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Liquid–Liquid Phase Equilibria of Systems of Palm and Soya Biodiesels: Experimental and Modeling

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Supporting Information

ABSTRACT: Liquid–liquid phase equilibria of two systems of concern in the biodiesel production process are determined experimentally. The first system is the binary mixture of water + biodiesel within a temperature range of 297.2 to 333.2 K, in order to determine water solubilities in two biodiesels prepared from palm and soya oil. The experimental results showed that water solubilities were limited to values below 0.05 mol % and that the solubility increased with increasing temperature and biodiesel unsaturation. Next, the phase diagrams of ternary mixtures of glycerol + methanol + mentioned biodiesels were determined at three temperatures (293.2, 303.2, and 313.2 K). The reliability of the experimental data of tie lines was ascertained using the Othmer–Tobias relation. The UNIQUAC model was then used to model both the binary and ternary experimental data. Results showed the suitability of this model in correlating the phase behavior of such systems.

■ INTRODUCTION

The production of alternative fuels from renewable sources is becoming attractive because of the high prices of fossil fuels, the decline of fuel reserves, and the concern about the environment.¹ Nowadays, biodiesel is receiving increasing attention as a renewable fuel, because of particular advantages over petrodiesel: In contrast to diesel fuel, biodiesel contains long-chain alkyl esters with oxygen in their structures, which results in more complete burning. In addition, it has a higher flash point compared to petrodiesel. Therefore, this fuel is less flammable and more safe. In addition, its cetane number is higher than that of petrodiesel because the fatty acid methyl esters used as biodiesels contain long-chain compounds similar to long-chain alkanes such as hexadecane, which make for a higher-quality diesel.²

There are four basic methods for biodiesel production from oils and fats: base-catalyzed transesterification, direct acid-catalyzed transesterification, conversion of the oil into its fatty acids and then into biodiesel, and noncatalytic transesterification of oils and fats such as the BIOX process or the supercritical alcohol process.³ In the base-catalyzed transesterification method, biodiesel is obtained via a transesterification reaction of triglycerides from oils and fats with an excess of alcohol, and using a catalyst to accelerate the reaction. The reaction product is composed of fatty acid methyl esters and glycerol as a byproduct. After biodiesel production, some steps are carried out for the separation and purification of the desired product. This includes respectively, the separation of the biodiesel phase from the glycerol phase, recycling the unreacted alcohol, water-washing, and drying.

Therefore, accurate information on the phase equilibria of the components involved in biodiesel production, and the ability to predict equilibria where information is not available, is necessary in order to determine optimum operating conditions for the separation and purification units of biodiesel production. Some studies have been carried out in this respect. Oliveira et

al.⁴ measured water solubility in eleven pure alkyl esters and six commercial biodiesels in the temperature range from 288.2 to 323.2 K and modeled them using the Cubic Plus Association (CPA) equation of state. They showed that water solubility decreases with a decrease in polarity of the esters and increases with ester unsaturation. In 2008, Andreatta et al.¹ determined liquid–liquid equilibrium data for the ternary system consisting of methyl oleate, methanol, and glycerol. Their experiments were carried out at temperatures between 313 and 393 K. They also modeled their experimental results using the Group Contribution with Association Equation of State (GCA-EoS) and the A-UNIFAC model and concluded that the GCA-EoS model, in particular, has good predictive capability. In other work by Negi et al.,⁵ liquid–liquid phase equilibrium data for glycerol + methanol + methyl oleate ternary systems were determined experimentally at 60 °C and compared with predictions of the UNIFAC and UNIFAC-Dortmund models. For this system, the predictions of UNIFAC and UNIFAC Dortmund were in good agreement with the experimental results. In 2010, Lee et al.⁶ studied the liquid–liquid equilibria for ternary systems of glycerol + methanol + methyl oleate, and glycerol + methanol + methyl linoleate at temperatures from 298.2 to 318.2 K under atmospheric pressure, including phase boundaries and tie-lines. They showed that these ternary systems behave as type I of liquid–liquid equilibria and that the two-phase region decreases in size with increasing temperature. They also found that the mutual solubilities of fatty acid methyl ester (FAME) and glycerol are very small. Further, they applied the UNIFAC model and its modified versions, NRTL and UNIQUAC, to model the experimental data.

Received: January 11, 2012

Revised: May 9, 2012

Accepted: May 14, 2012

Published: May 14, 2012

In the present work, liquid–liquid equilibria of four systems of concern in biodiesel production were studied experimentally: the binary systems of water + palm oil biodiesel and water + soya oil biodiesel, and the ternary systems of each mentioned biodiesel + glycerol + methanol. Further, the UNIQUAC model was applied to correlate all four systems.

EXPERIMENTS

Materials. The chemicals used for experiments included distilled water, glycerol (>99% GC, supplied by Sigma Aldrich), methanol (99.5%, Supplied by Arman Sina), and two biodiesels from palm and soya oils. These biodiesels were produced in the laboratory via the transesterification reaction of palm and soya oils. The catalyst used was KOH (85%, supplied by BDH (British Drug House)). This reaction was carried out based on the international standard method of ISO 5509/1978 (E) for biodiesel preparation.⁷ The produced biodiesels were washed four times with water and then dried in an oven at 333.2 K to remove the water and any remaining methanol. The prepared biodiesels were then analyzed using a gas chromatograph under the following conditions: the injector, detector and column temperatures were set at 483, 523, and 473 K, respectively. The column used was capillary-type (C.P.88) with a length of 100 m in a Varian 3400 model apparatus. The results of the analysis are given in Table 1.

Table 1. Composition of the Two Biodiesels Investigated, As Indicated by GC

structure	common acronym (C:x:y) ^b	composition (wt %)	
		palm	soya
^a R-(CH ₂) ₁₀ -CH ₃	C12:0	0.29	
R-(CH ₂) ₁₂ -CH ₃	C14:0	1.05	0.07
R-(CH ₂) ₁₄ -CH ₃	C16:0	40.01	11.49
R-(CH ₂) ₆ CH=CH(CH ₂) ₆ -CH ₃	C16:1	0.11	0.11
R-(CH ₂) ₆ CH=CH(CH ₂) ₇ -CH ₃	C17:1		
R-(CH ₂) ₁₆ -CH ₃	C18:0	4.17	5.08
R-(CH ₂) ₇ CH=CH(CH ₂) ₇ -CH ₃	C18:1	43.09	25.37
R-(CH ₂) ₇ CH=CH-CH ₂ -CH=CH-(CH ₂) ₄ -CH ₃	C18:2T		0.12
R-(CH ₂) ₇ CH=CH-CH ₂ -CH=CH-(CH ₂) ₄ -CH ₃	C18:2C-C	11.09	51.06
R-(CH ₂) ₇ -(CH=CH-CH ₂) ₃ -CH ₃	C18:3C-C	0.19	5.95
R-(CH ₂) ₁₈ -CH ₃	C20:0		0.20
R-(CH ₂) ₈ CH=CH (CH ₃) ₈ CH ₃	C20:1		0.26
R-(CH ₂) ₂₀ CH ₃	C22:0		0.29

^aR is the COOCH₃ group. ^bx, number of carbons; y, number of double bonds.

Procedure. 1. Measurement of Water Solubility in Biodiesel. The water solubility of binary systems of each biodiesel + water was investigated within the temperature range of 297.2 to 333.2 K. After mixing 2 g each of biodiesel and distilled water (with accuracy of ± 0.001 g) at constant temperature in a shaker-incubator (IKA - Ks4000i) at 220 rpm for 35 min, the mixture was allowed to settle and separate at the same temperature for at least 20 h. The shaking time of 35 min was predetermined by tests to guarantee enough time to reach saturation solubility. Samples from the biodiesel phase were then carefully separated using a syringe and titrated using

a METTLER TOLEDO DL31 Karl Fischer titrator, having an accuracy of 0.01 ppm.

2. Ternary Systems of Biodiesel, Methanol, and Glycerol. The experiments of ternary systems include two parts: (a) phase diagram determination, and (b) tie-line determination.

a. Binodal Curves of Ternary Systems of Biodiesel + Methanol + Glycerol. Phase equilibria measurements on ternary system of biodiesel, methanol, and glycerol were carried out at the three temperatures of 293.2, 303.2, and 313.2 K for each biodiesel. The phase boundary of each phase diagram was determined by the titration method.⁸ In this procedure, which was carried out under isothermal conditions, binary mixtures of biodiesel and glycerol with known composition were titrated by methanol from a buret. All titration tests were carried out in closed tubes with latex covers. Isothermal conditions were applied using a water bath with a temperature uncertainty and fluctuation of ± 0.5 K. By slowly adding methanol to the binary mixture, the point at which the mixture of biodiesel, glycerol, and methanol changed from turbid to transparent was considered as a point on the saturation solubility curve. This is, in fact, a transition point from a two-phase region into a one-phase region.

Finally, to complete the phase boundary and determine the binary solubilities of biodiesel in glycerol and vice versa, a sonicator cleaner (model LUC-410, 500 W, 40 kHz) was used as a mixer to mix these two components to proper dispersion.

b. Tie Lines of the Ternary Systems of Biodiesel + Methanol + Glycerol. Determination of the tie-lines was carried out using the following procedure: After mixing a specific known mass fraction of biodiesel, methanol, and glycerol for 35 min (35 min is the predetermined time to ensure having reached saturation) at constant temperature in a shaker-incubator, the mixture was kept in an isothermal incubator at the same temperature for at least 20 h for adequate separation into two phases: a biodiesel-rich phase and a glycerol-rich phase. Samples from each phase were then carefully taken using syringes, weighed, and then kept in an oven at 348.2 K for 2.5 h to remove all methanol via evaporation until reaching a constant weight.⁸ The weight fraction of methanol was calculated as (mass of sample before evaporation – mass of sample after evaporation)/mass of sample before evaporation. The equilibrium biodiesel and glycerol mass fractions were then determined with the aid of the binodal curves of the phase diagram obtained in section a, using the mass fractions of methanol obtained in the two phases.

Thermodynamic Model. An appropriate activity coefficient-based model can be used to model the experimental data of both the binary and ternary systems. In this study, the UNIQUAC model⁹ was used due to its simplicity and wide range of applicability, as well as being recommended for nonideal systems at low temperatures and ambient pressures.^{10,11} The binary interaction parameters were optimized by minimizing the objective function described below in the case of binary mixture modeling

$$OF = \sum_{i=1}^N \sum_{j=1}^2 \left(\frac{|x_{i,j} - x_{i,j_e}|}{x_{i,j_e}} \right) + \sum_{i=1}^N |1 - y_{i,1}| \quad (1)$$

where N is the number of data points, x_{i,j_e} and $x_{i,j}$ are the experimental and calculated mole fractions of component j in

the biodiesel-rich phase, respectively, and $y_{i,1}$ is the theoretical water mole fraction in the water-rich phase.

For ternary systems, the following objective function was minimized

$$OF = \sum_{i=1}^N \sum_{j=1}^3 \left(\frac{|x_{i,j} - x_{i,j_e}|}{x_{i,j_e}} + \frac{|y_{i,j} - y_{i,j_e}|}{y_{i,j_e}} \right) \quad (2)$$

where N is the number of the tie lines, x_{i,j_e} and $x_{i,j}$ are the experimental and calculated mole fractions of component j in the biodiesel-rich phase, respectively, and y_{i,j_e} and $y_{i,j}$ are the same variables in the biodiesel-lean phase.

The optimization procedure consisted of a hybrid of Genetic Algorithm (GA) with the MATLAB function *fminsearch* which finds a minimum of an unconstrained multivariable function using the derivative-free method. GA was used to find a proper first assumption, followed by *fminsearch* to converge to the optimized answer.

The relative molecular volume (r) and relative molecular surface area parameters (q) required by UNIQUAC are calculated using eqs 3 and 4.

$$r = \sum_j x_i \sum_k^G v_k^{(i)} R_k \quad (3)$$

$$q = \sum_j x_i \sum_k^G v_k^{(i)} Q_k \quad (4)$$

where x_i is the mole fraction of any component in the biodiesel mixture, $v_k^{(i)}$ is the number of groups k in molecule i , C is the number of components in the biodiesel, and G is the total number of groups. R_k and Q_k are the UNIFAC-VLE subgroup parameters. For all the groups involved in this work, these group parameters were taken from the UNIFAC-VLE tables⁹ and the resulting values of r and q are given in Table 2 for the components of this study.

Table 2. Parameters r and q for the Studied Systems Obtained by UNIFAC Tables⁹ and Eqs 3 and 4

compd	r	q
palm biodiesel	12.83	10.59
soya biodiesel	13.02	10.72
methanol	1.43	1.43
glycerol	4.80	4.91
water	0.92	1.40

RESULTS AND DISCUSSION

Binary Systems. The experimental values of water solubility in both palm and soya biodiesels at ambient pressure are presented in Table 3. It is observed that water solubility in both biodiesels increases with an increase in temperature. These data are in good agreement with experimental results of Oliveira et al. on some commercial biodiesels.⁴ The saturation solubility of water in palm biodiesel is less than that of soya biodiesel. The higher C18:2 content in soya biodiesel is responsible of this increased solubility. The C18:2 molecules are unsaturated and have double bonds in their structure, resulting in higher polarity when present in higher concentrations, compared to a biodiesel that has less C18:2 content.

Table 3. Experimental Values of Water Solubilities in the Two Biodiesels at Various Temperatures, Where x is Mole Fraction

palm biodiesel		soya biodiesel	
T (K)	x_{H_2O}	T (K)	x_{H_2O}
297.2	0.025	297.2	0.031
308.2	0.029	308.2	0.034
318.2	0.032	318.2	0.040
328.2	0.039	328.2	0.046
333.2	0.041	333.2	0.049

Water solubilities were also correlated by the UNIQUAC model, and the results are compared with the experimental values in Figure 1 for both biodiesels.

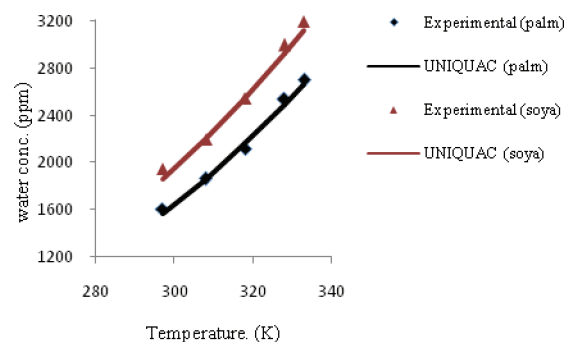


Figure 1. Experimental and calculated results of water solubility in the two biodiesels at various temperatures.

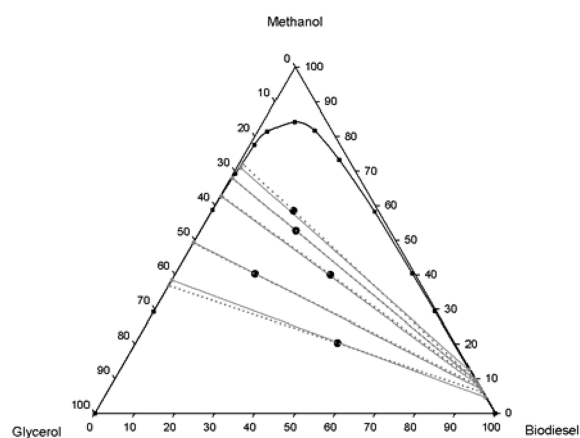
The modeling results indicate the suitability of the UNIQUAC approach for modeling such binary systems. The average absolute deviation (AAD) in the studied temperature range, according to eq 5, is 0.50% for the palm biodiesel + water system and 0.74% for the soya biodiesel + water system.

$$AAD = \frac{1}{N} \sum_{i=1}^N |x_i^{\text{exp}} - x_i^{\text{cal}}| \quad (5)$$

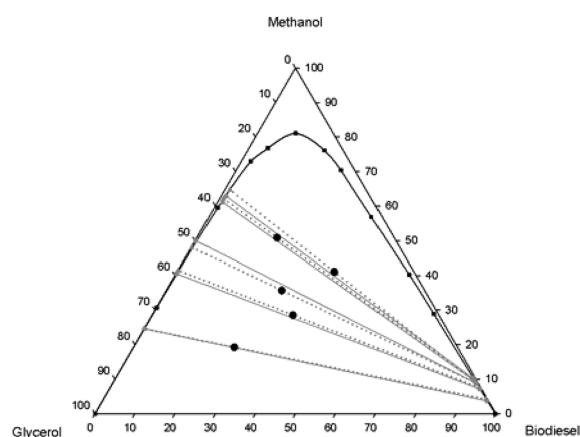
In this equation, x_i is the molar solubility of water in the biodiesel and N is the number of data points. Within the temperature range of 297.2 to 333.2 K, the values of the optimized binary interaction coefficients, U_{12} and U_{21} (where 1 represents water and 2 biodiesel), are -731.1 and 9031.1 J/mol, respectively for palm biodiesel, and -563.4 and 8447.0 J/mol, respectively, for soya biodiesel.

Ternary Systems. Three sets of experimental phase diagrams at 293.2, 303.2, and 313.2 K, are shown graphically in Figure 2 for the ternary system of palm biodiesel + methanol + glycerol, and in Figure 3 for the ternary system of soya biodiesel + methanol + glycerol. These diagrams include the binodal curves, and the tie lines in the form of solid lines, at the three above-mentioned temperatures. These results showed good agreement with literature data on a similar system in which only one representative component, namely methyl oleate, was used to represent the biodiesel.⁵

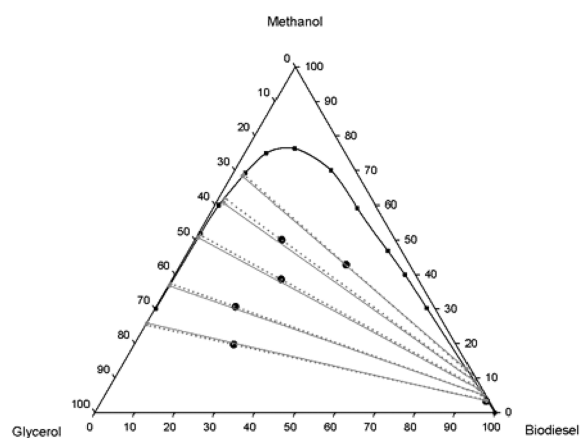
As can be observed, both biodiesel and glycerol are completely soluble in methanol. However, biodiesel and glycerol are partially miscible in one another. Therefore, these ternary systems behave as type I of liquid–liquid equilibria.



(a)



(b)

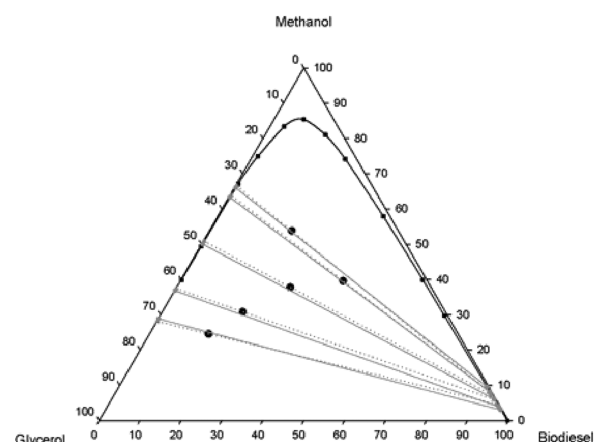


(c)

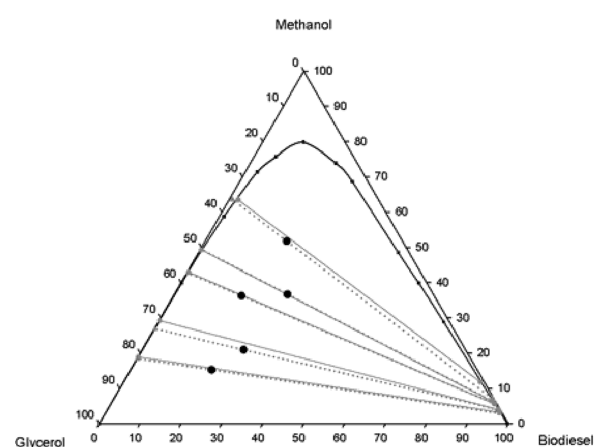
Figure 2. Phase diagrams (in wt %) and tie lines of the ternary system of palm biodiesel, glycerol, and methanol at: (a) 293.2, (b) 303.2, and (c) 313.2 K. Solid line, experimental; dashed line, UNIQUAC model.

The greater similarity between methanol and glycerol molecules compared to that of methanol and biodiesel molecules makes for the higher solubility of methanol in glycerol compared to methanol solubility in biodiesel. This is also apparent from the slopes of the tie lines.

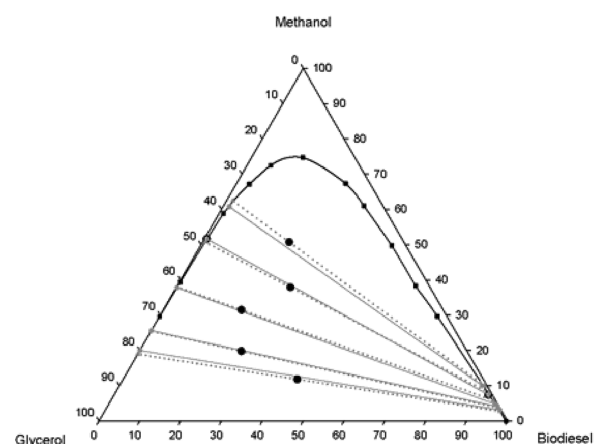
The experimental data show that the solubility of biodiesel in glycerol, and vice versa, is very low. However, the solubility of



(a)



(b)



(c)

Figure 3. Phase diagrams (in wt %) and tie lines of the ternary system of soya biodiesel, glycerol, and methanol at: (a) 293.2, (b) 303.2, and (c) 313.2 K. Solid line, experimental; dashed line, UNIQUAC model.

glycerol in the biodiesel phase is greater than that of biodiesel in the glycerol phase, for example at a temperature of 313.2 K, glycerol concentration in palm biodiesel is 0.24 wt %, while that of the biodiesel in glycerol is about 0.1%. Because of these small values, it can be concluded that it is possible to have a rather

clean separation of glycerol from biodiesel in the purification step.

The effect of temperature on the experimental results is apparent in Figures 2 and 3. The size of the two-phase region shrinks with increasing temperature since ternary solubilities of the studied systems increase with increasing temperature.

Figures 2 and 3 also include the result of modeling for each biodiesel system using the UNIQUAC model at 293.2, 303.2, and 313.2 K. These are shown as dashed lines, to be compared with the experimental values as solid lines at the same three temperatures. As the modeling results show, the UNIQUAC model is also applicable for the ternary systems. The optimized binary interaction coefficients and the AAD% of tie lines, calculated according to eq 6, are given as Supporting Information for all of the ternary systems studied.

$$\text{AAD} = \frac{1}{N} \sum_i |w_i^{\text{exp}} - w_i^{\text{cal}}| \quad (6)$$

In this equation w_i is the mass fraction of the components, and N is the number of tie lines.

The consistency of tie line data was ascertained by applying the Othmer–Tobias plots,¹² which are described as eq 7:

$$\log \frac{1-a}{a} = n \log \frac{1-b}{b} + c \quad (7)$$

where a is the weight fraction of glycerol in the glycerol-rich phase, b is the weight fraction of biodiesel in the biodiesel-rich phase, n is the slope on a $\log(1-a)/a$ vs $\log(1-b)/b$ graph, and c is a constant for each system. As an example, the Othmer–Tobias plot for soya biodiesel at 293.2 K is shown in Figure 4. The constants of Othmer–Tobias for each system at

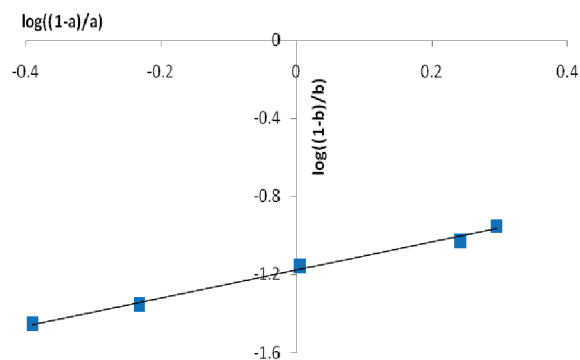


Figure 4. Othmer–Tobias plot of soya biodiesel at 293.2 K. a , weight fraction of glycerol in the glycerol-rich phase; b , weight fraction of biodiesel in the biodiesel-rich phase.

each temperature are given in Table 4. The results showed a good linear fit at all of the temperatures investigated with an R^2 value within the range of 0.9351 to 0.9932, which confirms the accuracy of the experimental tie line data. In addition, the Othmer–Tobias relation can be used as a useful tool to predict other tie lines which have not been measured experimentally.

According to the phase rule, at a fixed temperature and pressure, the degrees of freedom for a ternary system in two-phase equilibrium is equal to one. In other words, only one component can independently change in concentration. Therefore, the mass fraction of a component in a phase can be expressed as a function of another mass fraction in that phase. The relations between methanol and glycerol concentrations in the glycerol-rich phase can be expressed mathemati-

Table 4. Constants of the Othmer–Tobias Correlation (eq 7) for the Ternary Systems of Biodiesel, Methanol, And Glycerol

T (K)	n	c	R^2
Palm Biodiesel			
293.2	0.655	−1.134	0.954
303.2	0.584	−1.039	0.935
313.2	0.652	−1.080	0.987
Soya Biodiesel			
293.2	0.716	−1.177	0.993
303.2	0.642	−1.055	0.962
313.2	0.650	−1.058	0.984

cally according to eq 8, and between methanol and biodiesel concentrations in the biodiesel-rich phase according to eq 9. Table 5 shows the values of the constants A and B obtained for the investigated systems.

$$\text{In the glycerol-rich phase: } w_{\text{glycerol}} = Aw_{\text{MeOH}} + B \quad (8)$$

$$\text{in the biodiesel-rich phase } w_{\text{MeOH}} = Aw_{\text{biodiesel}} + B \quad (9)$$

Table 5. Constants A and B of the Linear Equations (eqs 8 and 9) for the ternary Systems of Biodiesels, Methanol, And Glycerol

T (K)	palm biodiesel			soya biodiesel		
	A	B	R^2	A	B	R^2
Glycerol-Rich Phase				Glycerol-Rich Phase		
293.2	−1.022	1.009	0.999	−1.005	1.000	1.000
303.2	−1.031	1.009	0.999	−1.040	1.014	0.999
313.2	−1.059	1.017	0.999	−1.032	1.013	0.999
Biodiesel-Rich Phase				Biodiesel-Rich Phase		
293.2	−0.986	0.984	0.999	−0.985	0.982	1.000
303.2	−0.968	0.966	0.999	−0.945	0.943	0.999
313.2	−0.968	0.963	0.999	−0.883	0.884	0.999

CONCLUSIONS

According to the experimental results obtained in this study on the solubility of water in palm and soya biodiesels at ambient pressure, it is concluded that the saturation solubility of water in both biodiesels is very low, not exceeding 0.041 and 0.049 in mol % within the temperature range of 297.2 to 333.2 for palm and soya biodiesels, respectively. This is due to the long chains and low polarities of the ester molecules in the biodiesels. The presence of double bond(s) was shown to have a large effect on water solubility in long-chain esters, whereas carbon chain length is a less effective parameter. The small values of water solubility in the biodiesels suggests that in the drying process, little energy is required if separation is carried out by evaporation. Such low concentrations of water even suggest the possibility to use an adsorbent for water removal. In addition, since the solubility of water in the biodiesel increases with increasing temperature, it is better to carry out the washing step of the process at low temperatures for less water contamination.

Liquid–liquid equilibria were also determined experimentally for the two ternary systems of the mentioned biodiesels + methanol + glycerol. On the basis that the size of the two-phase region was shown to shrink as temperature increased, it is concluded that more biodiesel will be obtained in the

purification steps of biodiesel production if such operations are carried out at the lowest economic temperatures.

The experimental ternary phase diagrams have also indicated that it is easy to separate glycerol (as a byproduct) after the removal of methanol from biodiesel, owing to the low solubilities of biodiesel and glycerol in one-another. It is possible to have a clean and rather complete separation.

The linearity of Othmer–Tobias plots, obtained in this work, prove the consistency of experimentally measured tie line data of the studied systems, and provide relations to predict other tie-lines.

The UNIQUAC model was used to correlate both the binary and ternary equilibrium data. The corresponding optimized binary interaction coefficients were determined for each system. Results showed that the UNIQUAC model is suitable for modeling such systems with AAD percentages of 0.50 and 0.74% for modeling water solubility in palm and soya biodiesels, respectively, and 3.93 and 4.30% in modeling the ternary phase equilibria in the studied systems of palm and soya biodiesels, respectively.

Linear correlations have also been obtained at each temperature which can be used to determine the unknown composition in both phases by having one known concentration in each phase.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental equilibrium data pertaining to phase boundaries at 293.2, 303.2, and 313.2 K for the ternary systems of each biodiesel + methanol + glycerol, are presented as Table S1. The corresponding data of the tie lines are provided as Table S2. The optimized binary interaction coefficients of the UNIQUAC model for all of the ternary systems studied, and the errors in modeling the tie lines with these optimized values are presented in Table S3. These values can be used for predicting equilibrium data at conditions where no data are available. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Mr. Ebrahim Lalehzari, Mr. Mohammad Ranjbaran, and Mr. Abdolreza Javidi-Alesaadi for their kind assistance.

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