Experimental Determination of Binodal Curves and Study of the Temperature in Systems Involved in the Production of Biodiesel with Ethanol

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Binodal curves of systems involved in the production of soybean oil biodiesel and castor oil biodiesel were obtained at different temperatures by the titration method under isothermal conditions. The measurements allow the analysis of the mutual solubility of the compounds present after the transesterification reaction and supply data for the process of separation and purification of biodiesel. The systems studied were soybean oil biodiesel + glycerol + ethanol at temperatures of (298.15, 333.15, and 343.15) K, soybean oil biodiesel + ethanol + water at temperatures of (298.15 and 323.15) K, and castor oil biodiesel + ethanol + glycerol to 333.15 K. The highest levels of biodiesel were obtained at 298.15 K, although small changes in temperature did not significantly affect the system behavior. The two-phase region for the system of ethanol + biodiesel + glycerol at 333.15 K using soybean oil as raw material was bigger than the two-phase region using castor oil, which allows us to separate higher amounts of biodiesel after the transesterification reaction at the stage of interest.

Introduction

The development of alternative fuels from renewable resources, like biomass, has received considerable attention in all countries, mainly in Brazil, due to its high biodiversity.[1−3] It is considered that biodiesel contributes much less to global warming than fossil fuels, being produced from renewable natural sources such as vegetable oils and animal fats consisting of the alkyl esters of fatty acids.[4,5] The transesterification reaction for biodiesel production typically uses vegetable oils, a short chain alcohol, and a catalyst.[6,7] Brazil stands out because of its soybean oil and castor oil. With respect to soybean oil, it is the second largest producer in the world and with the castor oil is the third largest producer. The castor oil is a vegetable oil with applications in the industrial area and also successful application as an energy source. Castor oil has been suitable for use as feedstock for biodiesel production, and its main advantage is to be the only vegetable oil totally soluble in alcohols. Consequently, the process of biodiesel production with castor oil does not require heating.[8] These two oils represent great importance to the economy of Brazil and represent good options to be used as feedstock in the production of biodiesel. The operation conditions can be responsible for contaminations of phases when reactants and products reach an inseparable mixture.[9,10] The solubility of involved compounds can signify that significant quantities of esters (biodiesel) remain in the glycerol-rich phase while those in the ester-rich phase can have impurities and become hard to purify and reach standard requirements for marketing.[11,12] Besides this, the mutual solubility can also hinder the recovery of the alcohol used for the reaction.

Phase diagrams of systems involved in the production of biodiesel have been previously studied. Lu et al.[13] measured the solubility of the ternary system soybean oil ethyl esters (FAEE) + ethanol + glycerol showing that the solubility is temperature-sensible in the range of (300.15 to 343.15) K. França et al.[14] investigated the solubility of the ternary system containing biodiesel derived from castor + glycerol + ethanol at (298.15 and 333.15) K and observed that the solubility of glycerol and alcohol in castor oil biodiesel gives more difficulty during separation and purification steps. Zhou et al.[15] measured the solubility of the ternary system *Jatropha curcas L.* oil methyl ester (FAME) + methanol + glycerol in the range from (298.15 to 333.15) K, showing that the solubility is temperature insensible in the temperature range of the transesterification reaction. However, in the literature there are no systems that compare the behavior of solubility over a vegetable oil for biodiesel; besides, there are no options showing use of ethanol as the alcohol and also no data to report the behavior of the solubility of the phases after the production of biodiesel in the presence of impurities such as water.

The objective of this work was to study the mutual solubility of some compounds that are generated during the production of biodiesel through the use of phase diagrams constructed at different temperatures. Binodal curves were determined experimentally using ethanol as alcohol and were divided into three ternary systems according to the combinations between some of these compounds present in biodiesel production. The systems studied were soybean oil biodiesel + glycerol + ethanol at temperatures of (298.15, 333.15, and 343.15) K, soybean oil biodiesel + ethanol + water at temperatures of (298.15 and 323.15) K, and castor oil biodiesel + ethanol + glycerin at 333.15 K. A comparison of temperatures was made to check how the change in temperature affects the solubility of compounds in the analysis of each of these systems.

Experimental Section

Materials. Water was purified by a Milli-Q system with a resistivity of less than 18 MΩ·cm. The alcohol and glycerol used in the experiments were used with a percentage of purity of 99.5 %. The soybean oil was used brand Liza, and castor oil was provided by Campestre Ind. and Co. The soybean oil

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Table 1. Concentration Range in the Calibration Curve

			$C_X{}^a$ (mg·mL^{-1})					
component	manufacturer	purity (%)	C_1	C_2	C_3	C_4	C_5	C_6
ethyl linoleate	Sigma	98.0	0.20	0. 90	6.00	12.00	18.00	24.80
ethyl palmitate	Sigma	99.0	0.30	0.60	1.00	3.00	4.00	5.60
ethyl oleate	Sigma	98.0	0.10	0.50	0.90	4.00	8.00	12.00
ethyl linolenate	Sigma	99.0	0.40	0.60	1.00	2.00	3.00	4.40
ethyl ricinoleate	Sigma	99.0	0.80	5.00	10.00	15.00	25.00	32.44

[a] C = concentration. X = level.

biodiesel was prepared in the laboratory by transesterification of soybean oil by keeping the following conditions: mole ratio of ethanol to oil of 10:1, alkaline catalysis with 1 % (w/w) of NaOH (calculated over the quantity of soybean oil), agitation of 370 rpm, and constant temperature of 343.15 K. In the case of castor oil, biodiesel was kept at the same conditions with the only difference being that the molar ratio of ethanol over oil was 12:1. In the next step, excess alcohol was removed by a vacuum distillation route evaporator at 353.15 K, and after that, two phases separated (esters and glycerol) were obtained in a decantation funnel. Then, the ester phase was washed with acidified water to remove catalyst traces, glycerol, alcohol, and other impurities present in biodiesel, and then sodium sulfate was added to remove residual humidity. The final water content was (0.043 and 0.048) % (w/w) for soybean oil biodiesel and castor oil biodiesel, respectively, being determined by Karl Fischer analysis.

a. Determination of Chemical Composition of Vegetable Oil and Biodiesel. Soybean Oil and Castor Oil. The fatty acid composition of soybean oil and castor oil was determined according to the official method 5 Ce 1f-96 of the AOCS.[16] The soybean oil and castor oil were submitted to chromatographic analysis, using gas chromatograph Varian Star 3600CXa flame ionization detector (FID), coupled to software Star WAS (workstation), column DB23 (50 % cyanopropylphenil and 50 % dimethyl polysiloxane), 30 m × 0.25 mm × 0.25 μm, and the following ramp heating: 323.15 K for 5 min, (323.15 to 453.15) K (rate of 10 K·min^{-1}), 453.15 K for 5 min, and (453.15 to 513.15) K (rate of 5 K·min^{-1}). The injector and detector temperatures were set in (523.15 and 573.15) K, respectively. The fatty acids were quantified by means of areas determined by calibration curves for standards of palmitic, stearic, oleic, linoleic, linolenic, and ricinoleic acids.

Soybean Oil Biodiesel and Castor Oil Biodiesel. The ethyl ester composition of soybean oil biodiesel and castor oil biodiesel was determined by gas chromatography using a GC Agilent 6850 Series GC system with an FID under the following experimental conditions: DB-225 Agilent capillary column (50 % cyanopropylphenil and 50 % dimethyl polysiloxane), 25 m × 0.32 mm × 0.25 μm, nitrogen as the carrier gas at a rate of 1 mL·min^{-1}, with the following ramp heating: 308.15 K for 0.5 min, (308.15 to 458.25) K (rate of 35 K·min^{-1}), (458.25 to 473.15) K (rate of 5 K·min^{-1}), 473.15 K for 2.5 min, (473.15 to 503.15) K (rate of 10 K·min^{-1}) for 1.75 min; and an injection volume of 1.0 μL. The injector and detector temperatures were set at 513.15 K. The ethyl esters were quantified by means of areas determined by calibration curves for standards of palmitate, oleate, linoleate, linolenate, and ricinoleate esters. The concentrations used for the construction of curve calibrations are presented in Table 1.

Procedures. Binodal curves of ternary systems were determined by the cloud point using the titration method under isothermal conditions. The experiments were performed in a cell liquid−liquid equilibrium and the temperature of the controlled movement of water from a thermostatic bath. For monitoring the cell temperature used a thermometer with an uncertainty of about ± 0.05 K. The cell of liquid−liquid equilibrium was placed above a sign of agitation, which was used in a magnetic stirrer, to allow complete homogenization of the mixture under study. The binodal curves were represented in mass fraction (w), and to do this it was necessary to measure the density of biodiesel produced. The density measurements were made using the apparatus Stanbirger viscosimer 3000 (Anton Paar) with an uncertainty of about ± 0.0001 g·cm^{-3}.

Phase Diagrams of Systems of Soybean Oil Biodiesel + Ethanol + Glycerol and Castor Oil Biodiesel + Ethanol + Glycerol. For the biodiesel-rich phase within the cell was added a known mass of biodiesel and ethanol which was the binary mixture titrated with glycerol until the cloud point was visible; in the case of the glycerol-rich phase were added glycerol and ethanol, and the binary mixture was titrated with biodiesel until the cloud point was visible. The turbidimetric analysis was complete when the mixture changed from transparent to turbid. The glycerol and biodiesel were added drop by drop through a buret with constant stirring until the turbidity of the mixture was visible. To carry out the titration it was stipulated that the time between drops added was 3 min to ensure that the solution was homogeneous, because sometimes the addition of a drop occasioned a slight turbidity which disappeared with continued agitation for a few minutes. The solutions were prepared by measuring the masses of the components in an analytical balance; the titration was performed with a buret, and the volume of the added mass has been transformed by its density, in which for the construction of binodal curve these masses were transformed to mass fractions. The measurements with biodiesel and soybean oil were made at temperatures of (298.15, 333.15, and 343.15) K, and biodiesel from castor oil was made to 333.15 K.

Phase Diagrams of Systems of Soybean Oil Biodiesel + Ethanol + Water. Measurement procedures were the same as referred to in item a. For the soybean oil biodiesel-rich phase a known mass of biodiesel and ethanol was titrated with water until the cloud point was visible; in the case of the water-rich phase were placed water and ethanol, and the binary mixture was titrated with soybean oil biodiesel until the cloud point was visible. Measurements were carried out at temperatures of (298.15 and 323.15) K.

Results and Discussion

The calibration curves obtained for the quantification of biodiesel used are presented in Table 2.

The fatty acid compositions of the vegetable oil are presented in Table 3, and the ethyl ester compositions of the biodiesel are presented in Table 4.

The values of density measured were 0.8801 g·cm^{-3} and 0.9102 g·cm^{-3} to 293.15 K for biodiesel from soybean oil and

Table 2. Calibration Curves Obtained for Quantification of Biodiesel[a]

component	calibration curves	R
ethyl palmitate	$y = 1000000.52x - 424.94$	0.9986
ethyl oleate	$y = 105294.30x - 5158.32$	0.9997
ethyl linoleate	$y = 108190.44x - 18609.62$	0.9991
ethyl linolenate	$y = 104905.15x - 434.36$	0.9997
ethyl ricinoleate	$y = 88790.97x + 5806.83$	0.9994

[a] y = area; x = concentration; R = correlation coefficient.

Table 3. Fatty Acid Compositions of the Vegetable Oils

fatty acids	Cx:y[a]	soybean oil % (w/w)	castor oil % (w/w)
palmitic	C16:0	11.3	1.35
stearic	C18:0	3.3	0.78
oleic	C18:1	24.7	2.42
linoleic	C18:2	54.5	3.08
linolenic	C18:3	0.8	0.24
ricinoleic	C18:1:OH	-	91.21
myristic[b]	C14:0	0.2	-
lauric[b]	C12:0	0.1	-
arachidic[b]	C20:0	0.2−0.5	-
behenic[b]	C22:0	0.3−0.7	-
lignoceric[b]	C24:0	0.4	-
gadol[b]	C20:1	0.1−0.3	-
palmitic[b]	C16:1	0.2	-
erucic[b]	C22:1	0.3	-

[a] Cx:y:OH. [b] Minor constituents. x = number of carbons. y = number of double bonds, and OH = number of hydroxyl groups.

Table 4. Ethyl Ester Composition of the Biodiesel

FAEE	Cx:y[a]	soybean oil biodiesel % (w/w)	castor oil biodiesel % (w/w)
palmitate	C18:1	12.33	1.10
oleate	C20:1	25.95	2.70
linoleate	C20:2	55.55	4.90
linolenate	C20:3	6.17	0.40
ricinoleate	C20:1:OH	-	90.90

[a] Cx:y. x = number of carbons. y = number of double bonds, and OH = number of hydroxyl groups.

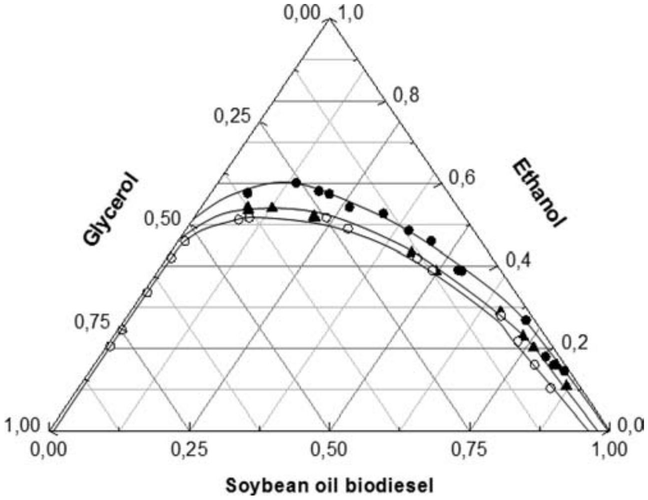

Figure 1. Phase diagram of the system of soybean oil biodiesel + ethanol + glycerol. ●, 298.15 K; ▲, 333.15 K; ○, 343.15 K.

Table 5. Binodal Curve of the System of Soybean Oil Biodiesel (1), Ethanol (2), and Glycerol (3)

w_1	w_2	w_3
	T/K = 298.15	
0.2648	0.5419	0.1934
0.4516	0.4595	0.0889
0.5421	0.3884	0.0695
0.7161	0.2685	0.0154
0.8205	0.1591	0.0204
0.3328	0.5268	0.1404
0.1902	0.5815	0.2284
0.8464	0.1448	0.0088
0.5345	0.3899	0.0756
0.2122	0.5744	0.2134
0.1402	0.6010	0.2588
0.0659	0.5761	0.3580
0.7955	0.1797	0.0247
0.3984	0.4855	0.1161
	T/K = 333.15	
0.1280	0.5394	0.3326
0.2119	0.5201	0.2679
0.4311	0.4311	0.1378
0.8691	0.1077	0.0232
0.0878	0.5349	0.3773
0.6607	0.2889	0.0504
0.7306	0.2289	0.0405
0.7633	0.2014	0.0353
0.4968	0.3869	0.1162
0.8262	0.1587	0.0151
0.2150	0.5177	0.2673
0.0830	0.5419	0.3750
	T/K = 343.15	
0.236	0.5167	0.2473
0.4475	0.4186	0.1339
0.0985	0.5164	0.3851
0.0820	0.5116	0.4060
0.6667	0.2789	0.0544
0.7276	0.2169	0.0555
0.7859	0.1597	0.0543
0.4887	0.3894	0.1219
0.2881	0.4899	0.222
0.8311	0.1015	0.0534
0.0079	0.4196	0.5724
0.0073	0.2452	0.7489
0.0064	0.2052	0.7884
0.0073	0.3354	0.6573
0.0121	0.4597	0.5282

castor oil, respectively. The binodal curves found experimentally for different types of systems are discussed separately.

Phase Diagrams of Systems of Soybean Oil Biodiesel + Ethanol + Glycerol. Figure 1 shows that the binary mixtures of soybean oil biodiesel−ethanol and glycerol−ethanol are completely soluble, but the solubility of glycerol in the soybean oil biodiesel-rich phase is considerably larger than this biodiesel in the glycerol-rich phase. For the analysis of the temperatures for the system of soybean oil biodiesel + glycerol + ethanol it is observed that a small difference in temperature is not important (as (333.15 to 343.15) K which represents only 10 K of difference) because the two-phase region remains almost equal, but bigger differences in temperature show bigger differences in two-phase region, as can be seen in Figure 1, where that of the two-phase region at 298.15 K is considerably bigger than of two-phase region at 343.15 K, showing also that a lower temperature represents a bigger two-phase region. Table 5 shows the experimental data found for this system at temperatures of study.

Phase Diagrams of Systems of Soybean Oil Biodiesel + Ethanol + Water. Figure 2 shows that the mixtures of soybean oil biodiesel−ethanol and ethanol−water are miscible in all proportions at the temperatures studied, and the solubility of the water in the soybean oil biodiesel-rich phase is slightly larger than the biodiesel in the water-rich phase. This amount of water that is still in the soybean oil biodiesel-rich phase may affect the purification of biodiesel by modifying the composition and reducing its quality. The water is introduced into biodiesel production during processing and washing and may remain in it if the drying procedure is not efficient.[17] A comparison (Figure

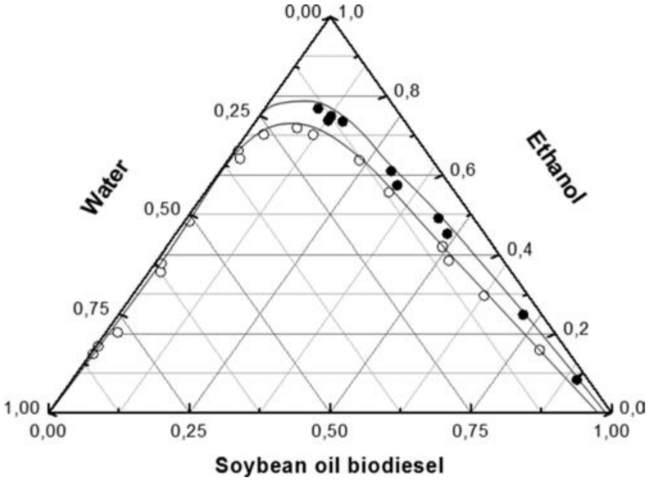

Figure 2. Phase diagram of the system of soybean oil biodiesel + ethanol + water. ●, 298.15 K; ○, 323.15 K.

Table 6. Binodal Curve of the System of Soybean Oil Biodiesel (1), Ethanol (2), and Water (3)

w_1	w_2	w_3
	T/K = 298.15	
0.3326	0.5734	0.0940
0.4477	0.4898	0.0624
0.7193	0.2476	0.0331
0.4830	0.4504	0.0666
0.1278	0.7373	0.1348
0.0951	0.7673	0.1376
0.1274	0.7483	0.1242
0.1550	0.7349	0.1102
0.8966	0.0835	0.0199
0.3040	0.6093	0.0867
	T/K = 323.15	
0.0207	0.3559	0.6233
0.0208	0.2033	0.7760
0.0114	0.3776	0.6110
0.0041	0.1492	0.8467
0.0092	0.4820	0.5088
0.0066	0.6610	0.3324
0.0193	0.6407	0.3399
0.0036	0.1684	0.8281
0.0310	0.7020	0.2670
0.5187	0.3845	0.0969
0.4901	0.4191	0.0908
0.3265	0.5561	0.1174
0.6257	0.2959	0.0783
0.1193	0.7013	0.1794
0.2336	0.6365	0.1299
0.0821	0.7183	0.1996
0.7927	0.1586	0.0486

2) of the temperatures (323.15 and 298.15) K for the system soybean oil biodiesel + ethanol + water demonstrates that the difference in the temperature of the system under consideration is important, affecting the two-phase region. Besides, it is possible to see that larger quantities of biodiesel in soybean oil biodiesel-rich phase are obtained when lower temperatures are used, like the temperature of 298.15 K, because the area of the heterogeneous phase decreases with increasing temperature. Table 6 shows the experimental data found for this system at temperatures of study.

Comparison of Binodal Curves of Systems Biodiesel + Ethanol + Glycerol Changing the Vegetable Oil. As the soybean oil biodiesel and castor oil biodiesel are made up of various esters, with the higher percentage of the ethyl linoleate and ethyl ricinoleate, respectively, it is possible to obtain different characteristics in the binodal curves and, as a result, the systems of liquid−liquid equilibrium. To understand the differences in solubility, the effect in the systems soybean oil biodiesel + glycerol + ethanol and castor oil biodiesel + ethanol + glycerol at 333.15 K (Figure 3) was studied. Analyzing the binodal curves for these systems is possible to check that the change of raw materials to obtain biodiesel has great influence on the solubility of the mixture. Biodiesel from castor oil has a two-phase region lower than the biodiesel from soybean oil, indicating that the solubility of castor oil biodiesel is worst causing difficulties in the purification. These results agree with those obtained previously in the literature.[14] This may be due to the fact that the largest proportion of ester in biodiesel from castor oil (ethyl ricinoleate) contains the presence of the hydroxyl group in the carbon chain, which makes biodiesel have a larger solubility in ethanol and consequently less heterogeneous area. The experimental data for the construction of the binodal curves of the system of oil castor biodiesel + ethanol + glycerol at 333.15 K are shown in Table 7.

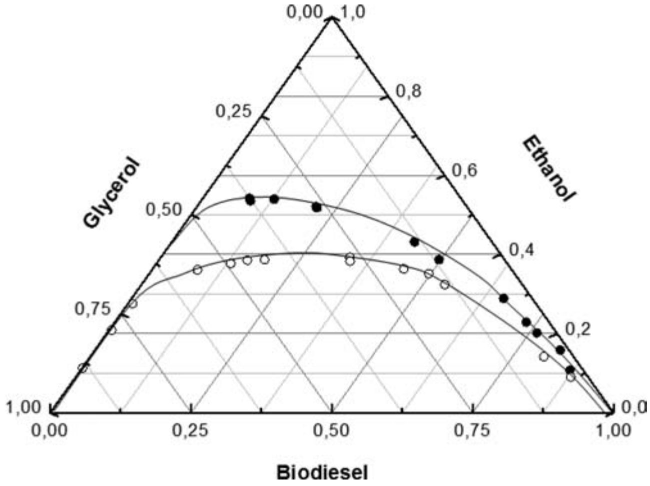

Figure 3. Comparison of phase diagrams of systems of biodiesel + ethanol + glycerol with soybean oil biodiesel (●) and castor oil biodiesel (○), at 333.15 K.

Table 7. Binodal Curve of the System of Castor Oil Biodiesel (1), Ethanol (2), and Glycerol (3)

w_1	w_2	w_3
	T/K = 333.15	
0.8058	0.1419	0.0523
0.3362	0.3920	0.2718
0.1869	0.3868	0.4263
0.4967	0.3511	0.1523
0.8791	0.0901	0.0308
0.1572	0.3851	0.4577
0.5386	0.3241	0.1373
0.4462	0.3635	0.1903
0.3409	0.3831	0.2760
0.1317	0.3771	0.4913
0.0044	0.2087	0.7869
0.0001	0.1127	0.8863
0.0082	0.2755	0.7163
0.0809	0.3610	0.5580

Conclusions

The analysis of solubility for the systems studied with biodiesel, ethanol, glycerol, and water show that the temperature difference does not have much influence in separation. It was seen that in a small temperature range (10 K) the change was almost insignificant, but at the large temperature differences (45 K) an increase in the region of two phases is observed, with higher quantities of biodiesel in the biodiesel-rich phase at temperatures of 298.15 K, which provides a better separation of the product of interest. Therefore, processes that use heat to encourage the separation of the components may not be the best alternative for these systems under study. The amount of water at the biodiesel-rich phase as was observed for the system of soybean oil biodiesel + ethanol + water is considerable, causing difficulties in future stages of separation and purification of biodiesel if it does not have a good drying process damaging the quality of biodiesel. It was also observed that the castor oil used raw material for the production of biodiesel also creates more difficulties in the separation of phases. It is known that the increase in carbon chain FAEE (ethyl esters of fatty acids) decreases the solubility in ethanol and glycerol. It was unexpected that castor oil biodiesel would present a two-phase region similar to soybean oil biodiesel exactly due to the presence of the hydroxyl group.

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