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Liquid–Liquid Equilibrium for Ternary Mixtures Methanol-Glycerol- Biodiesel from *Jatropha curcas*

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Abstract : With the emergence of new raw materials for biofuels production, it is important to study systems formed by the chemical species involved in order to improve the efficiency of processes for a viable large-scale production. This paper presents an experimental methodology developed for the determination of the liquid-liquid equilibrium (LLE) data of the ternary system methanol-glycerol-biodiesel obtained from the seeds of *Jatropha curcas*. UNIQUAC and NRTL models were fitted properly to experimental data with a mean deviation percentage of 2.29 % and 2.38 %, respectively. In addition, LLE was simulated at 30 and 60 °C, obtaining a correlation factor (R^2) of 0.9597 from Othmer-Tobias equation which shows the reliability of the data obtained. This research provides experimental information about crude oil, refined oil and biodiesel from *Jatropha curcas*crops produced in the Colombian Caribbean region, thermodynamic data and parameters for LLE calculations of the system described.

Keywords: Liquid-liquid equilibrium, Biodiesel, Transesterification, Gas chromatography, Interaction parameters..

Introduction

In recent years, the growing need to ensure energy supply has driven the search for renewable energy sources. Biodiesel obtained from second-generation oil plants such as *Jatropha curcas*[1,2], which represents many ecological advantages[3], is currently considered one of the main alternatives to fossil fuels due to is a renewable, biodegradable and environmentally friendly fuel[4]. Nevertheless, the production of these biofuels requires a great variety of studies, such as the separation processes based on precise data of thermo-physical properties and phase equilibrium. In literature are found different studies related to real systems containing methanol-glycerol-first generation biodiesel, however, it is evident the limitation of information to conventional biomass. This points the importance of evaluating the LLE of systems that include biodiesel obtained from *Jatropha curcas*, in order to provide essential information that allows carrying out its production on an industrial scale[5]. This work presents a methodology to obtain biodiesel from *J. curcas*, followed by the preparation of ternary mixtures and the quantification of the equilibrium concentrations at 45 °C. In addition, it was analyzed the correlation of the experimental data, methanol distribution coefficient and solvent selectivity. Finally, UNIQUAC and NRTL models were evaluated using a commercial process simulator.

Experimental

Oil extraction, refining and characterization

Fruits of *Jatropha curcas L.* were obtained from Sincerín-Bolívar (10°8’39’’N, 75°16’39’’W) located at 36 km from Cartagena (Colombia), with a maturation time of 12±2 weeks.The seeds were dried by direct exposure to the sun, husked, macerated and subjected to Sohxlet extraction with Hexane at 65 °C (purity 96% G.C., Emsure) for 6 hours, after which the solvent was removed by vacuum evaporation and by heating in a drying oven (Esco Isotherm, Model OFA-32-8) at 60 °C for 24 hours. The extracted oil was stored at -2 °C for physical-chemical analysis and refining in stages; that started with degumming, for which a known volume of oil was taken and 0.5 %v/v of H_3PO_4 (purity 85 %, Emsure) was added at 20%, 60 °C and 200 rpm for 30 minutes. The degummed oil was separated and removed by centrifuging at 300 rpm (GEMMYCO Model PLC-012E). Then, it was washed with distilled water at 60 °C until a pH near 7 was reached and heated to 110 °C and vacuum filtration to evaporate the remaining water. Finally, the lipid profile was determined based on the procedure developed by Gambia and Celis (2010)[6]. Measurements of some physicochemical oil properties were made, such as density, kinematic viscosity, acidity, cloud point and yield.

Oil esterification and transesterification to biodiesel

The esterification process[7]was carried out at 50 °C ± 2 °C for 1 h at 400 rpm using a ratio of 60 % wt methanol/oil (99.8 % purity, Panreac brand) and 1 % wt/wt H_2SO_4(97 % purity, Emsure brand)to reduce the FFA concentration below 2%.After esterification, the organic phase was washed with hot water (60-70 °C) in a ratio of 1:1 to remove traces of acid and alcohol; and kept in an oven for 1 hour at 110 °C to eliminate the water and traces of alcohol present.Then, the oil was transesterificated[8] using NaOH at 0.5%wt relative to the oil (Mark Panreac, 98%) and a molar ratio methanol/oil 8:1[9]. When the system reached 65 °C, the alkoxide was slowly added at a rate of 3.5 mL/min at 400 rpm for 90 minutes. After the reaction was complete, the mixture was allowed to cool and added to a settling funnelat room temperature for 2 hours to ensure phases separation, after which methanol traces were removed by evaporation at 85 °C for 30 minutes. Biodiesel obtained was washed using distilled water in a ratio of 1:1, stirred and standed for 24 hours, so that methyl and water phases were separated. Finally, acidity, density, viscosity and cloud point of biodiesel were measured based on ASTM D6751. The cetane index(CN) was determined from the biodiesel composition using Equation 1[10], where$x_2 =$ % Myristic acid,$x_3 =$ % Palmitic acid,$x_4 =$ % Stearic acid,$x_5 =$ % Palmitoleic acid,$x_6 =$ % Oleic acid,$x_7 =$ % Alpha-linoleic acid and$x_8 =$ % Linoleic acid.

$$CN=61.1+0.088x_2+0.133x_3+0.152x_4-0.101x_5-0.039x_6-0.243x_7-0.395x_8 \quad (1)$$

Mixtures preparation, and determination of equilibrium concentration

Mixtures used for the LLE study were prepared taking as reference the compositions reported by Silva et al., (2013)[11].A unifactorial design was carried out with 5 levels of variation, where the process and response variableswere the initial concentration of the ternary system and the concentration at equilibrium. Five experiments were performed in duplicate, for a total of 10 tests. Table 1 show the concentrations of each component, which were added to the containers in increasing order of volatility.

Table 1. Concentrations resulting from the experimental design

Number of experiment	FAME – Glicerol-Metanol (%wt)
1	50.73 - 42.47 - 6.80
2	42.51 - 37.26 - 20.23
3	37.11 - 33.09 - 29.80
4	31.52 - 28.53 - 39.95
5	25.84 - 14.34 - 59.83

After the blends were prepared, the LLE experiments were performed onshaking incubation equipment (Lab Shaking Incubator-GEMMYCO model IN-666) at 45 °C ± 0.1 °C, 1 atm pressure and 300 rpm for 3 hours. Then, the blends were kept in the equipment for 16 hours to allow the formation of two phases.For each system, the samples were taken using 50 mL syringes adapted to 6 cm needles, prior depressurizing of containers. An aliquot of the light and heavy phases was extracted and recorded to avoid alcohol evaporation.Then, the samples were injected into Petri dishes and taken to a forced convection oven (EscoIsotherm, model OFA 32) at 75 °C for 24 hours to evaporate the methanol present. The mass fraction of methanol was obtained from the ratio between the weight of the evaporated methanol and the initial weight of the samples; the amount of glycerol present in the biodiesel + glycerol mixtures was quantified by gas chromatography using a flame ionization detector.

Analysis of data obtained and adjustment of thermodynamic models

The data analysis was carried out using the free softwareProSim Ternary Diagram ®to obtain the distribution lines. The parameters of UNIQUAC and NRTL models were estimated by non-linear regression. The NRTL model presented three ($A_{ij}, B_{ij}, \alpha_{ij}$) for each binary pair, two interaction energy parameters (τ_{ij}, τ_{ji}) and anon-randomness parameterα_{ij}. For UNIQUAC model, two binary parameters were estimated (τ_{ij}, τ_{ij})by the binary interaction parameters (A_{ij}, B_{ij}), whereA_{ij} is a dimensional andB_{ij} has absolute temperature units[12]. Biodiesel was considered a pseudo-component and the methyl linoleate was taken as representativeethyl ester, due to it proved to be the methyl ester in the highest concentration in the biodiesel (40.62% wt)[11].

Results and discussion

Physicochemical characterization of crude and refined oil

The density value obtained for crude and refined oil did not present significant variation, being 884.16 and 882.23 g/cm^3, respectively; while acidity decreased from 9.1 to 6.3 %[13],however, high acidity justified esterification to reduce the FFAs content to guarantee the ideal conditions for the biodiesel production. Finally, the color light yellow of the refined oilproves the separation of gums and impurities, which might help to avoid the formation of soaps that tend to difficult biodiesel and glycerol separation.Table 2 shows the physicochemical properties of oil compared with some data reported in the literature. These variations may occur due to the *J. curcas*variety, which are toxic, non-toxic, African, American and some coming from a genetic modification process.Based on density and viscosity values is possible to infer a good trend in biodiesel properties, since the respective values are within the values reported in the literature[14].

Table 2. Physicochemical properties of *Jatropha curcas*crude oil

Property	Authors	Adapted from Okullo et al., (2012)[15]	Adapted from Parawira (2010)[16]	Adapted fromAchten et al., (2008)[17]
Color	Light yellow	-	Light yellow	-
Density (kg/m^3	884.16	910±2.64	920	860 - 933
Kinematic viscosity (mm^2/s)	34.28±0.36	33.86±1.92	37 - 39	37.00 - 54.80
Free Fatty Acids (%wt)	1.82	1.70±0.46	1.8	0.18 - 3.40
Saponification Index (KOH/g)	192.6±0.36	-	190 - 199	182.8
Cloud Point (°C)	1.7	2±0.21	-	2

Lipid profile of crude oil

Table 3 shows that fatty acid (FA) composition differ slightlyrespect somevalues reported in the literature,possibly due to differences in the climatic and soil conditions[18]. The high percentage of unsaturated FAs (85.62 %) indicates that the oil is suitable for biodiesel production because of their presence favors the conversion efficiency and can improve the properties such as decrease of cold filterobstruction[19].

Table 3. Fatty acid composition of *Jatropha curcas*crude oil

Fattyacids	Structure	Authors (%wt)	Adapted from Silva et al. (2013)[11] (%wt)
Myristic	14:0	0.1153	0.38
Palmitic	16:0	14.2566	12.82
Palmitoleic	16:1	0.6827	3.14
Stearic	18:0	0.0000	4.75
Oleic	18:1	38.0072	43.13
Linoleic	18:2	38.8222	35.27
Linolenic	18:3	8.1160	0.34
Arachidonic	20:0	0.0000	0.16

Obtaining and characterization of *Jatropha curcas* biodiesel

The profile of methylesterswas determined by gas chromatography following the protocol of AOAC method 969.63. According to Table 4, it is possible to state that biodiesel obtained has good flow properties, since it is composed of 80 % of methyl esters of unsaturated FA, with linoleic and oleic acids being present in greater quantity, which coincides with reported in literature.

Table 4. Composition of methyl ethyl esters of *Jatropha curcas* biodiesel

FAME	Authors (% wt)	Adapted from Berchmans and Hirata (2008)[20]	Adapted fromPedraza and Cayón (2010)[21]
Lauric acid	0.00	0.06	0.10
Capric acid	0.11	0.00	0.00
Myristic acid	0.01	0.10	0.10
Palmitoleic acid	0.82	1.10	0.70
Palmitic acid	14.40	14.96	13.50
Heptadecanoic acid	0.09	0.00	0.10
Linoleic acid	40.62	47.43	43.20
Stearic acid	7.46	3.85	7.40
Oleic acid	36.01	32.49	33.20
Gamma-linoleic acid	0.06	0.00	0.20
Arachidic acid	0.08	0.00	0.20
Marginic acid	0.21	0.00	0.20

Table 5 shows the physicochemical parameters that biofuel must have for its use and commercializationcompared to those reported by international standards and some researches.The viscosity value obtained is within the limits reported by ASTM D6751 and presents similar values to those reported by literature, with a relative difference lower than 9.5 %, which may possibly be influenced by the maturation stage of the fruit[22]. The fact that density is within the range of values reported by the European standard EN-14214 guarantees an optimum energy content for the biofuel, preventing that solidifies at temperatures around 25 °C[14]. On the other hand, the estimated value of the cetane index is located above the minimum limit established by the standards, so would expect to have lower emissions of NOx and a high ignition quality of the biodiesel. Finally, acidity index obtained was under than the limit allowed by standard EN-1421, possibly due to the purification processes employed and the chemical composition of the oil.

Table 5. Physicochemical properties of *Jatropha curcas* biodiesel

Property	**Authors**	**Adapted from Da Silva Araújo et al., (2014)[23]**	**Adapted fromOkullo et al., (2012)[15]**	**EN-14214**	**ASTM D6751**
Viscosity (cSt)	4.75	4.54	5.25	3.5-5	1.9-6
Density (g/cm^3)	873.75	875.90	871	860-900	-
Cetane Index	62.65	53.00	58.20	51 min	47 min
Acidity index (mg KOH/ g)	0.382	0.278	0.480	0.50 max	-
Total Glycerin (% mass)	0.045	0.098	-	0.25 max	0.24 max

Analysis of concentrations at equilibrium

The overall compositions for biodiesel+glycerol+methanol system are presented in Table 6.It can be deduced that glycerol+biodiesel are partially soluble to each other; however, the mixtures biodiesel+methanol and glycerol+methanol are completely miscible with each other. On the other hand, the relative distribution of methanol is higher in the glycerol phase than in the biodiesel phase and the solubility of FAME in the glycerol rich phase is slightly higher than glycerol in the FAME phase, behaviors similar to those reported by Silva et al., (2013)[11] and Oliveira et al., (2011)[24].

Table 6. LLE data for the system of *Jatropha curcas*biodiesel (A) + glycerol (B) + methanol (C) at T = (45 ± 0.2) °C and 1 atm

Number of experiment	**Biodiesel RichPhase**			**GlycerolRichPhase**			K_d	**S**
	A	**B**	**C**	**A**	**B**	**C**		
1	0.9827	0.0003	0.0171	0.0006	0.8556	0.1438	8.4273	13356.88
2	0.9630	0.0004	0.0366	0.0027	0.6762	0.3212	8.7701	3151.33
3	0.9476	0.0005	0.0519	0.0085	0.5215	0.4700	9.0508	1006.66
4	0.9349	0.0005	0.0646	0.0220	0.3857	0.5923	9.1629	389.19
5	0.9179	0.0005	0.0816	0.0708	0.2106	0.7186	8.8036	114.19

Values for the methanol distribution coefficient $K_d$was determined as the ratio between the methanol mass fraction in the glycerol and biodiesel phases. The fact that these values are greater than unity indicates that the glycerol phase is richer in alcohol than that methyl esters[11].Solvent selectivity (S) was calculated from Equation 2, wherew_1^{I} andw_1^{II} represent the biodiesel fraction in the rich phase in biodiesel and glycerol, respectively. In this system, glycerol can be considered as a solvent capable of extracting the methanol from the biodiesel phase, in this way, the selectivity reflects its efficiency in the methanol recovery from the lipophilic phase.

$$S=(K_d)\,\frac{w_1^{I}}{w_1^{II}} \qquad (2)$$

Figure 1 shows the distribution diagram for methanol in biodiesel + methanol + glycerol system, based on the mass fraction in the glycerol (w^G) and biodiesel (w^B) phase reported in Table 6. Although the results obtained experimentally and those reported by Silva et al., (2013)[11]have a similar trend, the graphs differ slightly.

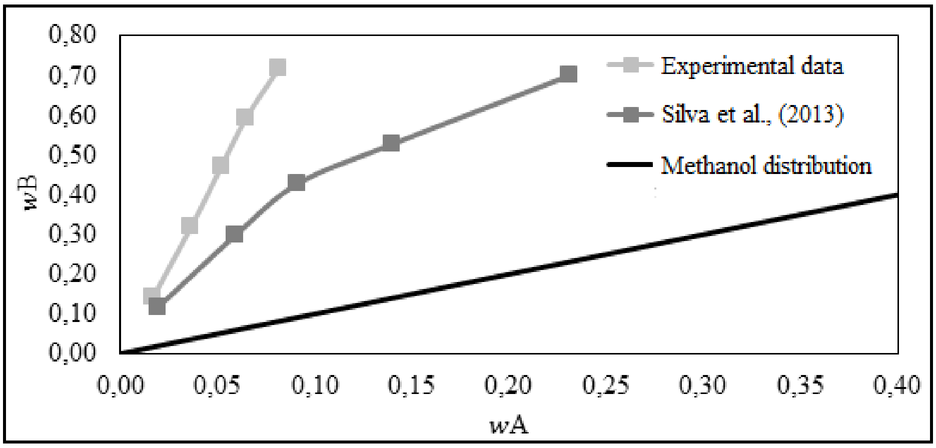


Figure 1. Representation of the methanol distribution coefficient

The black line represents the mutual solubility of methanol in the glycerol and biodiesel phase, based on the fact that the alcohol is distributed equally on both phases. The line representing the experimental data indicates a greater distribution of the alcohol in the glycerol phase compared to the one obtained by Silva et al., (2013)[11], which facilitates the separation process of the heavy phase. In the other hand, Figure 2 presents the ternary diagram for the equilibrium system, along with the distribution lines.

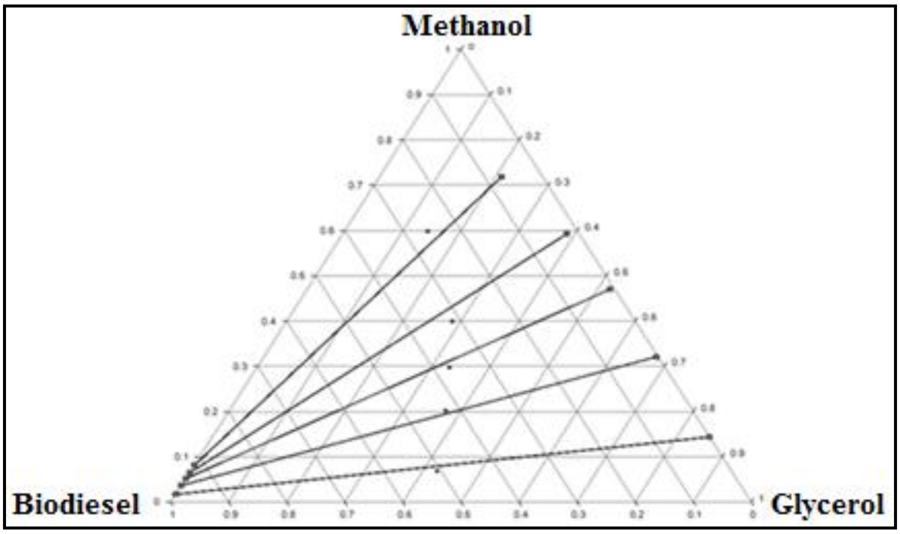


Figure 2. Ternary diagram for the *Jatropha curcas* biodiesel + methanol + glycerol system at T = 45 ° C

The consistency of the ELL experimental data was evaluated using the Othmer-Tobias correlation[25]given by Equation 3, wherew_A represents the biodiesel mass fraction in the biodiesel rich phase,w_B corresponds to the glycerol fraction in the glycerol rich phase,*a* and*b*are the angular and linear coefficients respectively.

$$\ln\left(\frac{1\text{-}w_A}{w_A}\right)=b\ln\left(\frac{1\text{-}w_B}{w_B}\right)+a \qquad (3)$$

Figure 3 shows the Othmer-Tobias diagramfor the ternary mixture at 45 °C, where the quality, reliability and consistency of the results is reflected in the approximation of the correlation factor to the unit ($R^2 = 0.9597$). Positive values of parameter *b* indicate an increase of w_A whenw_B increase, which is observed in the bonding lines of the ternary diagram showing a tendency for ternary mixtures to be separated into two phases, one rich in biodiesel and one in glycerol. The values obtained show that the selectivity of glycerol was high and in most cases above 100. However, this decreases with increasing methanol fraction in the biodiesel phase, due to higher amounts of methanol increase the mutual solubility of the glycerol and biodiesel in the rich phase[26.]

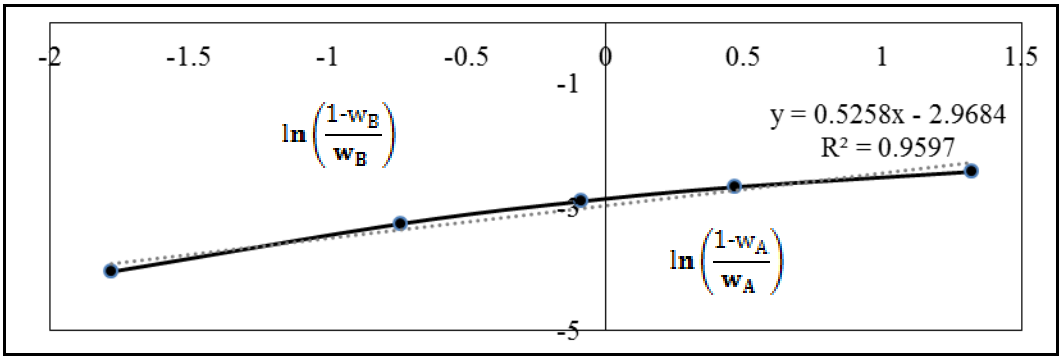


Figure 3. Othmer-Tobias diagram for *Jatropha curcas* biodiesel (A) + glycerol (B) +methanol (C) system at 45 °C and 1 atm

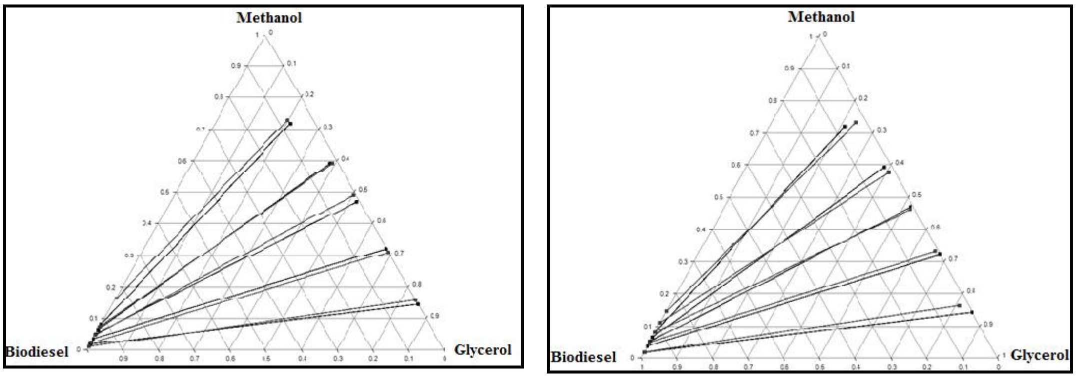
Adjustment and validation of parameters for thermodynamic models

Table 7 shows the binary interaction parameters obtained for the UNIQUAC and NRTL models, which are similar to those reported in literature[11, 27].

Table 7. Binary interaction parameters from the UNIQUAC and NRTL models to represent the biodiesel (A) + glycerol (B) + methanol (C)

	Binarypairij	A_{ij}	A_{ji}	B_{ij}	B_{ji}	
UNIQUAC	A/B	-2.5614	-0.1293	69.6944	-14.0108	
	A/C	-0.7451	0.0781	0.0000	0.0000	
	B/C	2.1837	-1.3823	-47.6493	-100.4220	
NRTL	**Binarypairij**	A_{ij}	A_{ji}	B_{ij}	B_{ji}	α_{ij}
	A/B	9.5127	14.2333	0	0	0.3
	A/C	-0.7665	4.9215	0	0	0.3
	B/C	-1.5673	3.6090	-218.522	547.83	0.3

The adjusted parameters were validated bypredicting and comparing the ELL of the analyzed system at 45 °C with the data calculated by the software. Figure 4 shows the phase diagrams for the ternary system using the UNIQUAC and NRTL models.It can be observed that thermodynamic models fitted the experimental data, so it was calculated the sum quadratics error (SCE), where was obtained a value of 0.0164 and 0.0216, respectively.Comparing these results with the one(0.0592) reported by Silva et al., (2013)[11], it is observed a discrepancy possibly due to the difference in the components distribution in the light and heavy phase or to the possible evaporation of the methanol at the moment of the extraction in each phase.



(b)

(a)

Figure 4. Prediction of the thermodynamic model a) UNIQUAC, b) NRTL for the ELL of biodiesel + glycerol + methanol system at 45 °C and 1 atm

With the adjusted parameters, comparisons were made between the calculated and experimental compositions of the two phases involved in the system using the root mean square deviation (RMSD) or mean percentage deviation (Δx), expressed by Equation 4; where, x_{ij}^{exp} and x_{ij}^{cal} represent the experimental and calculated mass fraction of each component; I, II the liquid phases in equilibrium; N indicates the number of connecting lines and M the number of system components.The RMS values for the UNIQUAC and NRTL models were 2.2901 % and 2.3827 %, respectively, while, Silva et al., (2013)[11] reported a RMS of 3.6880 %.

$$RMSD=\Delta x=100\sqrt{\frac{\sum_i^M \sum_j^{N-1} (x_{ij}^{I\,exp}-x_{ij}^{I\,cal})^2-(x_{ij}^{II\,exp}-x_{ij}^{II\,cal})^2}{2NM}} \quad (4)$$

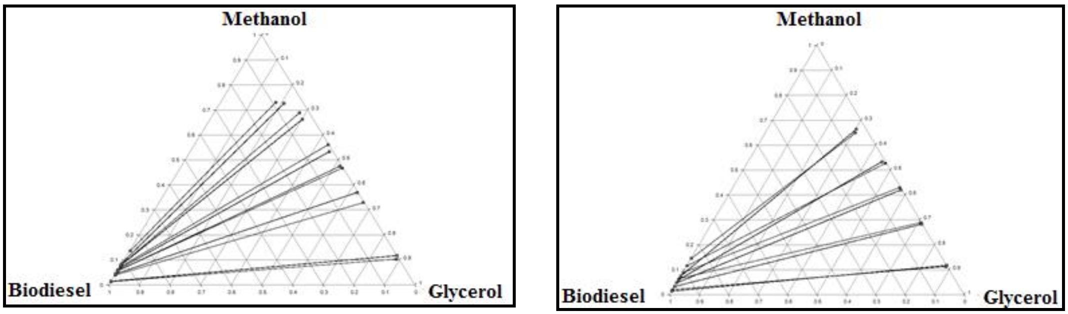
Simulation of thermodynamic behavior of the ternary system at 30 °C,60 °C and 1 atm

Table 8 presents the data for the thermodynamic behavior of system evaluated at 30 °C and 60 °C± 0.2 °C and 1 atm, based on the parameters obtained with the UNIQUAC model.

Table 8.LLE data for the ternary system biodiesel + glycerol + methanol at 30 °C and 60 °C ± 0.2 ° C

T (°C)	Rich Biodiesel Phase			Rich Glicerol Phase				
	A	B	C	A	B	C	K_d	S
30	0.9852	0.0002	0.0144	0.0004	0.8824	0.1171	8.1319	20028.9792
	0.9556	0.0004	0.0439	0.0035	0.6262	0.3701	8.4305	2301.7739
	0.9441	0.0004	0.0554	0.0079	0.5177	0.4743	8.5614	1023.1381
	0.9375	0.0005	0.0620	0.0123	0.4541	0.5334	8.6032	655.7337
	0.9215	0.0005	0.0779	0.0349	0.3016	0.6634	8.5160	224.8578
	0.9110	0.0005	0.0884	0.0644	0.2095	0.7259	8.2115	116.1601
60	0.9859	0.0003	0.0138	0.0005	0.8821	0.1174	8.4880	18289.7684
	0.9672	0.0003	0.0325	0.0018	0.7151	0.2832	8.7147	4724.0217
	0.9524	0.0004	0.0471	0.0052	0.5748	0.4201	8.9111	1646.6390
	0.9404	0.0005	0.0592	0.0122	0.4544	0.5334	9.0175	697.7842
	0.9252	0.0005	0.0743	0.0341	0.3023	0.6636	8.9261	242.3255

Figure 5 shows the ELL diagrams for the ternary system obtained by simulation at temperatures of 30 °C and 60 °C.



(a) **(b)**

Figure 5. Ternary diagram of the ELL data obtained by the simulation for the biodiesel + glycerol + methanol system at a) 30 ° C and b) 60 ° C

It is observed that the temperature influence on the mutual solubilities of the system was practically insignificant, similar behavior to the one reported by Oliveira et al., (2011)[24]. On the other hand, the results at 30 and 60 °C showed a similar trend for ELL experiments, which is reflected in the alcohol distribution, mainly in the glycerol rich phase. As reported by Gutierrez (2008)[28], the value of the distribution coefficient depends on the temperature. In this sense, Figure 6 shows that,an increase in the equilibrium temperature produces an increase in the methanol distribution coefficients because of at higher temperatures the translational energy of the glycerol-methanol molecules decreases the effect of the hydrogen bonds.

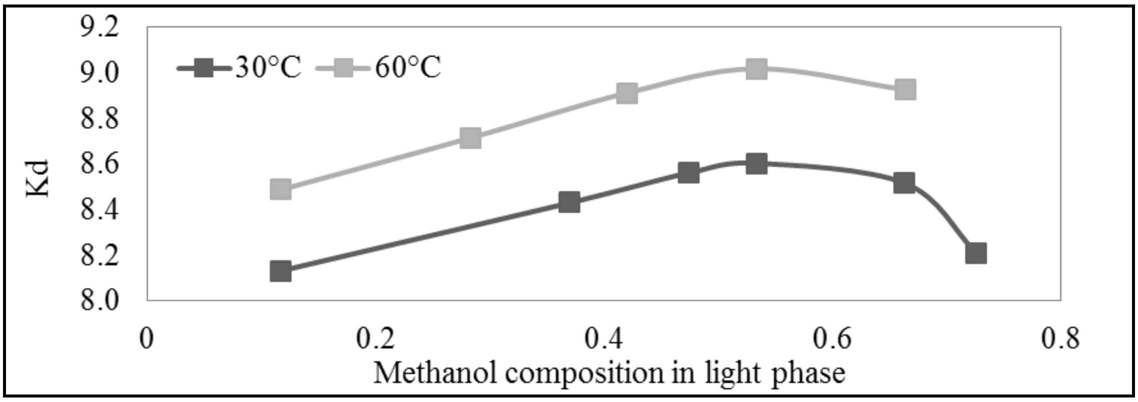


Figure 6. Representation of the methanol distribution coefficient at 30 °C and 60°C

Conclusions

The ELL experiments of the ternary system biodiesel + glycerol + methanol were carried out, obtaining reliable results and experimental distribution lines, verified through the Othmer-Tobias correlation (R^2= 0.9597). By adjusting parameters obtained from experimental data, it was demonstrated that the thermodynamic models UNIQUAC and NRTL are suitable for predicting the phase equilibrium of the ternary system with values below 2.3 % in the root of the mean square deviation.In addition, it was determined that two pairs are soluble (biodiesel-methanol and glycerol-methanol) and one is partially miscible (biodiesel-glycerol).Finally, a successful prediction of the phase equilibrium for the ternary systemat 30 °C and 60 °C was performed using the UNIQUAC model, demonstrating the validity of the adjusted model and showing its possible use as a thermodynamic model for the analyzed system at different temperature conditions, representing a suitable tool for the simulation of the separation and purification processes of biodiesel in further studies.

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