



## Prediction of near and supercritical fatty acid ester + alcohol systems with the CPA EoS

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### ARTICLE INFO

#### Article history:

Received 20 November 2009

Received in revised form 22 January 2010

Accepted 25 January 2010

#### Keywords:

Biodiesel

CPA EoS

Supercritical alcohols

Fatty acid esters

VLE

High pressures

High temperatures

### ABSTRACT

The use of supercritical alcohols has been proposed as a non-catalytic method to produce biodiesel, overcoming some of the shortcomings related to conventional catalytic methods.

In this work, the Cubic-Plus-Association equation of state is used to predict the vapor–liquid equilibria of several alcohol + fatty acid ester and alcohol + glycerol systems, in the temperature range 493–573 K and pressure range 2–12 MPa. The resulting predictions reproduce accurately the experimental data, within their experimental uncertainty.

The ability to predict these phase equilibria is of primary importance for designing, operating and optimizing biodiesel production at near or supercritical conditions. The CPA EoS is shown to be a powerful prediction tool for an adequate design of the operations involved in the biodiesel production with near or supercritical alcohols.

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### 1. Introduction

Several efforts have been made in order to find new alternative and renewable fuels to fulfill the global energy demands. The use of petroleum based fuels is becoming progressively more problematic, essentially due to the limited life span of fossil fuel resources, located in politically and economically instable regions, and to the imposed constraints to carbon dioxide emissions responsible by global warming [1,2].

One reliable alternative is the use of biofuels. The recent interest in biodiesel can be understood by its characteristics. Being easy to produce from renewable resources, and environmentally friendly, it may help to meet the increasing energy demand, as well as to keep under control greenhouse gas emissions. Additionally, it is non-toxic, sulfur-free and biodegradable, being used in unmodified diesel engines pure or as a blend [1,3].

The current process of choice to produce biodiesel is transesterification that consists in the reaction of a fat or oil with an alcohol, commonly methanol or ethanol [4], to produce fatty acid alkyl esters and a by-product, glycerol [5]. Biodiesel production created a new market for the excess production of vegetable oils and animal fats.

Typically, a catalyst is necessary to improve reaction speed and yield. Transesterification is usually carried out under an excess of alcohol in order to move the reaction towards the products [5,6]. Different types of catalysts can be used such as sodium or potassium hydroxides, sulfuric acid, ion exchange resins and lipases [7]. The most currently used are the basic catalysts in spite of their shortcomings [8]. The use of a basic catalyst makes necessary to remove the catalyst and formed soaps from the product, consequently having to manage waste streams with a high pH. Due to the sensitivity of basic catalysts to the fatty acids and water contents, no low-quality raw materials can be used. In addition, alkaline transesterification is low in selectivity leading to undesirable side reactions [9,10]. Equipment corrosion and the need of vigorous stirring (required for the mixing of the two-phase mixture of oil and alcohol) [8,11] are some of the technical problems that can also be implicated. In conclusion and in spite of being the preferred process from an industrial point of view, the basic catalysis is considered to be costly and energy demanding.

Acid catalysis and enzymatic based transesterifications have been widely pursued but are of limited application due to their still unsolved problems. Acid catalysis has long reaction times [12] and enzymatic reactions involve complex processing equipment and a high cost of enzymes [13].

Recently some work has been addressing the near/supercritical synthesis of biodiesel [2]. This process seems to have several advantages over the catalyzed approaches and could successfully overcome a number of the problems of conventional processes [14].

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The issues related to catalyst removal, replacement and sensibility to fatty acids and water are not a concern as no catalyst is used. Very good quality glycerol is produced and only a simple evaporation process of the excess amount of methanol is necessary to get fatty acid methyl esters (FAMES) within specified characteristics. The conversion is high, being the free fatty acids in the oil esterified simultaneously with the triglycerides, and the reaction duration is significantly shorter, only minutes, even with low-quality raw materials. Therefore, it requires a smaller reactor size to achieve the same production output of the conventional biodiesel production process [9].

Although the supercritical process requires high pressures and temperatures the advantages of a non-catalyzed process may make it competitive with the existing alkali catalyzed processes, especially for the conversion of inferior quality raw resources, rich in free fatty acids and water, such as waste cooking oils [15,16]. Fig. 1 shows the typical process of a biodiesel production by supercritical alcohol [15].

For a rational design and operation of biodiesel production processes with supercritical alcohols it is essential to have quantitative and reliable information about the phase equilibria of mixtures containing alcohols, fatty acid esters and glycerol, near or above the critical temperature of the alcohol.

Shimoyama et al. [17–21] performed several vapor–liquid equilibria measurements for systems of interest for the biodiesel supercritical production process. Data have been reported for the vapor–liquid equilibria of methanol+fatty acid methyl ester systems at 493–543 K [20], for the vapor–liquid equilibria of ethanol+ethyl laurate and ethanol+ethyl myristate systems at 493–543 K [19], for the vapor–liquid equilibria of methanol+glycerol and ethanol+glycerol systems at 493–573 K [18], and for the vapor–liquid equilibria of a methanol+FAMES mixture at 523–573 K [21]. Only the works of Shimoyama et al. have

been, up to now, focused on these kind of high pressure binary systems.

The same authors correlated the reported data for methyl ester + methanol systems with the PRASOG model (Peng–Robinson equation of state with an EoS–gE mixing rule based on the ASOG model) [20]. The first attempt by these authors was to set the binary interaction parameters  $l_{ij}$  and  $k_{ij}$  to zero. For the higher temperatures those predictions diverged from the experimental data in the vapor and liquid phases. Improved results were obtained adjusting the  $l_{ij}$ 's for each binary system using the provided experimental data at high pressures. Values for those parameters were found to be quite large and negative, in order to, as stated by the authors, include the contribution of the energy parameter and the very large differences of the molecular size between methanol and fatty acid methyl ester.

The data for ethyl ester + ethanol systems were modeled with the Peng–Robinson equation of state (PR–EoS) with two different mixing rules for the energy and size parameters, the van der Waals and the Wong–Sandler mixing rules, with different results obtained for the liquid and vapor phases [19]. The modified version of UNI-FAC was applied to calculate the excess Gibbs free energy. With the two binary interaction parameters,  $k_{ij}$  and  $l_{ij}$ , correlated from the high-pressure experimental data, the van der Waals mixing rule provided the best results for the liquid phase, but the  $k_{ij}$ 's used are temperature dependent. The Wong–Sandler mixing rule described better the vapor phase, however, requiring a temperature dependent and large binary interaction parameter, fitted from the provided experimental data.

For the glycerol systems the Peng–Robinson equation of state was used, adopting the van der Waals mixing rule and the PRASOG model [18]. Once more the van der Waals mixing rule better described the liquid phase data, using temperature dependent  $k_{ij}$ 's and  $l_{ij}$ 's determined from the high-pressure experimental data.

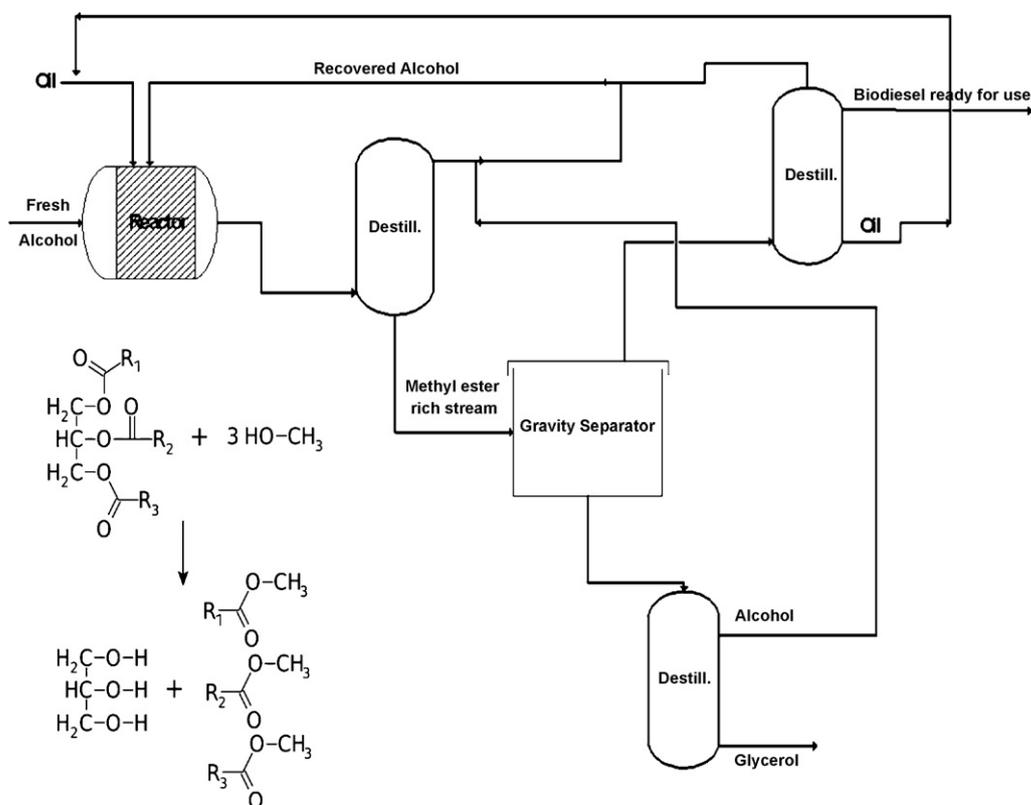


Fig. 1. Typical biodiesel production process by supercritical alcohol and transesterification reaction scheme.

The EoS–gE mixing rule provided a better description of the vapor phase, with no fitting parameters used.

The methanol + FAMES mixture was also successfully correlated with the PR-EoS and the van der Waals mixing rule [21]. The mixture was considered to be a pseudo-binary system and, in the same way as described above, the two binary interaction parameters were correlated from the experimental data, being the  $k_{ij}$ 's temperature dependent.

Shimoyama et al. have also attempted at correlating the experimental data using a combination of the Soave–Redlich–Kwong (SRK) equation of state with the Wong–Sandler (WS) mixing rules, using both the Conductor-like Screening Model (COSMO and the UNIFAC models [17]). Predictions for the liquid phase by SRK/WS/COSMO-SAC reproduced the experimental data more accurately than calculations made with SRK/WS/UNIFAC.

The results summarized above indicate that cubic equations of state with complex gE mixing rules provide the best results for the description of the vapor phase of ester + alcohol systems, in a broad range of temperatures and pressures. However, it is necessary to include temperature dependent binary interaction parameters that have to be correlated from experimental data due to the limited prediction capability of those approaches. On the other hand, the liquid phase description is poorer than the one provided by the conventional van der Waals mixing rules. In conclusion, there is not a single model able to simultaneously describe the liquid and vapor phases of these systems.

To overcome the use of empirical corrections to cubic EoSs or gE mixing rules, the breakthrough in the modeling of polar and highly non-ideal systems came with the development of more rigorous explicit association models.

Brignole and co-workers [22,23] applied the Group Contribution with Association Equation of State (GCA-EoS) to describe the phase equilibria involved in the supercritical methanolysis of vegetable oils. The use of this group contribution approach can be considered to be quite demanding while dealing with the amount of necessary regressed parameters and with the calculation of the association contributions for multiple associating groups.

Other association models are the statistical associating fluid theory (SAFT) [24], the associated-perturbed-anisotropic-chain-theory (APACT) [25] and the Cubic-Plus-Association (CPA) EoS [26,27]. NguyenHuyh et al. [28] used the GC-SAFT approach to describe small ester + 1-alkanol systems (from ethanol to butanol), with reasonable results obtained when considering the cross-association interaction between esters and alkanols. Grenner et al. [29] described the vapor–liquid equilibria at moderate conditions of several systems including small ester + alcohol mixtures in order to compare the accuracy of two association models. A lattice model that explicitly accounts for hydrogen bonding, the nonrandom hydrogen bonding (NRHB) theory, and the PC-SAFT equation were considered. Results show that none of the models is overall superior over the other.

None of these models that are theoretically sound approaches to the description of polar systems have been applied to the description of the phase equilibria of fatty acid ester + alcohol systems at high temperatures and pressures.

The CPA EoS, used in this work, is a combination of the Soave–Redlich–Kwong (SRK) EoS, used for the description of the physical interactions, with the Wertheim's first-order perturbation theory, which can be applied to different types of associating compounds [26,27]. The coupling of a simple cubic equation of state with the Wertheim association term that accurately describes the specific association interactions between like molecules (self-association) and unlike molecules (cross-association or solvation) provides the capability to describe complex systems, in broad temperature and pressure conditions, with no need of increasing the physical term complexity.

Previous results have shown the applicability of the CPA EoS for biodiesel systems. The CPA EoS has been successfully applied to described the water solubility in fatty acid esters and biodiesels [30], the mutual solubilities of water and fatty acid binary mixtures [31], the LLE of multicomponent systems containing fatty acid esters, alcohols and glycerol [32], the vapor–liquid equilibrium of several glycerol + alcohol and water + glycerol systems [33] and the vapor–liquid equilibria of fatty acid ester + methanol/ethanol systems [34], at atmospheric pressure.

The results for these last systems are relevant for the work developed here. It was shown that the CPA EoS can accurately describe the solvation interaction between the ester and the alcohol group, through a solvation scheme for the cross-association energy and volume [32,34]. In addition, the binary interaction parameters,  $k_{ij}$ 's, are shown to follow a linear trend with the ester carbon number when a single cross-association volume,  $\beta_{ij}$ , is used [34]. Also, a new association scheme for glycerol along with small and temperature independent binary interaction parameters provided a very good description of glycerol systems [33].

Those binary interaction parameters are used in this work to evaluate the predictive character of the model in the description of the systems composed of an ester and an alcohol or glycerol and an alcohol, at high temperatures and pressures, not yet attempted in our previous studies.

It will be shown that the CPA EoS is able to successfully predict the experimental data, proving a reliable model for the phase behaviour of systems for which no experimental data is available, even at conditions far removed from those used in the estimation of the model parameters.

## 2. Model

The Cubic-Plus-Association equation of state, first proposed by Kontogeorgis et al. [35], combines the simplicity and robustness of a cubic equation of state with the Wertheim term, in order to explicitly take into account molecular association.

With a Soave-type temperature dependency of the pure component energy parameter,  $a$ , the CPA EoS can be expressed as:

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

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

$b$  is the co-volume parameter,  $\rho$  is the density,  $g$  is a simplified radial distribution function [36],  $X_{A_i}$  is the mole fraction of pure component  $i$  not bonded at site  $A$ ,  $x_i$  is the mole fraction of component  $i$  and finally  $T_r$  is the reduced temperature.

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

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (3)$$

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp \left( \frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (4)$$

The simplified radial distribution function given by [36] is used:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (5)$$

$$\eta = \frac{1}{4} b\rho \quad (6)$$

**Table 1**  
CPA pure compound parameters, critical temperatures and modeling results.

Compound	$T_c$ (K)	$a_0$ (J m <sup>3</sup> mol <sup>-2</sup> )	$c_1$	$b$ ( $\times 10^5$ m <sup>3</sup> mol <sup>-1</sup> )	$\varepsilon$ (J mol <sup>-1</sup> )	$\beta$	AAD <sup>a</sup> %	
							$P$	$\rho$
Ethyl laurate	719.1	8.23	1.44	30.18				
Ethyl myristate	744.3	9.52	1.54	34.54				
Methyl laurate	712.0	7.46	1.37	24.04			0.8	1.31
Methyl myristate	742.4	8.84	1.51	27.95			3.66	
Methanol-set1 ( $T_r$ : 0.45–0.85)	512.7	0.43	0.75	3.22	20859	0.034	0.29	0.14
Methanol-set2 ( $T_r$ : 0.85–1)	512.7	0.41	1.18	3.25	19945	0.047	1.60	3.83
Ethanol	514.7	0.68	0.94	4.75	21336	0.019	0.35	0.51
Glycerol	766.1	1.21	1.06	6.96	19622	0.009	0.77	1.49

$$^a (\%AAD = \frac{1}{NP} \sum_{i=1}^{NP} ABS \left[ \frac{\exp_i - \text{calc}_i}{\exp_i} \right] \times 100).$$

CPA involves the knowledge of three pure component parameters in the physical part that are  $a_0$ ,  $c_1$  and  $b$ , and two more for the association term ( $\varepsilon$  and  $\beta$ ). These last two are only required for associating components. Either way, all these parameters are estimated through a simultaneous regression of liquid density and vapor pressure data.

In order to determine the pure compound parameters, as well as for phase equilibria calculations, it is necessary to assign an association scheme, that is, the number and type of association sites for the associating compound.

Following the nomenclature proposed by Huang and Radosz [37], for alcohols the two sites (2B) is the most successfully applied association scheme [27]. For glycerol, a recently proposed association scheme was applied, the  $3 \times 2B$ , that considers the glycerol molecule as having three equal hydroxyl groups, each one with two association sites [33]. That scheme already provided very good results for the liquid–liquid equilibrium of multicomponent systems containing fatty acid esters, alcohols and glycerol [32] as well as for the vapor–liquid equilibrium of several glycerol + alcohol and water + glycerol systems [33], at low pressures.

When dealing with mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules, and for mixtures composed solely by non-associating compounds the binary interaction parameter,  $k_{ij}$ , is the only adjustable parameter.

Otherwise, when CPA is employed to mixtures containing cross-associating molecules, combining rules for the association energy and volume parameters are required. Several combining rules have

been suggested and applied with different results for different phase equilibria and systems [38], being the Elliot rule or CR-4 [33] the most successful for glycerol containing systems.

Within the cross-associating systems, there is a special case that occurs when systems are constituted by a self-associating compound and an inert that can solvate with the associating component, as it is the case of ester + alcohol systems. Accordingly, for the ester compounds a single association site able to cross-associate with the alcohol is considered [30]. For that type of systems a procedure proposed by Folas et al. [39] has been used to obtain the cross-associating energy and volume. The cross-association energy between the ester and the alcohol is taken as half the alcohol association energy and the cross-association volume is used as an adjustable parameter, fitted to equilibrium data. Within the systems of relevance for the biodiesel research, the referred approach was successfully applied to model the water solubility in fatty acid esters and biodiesels [30] and the vapor–liquid equilibria of fatty acid ester + methanol/ethanol systems at atmospheric pressure [34].

### 3. Results and discussion

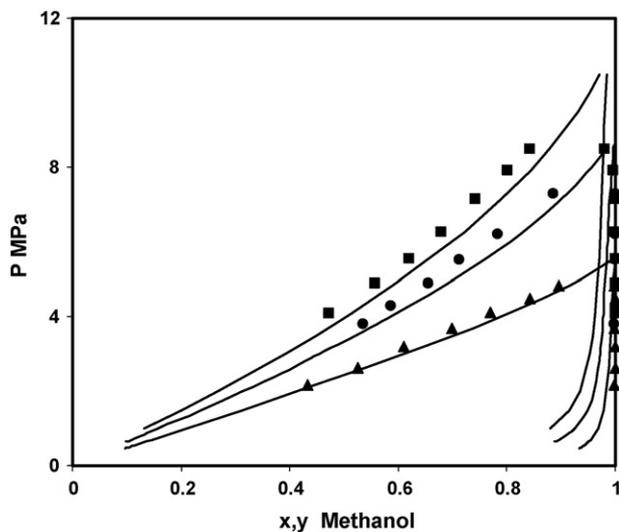
#### 3.1. CPA pure compound parameters

The ester compounds do not self-associate. Accordingly, there are only three pure component parameters to be estimated, the ones of the physical part. The CPA pure compounds parameters for the ester family were previously proposed for esters from 2 up to 19 carbons atoms [30], including methyl laurate and methyl myristate. These parameters were established through a simultaneous regression of vapor pressure and liquid density data, within the reduced temperature range of 0.45–0.85. These pure compound parameters lead to global average deviations inferior to 2% for liquid densities and 1% for vapor pressures [30].

In the same work [30] it was shown that the  $a_0$ ,  $c_1$  and  $b$  CPA parameters followed a trend with the ester carbon number, as previously observed for the n-alkanes and n-alcohols series. It was also observed that esters with the same carbon number have similar values for the pure compound parameters, being those either methyl, ethyl, propyl or butyl esters, acetates and even formates. Therefore, quadratic and linear correlations for the estimation of these parameters can be proposed, enabling to calculate the CPA pure compound parameters in the absence of vapor pressure and liquid density data, as happens for ethyl laurate and ethyl myristate.

In fact, for esters for which no vapor pressure and liquid density data were available, using pure compound parameters equal to the ones of another ester with the same carbon number provided very good results for the water solubility in binary ester systems [30].

Due to the lack of available literature data for the fatty acid esters critical temperatures, required in Eq. (2), the best group contribution model was previously assessed to be the one of Wilson and



**Fig. 2.** VLE for the methanol + methyl laurate system at 493 K (▲), at 523 K (●) and at 543 K (■) [20]. CPA results using the first set of parameters for methanol presented at Table 1 (—).

Jaspersion [40] for methyl esters and the one of Nikitin et al. [40] for ethyl esters, as discussed by Lopes et al. [41].

For methanol, ethanol and glycerol, two more pure compound parameters are required for the association term. Those parameters were also previously established and used in several works [33,42], considering the 2B association scheme for alcohols and the  $3 \times 2B$  scheme for glycerol. Those parameters provided very good results for binary VLE of fatty acid esters and alcohols [34], and of glycerol and alcohols [33], at low pressures.

All the CPA pure compound parameters used in this work are presented at Table 1 along with the deviations obtained for liquid densities and vapor pressures.

### 3.2. Predictions of high pressure vapor–liquid equilibria

Alcohol + fatty acid ester mixtures are not easy to model due to their differences in size and intermolecular interactions.

As discussed above, in a previous work [34] using new experimental data for the atmospheric pressure VLE of binary systems composed of esters (methyl laurate, methyl myristate, methyl oleate) and alcohols (methanol, ethanol), the performance of the CPA EoS in the description of these phase equilibria was studied. The cross-association between the ester group and the hydroxyl group was considered using the solvation scheme described before with the value for the cross-association energy,  $\beta_{ij}$ , being only alcohol dependent, and a linear correlation for the binary interaction parameter,  $k_{ij}$ , with the ester carbon number being also proposed [34].

In this work, this predictive character of the CPA EoS model is evaluated, by using the atmospheric pressure estimated binary interaction parameters to describe the phase equilibria at high pressures and temperatures.

Starting with the ester+alcohol binaries, high pressure and high temperature vapor–liquid equilibria data were available for the systems methanol + methyl laurate/methyl myristate [20], ethanol + ethyl laurate/ethyl myristate [19], and methanol + FAMES [21].

The first systems studied were those with methanol, in particular the mixture containing methyl laurate.

An acceptable prediction of the liquid and vapor phase compositions was initially achieved, but a degradation of the predictions with temperature was nevertheless observed (Fig. 2).

In order to obtain a better description of the liquid and vapor phases at near critical conditions, the methanol CPA parameters were re-estimated closer to the critical point, in the  $T_r$  range of 0.85–1. A new set of parameters for methanol that provided a better description of the critical region is here proposed and reported in Table 1 (set 2).

Improved results were obtained for the vapor–liquid equilibria of the methyl laurate + methanol system at all temperatures, particularly for the liquid phase, as shown in Fig. 3. It must be noticed that no degradation of the description with temperature is now observed. The new methanol CPA parameters (set 2) were thus used here for the calculations involving methanol systems.

Very good results for the vapor–liquid prediction of the methyl myristate + methanol system were achieved, as presented in Fig. 4 and Table 2. The small deviation observed in the liquid phase at low temperatures is probably related to the uncertainty of the experimental data. Nevertheless, the differences between experimental and CPA calculated values are lower than the reported experimental uncertainties for the liquid phase.

For the ethanol systems there was no need to re-estimate the ethanol CPA pure compound parameters, as they can successfully predict the high temperature region.

A good prediction of the liquid phase for fatty acid ester (ethyl laurate/ethyl myristate) + ethanol systems was also accomplished

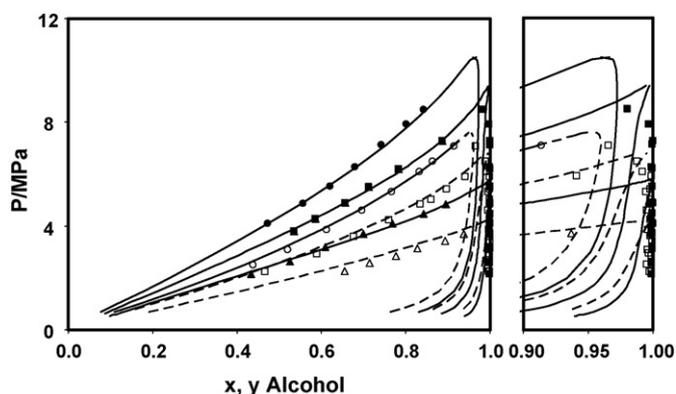


Fig. 3. VLE for methanol + methyl laurate [20] (full symbols) and ethanol + ethyl laurate [19] (empty symbols) systems (triangles, 493 K; squares, 523 K; circles, 543 K). CPA results (—, methanol systems; ---, ethanol systems).

(Figs. 3 and 4 and Table 2). The vapor phase description is worse than for methanol systems. This may be related to the difficulty in taking into account the dispersive interactions due to the additional methyl group of alcohols and fatty acid esters, or to the quality of the experimental data for the vapor phase, as no other data is available for these systems.

Considering all binary systems containing a fatty acid ester and an alcohol, global average deviations, AAD %, inferior to 2% were obtained for the alcohol compositions in both liquid and vapor phases, in the temperature and pressure ranges studied.

Shimoyama et al. [19] while correlating ethanol systems using the van der Waals and the Wong–Sandler mixing rules, with temperature dependent binary interaction parameters, reported an average deviation from the experimental data (given by the difference between the calculated and experimental ethanol compositions) of less than 0.02 for the liquid and vapor phases. For methanol systems no deviations between the experimental and the correlated results were reported.

The CPA EoS can predict the vapor–liquid equilibrium of ethanol systems with deviations inferior to 0.04 for both liquid and vapor phases, showing that there is no major advantage in increasing the complexity of equations of state through the use of gE mixing rules or temperature dependent binary interaction parameters. Excellent predictions can be achieved being only necessary a single binary interaction parameter for the physical part, that can be obtained from existing correlations developed at atmospheric pressure.

Experimental data were also available for methanol/ethanol + glycerol systems at high pressures [18]. Once more, the  $3 \times 2B$

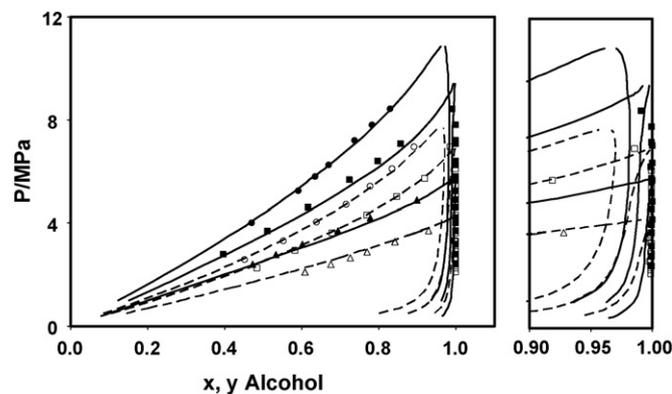


Fig. 4. VLE for methanol + methyl myristate [20] (full symbols) and ethanol + ethyl myristate [19] (empty symbols) systems (triangles, 493 K; squares, 523 K; circles, 543 K). CPA results (—, methanol systems; ---, ethanol systems).

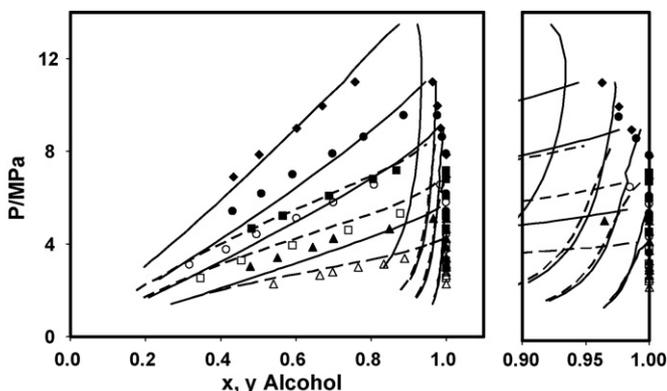
**Table 2**  
Modeling results for fatty acid ester + methanol/ethanol and ethanol/methanol + glycerol systems.

	$k_{ij}$ [34]	AAD <sup>a</sup> %	
		$y_{\text{Alcohol}}$	$x_{\text{Alcohol}}$
<b>Methyl laurate + methanol</b>			
493 K	-0.0326	0.91	1.77
523 K		1.91	0.99
543 K		2.84	0.81
<b>Methyl myristate + methanol</b>			
493 K	-0.0432	0.48	2.61
523 K		1.16	2.4
543 K		1.77	0.87
<b>Ethyl laurate + ethanol</b>			
493 K	-0.0080	1.4	5.3
523 K		2.93	2.91
543 K		4.37	1.74
<b>Ethyl myristate + ethanol</b>			
493 K	-0.014	0.93	3.75
523 K		2.17	1.66
543 K		3.39	1
<b>Glycerol + methanol</b>			
493 K	0.014	0.97	11.25
523 K		2.26	7.51
543 K		3.16	8.2
573 K		5.88	3.79
<b>Glycerol + ethanol</b>			
493 K	0.06	1.66	10.55
523 K		3.88	8.83
543 K		5.71	8.32
<b>FAMES + methanol</b>			
523 K		0.39	1.56
548 K		0.49	4.3
573 K		1.35	4.08

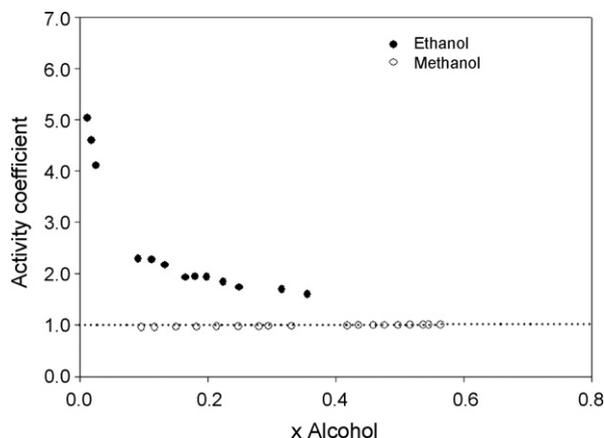
$$^a \left( \%AAD = \frac{1}{NP} \sum_{i=1}^{NP} ABS \left[ \frac{\exp_i - \text{calc}_i}{\exp_i} \right] \times 100 \right).$$

association scheme for glycerol and binary interaction parameters estimated from atmospheric pressure vapor–liquid equilibria were applied for high pressure predictions [33]. The predictions reported in Fig. 5 present a good description of the experimental data although with a slightly higher deviation when compared with the fatty acid ester systems studied before.

Comparing the experimental and the predictive high pressure results it can be seen that for the glycerol + methanol system the CPA results show a negative deviation from Raoult's law, whereas the experimental results reveal a positive deviation from Raoult's law. The inverse is shown for the glycerol + ethanol system.



**Fig. 5.** Experimental VLE for methanol + glycerol [18] (full symbols) and ethanol + glycerol [18] (empty symbols) systems (triangles, 493 K; squares, 523 K; circles, 543 K; diamond shape, 573 K). CPA results (—, methanol systems; ---, ethanol systems).

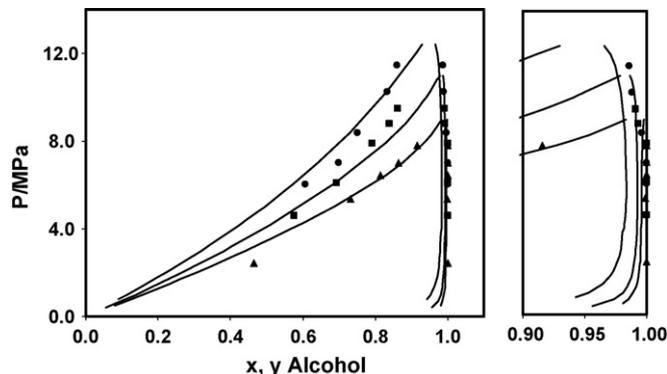


**Fig. 6.** Activity coefficients for methanol/ethanol systems vs. alcohol composition.

As seen in Fig. 6, where the activity coefficients for methanol/ethanol + glycerol systems are presented as a function of the alcohol composition, calculated from the atmospheric pressure experimental data [33], considering that activity coefficients for the methanol + glycerol system are lower or very close to unity, and for ethanol + glycerol are considerably higher than one, the above described deviations from the Raoult's law proposed by the CPA EoS are more likely to be correct than the experimental ones. In that way, while evaluating the model results it must be considered the somewhat low quality of the experimental results.

Although not usually successfully applied to alcohol containing systems, the proximity of the glycerol + methanol activity coefficients to unity (Fig. 6) can explain the success of the van der Waals mixing rule in correlating this mixture.

The very last test to the predictive character of the model was evaluated through the modeling of the vapor–liquid equilibria of the methanol + FAMES multicomponent mixture (85 wt% of  $C_{18}$  methyl esters (mainly methyl oleate) and the rest made of  $C_{16}$  and  $C_{14}$  methyl esters). The linear correlation with the ester carbon number was once more applied to generate the required binary interaction parameters. Good predictions were achieved for the three selected temperatures, as shown in Fig. 7, with global average deviations, AAD %, for the methanol composition inferior to 1% for the vapor phase and to 3% for the liquid phase. It should be recalled that the PR-EoS with the van der Waals mixing rule was only able to satisfactorily describe the vapor–liquid equilibria of the methanol + FAMES mixture considering the system to be a pseudo-binary and optimizing temperature dependent binary interaction parameters from the experimental data [21].



**Fig. 7.** Experimental VLE for the system methanol + FAMES [21] ( $\Delta$ ) 523 K; ( $\square$ ) 548 K; ( $\bullet$ ), 573 K). CPA results (—).

The results here reported show the importance of using an adequate contribution to take into account the polar interactions between esters and alcohols, as it is with the CPA EoS through the Wertheim association term, making possible to successfully predict the vapor–liquid equilibria of ester + alcohol/systems, in a large range of pressures and temperatures.

Having applied the CPA EoS to the modeling of different phase equilibria of binary and multicomponent systems composed of fatty acids, esters, water, glycerol and alcohols, the research work will move towards the description of mixtures with more complex components such as triglycerides.

#### 4. Conclusions

In this work the Cubic-Plus-Association EoS was used to predict the vapor–liquid equilibria of several fatty acid ester + ethanol or methanol and of glycerol + ethanol or methanol systems, at near/supercritical conditions.

A single and temperature independent binary interaction parameter (in the physical term) and a constant value for the cross-association volume in the case of fatty acid ester + alcohol systems, fitted to experimental VLE data at atmospheric pressure, was used to predict the experimental data. It was shown that it is possible to accurately predict the phase equilibria for the studied systems with global average deviations inferior to 2% for the alcohol compositions in both liquid and vapor phases. The model is able to correctly take into account the cross-association phenomena between the polar molecules here considered.

The CPA EoS proves to be a valuable alternative to the demanding EoS/gE models, typically employed for high pressure phase equilibria calculations, to evaluate the design, operation and optimization of biodiesel production facilities using supercritical conditions since it can successfully predict the phase equilibria observed on these processes.

#### Acknowledgements

Financial support was provided to LSRE by FEDER/POCI/2010. Mariana B. Oliveira acknowledges Fundação para a Ciência e a Tecnologia through her PhD (SFRH/BD/29062/2006) scholarship. A.J. Queimada acknowledges support from POCI/N010/2006.

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