Phase Equilibria of Highly Asymmetric Mixtures Involved in Biodiesel Production

Maria Cristina Annesini, Fausto Gironi, Walter Guerani*

Dipartimento Ingegneria Chimica Materiali Ambiente, Sapienza Università di Roma, Via Eudossiana 18, I-00184 Roma
walter.guerani@uniroma1.it

In recent years, hydroconversion of vegetable oils has been considered a promising route for biodiesel production. The process involves highly asymmetric mixtures of hydrocarbons and triglycerides which exhibit complex phase behaviours. In this work, thermodynamic modelling of C_3-C_{16} and C_3-triglyceride mixtures was performed by means of Peng-Robinson and PC-SAFT EOS. Critical properties and PC-SAFT parameters for triglycerides were estimated with group contribution methods; furthermore, an approach for evaluation of triglyceride PC-SAFT parameters, based on regression of experimental binary phase equilibrium data, was proposed. The PC-SAFT model showed its capacity to depict chain molecule phase behaviour providing better predictions for all the system investigated and it is recommended as reference EOS to represent phase equilibria involved in vegetable oils hydroconversion process.

1. Introduction

In recent years the emerging biodiesel production process, based on vegetable oils hydroconversion, has been extensively studied. The process deals with conversion of triglycerides contained in vegetable oils into diesel-range alkanes under high hydrogen pressure (40-80 atm) and relative high temperature (570-670 K). As stated by Guzman et al. (2010), reactions occur according to three main reactive pathways: hydrodeoxygenation (HDO), hydrodecarboxylation (HDC) and decarbonylation (DC). In Figure 1 the different reaction routes for triolein are depicted.
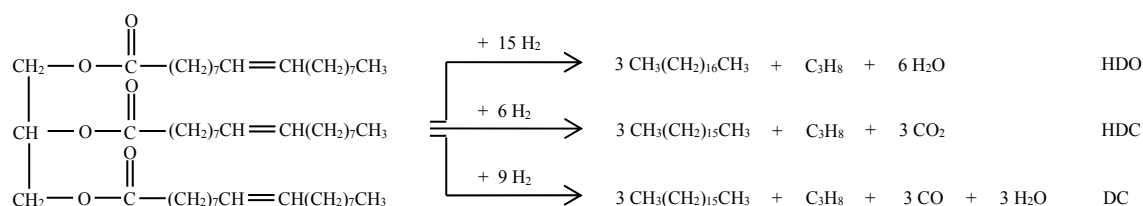

Figure 1: Main reaction pathways for triolein hydroconversion.

The mixture from the reaction step contains unreacted triglycerides, long and short chain alkanes, water and gaseous compounds such as hydrogen, carbon monoxide and carbon dioxide. Obviously separation steps must be carried out to separate long chain alkanes from triglycerides, which are recycled to the reaction step, and gaseous components. The process development needs a model to describe phase behaviour of such a complex mixture and, for this aim, a φ - φ approach based on equations of state seems the most suitable. Such an approach requires preliminary study of binary subsystems which characterize mixtures involved in the hydroconversion process. In particular, in these mixtures it is possible to recognize binary systems which exhibit complex phase behaviours and give rise to thermodynamic modelling difficulties. Among these, highly asymmetric mixtures of propane and long chain hydrocarbons (C_{15}-C_{18}) and propane-triglycerides must be investigated. The first ones exhibit solvent-solute size asymmetry and require models able to relate molecular features to macroscopic thermodynamic behaviour

(Ting et al., 2003). On the other hand, propane-triglyceride systems are characterized by a complex vapour-liquid-liquid phase equilibrium behaviour. In this work the classical cubic equation of state of Peng-Robinson (PR) and a specific implementation of the Statistical Associating Fluid Theory (SAFT) were employed to describe: a) vapour-liquid equilibrium of the C_3-C_{16} mixture, which is assumed to be representative of the different asymmetric systems which originate from vegetable oils hydroconversion reactions; b) phase equilibrium behaviour of C_3-triglyceride systems which exhibit a region of liquid partial miscibility at high propane concentration (Straver et al., 1998). Reliability of PR and PC-SAFT EOS was evaluated through comparison of model results relative to equilibrium conditions with experimental data available in the literature. Furthermore, parameters obtained from the study of binary systems were also employed to predict phase equilibrium of multicomponent mixture coming out from the first of the two reaction steps of the hydroconversion process scheme proposed by Abhari and Havlik (2009).

2. Equation of state

We employed standard version of PR EOS (Peng and Robinson, 1976) with pure components covolume and attractive parameter calculated from critical properties and Van der Waals one-fluid mixing rules, with no binary interaction parameters.

Furthermore equilibrium calculations were carried out by means of one of the most up-to-date version of the original EOS which is known as perturbed chain SAFT (PC-SAFT). SAFT is one of the most important association theory which belongs to the general perturbation category. It is based on the Wertheim's first order perturbation theory (Wertheim, 1984) and it has been implemented into useful expressions in several studies. SAFT EOS considers molecules as chains composed of freely jointed spherical segments and the basic idea underlying the model is the definition of an interaction potential to represent attraction and repulsion forces between segments. The molecular model can be refined by assuming the segments to have association sites and partial charges enabling the chains to associate or repulse by hydrogen bonds and dipole interactions. Consequently, the residual Helmholtz free energy, is made up by terms stemmed from each of these contributions. The PC-SAFT EOS main innovation relies on considering perturbation respect to spherical segments which are connected into rigid chains (hard-chain term) rather than disconnected segments (Gross and Sadowsky, 2001). Obviously this means considering interactions between chains instead of single segments and this would allow to capture the behaviour of chain molecule, such as hydrocarbons and polymers, more realistically. In this way, the residual Helmholtz free energy results

$$\frac{A^{res}}{NkT} = \frac{A^{hc}}{NkT} + \frac{A^{disp}}{NkT} + \frac{A^{assoc}}{NkT} \tag{1}$$

In Eq(1) the hard-chain reference term accounts for hard-sphere and chain formation contributions

$$A^{hc} = A^{hs}\sum_i x_i m_i + \sum_i x_i (1 - m_i) \ln g_{ii}^{hs}(\sigma_{ii}) \tag{2}$$

Where m_i and σ_i correspond to the number of segments which constitute the chain of the i-th component and to its diameter, respectively, while x_i is the component mole fraction. The dispersion term in Eq(1), according to Barker and Henderson (1967), consists of a first and second order contributions

$$\frac{A^{disp}}{NkT} = \frac{A^1}{NkT} + \frac{A^2}{NkT} = -2\pi\rho I_1(\eta, \overline{m}) \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)\sigma_{ij}^3 -$$

$$-\pi\rho m \left(1 + Z^{hc} + \rho\frac{\partial Z^{hc}}{\partial\rho}\right)^{-1} I_2(\eta, \overline{m}) \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)^2 \sigma_{ij}^3 \tag{3}$$

where Z^{hc} is the hard-chain contribution expressed in terms of compressibility factor, η is a packing factor and I_1 and I_2 are integral terms. Expressions of these terms depend on the choice of the interaction potential, which in PC-SAFT model is assumed to be a modified version of the classical square-well suggested by Chen and Kreglewski (1977). The interaction potential is then characterized by the three parameters, m_i, σ_i and ε_i, which is the well potential depth. For definition and exhaustive derivation of all the terms appearing in Eq(1) - Eq(3) we refer to Gross and Sadowsky (2001). Mixtures extension provided

in Eq(3) requires definition of mixing rules for a pair of unlike segments, which according to Berthelot-Lorentz, results

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right), \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right) \tag{4}$$

In this work, binary interaction parameter was not included. Also, the term A^{assoc} in Eq(1), which represents contribution from chains association, was neglected since we are assuming to deal with non-associative components.

2.1 Parameters estimation

Experimental data relative to critical properties and acentric factor of triglycerides are not available and, therefore, estimated values of these parameters are required. In this work group contribution methods proposed by Ambrose (1982) and Reid and Prausnitz (1987) were used. Predicted values of critical properties for several triglycerides are listed in Table 1 together with data for propane and hexadecane collected in Ambrose (1995).

PC-SAFT parameters for pure components are usually obtained by regression of experimental data of vapour pressure and liquid density. According to this approach Gross and Sadowsky (2001) reported regression results for 78 non-associative components including propane and hexadecane. For macromolecules, such as polymers or fatty acids, neither vapour-pressure data nor heats of vaporization are available (Gross and Sadowsky, 2002); consequently, the above procedure cannot be applied. On the other hand, it is well known that derivation of parameters relying only on density data usually results in poor prediction of phase equilibria (Tihic et al., 2008). Therefore, in this work, two different approaches were followed. In the first one, the group contribution method developed by Nguyen et al. (2013) was applied and PC-SAFT parameters were estimated according to

$$\varepsilon_{molecule} = \sqrt[\sum_h n_h]{\prod_{h=1}^{n_{group}} \varepsilon_h^{n_k}} \ , \quad \sigma_{molecule} = \frac{\sum_{h=1}^{n_{group}} n_h \sigma_h}{\sum_{h=1}^{n_{group}} n_h} \ , \quad m_{molecule} = \sum_{h=1}^{n_{group}} n_h R_h \tag{5}$$

where ε_h, σ_h and R_h are the group contribution values listed in Nguyen et al. (2013). We referred to the PC-SAFT EOS whose parameters are obtained by group contribution method as GC-PC-SAFT.

The second approach was based on estimation of the PC-SAFT parameters for triglycerides by regression of experimental phase equilibrium data according to the 'Maximum Likelihood' criterium:

$$\min_{(\varepsilon_i, \sigma_i, m_i)} \Omega = \sum_{i=1}^{N_{exp}} \left[\left(\frac{T_{exp,i} - T_{cal,i}}{S_{T,i}}\right)^2 + \left(\frac{P_{exp,i} - P_{cal,i}}{S_{P,i}}\right)^2 + \sum_{j=1}^{N_c-1}\left(\frac{x_{exp,i,j}^{\alpha} - x_{cal,i,j}^{\alpha}}{S_{\alpha,i}}\right)^2 + \sum_{j=1}^{N_c-1}\left(\frac{x_{exp,i,j}^{\beta} - x_{cal,i,j}^{\beta}}{S_{\beta,i}}\right)^2 \right] \tag{6}$$

In Eq(6) $T_{exp,i}$, $P_{exp,i}$, $x^{\alpha}_{exp,i,j}$ and $x^{\beta}_{exp,i,j}$ are the i-th experimental values of temperature, pressure and mass fractions of j-th component in α and β phases at equilibrium, whereas S is the standard deviation of the different experimental variables considered. Obviously this procedure is no more predictive but, as we will point out later on, it significantly enhances the model fitting capacity. The PC-SAFT EOS with parameters calculate by the above procedure is named REG-PC-SAFT. PC-SAFT parameters obtained with group contribution method and regression procedure are reported in Table 2.

3. Results and discussion

We firstly tested suitability of PR and PC-SAFT EOS to describe vapour-liquid equilibria for the C_3-C_{16} system. Experimental data taken from Thies (2004) are used for comparison.

Table 1: Critical temperature (T_c), critical pressure (P_c) and acentric factor (ω) used in PR EOS

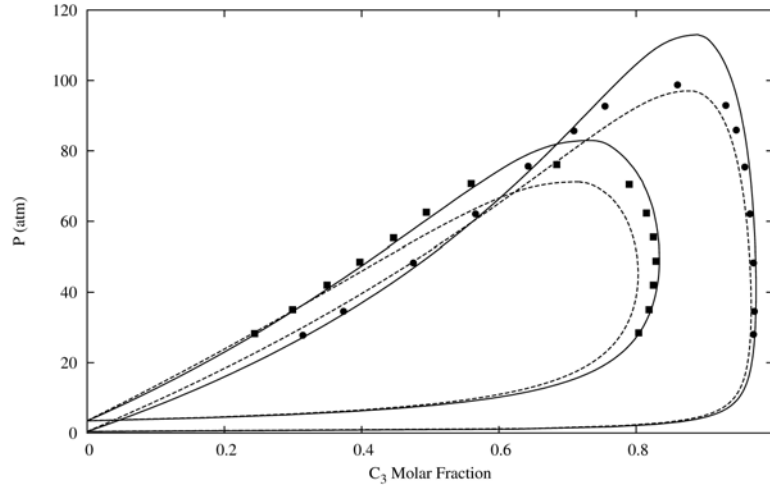| Component	T_c [K]	P_c [atm]	ω
Triolein	947.07	4.619	1.686
Tristearin	900.95	4.520	1.737
Tripalmitin	889.14	5.024	1.819
Hexadecane	723.00	13.92	0.717
Propane	369.83	41.93	0.152

Figure 2: Comparison between VLE and LLE experimental data, relative to C3-C16 mixture, at 522.9 K (●) and 625.8 K (■), and phase equilibrium conditions calculated with PR (−−) and PC-SAFT (—) EOS.

It is worth noting that the temperature range considered comprises operating conditions of the vegetable oil hydroconversion process. The reliability of the different thermodynamic models is evaluated in terms of average absolute percentage deviation between experimental and calculated values of liquid (AAPDx) and vapour (AAPDy) phase composition, at fixed temperature and pressure. In Table 3 AAPD values obtained for PR and PC-SAFT EOS are reported. As also shown in Figure 2, PC-SAFT reproduces VLE data more accurately than PR EOS for all temperatures considered. In particular, while calculation results for vapour phase composition are quite similar, PR predictions of liquid phase composition are considerably worse. On the other hand, we observed that PC-SAFT, which does not account for critical properties in parameter estimation, overestimates mixture critical pressure for all temperatures investigated.

Thermodynamic models based on PR and PC-SAFT EOS were then used to evaluate vapour-liquid and liquid-liquid phase equilibria in mixtures of triglycerides and propane close to critical conditions. The isothermal experimental data used for comparison with simulation results were taken from Bottini et al. (1999) and refer to different triglycerides in a temperature range between 340 K and 400 K and pressure up to 160 atm. As we outlined previously, above the lower critical end point, at high pressure, vapour-liquid-liquid equilibrium takes place (Straver et al., 1998).

In Figure 3 comparisons between experimental and calculated equilibrium data obtained by means of PR, GC-PC-SAFT and REG-PC-SAFT EOS are shown. As expected, PR is less accurate than PC-SAFT in the evaluation of the bubble point curve while the results obtained with GC-PC-SAFT and REG-PC-SAFT models are quite similar. The main PR EOS inaccuracies arise in liquid-liquid equilibrium calculations: in fact PR does not predict liquid phase splitting for both systems considered. On the other hand GC-PC-SAFT and REG-PC-SAFT models correctly predict heteroazeotrope conditions while provide quite different results concerning composition of the two liquid phases. In particular, REG-PC-SAFT model results are much more accurate in evaluation of liquid phase composition and critical solution conditions.

Table 2: Pure components parameters used in PC-SAFT EOS

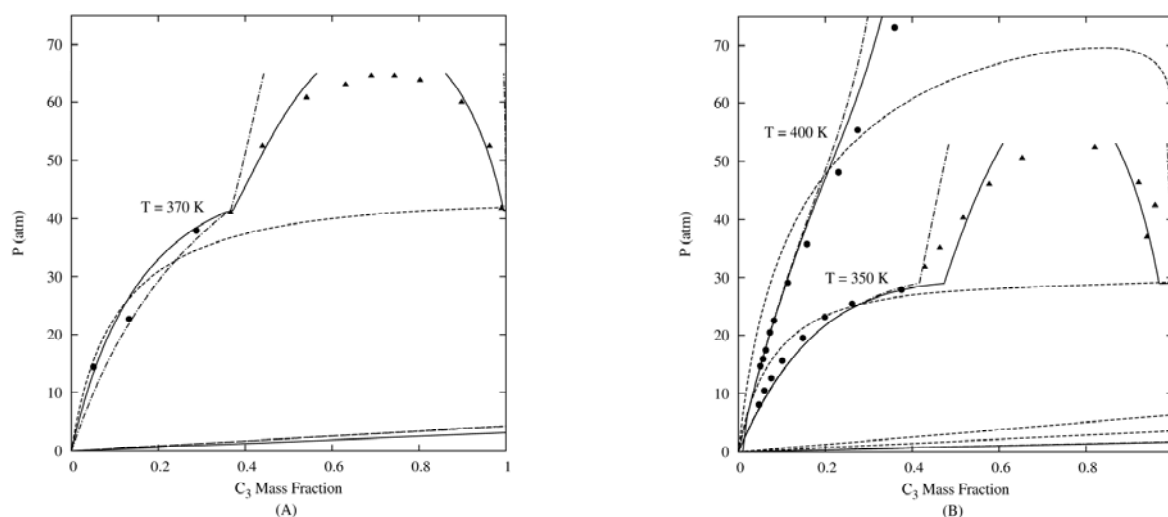| Method	Component	m[-]	σ[Å]	ε/k[K]
Group contribution	Triolein	23.728	3.887	265.9
	Tristearin	24.314	3.894	263.23
	Tripalmitin	21.851	3.891	263.48
Regressed	Triolein	26.368	3.335	205.176
	Tristearin	20.985	3.459	214.82
	Tripalmitin	12.511	3.898	265.99
Gross and Sadowsky (2001)	Hexadecane	6.6485	3.9552	254.7
	Propane	2.002	3.6184	208.11

Figure 3: Comparison between VLE (●) and LLE (▲) experimental data, relative to C_3-Tripalmitin (A) and C_3-Triolein (B) mixtures, and phase equilibrium conditions calculated with PR (−−), GC-PC-SAFT (−·−) and REG-PC-SAFT (—) EOS.

Since REG-PC-SAFT seems to be the more suitable EOS to describe the binary systems investigated, it was chosen to carry out a preliminary study of the hydroconversion two stages process proposed by Abhari and Havlik (2009). According to the results reported in their work, in the first reactor partial conversion takes place and reaction products such as water, propane and gaseous compounds need to be removed to allow the reaction to approach chemical equilibrium into the second reaction step. To this end, the stream from the first reactor is separated in a flash drum. In this work, we simulated the process assuming an inlet stream composition as reported in Table 4. In the same table, the separation results, calculated with REG-PC-SAFT model at 58 atm and temperature from 313 K to 383 K are reported. As expected, the higher the temperature the lower is the propane fraction into the oil-rich liquid phase.

4. Conclusions

The study carried out on highly asymmetric mixtures of alkanes involved in vegetable oil hydroconversion shows that the PC-SAFT with parameters regressed, as usual, from pure components physical properties is the most appropriate EOS for predicting phase behaviour of such a system. Concerning C_3-triglycerides systems it was proven that a fully predictive PC-SAFT EOS, with parameters obtained from a group contribution method, gives adequate vapour-liquid-liquid phase equilibrium predictions. On the other hand, PC-SAFT EOS with regressed parameters, better fits liquid partial miscibility limits and, in spite of loss of predictive quality, appears the most suitable EOS to model phase equilibria involved into the vegetable oils hydroconversion process.

Table 3: Average absolute percentage deviations (AAPD) between experimental data and phase composition calculated with PR and PC-SAFT EOS for the C_3-C_{16} system.

EOS	T[K]	AAPDx	AAPDy
PR	472.9	4.396	0.352
	522.9	4.436	1.621
	573.6	8.345	2.951
	625.8	7.785	5.297
PC-SAFT	472.9	3.401	0.355
	522.9	1.665	1.834
	573.6	1.282	2.553
	625.8	2.195	2.73

Table 4: Mass fractions of the outlet streams of the three-phase separator calculated with REG-PC-SAFT EOS at 58 atm and different temperatures for a given inlet stream.

Streams	T[K]	Stream to feed flow ratio	Triglycerides	Fatty acids	Alkanes $(C_{15}-C_{18})$	Water	Propane	Gaseous (H_2, CO_2, CO)
Inlet			0.255*	0.084**	0.538°	0.047	0.032	0.044°°
Vapour phase	313.2	0.044	-	-	-	0.007	0.267	0.726
	353.2	0.054	-	-	-	0.035	0.313	0.652
	383.2	0.066	-	-	0.002	0.122	0.312	0.564
Oil-rich liquid phase	313.2	0.910	0.281	0.093	0.591	0.001	0.021	0.013
	353.2	0.905	0.282	0.094	0.594	0.005	0.016	0.009
	383.2	0.907	0.282	0.093	0.592	0.014	0.012	0.007
Water-rich liquid phase	313.2	0.046	-	-	-	0.99901	2e-4	7.9e-4
	353.2	0.041	-	-	-	0.99894	3e-4	7.6e-4
	383.2	0.027	-	-	-	0.99888	4e-4	7.2e-4

(*) Triolein 25.9%, Tripalmitin 58%, Trilinolein 16.1%, (**) Oleic acid 100%, (°) C_{18} 42.7%, C_{17} 15.1%, C_{16} 32.1%, C_{15} 10.1%, (°°) CO_2 48.8%, CO 0.3%, Hydrogen 50.9%.

References

Abhari R., Havlik P., 2009, Hydrodeoxygenation Process, US Patent 2009/0163774.

Ambrose D., 1982, Correlation and Estimation of Vapour-Liquid Critical Properties, I. Critical Temperature of Organic Compounds, The Journal of Chemical Thermodynamics 14, 61-76.

Ambrose D., 1995, Vapor-Liquid Critical Properties of Elements and Compounds. II. Normal Alkanes, Journal of Chemical Engineering Data 35, 531-546.

Barker J.A., Henderson D., 1967, Perturbation Theory and Equation of State for Fluids: A Successful Theory of Liquids, The Journal of Chemical Physics 47, 2856-2861.

Bottini S.B., Fornari T., Brignole E.A., 1999, Phase Equilibrium Modelling of Triglycerides with Near Critical Solvents, Fluid Phase Equilibria 158-160, 211-218.

Chen S.S., Kreglewski A., 1977, Applications of the Augmented van der Waals Theory of Fluids. I. Pure Fluids, Ber. Bunsenges. Phys. Chem. 81, 1041.

Gross J., Sadowsky G., 2001, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules, Industrial and Engineering Chemistry Research 40, 1244-1260.

Gross J., Sadowsky G., 2002, Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State, Industrial Engineering Chemistry Research 41, 1084-1093.

Guzman A., Torres J.E., Prada L.P., Nuñez M.L., 2010, Hydroprocessing of crude palm oil at pilot plant scale, Catalysis Today 156, 38-43.

Nguyen T.B., De Hemptinne J.C., Creton B., Kontogeorgis G.M., 2013, GC-PPC-SAFT equation of state for VLE and LLE of Hydrocarbons and Oxygenated Compounds. Sensitivity analysis, Industrial Engineering Chemistry Research 52, 7014-7029.

Peng D.Y., Robinson D.B., 1976, A New Two-Constant Equation of State, Industrial and Engineering Chemistry Fundamentals 15, 59-64.

Reid R.C.; Prausnitz J., Poling B., 1987, The Properties of Gases and Liquids, McGraw Hill, New York.

Straver E.J.M., de Roo J.L., Peters C.J., de Swaan Arons J., 1998, Phase behaviour of the binary system propane and tristearin, Journal of Supercritical Fluids 11, 139-150.

Thies M.C., 2004, VLE measurements for asymmetric mixtures of Fischer-Tropsch hydrocarbons, Technical Report, United States, DOI 10.2172/828222.

Tihic A., Kontogeorgis M.G., van Solms N., Michelsen M.L., 2008, A Predictive Group-Contribution Simplified PC-SAFT Equation of State: Application to Polymer Systems, Industrial and Engineering Chemistry Research 47, 5092-5101.

Ting P.D., Joyce P.C., Prasanna K.J., Chapman W.G., Thies M.C., 2003, Phase equilibrium modeling of mixtures of long-chain and short-chain alkanes using Peng-Robinson and SAFT, Fluid Phase Equilibria 206, 267-286.

Wertheim M.S., 1984, Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations, Journal of Statistical Physics 35, 35-47.