

A PHASE EQUILIBRIA STUDY OF SUNFLOWER OIL TRANSESTERIFICATION USING SUPERCRITICAL ALCOHOLS WITH CARBON DIOXIDE AS COSOLVENT

A.Santana^a, F. Recasens^a, E. Ramírez^b, M.A. Larrayoz^{a,*}

^a*Chemical Engineering Department, Universitat Politècnica de Catalunya,
Av. Diagonal 647, ETSEIB. Pab. G-2. 08028. Barcelona, Spain.*

^b*Chemical Engineering Department, Faculty of Chemistry, Universitat de Barcelona
Martí I Franquès 1. 08028. Barcelona Spain*

[*m.angeles.larrayoz@upc.edu](mailto:m.angeles.larrayoz@upc.edu)

Abstract. Vapor-liquid equilibria for supercritical modified alcohol + fatty acid ester systems were predicted by ASPEN software using Peng Robinson Equation of State (PR-EOS) with one k_{ij} binary parameter. The model has been employed to predict the operating conditions in the supercritical phase when different alcohols are present in the mixture. The effect of several alcohols (e.g. methanol, ethanol, propanol and butanol) using CO₂ as cosolvent, is theoretically studied for obtaining mild operating conditions that increase the feasibility of continuous single-phase transesterification. Compared with the conventional supercritical alcohols technique less energy consumption required for the process. Furthermore, the reaction pressure required is significantly reduced, which makes the process safer and lowers production costs. For specific operating conditions (feed composition, concentration of cosolvent, pressure and temperature).

1. Introduction

Biodiesel is defined as the fatty acid alkyl monoesters derived from renewable feedstocks, such as vegetable oils, animal fats, etc. There are four chemical processes used to solve the high viscosity problem of triglycerides: dilution, microemulsification, pyrolysis (thermal cracking), and transesterification [1]. Among these four ways, the most commonly preferred process is transesterification. Transesterification is an ester conversion process that splits up the triglycerides; that is, takes the glycerol of the triglyceride and replaces it with alkyl radical of the alcohol used. Through transesterification, high viscosity is reduced to a value closer to that of diesel fuel while cetane number and heating value are saved. As seen in Fig. 1, three moles of alcohol are used per mole of triglyceride for the stoichiometric transesterification reaction. This reaction results in three moles of fatty acid alkyl monoester (biodiesel) and a mole of glycerol that is the by-product of this reaction. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however, methanol is lower in cost and has some physical and chemical advantages like more polarity and the shortest alcohol chain length.

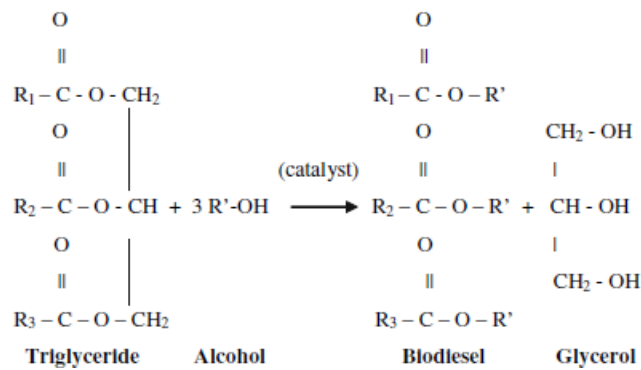


Figure 1. Stoichiometric transesterification reaction

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature, environmental friendly and can be produced locally. The most widely used vegetable oils for the production of biodiesel are taken from rape seeds, sunflowers, and soybeans. The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines.

Biodiesel has recently attracted considerable attention due to its environmental benefits and the fact that it comes from renewable resources. The different stages in the production of sunflower seed methyl esters generate by-products which offer further outlets. The supercritical fluids (SCFs) have been shown to be a promising technique for future large-scale biofuel production, especially for biodiesel production from oils and fats. Compared with conventional biofuel production methods, the SCFs technology has a number of advantages that includes fast kinetics, high fuel production rate and ease of continuous operation.

The supercritical method requires high molar ratios of alcohol to oil and the adoption of high temperatures and pressures for the reaction to present satisfactory conversion levels, leading to high processing costs and causing, in many cases, the degradation of the fatty acid esters formed [2], hence decreasing the reaction conversion [3]. Attempts to reduce the expected high operating costs and product degradation have been made through the addition of cosolvents [4-6], a two-step process with removal of glycerol generated in the first step [7], and adopting a two-step process comprising hydrolysis of triglycerides in subcritical water with subsequent esterification of fatty acids [8,9].

The use of cosolvents can decrease the mixture critical point and allow the reaction to be carried out under milder conditions, enhancing the mutual solubility of the oil-alcohol mixture [4, 5], reducing the transport limitations, and increasing the reaction rates. Just a few works are available in the open literature regarding the use of cosolvents in the supercritical transesterification, such as the use of carbon dioxide [5, 10-12] and propane [4,13,14] all of them with methanol. In those studies, it has been shown that the use of the aforementioned cosolvents led to a decrease in the operational conditions with high reaction yields. It is well-known that supercritical carbon dioxide, besides its low-cost, non-toxicity, favorable critical parameters and transport

coefficients, may be a good cosolvent for short and intermediate chain length organic molecules, and it is a low-cost and facile material [5, 15-19].

In this work, we studied in a preliminary way, the phase behaviour of modified methanol ethanol/propanol/butanol systems at different temperatures and pressures. The Peng-Robinson [20] equation of state (PR-EOS) was used to estimate the vapour-liquid equilibria of the reactants and the possible operating conditions to assure the presence of a single phase in the reactor.

2. Modelling Phase Equilibria

The transesterification rate is low at subcritical (multiphase) conditions but significantly accelerated at supercritical (single phase) conditions. A portion of this acceleration is due to temperature effects, but a portion is also due to the presence of single supercritical phase at supercritical conditions. Therefore, the phase behavior of the mixture in the system is an important consideration in biodiesel production. Large excess amounts of alcohol have been used in previous supercritical transesterification research because this practice reduces the critical temperature of the mixture. The critical properties of triglyceride-alcohol mixtures have not been a topic of much research, so the precise amount of alcohol needed to achieve supercritical conditions at a given temperature is not readily available. Bunyakiat *et al.* [21] report results from an investigation that was intended to address this issue. They used Lydersen's method of group contributions to estimate the critical temperature and pressure of vegetable oil and then used Lorentz-Berthelot type mixing rules to calculate what they took to be the critical values for mixtures of oil and alcohol. The properties they calculated, though, are actually pseudocritical properties, not true critical points. Therefore, the results from their thermodynamic calculations have no bearing on the actual phase behavior. Pseudocritical properties are used to parameterize equations of state for mixtures, but these values are not the same as the true thermodynamic critical point of a mixture. The two are often quite different. To determine the actual critical point of a mixture, one can use an appropriate equation of state. It is important to recognize, as well, that the critical temperature of the mixture will change as the transesterification reaction progresses, because the reaction changes the identities of species present in the mixture and their mole fractions. Thus, if one intends to examine or use supercritical conditions for transesterification, it is not adequate to simply choose a reaction temperature that exceeds the critical temperature of the alcohol being used. Rather, one needs to know the critical temperature of the mixture as the reaction progresses and ensure that the reaction temperature remains above these values throughout.

The phase behavior and critical points for some binary mixtures important in supercritical transesterification have been studied. Shimoyama *et al.* [22] examined methanol-methyl ester systems, which reflect the final products from transesterification. They provide experimental measurements for the compositions of the coexisting liquid and vapor phases, and they correlated the results using the Peng-Robinson equation of state. Glisic *et al.* [23] examined systems that reflect the reactants. They measured the phase equilibria for methanol-sunflower oil mixtures. The best correlation of the experimental results was by the Redlich-Kwong-ASPEN equation of state with van der Waals mixing rules. It must be noted, however, that the system examined is a reactive

one and that sunflower oil is a mixture but it was treated thermodynamically as a single pseudocomponent. The effect of these items on the conclusion about the best equation of state to use is not clear. The conditions examined by these authors always resulted in only a single liquid phase being present. They provide no data for liquid-liquid-vapour equilibrium, which would exist when there are separate oil-rich and methanol-rich liquid phases. Despite these limitations, this article is significant because it explores the use of different equations of state and it begins to address key issues in supercritical synthesis of biodiesel. Tang *et al.* [24] reported liquid-liquid equilibrium data of the system methanol-triolein in the temperature range between 353 and 463K at three different pressures 6, 8 and 10MPa that were above the bubble pressure of the binary mixture. Hegel *et al.* [25] examined mixtures of soybean oil, methanol, and propane. They showed visually how the system evolves from three phases (LLV) to two (LV) to one (supercritical) as the mixture is heated and reacts. A single liquid phase was observed to exist for several mixtures at temperatures as low 160°C. Supercritical temperatures are not required to have a single homogeneous fluid phase containing the reactants.

Taking into account the facts mentioned above, the phase equilibria was modelled as follows: sunflower oil is composed mainly of triolein and trilinolein, with minor contents of tripalmitin, tristearin and other triglycerides. However, to simplify the problem, it is convenient to represent the complex composition of sunflower oil with a pseudo component. In this case, the selected pseudo component was triolein and not trilinolein, since it is the components for which more thermodynamic data is available in the literature [26]. The critical constant of the pure components are needed for the calculation of $a(T)$ and $b(T)$, but these constants are not available for compounds such as fats, since they are chemically unstable and decompose at high temperatures. The critical properties and other parameters of the pure components are listed in Table 1.

Table 1. Critical properties and substance parameters in equation of state.

| Components | M/kg kmol ⁻¹ | T _c /K | P _c /bar | ω |
|-----------------|-------------------------|-------------------|---------------------|--------|
| Methanol | 32 | 512.6 | 80.1 | 0.5659 |
| Ethanol | 46 | 513.9 | 61.4 | 0.6436 |
| Propanol | 60 | 508 | 47.6 | 0.6689 |
| Butanol | 74 | 536 | 41.9 | 0.5711 |
| CO ₂ | 44 | 304.2 | 73.8 | 0.225 |
| Triolein* | 884 | 977.8 | 3.34 | 1.9780 |

The PR-EOS was used to correlate the experimental data. The equation can be expressed as following:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + 2bV - b^2} \quad (1)$$

For a pure component i , the parameters a_i and b_i in the PREOS are the function of the critical temperature, critical pressure and acentric factor of the component. To model the molecular interactions between components i and j , the binary interaction parameters ($k_{a,ij}$, $k_{b,ij}$) are introduced through the mixing rules as follows [27]:

$$(2)$$

$$\begin{aligned}
 a &= \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{a,ij}) \\
 b &= \sum \sum x_i x_j \frac{b_i + b_j}{2} (1 - k_{b,ij})
 \end{aligned}
 \tag{3}$$

where P is the pressure, R is the gas constant, T is the temperature, and V is the molar volume. The parameters a and b are the energy and size parameters, respectively. The subscript c denotes the critical properties. The experimental data of the critical properties and the acentric factor (ω) for alcohols and sunflower oil are available from the literatures [26, 28].

The PT-diagrams for each system (Sunflower oil-alcohols) were generated using the standard Peng-Robinson equation of state (PR-EOS). Each isopleth plotted in these diagrams represents the phase limit between the two-phase and the one-phase regions. From these curves it is possible to find, for a given temperature and feed composition, the minimum pressure required to assure complete miscibility in the reactive mixture.

The experimental information available in the literature on high-pressure phase equilibria of reactive mixtures is very scarce, which made difficult to determine the model parameters. Because of vegetable oil properties such as vapor pressure and critical properties are experimentally unattainable it was necessary to make a rough theoretical estimation of its critical properties according to the Chueh–Prausnitz approximation [29].

3. Results

The binary vapor–liquid equilibrium (VLE) diagrams for sunflower oil in CO₂ + alcohols are shown in terms of the VLE constants as a function of pressure at constant temperature in Figure 2. These diagrams were calculated for the system CO₂+alcohols–sunflower oil, estimating the K_i values from the fugacity coefficients calculated with the PR-EOS [30,31]. The calculations were performed with a PE 2000 [32] in terms of the convergence pressure [33].

Methanol, ethanol and propanol practically have the same convergence pressure of around 12 MPa, which is significantly higher than that for butanol-oil system. Nimcevic et al. [34] found that transesterification of oils by propanol or alcohol with longer alkyl chain always failed even after several hours of treatment at the boiling point of alcohol.

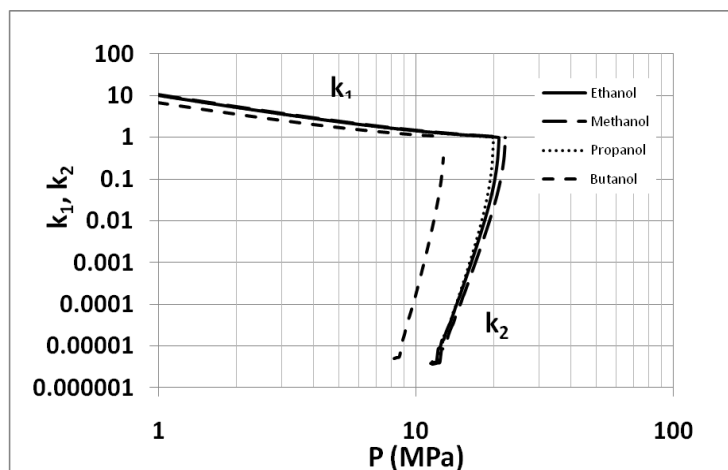


Figure 2. VLE binary systems. Sunflower (K_1) and SC- CO_2 + Alcohols (K_2) VLE constants vs. pressure at constant temperature.

Another factor to be considered is the alcohol size. The smaller size of the alcohols could facilitate the simultaneous attack of alcohol on all three chains of triglycerides, resulting in the higher reaction rate of fatty acid alkyl ester formation [35]. For this reason, we studied in a preliminary way, the phase behavior of methanol/ethanol- CO_2 systems at different pressures, temperatures and alcohols composition (see Table 2).

Table 2. Measured vapor liquid equilibrium data for methanol and ethanol – CO_2 system.

| Alcohols (%wt) | Methanol | Ethanol |
|------------------|----------|---------|
| | P (MPa) | |
| T = 343 K | | |
| 5 % | 14 | 13 |
| 20 % | 17 | 16 |
| 30 % | 19 | 17 |
| T = 373 K | | |
| 5 % | 20 | 19 |
| 20 % | 25 | 24 |
| 30 % | 27 | 25 |
| T = 423 K | | |
| 5 % | 29 | 27 |
| 20 % | 34 | 33 |
| 30 % | 36 | 34 |

Isotherms at 343, 373 and 423 K for different concentration of methanol + CO_2 and ethanol + CO_2 systems were estimated with PR-EOS. From the results in Table 2, it can be observed that on increasing the amount of alcohol and temperature, involves an increase in the convergence pressure.

There are no previous experimental studies in the open literature on high-pressure equilibria of these systems (alcohols+ CO_2 as cosolvent). The most similar application is

the supercritical alcohols with propane or dimethylether as cosolvents. The estimated data of this study were compared with the literature data reported by Joung et al. [36], the comparisons were made for the CO₂-methanol and CO₂-ethanol systems. At 13 MPa and 343 K and at 11.97 MPa and 344.75 K, Joung et al. [36] reported the vapor phase of the system CO₂-methanol and CO₂-ethanol respectively, which favorably agrees with the vapor phase estimated in this study.

4. Conclusion

In this work, the phase equilibria of the sunflower oil-methanol/ethanol-CO₂ ternary system was investigated using the PR-EOS. This model is applied to the prediction of phase equilibria in the supercritical alcohols-CO₂ of sunflower oil for the transesterification process.

Compared with the conventional supercritical methanol/ethanol technique, less energy is required for the process. Furthermore, the reaction pressure required is significantly reduced, which makes the process safer and lowers production costs. The supercritical process with cosolvent leads to milder conditions (160 K lower temperature) compared with conditions without cosolvent at higher pressure. At present, experiments are being conducted in our laboratory and experimental data will be used to tune the PR-EOS model.

Acknowledgments

The authors would like to acknowledge Spanish Ministry of Science, Technology and Innovation (Grant N^o. ENE 2009-14502) for the financial support given.

Reference

- [1] Ramadhas AS, Jayaraj S, Muraleedharan C., (2004), Use of vegetable oils as IC engine fuels—a review. *Renew Energy* 29:727–742
- [2] Imahara, H.; Minami, E.; Hari, S.; Saka, S. *Fuel* (2007), 87, 1–6.
- [3] Kusdiana, D.; Saka, S. *Fuel* (2001), 80, 693–698.
- [4] Cao, W.; Han, H.; Zhang, J. *Fuel* (2005), 84, 347–351.
- [5] Han, H.; Cao, W.; Zhang, J. *Process Biochemistry* (2005), 40, 3148–3151.
- [6] Hegel, P.; Mabe, G.; Pereda, S.; Brignole, E. A. *Ind. Eng. Chem. Res.* (2007), 46, 6360–6365.
- [7] D' Ippolito, S.A.; Yori, J.C.; Iturria, M.E.; Pieck, C.L.; Vera, C.R. *Energy Fuels* (2007), 21, 339–346.
- [8] Kusdiana, D.; Saka, S. *Appl. Biochem. Biotechnol.* (2004), 113, 781–791.
- [9] Minami, E.; Saka, S. *Fuel* (2006), 85, 2479–2483.
- [10] Yin, J. Z.; Xiao, M.; Song, J. B. *Energy Convers. Manage.* (2007), 49, 908–912.
- [11] Anitescu, G.; Deshpande, A.; Tavlarides, L. L. *Energy Fuel* (2008), 22, 1391–1399.
- [12] Imahara, H.; Xin, J.; Saka, S. *Fuel* doi:10.1016/j.fuel. 2009.01.002.
- [13] Hegel, P.; Mabe, G.; Pereda, S.; Brignole, E. A. *Ind. Eng. Chem. Res.* (2007), 46, 6360–6365.

- [14] van Kasteren, J. M. N.; Nisworo, A. P. *Resourc. Conserv. Recyc.* (2007), 50, 442–458.
- [15] Oliveira, D.; Oliveira, J. V. J. *Supercrit. Fluids* (2001), 19, 141–148.
- [16] Guc-lu- Ustundac_g, O.; Temelli, T. J. *Supercrit. Fluids* (2006), 38, 275–288.
- [17] Ndiaye, P. M.; Franceschi, E.; Oliveira, D.; Dariva, C.; Tavares, F. W.; Oliveira, J. V. J. *Supercrit. Fluids* 2006, 37, 29–37.
- [18] Jackson, M. A.; Mbaraka, I. K.; Shanks, B. H. *Appl. Catal., A* 2006, 310, 48–53.
- [19] Hernandez, E. J.; Mabe, G. D.; Senorans, F. J.; Reglero, G.; Fornari, T. J. *Chem. Eng. Data* 2008, 53, 2632–2636.
- [20] Peng, D. Y., Robinson, D. B. (1976). A new two-constant equation of state, *Ind. Eng. Chem. Fundam.*, 15 59-64.
- [21] Bunyakiat, K.; Makmee, S.; Sawangkeaw, R.; Ngamprasertsith, S. (2006). Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. *Energy Fuels*, 20, 812–817.
- [22] Shimoyama, Y., Iwai, Y., Jin, B. S., Hirayama, T., Arai, Y. (2007). Measurement and correlation of vapor-liquid equilibria for methanol+methyl laurate and methanol+methyl myristate systems near critical temperature of methanol. *Fluid Phase Equilib.* 257, 217–222.
- [23] Glisic, S.; Montoya, O.; Orlovic, A.; Skala, D. (2007). Vapor-liquid equilibria of triglycerides-methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol. *J. Serb. Chem. Soc.*, 72, 13–27.
- [24] Tang Z., Du Z, Min E., Gao L., Jiang T., Han B. (2006). Phase equilibria of methanol-triolein system at elevated temperature and pressure, *Fluid Phase Equilibria* 239 8–11.
- [25] Hegel, P.; Mabe, G.; Pereda, S.; Brignole, E. A. (2007). Phase transitions in a biodiesel reactor using supercritical methanol. *Ind. Eng. Chem. Res.*, 46, 6360–6365.
- [26] Weber, W., Petrov, S., Brunner, G. (1999). Vapour-liquid-equilibria and calculations using the Redlich-Kwong-Aspen-equation of state for tristearin, tripalmitin, and triolein in CO₂ and propane. *Fluid Phase Equil.*, 158-160, 695-706.
- [27] Prausnitz, J.M., Lichtenthaler, R.N. De Azevedo, E.G. (1986). *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall.
- [28] Poling, B. E., Prausnitz, J. M., O’Connell, J. P. (2001). *The properties of Gases and Liquids* 5th edition, McGraw-Hill, New York, , p. A.5.
- [29] Reid, R., Prausnitz J., Poling B. (1987). *The properties of gases & liquids*, 4th edn, McGraw Hill, New York .
- [30] McHugh M., and V. Krukoni, *Supercritical Fluid Extraction*, 2nd Edition, Butterworth–Heinemann, Stoneham, UK (1994).
- [31] Sandler, S. I., *Chemical and Engineering Thermodynamics*, 3rd Edition, Wiley, New York (1999).
- [32] Pfohl, O., S. Petkov, and G. Brunner, *PE 2000: A Powerful Tool to Correlate Phase Equilibria*, Herbert Utz Verlag, Munich (2000).
- [33] Hougen, O. A., K. M. Watson, and R. A. Ragatz, *Principios de los procesos quimicos*, Vol. 2, Editorial Reverte, S. A., Madrid (1954).
- [34] Nimcevic, D., Puntigam, R., Wörgetter, M., and Gapes, R.J. (2000), *JAOCS* 77, 275-279.
- [35] Freedman, B., Butterfield, R.O., and Pryde, E.H. (1986), *JAOCS* 63, 1375-1380.

[36] S. N. Young, C. W. Yoo, H. Y. Shin, S. Y. Kim, K-P. Yoo, C. S. Lee, W. S. Huh, *Fluid Phase Equilibria*, 185, (2001), 219-230.