

Modeling of Biodiesel Multicomponent Systems with the Cubic-Plus-Association (CPA) Equation of State

Mariana B. Oliveira,[†] António J. Queimada,[‡] and João A.P. Coutinho^{*†}

CICECO, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal, and LSRE - Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia, Universidade do Porto, Rua do Doutor Roberto Frias, 4200 - 465 Porto, Portugal

To supply biodiesel with the quality levels required by the standards for alternative fuels, the separation and purification units are extremely important in the biodiesel production plants. The correct knowledge and description of the phase equilibria in systems composed by transesterification products is essential for a correct operation and optimization of the purification process. For that purpose, the cubic-plus-association equation of state (CPA EoS) was here applied to model the phase equilibria of multicomponent systems common to biodiesel production and purification processes. It is shown that the CPA EoS can provide a good description of the liquid–liquid equilibria of multicomponent mixtures containing alcohols, glycerol, and fatty acid esters in the temperature range of operation of the separation units in biodiesel plants. As the liquid–liquid phase equilibrium description depends on the EoS parameters, a discussion is also presented about the best set of parameters and the method to estimate them.

Introduction

The various environmental, economical, and political problems related to the use of conventional fossil fuels are leading toward the search for new renewable energy sources. Carbon dioxide emissions contributing to global warming; countries depending on petroleum-based fuel imported from socially, politically, and economically unstable regions; and current reserves of crude oil based fuels that will only last a few more decades¹ (global production will decline sometime between 2010 and 2032²) are focusing the attention on alternative fuels.³

Biodiesel is at the forefront of the alternatives to petroleum-based fuels being environmentally acceptable and easily available. When using adequate raw materials and production processes along with the recovering and valorization of byproducts, biodiesel can be considered economically competitive⁴ and a socially and ethically acceptable alternative. It is biodegradable, nontoxic, and able to considerably decrease the emissions of noxious gases. It consists of a blend of fatty acid alkyl esters that can also be mixed in all proportions with regular diesel.⁵

Among the various approaches to produce biodiesel, transesterification is the preferable method. It consists of the reaction of an oil or fat with an alcohol producing fatty acid esters and glycerol. As the reaction rate is very slow, a catalyst is required for industrial applications (usually an alkaline catalyst) to increase reaction speed and yield.^{5,6} The reaction occurs with an excess of alcohol, and commonly used alcohols are methanol and ethanol although the use of higher alcohols has already been proposed.⁷

The majority of the European countries regulate the biodiesel properties under the European Union (EU) standards for alternative diesel fuels (DIN EN 14214:2003⁸) since the biodiesel purity level has important effects on its performance as a fuel. Among the restrictions imposed by these standards are the free fatty acids, methanol, glycerin, and water contents. Consequently, regardless of the technologies used for biodiesel

production, the raw materials or the catalysts, the operation of the biodiesel purification units in the biodiesel production plants is particularly important to produce a fuel with the quality levels required by the standards for alternative fuels. Moreover, the excess methanol recovery reduces the operating costs and the environmental impact while improving biodiesel characteristics since the alcohol content controls the fuel flammability.⁵

The glycerol recovery section is also required to minimize its presence in the fuel since a high glycerol content leads to several fuel problems, such as blocking of fuel filters and fuel pressure drops. Glycerol is also seen as a versatile and valuable chemical with a wide variety of uses and applications, namely, in medical and pharmaceutical preparations and in cosmetics among others.⁹ The inclusion of a glycerol recovery and purification unit allows selling this byproduct as a good instead of having to manage it as a waste.

A succinct description of the involved purification processes may be summarized as follows^{5,10} (Figure 1): after the transesterification reaction, the glycerol formed separates from the oil phase, and at the outlet of the reactor, two liquid phases coexist, one of them rich in glycerol and the other rich in fatty acid esters (biodiesel). The unreacted alcohol is distributed between these two liquid phases. These phases are afterward separated by settling, and the glycerol-rich phase is sent to the alcohol recovery section where it is recovered by distillation and is recycled into the transesterification reactor. The glycerol-rich stream coming from the distillation process is then evaporated to decrease its water content and to meet the specifications of the glycerol market.

Simultaneously, the fatty acid ester stream leaving the transesterification reactor is washed with acidified water to neutralize the catalyst and to convert any existing soaps into free fatty acids. After the alcohol recovery, the methyl ester product is finally dried to reduce the water content to meet the biodiesel required standards.

Using thermodynamic models in simulation of biodiesel purification processes allows an easy evaluation and optimization of the operating variables and process configurations thereby giving more insight into the influence of important parameters on process design and operation. It makes possible the identi-

* To whom correspondence should be addressed. E-mail: jcoutinho@ua.pt. Tel.: +351 234401507. Fax: +351 234370084.

[†] University of Aveiro.

[‡] Universidade do Porto.

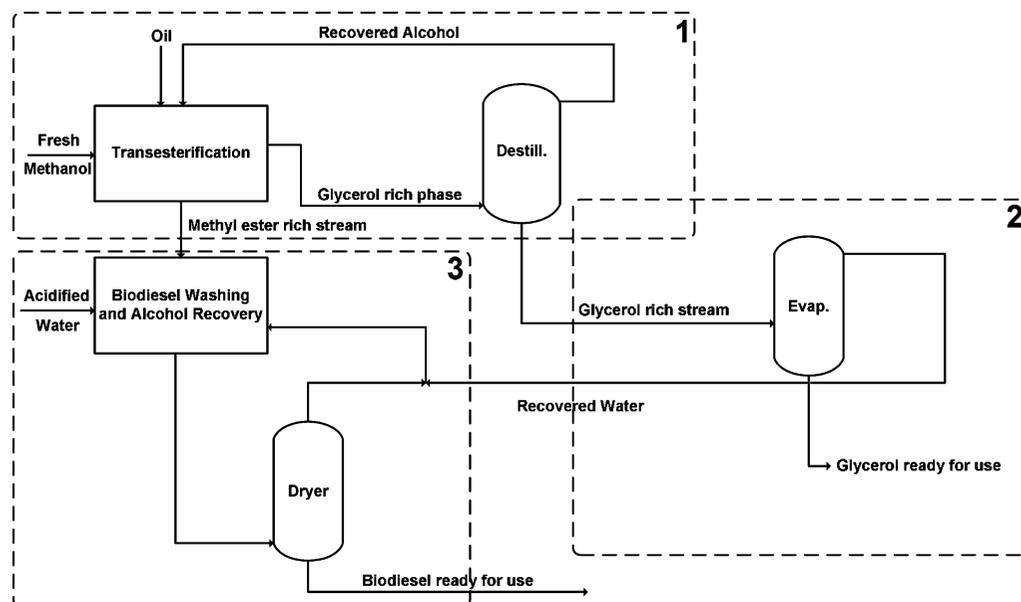


Figure 1. Biodiesel production and purification simplified flowsheet.

fication of process bottlenecks early in the design stage or existing ones allowing to operate with higher productivity within product specifications while minimizing environmental impacts therefore improving profits, reducing operating costs, and justifying the industrial feasibility of the process.

For that purpose, a thermodynamic model is necessary to correctly describe the transesterification products distributed between the two formed immiscible phases, one rich in glycerol and the other rich in biodiesel, in a broad range of thermodynamic conditions.

Up to now, only limited experimental phase equilibrium data has been made available for the separation processes of interest, and essentially, the conventional activity coefficient models have been applied to predict these data. The UNIFAC and UNIFAC-Dortmund models were applied with satisfactory results to the prediction of the system glycerol + methanol + methyl oleate.¹¹ Andreatta et al.¹² used the UNIFAC with association (A-UNIFAC) model and also the group contribution with association equation of state (GCA-EoS) to describe this same system. A good agreement with the experimental data was obtained particularly with the GCA-EoS model. The Wilson activity coefficient model was also applied to describe mixtures of biodiesel and glycerol as well as biodiesel + glycerol + methanol.^{13,14}

To analyze the possibility to use hexane for biodiesel extraction, Tizvar et al.¹⁵ experimentally measured the liquid–liquid equilibria (LLE) of the methyl oleate + glycerol + methanol + hexane system and modeled it with the UNIFAC and modified UNIFAC models.

Recently, França et al.¹⁶ reported new experimental data for methyl ricinoleate + methanol + glycerol and methyl ricinoleate + ethanol + glycerol systems and their satisfactory correlation with the UNIQUAC model.

Experimental results for other useful systems for the biodiesel purification processes were also presented by Zhou et al.¹⁷ and Liu et al.¹⁸

The change from oil to vegetable oils or animal fats as raw materials for diesel production represents a minor change in terms of fuel properties but a significant change in complexity in terms of intermolecular interactions. While in the conventional oil industry vapor–liquid is the dominant phase equilibria, in biodiesel production both vapor–liquid and liquid–liquid

equilibria are involved and water becomes an important component. To describe these highly nonideal systems in broad temperature, pressure, and composition conditions, associating equations of state are required.

During the last two decades, several equations of state have been proposed to explicitly consider association. Among these, there are the several versions of the statistical associating fluid theory (SAFT),¹⁹ the associated perturbed anisotropic chain theory (APACT),²⁰ and more recently, the cubic-plus-association equation of state (CPA EoS).^{21,22} The CPA EoS had already demonstrated to be a flexible and reliable thermodynamic tool for correctly modeling the phase equilibria of mixtures containing both associative and nonassociative components distributed by different fluid phases. In fact, the results obtained until present seem to indicate that within the association equations of state, the CPA EoS is the most successful association model for aqueous systems^{21–23} and is also mathematically simpler thus substantially simplifying and accelerating the phase equilibrium calculations.

The CPA EoS was previously successfully applied to model the phase equilibria of mixtures containing hydrocarbons, alcohols, glycols, water, amines, organic acids, aromatic or olefinic hydrocarbons, perfluorocarbons, esters, and phenolic compounds. It provided very good results in modeling the vapor–liquid equilibria (VLE) of the glycol + water system,²⁴ the LLE and VLE of water + heavy alcohol systems,²⁵ the LLE of water + amine systems,²⁶ the VLE and solid–liquid equilibria (SLE) of water + small alcohols systems,²⁵ the VLE of small acids + water or small acids + alcohol systems,²⁷ the VLE of amine + alcohol²⁶ systems, the SLE of the monoethylene glycol (MEG) + water systems,²⁴ and the LLE of water + hydrocarbon systems.²³ The CPA EoS had also shown to be able to take into account the solvation phenomena occurring between water and aromatic hydrocarbons^{23,28} and perfluorocarbons.²⁹

It has also been previously demonstrated that this model can be adequately applied to the description of several binary systems present at the operation units of biodiesel production processes. Very good results were reported for the description of the LLE and SLE of water and free fatty acids systems³⁰ and for the description of the water solubility in fatty acid methyl

Table 1. CPA Pure Compound Parameters and Modeling Results

compound	T_c (K)	a_0 (J m ³ mol ⁻²)	c_1	$b \times 10^5$ (m ³ mol ⁻¹)	ϵ (J mol ⁻¹)	$\beta \times 10^3$	AAD %	
							P^o	ρ
glycerol	766.1	1.21	1.06	6.96	19 622	9	0.77	1.49
methyl laurate	712.0	7.46	1.37	24.04			0.80	1.31
methyl myristate	742.4	8.84	1.51	27.95			3.66	
methyl stearate	788.6	11.64	1.72	35.07			3.53	
methyl oleate	764.0	10.70	1.86	33.39			4.81	1.74
methyl ricinoleate	798.2	9.41	1.36	32.76	22 665	90.30	0.58	0.31
methanol	512.7	0.43	0.75	3.22	20 859	34	0.29	0.14
ethanol	514.7	0.68	0.94	4.75	21 336	19	0.35	0.51

esters and biodiesels.³¹ The VLE of several glycerol + alcohol systems and of the glycerol + water system, essential for the design of the separation and purification processes of the glycerol recovery section, were also successfully described with the CPA EoS.³²

In the present work, the CPA EoS capability to model the phase equilibria of systems of transesterification products will, for the first time, be evaluated. Modeling results will be presented for several multicomponent systems composed of glycerol, fatty acid esters, ethanol, methanol, and n-hexane. The CPA EoS is summarized in Appendix A.

Two approaches were considered to evaluate the binary interaction parameters for all possible component pairs for each multicomponent system, and a discussion about the best approach to carry the parameter estimation is provided.

Results and Discussion

1. Pure Component CPA Parameters. The initial step to apply the CPA EoS to the description of mixture phase equilibria is the estimation of the CPA parameters of the pure compounds involved. Both self-associating and non-self-associating compounds constitute the multicomponent systems studied here. For most of these compounds, the three or five CPA pure compound parameters were already estimated in previous works, and these are presented along with the correspondent critical temperatures in Table 1. For the ester compounds, because of the lack of available literature data for critical properties, the best group contribution models to estimate these properties were previously assessed for several methyl and ethyl esters.³³ With these parameters, CPA provided very good results for correlating the LLE of water + fatty acid ester systems³¹ and the VLE of glycerol + n-alcohol systems.³²

For methyl ricinoleate, no CPA pure compound parameters were previously estimated. For this compound, vapor pressure and liquid density data were calculated by literature group contribution methods: the SIMPOL.1³⁴ model for vapor pressures and the GCVOL³⁵ model for liquid densities. The SIMPOL.1 was developed using a set of 277 compounds and was examined using a test set of 184 compounds. The average overall points of the absolute difference between experimental and predicted values of $\log_{10} P$ was 0.34. Elbro et al.³⁵ showed that liquid densities can be predicted with an error of approximately 1% for several compounds of different families (alkanes, aromatics, alkenes, ketones, ethers, esters, chlorides, etc).

Its critical temperature was estimated through the Constantinou and Gani group-contribution method.³⁶ This unsaturated fatty ester has a hydroxyl group, and so, the 2B association scheme was used for this compound. A satisfactory description of pure component vapor pressure and liquid density data was obtained covering the range of reduced temperatures from 0.45 to 0.85 with global average deviations of 0.6% and 0.3% for

vapor pressure and liquid density, respectively. The five CPA parameters and the critical temperature for methyl ricinoleate are also presented in Table 1.

2. Binary Interaction Parameters from Binary Data. Having the pure component parameters, the remaining parameters to be fitted are the binary interaction parameters to be regressed from experimental data. Although the liquid–liquid equilibria of ester + glycerol + alcohol systems are important to evaluate the separation of transesterification products in biodiesel production, not much experimental data is available. Data was found for the ternary systems methyl oleate + glycerol + methanol,^{11,12,37} methyl myristate + ethanol + glycerol,³⁸ methyl laurate + ethanol + glycerol,³⁸ methyl stearate + ethanol + glycerol,³⁸ methyl ricinoleate + glycerol + methanol,¹⁶ and methyl ricinoleate + glycerol + ethanol.¹⁶ Data for the quaternary system methyl oleate + glycerol + methanol + n-hexane was also accessible in literature.¹⁵

The first approach to model those systems was to use binary interaction parameters for the binary subsystems obtained from binary equilibria data. The subsystems possible comprise fatty acid ester + glycerol, glycerol + alcohol, and fatty acid ester + alcohol mixtures. For fatty acid ester + glycerol mixtures, phase equilibria data was only available for two LLE systems, namely, methyl dodecanoate + glycerol and methyl hexanoate + glycerol.³⁹ The cross-association between the ester group and the glycerol was taken into account as previously described in the model section with both the binary interaction k_{ij} and the cross-association β_{ij} parameters fitted to the mutual solubility data. As the majority of the regressed values for β_{ij} were close to 0.1, this parameter was fixed, and afterward the k_{ij} 's were refitted. Satisfactory results were obtained as seen in Figure 2. As no other binary systems composed by ester and glycerol were available in the literature, the results obtained for methyl dodecanoate + glycerol were considered to represent binary subsystems glycerol + ester.

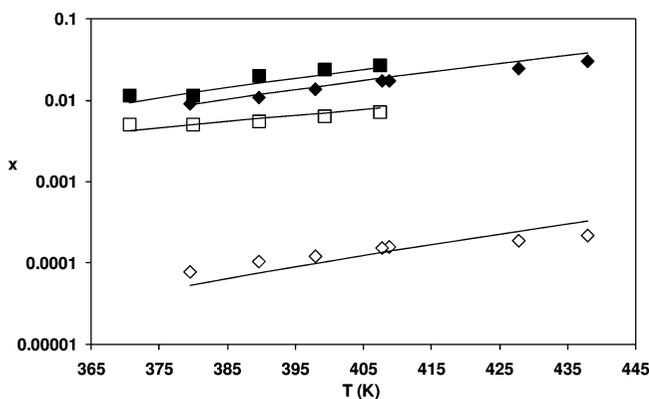


Figure 2. CPA (—) results for the mutual solubilities of methyl hexanoate + glycerol ($k_{ij} = 0.102$) (squares) and methyl dodecanoate + glycerol ($k_{ij} = 0.129$) (lozenges). Open symbols correspond to the glycerol phase, and closed symbols correspond to the ester phase.

Table 2. Binary Interaction Parameters Correlated from Ester + Methanol/Ethanol VLE Data

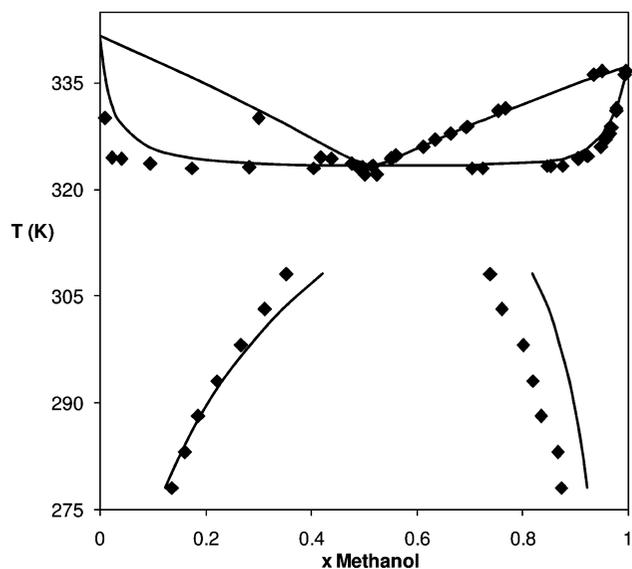
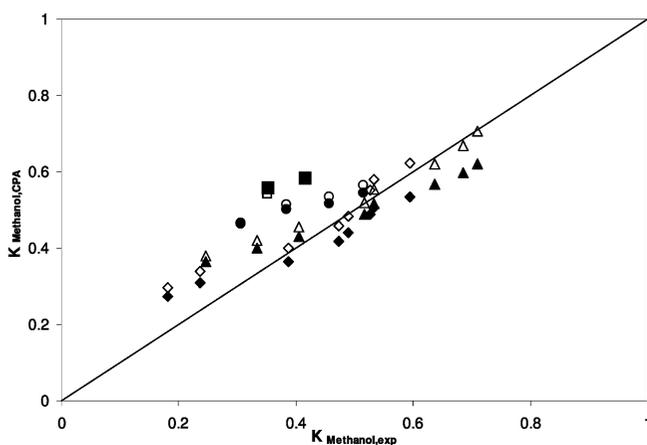
	k_{ij}
methyl laurate + methanol	-0.0326
methyl myristate + methanol	-0.0432
methyl oleate + methanol	-0.0589
methyl laurate + ethanol	-0.0002
methyl myristate + ethanol	-0.0046
methyl oleate + ethanol	-0.0197

Glycerol + methanol and glycerol + ethanol systems were previously studied with the CPA EoS and the new association scheme proposed for glycerol, the $3 \times 2B$ scheme.³² With a single and temperature independent binary interaction parameter, it was possible to successfully correlate the VLE data of these systems.

The last binary subsystems for the ternary modeling are the fatty acid ester + methanol (or ethanol) binary mixtures. The CPA EoS has already been applied to the description of the VLE of these systems.⁴⁰ Studying ester + methanol and ester + ethanol systems with ester carbon numbers from 5 up to 19 for ethanol systems and from 3 up to 19 for methanol systems, it was possible to establish a linear correlation for the binary interaction parameter with the ester carbon number. Also, a constant value for the cross-association volume was found being 0.10 for the ethanol systems and 0.13 for methanol systems. The use of this constant value and the linear correlation for the k_{ij} binary interaction parameter provides the CPA EoS with a predictive capability to model multicomponent systems containing these binaries. Values for the temperature independent binary interaction parameters are presented in Table 2.

To model the quaternary system composed by methyl oleate + methanol + glycerol + hexane,¹⁵ it was also necessary to describe the binary systems hexane + methanol and hexane + glycerol. For the binary system hexane + methyl oleate, the k_{ij} value was set to zero, as the cross-energy parameter between these components is expected to be well described solely by the geometric mean combining rule (eq 3 of Appendix A). Experimental data was available for the VLE and LLE of the methanol + hexane mixture,^{41,42} and with a low and temperature independent binary interaction parameter fitted to the mutual solubility data of -0.00174, it was possible to provide a good description of LLE and to successfully predict the VLE as can be seen in Figure 3. Scarce experimental data is available for the hexane + glycerol system with only one point for the LLE of this system being available in the literature.⁴³ Even so, the CPA EoS was applied to correlate this system with the binary interaction parameter estimate being -0.0205.

With the binary interaction and cross-association parameters evaluated from binary equilibria data, it is then possible to attempt modeling multicomponent systems. Starting with the methyl oleate + methanol + glycerol system, experimental tie-line data from different authors were available at five different temperatures.^{11,12,37} Promising results for this system were previously reported with the CPA EoS using the association scheme recently proposed for glycerol,³² and because of the lack of binary data, using either binary parameters set to zero or obtained from similar systems, and a k_{ij} for the methyl oleate + methanol fitted from the ternary data. As seen in Figures 4–6, improved results were obtained using the CPA EoS and the binary interaction parameters k_{ij} and β_{ij} correlated from binary equilibrium data. The CPA EoS can correctly predict the immiscibility between glycerol and methyl oleate and the formation of a glycerol phase richer in alcohol than the ester phase. Higher deviations are obtained for the methyl oleate

**Figure 3.** VLE and LLE CPA EoS correlation for the system hexane + glycerol. Experimental data (◆).**Figure 4.** Methanol distribution coefficient from the CPA EoS versus the experimental methanol distribution coefficient (◆◇, 313 K; ▲△, 333 K; ●○, 353 K; ■□, 373 K). Full symbols represent CPA EoS results using interaction parameters correlated to the ternary data, and the empty symbols represent the CPA EoS results using interaction parameters correlated from binary data.

solubility in the glycerol-rich phase, but these were already expected as these solubility values are typically small at about 10^{-3} .

For the quaternary system methyl oleate + methanol + glycerol + n-hexane, experimental data at 293.15 K were available from Tizvar et al.,¹⁵ and similar good results were also obtained when using the CPA EoS with the k_{ij} 's and β_{ij} 's correlated from binary data as observed in Figure 7, where the predicted mole fractions are plotted versus the experimental mole fractions for both phases. As the authors of the experimental data state, the precision for the reported glycerol content on the methyl oleate rich phase was too low to allow the evaluation of model performance in predicting that data. Still, the plots of the two equilibrium phases in Figure 7 clearly illustrate the good performance of the proposed model for these biodiesel systems.

Other systems of interest for the biodiesel industry are those constituted by a fatty acid ester, ethanol, and glycerol. Saturation lines for methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol systems were available at 303.15 K.³⁸ The approach described above for considering the k_{ij} 's and β_{ij} 's

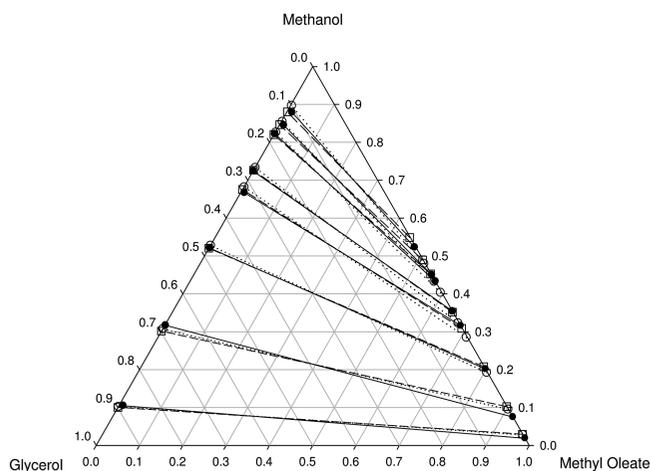


Figure 5. CPA results for methyl oleate + methanol + glycerol at 313 K (k_{ij} and β_{ij} correlated from binary data (O, $\bullet\bullet$); k_{ij} 's and/or β_{ij} 's correlated from this ternary (□, ---); experimental data (\bullet , —)).

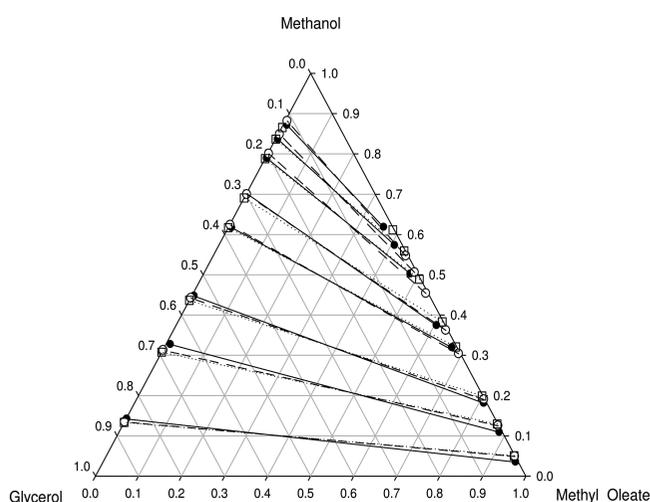


Figure 6. CPA results for methyl oleate + methanol + glycerol system at 333 K (k_{ij} and β_{ij} correlated from binary data (O, $\bullet\bullet$); k_{ij} 's and/or β_{ij} 's correlated from this ternary system data (□, ---); experimental data (\bullet , —)).

poorly predicts these saturation lines, as seen in Figure 8, opposed to the good tie-line results presented before. This is particularly the case for the ethanol-rich zone.

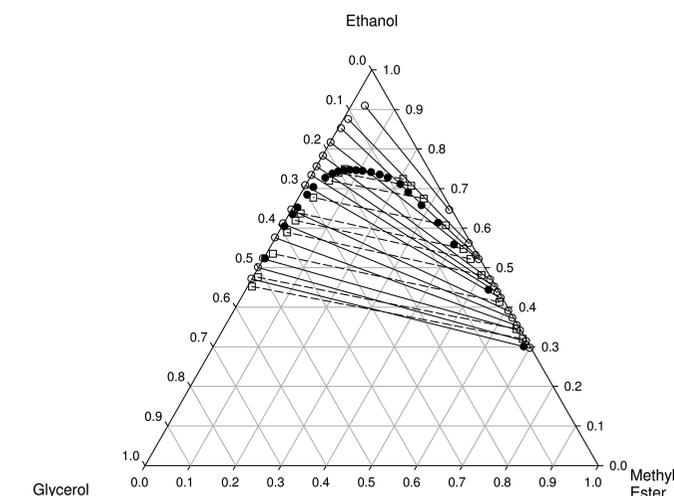
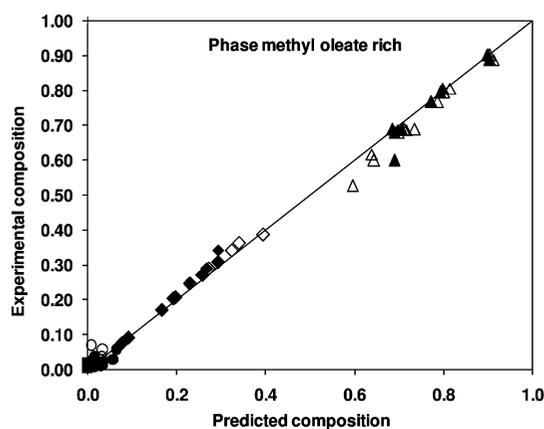


Figure 8. CPA results for methyl myristate + ethanol + glycerol at 303.15 K (k_{ij} 's and β_{ij} 's correlated from binary data (O, —); k_{ij} 's and/or β_{ij} 's correlated from methyl oleate + ethanol + glycerol LLE data and k_{ij} (ester + ethanol) = -0.0317 (□, ---). Experimental data (\bullet)).

Table 3. Binary Interaction and Cross-Association Parameters Correlated from Methyl Oleate + Glycerol + Methanol LLE Data

k_{ij} (methyl oleate + glycerol)	-0.098
β_{ij} (methyl oleate + glycerol)	0.011
k_{ij} (glycerol + methanol)	-0.037
k_{ij} (methyl oleate + methanol)	-0.022
β_{ij} (methyl oleate + methanol)	0.245

3. Binary Interaction Parameters from Multicomponent Data. Another possible approach to consider binary interaction parameters and cross-association parameters is to evaluate them directly from the ternary data. At Table 3, the binary interaction k_{ij} and the cross-association β_{ij} parameters estimated when correlating the LLE data of the system methyl oleate + methanol + glycerol are presented. All data at all temperatures were considered for evaluating the k_{ij} 's and β_{ij} 's. Using these new temperature independent k_{ij} 's and β_{ij} 's, the model performance is enhanced, as noticed in Figures 4–6, specially for the glycerol-rich phase in particular for the mole fraction of methyl oleate that was not so well described using the binary interaction parameters obtained from binary data.

Using the same k_{ij} 's and β_{ij} 's from Table 3, similar good results are obtained for the quaternary system as can be seen in Figure 7.

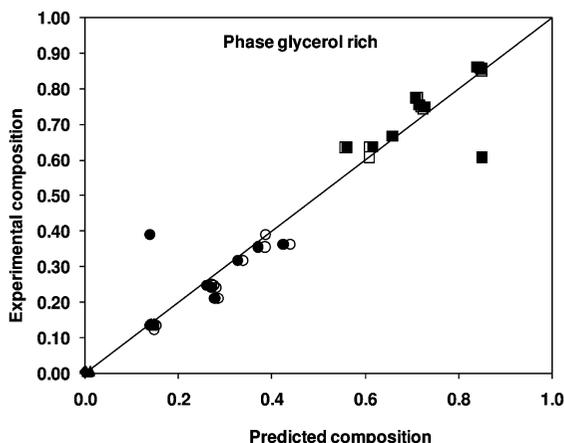


Figure 7. Experimental versus CPA EoS estimated mole fractions for the quaternary system methyl oleate + glycerol + methanol + n-hexane. (Full symbols, binary parameters from binary data; empty symbols, binary parameters from methyl oleate + methanol + glycerol system. Compositions: glycerol, \blacksquare ; methanol, \bullet ; methyl oleate, \blacklozenge ; hexane, \blacktriangle).

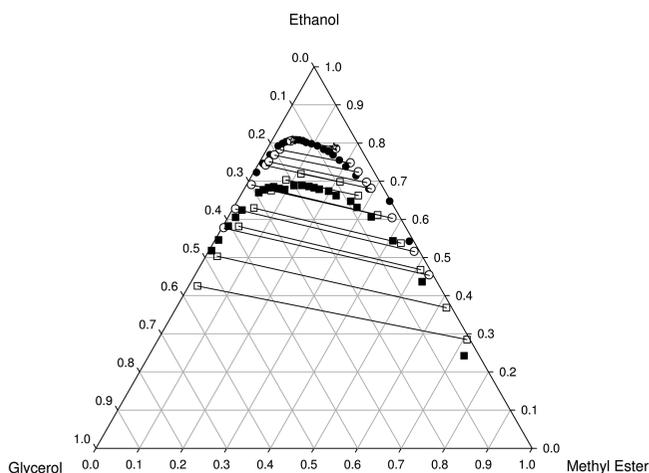


Figure 9. LLE for methyl stearate + ethanol + glycerol (●) and for methyl laurate + ethanol + glycerol (■) systems at 303.15 K. CPA results using k_{ij} 's and/or β_{ij} 's correlated from the methyl oleate + methanol + glycerol system and k_{ij} (methyl stearate + ethanol) = -0.0425 and k_{ij} (methyl laurate + ethanol) = -0.02173 (empty symbols, —).

Table 4. Binary Interaction Parameters Correlated from Methyl Ricinoleate + Glycerol + Methanol LLE Data

k_{ij} (methyl ricinoleate + glycerol)	-0.074
k_{ij} (methyl ricinoleate + methanol)	-0.131
k_{ij} (glycerol + methanol)	-0.026

As no tie-line data were available for the methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol systems, it is more difficult to use these LLE ternary data to evaluate the binary interaction and cross-association parameters. Taking advantage of the predictive capacity of the model, the same parameter set obtained before from the tie-line data of the system methyl oleate + methanol + glycerol was investigated leaving only as an adjustable parameter the ester + ethanol k_{ij} parameter.

As can be seen from Figures 8 and 9, the interaction and cross-association binary parameters are easily transferable as seen by the overall agreement between the experimental data and the model calculations.

Other relevant systems are the ones derived from castor oil, which is one of the most important nonedible biodiesel feedstocks and which is widely available in Brazil and in other regions; methyl ricinoleate is the major component of castor oil biodiesel at about 90% of its composition.¹⁶ As far as methyl ricinoleate + methanol + glycerol and methyl ricinoleate + ethanol + glycerol systems are concerned, experimental tie lines and saturation curves were only available from França et al.¹⁶ Starting with the methyl ricinoleate + methanol + glycerol system for which tie-line data were available at 298 K, the second approach used before was adopted, that is, the estimation of binary interaction parameters for all the three subsystems from the ternary LLE data. That decision was supported by the good results obtained for other systems by this method and the absence of binary data in literature for mixtures with methyl ricinoleate. Results for these k_{ij} 's are presented in Table 4, and modeling results are presented in Figure 10. Very good tie-line results were accomplished. For methyl ricinoleate + ethanol + glycerol, the authors did not present tie-line data and, as done before for the methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol systems, the k_{ij} 's calculated from the methyl ricinoleate + methanol + glycerol system were evaluated to predict this mixture at 298 and 333.15 K. Good predictive results were obtained as shown in Figure 11.

Several attempts were made to describe two other systems available in literature constituted by fatty acid methyl esters,

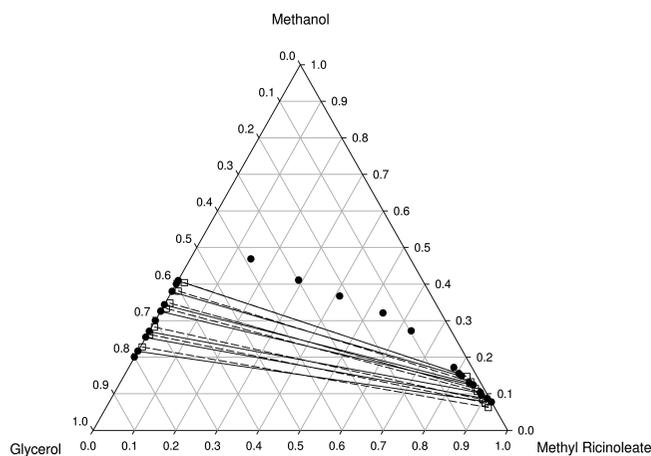


Figure 10. CPA results for methyl ricinoleate + methanol + glycerol system at 298.15 K using k_{ij} 's correlated from this ternary system data (□, ●●). Experimental data (●, —).

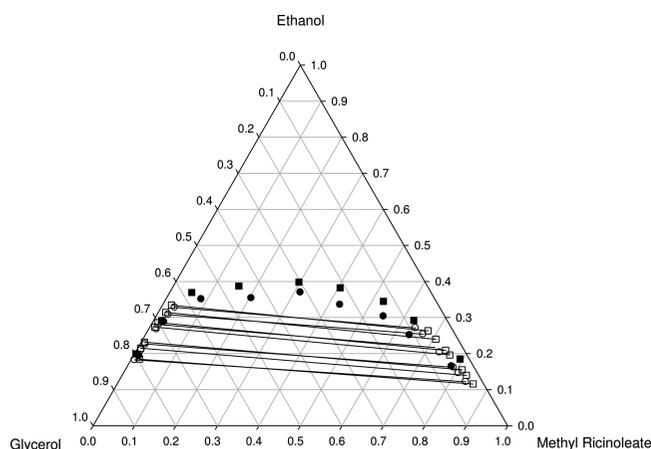


Figure 11. CPA results for methyl ricinoleate + ethanol + glycerol system using k_{ij} 's correlated from the ternary methyl ricinoleate + methanol + glycerol system data (□, 298.15 K; ○, 333.15 K). Experimental data (closed symbols).

methanol, and glycerol and by fatty acid ethyl esters, ethanol, and glycerol presented by Zhou et al.¹⁷ and Liu et al.,¹⁸ respectively. None of the approaches presented before were able to satisfactorily correlate this data. However, and as already stated in other experimental papers, the data presented by Zhou et al. and Liu et al. are in total disagreement with other literature available experimental data.^{11,12,37} Zhou et al. also stated that glycerol and methyl ester separation is temperature independent, which totally diverges from what Negi et al.,¹¹ Andreatta et al.,¹² and Cerce et al.³⁷ concluded for the same temperature range.

The results presented here clearly demonstrate that the CPA EoS can be used to describe ternary and multicomponent systems of transesterification products. This follows other good results already published from our group in several binary subsystems of interest for the biodiesel industry. As there is still a considerable lack of data for many of the binary subsystems, and even more ternary and multicomponent systems of interest, the results presented so far are expected to be improved when more (and accurate) data become available.

Conclusions

In this work, the performance of the CPA EoS is evaluated for the modeling of several multicomponent systems of relevance for the biodiesel industry using experimental data for multicomponent systems that appeared recently in literature.

Two approaches were used to estimate binary interaction and cross-association parameters. The first, and more generalized approach that was considered here, was to use binary parameters estimated from experimental data of the corresponding binary subsystems. The second was to use multicomponent data for the regression of the model parameters. To apply the first approach, several binary systems were also successfully modeled here with the CPA EoS.

Different results are obtained for multicomponent systems depending on the set of binary interaction parameters chosen. The second approach seems to be the best one providing very good results for several systems such as methyl oleate + methanol + glycerol, methyl oleate + methanol + glycerol + hexane, methyl myristate/methyl stearate/methyl laurate + ethanol + glycerol, methyl ricinoleate + methanol + glycerol, and methyl ricinoleate + ethanol + glycerol although at the expense of an increased correlative character.

The predictive performance of the model was also verified while using the same binary interaction and cross-association parameters to adequately model different ternary systems.

The CPA equation of state was found to give good correlation results and can safely extrapolate and even predict the liquid–liquid behavior of different complex ternary systems using the same binary interaction and cross-association parameters.

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Nomenclature

a = energy parameter in the physical term
 a_0, c_1 = parameters for calculating a
 A_i = site A in molecule i
 b = covolume
 g = simplified hard-sphere radial distribution function
 k_{ij} = binary interaction parameter
 P = vapor pressure
 R = gas constant
 T = temperature
 x = mole fraction
 X_{Ai} = fraction of molecule i not bonded at site A
 Z = compressibility factor

Greek Symbols

β = association volume
 ε = association energy
 η = reduced fluid density
 ρ = mole density
 Δ = association strength

Subscripts

c = critical
 i, j = pure component indexes
 r = reduced

Superscripts

assoc. = association
 phys. = physical

List of Abbreviations

AAD = average absolute deviation (%AAD = $(1/NP)\sum_{i=1}^{NP} \text{ABS}[(\text{exp}_i - \text{calc}_i)/(\text{exp}_i)] \times 100$)
 APACT = associated perturbed anisotropic chain theory
 CPA = cubic-plus-association
 CR = combining rule
 ECR = Elliot combining rule
 EoS = equation of state
 FAME = fatty acid methyl ester
 GCA-EoS = group contribution with association equation of state
 K_{Methanol} = methanol distribution coefficient $K_{\text{Methanol}} = (x_{\text{methanol}}^{\text{fatty phase}})/(x_{\text{methanol}}^{\text{glycerol phase}})$
 LLE = liquid–liquid equilibria
 MEG = monoethylene glycol
 NP = number of points
 SAFT = statistical associating fluid theory
 SLE = solid–liquid equilibria
 SRK = Soave–Redlich–Kwong
 UNIQUAC = universal quasi-chemical activity coefficient model
 UNIFAC = universal functional activity coefficient model
 VLE = vapor–liquid equilibria

Appendix A

In this work, the cubic-plus-association equation of state proposed by Kontogeorgis et al.⁴⁴ is used. In terms of the compressibility factor, it can be expressed as the sum of two contributions: one of them describing the physical interactions, that in the current work are taken into account by the SRK EoS, and the other accounting for association interactions, the Wertheim association term:^{45–49}

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

where a is the energy parameter, b is the covolume parameter, ρ is the molar density, g is a simplified hard-sphere radial distribution function, X_{A_i} is 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

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

where a_0 and c_1 are regressed (simultaneously with b) from pure component vapor pressure and liquid density data.

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

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

and

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

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

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (5)$$

where

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

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and the association volume, respectively.

The simplified radial distribution function, $g(\rho)$, is given by⁵⁰

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

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

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

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.^{25,51} In this work, the Elliott combining rule (ECR)²⁵ is used

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (9)$$

Among other combining rules,²⁵ the Elliot combining rule performed better, for instance, in predicting the VLE and SLE of water + small alcohol systems,⁵¹ the VLE of small acids + water or small acids + alcohol systems,²⁷ the VLE of amine + alcohol²⁶ systems, and the SLE of the MEG + water systems.²⁴ It also provided very good results in modeling the phase equilibria of several systems of interest for the biodiesel production, such as the LLE of water + fatty acid systems³⁰ and the VLE of glycerol + alcohol systems.³²

Solvation can occur in some systems containing self-associating and non-self-associating compounds as in the case of the ester + self-associating compound mixtures investigated in this work. For this type of system, this solvation phenomenon is considered as a cross-association by the CPA EoS where the cross-association energy ($\varepsilon^{A_i B_j}$) is considered to be half 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 equilibrium data. This approach proposed by Folas et al.⁵² was successfully applied to several water + aromatic systems.²³ The same method was adopted to correlate water + fatty acid ester³¹ and water + perfluorocarbon²⁹ systems and to model the water solubility in biodiesels.³¹ In these cases, for estimating the k_{ij} and $\beta^{A_i B_j}$ parameters, the following objective function was minimized:

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

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. According to the nomenclature of Huang and Radosz,⁵³ two association schemes can be considered to represent alcohols, the 3B and the 2B schemes. Kontogeorgis et al.²² had already shown that there is not much to gain by using the more rigorous (3B) over the simpler (2B) association scheme. Therefore, 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. For the ester family, a single association site is considered that can cross-associate with self-associating molecules.

For glycerol, an association scheme recently suggested is here adopted.³² It considers the glycerol molecule as having three identical alcohol groups with each of them having two association sites. The proposed $3 \times 2B$ scheme proved to be the most successful association scheme in describing the VLE for the glycerol + water system and for different glycerol + alcohol (from methanol to butanol) systems.³²

Literature Cited

- (1) Bentley, R. W.; Mannan, S. A.; Wheeler, S. J. Assessing the date of the global oil peak: The need to use 2P reserves. *Energy Policy* **2007**, *35*, 6364.
- (2) Kaufmann, R. K.; Shiers, L. D. Alternatives to conventional crude oil: When, how quickly, and market driven. *Ecol. Econ.* **2008**, *67*, 405.
- (3) Demirbas, A. Importance of biodiesel as transportation fuel. *Energy Policy* **2007**, *35*, 4661.
- (4) Duffield, J. A. Biodiesel: Production and economic issues. *Inhalation Toxicol.* **2007**, *19*, 1029.
- (5) Ma, F. R.; Hanna, M. A. Biodiesel production: a review. *Bioresour. Technol.* **1999**, *70*, 1.
- (6) Meher, L. C.; Sagar, D. V.; Naik, S. N. Technical aspects of biodiesel production by transesterification - a review. *Renewable Sustainable Energy Rev.* **2006**, *10*, 248.
- (7) Foglia, T. A.; Nelson, L. A.; Dunn, R. O.; Marmer, W. N. Low-temperature properties of alkyl esters of tallow and grease. *J. Am. Oil Chem. Soc.* **1997**, *74*, 951.
- (8) CEN - European Committee for Standardization. Automotive fuels - Fatty acid methyl esters (FAME) for diesel engine - Requirements and test methods; E.S.E. EN 14214; Brussels, Belgium, 2003.
- (9) Morrison, L. R.; Kirk, R. E.; Othmer, D. F. *Encyclopedia of Chemical Technology: Glycerol*, 4th ed.; John Wiley & Sons, Inc.: Boston, MA, 1997.
- (10) Haas, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. A process model to estimate biodiesel production costs. *Bioresour. Technol.* **2006**, *97*, 671.
- (11) Negi, D. S.; Sobotka, F.; Kimmel, T.; Wozny, G.; Schomacker, R. Liquid-liquid phase equilibrium in glycerol-methanol-methyl oleate and glycerol-monoolein-methyl oleate ternary systems. *Ind. Eng. Chem. Res.* **2006**, *45*, 3693.
- (12) Andreatta, A. E.; Casas, L. M.; Hegel, P.; Bottini, S. B.; Brignole, E. A. Phase equilibria in ternary mixtures of methyl oleate, glycerol, and methanol. *Ind. Eng. Chem. Res.* **2008**, *47*, 5157.
- (13) Di Felice, R.; De Faveri, D.; De Andreis, P.; Ottonello, P. Component distribution between light and heavy phases in biodiesel processes. *Energy Policy* **2008**, *47*, 7862.
- (14) Chiu, C. W.; Goff, M. J.; Suppes, G. J. Distribution of methanol and catalysts between biodiesel and glycerin phases. *AIChE J.* **2005**, *51*, 1274.
- (15) Tizvar, R.; McLean, D. D.; Kates, M.; Dube, M. A. Liquid-liquid equilibria of the methyl oleate-glycerol-hexane-methanol system. *Ind. Eng. Chem. Res.* **2008**, *47*, 443.
- (16) França, B. B.; Pinto, F. M.; Pessoa, F. L. P.; Uller, A. M. C. Liquid-liquid equilibria for castor oil biodiesel + glycerol + alcohol. *J. Chem. Eng. Data* **2008**, *54*, 2359.
- (17) Zhou, H.; Lu, H. F.; Liang, B. Solubility of multicomponent systems in the biodiesel production by transesterification of *Jatropha curcas* L. oil with methanol. *J. Chem. Eng. Data* **2006**, *51*, 1130.
- (18) Liu, X. J.; Piao, X. L.; Wang, Y. J.; Zhu, S. L. Liquid-liquid equilibrium for systems of (fatty acid ethyl esters plus ethanol plus soybean oil and fatty acid ethyl esters plus ethanol plus glycerol). *J. Chem. Eng. Data* **2008**, *53*, 359.
- (19) de Hemptinne, J. C.; Mougin, P.; Barreau, A.; Ruffine, L.; Tamouza, S.; Inchekel, R. Application to petroleum engineering of statistical thermodynamics - Based equations of state. *Oil Gas Sci. Technol.-Revue de l'Institut Francais du Petrole* **2006**, *61*, 363.
- (20) Economou, I. G.; Tsonopoulos, C. Associating models and mixing rules in equations of state for water/hydrocarbon mixtures. *Chem. Eng. Sci.* **1997**, *52*, 511.
- (21) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; von Solms, N.; Stenby, E. H. Ten years with the CPA (Cubic-Plus-

Association) equation of state. Part 1. Pure compounds and self-associating systems. *Ind. Eng. Chem. Res.* **2006**, *45*, 4855.

(22) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; von Solms, N.; Stenby, E. H. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part 2. Cross-associating and multicomponent systems. *Ind. Eng. Chem. Res.* **2006**, *45*, 4869.

(23) Oliveira, M. B.; Coutinho, J. A. P.; Queimada, A. J. Mutual solubilities of hydrocarbons and water with the CPA EoS. *Fluid Phase Equilib.* **2007**, *258*, 58.

(24) Folas, G. K.; Derawi, S. O.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Recent applications of the cubic-plus-association (CPA) equation of state to industrially important systems. *Fluid Phase Equilib.* **2005**, *228*, 121.

(25) Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. Prediction of phase equilibria in water/alcohol/alkane systems. *Fluid Phase Equilib.* **1999**, *160*, 151.

(26) Kaarsholm, M.; Derawi, S. O.; Michelsen, M. L.; Kontogeorgis, G. M. Extension of the cubic-plus-association (CPA) equation of state to amines. *Ind. Eng. Chem. Res.* **2005**, *44*, 4406.

(27) Derawi, S. O.; Zeuthen, J.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Application of the CPA equation of state to organic acids. *Fluid Phase Equilib.* **2004**, *225*, 107.

(28) Oliveira, M. B.; Oliveira, V. L.; Coutinho, J. A. P.; Queimada, A. J. Thermodynamic modeling of the aqueous solubility of PAHs. *Ind. Eng. Chem. Res.* **2009**, *48*, 5530.

(29) Oliveira, M. B.; Freire, M. G.; Marrucho, I. M.; Kontogeorgis, G. M.; Queimada, A. J.; Coutinho, J. A. P. Modeling the liquid-liquid equilibria of water plus fluorocarbons with the cubic-plus-association equation of state. *Ind. Eng. Chem. Res.* **2007**, *46*, 1415.

(30) Oliveira, M. B.; Melo, M. J. P.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Description of the mutual solubilities of fatty acids and water with the CPA EoS. *AIChE J.* **2008**, *55*, 1604.

(31) Oliveira, M. B.; Varanda, F. R.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Prediction of water solubility in biodiesel with the CPA equation of state. *Ind. Eng. Chem. Res.* **2008**, *47*, 4278.

(32) Oliveira, M. B.; Teles, A. R. R.; Queimada, A. J.; Coutinho, J. A. P. Phase equilibria of glycerol containing systems and their description with the cubic-plus-association (CPA) equation of state. *Fluid Phase Equilib.* **2009**, *280*, 22.

(33) Lopes, J. C. A.; Boros, L.; Krahenbuhl, M. A.; Meirelles, A. J. A.; Daridon, J. L.; Pauly, J.; Marrucho, I. M.; Coutinho, J. A. P. Prediction of cloud points of biodiesel. *Energy Fuels* **2008**, *22*, 747.

(34) Pankow, J. F.; Asher, W. E. SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds. *Atmos. Chem. Phys.* **2008**, *8*, 2773.

(35) Elbro, H. S.; Fredenslund, A.; Rasmussen, P. Group contribution method for the prediction of liquid densities as a function of temperature for solvents, oligomers, and polymers. *Ind. Eng. Chem. Res.* **1991**, *30*, 2576.

(36) Poling, B.; Prausnitz, J.; O'Connell, J. *The Properties of gases and liquids*, 5th ed.; Mc-Graw Hill: New York, 2001.

(37) Cerce, T.; Peter, S.; Weidner, E. Biodiesel-transesterification of biological oils with liquid catalysts: Thermodynamic properties of oil-methanol-amine mixtures. *Ind. Eng. Chem. Res.* **2005**, *44*, 9535.

(38) Carvalho, S. Equilíbrio Líquido-Líquido na Produção de Biodiesel. Master Dissertation, Aveiro University, 2007.

(39) Korgitzsch, F. M. Study of Phase Equilibria as a Fundamental for the Refinement of Vegetable Fats and Oils. Ph.D. Dissertation, TU Berlin, 1993.

(40) Oliveira, M. B.; Miguel, S. I.; Coutinho, J. A. P.; Queimada, A. J. Phase equilibria of ester + alcohol systems and their description with the cubic-plus-association (CPA) equation of state. *Ind. Eng. Chem. Res.* Submitted for publication, **2009**.

(41) Raal, J. D.; Best, D. A.; Code, R. K. Examination of Ethanol-Heptane, Methanol-Hexane Systems Using New Vapor-Liquid Equilibrium Still. *J. Chem. Eng. Data* **1972**, *17*, 211.

(42) Macedo, E. A.; Rasmussen, P. Liquid-Liquid Equilibrium Data Collection Supplement 1. *DECHEMA* **1987**, *1*, 91.

(43) Venter, D. L.; Nieuwoudt, I. Liquid-liquid equilibria for m-cresol plus o-toluenitrile plus hexane plus water plus (glycerol or triethylene glycol) at 313.15K. *J. Chem. Eng. Data* **1998**, *43*, 676.

(44) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An equation of state for associating fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310.

(45) Michelsen, M. L.; Hendriks, E. M. Physical properties from association models. *Fluid Phase Equilib.* **2001**, *180*, 165.

(46) Voutsas, E. C.; Boulougouris, G. C.; Economou, I. G.; Tassios, D. P. Water/hydrocarbon phase equilibria using the thermodynamic perturbation theory. *Ind. Eng. Chem. Res.* **2000**, *39*, 797.

(47) Wu, J. Z.; Prausnitz, J. M. Phase equilibria for systems containing hydrocarbons, water, and salt: An extended Peng-Robinson equation of state. *Ind. Eng. Chem. Res.* **1998**, *37*, 1634.

(48) Wertheim, M. S. Fluids with highly directional attractive forces. 2. Thermodynamic perturbation-theory and integral-equations. *J. Stat. Phys.* **1984**, *35*, 35.

(49) Wertheim, M. S. Fluids with highly directional attractive forces. 3. Multiple attraction sites. *J. Stat. Phys.* **1986**, *42*, 459.

(50) Kontogeorgis, G. M.; Yakoumis, I. V.; Meijer, H.; Hendriks, E.; Moorwood, T. Multicomponent phase equilibrium calculations for water-methanol-alkane mixtures. *Fluid Phase Equilib.* **1999**, *160*, 201.

(51) Folas, G. K.; Gabrielsen, J.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Application of the cubic-plus-association (CPA) equation of state to cross-associating systems. *Ind. Eng. Chem. Res.* **2005**, *44*, 3823.

(52) Folas, G. K.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Application of the cubic-plus-association (CPA) equation of state to complex mixtures with aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **2006**, *45*, 1527.

(53) Huang, S. H.; Radosz, M. Equation of state for small, large, polydisperse, and associating molecules. *Eng. Chem. Res.* **1990**, *29*, 2284.

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