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Modeling Systems Relevant to the Biodiesel Production Using the CPA Equation of State. Part 2. Systems with Supercritical CO₂

Ioannis Tsivintzelis^{*1,2}, Shahid Ali^{1,3} and Georgios M. Kontogeorgis¹

¹*Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

²*Aristotle University of Thessaloniki, Department of Chemical Engineering, 54124, Greece*

³*Current address: Department of Energy Technology, Aalborg University, Pontoppidanstræde 111, 9220 Aalborg, Denmark*

**Corresponding author: Ioannis Tsivintzelis: E-mail: gtsivint@eng.auth.gr*

Abstract

The CPA EoS is applied to binary mixtures of CO₂ with fatty acids and their methyl- or ethyl- esters. The model, using one temperature independent binary interaction parameter, satisfactorily describes the phase behavior of such systems. Correlations of the binary interaction parameters with the number of esters' or acids' carbon atoms, or with the number of double bonds for compounds with the same number of carbon atoms, were developed in order to make predictions feasible in cases of lack of experimental data. Subsequently, the model was applied for predicting the phase behavior of ternary and multicomponent mixtures. The model rather satisfactorily predicts the vapor-liquid equilibrium of such systems. In accordance with the first part of this series of articles [Tsivintzelis et al. 430 (2016) 75-92], since the binary parameters were optimized solely using experimental data for binary mixtures, CPA results for the ternary mixtures are pure predictions.

Keywords: Supercritical CO₂, Biodiesel, Fatty acids, Esters of Fatty acids, CPA, Phase Equilibrium

1. Introduction

The processing of vegetable oils with supercritical CO₂ is attracting considerable attention mainly from the food, but also from the pharmaceutical, nutraceutical and biodiesel industries. The extraction of vegetable oils, the selective extraction of valuable ingredients and the fractionation of fatty acids and fatty acid esters are now well studied processes [1]. However, such compounds are found in many pharmaceutical or nutraceutical products of high added value, where the purity of the products is of high importance, rendering such applications ideal for processing with supercritical CO₂ (which is nontoxic and can be easily separated from the final product material).

Biodiesel is usually produced from vegetable oils by the transesterification of triglycerides using excess of methanol or ethanol. Recently, several studies investigated the potential of using supercritical CO₂ as a co-solvent or as a reaction medium in the transesterification reactions [2-4]. Moreover, supercritical CO₂ has also been suggested for biodiesel purification processes, aiming to the removal of glycerol and other polar contaminants [5].

Vegetable oil and biodiesel related mixtures include many compounds such as fatty acids, alkyl esters of fatty acids, glycerides, glycerol, low molecular weight alcohols and water. The thermodynamic modeling of such multicomponent mixtures is rather demanding, mainly due to the highly non-ideal behavior of some systems (for example aqueous systems of organic acids), but also due to the lack of data, or due to the quality of some available data. In more detail, mainly due to the decomposition of high molecular weight compounds at relatively high temperatures, there is lack of experimental data for critical temperatures or vapor pressures for fatty acids, glycerides and esters of fatty acids. Moreover, such compounds are usually obtained in mixtures of various isomers, since compounds of the same family and similar molecular weight present similar physical properties rendering their purification rather demanding. Consequently, experimental data are often based on low purity samples. Furthermore, many mixtures of interest are reactive (i.e. mixtures of esters with alcohols, or alcohols with fatty acids) rendering the measurement of the phase behavior very demanding. Nevertheless, many experimental data of good quality were measured during the last years.

The Cubic-Plus-Association (CPA) equation of state (EoS) [6] is a combination of the SRK cubic Equation of State (EoS) with the association term that is used in the SAFT type models [11] (developed by Wertheim [7-10]). The CPA model has been extensively reviewed in literature [12-16] and is not presented here. Readers are referred to the original studies and should be familiar with concepts such as the association schemes and the combining rules used in the CPA model [12-16].

This study is a continuation of our previous study in modeling mixtures relevant to the production of biodiesel [17], where CPA pure fluid parameters for fluids, such as glycerides, organic acids, heavy esters and glycerol, were presented, along with trends of those parameters with the van der Waals volume. The performance of CPA in modeling the vapor – liquid (VLE) and the liquid – liquid equilibrium (LLE) of binary mixtures, containing water, glycerol, or alcohols with fatty acids, esters of fatty acids or glycerides, was evaluated and trends of such binary parameters with the molecular weight (or the carbon chain length) were obtained. Such estimated binary parameters and their correlations were used for predicting the liquid-liquid equilibrium of ternary and multicomponent mixtures [17].

In this study we present the application of CPA to describe binary, ternary and multicomponent systems that contain CO₂ and biodiesel-related compounds (fatty acids, heavy esters and methanol). Similarly to our previous study, emphasis is put on the establishment of systematic trends of the binary interaction parameters, in order to

enhance the predicting ability of the model for multicomponent systems. Moreover, all results for the ternary and multicomponent systems are considered as pure predictions, since binary parameters fitted only to binary data are used and there is no fine tuning of any parameter based on ternary or multicomponent data.

2. Binary systems with CO₂

Having the pure fluid parameters for low molecular weight acids or fatty acids and their esters from our previous study [17], the CPA EoS was applied to correlate the vapor – liquid equilibrium (VLE) of their mixtures with CO₂. In more detail, the pure fluid parameters for saturated esters and unsaturated esters were adopted from Tables 2 and 3, respectively, of reference 17, while parameters for acids were adopted from Table 4 of reference 17. The pure fluid parameters of CO₂ and methanol were adopted from literature [18]. In all cases one temperature independent binary interaction parameter (k_{ij}) was used.

2.1. CO₂ – Esters of Fatty Acids

Mixtures of CO₂ with methyl- and ethyl- esters of low molecular acids and fatty acids were modeled using available experimental data from literature. Such data, especially for mixtures with high molecular weight fatty acids, are in some cases contradictory and, thus, data from different studies are not in good agreement to each other. An example is shown in Figure 1. Nevertheless, many experimental data of good quality were measured during the last years.

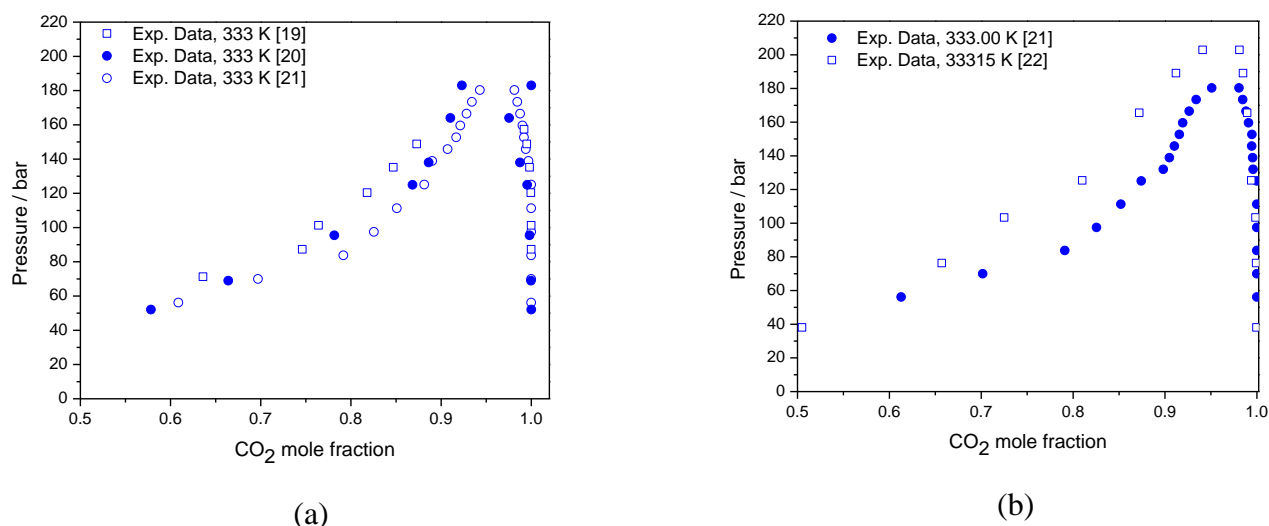


Figure 1. CO₂ - methyl oleate (a) and CO₂ - methyl linoleate (b) VLE. Experimental data from various literature sources [19-22].

The CPA equation of state was applied to model all the systems for which it was possible to find experimental data. In all cases, CO₂ and esters were modeled as inert compounds and one temperature independent binary interaction parameter (k_{ij}) was optimized by the experimental data. The results are presented in Table 1. The model

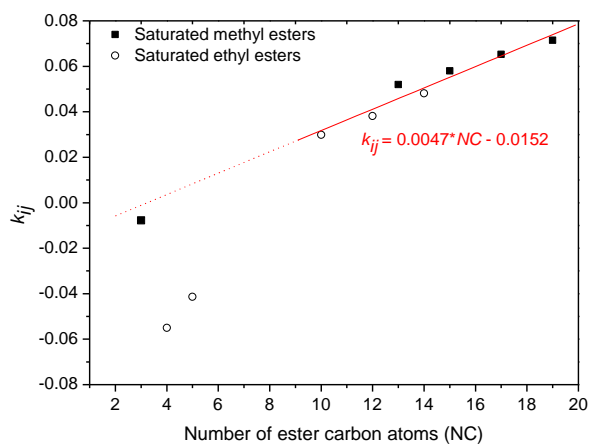
satisfactorily describes the vapor (fluid) - liquid equilibrium of such systems. Higher deviations are obtained for the ester fraction of the vapor phase. Most of such deviations are due to some low pressure data, where the ester mole fraction of the vapor phase is very low (of the order of 10^{-4} or less). However, they also reveal the difficulty in modeling such low concentrations using only one temperature independent parameter with the CPA model.

Since the aim of this study is to enhance the predictive capabilities of the CPA model, the estimated binary parameters of Table 1 are plotted against the number of carbon atoms of esters in Figure 2a. The k_{ij} s for saturated esters with more than eight carbon atoms, as for almost all biodiesel related compounds (see Tsivintzelis et al. [17]), follow a linear trend, which is more pronounced for high molecular weight compounds. In Figure 2b, the k_{ij} s are plotted against the number of double bonds for methyl- and ethyl- esters of C18- x fatty acids, i.e. 18 is the number of carbon atoms and x is the number of double bonds. As it was expected, the binary interaction parameter becomes lower as the number of double bonds increases. This is reasonable, since interactions that are more favorable should occur between the π -electrons of ester molecules and the charged (positive) carbon atom of CO₂. Results for the vapor – liquid equilibrium of CO₂ – methyl and ethyl- esters are presented graphically in Figures 3-7.

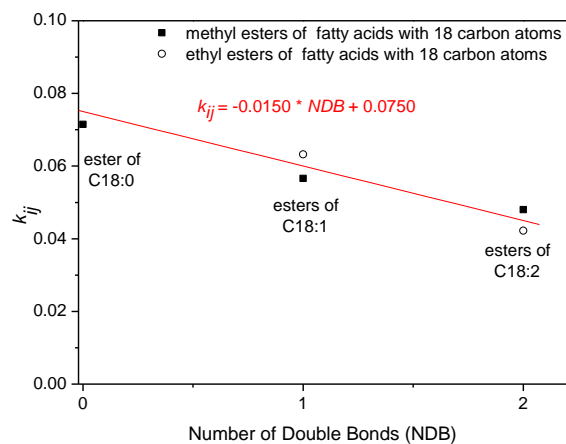
Table 1. Binary interaction parameters (k_{ij}) and deviations from experimental data for CO₂ (1) – Methyl- or Ethyl- Esters (2).

Ester	Temp. Range / K	k_{ij}	% AAD ^a in x_1	% AAD ^a in y_1	% AAD ^a in y_2	References
CO ₂ (1) – Methyl Esters (2)						
Methyl Ethanoate	298 - 313	-0.0078	11	0.36	19	[23]
Methyl Laurate	323 - 333	0.0520	4.8	6.4	59	[24]
Methyl Myristate	323 - 333	0.0580	7.8	0.13	80	[19, 25]
Methyl Palmitate	323 - 343	0.0653	13	0.11	48	[19, 25]
Methyl Stearate	323 - 343	0.0715	10	0.18	33	[19]
Methyl Oleate	323 - 343	0.0566	9.5	0.20	67	[19-22]
Methyl Linoleate	333	0.0480	8.8	0.17	77	[21, 22]
CO ₂ (1) – Ethyl Esters (2)						
Ethyl Ethanoate	323 - 393	-0.0550	10	1.3	31	[26, 27]
Ethyl Propanoate	333 - 373	-0.0414	3.8	0.80	62	[27]
Ethyl Octanoate	318 - 328	0.0299	2.4	2.3	49	[28]
Ethyl Decanoate	318 - 328	0.0381	2.4	1.9	75	[28]
Ethyl Dodecanoate	318 - 328	0.0481	2.5	2.6	65	[29]
Ethyl Oleate	323 - 333	0.0632	9.4	10	29	[30]
Ethyl Linoleate	323 - 333	0.0422	6.3	0.13	40	[30]

$$^a\% \text{AAD} = \frac{1}{n} \sum_i \left| \frac{X_i^{\text{cal}} - X_i^{\text{exp}}}{X_i^{\text{exp}}} \right| \times 100 \text{ where } X \text{ stands for the CO}_2 \text{ mole fraction of the liquid phase } (x_1) \text{ and the ester mole fraction } (y_2) \text{ of the vapor phase, while } n \text{ is the number of experimental data points}$$

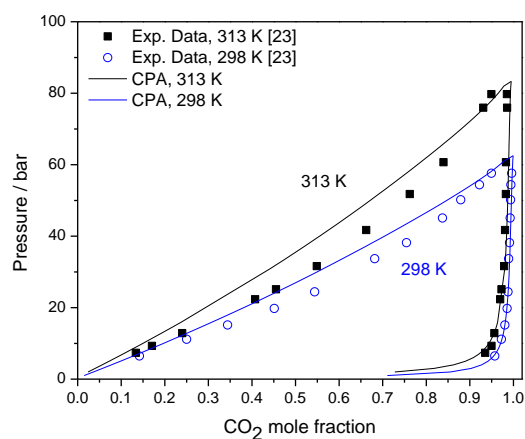


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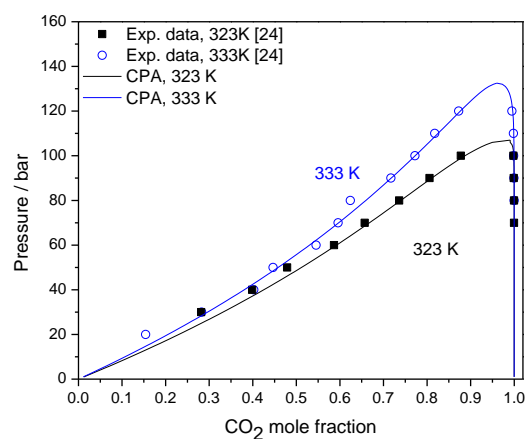


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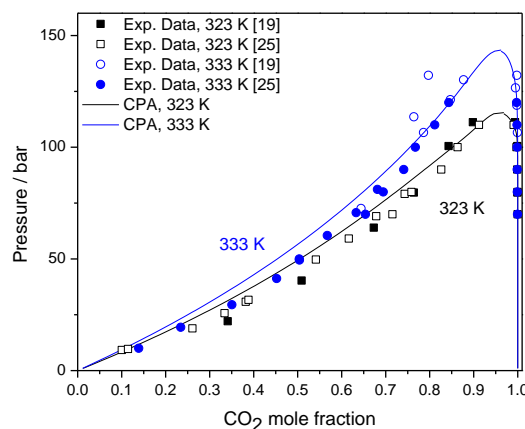
Figure 2. Binary interaction parameters (k_{ij} s) against the number of ester carbon atoms (NC) (a) and against the number of double bonds (NDB) for methyl- and ethyl- esters of C18- x fatty acids (stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2)) (b).



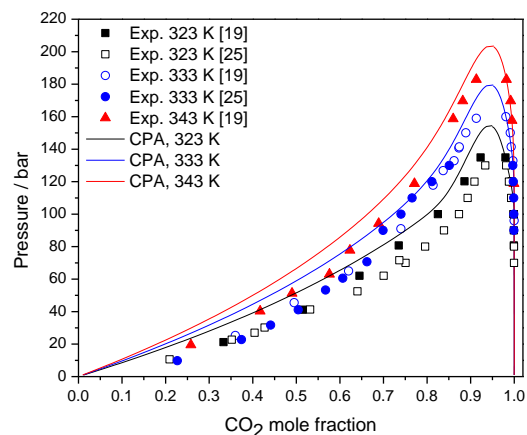
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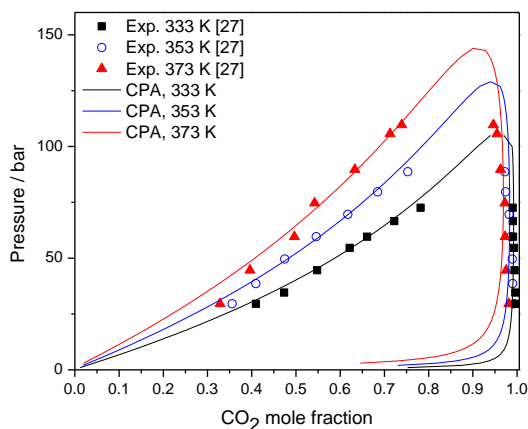


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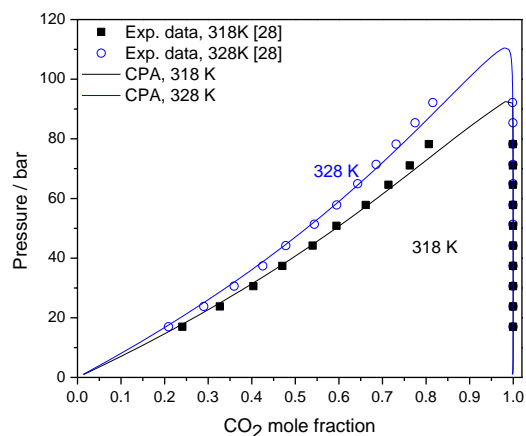


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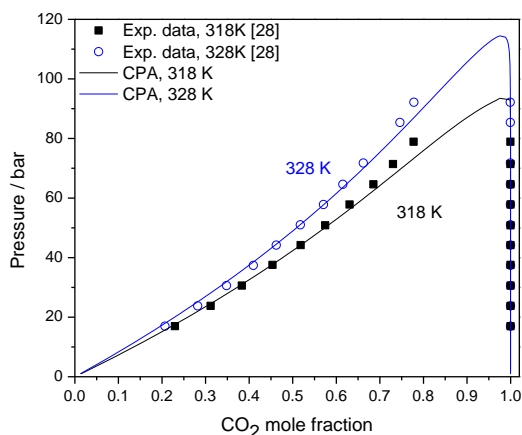
Figure 3. CO₂ – methyl- esters VLE. Experimental data (points) and CPA calculations (lines). CO₂ – methyl-ethanoate (a), CO₂ – methyl-laurate (b), CO₂ – methyl-myristate (c) CO₂ – methyl-palmitate (d). The interaction parameters are available in Table 1.



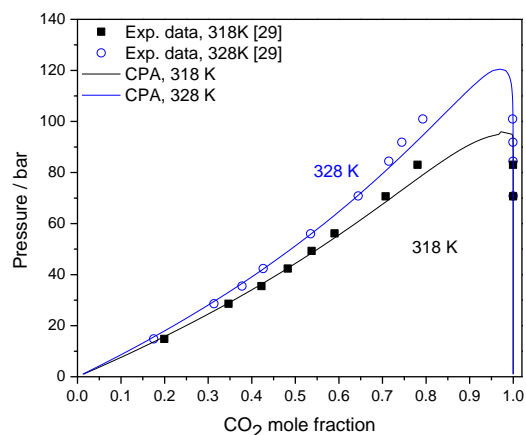
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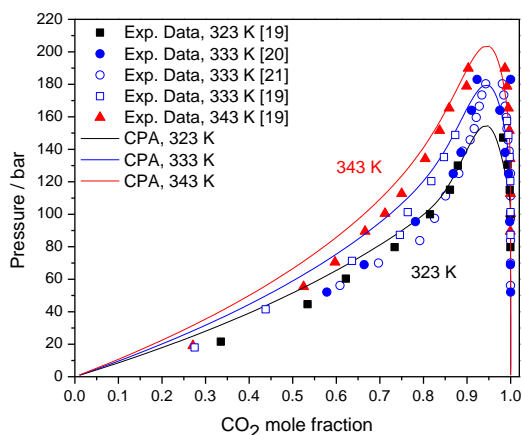


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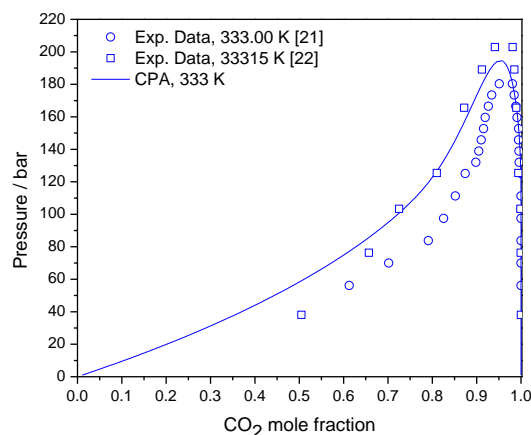


(d)

Figure 4. CO₂ – ethyl- esters VLE. Experimental data (points) and CPA calculations (lines). CO₂ – ethyl-propanoate (a), CO₂ – ethyl-octanoate (b), CO₂ – ethyl-decanoate (c) CO₂ – ethyl-laurate (d). The interaction parameters are available in Table 1.



(a)



(b)

Figure 5. CO₂ – methyl- esters of *C18-x* fatty acids VLE. Experimental data (points) and CPA calculations (lines). CO₂ – methyl-oleate (a) and CO₂ – methyl-linoleate (b). The interaction parameters are available in Table 1.

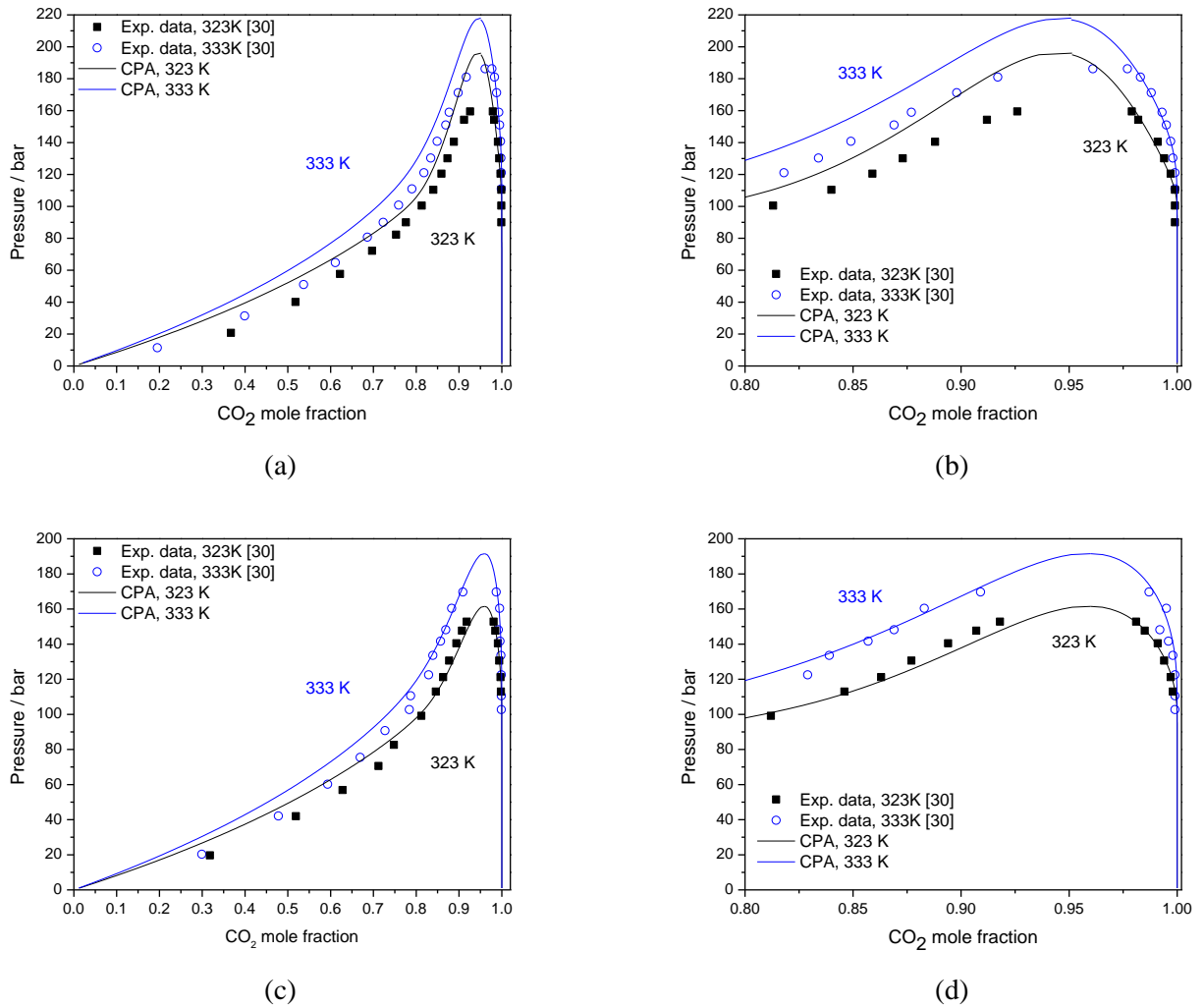


Figure 6. CO₂ – ethyl- esters of *C18-x* fatty acids VLE. Experimental data (points) and CPA calculations (lines). CO₂ –ethyl-oleate (a and b) and CO₂ – ethyl-linoleate (c and d). Interaction parameters of Table 1 were used.

The modeling of the VLE of binary systems containing CO₂ and esters is usually performed with cubic equations of state [20, 21, 31-38]. In order to enhance the correlation ability of the cubic equations of state, more complicated mixing rules and EoS/ G^E models are used [34,35]. In this direction, the Huron-Vidal first-order (MHV1) and second-order (MHV2) mixing rules, as well as the LCVM method have been investigated by combining cubic equations of state with various activity coefficient models [34,35].

In such approaches, attempts to use predictive models are of particular interest [32, 33, 38]. Jaubert and Coniglio suggested a purely predictive model, based on the Peng-Robinson equation of state. They have used a group contribution method to predict the binary interaction parameters and applied the model to predict the phase equilibria data of ternary and quaternary systems containing fatty acids and supercritical CO₂ [33]. Furthermore, Jaubert and coworkers used a predictive version of the Peng – Robinson EoS (PPR78) to model CO₂ – ethyl ester binary mixtures [38]. They conclude that the

predictive ability of the model slightly deteriorates in the critical region of mixtures with high molecular weight esters.

In addition, Oliveira et al. [37], used the CPA equation of state to model the VLE of CO₂ – ester binary mixtures. The authors considered seven binary systems and concluded that CPA can satisfactorily describe the phase behavior using one binary adjustable parameter. However, according to their approach, the critical region of CO₂ mixtures with higher esters cannot be accurately described using CO₂ pure fluid parameters adjusted to vapor pressure and density data (which overpredict the CO₂ critical point) and, thus, the authors used the critical properties of CO₂ (T_c , P_c and acentric factor) in order to calculate the pure fluid parameters of this compound.

Furthermore, the VLE of CO₂ with fatty acid methyl esters was modeled using a polar version of PC-SAFT [39]. Using a single binary adjustable parameter, the model satisfactorily describes the experimental data, but the description of the critical point region is not shown. In order to enhance the predicting ability of the approach, in a second step, the authors used a single binary parameter for all CO₂ mixtures with fatty acid esters, without significantly compromising the performance of the model [39].

Finally, Haley and McCabe used a group contribution SAFT-VR (GC-SAFT-VR) model to predict the VLE of CO₂ mixtures with methyl myristate, methyl oleate, methyl stearate, and methyl palmitate. Without using binary adjustable parameters (pure predictions), their model presented a satisfactory agreement with the experimental data away from the critical region, but resulted in an over prediction of the critical point, which is typical of all equations of state of this type [40].

Such observations are in agreement with the findings of this study, i.e. the CPA, using the pure fluid parameters of Tsivintzelis et al. [17], in many cases results in an overprediction of the critical region (see for example Figures 6a and 6b). However, it is well known that the CPA model, which unlike to other cubic equations does not use the experimental values of the critical properties for obtaining the pure fluid parameters, overpredicts the critical point of pure compounds and, as a consequence, present similar behavior for mixtures. This is a common limitation of many advanced models, such as the SAFT type models, and due to that many cross-over theories appeared in literature. In this direction, Llorell and Vega used a cross-over version of the soft SAFT EoS and modeled four CO₂ – fatty acid ester binary mixtures using with two adjustable parameters per binary system [41].

2.2 CO₂ – Fatty acids

Next the model was applied to describe the vapor – liquid equilibrium of CO₂ - acid mixtures. All the CO₂ – linear acid mixtures, for which experimental data were available in the literature, were investigated. However, as it was observed for CO₂ – fatty acid ester mixtures, in some cases contradictory experimental data are found in literature, especially for higher acids. An example is shown in Figure 7.

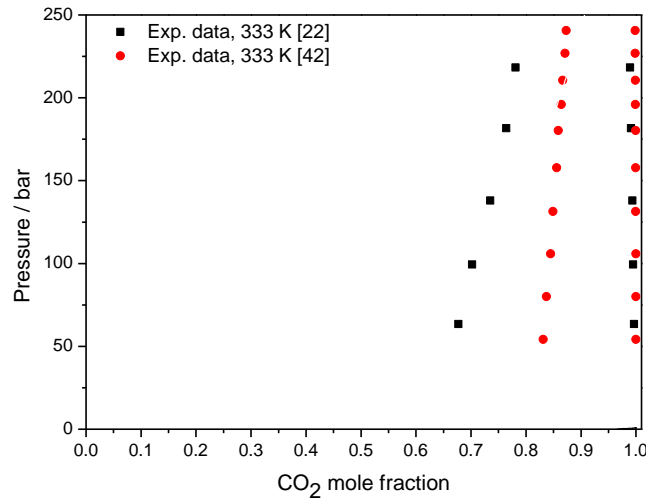


Figure 7. CO₂ - linoleic acid VLE at 333 K. Experimental data from literature [22,42].

Table 2. Binary interaction parameters and deviations of model correlations from experimental data for CO₂ (1) – Acid (2) systems.

Acid	Temp. Range / K	k_{ij}	% AAD ^a in x_1	% AAD ^a in y_1	% AAD ^a in y_2	References
Acetic Acid (C2:0)	333-353	0.0190	4.3	1.3	5.9	[43]
Butanoic Acid (C4:0)	333-393	-0.0220	13.4	2.7	71	[44]
Pentanoic Acid (C5:0)	333-393	-0.0318	13.0	3.4	80	[44]
Hexanoic Acid (C6:0)	328-373	-0.0220	9.6	0.8	73	[44, 45]
Octanoic Acid (C8:0)	328-373	-0.0030	4.8	0.8	55	[44]
Decanoic Acid (C10:0)	323-353	0.0200	6.9	-	-	[46]
Lauric Acid (C12:0)	333-353	0.0380	2.6	0.2	44	[45]
Palmitic Acid (C16:0)	353-373	0.0820	7.3	0.1	39	[45]
Oleic Acid (C18:1)	323-333	0.0641	12.9	0.3	56	[22,25]
Linoleic Acid (C18:2)	333	0.0500	11.4	0.4	>100	[22, 42]

^a%AAD = $\frac{1}{n} \sum_i \left| \frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}} \right| \times 100$ where X stands for the CO₂ mole fraction on the liquid phase (x_1) and the acid mole fraction (y_2) in the vapor phase, while n is the number of experimental data points

Hydrogen bonding interactions were accounted for carboxylic acids. All acids were modeled using the 1A association scheme, which is a very popular association scheme in the SAFT type models to account the possible dimerization of carboxylic acids, using the parameters reported by Tsivintzelis et al [17]. The vapor – liquid equilibrium of CO₂ - acid mixtures was modeled assuming that CO₂ is an inert compound. Thus, no cross association interactions (of electron donor-acceptor type) were assumed between CO₂ and acid molecules, although such interactions may occur, especially for mixtures with low molecular weight acids. However, because the aim of this study is to model systems with high molecular weight acids (compounds relevant to biodiesel production) and since the CPA rather satisfactorily describes such mixtures using only one adjustable parameter, cross interactions were not accounted for. All acids were modeled using the 1A association scheme and the parameters are given by Tsivintzelis

et al [17]. All the CO₂ – linear acid mixtures, for which experimental data were available in the literature, were investigated and the results are presented in Table 2.

In Figure 8a, the binary interaction parameters of Table 2 are plotted against the number of carbon atoms in acid molecules. It is shown that the k_{ij} s follow a linear trend for acids with more than four carbon atoms. For acids with less than four carbon atoms, the correlation shown in Figure 8a cannot be used and this happens, probably, due to the peculiar hydrogen bonding interactions in such systems. We have seen such behavior for many homologous series, see for example ester-alcohol systems in reference [17], and with many models. In Figure 8b, the k_{ij} s are plotted against the number of double bonds for C18-*x* fatty acids. As it was also observed for the esters of C18-*x* fatty acids, the binary interaction parameter becomes lower as the number of double bonds increases.

The results are illustrated in Figures 9 and 10. In most cases, the model satisfactorily describes the experimental data. For mixtures with C4:0, C5:0 and C6:0 acids, the model significantly overestimates the mixtures' critical point, however, the results are better for mixtures with C8:0, C10:0 and C12:0 acids.

Oliveira et al. also modeled the VLE of binary systems containing CO₂ with propanoic acid, hexanoic acid, octanoic acid or oleic acid and concluded that the CPA can satisfactorily describe the phase behavior using one binary adjustable parameter [37]. Byun et al. used the SAFT EoS and the PR EoS to model the VLE of binary mixtures containing CO₂ and organic acids with up to eight carbon atoms [44]. They conclude that the SAFT EoS satisfactorily predicts the phase behavior of the studied mixtures using two temperature independent adjustable parameters.

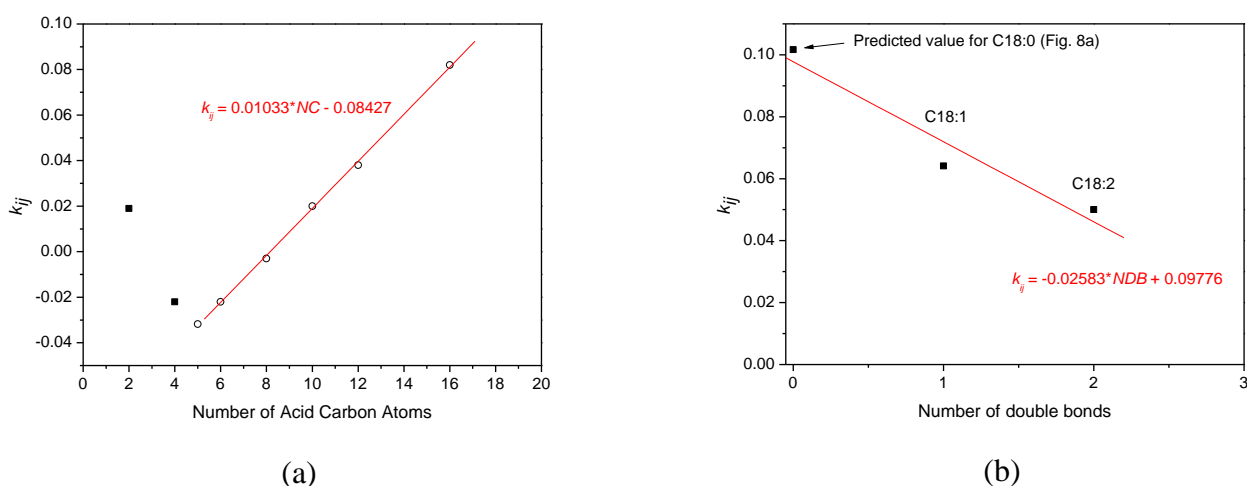
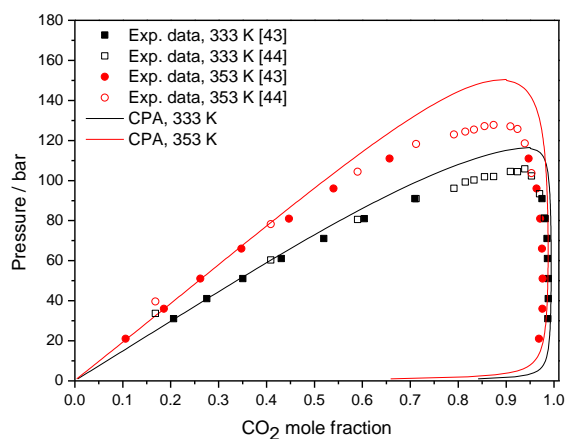
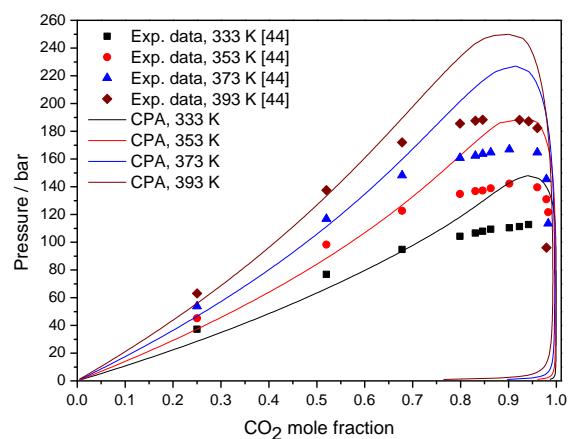


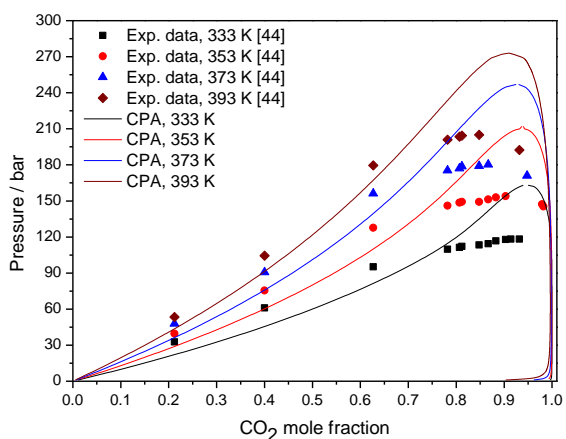
Figure 8. Binary interaction parameters (k_{ij} s) against the number of acid carbon atoms (left) and against the number of double bonds for C18-*x* fatty acids (stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2)) (right).



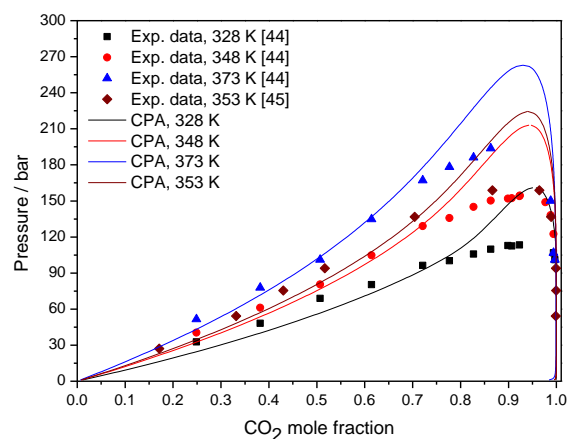
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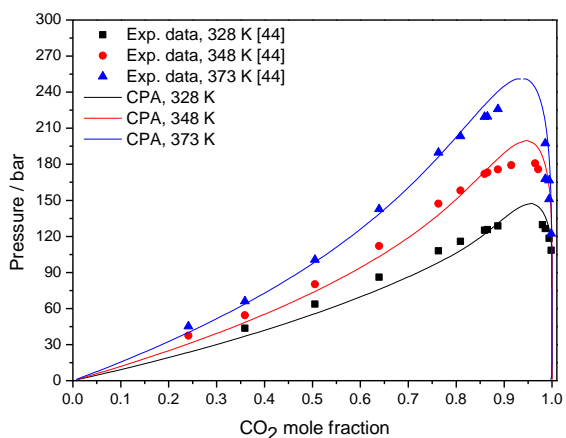
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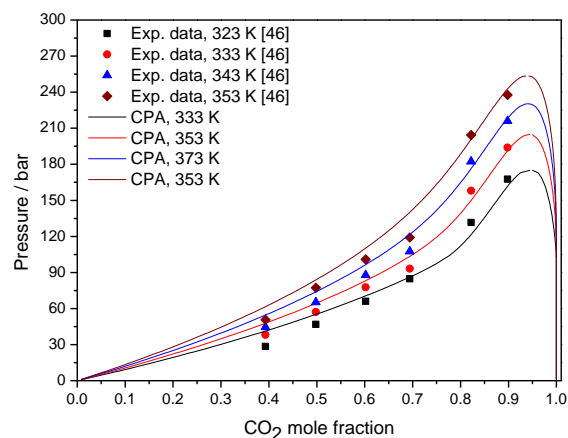
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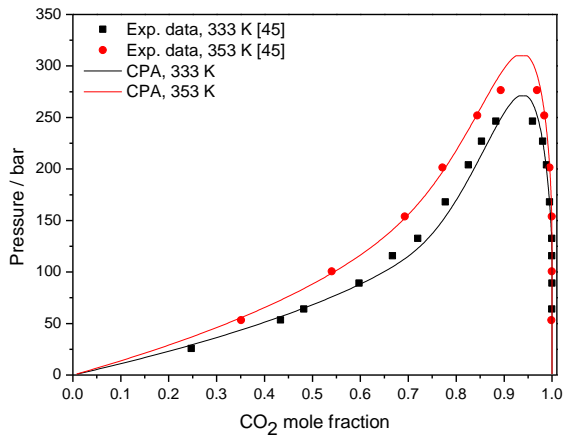


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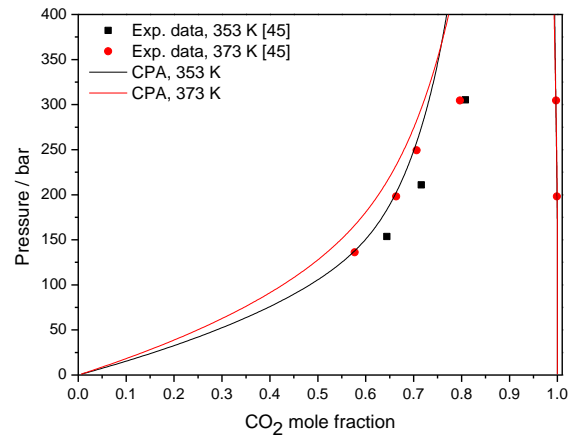


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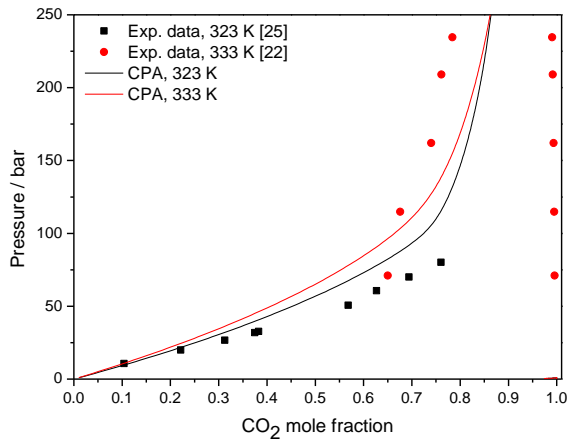
Figure 9. CO₂ – fatty acids VLE. Experimental data (points) and CPA calculations (lines). Binary mixtures of CO₂ with acetic acid (a), butanoic acid (b), pentanoic acid (c), hexanoic acid (d), octanoic acid (e), decanoic acid (f). The interaction parameters are available in Table 2.



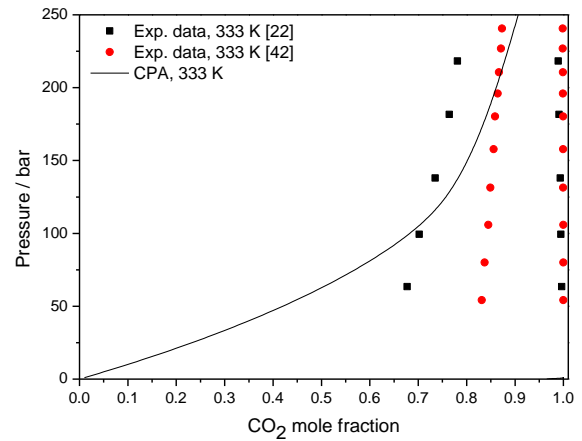
(a)



(b)



(c)



(d)

Figure 10. CO₂ – fatty acids VLE. Experimental data (points) and CPA calculations (lines). Binary mixtures of CO₂ with lauric acid (a), palmitic acid (b), oleic acid (c) and linoleic acid (d). The interaction parameters are available in Table 2.

3. Ternary and multicomponent mixtures

Next the model was applied to predict the phase behavior of ternary and multicomponent mixtures containing CO₂ with fatty acids or esters of fatty acids. In all cases no parameters were adjusted to ternary systems' data and all binary parameters were adopted from the corresponding sub-binary systems. Consequently, the results presented in this section are pure predictions.

Initially, a ternary mixture that contains CO₂ with two saturated fatty acid esters (methyl myristate and methyl palmitate) was modeled using the data of Lockemann [25]. As it is observed in Figure 11, the experimental data are scattered, similarly to the majority of experimental data for such systems, as discussed in section 2.1. The vapor – liquid equilibrium of such system was modeled using pure fluid parameters from literature [17,18] and the binary parameters of Table 1. The methyl myristate – methyl

palmitate binary interaction parameter was set equal to zero, which is reasonable, since such compounds present very similar molecular structure. In all cases flash calculations were performed using as feed compositions the center of the experimental tie lines. The results are presented in Figure 11 and in Table 3. The CPA model predicts the liquid phase compositions with reasonable accuracy. However, in both investigated pressures, it underestimates the CO₂ content of the liquid phase, following the behavior observed in Figure 3, i.e the model slightly underestimates the CO₂ content of the liquid phase of the corresponding sub-binary mixtures at 323 K. Moreover, the model presents better agreement with the experimental data at 110 bar, than at 70 bar. The vapor phase contains very small amounts of fatty acid esters. According to the experimental data [25], the mole fractions of esters are in the order of 10⁻⁴ at 323 K and 70 bar and 10⁻³ at 323 K and 110 bar. The model underpredicts, approximately one order of magnitude, the ester composition of the vapor phase at 70 bar. However, as shown in Table 3, results are significantly more accurate for 110 bar.

Table 3. Deviations^a from experimental data for ternary systems.

Temp. / K	Pressure / bar	AAD in x ₁	AAD in x ₂	AAD in x ₃	AAD in y ₁	AAD in y ₂	AAD in y ₃
CO ₂ (1) - methyl myristate (2) - methyl palmitate (3)							
323	70	7.6	15	19	0.1	86	98
323	110	2.2	15	21	0.3	23	31
CO ₂ (1) - methyl oleate (2) - methyl linolate (3)							
333	~148	2.2	81	81	0.4	37	38

$$^a\% \text{AAD} = \frac{1}{n} \sum_i \left| \frac{X_i^{\text{cal}} - X_i^{\text{exp}}}{X_i^{\text{exp}}} \right| \times 100 \text{ where } X \text{ stands for mole fraction of the liquid phase } (x_i) \text{ or the vapor phase } (y_i), \text{ while } n \text{ is the number of experimental data points}$$

Next, the model was applied to predict the vapor – liquid equilibrium of a ternary mixture containing CO₂ and two unsaturated fatty acid esters (methyl oleate and methyl linoleate). The calculated results were compared to the experimental data [47] in Figure 12. Similarly to the previous system, the model slightly underestimates the CO₂ content of the liquid phase, which is a behavior that arises from the corresponding sub-binary mixtures (see Figure 5). As shown in Table 3, the model predicts the very small fraction of esters in the vapor phase (of the order of 10⁻³, according to the experimental data [41]) with reasonable accuracy.

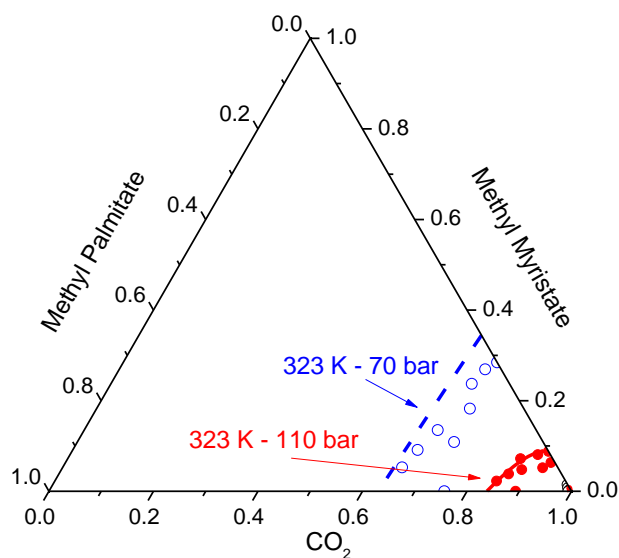


Figure 11. CO₂ methyl myristate – methyl palmitate VLE at 323 K. Experimental data [25] for 70 bar (open symbols) and 110 bar (solid symbols), as well as CPA correlations (lines).

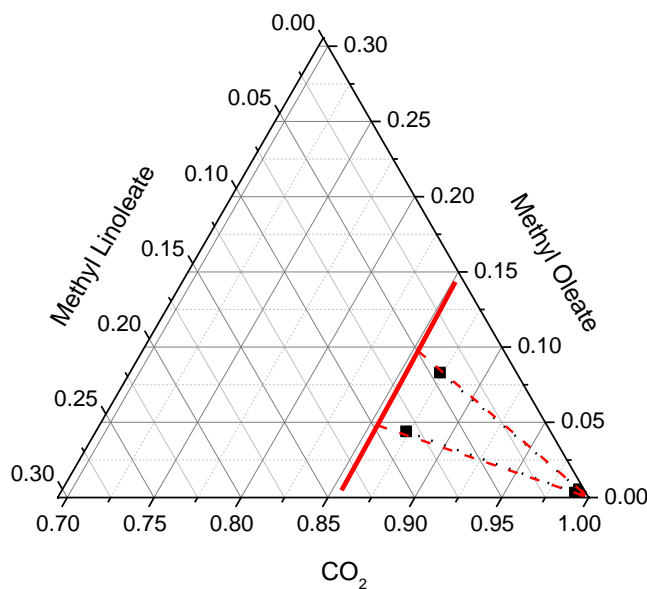


Figure 12. CO₂ – methyl oleate – methyl linoleate VLE at 333 K and approximately 148 bar. Experimental data [47] (symbols) and CPA correlations (solid lines). The experimental tie lines (black dot line) and the calculated tie lines (red dash lines) are also shown.

Next, the model was applied to predict the phase behavior of a ternary system that contains CO₂ with methanol and lauric acid, which is a reactive mixture, rendering the

modeling of the phase behavior a challenging task. Such system was experimentally investigated by Ferreira et al. [48], who report vapor – liquid – liquid (VLLE), liquid-liquid (LLE) and vapor-liquid (VLE) equilibrium data for various mixture compositions. The model was applied using binary parameters adopted from the sub-binary mixtures. In more detail, for CO₂ – lauric acid, the binary interaction parameter of this study was used. For CO₂ – methanol, cross association interactions were accounted for assuming one positive and one negative association sites on CO₂ and using an experimental value for the association energy [18]. Binary parameters for CO₂ – methanol were adopted from Tsivintzelis et al. [18]. In absence of binary parameters for the sub-binary methanol – lauric acid system, the model was applied using the parameters for the methanol – methyl laurate [17]. Results for two representative systems are presented in Figures 13 and 14. Ferreira et al. used two binary parameters per sub-binary system (in total six parameters, while the parameters for the methanol – lauric acid were adjusted to the ternary system's data) in order to model the ternary mixture with the Peng-Robinson EoS [48]. According to their results, the VLE data are accurately correlated, while the VLLE is qualitatively described.

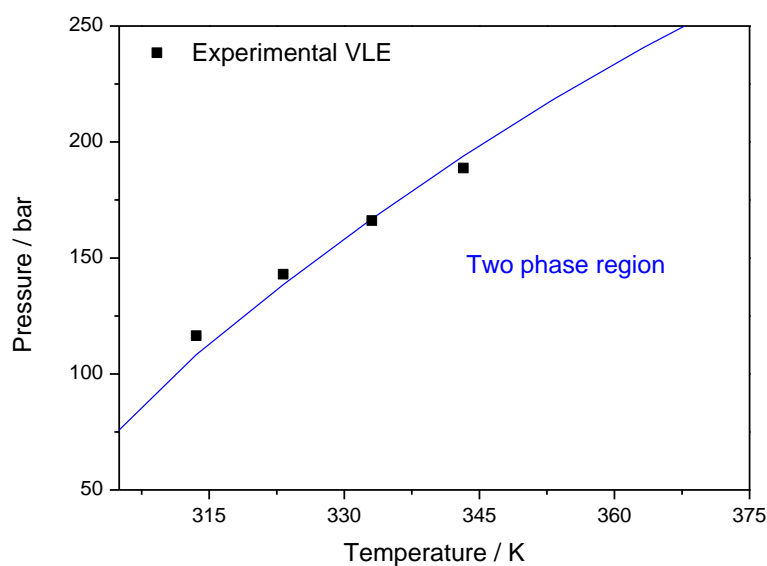


Figure 13. VLE of CO₂ – methanol – lauric acid system. Experimental data (points [48], for a mixture containing CO₂: 85.90% mol, methanol: 9.40% mol and lauric acid 4.7% mol) and CPA predictions (lines).

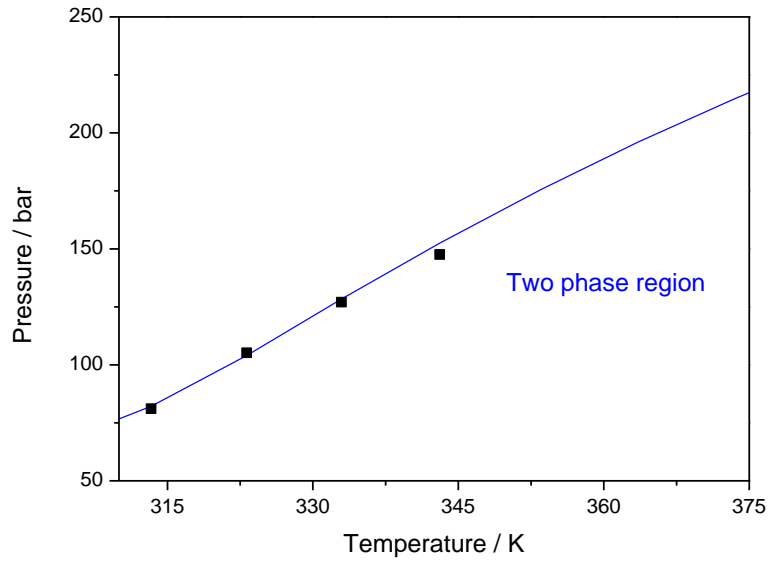


Figure 14. VLE of CO₂ – methanol – lauric acid system. Experimental data (points [48], for a mixture containing CO₂: 74.74% mol, methanol: 21.05% mol and lauric acid 4.21 % mol) and CPA predictions (lines).

Finally, the model was applied to predict the phase behavior of a multicomponent mixture containing CO₂ and a real biodiesel sample. The experimental data were taken from Pinto et al. [49]. Biodiesel was considered as a mixture of methyl esters of fatty acids (C16:0, C18:0, C18:1, C18:2, C18:3), according to the analysis performed by the authors. In all cases the binary interaction parameters of CO₂ with the various fatty acid esters were adopted from Table 1, while binary interaction parameters between fatty acids were set equal to zero, which is reasonable, since such compounds have very similar molecular structure. The deviations of model predictions from the experimental data are presented in Table 4, while results are illustrated in Figure 15.

Table 4. Deviations^a from experimental data [49] for CO₂ – biodiesel multicomponent system.

Temperature / K	AAD ^a in x _{CO2}	AAD ^a in y _{CO2}	AAD ^a in y _{ester}
323.15	6.6	0.4	39
333.15	6.7	0.3	25
343.15	7.2	0.5	24

^a%AAD = $\frac{1}{n} \sum_i \left| \frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}} \right| \times 100$ where X stands for mole fraction of the liquid phase (x_i) or the vapor phase (y_i), while n is the number of experimental data points

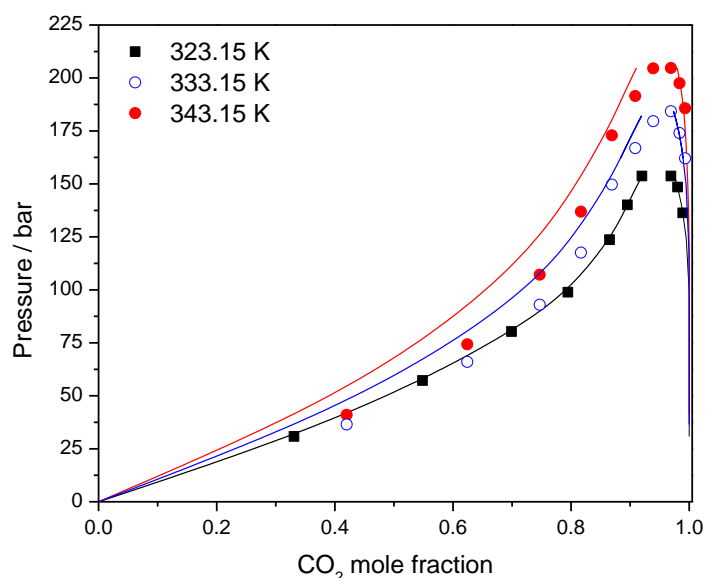


Figure 15. Phase behavior of CO₂ – biodiesel system. Experimental data (points, [49]) and CPA predictions (lines).

4. Conclusions

In this study, the application of the CPA equation of state to CO₂ – ester and CO₂ – fatty acid systems was investigated. The model, using one temperature independent binary interaction parameter, rather satisfactorily describes the phase behavior of the investigated CO₂ systems, however overpredicts the mixtures' critical point. In such systems, correlations of the binary interaction parameter with the number of esters' carbon atoms, or, where it was possible, with the number of double bonds for esters or fatty acids with the same number of carbon atoms, were obtained. In order to further test the predictive ability of the model coupled with the modeling approaches described here, as well as in our previous studies [17,18], the CPA equation of state was applied to predict the phase behavior of three ternary mixtures. All the binary parameters were adopted from the corresponding sub-binary mixtures and, overall, satisfactory predictions were obtained.

This study is a continuation of our previous study in modeling mixtures relevant to the biodiesel production [17]. In such study, all the most important mixtures in biodiesel processes were investigated and pure fluid and binary parameters were obtained. In addition, correlations for predicting the pure and binary parameters in cases of lack of experimental data were developed. In this way, the predictive ability of the model is enhanced and the application of the CPA model to real systems relevant to biodiesel production becomes more feasible.

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