PHASE EQUILIBRIA OF TRIOLEIN TO BIODIESEL REACTOR SYSTEMS

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Abstract

The phase equilibria of biodiesel systems, which are comprised of mixtures of triolein, methanol, carbon dioxide, methyl-oleate, glycerol, and water, are analyzed using PC-SAFT in ASPEN PLUS and SAFT- γ Mie in gPROMS (gSAFT) for systems in the vicinity of their critical point. Pure-species density and liquid vapor-pressure data were used to regress pure-species parameters for both variants of the SAFT equations. Binary vapor-liquid and liquid-liquid equilibrium data for the six species were used to obtain binary interaction parameters in PC-SAFT and cross parameters in SAFT- γ Mie. Vapor-liquid and liquid-liquid equilibria data from the literature were supplemented with experimental data taken herein to obtain a complete set of binary parameters. Overall, SAFT- γ Mie gave the best agreement with binary data, but had difficulty predicting liquid-liquid behavior in ternary systems. PC-SAFT showed good agreement with experimental data, especially for LLE systems. However, the *Gibbs flash method* in ASPEN PLUS yielded poor predictions for the triolein, methanol, and carbon dioxide mixture in the VLE and VLLE regions – but, addition of a tangent-plane-distance code revealed the prediction of unstable phases. Similarly, gSAFT in gPROMS, was unable to predict correct phase distributions, using parameters regressed in prior studies. Consequently, to examine the conversion of triolein to methyl-oleate observed experimentally at VLLE conditions (95°C 9.65 MPa), RK-ASPEN (without binary interaction parameters) was used in a custom-written FORTRAN reactor program.

Keywords: SAFT, GXL, supercritical, CO₂

1. Introduction

Biodiesel offers a renewable, carbon-neutral alternative to its fossil fuel counterpart. However, with plummeting oil prices, alternative fuels have become less competitive, and thus, improved processes are needed to reduce costs. In a previous study, which examined algae-to-biodiesel ventures, the extraction step was found to be energy intensive and have widely variable economic estimates [1]. An alternative, using high-pressure CO_2 , has been demonstrated experimentally [2] and found to be highly-effective and also selective at extracting algae-oil. Similarly, several studies have shown the potential of supercritical CO_2 as a co-solvent in the transesterification reactions [3-5], allowing high conversions at relatively low temperatures. It is thus possible that these two steps could be combined, although this has not been demonstrated yet. However, performing the oil-extraction and conversion in the same step or at least the same process should yield considerable cost savings by eliminating pre-processing and purification steps that are currently required [1].

This paper focuses on the conversion of triglyceride to biodiesel using supercritical CO_2 — with the kinetic mechanism shown in Figure 1, rather than the extraction of oil from algae. Given that the objective is to use algae-derived oils, water is assumed to be present. Due to lack of data, diglycerides and monoglycerides are excluded from the calculations herein. Further, triolein and methyl-oleate were used as exemplars of algal oil and biodiesel for this study as they are the only triglyceride and fatty acid methyl ester (FAME) molecules having sufficient data to be included. As such, this analysis involves just six chemical species: triolein, methyl-oleate, methanol, glycerol, water, and carbon dioxide. In future studies, the number of triglycerides will be increased to accurately represent algae-oils, allowing the extraction step to be modeled.

Kinetic pre-exponential factors and activation energies for the conversion of algae-oils to biofuels are available [5-7]. However, previous studies that modeled the phase behavior for transesterification reactions used crude models (like Redlich-Kwong in ASPEN PLUS [3, 4, 8], which are not suitable in the critical region or with large, asymmetric molecules. The most advanced equations-of-state (EoS) used for supercritical systems have been the Cubic Plus Association (CPA) EoS, which was used to study supercritical alcohols [9-15], and the soft-SAFT, which was used to study binary systems of CO_2 and water, and CO_2 and FAME [16].

The objective of this transesterification study is to use the SAFT EoSs to model the phase behavior of a biodiesel reactor [up to three phases (vapor, polar liquid, nonpolar liquid) or as few

as one supercritical phase [17]]. The miscibility between the phases has drastic effects on the concentrations (and reaction rates). It will be shown that a reliable phase equilibria model is needed to describe the reactor conversions; however, predictions with commercially-available SAFT phase-equilibria models are not yet sufficiently reliable in the critical region for triolein, methanol and CO₂. This paper presents experimental data and shows the reason for the inadequacy of their predictions, along with suggestions to improve their predictive capability in future work.

Figure 1. Triolein to biodiesel conversion mechanism. TG is triglyceride (triolein), MEOH is methanol, DG is diglyceride, FAME is fatty-acid methyl-ester (biodiesel), MG is monoglyceride, GLY is glycerol, and critical CO₂ is carbon dioxide in or near the critical region.

In the sections that follow, cubic and SAFT equations-of-state are reviewed, the latter designed for use with long-chain hydrocarbons. Experimental methods are presented, which were used to generate data herein for binary systems, where data were unavailable or unreliable. Most of these data were for liquid-liquid systems, although one vapor-liquid system was studied

experimentally. Then, pure-species, binary, and ternary data are used to compare two SAFT variants [PC-SAFT in ASPEN PLUS [18, 19] and SAFT- γ Mie in gPROMS (gSAFT¹) [20, 21]] and RK-ASPEN. Finally, a multiphase-reactor model, using approximate RK-ASPEN to model VLLE, is formulated and evaluated with experimental data.

2. Theory

2.1. Cubic Equations-of-State

Cubic equations-of-state (EoS) were first developed roughly 130 years ago and have become the industry standard since the development of computer-aided process design in the 1970s. The cubic EoSs are named as such because they contain a cubed molar volume term (Eq. 1). Numerous variants exist, the most popular of which are the van der Waals equation, Soave-Redlich-Kwong [22], and Peng-Robinson [23]. Herein, a variant of Soave-Redlich-Kwong (RK-ASPEN) will be used for comparative purposes with the SAFT EoSs. The equations that describe RK-ASPEN are shown below.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (1)$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - K_{a,ij}) \quad (2)$$

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - K_{b,ij}) \quad (3)$$

where R is the gas constant (8.314 J/mol-K), T is temperature, V is the molar volume, P is the pressure, $K_{a,ij}$ and $K_{b,ij}$ are binary interaction parameters, and a_i and b_i are empirical parameters, calculated using Eq. 4-7. The attractive parameter, a_i , depends on the reduced temperature ($T_{ri} = T/T_{ci}$), the critical temperature (T_{ci}) and critical pressure (P_{ci}), the accentric factor (ω_i), and an extra polar parameter (η_i). The size parameter, b_i , depends only on the critical temperature and critical pressure. γ_i is a parameter that accounts for accentricity of the molecule.

$$a_i = 0.42747 \propto_i \frac{R^2 T_{ci}^2}{P_{ci}} \quad (4)$$

$$\propto_i = [1 + \gamma_i (1 - T_{ri}^{0.5}) - \eta_i (1 - T_{ri})(0.7 - T_{ri})]^2 \quad (5)$$

$$\gamma_i = 0.48508 + 1.5517\omega_i - 0.15613\omega_i^2 \quad (6)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (7)$$

¹ Note that the equation-of-state is known as SAFT- γ Mie. gSAFT is the thermodynamics package developed by Process System Enterprise, which contains the SAFT- γ Mie equation-of-state. Note that these two terms are used interchangeably throughout this paper.

The binary interaction parameters, $K_{a,ij}$ and $K_{b,ij}$, are determined from Eq. 8 and 9, in which $K_{a,ij}^0$, $K_{a,ij}^1$, $K_{b,ij}^0$, and $K_{b,ij}^1$ are all parameters regressed using binary vapor-liquid equilibrium (VLE) or liquid-liquid equilibrium (LLE) data [24].

$$K_{a,ij} = K_{a,ij}^0 + K_{a,ij}^1 \frac{T}{1000} \quad (8)$$

$$K_{b,ij} = K_{b,ij}^0 + K_{b,ij}^1 \frac{T}{1000} \quad (9)$$

2.2. PC-SAFT

More recently, new EoSs were derived using statistical mechanics to represent complex fluid mixtures. The statistical associating fluid theory (SAFT), which treats molecules as freely jointed spherical segments [25], is prominent among them. Gross and Sadowski modified the original SAFT formulation by: (1) adding a dispersion expression for chain molecules based on perturbation theory [26-29], (2) readjusting the other pure-species parameters to improve accuracy [18], and (3) adding an association term [19]. Their EoS is referred to as the perturbed chain-SAFT, or PC-SAFT.

In PC-SAFT, molecules are modeled as chains of spherical segments. The pair-potential of a segment is described by Eq. 10, which uses a modified square-well potential, in which $u_{ij}(r)$ is the pair-potential, r is the radial distance between segments, σ_{ij} is the segment diameter, ε_{ij} is the energy of the square-well interaction, and λ_{ij} is the attractive range of the interaction [18]. In this case, $S_{ij} = 0.12\sigma_{ij}$. Note that the variable, λ_{ij} , is not actually used in the final version of the equation since it is regressed out, but is included here for completeness.

$$u_{ij}(r) = \begin{cases} \infty, & r < (\sigma_{ij} - S_{ij}) \\ 3\varepsilon_{ij}, & (\sigma_{ij} - S_{ij}) \leq r < \sigma_{ij} \\ -\varepsilon_{ij}, & \sigma_{ij} < r \leq \lambda_{ij}\sigma_{ij} \\ 0, & r > \lambda_{ij}\sigma_{ij} \end{cases} \quad (10)$$

The EoS is formulated in terms of the Helmholtz free energy, as shown in Eq. 11. Four terms account for four phenomena: an ideal-gas contribution (ig); a hard-chain contribution (hc), which accounts for repulsive forces between chains (individual species in this work); a

dispersion (disp) contribution, which accounts for attractive forces between species; and an association contribution (assoc) for species that can hydrogen bond or those with electron lone pairs. For Eq. 11, A is the Helmholtz free energy, N is the number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature.

$$\frac{A}{Nk_BT} = \frac{A^{ig}}{Nk_BT} + \frac{A^{hc}}{Nk_BT} + \frac{A^{disp}}{Nk_BT} + \frac{A^{assoc}}{Nk_BT} \quad (11)$$

For non-associating molecules, the equation is described by three pure-species parameters: the segment diameter, σ_{ij} , the energy of the square-well potential ε_{ij} , and the number of segments per chain, m_i . The like (ε_{ii} , σ_{ii} , and m_i) parameters are regressed from pure-species densities and liquid vapor pressures. The unlike parameters (ε_{ij} and σ_{ij}) are calculated using:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1 - K_{ij}) \quad (12)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (13)$$

where K_{ij} represents the binary interaction parameter for molecules i and j , which is regressed using experimental binary data and calculated using Eq. 14. Note that these parameters are symmetric ($K_{ij} = K_{ji}$) [24].

$$K_{ij} = K_{ij}^{(1)} + K_{ij}^{(2)}T + \frac{K_{ij}^{(3)}}{T} \quad (14)$$

The hard-chain contribution is dependent on reduced densities:

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i D_{ii}^n \quad n \in (0, 1, 2, 3) \quad (15)$$

where ζ_n is the reduced density, ρ is the number density (molecules/m³), x_i is the mole fraction of chemical species i , m_i is the number of segments in species i , and D_{ii} is a temperature-dependent collision diameter of i (in meters), which is defined in Eq. 16. Note that for a value of $n = 3$, ζ_3 is a dimensionless density, more commonly referred to as the packing fraction.

$$D_{ii} = \int_0^{\sigma_{ii}} \left[1 - \exp\left(-\frac{u_{ii}(r)}{k_BT}\right) \right] dr \quad n \in (0, 1, 2, 3) \quad (16)$$

The dispersion contribution is characterized as the sum of the first and second order Helmholtz perturbation expansions:

$$\frac{A^{disp}}{Nk_BT} = \frac{A_1}{Nk_BT} + \frac{A_2}{Nk_BT} \quad (17)$$

where the first and second order Helmholtz functions depend on the interacting segments' radial distributions, hard-chain Helmholtz energies, reduced radial distance, and reduced potential function [18]. The universal model constants (not described in this paper) used to calculate the

two Helmholtz terms were adjusted using pure-species data from the n-alkane series. These adjustments eliminate the parameter, λ_{ij} . For further discussion of this topic, see the original PC-SAFT paper [18].

Finally, the association term is:

$$\frac{A^{assc}}{Nk_B T} = \sum_i x_i \left[\sum_A [\text{Ln}(X_{A_i}) - \frac{X_{A_i}}{2}] + \frac{1}{2} M_i \right] \quad (18)$$

where M_i is the number of association sites on each molecule and X_{A_i} is the mole fraction of molecules i not bonded at an individual site, A . The summation is performed over all associating sites for each molecule. X^{A_i} is dependent on a bonding volume term, $\kappa^{A_i B_j A}$, and a dimensionless association energy term, $\varepsilon^{A_i B_j}/k_B T$, which are the other pure-species parameters required for an associating molecule. For cross-associating mixtures, these terms are described by simple combining rules:

$$\varepsilon^{A_i B_j} = \frac{1}{2} (\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}) \quad (19)$$

$$\kappa^{A_i B_j A} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left(\frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{0.5(\sigma_{ii} + \sigma_{jj})} \right)^3 \quad (20)$$

There is also a dipole-dipole component of the equation that depends on the dipole-moment and dipole-fraction parameters. The polar Helmholtz term depends on the second- and third-order terms in a Helmholtz perturbation expansion:

$$A^{\text{polar}} = \frac{A_2}{1 - \frac{A_3}{A_2}} \quad (21)$$

where the second- and third-order perturbation expansions depend on the summation of the dipole-moment and dipole-fraction parameters over all species [24, 30]. Because the dipole-dipole portion of the equation led to numerical instability when performing phase equilibria calculations, it was not used herein. Consequently, three pure-species parameters are required for non-hydrogen bonding systems (ε_{ii} , σ_{ii} , and m_i), five pure-species parameters are required for hydrogen bonding systems (ε_{ii} , σ_{ii} , and m_i , $\kappa^{A_i B_j A}$, $\varepsilon^{A_i B_j}$), and up to $3NC$ binary parameters are required, where NC is the number of species. The factor of 3 takes into account all binary parameters in Eq. 14.

2.3. SAFT- γ Mie

An alternative to modeling molecules as chains of spherical segments is to model them as combinations of different functional groups. This approach has been used previously for both

pure-species parameters (i.e., Joback or Marrero and Gani methods) [31] activity coefficient models (like UNIFAC) [32], and cubic EoS [33]. The advantages of this approach are that the assumption of perfectly spherical segments can be relaxed by introducing a shape factor, and parameters do not need to be regressed for every molecule in the system. As long as all of the functional groups in a molecule are known, the molecule's thermodynamic properties and behavior in mixtures can be predicted. This is useful for systems where large numbers of similar molecules are present, as is often seen in biological systems. When working with the biodiesel system, the group methodology is helpful to represent the large ranges of fatty-acid methyl-esters (FAMES) and triglycerides.

The most recent implementation of the group-contribution methodology within the SAFT framework is in the SAFT- γ Mie EoS [21]. Like PC-SAFT, SAFT- γ Mie is formulated in terms of the Helmholtz free energy. However, the formulation is different as it involves terms for the monomeric functional-group interactions. The SAFT- γ Mie equation is:

$$\frac{A}{Nk_B T} = \frac{A^{\text{ig}}}{Nk_B T} + \frac{A^{\text{mono}}}{Nk_B T} + \frac{A^{\text{chain}}}{Nk_B T} + \frac{A^{\text{assoc}}}{Nk_B T} \quad (22)$$

where A is the Helmholtz free energy, N is the number of molecules, k_B is Boltzmann's constant, T is the absolute temperature, A^{ig} is the ideal gas contribution, A^{mono} is the contribution of the individual functional groups, A^{chain} is the contribution of the full molecules, and A^{assoc} is the association contribution. Unlike PC-SAFT, there is no term to account for the dipole-dipole interactions that occur in molecules having lone electron pairs. However, since this term was set to zero in PC-SAFT, it allows a more symmetric comparison of the models.

Another major difference between the two SAFT EoSs, is that SAFT- γ Mie replaces the square-well potential energy function with the Mie function (a generalized form of the Lennard-Jones equation). The Mie potential energy function is displayed in:

$$U_{kl}(r) = \Omega_{kl}^{\text{Mie}} \varepsilon_{kl} \left[\left(\frac{\sigma_{kl}}{r} \right)^{\lambda_{R,kl}} - \left(\frac{\sigma_{kl}}{r} \right)^{\lambda_{at,kl}} \right] \quad (23)$$

$$\Omega_{kl}^{\text{Mie}} = \frac{\lambda_{R,kl}}{\lambda_{R,kl} - \lambda_{at,kl}} \left(\frac{\lambda_{R,kl}}{\lambda_{at,kl}} \right)^{\left(\frac{\lambda_{at,kl}}{\lambda_{R,kl} - \lambda_{at,kl}} \right)} \quad (24)$$

where σ_{kl} is the group segment diameter, ε_{kl} is the depth of the potential well between groups, $\lambda_{R,kl}$ and $\lambda_{at,kl}$ are the repulsive and attractive exponents of the intergroup interactions, respectively, and Ω_{kl} is a function of $\lambda_{R,kl}$ and $\lambda_{at,kl}$, which ensures that the minimum interaction energy is ε_{kl} .

The hard-sphere diameter is calculated using Eq. 16, with the Mie potential replacing the square well potential used in PC-SAFT. However, unlike with the case of the square-well potential, Eq. 16 cannot be solved analytically for the Mie potential, and a Gauss-Legendre procedure has been applied [34] to allow incorporation into the code. As before, the hard-sphere diameter is used to calculate the reduced densities (Eq. 15), which are used in both the monomeric and chain contribution terms.

The monomer contribution in Eq. 22 is analogous to the hard-sphere and dispersion contributions from Eq. 11, but for functional groups instead of molecules. The dispersion contribution is also calculated using a perturbation expansion, but SAFT- γ Mie uses a third-order perturbation expansion, compared with the second-order expansion in Eq. 17. The chain contribution is determined by calculating molecule-averaged quantities for σ_{kl} , ε_{kl} , $\lambda_{R,kl}$, $\lambda_{at,kl}$, D_k , and ζ_n . These averaged molecule parameters are used to calculate a pair potential function that is summed over the number of species to yield the chain contribution of the Helmholtz free energy. The association term is similar to Eq. 18, only its formulation is in terms of the associating sites per functional group, which is summed over the various molecules in the solution:

$$\frac{A^{\text{assoc}}}{Nk_B T} = \sum_{i=1}^{NC} x_i \sum_{k=1}^{NG_i} ng_{k,i} \sum_{A=1}^{N_{ST,k}} nsg_{k,A} \left(\ln X_{i,k,A} + \frac{1 - X_{i,k,A}}{2} \right) \quad (25)$$

where NC is the number of chemical species, NG_i is the number of groups for species i , $ng_{k,i}$ is the number of groups of type k in molecule i , $N_{ST,k}$ is the total number of site types on a given group k , and $nsg_{k,A}$ is the number of sites of type A on group k . $X_{i,k,A}$ represents the fraction of molecules of species i that are not bonded at a site of type A on group k . $X_{i,k,A}$ is a complex function of $\varepsilon_{kl,AB}^{\text{HB}}$ (the interaction energy between two bonding sites) and $r_{kl,AB}^c$ (the interaction range between two bonding sites) for associating sites A and B on groups k and l respectively. The potential energy function which characterizes the association energy is described by the square-well potential energy function:

$$u_{kl,AB}^{\text{HB}}(r_{kl,AB}) = \begin{cases} -\varepsilon_{kl,AB}^{\text{HB}}, & r_{kl,AB} \leq r_{kl,AB}^c \\ 0, & r_{kl,AB} > r_{kl,AB}^c \end{cases} \quad (26)$$

Overall, for each group, four like parameters need to be regressed for a non-associating system (σ_{kk} , ε_{kk} , $\lambda_{R,kk}$, $\lambda_{at,kk}$) and six like parameters need to be regressed for an associating system

$(\sigma_{kk}, \varepsilon_{kk}, \lambda_{R,kk}, \lambda_{at,kk}, \varepsilon_{kl,AB}^{HB}, r_{kl,AB}^c)$. The unlike parameters can either be regressed from data or calculated using the following equations:

$$\sigma_{kl} = \frac{1}{2}(\sigma_{kk} + \sigma_{ll}) \quad (27)$$

$$\varepsilon_{kl} = \frac{\sqrt{\sigma_{kk}^3 \sigma_{ll}^3}}{\sigma_{kl}^3} \sqrt{\varepsilon_{kk} \varepsilon_{ll}} \quad (28)$$

$$\lambda_{R,kl} = 3 + \sqrt{(\lambda_{R,kk} - 3)(\lambda_{R,ll} - 3)} \quad (29)$$

$$\lambda_{at,kl} = 3 + \sqrt{(\lambda_{at,kk} - 3)(\lambda_{at,ll} - 3)} \quad (30)$$

$$D_{kl} = \frac{1}{2}(D_{kk} + D_{ll}) \quad (31)$$

$$\varepsilon_{kl,AB}^{HB} = \sqrt{\varepsilon_{kk,AA}^{HB} \varepsilon_{ll,BB}^{HB}} \quad (32)$$

$$r_{kl,AB}^{HB} = \frac{1}{2}(r_{kk,AA}^c + r_{ll,BB}^c) \quad (33)$$

Note that instead of Eq. 31, Eq. 16 could be used to calculate the unlike hard-sphere diameter. However, Eq. 31 is used to decrease the numerical complexity. It is also important to realize that while it appears that SAFT- γ Mie requires many more parameters than PC-SAFT (4 compared to 3 for non-associating systems, or 6 compared to 5 for associating systems), the SAFT- γ Mie parameters are for groups, which can be used for multiple molecules. SAFT- γ Mie also does not require separate binary parameters (K_{ij}), which further decreases the number of regressed parameters required for complex systems.

2.4. Tangent-Plane-Distance Criterion

The equations-of-state are used to calculate thermodynamic properties, such as fugacity coefficients and liquid molar volumes. However, determining the phase distribution and compositions in a multiphase mixture requires that the Gibbs free energy be minimized subject to mass-balance constraints [35-39]. For this purpose, the *Gibbs flash method*² in ASPEN PLUS was used [35, 38] with PC-SAFT and RK-ASPEN, and a proprietary algorithm was used in gPROMS. While, with good initial guesses, it is possible to find the correct phase distribution through direct minimization of the Gibbs free energy [40], it is preferable to check the stability

²Two flash convergence algorithms are available: "Inside-Out" (Boston and Britt, 1976) and direct minimization of Gibbs free energy (Gautam and Seider, 1979). The former is implemented in the FLASH2 and FLASH3 blocks and the latter in the RGIBBS block. To our knowledge, the latter uses an approximate phase-splitting algorithm as the free energy is minimized.

of the resulting phases by using the Gibbs free energy of mixing to estimate the tangent-plane-distance function [41-43]. The tangent-plane-distance function compares the total Gibbs free energy after creating a new, infinitesimal phase with the Gibbs free energy of the initial phase, shown as Eq. 34, where ΔG is the total Gibbs free energy of the phase, $\bar{Z}$ is the vector of moles in the initial phase, and $\bar{Y}$ is the vector of moles in the infinitesimal phase. This expression can be reformulated in terms of the Gibbs free energies of mixing as Eq. 35 [43], where $\bar{y}$ is the vector of mole fractions in the infinitesimal phase, $\bar{z}$ is the vector of mole fractions in the initial phase, $\Delta G_m(\bar{y})$ is the Gibbs free energy mixing surface, $\Delta G_m^T(\bar{z})$ is the tangent plane, and $F(\bar{y})$ is the tangent-plane-distance function (the difference between the tangent plane and the Gibbs free energy of mixing surface). If $F(\bar{y})$ is greater than zero for all values of $\bar{y}$, the initial phase is stable. Otherwise, the initial phase is unstable, guesses for another phase are estimated, and the Gibbs free energy is re-minimized.

A more common formulation of the tangent-plane-distance function is shown as Eq. 36, where μ_i is the chemical potential of species i in the phase [43]. Finally, the tangent-plane-distance function is reformulated using Eq. 37 and 38 to give Eq. 39, where $\mu_{i,ref}$ is the chemical potential of species i in the pure ideal gas evaluated at T , R is the gas constant, T is the absolute temperature, f_i is the fugacity of species i in the phase, P is the pressure of the system, ϕ_i is the fugacity coefficient of species i in the phase, x_i is the mole fraction of species i in the phase, and $\phi_{o,i}$ is the fugacity coefficient of species i in the original phase.

Eq. 39 is used herein in a FORTRAN algorithm written by Prof. Romain Privat [44], which examines the stability of every phase separately. The code uses the objective function, Φ , defined by Michelsen [42], in Eq. 40, where W_i is the non-normalized concentration for the infinitesimal phase. Since the minimum of the objective function satisfies the necessary constraint [42], Eq. 41 – the minimum can be found by minimizing the sum of the squares, shown in Eq. 42. The objective function, Γ , is minimized using a custom-written NLP solver with numerous initial guesses. If the minimum of Eq. 39 is found to be negative, the initial phase(s) is unstable. Otherwise, the phase(s) is assumed to be stable. This code was incorporated within ASPEN PLUS by the authors, permitting ϕ_i and $\phi_{o,i}$ to be calculated using the ASPEN PLUS physical property system.

$$\Delta G(\bar{Y}) = \Delta G(\bar{Z} - \bar{Y}) + \Delta G(\bar{Y}) - \Delta G(\bar{Z}) \geq 0, \forall \bar{Y} \quad (34)$$

$$F(\bar{Y}) = \Delta G_m(\bar{Y}) - \Delta G_m^T(\bar{Z}) \geq 0, \forall \bar{Y} \quad (35)$$

$$F(\bar{Y}) = \sum_{i=1}^{NC} y_i (\mu_i(\bar{Y}) - \mu_i(\bar{Z})) \geq 0, \forall \bar{Y} \quad (36)$$

$$\mu_i = \mu_{i,ref} + RT \ln(f_i) \quad (37)$$

$$f_i = P \phi_i x_i \quad (38)$$

$$F(\bar{Y}) = RT \sum_{i=1}^{NC} y_i (\ln(y_i) + \ln(\phi_i) - \ln(z_i) - \ln(\phi_{o,i})) \quad (39)$$

$$\Phi(T, P, z, W) = 1 + \sum_{i=1}^{NC} W_i * (\ln(W_i) + \ln(\phi_i) - \ln(z_i \phi_{o,i}) - 1) \quad (40)$$

$$\ln(W_i) + \ln(\phi_i) - \ln(z_i \phi_{o,i}) = 0, \forall i \quad (41)$$

$$\Gamma(T, P, z, W) = \sum_{i=1}^{NC} (\ln(W_i) + \ln(\phi_i) - \ln(z_i \phi_{o,i}))^2 \quad (42)$$

3. Experimental

3.1. Vapor-Liquid Equilibria

Methyl-oleate and methanol equilibrium data were measured using a 500 mL bulb connected to a condenser and setup for total or partial reflux. The bulb was heated with an electric heating jacket, and the cooling water was circulated at 7°C. The well-insulated apparatus was mixed by a magnetic stir bar in the liquid phase and heated to obtain a low boil. The system was then operated at total reflux for 1-hour to attain equilibrium. A small sample of the condensed vapor was collected using a 3-way valve. The liquid was sampled from a stopcock at the bottom of the bulb. Following sampling, methanol was added through the condenser to obtain data at a higher methanol composition.

3.2. Liquid-Liquid Equilibria

Each species was added at equal mass loadings to a 10 mL separatory funnel that was used for equilibration and sampling. The apparatus was affixed to a rotisserie-style rotor inside a preheated oven and rotated for at least 3 hours to provide adequate contact between the two liquids. The samples were then left to equilibrate for at least 5 hours. The top phase was sampled using a pipette and the bottom phase was sampled through the funnel's stopcock. During sampling, the first few drops of sample were discarded to insure a representative sample was taken. All experiments were run at least in duplicate.

3.3. Sample Preparation

To obtain the methyl-oleate concentration, samples were diluted in heptane containing 0.05 g/L of methyl-laurate as an internal standard. For the analysis of triolein, samples were diluted in 1:1 chloroform:methanol containing 0.1 g/L tripalmitin as an internal standard. They were then transesterified using 14% boron trifluoride in methanol. The sample headspace was sparged with nitrogen, and the reaction took place at 100°C for 1-hour. The reacted samples were diluted with heptane containing 0.05 g/L of methyl-laurate as an internal standard. For analysis of glycerol, samples were silylated using ASTM Standard test method D6584 – 13 [45].

3.4. Analysis

The sample analysis was performed using a Perkin-Elmer AutoSystem XL Gas Chromatograph and Gold Mass Spectrometer (GC-MS). The GC was fitted with a 15m × 0.25mm × 0.25µm 5% phenyl polydimethylsiloxane column (Agilent, DB-5ht) and joined with a 5m × 0.53mm deactivated, Hi-Temp guard column using a press fit union. All analytical samples were run on the GC-MS using ASTM Standard test method D6584 – 13 [45]. Methyl-oleate and silylated glycerol were analyzed at a mass-to-charge ratio (m/z) of 264 and 205 with retention times of 11.00 and 5.87 minutes, respectively. The results of the analysis are shown as Appendix A.

4. Regression Methodology

This section discusses the techniques used to regress the pure-species and binary-interaction parameters necessary for PC-SAFT in ASPEN PLUS and SAFT- γ Mie in gPROMS. The same pure-species and binary data sets were used to regress parameters in both PC-SAFT and SAFT- γ Mie. The Britt-Luecke method [46] in ASPEN PLUS was used to regress the parameters for PC-SAFT. The Levenberg-Marquardt algorithm [47] was used in gPROMS for SAFT- γ Mie.

4.1. Pure Species

The majority of the pure-species data were obtained from the NIST database within ASPEN PLUS [48]. For methyl-oleate [49-52], glycerol [53, 54], CO₂ [55], and triolein [56, 57], sufficient data were not present in the NIST databanks. Supplementary data were obtained from

the literature [58-60]. For all species except carbon dioxide, liquid density and liquid vapor-pressure data were used to regress the pure-species parameters. Liquid density data were weighted more heavily (roughly 200 times) than vapor-pressure data, leading to more accurate representation of liquid phase behavior, and in particular liquid-liquid equilibria. The liquid phase behavior must be accurate, because in a biodiesel production reactor, the reactions occur exclusively in the liquid phases (and only at the surface of a catalyst bead) due to the nonvolatile triglycerides. It is also essential to capture the liquid-liquid behavior of the aqueous (methanol) phase and the nonpolar (oil) phase to obtain an accurate prediction of the reaction rates.

With regard to carbon dioxide, the pure-species parameters were regressed entirely from densities for the three phases (vapor, liquid, and supercritical). Because ASPEN PLUS accepts data input as either a vapor or a liquid phase, the supercritical region needed to be partitioned into these two categories. Densities greater than the critical density (467.6 kg/m^3) [61] were classified as liquid, while all others were classified as vapor. Plots of the density as a function of temperature were also generated to visualize the phase distribution, as shown in Figure 2. From these, good agreement between the data points and the PC-SAFT method is observed.

Figure 2. CO₂ density as a function of temperature using the PC-SAFT EoS

4.2. *Binary*

Binary data were obtained from the NIST interface in ASPEN PLUS [48], the literature [62-64], as well as the experiments in Section 3 (data listed in Appendix A). The regressed

binary interaction parameters for PC-SAFT are shown below. Only b_{ij} and c_{ij} were regressed, with the others set to zero. For SAFT- γ Mie, the cross-interaction energies for unlike groups, ε_{ij} , were regressed using binary data. In some cases, unlike well-distance parameters, λ_{ij} , were added to improve the fit.

$$\varepsilon_{ij} = (1 - K_{i,j})\sqrt{\varepsilon_i \varepsilon_j} \quad (43)$$

$$K_{i,j} = a_{i,j} + \frac{b_{i,j}}{T_r} + c_{i,j} \ln(T_r) + d_{i,j} T_r + e_{i,j} T_r^2 \quad (44)$$

$$T_r = \frac{T}{T_{\text{ref}}} \quad (45)$$

where ε_{ij} is the square-well potential energy constant for two unlike molecules i and j , ε_i and ε_j are the square-well potential energy constants for pure species i and j , respectively, $K_{i,j}$ is the binary interaction parameter for molecules i and j , $a_{i,j}$, $b_{i,j}$, $c_{i,j}$, $d_{i,j}$, and $e_{i,j}$ are empirical constants that are fit to binary data for molecules i and j , T_r is the reduced temperature, T is the system temperature, and T_{ref} is the chosen reference temperature (298.15 K).

5. Results

5.1. Parameter Results

The pure-species PC-SAFT parameters are shown in Table 1. A similar set of parameters were regressed for SAFT- γ Mie (the gSAFT package in gPROMS); however, at this time, those parameters cannot be released for intellectual property reasons. The groups that were used by SAFT- γ Mie are shown in Table 2. Where “R” represents a set of parameters that were regressed from data herein, “P” represents a set of parameters that were regressed in earlier work, and “X” indicates no parameters were regressed, because the necessary data does not exist.

In Table 1, PCSFTM is m_i in Eq. 15, representing the length of the molecule. Note that fits are empirical and while they follow a logical trend, the parameter values presented herein are not meant to agree with theoretical molecular properties. PCSFTU is the interaction energy, ε_i . PCSFTV is the characteristic diameter, σ_i . PCSFAU is the association site interaction energy (for hydrogen bonding molecules), $\varepsilon^{A_i B_i}$. PCSFAV is the association site interaction volume (for hydrogen-bonding molecules), $\kappa^{A_i B_i}$. PCSFMU and PCSFXP are the characteristic dipole-moment and the characteristic dipole-fraction parameters, respectively. The latter two

parameters are not used herein because they led to numerical instability for regressions and simulations. The effect of lone pairs was not accounted for in SAFT- γ Mie for similar reasons.

Table 1. Pure-Species Parameters for PC-SAFT

PURE COMPONENT								
Parameters	ASPEN PLUS Name	Units	Component	Component	Component	Component	Component	Component
			Methyl-oleate	Triolein	Glycerol	Methanol	Water	Carbon dioxide
m_i	PCSFTM	-	9.0390	16.184	2.1512	0.55347	0.33444	1.8102
ε_i	PCSFTU	K	248.47	282.84	472.16	120.97	139.50	179.83
σ_i	PCSFTV	-	3.7465	4.4475	3.7517	4.6043	4.5938	2.9107
ε^{AiBi}	PCSFAU	K	0	0	3832.4	3602.3	3965.5	0
κ^{AiBi}	PCSFAV	-	0	0	0.00189	0.01171	0.00634	0
μ	PCSFMU	-	0	0	0	0	0	0
X_p	PCSFXP	-	0	0	0	0	0	0

Table 2. SAFT- γ Mie groups.

Group	CH ₃	CH ₂	CH=	COO	C ₉ H ₁₁ O ₆	C ₃ H ₈ O ₃	CO ₂	CH ₃ OH	H ₂ O
CH ₃	P	P	P	R	R	R	R	R	R
CH ₂	P	P	P	R	R	R	R	R	R
CH=	P	P	P	R	R	R	R	R	R
COO	R	R	R	R	X	R	R	R	R
C ₉ H ₁₁ O ₆	R	R	R	X	R	R	R	R	R
C ₃ H ₈ O ₃	R	R	R	R	R	R	X	R	R
CO ₂	P	P	P	R	R	X	R	R	R
CH ₃ OH	P	P	P	R	R		R	R	R
H ₂ O	P	P	P	R	R	R	R	R	R

The binary interaction parameters regressed from vapor-liquid and liquid-liquid equilibria data are shown in Tables 3 and 4. Only b_{ij} and c_{ij} (in Eq. 44) were regressed to avoid over-regressing parameters.

Table 3. Binary-Species Parameters for PC-SAFT (from VLE data)

Species i	Methanol	Glycerol	Glycerol	Water
Species j	Carbon Dioxide	Methanol	Water	Methanol
Temp. units	°C	°C	°C	°C
$a_{i,j}$	0	0	0	0
$b_{i,j}$	-0.1317	-0.3297	0.21467	-0.5846
$c_{i,j}$	0.3591	-0.1476	-1.6503	2.7260
$d_{i,j}$	0	0	0	0
$e_{i,j}$	0	0	0	0
T_{ref}	25	25	25	25
Species i	Carbon Dioxide	Methanol	CO ₂	CO ₂
Species j	Water	Methyl-oleate	FAME	TG
Temp. units	°C	°C	°C	°C
$a_{i,j}$	0	0	0	0
$b_{i,j}$	-0.4504	-0.1658	-0.0429	0.13616
$c_{i,j}$	-0.0191	-1.463	1.0185	0.29994
$d_{i,j}$	0	0	0	0
$e_{i,j}$	0	0	0	0
T_{ref}	25	25	25	25

The pure-species parameters for RK-ASPEN are in Table 5. They were taken from the NIST databank, with the exception of triolein, which decomposes before reaching its critical point. Consequently, its critical properties were generated using group-contribution methods [3, 4, 8]. The binary interaction parameters (in Eqs. 8 and 9) are in Table 6. They were regressed using the same data and algorithm as for those in PC-SAFT.

5.2. *Pure Species*

Figure 3 shows the plots of pure-species liquid densities and vapor pressures for triolein, with similar plots for water, methanol, glycerol, and methyl-oleate in Figures S1-S4 in the

Supplement to this paper. In these plots, pure component properties were generated over the range of temperatures and pressures for each species using PC-SAFT, SAFT- γ Mie (gSAFT), and RK-ASPEN. All three EoS provide excellent agreement with vapor pressures, with the exception of triolein; however, the cubic EoS (RK-ASPEN), yields poor predictions of liquid densities. This underestimation of liquid density by RK-ASPEN would lead to drastic underestimations of process-vessel sizes.

Table 4. Binary-Species Parameters for PC-SAFT (from LLE data)

Species i	Triolein	Methyl-oleate	Methyl-oleate	Triolein	Triolein
Species j	Methanol	Water	Glycerol	Glycerol	Water
Temp. units	°C	°C	°C	°C	°C
$a_{i,j}$	0	0	0	0	0
$b_{i,j}$	-0.06820	-0.31655	-0.03783	-0.10413	-0.17356
$c_{i,j}$	0.01725	-0.12144	0.01543	-0.01823	0.20112
$d_{i,j}$	0	0	0	0	0
$e_{i,j}$	0	0	0	0	0
T_{ref}	25	25	25	25	25

Table 5. Pure-Species Parameters for RK-ASPEN

Parameters	Units	Component	Component	Component	Component	Component	Component
		Methyl-oleate	Water	Methanol	Triolein	Glycerol	CO ₂
ω	-	0.96055	0.34407	0.55850	1.6862	0.55381	0.22567
V_C	m ³ /kmol	1.2339	0.05870	0.11800	3.0070	0.24470	0.09431
P_C	Pa	1.1726E+06	2.2094E+07	8.0099E+06	4.6820E+05	7.5025E+06	7.3817E+06
T_C	K	768.00	647.11	512.70	947.10	850.00	304.16

In Figure 4, liquid, vapor, and supercritical phase densities of CO₂ are plotted as a function of pressure at various temperatures. Both versions of the SAFT EoS show excellent agreement with the data in all three regimes (vapor, liquid, and supercritical). By contrast, RK-ASPEN is accurate in the vapor regimes and at temperatures far above the critical region, which limits its ability to predict gas-expanded liquid (GXL) [65] systems.

Table 6. Binary Interaction Parameters for RK-ASPEN (using VLE or LLE data)

$K_{a,ij}^1$	Glycerol	Water	0.0815	$K_{a,ij}^1$	Glycerol	MEOH	0.0049
$K_{b,ij}^1$	Glycerol	Water	0.1925	$K_{b,ij}^1$	Glycerol	MEOH	0.0380
$K_{a,ij}^1$	Methyl-oleate	Water	-4.8307	$K_{a,ij}^1$	Methyl-oleate	MEOH	-1.3533
$K_{b,ij}^1$	Methyl-oleate	Water	-1.6375	$K_{b,ij}^1$	Methyl-oleate	MEOH	-0.6083
$K_{a,ij}^1$	Water	Methanol	0.1295	$K_{a,ij}^1$	Water	CO ₂	-1.9801
$K_{b,ij}^1$	Water	Methanol	0.3595	$K_{b,ij}^1$	Water	CO ₂	-0.9809
$K_{a,ij}^1$	Methanol	CO ₂	0.2373	$K_{a,ij}^1$	CO ₂	FAME	0.1983
$K_{b,ij}^1$	Methanol	CO ₂	0.0316	$K_{b,ij}^1$	CO ₂	FAME	-0.2123
$K_{a,ij}^1$	CO ₂	Triolein	0.2086	$K_{a,ij}^1$	Methanol	T-OLE	-1.7758
$K_{b,ij}^1$	CO ₂	Triolein	0.1955	$K_{b,ij}^1$	Methanol	T-OLE	-0.7823
$K_{a,ij}^1$	Methyl-oleate	Glycerol	-11.177	$K_{a,ij}^1$	Glycerol	T-OLE	-1.1270
$K_{b,ij}^1$	Methyl-oleate	Glycerol	-8.2022	$K_{b,ij}^1$	Glycerol	T-OLE	-0.7685
$K_{a,ij}^1$	Triolein	Water	97.529				
$K_{b,ij}^1$	Triolein	Water	-11.754

(a) Liquid density

(b) Liquid vapor pressure

Figure 3. Triolein properties

Figure 4. CO₂ densities (see color e-copy to distinguish curves)

5.3. Binary VLE Mixtures

Figures 5-8 show bubble- and dew-point curves for binary mixtures involving the six species in the biodiesel system considered herein. Note that more binary VLE plots are listed in the Supplement (Figures S6-S9). For systems that do not involve CO₂ (Figures S6-S8), the data are in excellent agreement with all three equations-of-state. Note that one of the systems, water and CO₂, was also studied using the soft-SAFT EoS, and a similar level of agreement was obtained [16].

Introducing CO₂ drives the mixtures toward their critical points, which are more difficult to model in the critical region. RK-ASPEN performs well for CO₂ and methanol (Figure 6) because the molecules are small and do not associate. All of the EoSs perform somewhat poorly for triolein and CO₂ around 313 K because of the proximity to the CO₂ critical point and the size-difference of the molecules. At higher temperatures, the EoSs are in much closer agreement with the data. The same effect is seen for FAME and CO₂ around the critical point, although even in this region, gSAFT performs well. Note that the methyl-oleate and CO₂ system was also studied using the soft-SAFT EoS, with a high level of agreement (comparable to that of gSAFT) obtained [16]. For Figure 8c, PC-SAFT yields poor performance, likely due to the high emphasis on liquid phase behavior using weighting factors. While the same weighting factors were used for SAFT- γ Mie for the groups regressed herein, it was less sensitive to the effects of

weighting because certain groups (like CH_3 and CH_2) had already been regressed previously and were not weighted.

Overall, the largest advantage of a SAFT EoS relative to a cubic EoS arises for the long-chain species (triolein and methyl-oleate) in Figures 7 and 8. RK-ASPEN gave comparable performance for small molecules (for example, methanol and water); however, RK-ASPEN fails to accurately model the behavior of long-chain molecules as seen in Figures 7a, c, and 8 (but, not 7b). It should be noted that alpha factors were not used herein to improve RK-ASPEN's behavior, because it was meant to be a benchmark against previous calculations [3, 4, 8].

Figure 5. Methanol and methyl-oleate VLE at 1 atm (see color e-copy to distinguish curves)

5.4. Binary LLE Mixtures

Figures 9-13 display liquid-liquid equilibria for the six species in the biodiesel system. In Section 5.3, all of the data, except for methanol and methyl-oleate, were obtained from the NIST databank or the literature, with numerous datasets for each binary pair. All of the LLE data, except for methyl-oleate and water, were measured by the authors (see Appendix A). Error bars are provided in Figures 9-12 with their width being equal to 1 standard deviation on each side. While a dataset for triolein and methanol existed, it was of questionable accuracy [66]. Overall, as anticipated, the EoSs were less effective in modeling LLE than VLE data.

(a) At 313.14 K (full-scale)

(b) At 313.14 K (expanded vapor region)

(c) At 398.06 K

Figure 6. Methanol and CO₂ VLE (see color e-copy to distinguish curves)

(a) At 313 K (bubble-point curve)

(b) At 333 K (bubble-point curve)

Figure 7. Triolein and CO₂ VLE (see color e-copy to distinguish curves)

(c) At 363 K (bubble-point curve)

Figure 7. Triolein and CO₂ VLE (see color e-copy to distinguish curves) (Cont'd.)

(a) At 313 K

(b) At 333 K

(c) At 343 K

Figure 8. Methyl-oleate and CO₂ VLE (see color e-copy to distinguish curves)

For methyl-oleate and water (Figure 13), the two available datasets differed by an order of magnitude [13, 67]. The former is displayed because all three EoSs provided reasonable agreement. However, there were only three datapoints, and the EoS estimates did not fully agree with the data. Thus, these methyl-oleate and water LLE systems should be investigated more thoroughly in future studies.

Reasonable agreement with the triolein and water LLE data (Figure 10) were obtained by both SAFT equations. RK-ASPEN failed to yield LLE predictions at these conditions. Similarly, in Figure 9, both SAFT equations provide much better agreement with the triolein-methanol LLE data.

The systems involving glycerol (Figures 11 and 12) were the most challenging to sample. It was difficult to determine when the phases had reached their equilibrium separation. As a result, the datasets exhibited large standard deviations for some points. Measurements for triolein in the glycerol bulk phase were particularly difficult, leading to only one useable datapoint at many temperatures. Note that although the error bars appear small in Figures 11 and 12, the x-axes (concentrations) are on a log-scale. See Appendix A for tabulated data. For these glycerol systems, PC-SAFT provides the best agreement with the data (as with the other LLE data), but surprisingly, all three EoSs (without binary interaction parameters) provide better estimates for the apolar bulk phases (a in both Figures 11 and 12). It was not possible to confirm this observation for the triolein - methanol or triolein-water systems (Figures 9 and 10) as the apolar phase could not be sampled.

Figure 9. Triolein in the methanol phase (LLE at 1 atm)

Figure 10. Triolein in the water phase (LLE at 1 atm)

(a) Glycerol in the triolein phase

(b) Triolein in the glycerol phase

Figure 11. Glycerol and triolein LLE at 1 atm. (note that the two gSAFT curves overlap in (b), and it is difficult to distinguish them - see color e-copy to distinguish curves)

5.5. Ternary LLE Mixtures

LLE data and model predictions for water, methanol, and methyl-oleate at 318.2 K and 1 atm are shown in Figure 14. For RK-ASPEN, significant deviations occur at high water concentrations in the aqueous phase, because RK-ASPEN doesn't accurately represent strongly associating mixtures. Good agreement is obtained by both SAFT EoSs, especially for regions of high water concentrations. PC-SAFT slightly under-predicts the solubility of methanol and

methyl-oleate at high concentrations of both, while gSAFT over-predicts their solubility. However, the latter does a much better job of predicting the shape of the phase boundary curve.

(a) Glycerol in the methyl-oleate phase

(b) Methyl-oleate in the glycerol phase

Figure 12. Glycerol and methyl-oleate LLE at 1 atm (see color e-copy to distinguish curves).

(a) Methyl-oleate in the water phase

(b) Methyl-oleate in the water phase

Figure 13 Methyl-oleate and water LLE at 1 atm.

For glycerol, methanol, and methyl-oleate at 333 K and 1 atm (Figure 15) poor agreement is achieved with RK-ASPEN, again because of its difficulty in representing associating systems. Good agreement is achieved with PC-SAFT, but not with gSAFT. The poor predictions shown for gSAFT could be due to either over-regression of parameters, because glycerol has two different associating sites (primary and secondary alcohol groups), for which separate parameters were regressed — as opposed to PC-SAFT, where the two standard associating parameters were regressed for the entire molecule. The inaccuracy shown for gSAFT could also result from the fact that methyl-oleate was represented using an assembly of groups, instead of unique parameters for the complete molecule, as was done for PC-SAFT. Between these two explanations, the first is more likely, as it explains the disparity in performance by gSAFT between Figures 14 and 15 - suggesting future attempts use fewer parameters. Note that the PC-SAFT binary interaction parameters for glycerol and methyl-oleate were not used because they detract from the model performance when the glycerol, methyl-oleate, and methanol are present [63, 67].

These two ternary mixtures are typical of the effluent streams from the biodiesel reactor. Clearly, PC-SAFT should yield the best predictions for liquid-liquid phase distributions in the reactor effluent and product separation and purification units of a biodiesel process. Although, in further investigations, the regression of group parameters in gSAFT needs to be examined more closely.

5.6. Ternary Inlet Mixtures

Figure 16 examines the phase distributions of triolein, methanol, and CO₂ mixtures at various pressures and compositions typical of the inlet conditions for a biodiesel reactor using CO₂ to increase conversion rates [5, 68]. Only the triolein mole fraction is shown. The mole fractions of methanol and CO₂ are based on the triolein mole fraction with the triolein:methanol molar ratio fixed at 1:4,032. As shown in the legend, each symbol represents a different phase distribution at equilibrium, where dashes (V) represent a vapor (or supercritical) phase, triangles (L) a liquid (or supercritical) phase, stars (VLE) vapor and liquid phases at equilibrium, diamonds (LLE) two liquid phases at equilibrium, and circles (VLLE) vapor-liquid-liquid equilibria. Open spaces arise when the *Gibbs flash method* in ASPEN PLUS (see footnote 1) algorithm did not converge. Note that a supercritical phase can be classified as either a vapor or

liquid by the equilibrium algorithm, and therefore, for example, the transition from vapor to liquid at elevated pressures in Figure 16 (c and d) is not physically realistic.

(a) Predicted with RK-ASPEN

(b) Predicted with PC-SAFT

(c) Predicted with SAFT- γ Mie (gSAFT)

Figure 14. LLE for water, methanol, and methyl-oleate at 318.2 K and 1 atm (see color e-copy images to distinguish the data and curves).

Figure 15. LLE for glycerol, methanol, and methyl-oleate at 333 K and 1 atm (see color e-copy images to distinguish the data and curves).

The lines, which represent approximate phase boundaries, connect experimental phase transition datapoints [5]; that is, orange circles (showing a transition from supercritical phase to VLE) and purple crosses (showing a transition from VLE to VLLE). Unfortunately, as can be seen in the five sub-figures, none of the EoSs accurately predict all three of these regions.

RK-ASPEN with no binary interaction parameters (Figure 16(a)) is most effective in predicting the VLLE region, but the *Gibbs flash method* fails to converge in much of the VLE or supercritical regions. RK-ASPEN with binary interaction parameters (Figure 16(b)) is more robust in terms of convergence, and correctly represents most of the supercritical region and the VLE region, but fails to predict any VLLE behavior.

gSAFT (Figure 16(e)) predicts the supercritical region and the VLE region, as well as their transition, almost perfectly. However, like RK-ASPEN with binary interaction parameters, it fails to predict any VLLE behavior, because it does not predict a liquid-liquid split between methanol and triolein at these conditions (as opposed to those in Figure 9). The poor predictions in the VLLE region are likely due to two factors: (1) the weighting factors for the liquid density [200] and vapor pressure [1] used during the regressions herein (Section 4) were not applied to groups that had been regressed in prior studies (CH_3 and CH_2 , which are crucial for triolein and methyl-oleate property estimation); (2) the group contribution method is not as accurate as regressing parameters for individual molecules. Thus future studies should regress “groups” that are equivalent to triolein and methyl-oleate, and ranges of weighting factors should be adjusted to compare the estimates of PC-SAFT and gSAFT. If gSAFT were shown to be more accurate using “molecular” groups, which is likely given the binary systems diagrams in Sections 5.2 and 5.3, the molecules could be dissected into various groups, with the objective of increasing flexibility without significantly decreasing accuracy.

PC-SAFT with no binary interaction parameters (Figure 16(c)) accurately predicts the supercritical region and much of the VLLE region, but fails to predict any part of the VLE region. PC-SAFT with binary interaction parameters clearly improves predictions in the VLE region, but only at low triolein mole fractions, as shown in Figure 16(d). The supercritical region is predicted as a liquid phase, and the transition from VLE to VLLE is predicted properly – but VLE is predicted in a significant portion of the VLLE region. After adjusting convergence tolerances and flash algorithms, but obtaining the same incorrect phase distributions, phase stability checks were implemented for PC-SAFT with binary interaction parameters

To check phase stability, the tangent-plane-distance criteria [42, 43], as discussed in Section 2, was implemented, using the FORTRAN code provided by Prof. Romain Privat (Webpage: Prof. Romain Privat's Homepage). When using PC-SAFT with binary interaction parameters (Figure 16(d)), the Privat code showed that the liquid phase in the VLE predictions (in the intermediate portion of the VLLE region) is unstable, as shown in the lower enclosed region of Figure 17. Similarly, it showed that the liquid phases predicted for high triolein concentrations in the VLE region are unstable. Note, however, that negative tangent-plane distances were observed at higher triolein mole fractions in the supercritical region, indicating that a second phase at equilibrium is incorrectly predicted by PC-SAFT with interaction parameters.

Additional code was not written to reinitialize the flash calculations with improved guesses for the phases at equilibrium – primarily because the effect of the phase distribution on the rate of the transesterification reaction(s) in the VLLE region is demonstrated sufficiently well, next in Section 6. However, improvements in the ASPEN PLUS flash algorithms (RGIBBS and FLASH3) in the critical region would allow higher fidelity EoSs (like PC-SAFT) to be used more effectively for these mixtures – thus yielding more accurate predictions for reactor conversions.

Note that phase stability was not examined for gSAFT – as Process Systems Enterprise (PSE), creator of gSAFT, performs tangent-plane distance phase-stability checks.

6. Kinetics and Reactor Design

For the transesterification reaction involving triolein, methanol, and CO₂, overall composition data were measured dynamically at various catalyst loadings, using a Nafion solid-acid catalyst in both bead and powder form at 95°C and 9.65 MPa [68]. These data include triolein, diolein, monoolein, and methyl-oleate concentrations. Glycerol, methanol, and CO₂ concentrations at each time were calculated using initial substrate loadings and mole balances. Because phase equilibrium data involving diolein and monoolein were unavailable, the simplified reaction:

(a) RK-ASPEN (no binary interaction parameters)

(b) RK-ASPEN (with binary interaction parameters)

(c) PC-SAFT (no binary interaction parameters)

(d) PC-SAFT (with binary interaction parameters)

(e) SAFT- γ Mie (gSAFT)

Figure 16. Triolein, methanol, and CO₂ phase equilibria at 353.15 K.

Figure 17. Tangent-plane-distance regions of stability and instability (PC-SAFT with binary parameters at 353.15 K). The unstable regions are enclosed in two polygons.

was used in place of the kinetic mechanism in Figure 1. The mechanism is formulated in terms of the triglyceride-branch species, TG_{branch} , where three moles of TG_{branch} are equivalent to a mole of triolein, two moles of TG_{branch} and one-third of a mole of glycerol is equivalent to a mole of diolein, and one mole of TG_{branch} and two-thirds of a mole of glycerol is equivalent to a mole of monoolein.

This reaction mechanism was translated into the intrinsic reaction-rate:

$$rxn = k_f [cat]^{n_f} [TG_{branch}] [methanol] - k_r [cat]^{n_{rev}} [methyl_oleate] [glycerol]^{\frac{1}{3}} \quad (46)$$

with the ODE mass balances:

$$\frac{d[C_i]}{dt} = \nu_{R1,i} * rxn \quad (47)$$

where k_f is the forward rate constant, k_r is the reverse rate constant, $[cat]$ is the catalyst concentration, n_f is the exponent of the catalyst concentration in the forward direction, n_{rev} is the exponent of the catalyst concentration in the reverse direction, $[C_i]$ is the concentration of species i , and $\nu_{R1,i}$ is the stoichiometric coefficient of species i in reaction R1.

Initially, k_f , k_r , n_f , and n_{rev} were regressed using the bulk concentrations in the experimental 50 mL, agitated reactor vessel [68]. An explicit Euler integration was used in MS

Excel with a time-step of 18 seconds. The sum-of-the-square differences between the concentration data and the integrated concentrations for triolein, methanol, and methyl-oleate (for the entire stirred tank) were incorporated into a relative, weighted least-squares objective function, which weighted the concentration differences more heavily as reaction time increased [1]. Note that triolein, methanol, and methyl-oleate concentrations were weighted equally. Also, glycerol concentrations were not included in the objective function because the calculated moles of glycerol were substantially larger than experimental values – with each mole of diolein replaced by two moles TG_{branch} and two-thirds mol glycerol and each mole of monoolein replaced by one mole TG_{branch} and one-third mol glycerol.

The minimization of the objective function yielded the kinetic constants in column 2 of Table 7. These constants served as initial guesses in a custom-written FORTRAN subroutine in ASPEN PLUS that incorporates the effect of the phase behavior on the reaction kinetics using the algorithm in Figure 18.

Figure 18. Multiphase-kinetic reactor algorithm created for ASPEN PLUS.

As with the MS Excel model, experimental data for eight loadings, over a 4-hour reaction time, were used. The reaction temperature was maintained at 95°C. The total vessel volume was the sum of the three “phase” batch reactors, and was calculated every 10 time-steps (18 seconds per time-step) along with the phase equilibria. The phase volumes remained nearly constant during the 4-hour reaction, with the vapor phase (methanol and CO₂) taking about two-thirds of the vessel volume. The aqueous liquid (methanol and glycerol) accounted for most of the remaining third, with the apolar liquid (triolein, methyl oleate, with some methanol) never exceeding 0.25% of the total volume. The change in vessel volume throughout the reaction was less than 1%, with no volume adjustments implemented.

Because RK-ASPEN with no binary interaction parameters (Figure 16a) is the only thermodynamics package to predict VLLE at the reactor conditions (95°C and 9.65 MPa), it was used to determine the four kinetic constants in column 3 of Table 7 – again using a relative, weighted least-squares regression. The concentration profiles for triolein, methanol, and methyl-oleate are shown in Figure 19, and the reaction rate profiles are shown in Figure 20. Note that the CO₂ concentration profiles in each phase do not change appreciably. CO₂ accounts for roughly 92.5 mol% in the vapor phase, 61.7 mol% in the apolar liquid phase, and 43.7 mol% in the aqueous liquid phase. Overall, 63.3% of the total CO₂ moles are in the vapor phase, 0.57% in the apolar liquid phase, and 36.11% in the aqueous liquid phase.

Table 7. Kinetic Parameters

Constant	MS Excel	ASPEN PLUS	Units
k_f	0.063	0.104	(m ³) ² /(kmol ² s)
k_r	0.006	0.114	(m ³) ² /(kmol ² s)
n_f	1.253	1.269	-
n_{rev}	0.700	0.700	-

Liquid 1 is the triolein (apolar liquid) phase and liquid 2 is the aqueous phase. Note that methanol distributes between the two phases, due to CO₂ increasing its solubility in the apolar phase. The forward reaction occurs almost exclusively in the apolar liquid phase. The vapor phase has a negligible reaction rate because of triolein’s low vapor pressure. The reverse reaction occurs in the second liquid, because essentially all produced glycerol moves to the

aqueous phase and there is negligible triolein present to drive the forward reaction. Note that the system is predicted to remain in the 3-phase region throughout the course of the reaction.

(a) TG_{branch} concentration profiles

(b) Methanol concentration profiles

(c) Methyl-oleate concentration profiles

Figure 19. Concentrations with time (see color e-copy to distinguish curves)

Figure 20. Reaction rates (see color e-copy to distinguish curves)

Although conversions are comparable when using the same kinetic constants, the reaction proceeds slower in this 3-phase model than in the 1-phase model in MS Excel, with 77.3% of triolein converted compared to 81.6%), which does not agree with the experimental data [5]. This is likely because RK-ASPEN under-predicts the solubility of methanol in the triolein phase. The high solubility also explains why the *Gibbs flash method* predicts only one liquid phase, because it has difficulty distinguishing between two phases with high mutual solubility. Clearly, more robust phase equilibria algorithms, which check the phase stability, are needed to analyze this system.

7. Conclusions

Biodiesel production, using supercritical fluids, has gained interest in the last several years [5-7]. Numerous attempts have been made to model this system, but almost all previous studies used cubic equations-of-state [3, 4, 8-15]. It should be noted herein that the cubic plus EoS is more advanced than RK-ASPEN, and in future studies it would be instructive to compare the SAFT equations to this EoS [9-15]. Another study has also examined several binary systems (including CO₂ and water, and CO₂ and FAME) using the soft-SAFT EoS [16]. This work, however, was the first to examine a complete biodiesel system with two versions of SAFT. Herein, PC-SAFT in ASPEN PLUS and SAFT- γ Mie (gSAFT) in gPROMS were compared to RK-ASPEN in ASPEN PLUS for pure-species, binary, and ternary systems.

A simplified biodiesel system using six species (triolein, methanol, carbon dioxide, methyl-oleate, glycerol, and water) has been studied. For the pure species, all three equations matched the liquid vapor-pressure data, but only the SAFT EoSs correctly predicted the liquid densities. PC-SAFT's VLE predictions were poorer on average than those of gSAFT and RK-ASPEN, but it provided the best agreement with LLE data. PC-SAFT gave good predictions for the ternary LLE systems, and for portions of the triolein, methanol, carbon dioxide mixture phase map, but ultimately none of the EoSs studied herein gave accurate predictions for the triolein, methanol, and CO₂ mixtures. For PC-SAFT, this shortcoming was attributed to phase instability. Whereas, for gSAFT, the poor predictions in the VLLE region are likely to be a combination of improper weighting factors in regression of parameters from experimental data and the lower accuracy of using a group-contribution methodology. However, the SAFT EoSs are clearly more robust than RK-ASPEN, and given Figure 16(d) and the unstable phase distributions in the two

polygons in Figure 17, it is likely that PC-SAFT can correctly representing the phase distribution for this system. In future work, a single-group molecule approach should be used in gSAFT to determine the full extent of its predictive capabilities, as it incorporates a more robust phase equilibria algorithm than ASPEN PLUS; that is, gSAFT checks the phase stability after convergence of flash calculations.

RK-ASPEN (with no binary parameters) gave reasonable agreement with experimental results in the VLLE region, and thus, was used in the thermo-kinetic reactor model. The model showed comparable conversions in the VLLE and supercritical regions. This is economically promising, suggesting that the much lower pressure VLLE systems can achieve high conversions. As newer flash algorithms are introduced in ASPEN PLUS and the parameter databank in gSAFT becomes more refined, it will become possible to model these reactions and the accompanying separations with greater accuracy, eventually allowing an extraction-transesterification process to be synthesized, optimized, and economically evaluated.

8. Nomenclature

<u>Variables and Parameters</u>	<u>Meaning</u>	<u>Units</u>
$[C]$	Concentration	kmol/m^3
$[cat]$	Catalyst concentration	kmol/m^3
$[glycerol]$	Concentration of glycerol	kmol/m^3
$[methanol]$	Concentration of methnaol	kmol/m^3
$[methyl-oleate]$	Concentration of methyl-oleate	kmol/m^3
$[TG_{\text{branch}}]$	Concentration of TG_{branch}	kmol/m^3
a	EoS parameter	-
A	Helmholtz free energy	J
b	EoS parameter	-
c	EoS parameter	-
d	EoS parameter	-
D	Collision diameter	m
e	EoS parameter	-
F	Tangent-plane-distance function	J

f	Fugacity	Pa
G	Gibbs free energy	J
K	Binary interaction parameter	-
k	Rate constant	$(\text{m}^3)^2/(\text{kmol}^2\text{-s})$
k_B	Boltzmann's constant	J/molecule-K
m	Segment length	-
M	No. of association sites on each molecule	-
N	Number of molecules	molecules
n	Exponent	-
NC	Number of chemical species	-
NG	Number of groups	-
ng	Number of groups in a molecule	-
nsg	Number of sites on a group	-
NST	Number of sites	-
P	Pressure	Pa
R	Universal gas constant	J/mol-K
r	Radial distance between segments	m
rxn	Intrinsic reaction rate	$\text{kmol}/\text{m}^3\text{-s}$
S	Empirical square-well parameter	m
s	Shape parameter	-
T	Temperature	K
t	Time	s
u	Square-well potential energy	J
V	Volume	m^3
W	Non-normalized mole fraction	-
x	Mole fraction	-
X	Association mole fraction	-
y	Mole fraction	-
Y	Moles	mol
z	Mole fraction	-

Z	Moles	mol
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<u>Greek Symbols</u>	<u>Meaning</u>	<u>Units</u>
α	Temperature fitting parameter	-
γ	Accentricity fitting parameter	-
Γ	Objective function	-
ε	Energy of the square-well interaction	J
ζ	Reduced density	-
η	Extra polar parameter	-
κ	Association bonding volume	m ³
λ	Range of the interaction	m
μ	Chemical potential	J/mol
ν	Stoichiometric coefficient	-
ρ	Number density	Molecules/m ³
σ	Segment diameter	m
ϕ	Fugacity coefficient	-
Φ	Objective function	-
ω	Accentric factor	-
Ω	Minimum interaction parameter	-

<u>Subscript</u>	<u>Meaning</u>
1	Order of perturbation term
2	Order of perturbation term
a	Relating to parameter a
A	Association
at	Attractive
b	Relating to parameter b
B	Association
c	Critical
f	Forward
m	Mixing

n	Power of the collision diameter
r	Reduced
R	Repulsive
R1	Relating to reaction R1
ref	Reference
rev	Reverse

Superscript

Meaning

0	Binary interaction coefficient order
1	Binary interaction coefficient order
A	Associating group
assoc	Association contribution
B	Associating group
chain	Chain contribution
disp	Dispersion contribution
HB	Associating
hc	Hard-chain contribution
ig	Ideal-gas contribution
mono	Monomer contribution
polar	Polar contribution
T	Tangent

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Appendix A. Experimental Data

The data measured according to the methods described in Section 3 are listed in Tables A.1-A.5. Table A.1 provides the only vapor-liquid equilibrium dataset. All others provide liquid-liquid equilibria. For the LLE datasets, each temperature was measured twice; however, some experiments resulted in physically impossible concentrations. A dash is used to denote this in the tables. Finally, for the methanol and triolein (Table A.2) and water and triolein (Table A.5) LLE datasets, only one of the liquid phases could be sampled. The data in all tables is accurate to three significant figures.

Table A.1. Methanol and Methyl-oleate VLE (mole fractions)

T(K)	x , Methanol	x , Methyl-oleate	y , Methanol	y , Methyl-oleate
342.25	0.672	0.328	1.000	0.000291
346.95	0.484	0.516	1.000	0.000271
356.75	0.346	0.654	0.999	0.00141
362.65	0.239	0.761	0.999	0.000840
372.85	0.145	0.855	0.999	0.000955
384.15	0.104	0.896	0.998	0.00153
394.65	0.0759	0.924	0.998	0.00218
414.85	0.0528	0.947	0.997	0.00284
435.15	0.0552	0.945	0.996	0.00362

Table A.2. Methanol and Triolein LLE (mole fractions)

T(K)	x_1 , Methanol	x_1 , Triolein
303.15	1.000	0.0000758
303.15	1.000	0.0000877
303.15	1.000	0.0000879
308.15	1.000	0.000110
308.15	1.000	0.000147
308.15	1.000	0.000148
313.15	1.000	0.000082
313.15	1.000	0.000128
318.15	1.000	0.000118
318.15	1.000	0.000120
318.15	1.000	0.000140
313.15	1.000	0.000305

328.15	1.000	0.000168
328.15	1.000	0.000259
333.15	1.000	0.000173
333.15	1.000	0.000207

Table A.3. Glycerol and Methyl-oleate LLE (mole fractions)

Temperature (K)	x_1 , Glycerol	x_1 , Methyl-oleate	x_2 , Glycerol	x_2 , Methyl-oleate
323.15	0.00231	0.998	-	-
323.15	0.00389	0.996	0.989	0.0111
333.15	0.00317	0.997	0.992	0.00811
333.15	0.00309	0.997	0.997	0.00318
343.15	0.00513	0.995	0.999	0.00140
343.15	0.00419	0.996	0.999	0.00122
353.15	0.00510	0.995	0.996	0.00376
353.15	0.00542	0.995	0.992	0.00792
363.15	0.00627	0.994	0.998	0.00207
363.15	0.00690	0.993	0.984	0.0161
373.15	0.00993	0.990	0.995	0.00470
373.15	0.00906	0.991	0.956	0.0445
383.15	0.0121	0.988	1.000	0.000208
383.15	0.0128	0.987	0.997	0.00272

Table A.4. Glycerol and Triolein LLE (mole fractions)

Temperature (K)	x_1 , Triolein	x_1 , Glycerol	x_2 , Triolein	x_2 , Glycerol
323.15	0.000371	1.000	-	-
323.15	0.000421	1.000	0.997	0.00306
333.15	0.0252	0.975	0.995	0.00499
333.15	-	-	0.995	0.00453
343.15	0.00255	0.997	0.993	0.00716
343.15	0.0134	0.987	0.994	0.00559
353.15	0.00459	0.995	0.993	0.00713
353.15	-	-	0.994	0.00562
363.15	0.00224	0.998	0.993	0.00719
363.15	-	-	0.993	0.00688
383.15	0.000820	0.999	0.981	0.0191
383.15	0.000767	0.999	0.975	0.0254

Table A.5. Water and Triolein LLE (mole fractions)

Temperature (K)	x_1 , Triolein	x_1 , Water
323.15	1.87E-04	1.000
333.15	3.96E-05	1.000
333.15	8.99E-06	1.000
333.15	2.33E-04	1.000
341.15	1.83E-05	1.000
341.15	6.17E-06	1.000
341.15	1.10E-05	1.000
348.15	2.00E-05	1.000
348.15	5.78E-05	1.000
348.15	3.48E-06	1.000
355.15	1.85E-05	1.000
355.15	7.50E-06	1.000
355.15	2.01E-05	1.000
363.15	1.76E-05	1.000
363.15	7.00E-06	1.000

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