Experimental Investigation and Modeling of Liquid-Liquid Equilibria in Biodiesel + Glycerol + Methanol

Masoume Rostami, Maziyar Mahmoudi and Sona Raeissi[+]

School of Chemical & Petroleum Engineering, Department of Gas Engineering, Shiraz University, Iran.

Abstract. The direct product of the biodiesel production process can be assumed to be a ternary mixture of biodiesel, glycerol, and methanol. The liquid-liquid equilibria of ternary systems of glycerol + methanol + corn oil biodiesel have been investigated experimentally in this study. Measurements were carried out at three temperatures of 20, 30 and 40°C. The binodal curves were determined by the cloud point titration method and the tie-lines were measured by evaporation of methanol in an oven. The results showed that the solubility curves are not situated far from the axes and that the two–phase region shrinks with increasing temperature. The ternary data obtained were modeled using the UNIQUAC model and the binary interaction coefficients were optimized. Results indicated that UNIQUAC is a suitable model for such systems, capable of satisfactory correlations with a maximum error of 4.4% for the 3 set of data investigated in this study. Further, the Othmer-Tobias correlations were applied to this mixture and the constants were obtained at each temperature. The results validated the consistency of tie-line data obtained experimentally in this work.

Keywords: phase behavior, solubility, corn oil, biodiesel, glycerol, methanol, UNIQUAC model.

1. Introduction

In recent years, biodiesel is gaining attention in the world as an alternative fuel for diesel engines. Its primary advantages are that it is one of the renewable fuels. Compared with petro-diesel, biodiesel is a non-toxic fuel, free of aromatics and sulphur and is also more biodegradable. Biodiesel is produced by the transesterfication reaction of vegetable oils with alcohol (ethanol or methanol) in the presence of a catalyst. The most common alcohol used in biodiesel production is methanol. The biodiesel production reaction is carried out with an excess of alcohol to make the reaction more complete. This reaction produces a mixture of fatty acid methyl esters (FAME), and glycerol as a byproduct [1].

After reaction, the desired product is contaminated with some impurities such as glycerol and the non-reacted alcohol. Therefore**,** some steps are carried out following reaction to recover the desired product. The first step of product recovery is the separation of biodiesel and glycerol. Alcohol recovery and recycling is the next step of the process. Therefore, knowledge of accurate phase equilibria of the components involved in biodiesel production is essential to determine optimum operating conditions for the processes of separation and purification of the biodiesel. In this respect, Franc et al. [2] measured the solubility of castor oil biodiesel, glycerol, and alcohol (methanol and ethanol) at different temperatures and showed that biodiesel solubility in the glycerol-rich phase is slightly higher for ternary mixtures containing ethanol compared to methanol. Ardila et al. [3] studied the ternary system of soybean oil biodiesel, glycerol, and ethanol to investigate the temperature effect and showed that a small temperature change (10 K) does not have much influence in the solubilities. Liu et al. [4] determined the phase diagram and tie lines of ternary mixtures of soybean oil biodiesel, ethanol, and glycerol in the temperature range from 300 to 343 K and showed that the distribution coefficient of ethanol between the biodiesel-rich phase and the glycerol-rich phase decreases with increasing ethanol concentration.

[+] Corresponding author. Tel.: +98-711-2303071; fax: +98-711-6473180.
E-mail address: raeissi@shirazu.ac.ir

In this work, a ternary system of concern in biodiesel production, consisting of corn oil biodiesel + glycerol + methanol was studied experimentally regarding its liquid-liquid equilibria. The binodal curves and tie lines were determined at the three temperatures of 20, 30 and 40°C and the resulting tie lines were correlated using the UNIQUAC model.

2. Experimental section

2.1. Materials

The chemicals used were glycerol (> 99% GC, from Sigma Aldrich), methanol (99.5%, from Arman Sina), and biodiesel prepared in the laboratory by transesterification of corn oil with methanol and KOH as catalyst. The produced biodiesel was washed with water to remove all impurities and then dried in an oven to remove the water and any remaining methanol by evaporation.

2.2. Procedure

a. phase diagram of the ternary system of biodiesel+ methanol + glycerol

The binodal curves were determined by the cloud point titration method under isothermal conditions [4], where the test cell was placed in a water bath with a temperature uncertainty of 0.1 K. Mixtures having different initial mass fractions of biodiesel and glycerol were titrated with methanol in a buret. A magnetic stirrer was used to agitate the mixture during titration. The point when the mixture changed from turbid to transparent was considered as a point on the binodal curve. In order to determine the binary solubilities of biodiesel in glycerol, and vice versa via the titration method, an ultrasonic mixer was used to mix these two components to proper dispersion owing to the large difference between biodiesel and glycerol densities.

b. tie lines of the ternary system of biodiesel+ methanol + glycerol

After mixing a specific known mass fraction of biodiesel, methanol, and glycerol for 35 minutes at constant temperature in a shaker-incubator, the mixture was kept in an isothermal incubator at the same temperature for at least 20 hours for adequate separation into two phases: a biodiesel-rich phase and a glycerol-rich one. Samples from each phase were then withdrawn using syringes, weighed, and kept in an oven at 75°C for 2.5 hours to remove all methanol via evaporation until reaching a constant weight. By weighing the remaining sample, the amounts of methanol in each phase were determined. The biodiesel and glycerol mass fractions were also determined with the aid of the phase diagram obtained in section (a) using the determined mass fractions of methanol obtained in the two phases.

3. Thermodynamics model

An activity coefficient-based model can be applied to model the experimental data. In this study, the UNIQUAC model [5] was used and the binary interaction parameters were optimized. This model is used due to its simplicity and wide range of applicability and is recommended for non-ideal systems at low temperatures and ambient pressures [2], [6].

4. Results and discussions

The three experimental phase diagrams of the ternary system of corn oil biodiesel + methanol + glycerol, including tie line data in the form of solid lines, are presented in Figure 1 (a, b, and c) at 20, 30, and 40° C, respectively. It is seen in these figures that both biodiesel and glycerol are completely soluble in methanol. However, biodiesel and glycerol are partially soluble in one another.

Solubility in the ternary mixture increases with increasing temperature and thus, the size of the two-phase region shrinks. The results of these experiments indicate that the solubility of biodiesel in glycerol and vice versa is very low; however, the solubility of glycerol in the biodiesel phase is greater than that of biodiesel in the glycerol phase. Therefore, it is possible to have a clean and complete separation of glycerol from biodiesel. In addition, it is seen that the solubility of methanol in the glycerol-phase is more than in the biodiesel phase. This is evident from the slopes of the tie lines.
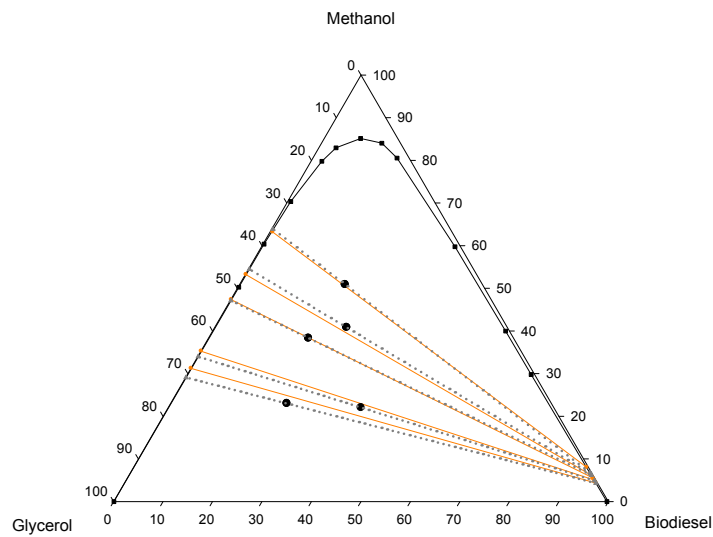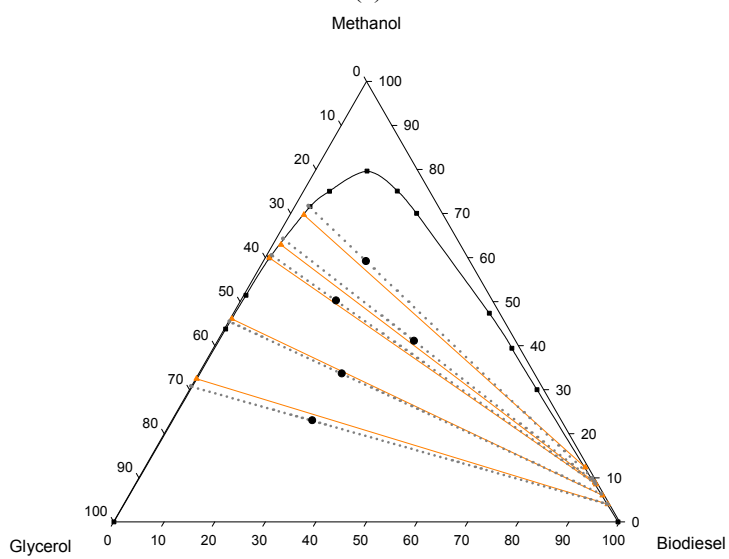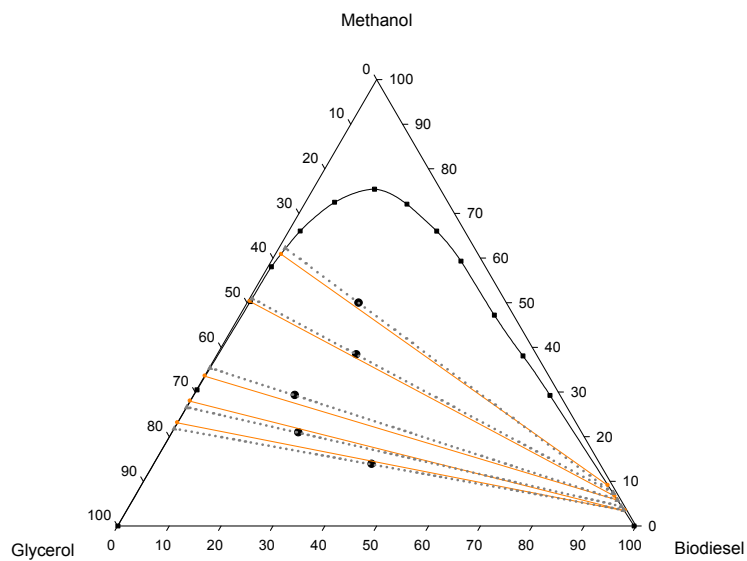
Fig. 1: Phase diagram and tie lines of the ternary system of corn oil biodiesel, glycerol, and methanol at: (a) 20^0 C, (b) 30^0 C, and (c) 40° C. solid line: experimental, dashed line: UNIQUAC model.

Figure 1 (a, b, and c) also shows the correlation results by the UNIQUAC model at 20, 30, and 40º C, respectively, shown as dashed lines, which can be compared to the experimentally determined values (solid lines) at the corresponding temperatures. These results indicate the applicability of this model with a maximum global AAD (average absolute deviation) of 4.4% in the studied system calculated according to the following equation:

$$AAD = \frac{1}{N} \sum_i \left| w_i^{exp} - w_i^{cal} \right|$$

Where w_i is the mass fraction of the components, and N is the number of the tie lines.
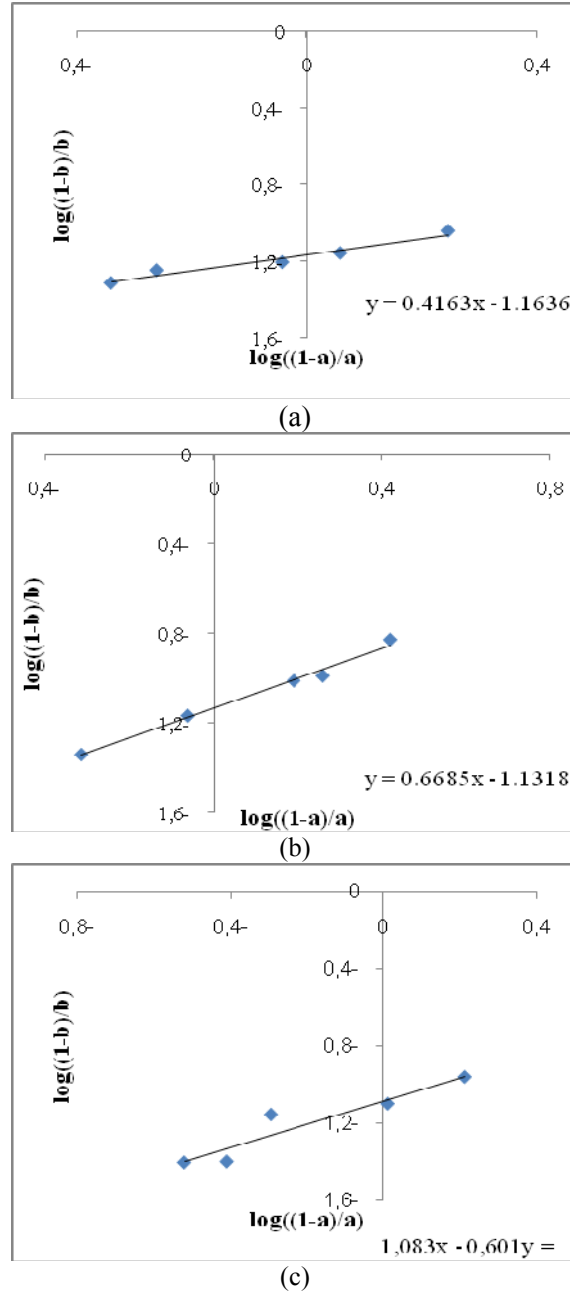

(a)

(b)

(c)

Fig. 2: Othmer-Tobias plot: at (a) 20º C, (b) 30º C, and (c) 40º C where "a" is the mass fraction of glycerol in the glycerol-rich phase, and "b" is the ma`ss fraction of biodiesel in the biodiesel-rich phase

The consistency of tie line data was validated by applying the Othmer-Tobias plot [7]. As seen in Figure 2 (a, b, and c) these plots showed a good linear fit, at 20, 30, and 40º C, respectively.

According to the phase rule, when a ternary system has two-phase equilibrium at constant pressure and temperature, the degree of freedom is one. This indicates that only one component can change independently. In fact, the mass fraction of a component in a phase can be expressed as a function of another mass fraction

in that phase. Therefore, the relations between methanol and glycerol in the glycerol-rich phase and between methanol and biodiesel in the biodiesel-rich phase can be expressed mathematically as:

In glycerol-rich phase at 20° C: $w_{Glycerol} = -1.063\,w_{MeOH} + 1.022$

In biodiesel-rich phase at 20° C: $w_{MeOH} = -0.972 w_{Biodiesel} + 0.9701$

In glycerol-rich phase at 30° C: $w_{Glycerol} = -1.028\,w_{MeOH} + 1.006$

In biodiesel-rich phase at 30° C: $w_{MeOH} = -0.924 w_{Biodiesel} + 0.9223$

In glycerol-rich phase at 40° C: $w_{Glycerol} = -1.032\,w_{MeOH} + 1.007$

In biodiesel-rich phase at 40° C: $w_{MeOH} = -0.883 w_{Biodiesel} + 0.8840$

5. Conclusions

The experimental results have indicated that it is easy to separate glycerol (as a byproduct) after the removal of methanol from biodiesel, owing to the low solubility of biodiesel and glycerol in each other. The Othmer-Tobias plots proved the consistency of tie line data obtained experimentally. Since the size of the two-phase region shrinks with a temperature increase, larger quantities of biodiesel in the biodiesel-rich phase can be obtained at lower temperatures. Good agreement was found between experimental data and correlations using the UNIQUAC modeling, indicating the applicability of this model for such systems. Linear correlations have also been proposed at each temperature which can be used to predict tie lines. By using the linear correlations above, it is possible to determine the unknown composition in both phases.

6. Acknowledgements

7. References

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