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Liquid–liquid equilibria for the canola oil biodiesel + ethanol + glycerol system

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ABSTRACT

The knowledge and accurate description of the phase equilibria of systems containing transesterification products are essential for a correct operation and optimization of the biodiesel production and purification units.

To overcome the lack of phase equilibria information concerning systems from the transesterification reaction with ethanol, in this work, liquid–liquid equilibria data, tie-lines and phase boundaries, have been measured for the ternary system canola oil biodiesel + ethanol + glycerol at temperatures between 303.15 and 333.15 K.

Following previous successful applications to other biodiesel systems, the Cubic-Plus-Association (CPA) equation of state was also applied here to predict the experimental data, using previously established interaction parameters, with average deviations inferior to 3%.

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1. Introduction

Biodiesel is nowadays seen as one of the most worthy alternatives to conventional fossil fuels. It is generally accepted that the available fossil fuel reserves will only last for a few more decades instigating the search for reliable alternatives. In addition, most of the accessible petroleum fuel comes from politically instable countries raising the uncertainty of its availability and price [1–3].

The use of renewable energy sources, such as biodiesel, can also decrease greenhouse gases and emissions of other air contaminants contributing to reduce the global warming problem [4,5].

Biodiesel, a blend of fatty acid alkyl esters, is industrially produced by transesterification, that is, a reaction of an oil or a fat with an alcohol to produce fatty acid esters and glycerol [6]. An excess of alcohol is used to shift the reaction towards the formation of products [5] and an alkaline catalyst is required in order to increase reaction speed and yield [7].

Methanol is the most commonly used alcohol due to its low cost and physical and chemical advantages in the process [5,8]. However, ethanol can prevail in regions where it is easily produced and available [9]. Its use can be more advantageous than the use of methanol, since it has a superior dissolving capability and is less toxic [8,10]. There are also other advantages of using ethyl ester

based biodiesel over methyl esters. Due to the extra carbon added, fatty acid ethyl esters have a higher heat content and cetane number and improved storage properties, as a result of lower cloud and pour points [11–13]. The use of biodiesel composed of fatty acid ethyl esters is also more environmentally friendly due to lower emissions of nitrogen oxides and carbon monoxide [8]. Additionally, as most of the available methanol is derived from natural gas or from coal via synthesis gas, biodiesel produced from methanol cannot be considered entirely carbon–neutral as happens with the ethyl ester biodiesel that is totally derived from agricultural sources [14,15].

The production of biodiesel by an alkaline catalyzed reaction takes place in a multiphase reactor where the oil reacts with an alcohol, in presence of a catalyst, to form fatty acid esters and glycerol [16]. The glycerol formed separates from the oil phase and at the outlet of the reactor two liquid phases co-exist: one of them rich in glycerol and the other in fatty acid esters. The unreacted alcohol is distributed between these two liquid phases [6].

An adequate description of the distribution of the transesterification products between the two immiscible phases, in a broad range of thermodynamic conditions, is essential for a correct study and design of the equipment involved on the production and purification of biodiesel. However, the presence of polar compounds with strong associative interactions increases the complexity of these systems, hindering the use of conventional thermodynamic models. In addition, there is still a considerable lack of experimental equilibria data for the two phases formed at the transesterification

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Nomenclature

Abbreviations

AD	average deviation
AOCS	American Oil Chemists' Society
CPA	Cubic-Plus-Association
EoS	equation of state
DIPPR	Design Institute for Physical Property Data
FAEE	fatty acid ethyl ester
GC	gas chromatography
LLE	liquid–liquid equilibrium
SRK	Soave–Redlich–Kwong

Symbols

a	energy parameter in the physical term of the CPA EoS ($J\,m^3\,mol^{-2}$)
a_0	parameter for calculating a ($J\,m^3\,mol^{-2}$)
A_i	site A in molecule i
b	co-volume parameter in the physical term of the CPA EoS ($m^3\,mol^{-1}$)
g	radial distribution function
k_{ij}	binary interaction parameter
n	tie line number in Eq. (11)
N	total number of tie lines in Eq. (24)
P	vapor pressure (Pa)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
R	total number of components in Eq. (11)
T	temperature (K)
x	mole fraction

X_{Ai}	fraction of molecule i not bonded at site A
w	mass fraction
Z	compressibility factor

Greek symbols

β	association volume in the association part of the CPA EoS
Δ^{AiBj}	association strength between site A in molecule i and site B in molecule j in the association part of the CPA EoS ($m^3\,mol^{-1}$)
ε	association energy in the association part of the CPA EoS ($J\,mol^{-1}$)
η	reduced fluid density

Subscripts

c	critical
i,j	pure component indexes
r	reduced

Superscripts

assoc.	association
calcd	calculated
exptl	experimental
EP	ester rich phase
GP	glycerol rich phase
phys.	physical

reactor, especially when using ethanol in the production process, hampering the development of thermodynamic models.

Recently, the Cubic-Plus-Association equation of state (CPA EoS) was successfully applied to model the liquid–liquid equilibria of systems containing transesterification products. Ternary and quaternary systems composed of fatty acid methyl esters, alcohols, glycerol and alkanes, in a broad temperature range were considered [17].

In this work, with the purpose of increasing the available data concerning systems from the transesterification reaction with ethanol, new measurements were carried out at three different temperatures for the ternary system canola oil ethyl ester biodiesel + ethanol + glycerol.

Taking advantage of the excellent extrapolation and predictive performance of the CPA EoS, the model pure compound and binary interaction parameters previously used to describe biodiesel multicomponent systems [17], were also applied here to successfully predict the new experimental data.

2. Experimental

2.1. Chemicals

Ethanol (from QHEMIS, ⩾99.3%), glycerol (from Fmaia, ⩾99.5%) and refined canola oil (from BUNGUE).

The composition of the oil with regard to fatty acid content was determined by gas chromatography (GC) using the AOCS official method [18] Ce 1-62 and Ce 2-26.

The canola oil fatty acid composition is reported in Table 1.

Canola oil based ethyl ester biodiesel was prepared by the transesterification of the canola oil with ethanol using sodium hydroxide (NaOH) as the catalyst. The amount of NaOH used was 1.5 wt% of the oil. Oil and ethanol with a mole ratio of 1:10 reacted at 323.15 K for 90 min.

Table 1
Canola oil fatty acid composition.

Fatty acid		% mass
Myristic	C14:0	0.14
Palmitic	C16:0	4.98
Palmitoleic	C16:1	0.32
Stearic	C18:0	2.14
Oleic	C18:1	60.86
Linoleic	C18:2	22.42
Linolenic	C18:3	8.11
Arachidic	C20:0	0.88
Others		0.15

Fatty acid ethyl esters (FAEEs) obtained from the transesterification reactions were analyzed by gas chromatography using a Varian (USA) model CX 3400 instrument equipped with a Varian VF-1 ms non-polar dimethylpolysiloxane capillary column (2.2 m × 0.32 mm i.d.) and a flame ionization detector (FID) operated at 250 °C. The capillary injection system was maintained at 240 °C, the split ratio was 100:1, the sample size was 1 μL and the carrier gas was high-purity hydrogen. The temperature program applied to the column was: initial temperature 50 °C held for 1 min, then raised to 180 °C at 15 °C/min, to 230 °C at 7 °C/min, and finally to 340 °C at 30 °C/min. The total analytical run time was 20 min.

In order to determine the yield of biodiesel (in terms of percentage of FAEEs) obtained by transesterification, a ∼0.15 g sample of the dried reaction product was weighed accurately into a vial and 1.0 mL of a solution of the internal standard, tricaprylin in n-hexane (0.100 g/100 mL) was added. Aliquots of the mixture were analyzed by GC as outlined above, and the peak areas of the separated components determined. Each experiment was performed in duplicate and each sample was assayed as the average of two injections.

The transesterification reaction of canola oil was obtained with a yield of 100% in biodiesel. The products were washed with a diluted solution of sulfuric acid. After settling, the upper ester layer was collected and washed several times with deionized water until the FAEEs phase was free of ethanol and catalyst. Finally, the biodiesel was dried with anhydrous magnesium sulfate.

2.2. Saturation curve of the canola oil biodiesel + ethanol + glycerol system

Phase boundaries at 303.15, 318.15 and 333.15 K were determined by turbidimetric analysis using the titration method under isothermal conditions. The equilibrium flask was immersed in a constant-temperature water bath (Model T-184) equipped with a temperature controller that was capable of maintaining the temperature within a fluctuation of ±0.2 K.

For the biodiesel rich phase, a known mass of biodiesel and ethanol where added to the flask and titrated with glycerol, while stirring with a mechanical agitator, until the mixture changed from transparent to turbid. This point is considered as the saturation point of glycerol in the biodiesel + ethanol mixture.

In the case of the glycerol rich phase, a mixture of glycerol and ethanol was titrated with biodiesel until the cloud point was visible.

Knowing the volumes of glycerol or biodiesel used in the titrations, the corresponding solubility curve was calculated by the amount of each component added.

2.3. Tie-lines of the canola oil biodiesel + ethanol + glycerol system

For the tie-line determination, compositions in the two phase region were selected keeping the molar relation between glycerol and biodiesel constant and changing the ethanol proportion.

The two immiscible components, glycerol and biodiesel, were added to the equilibrium vessel at a specific molar ratio and different amounts of ethanol were added to obtain the different global phase compositions for measuring a series of tie-lines. The mixture was stirred vigorously with a magnetic stirrer and left to rest for 12 h. This led to the formation of two phases with a well defined interface, and finally, samples of the phases were carefully collected for subsequent quantification of the components.

According to the phase rule, at a fixed temperature and pressure, only one component can independently change its composition. The mixture composition is determined identifying in the binodal curves previously measured, the point which represents the composition of the specified component. Ethanol was quantified from the amount removed by evaporation. For each sample and for each phase, at least three individual measurements were performed, with an average uncertainty within 1 wt%.

On the basis of the total system mass and of the phase and overall compositions, the mass balances were also checked.

3. Thermodynamic modeling

The use of association equations of state that explicitly take into account specific interactions between like (self-association) and unlike (cross-association) molecules was the step forward in the modeling of polar and highly non ideal systems in wide ranges of temperature and pressure. One of the most successful models of this kind, considering its accuracy and simplicity, is the Cubic-Plus-Association (CPA) equation of state.

It can be expressed as the sum of the SRK EoS, to describe the physical interactions, and the Wertheim association term, to describe association interactions [19–22]:

$$Z = Z^{phys.} + Z^{assoc.}$$
$$= \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{Ai}) \quad (1)$$

where a is the energy parameter, b the co-volume parameter, ρ is the molar density, g a simplified hard-sphere radial distribution function, X_{Ai} the mole fraction of pure component i not bonded at site A, and x_i is the mole fraction of component i.

The pure component energy parameter, a, is obtained from a Soave-type temperature dependency:

$$a(T) = a_0\left[1 + c_1\left(1 - \sqrt{T_r}\right)\right]^2 \quad (2)$$

When CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (3)$$

$$b = \sum_i x_i b_i \quad (4)$$

X_{Ai} is related to the association strength $\Delta^{A_iB_j}$ between sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{Ai} = \frac{1}{1 + \rho\sum_j x_j \sum_{Bj} \Delta^{A_iB_j}} \quad (5)$$

where

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right]b_{ij}\beta^{A_iB_j} \quad (6)$$

where ε^{AiBj} and β^{AiBj} are the association energy and the association volume, respectively.

The simplified radial distribution function, $g(\rho)$, is given by [23]:

Table 2
Binodal curves for the system canola oil biodiesel (1) + ethanol (2) + glycerol (3).

w_1	w_2	w_3
303.15 K		
0.068	0.602	0.330
0.153	0.609	0.238
0.242	0.562	0.196
0.337	0.516	0.147
0.447	0.447	0.106
0.562	0.374	0.064
0.684	0.293	0.023
0.781	0.196	0.023
0.887	0.098	0.015
318.15 K		
0.070	0.623	0.307
0.157	0.624	0.219
0.248	0.573	0.179
0.344	0.514	0.142
0.442	0.442	0.116
0.552	0.368	0.08
0.667	0.287	0.046
333.15 K		
0.061	0.547	0.392
0.130	0.561	0.309
0.232	0.531	0.237
0.316	0.491	0.193
0.418	0.439	0.143
0.562	0.352	0.086
0.657	0.287	0.056
0.717	0.246	0.037
0.877	0.108	0.015

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \text{where} \quad \eta = \frac{1}{4}b\rho \tag{7}$$

For non-associating components CPA has only the three pure component parameters, the ones of the cubic term (a_0, c_1 and b), while for associating components it has two additional parameters from the association term (ε and β). In both cases, these parameters are regressed simultaneously from vapor pressure and liquid density data, minimizing the following objective function:

$$\text{OF} = \sum_i^{NP} \left(\frac{P_i^{\exp} - P_i^{calc}}{P_i^{\exp}} \right)^2 + \sum_i^{NP} \left(\frac{\rho_i^{\exp} - \rho_i^{calc}}{\rho_i^{\exp}} \right)^2 \tag{8}$$

For a binary mixture composed solely by non-associating compounds, the binary interaction parameter, k_{ij} (Eq. (3)), is the only adjustable parameter.

When CPA is employed to mixtures containing two self-associating compounds, combining rules for the association term are required [24,25]. In this work, the Elliott Combining Rule (ECR) [25] is used:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \tag{9}$$

To consider systems containing self-associating and non self-associating compounds that can solvate with the associating compound, as in the case of ester + self-associating compound mixtures, the cross-association energy ($\varepsilon^{A_i B_j}$) is considered to be half

Table 3
Tie line data for the system canola oil biodiesel (1) + ethanol (2) + glycerol (3) at 303.15 K.

Biodiesel rich phase			Glycerol rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.821	0.162	0.017	0.024	0.557	0.419
0.828	0.155	0.017	0.013	0.483	0.504
0.883	0.104	0.013	0.010	0.388	0.602
0.918	0.066	0.016	0.009	0.266	0.726
0.964	0.026	0.010	0.014	0.118	0.867

the value of the association energy for the self-associating component and the cross-association volume ($\beta^{A_i B_j}$) is left as an adjustable parameter, fitted to equilibria data. This approach proposed by Folas et al. [26] was successfully applied to describe the LLE of systems such as methyl oleate + methanol + glycerol and methyl laurate/myristate/stearate + ethanol + glycerol [17].

For estimating the k_{ij} and $\beta^{A_i B_j}$ parameters the following objective function was minimized:

$$\text{OF} = \sum_i^{NP} \left(\frac{x_i^{calc.} - x_i^{\exp.}}{x_i^{\exp.}} \right)^2 \tag{10}$$

where single phase or all phase data can be selected during the parameter optimization. The association term depends on the number and type of association sites. For alcohols, the two-site (2B) association scheme is applied, which proposes that hydrogen bonding occurs between the hydroxyl hydrogen and one of the lone pairs of electrons from the oxygen atom in another alcohol molecule [27,28]. For the ester family a single association site is considered that can cross-associate with a self-associating molecules [29].

For glycerol an association scheme recently suggested is adopted [30]. It considers the glycerol molecule as having three identical hydroxyl groups, each of them with two association sites ($3 \times B$ scheme).
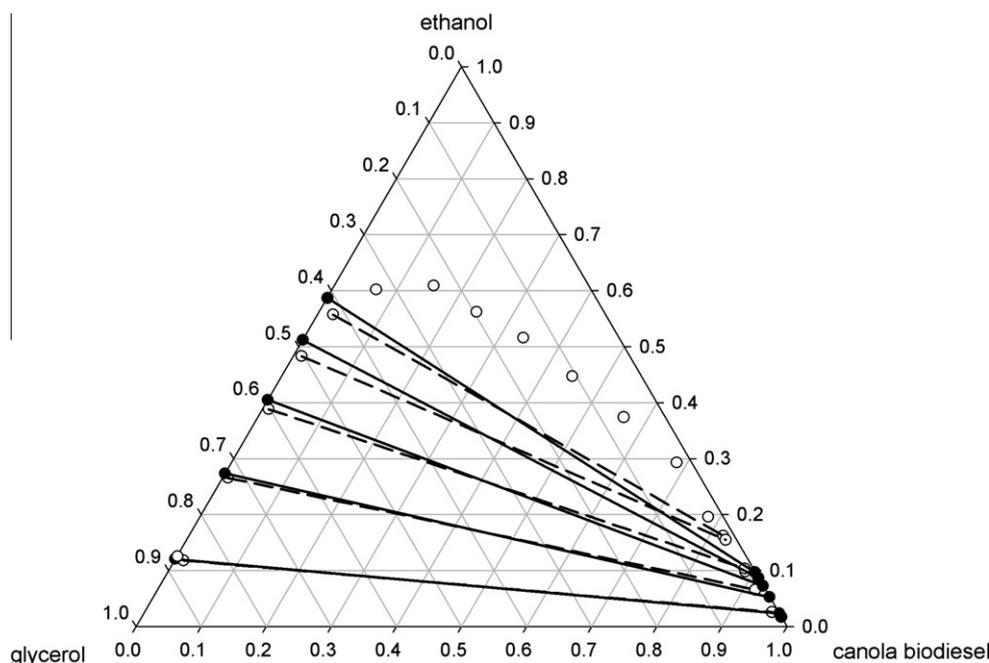
The average deviations (AD) between the experimental compositions and those estimated by the CPA EoS were calculated according to Eq. (11):

$$\text{AD} = \sqrt{ \frac{\sum_n^N \sum_i^R \left[\left(w_{i,n}^{\text{GP,exptl}} - w_{i,n}^{\text{GP,calcd}} \right)^2 + \left(w_{i,n}^{\text{EP,exptl}} - w_{i,n}^{\text{EP,calcd}} \right)^2 \right]}{2N \times R} } \tag{11}$$

where AD is the average deviation for each system, N is the total number of tie lines of the corresponding system, R is the total number of components ($R = 3$), w is the mass fraction, i is the component, the subscript n stands for the tie line number, the superscripts exptl and calcd refer to the experimental and

Fig. 1. LLE for the system canola oil biodiesel + ethanol + glycerol at 303.15 K. Experimental (empty symbols and dashed line) and CPA EoS results using interaction parameters correlated from binary data (full symbols and solid line).

calculated compositions and GP and EP to the glycerol and ester rich phases, respectively.

4. Results and discussion

4.1. Experimental results

Liquid–liquid equilibria data at atmospheric pressure for the canola oil biodiesel + ethanol + glycerol system were measured at 303.15, 318.15 and at 333.15 K. Experimental results for the phase boundaries in the temperature range selected are presented in Table 2 and the tie-line results at 303.15 K in Table 3. Results are also depicted in Figs. 1–4 along with the CPA EoS predictions.

Othmer and Tobias introduced an equation that reproduced the tie-lines in a straight line plotting $((1 - a)/a)$ against $((1 - b)/b)$, being a the mole fraction of canola oil biodiesel in the canola oil biodiesel rich phase and b the glycerol mole fraction in the glycerol rich phase, that can be used to test the reliability of the LLE
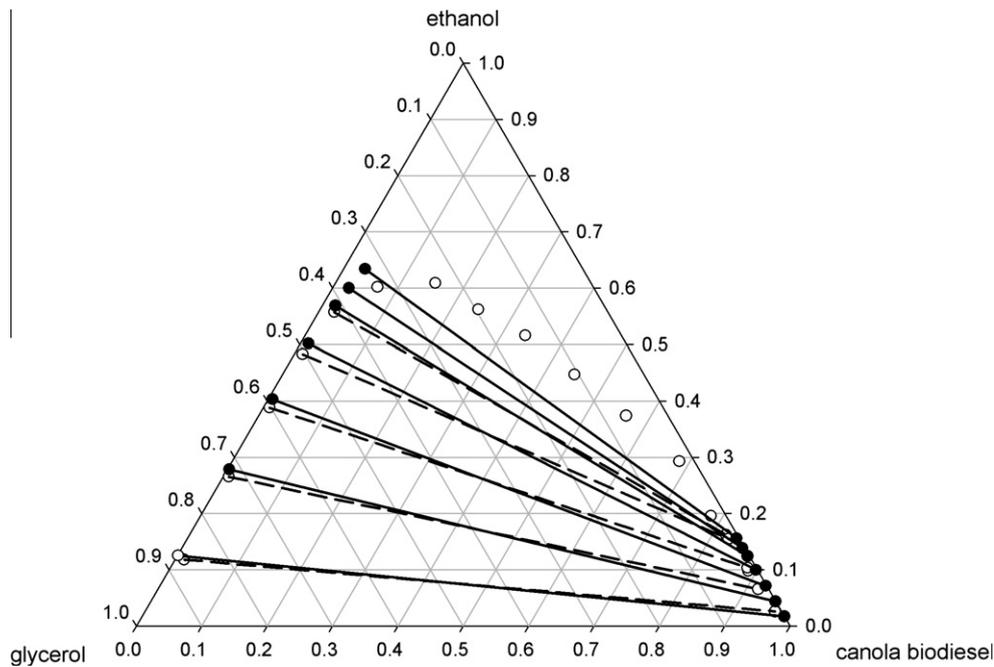

Fig. 2. LLE for the system canola oil biodiesel + ethanol + glycerol at 303.15 K. Experimental (empty symbols and dashed line) and CPA EoS results (full symbols and solid line).
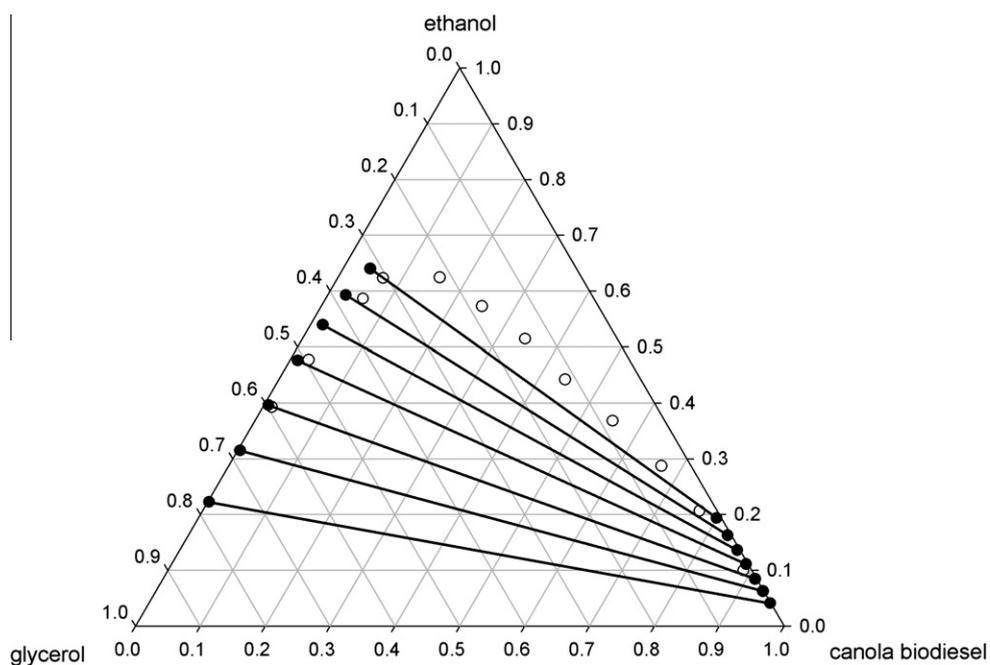

Fig. 3. LLE for the system canola oil biodiesel + ethanol + glycerol at 318.15 K. Experimental (empty symbols) and CPA EoS results (full symbols and solid line).

experimental data of a ternary system [31]. As presented in Fig. 5, the good linear fit with the Othmer–Tobias equation indicates the consistency of the experimental tie-lines and binodal curves.

The tie-lines show, in agreement with previously published data concerning the phase equilibria of the methyl oleate + methanol + glycerol system [32–34], that the glycerol phase is richer in ethanol than the fatty acid ethyl ester phase. From the experimental results it is also possible to see that the biodiesel phase is richer in glycerol than the glycerol phase is in biodiesel.

The temperature influence on the mutual solubilities of the ternary system is insignificant in the temperature range from 303.15 to 318.15 K. At 333.15 K it is observed a small decrease on the immiscibility region.

4.2. Thermodynamic modeling

Following the work by Oliveira et al. [17,29,30,35–38] focused on developing a thermodynamic model to be applied for the evaluation of the design and optimization of biodiesel production processes, the CPA EoS was shown to be the best model to describe complex multicomponent associating systems, such as those considered here, given its accuracy, predictivity and simplicity.

The first step in using the CPA EoS in the description of a multicomponent system is the estimation of the pure compound parameters through a simultaneous regression of vapor pressure and liquid density data. Concerning the self-associating components here involved, namely ethanol and glycerol, their five CPA pure compound parameters were previously determined and applied to model the VLE and LLE of several binary and multicomponent systems [17,30,35,37]. The five CPA parameters for ethanol were previously computed when evaluating the pure compound parameters for the n–alcohol family, from methanol to n–eicosanol [28], and the glycerol CPA parameters calculated while describing the VLE of glycerol binary systems containing alcohols and water [30]. These parameters, presented at Table 4, provided a very good description of pure compound vapor pressures and liquid densities and the LLE of ternary systems constituted of fatty acid methyl esters, ethanol and glycerol in a broad temperature range [17].
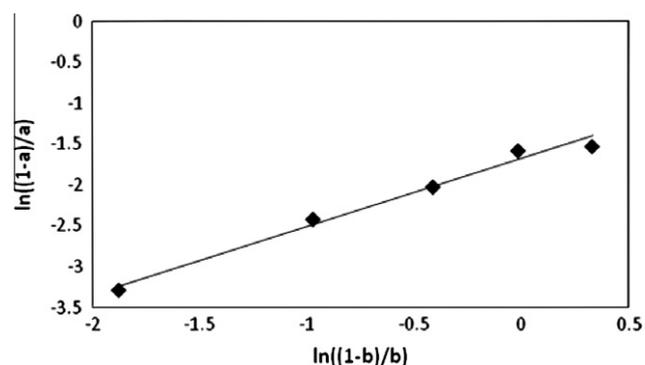

Fig. 5. Othmer–Tobias plot. *a* is the mole fraction of canola oil biodiesel in the canola oil biodiesel rich phase, and *b* is the glycerol mole fraction in the glycerol rich phase.

From the canola oil fatty acid composition, presented at Table 1, the canola oil biodiesel was considered to be constituted by the following ethyl esters: palmitate, stearate, oleate, linoleate and linolenate. As mentioned in the model section, esters are non-self-associating compounds that can solvate with associating components. In a previous work [29], it was shown that the a_0, c_1 and b CPA parameters for esters followed the same trend with the carbon number, for the different ester families considered. Correlations for the estimation of these parameters were then proposed enabling the estimation of the ester CPA pure compound parameters in the absence of liquid density and vapor pressure data, as it is the case of the fatty acid ethyl esters here considered. The critical temperature for the fatty acid esters was computed through the Nikitin et al. [39] group contribution method, previously assessed to be the best model to compute that property for ethyl esters [40]. CPA parameters and critical temperatures for esters are presented at Table 4.

Having the CPA pure compound parameters it was then possible to model the phase equilibria determined experimentally. In a first attempt, k_{ij}'s and β_{ij}'s values previously established when modeling the VLE and the LLE of binary systems composed of fatty esters,
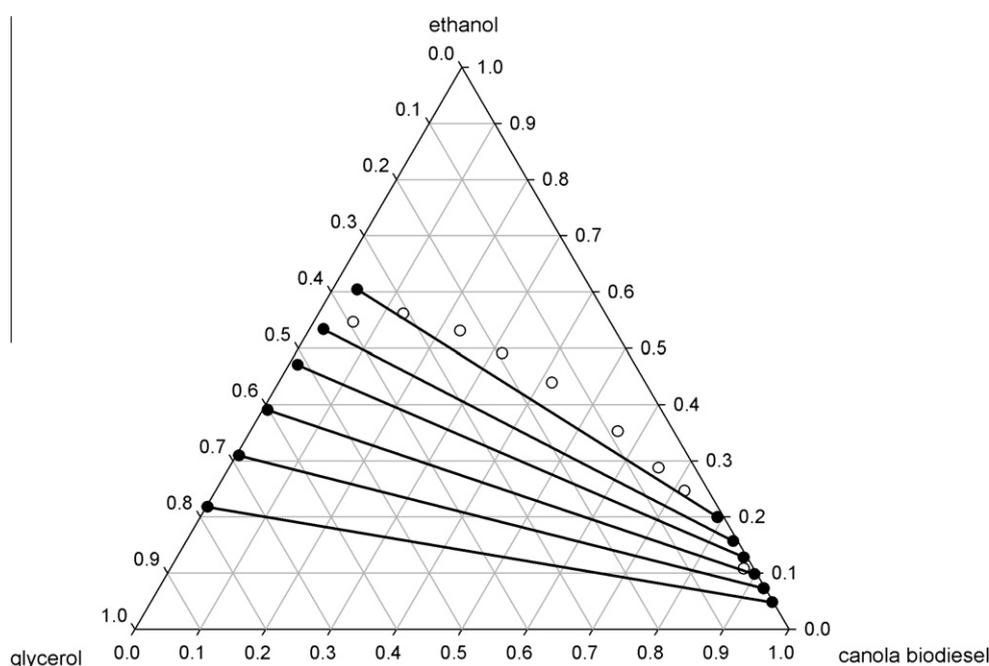

Fig. 4. LLE for the system canola oil biodiesel + ethanol + glycerol at 333.15 K. Experimental (empty symbols) and CPA EoS results (full symbols and solid line).

Table 4
Critical temperatures, CPA pure compound parameters and modeling results for fatty acid esters, ethanol and glycerol.

Compound							AAD%	
	T_c (K)	a_0 (J m^3 mol^{-2})	c_1	$b \times 105$ (m^3 mol^{-1})	ε (J mol^{-1})	β	P^σ	ρ
Glycerol	766.1[a]	1.21	1.06	6.96	19,622	0.009	0.77	1.49
Ethanol	514.7 [a]	0.68	0.94	4.75	21,336	0.019	0.35	0.51
Ethyl palmitate	766.4 [b]	10.80	1.65	33.37				
Ethyl stearate	786.1 [b]	12.09	1.75	37.17				
Ethyl oleate	771.1 [b]	12.09	1.75	37.17				
Ethyl linoleate	785.9 [b]	12.09	1.75	37.17				
Ethyl linolenate	800.7 [b]	12.09	1.75	37.17				

[a] From DIPPR database [41].
[b] From Nikitin et al. group contribution method [39].

glycerol and ethanol were used. For the binary subsystems fatty acid ethyl ester + ethanol the ester carbon number correlation for the k_{ij}'s and a constant value for the β_{ij}'s, previously determined when describing the VLE of fatty acid ester + ethanol systems [35], were used. Binary subsystems fatty acid ethyl ester + glycerol were represented by the k_{ij}'s and β_{ij}'s values obtained for the LLE of the binary system methyl dodecanoate + glycerol, as previously suggested [17]. Finally, the k_{ij} between ethanol and glycerol was taken from the VLE of the referred system [30]. Modeling results are presented in Fig. 1 and in Table 5 at 303.15 K. Table 5 also presents the values for the interaction and cross-association parameters obtained from binary phase equilibria data. Good results are obtained for the glycerol rich phase but the biodiesel phase is poorly predicted. In fact, Oliveira et al. [17], while modeling multicomponent systems of relevance for biodiesel production, have shown that the best approach to regress the binary interaction parameters needed is to use multicomponent data instead of equilibria data of the corresponding binary subsystems. It was however also shown that these parameters were transferable and the LLE of the methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol systems could be successfully predicted using interaction parameters obtained from the tie-line data of the system methyl oleate + methanol + glycerol.

The same approach was subsequently used to study the predictive capability of the CPA EoS and the transferability of the binary parameters to predict the new experimental LLE data for the canola oil biodiesel + ethanol + glycerol system, at the three temperatures selected.

Most values for the interaction parameters used were taken from the tie-line data of the system methyl oleate + methanol + glycerol studied in a previous work [17]. These are the β_{ij}'s values for the binaries fatty acid ester–glycerol/ethanol, the k_{ij} value for the binary glycerol–ethanol and the k_{ij}'s between the unsaturated fatty acid esters and ethanol/glycerol. For the k_{ij} between ethyl palmitate and ethanol the value regressed from the ternary system methyl myristate + ethanol + glycerol [17] was used, and for the k_{ij} between ethyl stearate and ethanol the value regressed

from the ternary system methyl stearate + ethanol + glycerol [17] was used.

The same interaction and cross-association binary parameters were used at the three temperatures studied of 303.15, 318.15 and 333.15 K. Parameter values are presented in Table 5.

An excellent prediction of both the saturation curves and tie lines was obtained at all the temperatures studied, as reported in Figs. 2–4. Average deviations (AD) of only 2.6% are obtained for the tie-lines at 303.15 K. The predictions obtained by the CPA EoS show that this is an accurate and simple model to describe the phase equilibria of ternary systems formed at the biodiesel production process. With a single set of temperature independent, transferable interaction parameters, obtained from other fatty acid ester + alcohol + glycerol systems, the CPA EoS is able to accurately predict the experimental data here reported in the temperature range studied.

5. Conclusions

New experimental measurements were carried out for the phase equilibria of the ternary system canola oil ethyl ester biodiesel + ethanol + glycerol at 303.15, 318.15 and 333.15 K. The reliability of the experimental tie lines was established through the Othmer–Tobias correlation.

The Cubic-Plus-Association equation of state (CPA EoS) was shown to be an adequate model to predict phase equilibria of relevance for the biodiesel production and purification processes. Using previously assessed temperature independent binary interaction and cross-association parameters, the experimental data was successfully predicted with the CPA EoS with average deviations inferior to 3%.

Acknowledgement

Appendix A. Supplementary material

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Table 5
Binary interaction and cross-association parameters from binary VLE and LLE data and ternary LLE data and respective modeling results at 303.15 K.

	From binary VLE and LLE data AD% = 3.2	From ternary LLE data AD% = 2.6
k_{ij} (fatty acid ester–glycerol)	0.129	−0.098
k_{ij} (unsaturated fatty acid ester–ethanol)	−0.026	−0.022
k_{ij} (ethyl palmitate–ethanol)	−0.020	−0.032
k_{ij} (ethyl stearate–ethanol)	−0.026	−0.043
k_{ij} (glycerol–ethanol)	0.060	−0.037
β_{ij} (fatty acid ester–glycerol)	0.100	0.011
β_{ij} (fatty acid ester–ethanol)	0.130	0.245

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