

## Modeling of Phase and Chemical Equilibria for Systems Involved in Biodiesel Production

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In recent years, the interest in the use of renewable energy has encouraged the growth of studies into renewable sources, such as the production of biofuels. This work investigates the vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE) of binary, ternary, quaternary and pseudo-quaternary systems using an optimization approach for components found in biodiesel production, which consists in vegetable oils, fatty acids, esters and alcohols. A methodology has been developed based on the Gibbs energy minimization and the discretization of the molar fraction domain, which incorporates a thermodynamic model to describe the phase equilibria. This work used the Soave-Redlich-Kwong equation of state (SRK-EOS) for phase equilibria calculation, where the compressibility factor was used to determine the phase present in the system (liquid, vapor or supercritical fluid). The chemical and phase equilibrium problem is solved using linear programming and satisfies the mass balance constraints. It was found that the proposed methodology adequately represents the selected experimental data, with an average absolute deviation of 1.31 % obtained.

### 1. Introduction

The most used energy sources worldwide are still non-renewable, such as oil, coal and natural gas. Factors such as environmental problems encourage the growth of studies in renewable sources such as biofuels. In large development, biodiesel has the main advantages: 1) It is biodegradable and non-toxic; 2) It contributes to the reduction of greenhouse gases, emissions of particulate matter and acid rain. The biodiesel production involves a number of processing steps that require knowledge of chemical or phase equilibrium.

When a system is in equilibrium, the Gibbs energy has a minimum value for a given pressure and temperature. The calculation of the correct number of phases in equilibrium and its composition can be divided in two mainly categories: through the equation-solving approach for searching same fugacity or chemical potential in all the present phases in equilibrium, or through the direct minimization of the Gibbs energy (Teh and Rangaiah, 2002). The first approach solves the necessary conditions to guarantee chemical equilibrium, but only one solution minimizes the Gibbs energy and satisfies the second law of thermodynamics. Considering the minimization of Gibbs energy, a common problem observed is the convergence in a global solution and a good estimate of the composition as a starting point is required.

This work presents a linear program model formulation for phase and chemical equilibria calculation in quaternary and pseudo-quaternary systems, based on a discretization of the molar fraction domain. The proposed approach can be applied to any thermodynamic model such as equations of state or excess Gibbs energy models. However, in this work, the equation of state of Soave-Redlich-Kwong (SRK-EOS) with the mixing rule of van der Waals two adjustable parameters (VDW-2) was employed. The use of this equation of state allows the calculation of both vapor-liquid equilibrium in elevated conditions of pressure and temperature, vapor-liquid in lower conditions of pressure and temperature, and liquid-liquid equilibrium. In the second part of this work, the performance of the proposed method in predicting phase and chemical

equilibrium was analyzed for eight types of vegetable oils (cotton, peanut, canola, coconut, sunflower, corn, palm and soybean) and their respective methyl and ethyl esters.

## 2. Methodology

### 2.1 Thermodynamic Equilibrium

The chemical and phase equilibria, in a multiphase and multicomponent closed system, at constant pressure and temperature, can be calculated by the minimization of the Gibbs energy in terms of fugacity:

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_i^k \cdot \left[ \mu_i^\circ + R \cdot T \cdot \ln \frac{\hat{f}_i^k}{f_i^\circ} \right] \quad (1)$$

where  $n_i^k$  is the number of moles of each component  $i$  at each phase  $k$ ,  $NC$  is the number of compounds and  $NP$  is the number of phases. In this work, the SRK equation of state was considered to represent both vapor and liquid phases.

The minimization of the Gibbs energy must satisfy some constraints:

- the number of moles cannot be negative, for any component in any phase:

$$n_i^k \geq 0 \quad \text{for } i = 1, 2, \dots, NC \text{ and } k = 1, 2, \dots, NP \quad (2)$$

- the molar balance for each component in the system:

$$\sum_{k=1}^{NP} n_i^k = n_i^0 - \nu_i \cdot \xi \quad \text{for } i = 1, 2, \dots, NC \quad (3)$$

where  $\nu_i$  is the stoichiometric coefficient of each compound  $i$  in the reaction and  $\xi$  is the extent of the reaction. If some compound does not react, then  $\nu_i$  is zero.

### 2.2 Discretization of the molar fraction domain

The problem of minimizing the Gibbs energy was formulated as a linear programming model through a discretization of the molar fraction domain, as seen in Rossi et al. (2009). However, in this work the methodology was extended to consider quaternary systems. The system is considered to have a potential number of phases, each one with molar fractions given by:

$$z_1 = 1 - \delta \cdot (p_1 - 1) \quad \text{for } p_1 = 1, 2, \dots, N + 1 \quad (4)$$

$$z_2 = 1 - z_1 - \delta \cdot (p_2 - 1) \quad \text{for } p_2 = 1, 2, \dots, p_1 \quad (5)$$

$$z_3 = 1 - z_1 - z_2 - \delta \cdot (p_3 - 1) \quad \text{for } p_3 = 1, 2, \dots, p_2 \quad (6)$$

$$z_4 = 1 - z_1 - z_2 - z_3 \quad (7)$$

where  $\delta$  is  $1/N$ . At each point in the molar fraction domain, all roots of the SRK equation of state are calculated and for each possible real root a potential phase is assigned. In this way, discontinuities are considered, since for the same molar fraction it may exist a liquid or a vapour phase.

### 2.3 Differentiation of the phases

The differentiation of the phases present in the system was performed considering the root of the cubic equation. When the cubic equation has three real roots, more than one phase is present in the system. These roots were dealing with the compressibility factors calculated by the algorithm. For SRK-EOS, the compressibility factors are calculated as:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (8)$$

where:

$$A = \frac{a_m P}{(RT)^2}, \quad B = \frac{b_m P}{RT} \quad (9)$$

The smallest root represents the liquid phase in the case of vapor-liquid equilibrium (VLE) systems. For liquid-liquid equilibrium (LLE) systems, the values of the molar fractions should be observed to differentiate the liquid phases. In the cases where the equation does not have three real roots, but just one, the isothermal

compressibility was considered to define if the phase is liquid or vapour. The SRK-EOS equation has the following isothermal compressibility coefficient:

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{V(V^2 - b^2)^2}{RTV^2(V+b)^2 - a(2V+b)(V+b)^2/\sqrt{T}} \quad (10)$$

For pressures close to atmospheric, the Poling et al. (1981) criterion for the phase definition is:

$$\beta < 0.005 / \text{atm}, \quad \text{indicates liquid phase} \quad (11)$$

$$0.9 / P < \beta < 3.0 / P, \quad \text{indicates vapor phase} \quad (12)$$

To identify whether the phase lies in the critical region, mixing rule were used for critical properties of the mixture (temperature and pressure). If the temperature and pressure of the chosen system are above of the critical values calculated, the result indicates a supercritical fluid.

### 3. Results and Discussion

Not all physical properties of fatty acids, esters, oils and biodiesel are available in the literature. However, it is possible to use predictive methods such as group contribution methods to estimate these properties. A detailed discussion of the analysis of the estimation of the properties can be seen in our previous work (Cunico et al., 2013). The values used for the compounds utilized in this work can be seen in Table 1.

Table 1: Pure component properties considered in the phase equilibrium calculations.

Component	$T_c$ (K)	$P_c$ (KPa)	$V_c$ (cm <sup>3</sup> /mol)	$\omega$	$\Delta_f H^0$ (J/mol)	$\Delta_f G^0$ (J/mol-)	$cp^0$ (J/mol.K) at 298 K
Triolein	977.88 <sup>a</sup>	334 <sup>a</sup>	3,250	1.978	-44,0727	-411,807	304.87
Methanol	512.60 <sup>a</sup>	8,090 <sup>a</sup>	117 <sup>a</sup>	0.566 <sup>a</sup>	-200,940 <sup>a</sup>	-162,320 <sup>a</sup>	43.99 <sup>a</sup>
Glycerol	850.00 <sup>a</sup>	7,500 <sup>a</sup>	264 <sup>a</sup>	0.513 <sup>a</sup>	-138,121 <sup>a</sup>	-106,859 <sup>a</sup>	115.28 <sup>a</sup>
Methyl oleate	764.00 <sup>a</sup>	1,280 <sup>a</sup>	1,060 <sup>a</sup>	1.049 <sup>a</sup>	-626,000 <sup>a</sup>	-170,900 <sup>a</sup>	442.64 <sup>a</sup>
Methyl laurate	708.91	1,746	784	0.718	-643,620	-254,967	324.76
Methyl myristate	735.98	1,561	897	0.790	-685,278	-238,839	373.22
Methyl linoleate	788.88	1,329	1,094	0.940	-543,052	-65,030	418.68
Ethyl laurate	734.90	1,648	840.55	0.754	-664,449	-24,6903	349.15
Ethanol	514.00 <sup>a</sup>	6,137 <sup>a</sup>	168.00 <sup>a</sup>	0.644 <sup>a</sup>	-159,860 <sup>a</sup>	-17,3860 <sup>a</sup>	65.00 <sup>a</sup>
Ethyl myristate	759.85	1,485	953.11	0.825	-706,107	-23,0775	397.61
Oleic acid	781.00 <sup>a</sup>	1,390 <sup>a</sup>	1,000.00 <sup>a</sup>	1.182 <sup>a</sup>	-762,120 <sup>a</sup>	-26,100 <sup>a</sup>	417.63 <sup>a</sup>
Hexane	507.60 <sup>a</sup>	3,025 <sup>a</sup>	371 <sup>a</sup>	0.301 <sup>a</sup>	-166,940 <sup>a</sup>	-415,400 <sup>a</sup>	141.79 <sup>a</sup>
Water	647.13 <sup>a</sup>	22,055 <sup>a</sup>	55.9 <sup>a</sup>	0.345 <sup>a</sup>	-241,810 <sup>a</sup>	-237,210 <sup>a</sup>	33.58 <sup>a</sup>

<sup>a</sup>Experimental values from DIADEM (2000) and NIST (in: <http://webbook.nist.gov>, 2010).

The results of the proposed methodology and the compounds present in biodiesel production were compared with experimental data found in literature considering the average absolute deviation - AAD (%):

$$AAD (\%) = 100 \cdot \sum_{k=1}^{NP} \sum_{i=1}^{NC} \frac{|x_{ik}^{lit} - x_{ik}^{work}|}{NP \cdot NC} \quad (13)$$

where  $x_{ik}^{lit}$  refers to the value of the molar fraction found in the literature and  $x_{ik}^{work}$  this work.

The problem of minimizing the Gibbs energy, subject to the restrictions of molar balances and non negativity of mol number, was solved using the software GAMS® 23.1.3 (General Algebraic System Model) with CPLEX as solver. The CPU time was low (maximum 6.68 seconds - Pentium III, 512MB, 900MHz, OS UNIX, parallel run). For binary and ternary systems,  $\delta$  was set to 0.002, and for quaternary systems it was set to 0.02.

### 3.1 Case Studies - Phase Equilibrium

Phase equilibrium data sets available in literature were chosen to analyze the proposed methodology. Representative binary and ternary experimental data of phase equilibrium for systems containing components present in biodiesel production were selected to validate the methodology. For quaternary systems, Tizvar et al. (2008) work was considered for compounds used in the process of purification of the biodiesel, where water is commonly used in the wash step of the biodiesel. The work of Felice et al. (2008) was considered for compounds combined with an organic solvent, as hexane. Figure 1 brings an example of the model representation of binary system considering the proposed methodology, while the difference observed for the phase calculations by the methodology can be seen in Figure 2 for ternary systems.

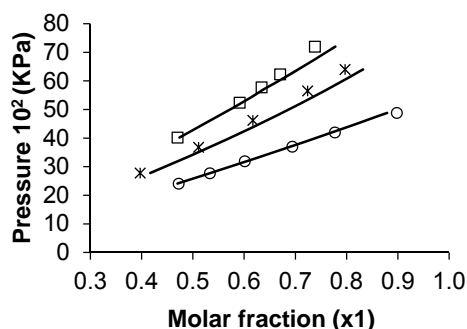


Figure 1. VLE of binary system: methyl myristate (1) and methanol (2). Experimental data (Shimoyama et al., 2007):  $\circ$   $T=493\text{K}$ ,  $*$   $T=523\text{K}$  and  $\square$   $T=543\text{K}$ , — Calculated: SRK-EOS,

The approach considering SRK-EOS equation of state showed good agreement with experimental data. The absolute average deviation (% mole fraction) does not exceed 2.2 % and is less than 1 % for some of the systems. Good representation of experimental data was also obtained for VLE and binary system. Both isothermal and isobaric data could be fitted considering the proposed methodology. It was observed better representation by the methodology for the glycerol phase data in comparison with the same methodology for the biodiesel phase, which can be explained by the difficulty of some models in representing systems containing major carbonic chains components. Note that some of the systems had the pure component properties, such as critical temperature ( $T_c$ ), estimated by group contribution method. In those systems, there was a higher deviation in the phase equilibrium data representation.

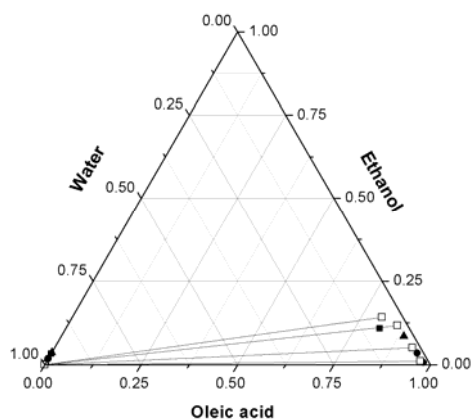


Figure 2: LLE of ternary system: Oleic acid, ethanol and water. Experimental data (Zhang and Hill, 1991):  $\bullet$   $T=293.15\text{K}$ ,  $\blacktriangle$   $T=303.15\text{K}$  and  $\blacksquare$   $T=333.15\text{K}$ ,  $\square$  Calculated using SRK-EOS

For some of the systems where the values of the binary parameter ( $k_{ij}$ ) were not available in literature, the relationship of Chueh and Prausnitz (1967) was considered. The average absolute deviation and computational time in seconds (s) for the proposed methodology and quaternary systems can be seen in Table 2.

Table 2: Average absolute deviation and computational time for quaternary systems

Systems	AAD (%)	CPU time (s)
Methyl oleate-Methanol-Glycerol-Hexane	1.40	6.68
Methyl oleate-Methanol-Glycerol-Water	1.20	6.23

### 3.2 Case Studies - Chemical Equilibrium

In this part of the work, combined chemical and phase equilibria calculations are presented. The molar balances in the Gibbs minimization considers the stoichiometric coefficients. Experimental data of molar ratios (oil: alcohol) and its conversion in biodiesel found in literature were compared with the calculated values. Different operating conditions (temperature, pressure, molar ratio of oil: alcohol) were considered to see how they affect the conversion into biodiesel. All physical properties of pseudo-components (vegetable oils and esters) necessary in the modeling were calculated using group contribution methods.

First, the calculated values were compared with available data for biodiesel conversion found in literature, as can be seen in Table 3. Then, calculated values obtained for a molar ratio of alcohol equal to 1:6 and using the proposed method were compared for both methanol and ethanol, and the results are presented in Table 4.

Table 3: Conversion in biodiesel at 101.3 KPa using the proposed methodology and comparison with experimental values

Temperature(K)	Vegetable Oil	Calculated (%)	Experimental (%)
323.15	Soybean	95.33	90 – 95 (Santos et al., 2013)
333.15	Coconut	79.25	76.1 (Ribeiro et al., 2012)

A good agreement was observed between experimental data and calculated chemical and phase equilibria, with similar conversions in biodiesel as showed in Nouredini and Zhu (2009) which considered the kinetics reaction and presented values close to 90 to 100% of conversion in biodiesel for the molar ratio oil: methanol equal to 1:6.

Table 4: Biodiesel conversion obtained for each vegetable oil (molar ratio of oil: alcohol 1:6) at 101.3 KPa.

Temperature (K)	Vegetable Oil	With Methanol	With Ethanol
298.15	Coconut	81.25	78.49
	Palm	84.79	92.60
	Cottonseed	96.66	100.00
	Soybean	97.33	100.00
	Corn	94.09	100.00
	Sunflower	95.97	97.95
	Canola	94.04	100.00
	Peanut	86.93	97.33
342.15	Coconut	84.65	100.00
	Palm	88.24	94.00
	Cottonseed	97.33	100.00
	Soybean	97.33	100.00
	Corn	96.70	100.00
	Sunflower	97.33	100.00
	Canola	100.00	100.00
	Peanut	100.00	100.00

It is important to highlight that in the pseudo-components, just the triacylglycerols (TAGS) were considered, since TAGS represent around 95 % of vegetable oils total composition. For vegetable oils, pure fatty acid properties were used to estimate the probable triacylglycerols (TAGS) composition according to Ceriani (2005); for biodiesels, the composition in methyl and ethyl esters followed the fatty acid composition reported by Ceriani (2005). Properties of these mixtures were considered as simple molar averages of the individual properties of each component.

#### 4. Conclusion

The proposed methodology was able to find the chemical and phase equilibrium using an approximation of the Gibbs energy based on the discretization of the molar fraction domain. Since the problem is formulated as a linear programming model, the solution is easy to find. The methodology proposed does not restrict the use of any thermodynamic model, although in this work it focused on the SRK equations of state. The use of a cubic EOS allows the model to consider discontinuities such as a liquid and vapour phase for the same molar fraction.

The number of phases in equilibrium and the number of moles of each compound in each phase were satisfactorily calculated and compared with available experimental data in literature, with deviations often less than 1 % and not exceeding 2.5 %. The computational time was low (maximum 6.68 seconds), even for the more complex systems, as the ones with four compounds. The estimate of the physical properties of pure compounds present in the production of biodiesel, as for fatty acids, methyl and ethyl esters, was satisfactorily calculated using group contribution methods. The prediction of chemical equilibrium and phase for eight different types of oils (peanut, cotton, canola, coconut, sunflower, corn, palm and soybean) was performed satisfactorily for systems containing methanol and ethanol. The conversion observed (90 or 100%) into biodiesel reached the results expected in the literature, even though the results in literature consider reaction kinetics.

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