

Parameter Estimation and Thermodynamic Model Fitting for Components in Mixtures for Bio-diesel Production

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There is a growing interest in the search of clean, sustainable and renewable energy sources. Among them, the use of bio-diesel from vegetable oils is being considered. The knowledge of the phase equilibrium in mixtures found in the bio-diesel production is essential for the correct design and operation of the process. However, there is still a lack of information about the parameter values for the models used to describe the phase equilibrium, which could lead to incorrect design of the reactors and the separation processes, and to low efficiency caused by low mass transfer due to the presence of heterogeneous mixtures. Therefore, for the correct calculation of phase equilibrium it is necessary to have reliable estimates of the thermodynamic model parameters. In this work, two algorithms are described for the model fitting and parameter estimation, which were used to estimate the values of the parameters in the UNIQUAC model for a mixture of vegetable oils and bio-diesel. One of the algorithms uses the Simulated Annealing method, in order to find initial estimates, without any previous knowledge of the parameters. Another algorithm uses successive quadratic programming, using the estimates calculated in the SA algorithm to refine these estimates. In both algorithms, the criterion for fitting is the minimization of the square of the difference between calculated and experimental values. Also, in both algorithms the equilibrium is calculated using the direct global minimization of the Gibbs free energy with respect to the number of moles of each component, at constant T and P, due to the non-linearity and non-convexity of the model. The minimization of the Gibbs free energy model was done using the software GAMS/CONOPT2. The results obtained were able to correctly reproduce the experimental values of phase equilibrium composition.

1. Introduction

Nowadays, there is a growing concern with the environment and the preservation of nonrenewable natural resources. At present, fossil fuels, such as oil, coal and natural gas, are still the largest source of energy in the world. These fossil fuels are finite,

which means that they will run out at some time, and they contribute to carbon dioxide emissions. Due to these concerns, there is an interest for clean and renewable energy sources, such as bio-diesel (Lee et al., 2010; Liu et al., 2008; Demirbas, 2005).

Considering the vegetable oils studied for the bio-diesel production, such as soybean, sunflower seeds, castor bean, corn, canola, etc. (Porte et al., 2010; Barbosa et al., 2010; Sun et al., 2008), studies consider the *Jatropha curcas*, which is not used for food and grows naturally in less fertile soils (Parawira, 2010). However, the choice will depend on the yield and soil adaptation (Ramos et al., 2003), and the economical feasibility. Another possibility is the use of recycled oil from fried food use, which would be discarded anyway.

Despite the existence of a number of studies about the production of bio-diesel from several vegetable oils, there is still a lack of thermodynamic data for the phases that are present in the processes involving bio-diesel (Liu et al., 2008; Valle et al., 2010). Reliable thermodynamic data are necessary for the modeling and design of the process. The lack of such reliable information, in the bio-diesel production, could lead to the formation of undesirable phases in the reacting mixture, such as liquid-vapor, liquid-liquid, and liquid-liquid-vapor. In a heterogeneous system, the resistance to mass transfer is higher among the different phases, so that the mixing conditions could not be adequate to get the desirable conversion. Therefore, it is essential to be able to correctly predict phase and reacting equilibrium for such systems.

The present work presents an approach for the parameter fitting that does not depend on initial estimates. This is an important point, since there are few values available in the literature for the case of bio-diesel mixtures.

The main objective of this work is estimating reliable parameters for the UNIQUAC model, to predict the liquid-liquid equilibrium (LLE) for a system with components found in the bio-diesel production, using curve fitting with two different approaches to minimize the errors between experimental values and predicted values.

2. Proposed Approach

Parameters for the UNIQUAC model were fitted based on the minimization of the squared residuals, using experimental data from Batista et al. (1999). Those authors obtained 5 experimental points at temperature of 20 °C and pressure of 1 atm. At equilibrium, there were two liquid phases, one rich in alcohol and another rich in oil. The approach proposed in this work was used to fit the τ_{ij} parameters. The parameters r_i and q_i were taken from Batista et al. (1999), shown in Table 1.

Table 1: Parameters r_i and q_i (Batista et al., 1999).

Compound	r_i	q_i
Canola Oil	38.58241	31.25989
Oleic Acid	12.27447	10.42610
Methanol	1.90110	2.04799

The fitting was done by the minimization of the sum of the squared errors of moles number between experimental and calculated points. The equilibrium values were calculated by the direct minimization of the Gibbs free energy of the system with respect to moles number, at a given temperature and pressure.

The minimization of the error was done using two algorithms. Initially, a Simulating Annealing (SA) algorithm was used to estimate the parameters, without any previous knowledge of their values. Then, a Successive Quadratic Programming (SQP) algorithm was used, using the previous values as initial estimates.

The SA algorithm was used since it is robust and can start even with bad initial estimates, and can avoid local minimum points, getting close to the global minimum point (Aarts and Korst, 1989). However, it does not guarantee finding the global minimum. The SQP algorithm can get better values for the parameters, since it considers the necessary conditions for a minimum. For both algorithms, the objective function minimized was given by Eq. (1):

$$\min Z = \sum_{m=1}^{NT} \sum_{i=1}^{NC} \sum_{k=1}^{NP} \left(n_{ik}^{m,\text{exp}} - n_{ik}^{m,\text{calc}} \right)^2 \quad (1)$$

where NT is the number of tie-lines, NP is the number of phases, NC is the number of components (or pseudo-components), $n_{ik}^{m,\text{exp}}$ is the experimental moles number, and $n_{ik}^{m,\text{calc}}$ is the calculated moles number.

In the minimization of Eq. (1), the decision variables are τ_{ij} , subject to the restrictions given by thermodynamic equilibrium, using the UNIQUAC model, which calculates the values of $n_{ik}^{m,\text{calc}}$ for a given value of τ_{ij} .

For both SA and SQP algorithms, each calculated equilibrium point uses a subroutine, where the LLE is calculated by the direct minimization of the Gibbs free energy of the system with respect to the moles number, at a given temperature and pressure, for each point (Castillo and Grossmann, 1981). For each minimization of G , the set of parameters τ_{ij} are considered as fixed (parameters, not decision variables). Each LLE problem was solved using GAMS[®] 21.6, with CONOPT2 as solver. Also, both AS and SQP algorithm were solved using the GAMS[®] 21.6 software, using the commands for external subroutines.

In order to compare the results from this work with results found in literature, which use different approaches, it was used the mass fraction deviation given by Eq. (2):

$$\Delta w = 100 \cdot \sqrt{\frac{\sum_{m=1}^{NT} \sum_{i=1}^{NC} \sum_{k=1}^{NP} \left(w_{ik}^{m,\text{exp}} - w_{ik}^{m,\text{calc}} \right)^2}{NP \cdot NC \cdot NT}} \quad (2)$$

3. Results And Discussion

The system canola oil (1) + oleic acid (2) + methanol (3) was chosen in this work, which is one of the systems found in bio-diesel production. This system was studied

experimentally by Batista et al. (1999), who also did a parameter fitting using the UNIQUAC and NRTL models. The mass fraction deviation found by those authors using the UNIQUAC model was 0.55 %.

The parameters were obtained at 20 °C and 1 atm. Table 2 shows the results of the fitting, comparing the ones calculated in this work with the ones from the fitting by Batista et al. (1999). The mass fraction deviation found in this work was 0.20 %, which is lower than the one using the parameters fitted by Batista et al. (1999).

Table 3 shows the mass fraction values calculated at LLE, using the parameters fitted by the approach proposed in this work. Experimental values of mass fractions for this three component system at LLE are compared with the calculated values in Figure 1. It can be seen that there is a good agreement for all points considered. Therefore, the values of the parameters fitted in this work can be used for a reliable modeling and design for equipment used in bio-diesel production with the system studied.

Table 2: UNIQUAC interaction parameters between canola oil (1) + oleic acid (2) + methanol (3) at 20 °C and 1 atm.

Pair ij	This work		Batista et. al (1999)	
	τ_{ij}	τ_{ji}	τ_{ij}	τ_{ji}
12	0.36849182	2.17675148	0.38887419	2.15361952
13	0.26516613	1.24780895	0.26372006	1.23784081
23	0.66963352	1.18863762	0.63547302	1.23847858

Table 3: Mass fraction values predicted by the minimization of the Gibbs free energy, using the parameters fitted in this work.

Alcohol phase			Oil phase		
$100w1$	$100w2$	$100w3$	$100w1$	$100w2$	$100w3$
1.452	0.000	98.548	95.049	0.000	4.951
1.959	4.146	93.896	87.201	5.555	7.244
2.620	8.244	89.136	79.343	10.686	9.971
5.208	17.681	77.112	61.706	20.625	17.669
7.590	22.428	69.982	52.382	24.916	22.703

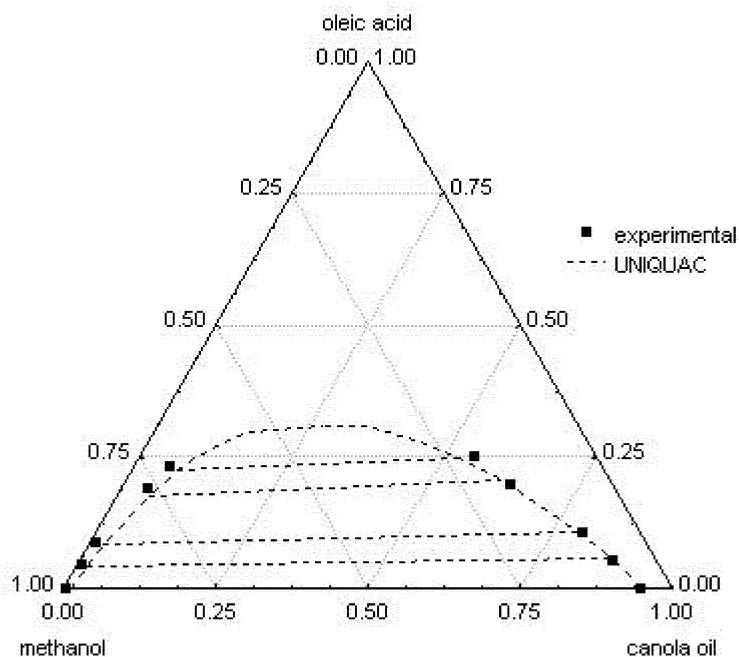


Figure 1: Canola oil (1) + oleic acid (2) + methanol (3) system at 20 °C. Experimental and calculated points are compared, using the parameter values fitted in this work.

4. Conclusions

The fitting of the parameters, using the UNIQAC model, was done for a three component system, with canola oil, oleic acid and methanol, at 20 °C and 1 atm. The LLE values calculated with these parameters were very close to the experimental values found by Batista et al. (1999), with a better fitting than the one found by those authors.

The fitting was done using two algorithms, initially SA and then SQP. Although this work has focused on the UNIQAC model, the approach can be applied to any thermodynamic model, such as NRTL, Peng-Robinson, and Soave-Redlich-Kwong.

This approach was useful to start the fitting without any previous knowledge of the values of the parameters, and then to more accurately refine the fitting. The fitted parameters were able to reproduce the experimental values more accurately.

The proposed approach was able to fit the parameters, with reliable results. The calculated LLE values are very close to the experimental values, and the model can be used to simulate the LLE in the production of bio-diesel.

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References

- Aarts E. and Korst J., 1989, *Simulated Annealing and Boltzmann Machines: A Stochastic Approach to Combinatorial Optimization and Neural Computing*. John Wiley and Sons, New York, the USA.
- Barbosa D.D., Serra T.M., Meneghetti S.M.P. and Meneghetti M.R., 2010, Biodiesel production by ethanolysis of mixed castor and soybean oils, *Fuels*, 89, 3791-3794.
- Batista E., Monnerat S., Kato K., Stragevitch L. and Meirelles A.J.A., 1999, Liquid-Liquid Equilibrium for Systems of Canola Oil, Oleic Acid, and Short-Chain Alcohols. *Journal of Chemical and Engineering Data*, 44, 1360-1364.
- Demirbas A., 2005, Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods, *Progress in Energy and Combustion Science*, 31, 466-487.
- Gonçalves C.B. and Meirelles A.J.A., 2004, Liquid-liquid equilibrium data for the system palm oil + fatty acids + ethanol + water at 318.2K. *Fluid Phase Equilibria*, 221, 139-150.
- Lee M., Lo Y. and Lin H., 2010, Liquid-liquid equilibria for mixtures containing water, methanol, fatty acid methyl esters, and glycerol, *Fluid Phase Equilibria*, 299, 180-190.
- Liu X., Piao X., Wang Y. and Zhu S., 2008, Liquid-liquid equilibrium for systems of (fatty acid ethyl esters + ethanol + soybean oil and fatty acid ethyl esters + ethanol + glycerol), *Journal of Chemical and Engineering Data*, 53, 359-362.
- Magnussen T., Rasmussen P. and Fredenslund A., 1981, *Industrial and Engineering Chemistry Process Design and Development*, 20, 331-339.
- NIST Chemistry WebBook, NIST Standard Reference Database Number 69, <webbook.nist.gov/chemistry> accessed 05.05.2010.
- Parawira W. 2010, Biodiesel production from jatropha curcas: A review, *Scientific Research and Essays*, 5, 1796-1808.
- Porte A.F., Scheneider R.D.D., Kaercher J.A., Klamt R.A., Schmatz W.L., da Silva W.L.T. and Severo W.A., 2010, Sunflower biodiesel production and application in family farms in Brazil, *Fuel*, 89, 3718-3724.
- Silva C. 2008, Continuous production of biodiesel by non-catalytic transesterification of soybean oil. PhD Thesis, State University of Maringá – Brazil (in Brazil)
- Sun H., Hu K., Lou H. and Zheng X., 2008, Biodiesel Production from Transesterification, of rapessed oil using KF/Eu₂O₃ as a catalyst, *Energy and Fuels*, 22, 2756 – 2760.
- Valle P; Velez A, Hegel P, Mabe G. and Brignole E.A., 2010, Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor, *Journal of Supercritical Fluids*, 54, 61-70.