Isobaric vapor-liquid equilibrium of methanol + glycerol binary mixture at 31.3 kPa

M A Batutah, K Kuswandi and G Wibawa

Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology (ITS), Kampus ITS Surabaya 60111. Indonesia
gwibawa@chem-eng.its.ac.id

Abstract. In this study the binary vapor-liquid equilibrium (VLE) data of methanol + glycerol system were determined experimentally using modified Glass Otther - Still. The equilibrium compositions of liquid and vapor phases were analysis using refractometer index type Bausch and Lomb ABBE. The experimental data obtained in this work were thermodynamically consistent based on the area test. The experimental data were correlated well with the Wilson and Non Random Two Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) models. The performance of Universal Chemical Functional Group Activity Coefficients (UNIFAC) in predicting VLE of the system studied were evaluated as well.

Keywords: vapor - liquid equilibrium, methanol, glycerol

1. Introduction

In the biodiesel production, process of transesterification, hydroesterification, enzymatic transesterification and supercritical transesterification process have been applied. However, transesterification is the most utilized process[1,2]. Transesterification refers to a chemical reaction of oil or fat with an excess of alcohols in the presence of a homogeneous or heterogeneous catalyst to yield biodiesel and glycerol [3,4]. After cooling to room temperature, the glycerol layer settles to the bottom and the ester-rich phase (FAME) forms the upper layer [5,6]. Separation of glycerol and unreacted alcohol is carried out to recover alcohol that may be recycled to transesterification reactor [7], where glycerol-rich phase will be further processed to produce crude glycerol. In the transesterification reaction, the glycerol is considered as commercial byproduct that may be used in food, pharmacy and cosmetics industries [8]. In order to rational design and optimize the glycerol production process, the VLE data for the binary system of alcohol + glycerol are required.

In the literatures the isobaric binary VLE data of alcohol + glycerol system have been published by several researchers [9-17]. The VLE data for this system at high temperature of 493–573 K were measured isothermally by Shimoyama et al. [12]. For higher chain alcohols, Oliveira et al. [9] measured the VLE data of 1-propanol + glycerol at atmospheric pressure with limited mole fractions ranges of (0.0418 to 0.4410). The VLE data for two binary systems of ethanol + glycerol and 2-propanol + glycerol have been measured at the temperatures of (323.15 and 333.15) K and (333.15 and 343.15) K, respectively by Wibawa et al. [13]. Heron et al. [14] measured Isobaric VLE data (P-T-W) where phase behaviors for three ternary systems (methanol + glycerol + methyl laurate/methyl myristate/methyl palmitate) were studied at elevated temperatures (about 493.0 K, 523.0 K) and pressures by a flow-type method. Saujanya et al. [16] the VLE data (T-x-y) behavior of the quaternary system, Methanol + Isopropyl alcohol (IPA) + Water + Glycerol (4) at 53.33, 66.66, 79.99 and 95.2 kPa has been studied experimentally using a Sweitoslawsky-type ebulliometer. Caroline et al. [17] measured experimentally VLE (P-x) of ethanol + glycerol and tertbutanol + glycerol systems using a static synthetic method over the temperature range of 423–523 K.
In this present study, the isobaric VLE data \((T-x-y)\) were measured using modified Glass Othmer-Still for binary systems of methanol + glycerol over the entire composition range at the constant pressure 31.3 kPa. The experimental data were correlated with the Wilson [18], NRTL [19] and UNIQUAC [20]. The performance of UNIFAC model [21] were studied as well.

2. Experimental apparatus and methods

2.1. Material
All material used in this work such as methanol and glycerol were supplied by Merck (Germany) and used without additional purification. The properties of each material are presented in Table 1.

| Component | Mass fraction purity | MW (g.mol\(^{-1}\)) | Boiling point (K) | Density (g.cm\(^{-3}\)) |
|-----------|----------------------|---------------------|-------------------|-----------------------|
| Methanol  | 0.999                | 46.069              | 351.80\(_a\)      | 0.78515\(_b\)         |
| Glycerol  | 0.995                | 92.095              | 563.00\(_c\)      | 1.25780\(_d\)         |

\(^a\) reference [23].
\(^b\) reference [24].
\(^c\) reference [25].
\(^d\) reference [26].

2.2. Apparatus and procedures
The VLE data were measured using a glass Glass Ohmber – Still [22]. Modified in this work as shown in Figure 1. The modified glass othmer still was made by flattening the bottom of ebulliometer so that the stirrer may be installed in order to mix homogeneously alcohol and glycerol solutions since the solutions is viscous. The experimental apparatus consist of 200 ml ebuliometer still, condenser, heating control system, two temperature sensors and indicators, pressure indicator and control, equipped with two sample ports to collect liquid and vapor phase samples. The pressure was controlled using a sensitive needle valve and was kept at a constant pressure with a precession of \(\pm 0.3 \text{ kPa}\). The solution was inserted into equilibrium cell and all valves were closed and heater system was turn on. Three hours after the equilibrium was achieved, the liquid phase and vapor phase samples were taken from sample ports (C1) and (C2) to be analyzed its composition using the Bausch and Lomb type refractometer ABBE. The equilibrium temperature is measured by Sokitech RTD 100 with diameter of 6 mm. the experiment was repeated for other compositions so that the composition range between 1 and 100% mole was obtained.

3. Result and Discussion
The VLE data obtained in this work for the binary system of methanol + glycerol at 31.3 kPa is listed in Table 2, the data presented in T-x-y diagram as shown in Figure3.

| \(T/K\)  | \(x_i\) | \(y_i\) | \(x_i\) | \(y_i\) |
|---------|--------|--------|--------|--------|
| 351.55  | 1.000  | 1.000  | 361.75 | 0.506  | 0.992  |
| 352.35  | 0.941  | 0.992  | 369.65 | 0.437  | 0.988  |
| 355.45  | 0.838  | 0.992  | 375.85 | 0.256  | 0.988  |
| 356.75  | 0.760  | 0.992  | 400.45 | 0.068  | 0.983  |
| 360.05  | 0.674  | 0.992  | 425.75 | 0.043  | 0.978  |

The experimental data were thermodynamically consistent based on Herrington test [27]. Presentation of the area test as shown in Figure 2 and Table 3. As shown in the Table 3 the value of \([D-J]\) is found to be less than 10% as the result, the experimental data obtained in this work are thermodynamically consistent.
Figure 1. Schematic diagram of experimental apparatus modified Glass Othmer – Still, (A) Ebulliometer Still, (B) Condenser, (C) sample ports, (D) Condensate Chamber, (H) Heater, (T) Thermocouple, (M) Magnetic Stirrer, (P) Pressure Indicator

Figure 2. Consistency of Herington test for methanol + glycerol

\[ D = 100 \frac{\int_0^1 \ln(y_1/y_2)dx}{\int_0^1 \ln(y_1/y_2)dx} \]  
(1)

\[ J = 150 \frac{T_{max} - T_{min}}{T_{min}} \]  
(2)
Where \( T_{\text{max}} \) and \( T_{\text{min}} \) represent the maximum and minimum temperatures in this study.

**Table 3. Thermodynamic Consistency Test with Herrington Method.**

| System            | Consistency Test |
|-------------------|------------------|
| Methanol + glycerol| 93.90961 101.94066 8.03105 Consistent |

The experimental VLE data were correlated with Wilson, NRTL, UNIQUAC models, the relationship of vapor and liquid phases in equilibrium is described as follows:

\[
y_i, \Phi_i, P = x_i, y_i P_{\text{sat}}
\]  

(3)

Where \( y_i, x_i, \Phi_i, y_i \) and \( P \) refer to vapor phase composition, liquid phase composition, fugacity coefficient, activity coefficient and equilibrium pressure, respectively. Since the pressure is less than 1 atm, the gas phase may be assumed to be ideal behavior then \( \Phi_i = 1 \).

The experimental data were correlated well with Wilson, NRTL and UNIQUAC models where binary parameter of each equation were determined by minimize the objective equation shown in equation (4). The parameters obtained in this work were listed in Table 4. Comparison between experimental data and correlated are presented in Figure 3.

**Figure 3. VLE phase (T-x-y) plots for binary system of methanol + glycerol at 31.3 kPa**

\[
OF = \sum \left( \frac{y_i^{\text{exp}} - y_i^{\text{cal}}}{y_i^{\text{exp}}} \right)^2 + \left( \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right)^2
\]

(4)

Where \( N \) is the number data points and the subscripts exp and cal refer to experimental and calculated values, respectively.

**Table 4. Fitted binary interaction parameters of activity coefficient models and Average Absolute Deviations (AAD) for binary system of methanol + glycerol at 31.3 kPa.**
The UNIFAC method is a prediction method that does not require experimental data [21], which is a development of the UNIQUAC model by modifying the interaction between components into interactions between functional groups making up the system. In this study the prediction method was used to obtain vapor-liquid equilibrium data for the binary system of methanol + glycerol at a pressure of 31.3 kPa. The performance of predictive UNIFAC model in predicting VLE of methanol + glycerol system at 31.3 kPa give satisfactory result with 3.1% AAD in temperatures.

| Method   | A12     | A11     | T%     | y%     |
|----------|---------|---------|--------|--------|
| Wilson   | -1107.587 | 257.543 | 0.12   | 0.001  |
| NRTL     | -170.050  | 1013.945 | 0.19   | 0.001  |
| UNIQUAC  | 605.835  | 4501.625 | 0.27   | 0.001  |

Figure 5. Plots for T-x-y prediction UNIFAC for the mixture methanol + glycerol at 31.3 kPa.

4. Conclusions
The isobaric VLE data were measured experimentally for the binary system of methanol + glycerol at 31.3 kPa by using modified Othmer recirculation still. The experimental data were correlated well with the Wilson, NRTL, and UNIQUAC, predictive UNIFAC model is satisfactory for predictive VLE of this system studied.

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