Equilibrium study for ternary mixtures of biodiesel

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Abstract. The liquid-liquid equilibrium (LLE) data for the ternary mixtures of methanol + fatty acid methyl ester (FAME) + palm oil and FAME + palm oil + glycerol at various temperatures from 35 to 55°C, the tie lines and binodial curves were also investigated and plotted in the equilibrium curve. The experimental results showed that the binodial curves of methanol + FAME + palm oil depended significantly with temperature while the binodial curves of FAME + palm oil + glycerol illustrated insignificant change with temperatures. The interaction parameters between liquid pair obtained for NRTL (Nonrandom Two-Liquid) and UNIQUAC (Universal Quasi-Chemical Theory) models from the experimental data were also investigated. It was found that the correlated parameters of UNIQUAC model for system of FAME + palm oil + glycerol, denoted as $a_{13}$ and $a_{31}$, were 580.42K and -123.69K, respectively, while those for system of methanol + FAME + palm oil, denoted as $a_{42}$ and $a_{24}$, were 71.48 K and 965.57K, respectively. The ternary LLE data reported here would be beneficial for engineers and scientists to use for prediction of yield and purity of biodiesel for the production. The UNIQUAC model agreed well with the experimental data of ternary mixtures of biodiesel.

1. Introduction

The development of alternative fuels from renewable resources, like biomass, has received considerable attention in all countries. It is considered that biodiesel contributes much less to global warming than fossil fuels, being produced from renewable natural sources such as vegetable oils and animal fats consisting of the alkyl esters of fatty acids [1, 2]. Tranesterification of triglyceride (TG) with methanol (MeOH) to produce biodiesel or fatty acid methyl ester (FAME) and glycerol is as following equation:

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{Glyceride} & \quad \text{Alcohol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{O} & \quad \text{O} \quad \text{R} \\
\text{Glyceride} & \quad \text{Alcohol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{Glyceride} & \quad \text{Alcohol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{Glyceride} & \quad \text{Alcohol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{CH}_2\text{OH} & \quad \text{O} \quad \text{R} \\
\text{Glyceride} & \quad \text{Alcohol} \\
\end{align*}
\]

(1)
The most widely used vegetable oils for the production of biodiesel are taken from rape seeds, sunflowers, and soybeans [3]. In Thailand, the most available feedstock is palm oil.

Knowledge about the phase equilibrium in these systems is essential for better understanding of the process and improvement of the reaction rate, the selectivity of the desired product, and the separation process for the product mixture [4]. Moreover, simulations for developing new processes for such systems require an activity coefficient model that can adequately describe these multiphase systems. Some authors have used UNIFAC for describing similar systems [4].

In this study, we present a phase behavior of liquid-liquid equilibrium by using an activity coefficient model to predict the new processes developing, however it is not investigated in kinetic study. In this paper, the experimental results of phase behavior for the methanol + FAME + palm oil and that for FAME + palm oil + glycerol systems are presented. The UNIQUAC interaction parameters \( w, a_{ij} \) (with the combinatorial parameters \( r_i \) and \( q_i \), calculated by UNIFAC-Dortmund) were estimated from the mutual solubility data.

2. Materials and methodology

2.1. Chemical

Chemical used in this experiment were palm oil (> 99.5%), methanol (99.5%), glycerol (> 99.0%) and FAME obtained from Bioenergy Plus Ltd, in Thailand, the composition of FAME is shown in Table 1 and its density is 0.88 g.cm\(^{-3}\).

| Components         | Composition (mass %) |
|--------------------|----------------------|
| Palmitic Acid ME   | 52.88                |
| Stearic Acid ME    | 4.670                |
| Oleic Acid ME      | 33.98                |
| Linoleic Acid ME   | 8.050                |
| Linolenic Acid ME  | 0.420                |

2.2. The binodial curve study

The binodial curves for both systems were investigated and then the thermodynamic model was used to analyse the biodiesel system.

2.2.1. The binodial curves of methanol + FAME + palm oil

The phase boundary or the binodial curve was determined by turbidimetric analyzing using the titration method under isothermal conditions at 35, 45 and 55°C. The experiment was conducted in a water bath equipped with a temperature controller within a fluctuation of ± 0.1°C, and the measurement of each phase is as followings:

*Palm oil-rich phase*: titrate methanol with a microburet into mixture of palm oil and FAME while the mixture was stirred by a mechanical agitator. The end point where the mixture changed from transparent to turbid was considered to be the saturation point of methanol in palm oil + FAME solution. The amount of methanol dissolved in the palm oil + FAME solution was calculated from the volume of methanol used. The solubility of methanol was measured in different compositions of the palm oil + FAME solution, and the equilibrium data were plotted in the triangular graph.

*Methanol-rich phase*: palm oil was titrated into a mixture of methanol + FAME until the turbidity was observed as described in the procedure of *Palm oil-rich phase*. The solubility of palm oil in the methanol + FAME solutions was obtained for various compositions of methanol and FAME.

2.2.2. The binodial curves of FAME + palm oil + glycerol

The same procedures as those for the binodial curves of methanol + FAME + palm oil were used for FAME + palm oil + glycerol.
2.3. Tie lines developing for methanol + FAME + palm oil system
Mixtures of methanol, FAME, and palm oil with various concentrations were intensively agitated for 2 hours after that they were left until they reached the two-phase equilibrium. The mixture was kept in an isothermal water bath for 12 hours until the ternary mixture was separated into two phases. The upper phase was enriched with methanol, while the lower layer was enriched with palm oil. The upper phase, methanol and FAME contents were measured by gas chromatography and the lower phase was determined from material balance. After obtaining the composition of the palm oil-rich phase and the methanol-rich phase, the tie lines were obtained by plotting the data in the phase diagram and connecting the two points with beeline.

2.4. Thermodynamic correlations
The LLE calculation is basically defined by equation 2.

\[ \gamma_i^I x_i^I = \gamma_i^II x_i^{II} \]  \hspace{1cm} (2)

\[ F'w_i = F'^I w_i^I + F'^II w_i^{II} \]  \hspace{1cm} (3)

Where \( \gamma_i \) and \( x_i \) represent the activity coefficient and mole fraction of component \( i \) presented in both phases \( I \) and \( II \), respectively.

The NRTL and the UNIQUAC models [5] were then applied in this study to correlate the LLE data with the material balance shown in equation 3, \( w_i \) and \( F \) represent the total feed mass fraction of component \( i \) and the total mass feed, respectively. The binary interaction parameters of the NRTL and UNIQUAC models were calculated by using nonlinear regression analysis. The objective function used for correlating of experimental data was in the following form of equation 4.

\[ \sum_{k=1}^{N} \sum_{i=1}^{3} (x_{ik,cal} - x_{ik,exp})^2 + \sum_{k=1}^{N} \sum_{i=1}^{3} (y_{ik,cal} - y_{ik,exp})^2 \]  \hspace{1cm} (4)

where \( x_{ik} \) is the mole fraction of component \( i \) in methanol-rich phase for the number of tie line \( k \), \( y_{ik} \) is the mole fraction of component \( i \) in palm oil-rich phase for the number of tie line \( k \), and the subscript \( cal \) and \( exp \) refer to the calculated and experimental values of the liquid phase concentrations, respectively.

3. Results and discussion

3.1. The solubility curves
Table 2 shows experimental data of methanol + FAME + palm oil ternary system at temperature of 35, 45, and 55°C. The data were plotted on a triangular phase diagram (Figure 1) to represent behavior of partially miscible ternary system of methanol + FAME + palm oil at each temperature. Any mixture whose overall composition falls in area below the equilibrium curve separates into two liquid phases coexist, while a single liquid phase occurs above the solubility curve. Methanol-FAME pair and FAME-palm oil pair are completely mutually soluble to form binary solutions as shown at the edges of the triangular phase diagram, but methanol-palm oil pair is partially soluble in each other.

Table 3 shows experimental data of FAME + palm oil + glycerol ternary system at temperature of 35, 45, and 55°C. The triangular phase diagram of this system at each temperature is illustrated in Figure 2. Most mixture is formed two phases. The results reveal that the binodial curves of methanol + FAME + palm oil depend significantly with temperature while the binodial curves of FAME + palm oil + glycerol change insignificantly with temperature as shown in Figures 1 and 2, respectively.
Generally, polar molecules, such as methanol and glycerol, tend to have high solubility parameters for example dielectric constant of fluids, while a nonpolar molecule, such as palm oil and FAME, has low solubility parameters. As a rough approximation, substances with solubility parameters difference by 3 (cal/cm\(^3\))\(^{1/2}\) or more will generate two liquid phases [6]. In the system of FAME + palm oil + glycerol, glycerol has very high dielectric constant while FAME or biodiesel and palm oil have low dielectric constant. As a result, the different polarity between FAME and palm oil pair is not much and then they can completely dissolve while the difference between FAME-glycerol and palm oil-glycerol pairs are high, the coexist can be observed.

Table 2. Experimental compositions of Methanol+FAME+Palm oil system along the Binodal Curve based on mass fraction

|          | 35 °C |          | 45 °C |          | 55 °C |
|----------|-------|----------|-------|----------|-------|
| Palm oil | FAME  | Methanol | Palm oil | FAME  | Methanol | Palm oil | FAME  | Methanol |
| 0.9418   | 0.0000| 0.0582   | 0.9172 | 0.0000  | 0.0828   | 0.9080  | 0.0000| 0.0920   |
| 0.8836   | 0.0465| 0.0699   | 0.8645 | 0.0454  | 0.0901   | 0.8589  | 0.0452| 0.0959   |
| 0.8338   | 0.0925| 0.0737   | 0.8141 | 0.0904  | 0.0955   | 0.7984  | 0.0889| 0.1127   |
| 0.7335   | 0.1834| 0.0831   | 0.7172 | 0.1774  | 0.1054   | 0.7000  | 0.1750| 0.1250   |
| 0.6352   | 0.2715| 0.0933   | 0.6191 | 0.2637  | 0.1172   | 0.6022  | 0.2582| 0.1396   |
| 0.5337   | 0.3564| 0.1099   | 0.5204 | 0.3471  | 0.1325   | 0.5054  | 0.3369| 0.1577   |
| 0.4354   | 0.4319| 0.1327   | 0.4250 | 0.4252  | 0.1498   | 0.4081  | 0.4076| 0.1843   |
| 0.3363   | 0.5046| 0.1591   | 0.3236 | 0.4853  | 0.1911   | 0.3078  | 0.4612| 0.2310   |
| 0.2402   | 0.5605| 0.1994   | 0.2735 | 0.5078  | 0.2188   | 0.2744  | 0.4743| 0.2513   |
| 0.1056   | 0.5778| 0.3166   | 0.2247 | 0.5241  | 0.2513   | 0.2056  | 0.4798| 0.3147   |
| 0.0892   | 0.5487| 0.3621   | 0.1328 | 0.5225  | 0.3447   | 0.2104  | 0.4757| 0.3139   |
| 0.0742   | 0.5169| 0.4089   | 0.1208 | 0.4907  | 0.3885   | 0.1762  | 0.4597| 0.3641   |
| 0.0593   | 0.4825| 0.4582   | 0.0929 | 0.4652  | 0.4419   | 0.1324  | 0.4449| 0.4227   |
| 0.0523   | 0.4247| 0.5230   | 0.0733 | 0.4153  | 0.5113   | 0.1069  | 0.4002| 0.4929   |
| 0.0333   | 0.3891| 0.5777   | 0.0590 | 0.3796  | 0.5614   | 0.0812  | 0.3698| 0.5490   |
| 0.0212   | 0.3484| 0.6304   | 0.0436 | 0.3405  | 0.6159   | 0.0609  | 0.3342| 0.6049   |
| 0.0179   | 0.2910| 0.6911   | 0.0223 | 0.2898  | 0.6879   | 0.0344  | 0.2861| 0.6796   |
| 0.0154   | 0.2457| 0.7389   | 0.0092 | 0.2000  | 0.7908   | 0.0120  | 0.1993| 0.7887   |
| 0.0092   | 0.1998| 0.7909   | 0.0055 | 0.0985  | 0.8961   | 0.0091  | 0.0983| 0.8927   |
| 0.0046   | 0.0985| 0.8969   | 0.0005 | 0.0000  | 0.9995   | 0.0005  | 0.0000| 0.9995   |
| 0.0005   | 0.0000| 0.9995   |        |         |          |         |       |          |
Table 3. Experimental compositions of FAME+Palm oil+Glycerol system along the Binodal Curve based on mass fraction

|       | 35 °C  |       | 45 °C  |       | 55 °C  |
|-------|--------|-------|--------|-------|--------|
| Glycerol | 0.9968 | Palm oil | 0.0032 | FAME  | 0.9975 | Glycerol | 0.0025 | Palm oil | 0.0000 | FAME  | 0.9977 | Glycerol | 0.0023 | Palm oil | 0.0000 |
| 0.9987 | 0.0000 | 0.0000 | 0.9887 | 0.0000 | 0.0013 | 0.9991 | 0.0000 | 0.0009 |
| 0.0016 | 0.0000 | 0.0000 | 0.9984 | 0.0000 | 0.0000 | 0.9984 | 0.0013 | 0.0000 | 0.9987 |
| 0.0019 | 0.00105| 0.0019 | 0.8976 | 0.0004 | 0.1004 | 0.8977 | 0.0025 | 0.0998 | 0.8977 |
| 0.0038 | 0.0025 | 0.0025 | 0.2987 | 0.0025 | 0.2995 | 0.6980 | 0.0019 | 0.2995 | 0.6986 |
| 0.0025 | 0.0025 | 0.0025 | 0.3990 | 0.0031 | 0.3990 | 0.5979 | 0.0025 | 0.3989 | 0.5986 |
| 0.0025 | 0.4986 | 0.4989 | 0.0025 | 0.4986 | 0.4989 | 0.4989 | 0.0025 | 0.4990 | 0.4985 |
| 0.0031 | 0.5981 | 0.3988 | 0.0025 | 0.5985 | 0.3990 | 0.5985 | 0.0025 | 0.5985 | 0.3990 |
| 0.0050 | 0.6967 | 0.2983 | 0.0044 | 0.6959 | 0.2997 | 0.0019 | 0.6986 | 0.2996 |
| 0.0044 | 0.7914 | 0.2042 | 0.0025 | 0.7973 | 0.2002 | 0.0019 | 0.7985 | 0.1996 |
| 0.0038 | 0.8967 | 0.0995 | 0.0025 | 0.8978 | 0.0997 | 0.0025 | 0.8977 | 0.0998 |
| 0.0041 | 0.9959 | 0.0000 | 0.0044 | 0.9956 | 0.0000 | 0.0044 | 0.9956 | 0.0000 |

Figure 1. The binodial curves of methanol + FAME + palm oil system based on mass fraction: ●; 35°C, ○; 45°C and ▼; 55°C.

Figure 2. The binodial curves of FAME + palm oil + glycerol system based on mole fraction: ●; 35°C, ○; 45°C and ▼; 55°C.
3.2. Tie lines
The lines connect phases in equilibrium with each other shown in phase diagram are called tie lines, the binodial curve with tie lines for methanol + FAME + palm oil system at 45°C is shown in Figure 3. However, the system of FAME + palm oil + glycerol, only the binodial was constructed without experimental tie lines due to its immiscible property. Two tie lines connect between two equilibrium compositions as open circle shown in Figure 3, as one can see, one tie line agrees well on the equilibrium curve while the other one shows a bit difference. The tie lines calculated by UNIQUAC Dortmund were used to verify experimental tie lines, and it was found that they agreed quite well. Therefore, the equilibrium curves and tie lines obtained from experimental data at various temperatures were used to evaluate the thermodynamic parameters for LLE of these two systems in section 3.3.

3.3. Activity coefficient model
The volume ($r$) and surface area ($q$) obtained from the UNIFAC-Dortmund [7, 8] are used to optimize values of model parameters by minimization method from equation 4 [9]. The $r$ and $q$ parameters of the NRTL and UNIQUAC models for each component are listed in Table 4. The interaction parameters of mutual solubility of the UNIQUAC model at 35, 45 and 55°C for these two systems are listed in Table 5 and Table 6.

| Components | $r_i$    | $q_i$    |
|------------|---------|---------|
| FAME       | 11.3629 | 13.3311 |
| Palm oil   | 34.3817 | 32.3022 |
| Glycerol   | 5.5881  | 4.4497  |
| Methanol   | 0.8585  | 0.9938  |
4. Conclusions
For the ternary mixture of methanol + FAME + palm oil system, the solubility curves change significantly with temperature in the range from 35°C to 55°C. On the other hand, the equilibrium curves for ternary mixture of FAME + palm oil + glycerol system change insignificantly with temperature and this is due to the polar properties of liquids. The activity coefficient models obtained from the UNIQUAC and NRTL model are used to correlate with the tie lines obtained from experimental data. They agree quite well, although some fluctuation can be observed.

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