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High pressure phase equilibria of supercritical alcohols with triglycerides, fatty esters and cosolvents

Pablo Hegel, Alfonsina Andreatta, Selva Pereda,
Susana Bottini, Esteban A. Brignole *

*Planta Piloto de Ingeniería Química, Universidad Nacional del Sur-CONICET, Camino La Carrindanga Km 7,
CC 717, 8000 Bahía Blanca, Buenos Aires, Argentina*

Abstract

The transesterification of vegetable oils, esterification of fatty acids and glycerolisis reactions, with supercritical alcohols, are of interest in the production of fine chemicals and biodiesel. The partial miscibility between the reactants and products of these processes have raised interest in the multiple phase behavior under reaction and separation conditions of mixtures of triglycerides and derivatives, fatty esters, alcohols and glycerin. In the present work, recent experimental studies under separation and reaction conditions are compared with modeling predictions using a group contribution with association equation of state.
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1. Introduction

The production of biodiesel by new synthesis approaches using reaction temperatures and pressures above the critical values of the alcohols has been an active research field in recent years [1–3]. The knowledge of phase equilibria under the various conditions of operation at low and high pressure, covering a wide range of temperatures is an obvious need for process development, design and optimization. A transesterification reaction with methanol is as follows:

$$\text{triglyceride} + 3CH_3OH \leftrightarrows 3\text{methylfattyesters} + \text{glycerin}$$
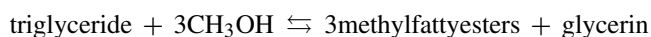
This is a reversible reaction and requires an important excess of methanol in the feed to obtain the desired product. This is more the case when the synthesis of biodiesel is carried out at supercritical methanol conditions under a catalyst-free process. When the reaction between the oil and methanol is carried out with basic or acid catalyst at moderate temperatures, the oil + methanol immiscibility cannot be avoided and this effect hinders the rate of reaction. A motivation behind operating at higher temperatures and pressures has been to obtain complete miscibility between the methanol (the most studied alcohol for this reaction) and the vegetable oil. However, recent experimental studies [4,5] indicate that complete oil + methanol miscibility can be achieved at temperatures between 470 and 480 K, below the critical temperature of methanol. Recent studies have also looked to the phase equilibria of the methyl esters + monoglycerides + glycerin and methanol [6,7]. Chiu et al. [6] used the Wilson activity coefficient model for predicting the methanol distribution among biodiesel and glycerin phase. Negi et al. [7] compare their experimental data with UNIFAC predictions and found reasonable good results with methyl oleate systems but not for monoglycerides. None of the models proposed in previous works take into account association or cross-association and are not suitable for application at high pressures or in the near critical region.

2. The thermodynamic modeling of natural products with association

Ferreira et al. [8,9] have extensively discussed the application of the Group Contribution with Association Equation of State (GCA-EOS) to the supercritical processing of fatty oil deriva-

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* Corresponding author. Tel.: +54 291 4861700; fax: +54 291 4861600.
E-mail address: ebrignole@plapiqui.edu.ar (E.A. Brignole).

tives with low molecular weight solvents. The GCA-EoS model can be written as the sum of three different contributions to the residual Helmholtz energy:

$$A = A^{\text{rep}} + A^{\text{att}} + A^{\text{assoc}} \tag{1}$$

The repulsive contribution (A^{rep}) is given by the Carnahan Starling term for hard spheres, the attractive (A^{att}) is a van der Waals term with a group-based local composition density dependent expression (NRTL) for the computation of the energy parameter, and the association part (A^{assoc}) is a group contribution term based on Wertheim Statistical Association Fluid Theory [10] as applied in the SAFT equation [11]. The association contribution is given by

$$\frac{A^{\text{assoc}}}{\text{RT}} = \sum_{i=1}^{\text{NGA}} n_i^* \left\{ \sum_{k=1}^{M_i} \left[\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right] + \frac{1}{2} M_i \right\} \tag{2}$$

In this equation NGA is the number of associating groups, n_i^* is the number of total moles of the associating group i, $X^{(k,i)}$ is the molar fraction of group i non-associated through site k and M_i is the number of associating sites of group i. The number of moles of associating group i is given by: $n_i^* = \sum_{m=1}^{\text{NC}} v_{\text{assoc}}^{(i,m)} n_m$, where $v_{\text{assoc}}^{(i,m)}$ is the number of associating groups i in the molecule m and n_m is the total number of moles of molecule m. The summation is over all the mixture components. The fraction of group i not associated through the site k is determined by the following expression:

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{\text{NGA}} \sum_{l=1}^{M_j} \rho_j^* X^{(l,j)} \Delta^{(k,i,l,j)} \right]^{-1} \tag{3}$$

Gross et al. [10] applied the GCA-EoS model to mixtures containing alcohols, water and any number of inert components by defining a single hydroxyl (OH) associating group. Later Ferreira et al. [8] extended the GCA-EoS model to several cross-associating mixtures containing esters, ketones, alcohols, water, acids, aromatics and alkanes. In those problems that present only self-association, the use of a group contribution approach leads to a simple analytical solution for the computation of the associating contribution. However, when dealing with problems of cross-association it is possible to find an analytical solution for the fraction of non-associated groups when two associating groups are present. In this case, a cubic or quartic equation is obtained that can be solved analytically. Kraska [12] presented a review on several analytical solutions. In dealing with multiple associating groups Michelsen and Hendriks [13] demonstrates that the calculation of the association contributions to pressure and chemical potential from statistical associating fluid theory can be simplified by the minimization of a conveniently defined state function, which does not require the calculation of first derivatives of the fraction of non-associating molecules X_A. Considering also that in the group contribution approach proposed by Gros et al. [10] the radial distribution function is assumed equal to unity, the group contribution expression for Z^{assoc} and $\ln \phi_i^{\text{assoc}}$ derived from this simplification of the GCA-EoS model

are [8]:

$$Z_{\text{assoc}} = -\frac{1}{2} \sum_{k=1}^{\text{NGA}} \sum_{l=1}^{M_k} \frac{n_k^*}{n} (1 - X^{(l,k)}) \tag{4}$$

$$\ln \hat{\phi}_i^{\text{assoc}} \equiv \frac{\partial}{\partial n_i} \left[\frac{A^R}{\text{RT}} \right]^{\text{assoc}} = \sum_{k=1}^{\text{NGA}} v^{(k,i)} \left\{ \sum_{l=1}^{M_k} \ln X^{(l,k)} \right\} \tag{5}$$

Phase equilibrium calculations normally involve the computation of first derivatives of fugacity coefficients with regard to process variables such as temperature, density and composition. This requires the calculation of the first derivatives of the non-bonded associating groups fraction $X^{(k,j)}$ with respect to these variables. According to Eq. (3) the fraction of non-bonded associating groups $X^{(k,j)}$ are obtained from a set of implicit equations that depend on the number of associating groups and on the assignment of associating sites to each associating group. The conventional procedure to solve for $X^{(k,j)}$ and its derivatives is to obtain a specific set of equations for each type of associating system, which makes the computation of association effects problem-dependent. Tan et al. [14] proposed a generalized procedure to calculate the fraction of non-bonded molecules and their derivatives, applicable to all associating systems, regardless of the number and type of associating sites and the number of components in the mixture. The application of this procedure to the GCA-EoS model is explained in detail by Andreatta et al. [15]. The computational procedure developed by Andreatta et al. allows the calculation of any type of association (self- and cross-association) in systems having up to a maximum of 12 different functional groups.

2.1. Associating parameters

Associating groups are considered to have one (electron donor or electron acceptor) or two (an electron donor and an electron acceptor) associating sites. Each water molecule or alcohol molecule is considered to have an associating group with two sites (an electronegative site O and an electropositive site H) as indicated in Table 1. This approximation resulted in very good representation of the properties of solutions containing these associating components [10].

Two additional associating groups are required to deal with triglycerides and derivatives [9]:

Table 1
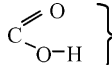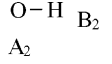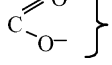Self-association models defined in the GCA-EoS

Association sites		Assumptions	Association parameters
RCOOH	C=O, O–H } A_1	$\Delta_{A_1 A_1} \neq 0$	$\varepsilon_{A_1 A_1}$, $\kappa_{A_1 A_1}$
ROH and H$_2$O	O–H B_2, A$_2$	$\Delta_{A_2 B_2} \neq 0$ $\Delta_{A_2 A_2} = \Delta_{B_2 B_2} = 0$	$\varepsilon_{A_2 B_2}$, $\kappa_{A_2 B_2}$
RCOOR	C=O, O– } A_3	$\Delta_{A_3 A_3} = 0$	–

Table 2
Groups self- and cross-association parameters

		Self-association	
		ε_{ij}/k (K)	κ_{ij} (cm^3/mol)
COOH		6300.0	0.0200
OH		2700.0	0.8621
i	*j*	Cross-association	
		ε_{ij}/k (K)	κ_{ij} (cm^3/mol)
COOH	OH	4500.0	0.1313
	COOR	3248.8	0.7786
OH	COOR	2105.3	0.9916

(a) The acid association group COOH, with one site capable of both self- and cross-associating.
(b) The ester association group COOR, with one site that does not self-associate but can cross-associate with groups that have an electropositive site.

Therefore, in dealing with mixtures of oils, fatty esters, alcohols and acids the model requires three possible associating groups as described in Table 1. In the first column the number of sites assigned to each associating group are represented schematically and, in the second column the different assumptions concerning the association strengths between each pair of sites. Finally, in the third column the association parameters that have to be fitted are shown.

As can be seen in Table 1, the double hydrogen bond of the acids is represented by a strong single bond between sites A_1. The ester group is represented by a unique electron-donor site A_3, which do not self-associate, *i.e.*, its self-association strength is zero. From the association point of view, the fatty oil + alcohol mixtures considered in this work contain at least one of the three groups that can hydrogen bond: the ester, the alcohol and the acid group. The corresponding self- and cross- association parameters used in this work are presented in Table 2.

2.2. Group parameters

The repulsive parameter of the GCA-EoS is the molecule critical diameter, which can be calculated from the component critical temperature and pressure when these properties are known. This is not the case for vegetable oils or derivatives. A correlation based on van der Waals volumes has been proposed by Bottini et al. [16]. The GCA-EoS group energy and interaction parameters used in this work for non-associating groups are those of Espinosa et al. [17,18]. For self-associating groups or for groups with cross-interactions the parameters reported by Ferreira el al. [8] and Gros et al. [10] are used. Table 3 reports specific parameters, obtained in the present work, for methanol and glycerin. A molecular description was used for glycerin in order to improve the liquid–liquid equilibria experimental data correlation, thus a new group 'glycerin' ($C_3H_8O_3$) has been defined in this work.

3. Experimental studies on biodiesel production with supercritical methanol

Saka and Kusdiana [1] used a small closed 5 cm^3 reactor, charged with rapeseed oil and methanol. Working at 620 K and 45 MPa these authors reported a high conversion to biodiesel, in a very short time. Recently Cao et al. [19] proposed the use of propane and CO_2 as cosolvents, they obtained high conversion with low reaction times operating at 540 K and pressures around 12 MPa. Other researchers [20,21] have proposed operating pressures ranging from 20 to 35 MPa and temperatures from 570 to 590 K. Except for the work of He et al. [20] that operate a continuous reactor, all of the reported experiments on supercritical methanol oil transesterification has been carried out in constant volume batch reactors without windows, therefore it has not been possible a direct observation of the phase behavior during the reaction process. In a recent work [4], we studied the evolution of phase behavior with temperature during the non-catalytic transesterification process of soy oil with supercritical methanol, with and without cosolvent (propane), under controlled reactor global density and composition. For this purpose, transesterification experiments were carried out in a see through two windows cylindrical reactor. The conversion achieved under different operating and phase conditions were measured. In this way it was possible to study the boundaries of the single and multiple phase regions of the reacting system vegetable oils + methanol and fatty ester + methanol + glycerol with the use or not of cosolvents.

Phase behavior predictions based on the GCA-EoS can now be compared with the direct observations reported by Hegel et al. [4]. The modeling of the phase equilibria of the reactants and reaction products in the two-phase region and the prediction of the boundaries of the homogeneous region is needed for process design. Also the distribution of components between phases in the heterogeneous region is of interest to understand the reaction mechanism and for the design of the separation train.

4. Evolution of phase transitions under reaction and separation conditions

The reaction system for the initial and final compositions gives rise in each case, to different pressure–temperature phase envelopes on which the trajectory of the pressure versus temperature of the experiments can be drawn. In this sense Hegel et al.

Table 3
New GCA-EOS pure-group and binary interaction parameters

Pure group parameters					
Group	T_i^*	q	g^*	g'	g''
$C_3H_8O_3$	850.0	3.060	510302.3	−0.3190	0.00

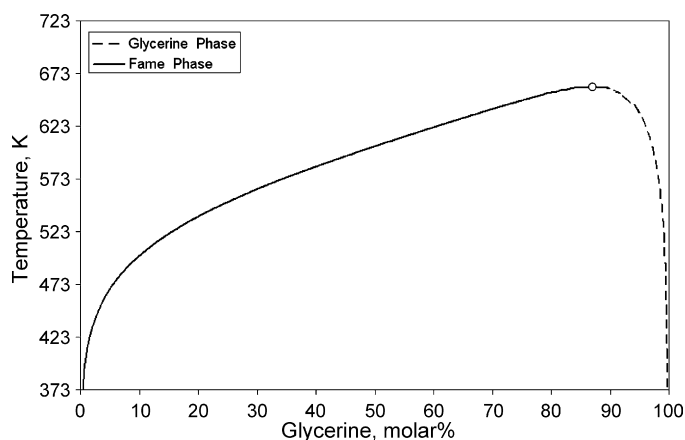| Binary interaction parameters					
Group *i*	Group *j*	k_{ij}	k'_{ij}	α_{ij}	α_{ij}
CH_3OH	CH_3	0.9760	0.00	0.00	0.00
	CH_2	1.0000	0.00	0.00	0.00
	$C_3H_8O_3$	1.0400	0.00	0.00	0.00
$C_3H_8O_3$	$COOCH_3$	1.0174	0.00	0.00	0.00
	CH_3/CH_2	1.0900	−0.02	0.00	0.00

Fig. 1. GCA-EoS prediction of liquid–liquid equilibria for the binary fatty acid methyl esters (FAME) + glycerin. (°) Critical solution temperture.

[4] observed phase transitions that ended either: in a homogeneous supercritical fluid, a dense liquid phase or a heterogeneous vapor–liquid system, depending mainly on the oil and methanol concentration, cell global density and the use or not of cosolvent.

4.1. Phase behavior of the system vegetable oil + methanol

Tang et al. [5] reported liquid–liquid equilibrium data of the system methanol–triolein in the temperature range between 353 and 463 K at three different pressures 6, 8 and 10 MPa that were above the bubble pressure of the binary mixture. Even though the plait point is not reported, complete liquid phase miscibility has been observed in the case of mixtures of methanol + soy oil at temperatures above 470 K [4]. The correlation of Tang et al. data with the GCA-EoS model indicates that complete liquid miscibility is achieved at 470 K when the total pressure is 8 MPa. From the direct observation of phase transitions by Hegel et al. [4] and the predictions of the GCA-EoS model, the phase behavior of the binary vegetable oil + methanol can be categorized as Type II according to the van Konynenberg and Scott classification [22], which presents liquid–liquid
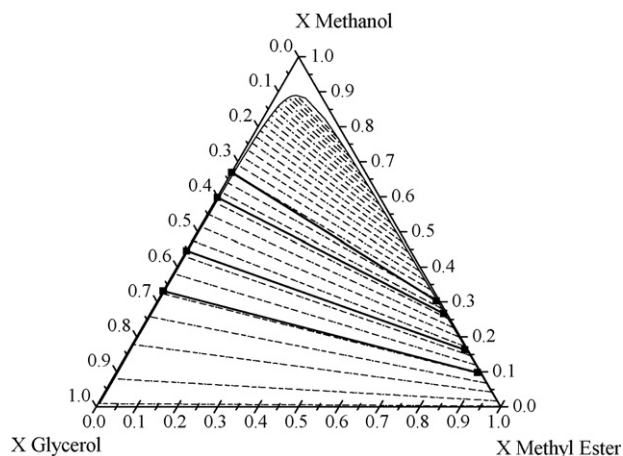

Fig. 2. GCA-EoS correlation of liquid–liquid equilibria for the ternary system methanol + methyl ester + glycerin at 333.15 K and 1 bar. Experimental data: Negi et al. [7].
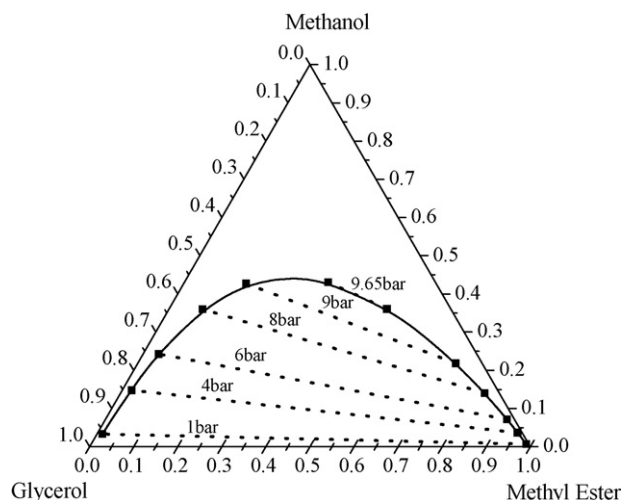

Fig. 3. GCA-EoS prediction of the liquid–liquid binodal curve of methyl esters + methanol + glycerin system at 423.15 K (fractions by-weight) from low pressure up to complete liquid miscibility at 9.65 bar (plait point).

equilibria at temperatures below the critical value of the light component (methanol, 516 K) and exhibit a continuous locus of liquid–vapor critical points.

4.2. Phase behavior of the system methyl esters, glycerin, methanol and propane

The binary of fatty ester + glycerin depicts liquid–liquid equilibria over a wide temperature range, this behavior has been experimentally observed at temperatures up to 500 K. In ternary mixtures with methanol the system presents a Type I [23] liquid–liquid equilibria behavior with one immiscible pair (glycerin + methyl ester) and two miscible pairs (methanol + methyl ester and methanol + glycerin). Fig. 1 shows GCA-EoS model prediction for the binary glycerin + methyl ester, which indicates that complete miscibility is achieved above 670 K.

Experimental data on LLE of the ternary methanol + methyl oleate + glycerin has been presented by Negi et al. [7] at 333.15 K and atmospheric pressure. These data were correlated with the GCA-EoS model (see Fig. 2) and new methanol and glycerin binary interaction parameters were estimated to improve the data correlation (Table 3). The association energy parameters were those of Table 2 and the glycerin molecule is also molecularly described for the attractive and repulsive contribution and three hydroxyl (OH) associating groups are assigned.

As expected, the partition coefficient of methanol in methyl ester and glycerin phases is lower than one (between 0.3 and 0.5 at 333.15 K according to Negi et al. [7] data). The L–L–V equilibrium of this mixture, at higher temperatures and pressures, is of interest at the reactor conditions and in the separation train of biodiesel high pressure processes. At a given temperature and pressure the L–L–V region of the ternary system has constant compositions. Therefore, keeping the temperature constant and increasing the pressure we can follow the evolution of the L–L–V region up to the point where complete liquid miscibility is achieved. In this way a binodal curve of the L–L compositions can be drawn on a ternary diagram, where each tie line corresponds
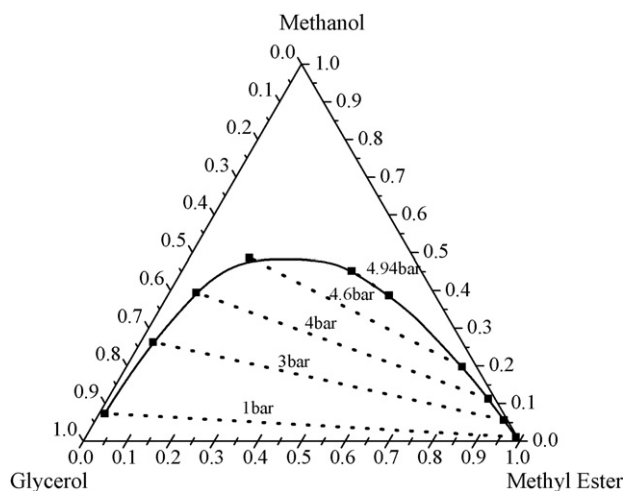
Fig. 4. GCA-EoS prediction of the liquid–liquid binodal curve of methyl esters + methanol + glycerin system at 393.15 K (fractions by-weight) from low pressure up to complete liquid miscibility at 4.94 bar (plait point).

Table 4
Experimental conditions of the transesterification experiments of soy oil with methanol cosolvent (propane)—almost complete conversion

Run #	MeOH/oil molar ratio	C$_3$/MeOH molar ratio	P (bar)	T (K)	Phase condition	Global density
1	23.5	0.0031	143	573	L	0.8051
2	65.88	0.0501	8.8	543.1	LV	0.5132

to a different pressure. Predictions of the binodal curve for two temperatures are given in Figs. 3 and 4.

The pressure at the plait point of these type of binodal curves will be low near the temperature of complete miscibility between the glycerin and the methyl ester, since almost no methanol (more volatile compound) will be required to achieved liquid miscibility. The plait point pressure will increase at lower temperatures due to the increasing methanol concentrations at the plait point, up to a certain maximum value and thereafter will decrease with temperature following the decrease of vapor pressure of methanol with temperature. In the temperature range between 400 and 640 K, predictions with the GCA-EoS model indicate that operating at pressures above 30 bar the system is outside of the LLV region.

For conditions in the vapor–liquid region above the LL miscibility pressure, it is of interest to study the bubble and dew point curves and critical conditions of the reaction products. The phase boundaries of the reaction products were obtained from phase envelope calculations of the mixtures of methyl oleate, methanol and glycerin and cosolvent (propane) at two reactor conditions observed experimentally by Hegel et al. [4] in which almost complete conversion is achieved (Table 4).

Even though there is no actual information on equilibrium phase composition in these experiments, the observation of

(a) 25°C 0.9 MPa

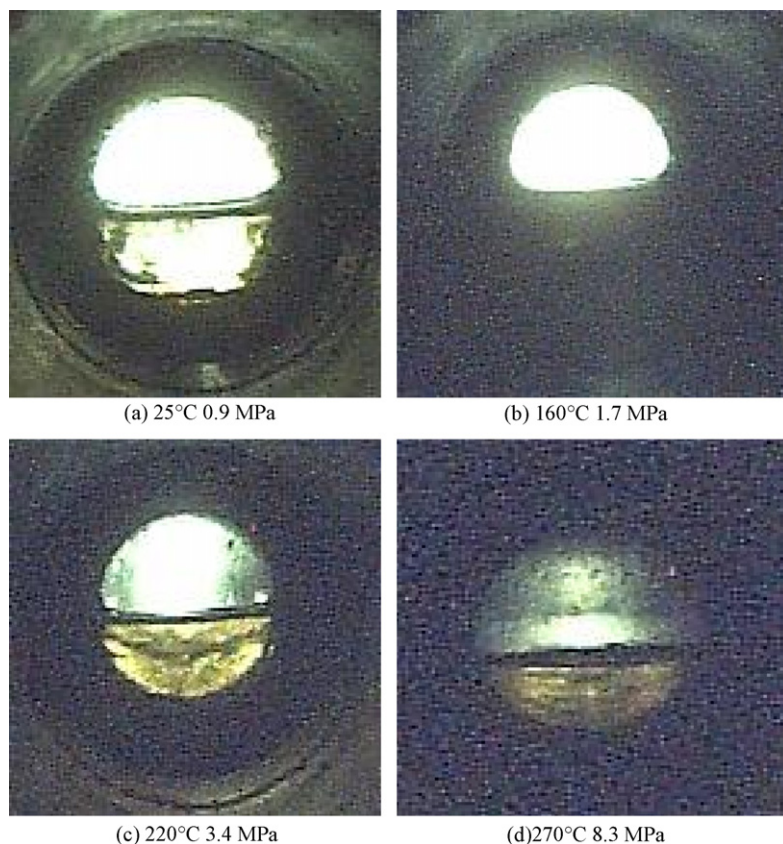(b) 160°C 1.7 MPa

(c) 220°C 3.4 MPa

(d)270°C 8.3 MPa

Fig. 5. Evolution of the phase behavior during the heating process of the reacting mixture (run 2): images (a, b and c) correspond to a two phase liquid–vapor equilibria. Image (d) shows the beginning of the transition to liquid–fluid equilibria (opalescence of light phase).
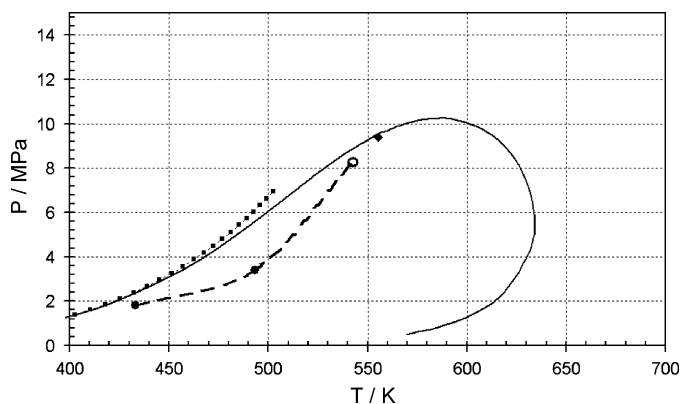
Fig. 6. Reactants (dotted line) and products (solid line) phase envelopes and the reaction trajectory (dashed line) for run 2 of Table 4. (♦) Critical point.
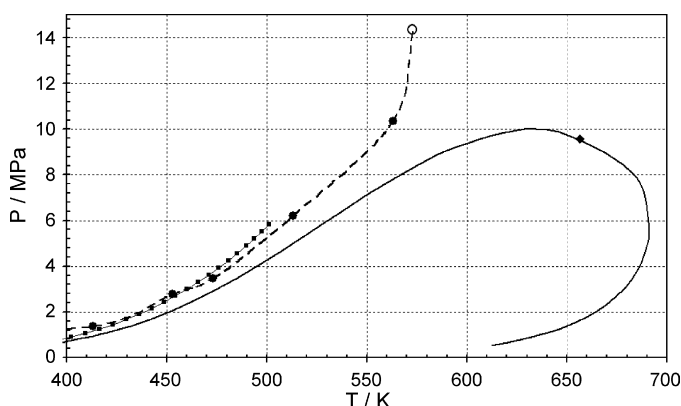

Fig. 7. Reactants (dotted line) and products (solid line) phase envelopes and reaction trajectory (dashed line) for run 1 of Table 4. (♦) Critical point.

regions of LLVE, LVE, critical transitions and supercritical and liquid like behavior is a challenge for the GCA-EoS model predicting capability. Pictures from a typical experiment of Hegel et al. [4] are shown in Fig. 5 for the conditions of run 2.

The phase envelope prediction (Fig. 6) for run 2 agrees well with the experimental trajectory of the reaction system. We can see from the pictures of run 2 and Fig. 6 that the system goes through liquid–vapor equilibrium at temperatures below 550 K and this agrees well with the predicted critical point of the products.
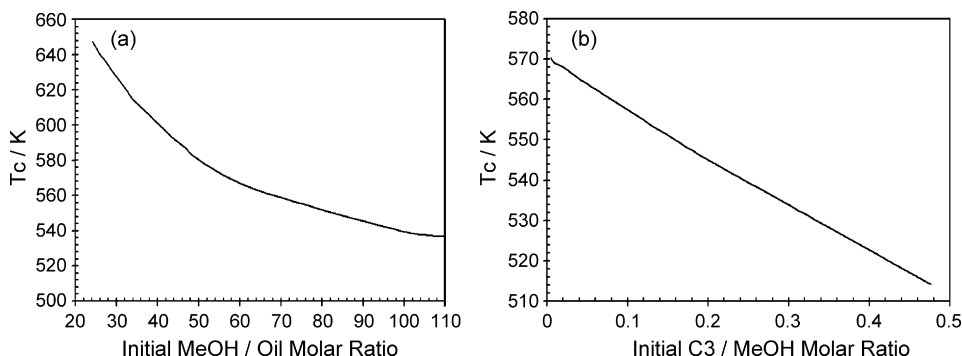
In the case of run 1 the vapor fraction in the system is low (high global density) and the process trajectory is very close to the mixture bubble point and ends in dense liquid condition (see Fig. 7) with an isochoric increment of pressure in the last stage of the reaction.

Another important property is the critical temperature of the reaction products. It is believed [1] that in the critical region the alcohol monomer fraction is high and this fact favors the kinetics of the methanolysis reaction. The critical temperatures are a function of the mixture composition and are obtained from phase envelope predictions using the GCA-EoS model. The predicted critical temperatures are shown in Fig. 8a and b. From these figures we can see that the critical temperature decreases with the methanol/oil ratio and with the propane concentration. This behavior justifies the use of a high methanol/oil ratio and of cosolvents like propane to achieve high conversions and high rates of reaction.

5. Conclusions

In this work an extended version of the GCA-EoS model is presented to predict high pressure phase equilibria of multicomponent associating systems and supercritical fluids, with multiple self- and cross-association groups. The model is applied to the prediction of phase equilibria in the supercritical methanolysis of vegetable oil for biodiesel production. GCA-EoS phase behavior predictions agree well with experimental observations for both reactants and products at high and low temperature and pressure. The effect of mixture composition on the reacting mixture critical properties gives a better understanding of the effect of alcohol and cosolvent composition on reaction rate and conversions. The GCA-EoS is found to be a suitable model for process design and optimization of biodiesel production plants.

Fig. 8. Effect of methanol/oil ratio (a: C_3/methanol = 0.05) and propane concentration (b: methanol/oil ratio = 65) on the products mixture critical temperature. GCA-EOS predictions.

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