76.70	1.76	68.69	9.34	21.61	0.36
4.00	49.98	0.02	48.00	2.00	2.55	0.02	93.22	4.21	89.96	0.02	9.83	0.19
	47.02	3.03	47.95	2.00	3.20	3.40	89.27	4.13	85.07	2.86	11.78	0.29
	43.90	5.96	48.13	2.01	4.35	6.45	85.33	3.87	80.26	5.35	14.01	0.38
	41.06	8.74	48.19	2.01	6.36	9.22	80.82	3.60	75.30	7.79	16.44	0.47
	38.16	11.70	48.13	2.01	8.55	12.53	75.47	3.45	69.43	10.47	19.50	0.60
					T = 308.15 K							
0.00	49.98	0.02	50.00		8.47	0.02	91.51		81.57	0.02	18.41	
	48.00	2.00	50.00		10.22	2.35	87.43		77.14	1.78	21.08	
	46.00	4.00	50.00		13.25	4.47	82.28		71.95	3.50	24.55	
	44.00	6.00	50.00		17.72	6.48	75.80		65.68	5.33	28.99	
	42.00	8.00	50.00		23.63	8.51	67.86		57.23	7.41	35.36	
2.00	49.79	0.02	49.16	1.03	5.02	0.02	92.86	2.10	85.58	0.02	14.21	0.19
	47.50	2.49	48.99	1.02	6.01	2.91	89.04	2.04	80.93	2.20	16.63	0.24
	45.00	4.98	49.00	1.02	8.24	5.79	84.07	1.90	75.81	4.53	19.36	0.30
	42.34	7.45	49.19	1.02	10.88	8.44	78.88	1.80	69.99	6.82	22.82	0.37
	39.95	10.02	49.01	1.02	14.31	11.38	72.68	1.63	63.29	9.23	27.00	0.48
4.00	49.93	0.02	48.05	2.00	3.23	0.02	92.65	4.10	88.08	0.02	11.64	0.26
	46.95	2.98	48.07	2.00	4.26	3.21	88.59	3.94	83.01	2.63	13.99	0.37
	43.96	5.98	48.06	2.00	5.37	6.37	84.52	3.74	77.61	5.31	16.61	0.47
	41.03	8.98	47.99	2.00	7.80	9.74	78.88	3.58	71.42	8.33	19.62	0.63
	38.03	11.98	47.99	2.00	10.88	12.84	72.98	3.30	64.48	11.17	23.53	0.82
					T = 318.15 K							
0.00	49.98	0.02	50.00		11.96	0.02	88.02		77.38	0.02	22.60	
	48.47	1.52	50.01		13.64	1.85	84.51		72.68	1.41	25.91	
	46.98	3.02	50.00		16.75	3.57	79.68		68.17	2.85	28.98	
	45.46	4.56	49.98		22.60	5.15	72.25		60.32	4.37	35.31	
2.00	49.61	0.02	49.34	1.03	6.58	0.02	91.24	2.16	82.74	0.02	16.98	0.26
	47.88	2.17	48.93	1.02	7.76	2.45	87.72	2.07	79.03	1.95	18.72	0.30
	45.92	4.10	48.96	1.02	9.85	4.78	83.42	1.95	74.63	3.80	21.20	0.37
	43.89	6.01	49.08	1.02	11.46	6.82	79.83	1.89	69.70	5.63	24.23	0.44
4.00	49.94	0.02	48.01	2.03	4.26	0.02	91.45	4.27	86.12	0.02	13.49	0.37
	47.45	2.55	47.98	2.02	5.03	2.91	88.13	3.93	81.75	2.42	15.39	0.44
	44.92	5.07	47.99	2.02	6.48	5.82	83.91	3.79	76.86	4.74	17.85	0.55
	42.89	7.56	47.55	2.00	8.83	8.42	79.15	3.60	71.55	6.92	20.86	0.67

[a] w_{4s} = water mass fraction in the alcoholic solvent.

samples of both the top and the bottom phases were collected separately using syringes. The FFA contents were determined by titration according to official method 2201 of International Union of Pure and Applied Chemistry (IUPAC)[36] using an automatic titrator (Metrohm, model Titrando 808, Herisan, Switzerland). Water content was determined by Karl Fisher titration, according to the AOCS method Ca23-55.[37] The solvent was evaporated in an oven (Marconi, model MA 035/3, Piracicaba/SP, Brazil) at atmospheric pressure and 383.15 K for 3 h, sufficient conditions for the remaining mixture to achieve a constant mass.[38] The quantity of triacylglycerols was then found by calculating the difference.

In this work, all measurements were performed with at least three triplicates. Type A standard uncertainties[39] of the equilibrium data ranged in mass fraction from (0.01 to 0.23) % for triacylglycerols, (0.01 to 0.09) % for oleic acid, (0.01 to 0.22) % for ethanol, and (0.01 to 0.07) % for water, where the lowest values were attained for the lowest compositions.

Table 4. Temperature-Dependent NRTL Parameters

pair ij^a	$A_{0,ij}$/K	$A_{0,ji}$/K	$A_{1,ij}$	$A_{1,ji}$	α_{ij}
12	–442 580.0	1411.3	1544.4	–5.21	0.6737
13	2453.5	1581.9	–8.726	–0.025	0.4307
14	3393.6	9274.9	–13.337	–19.723	0.1075
23	–214.4	–3000.0	0.000	0.000	0.3767
24	2424.1	1056.3	–4.745	0.000	0.1000
34	9696.6	–18 219.0	–31.695	61.455	0.6849

[a] *Jatropha curcas* oil (1), oleic acid (2), ethanol (3), and water (4).

Table 5. Mean Deviations Between the Experimental and the Calculated Compositions in Both Phases (Δw) for Systems Composed of *Jatropha curcas* Oil + Oleic Acid + Ethanol + Water, at Temperatures Ranging from (288.15 to 318.15) K

system	T/K	100 Δw
Jatropha curcas oil (1) + oleic acid (2) + ethanol (3)	288.15	0.96
	298.15	0.55
	308.15	0.53
	318.15	0.93
Jatropha curcas oil (1) + oleic acid (2) + ethanol (3) + water (4) (2.00 % in mass of water in anhydrous ethanol)	288.15	0.38
	298.15	0.39
	308.15	0.33
	318.15	0.55
Jatropha curcas oil (1) + oleic acid (2) +ethanol (3) + water (4) (4.00 % in mass of water in anhydrous ethanol)	288.15	0.29
	298.15	0.44
	308.15	0.59
	318.15	0.66
average overall deviation		0.56

Results indicated good precision and repeatability of the equilibrium data.

To test the quality of the obtained results, the procedure developed by Marcilla et al.[40] and previously applied for fatty systems by Rodrigues et al.[41] was utilized. The relative deviation ($E_{\mathrm{ri},N}$) for the mass balance of each component (i) in each tie line (N) was calculated according to:

$$E_{\mathrm{ri},N} = \frac{|m_N^{\mathrm{OC}} w_{i,N}^{\mathrm{OC}} - (m_N^{\mathrm{AP}} w_{i,N}^{\mathrm{AP}} + m_N^{\mathrm{OP}} w_{i,N}^{\mathrm{OP}})|}{m_N^{\mathrm{OC}} w_{i,N}^{\mathrm{OC}}} \tag{1}$$

where $w_{i,N}^{\mathrm{OC}}$ is the mass fraction of the component i associated to the overall mass composition m_N^{OC}, both being gravimetrically attained. m_N^{AP} and m_N^{OP} are, respectively, the masses of the alcoholic and oil phases, calculated using the procedure developed by Marcilla et al.[40] $w_{i,N}^{\mathrm{AP}}$ and $w_{i,N}^{\mathrm{OP}}$ are the mass fractions of the component i in the alcoholic and oil phases, experimentally determined.

The relative deviations ($E_{ri,N}$) varied within the following ranges: (0.01 to 0.08) % for triacylglycerols, (0.05 to 5.07) % for oleic acid, (0.01 to 0.10) % for ethanol, and (0.23 to 5.27) % for water, being that the lowest values were obtained for the greatest compositions. The relative deviation for the overall mass balance, attained between the sum of ($m_N^{\mathrm{AP}} + m_N^{\mathrm{OP}}$) and m_N^{OC}, was lower than 0.12 %, with an average value of 0.09 %, confirming the high quality of the experimental data.

Thermodynamic Modeling. The determined experimental data were used to adjust the binary interaction parameters of the NRTL model. Mole fractions have traditionally been used in this model, but mass fractions provide a more convenient composition unit because of the large difference in the molar masses of the components such as vegetable oil, oleic acid, ethanol, and water. Recently, several studies have been reported using this approach with the NRTL model.[22−25,28,41,42] In our previous work,[30] the activity coefficient equations for multicomponent mixtures expressed in terms of mass fraction was shown.

Adjustments were made by treating the system composed of *Jatropha curcas* oil + oleic acid + anhydrous ethanol as pseudoternary and the systems composed of *Jatropha curcas* oil + oleic acid + ethanol + water as pseudoquaternary. The systems were considered to be composed of a single triacylglycerol with the average molar mass of *Jatropha curcas* oil and a representative fatty acid with the molar mass of the oleic acid, ethanol, and water. This approach assumes that the different triacylglycerols and fatty acids present in the *Jatropha curcas* oil and the oleic acid, respectively, behave similarly in the liquid−liquid system under analysis. In this case, such compounds can be adequately replaced by a pseudocomponent with the corresponding average physical-chemical properties. This approach was previously evaluated by Lanza et al.[33] and Gonçalves and Meirelles,[42] whom proved the reliability of this hypothesis.

Estimation of the NRTL parameters was based on the minimization of the objective composition function following the procedure developed by Stragevitch and d'Ávila.[43] The objective function of composition and the equation defining the

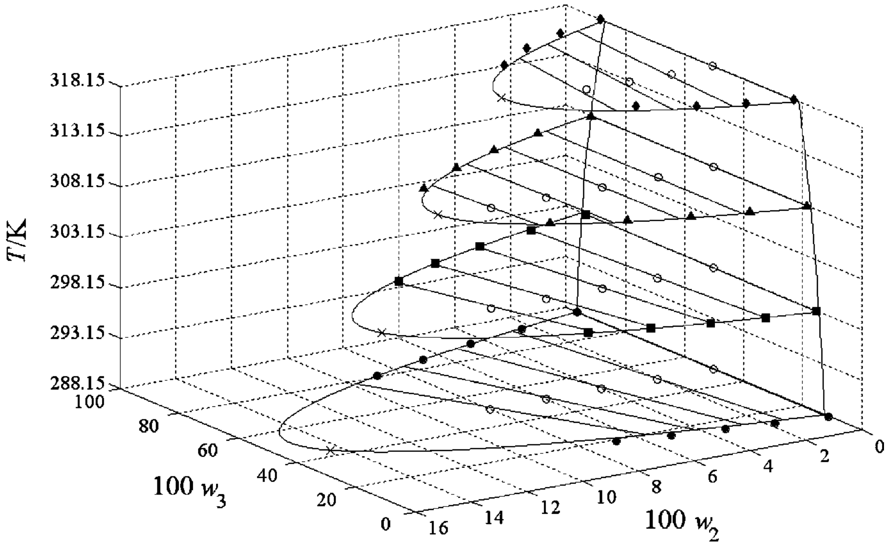

Figure 1. Liquid−liquid equilibrium for systems composed of *Jatropha curcas* oil (1) + oleic acid (2) + ethanol (3). Experimental phase compositions: ●, at 288.15 K; ■, at 298.15 K; ▲, at 308.15 K; ♦, at 318.15 K; —, NRTL; ○, experimental overall phase compositions; ×, calculated plait points.

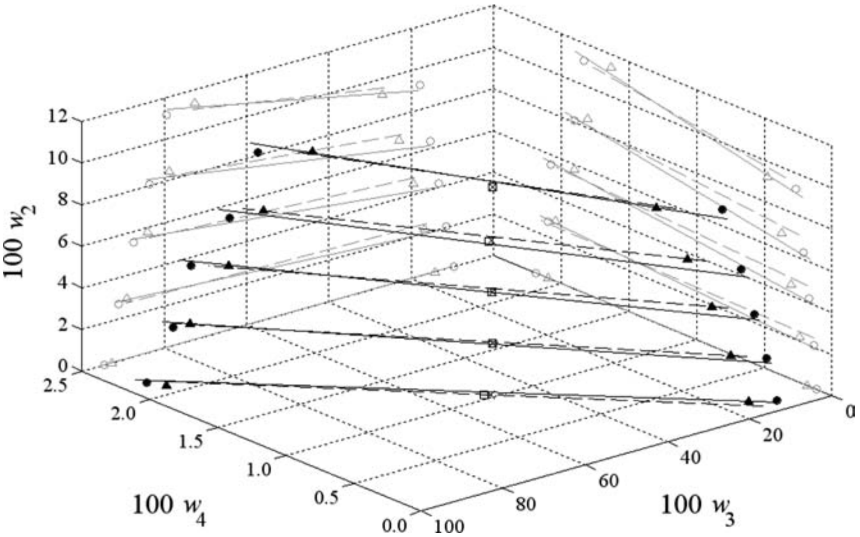

Figure 2. Liquid−liquid equilibrium for systems composed of *Jatropha curcas* oil (1) + oleic acid (2) + ethanol (3) + water (4), 100 w_{4s} = 2.00: ●, experimental phase compositions at 288.15 K; ▲, experimental phase compositions at 308.15 K; −, NRTL at 288.15 K; ----, NRTL at 308.15 K; □, experimental overall phase compositions at 288.15 K; ×, experimental overall phase compositions at 308.15 K.

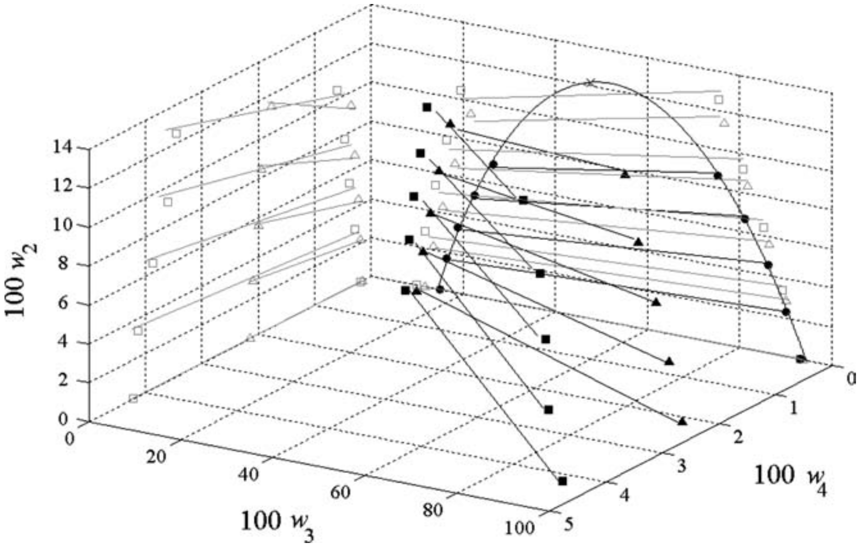

Figure 3. Liquid−liquid equilibrium for systems composed of *Jatropha curcas* oil (1) + oleic acid (2) + ethanol (3) + water (4) at 298.15 K: ●, experimental phase compositions (100 w_{4s} = 0.00); ▲, experimental phase compositions (100 w_{4s} = 2.00); ■, experimental phase compositions (100 w_{4s} = 4.00); −, NRTL; ×, calculated plait point.

average deviations between the experimental and the calculated compositions in both phases can be consulted in our previous work.[30]

Results and Discussion

In the present work, the following notations were given to the components used in the experiments: *Jatropha curcas* oil (1), oleic acid (2), anhydrous ethanol (3), and water (4). Table 3 presents the overall phase compositions and the corresponding tie lines for the pseudoternary and pseudoquaternary systems composed of *Jatropha curcas* oil + oleic acid + ethanol + water at different temperatures.

The adjusted parameters of the NRTL model are shown in Table 4. Average deviations between experimental and calculated compositions in both phases are shown in Table 5.

Figures 1 to 3 show the experimental points and calculated tie lines for the systems composed of *Jatropha curcas* oil + oleic acid + anhydrous ethanol + water at different temperatures for water mass fractions in the alcoholic solvent equal to (0.00, 2.00, and 4.00) %, respectively. The equilibrium diagrams were plotted in rectangular coordinates. In these figures, the composition in mass fraction of the *Jatropha curcas* oil can be obtained by difference:

$$w_1 = 1.00 - (w_2 + w_3 + w_4) \qquad (2)$$

Table 6. Estimated Model Coefficients for the Parameter k_2

	coefficient value	standard error of coefficients	t^a	Pr^b
C_0	1.5018	0.01307	114.94	0
C_1	–4.1623	0.7033	–5.92	0
C_2	–2.2798	0.0004	–11.59	0
C_3	–0.0042	0.1558	–14.63	0
C_4	–97.6500	13.36	–7.31	0
C_5				
C_6				
C_7	48.433	5.237	9.25	0
C_8	0.1327	0.0141	9.43	0
C_9				

[a] t = t-value of the Student test. [b] Pr = probability value.

From the diagrams presented in Figures 1 and 2, it can be noted that the enhancement of oleic acid mass fractions and temperature caused the decrease of the heterogeneous phase region. From Figure 3, it can be verified that the addition of water expands the phase splitting region. This occurs due to the decrease of mutual solubility between oil and solvent by the presence of water in the system.

Good alignment can be observed between phase and overall compositions. Tie lines based on experimental data were determined by linear regression of each corresponding set of overall, oil, and alcoholic phase compositions. Determination coefficients (R^2) higher than 96.7 % were obtained for all tie lines, indicating good alignment between the experimental data, relative to both overall and phase concentrations.

An important parameter in the selection of solvents for LLE processes is the distribution coefficient of the solute (k_2).[44,45] This parameter is also essential to define the individual film resistances according to the well-known two-film theory.[46] For closely linear distributions of solutes between phases, a behavior found in the studied systems, the oleic acid distribution coefficient at the film interphase can be easily calculated according to eq 3:

$$k_2 = \frac{w_2^{\mathrm{AP}}}{w_2^{\mathrm{OP}}} \tag{3}$$

where w_2 represents the mass fractions of oleic acid and the superscripts AP and OP stand for alcoholic and oil phases, respectively. The NRTL model accurately described the oleic acid distribution coefficient of the investigated systems, except for the experimental data at 318.15 K, where the experimental and estimated oleic acid distribution exhibits an opposing behavior. Thus, in an attempt to have a better insight on the effects of temperature (T), the water mass fraction of the solvent (w_{4s}), and the fatty acid mass fraction in the oil phase (w_2^{OP}) on parameter k_2, a complete second-order model was adjusted to the experimental data:

$$k_2 = C_0 + C_1 w_{4s} + C_2 w_2^{\mathrm{OP}} + C_3 T + C_4 w_{4s}^2 + C_5 w_2^{\mathrm{OP}2} + C_6 T^2 + C_7 w_{4s} w_2^{\mathrm{OP}} + C_8 w_{4s} T + C_9 w_2^{\mathrm{OP}} T \tag{4}$$

The C_i regression coefficients present in the model were then estimated by the least-squares fitting method and evaluated using the Student t test at 5 % of significance. Table 6 shows the

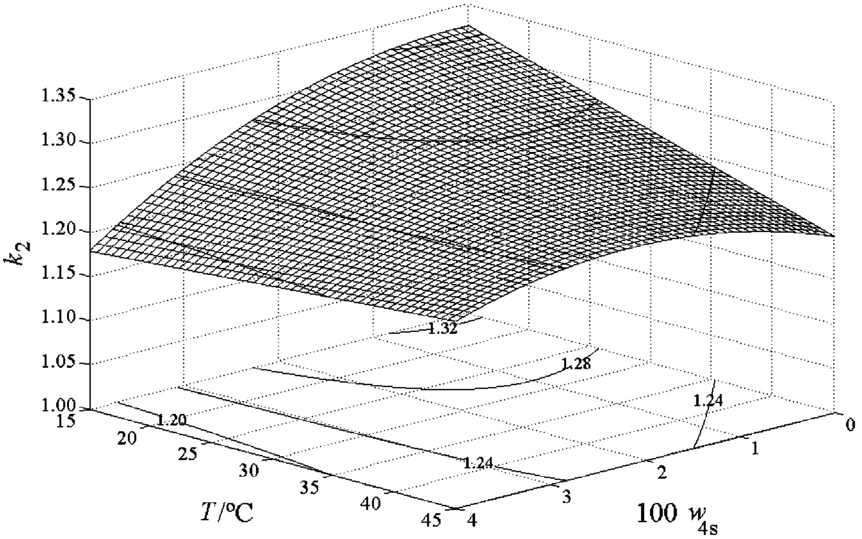

Figure 4. Effect of the water mass fraction in the solvent (w_{4s}) and temperature (T) on the oleic acid distribution coefficient (k_2); 100 $w_2^{\mathrm{OP}} = 5.00$; mesh, eq 4 using coefficients presented in Table 6.

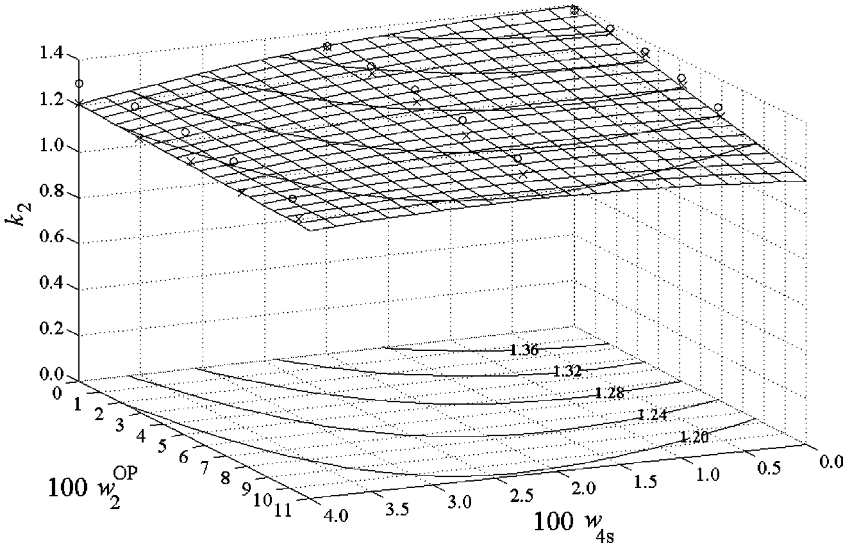

Figure 5. Effect of water mass fraction in the alcoholic solvent (w_{4s}) and oleic acid mass fraction in the oil phase (w_2^{OP}) on the distribution coefficient (k_2) at 298.15 K; ×, experimental data; ○, NRTL; mesh, eq 4 using coefficients presented in Table 6.

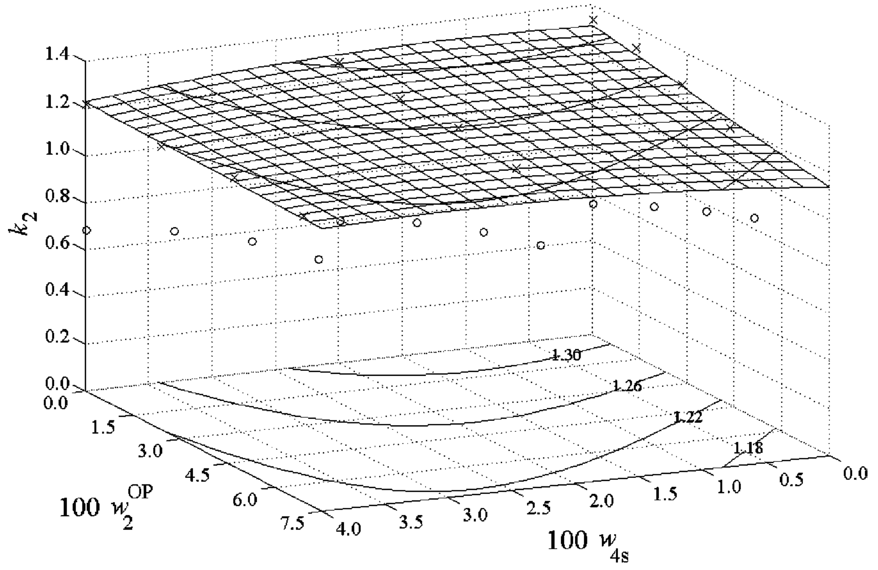

Figure 6. Effect of water mass fraction in the alcoholic solvent (w_{4s}) and oleic acid mass fraction in the oil phase (w_2^{OP}) on the distribution coefficient (k_2) at 318.15 K; ×, experimental data; ○, NRTL; mesh, eq 4 using coefficients presented in Table 6.

estimates of regression coefficients, the *t*-value, and probability (Pr) of each coefficient. The adjusted model had a determination coefficient (R^2) of 0.94.

As can be observed in Figure 4, for the range of studied variables, increases in w_{4s} values caused a decrease in the capacity of the solvent for extracting FFAs in higher proportions than T. On the other hand, the reduction of T led to an increase of k_2 in all of the levels of w_{4s}. But, in higher values of w_{4s}, the effect of T was verified to be smaller. These results are in accordance with previous results published by Sanaiotti et al.[38] and Cuevas et al.[47]

Figure 5 shows the oleic acid distribution coefficient (k_2) as a function of water mass fraction in the solvent (w_{4s}) and oleic acid mass fraction in the oil phase (w_2^{OP}) at 298.15 K. It can be observed that higher FFA content in the system decreases the distribution coefficient of oleic acid. This can be attributed to the increase of system solubility at higher FFA concentrations. On the other hand, the addition of water to ethanol reduces the solubility of oil in the alcoholic phase. In addition, it should be observed that in this case, the NRTL model accurately describes the oleic acid distribution coefficient. However, as previously mentioned, it is interesting to note that for experimental points at 318.15 K, the NRTL model underestimated the oleic acid distribution, as can also be verified in Figure 6. In this figure it can be observed that the NRTL model presents an opposing behavior for the oleic acid distribution coefficient.

Conclusions

Phase equilibrium data for upstream processes in biodiesel production were determined experimentally at (288.2 to 308.2) K. The good descriptive quality of the NRTL model was verified by lower values of the global deviations between calculated and experimental data.

As an alternative to the NRTL model, a second-order model was used to evaluate the oleic acid distribution coefficient at different conditions. The water mass fraction of the solvent presented a direct relationship with temperature and the fatty acid mass fraction in the oil. The reduction of temperature increased the oleic acid distribution coefficient in all systems, even more so in alcoholic solvents free of water.

Moreover, the results presented in this paper show that the deacidification of *Jatropha curcas* oil by LLE, using aqueous ethanol as solvent, allows the extraction of FFA with a slight loss of neutral oil, making the extraction process more economic and capable to be used for biodiesel production.

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