

Vapor-Liquid Equilibrium Measurement of Systems Containing Glycerol for Separation Process of Glycerol as a By-Product of Biodiesel

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Abstract. The most popular technique to produce biodiesel were uses alcohol as a catalyst to transesterify triglycerides. The biodiesel transesterification process has a by-product in the form of glycerol which has a high selling value. Equilibrium data of glycerol and alcohol mixtures is limited in equilibrium conditions and systems which causes the glycerol purification process may not be designed and operated optimally. This research aims to obtain experimentally isobaric vapor-liquid equilibrium of methanol + glycerol binary system at 31.3, 61.3, and 100.8 kPa. A modified Glass Othmer-Still was utilised to carry out the experiment. Refractometer index type Bausch and Lomb ABBE was used to examine the equilibrium composition of the liquid and vapor phases. Using the *L-W thermodynamic consistency test* method, the experimental data used in this work were shown to be thermodynamically consistent. The experimental data were correlated well with the Wilson, Non-Random Two Liquid (NRTL), and Universal Quasi-Chemical (UNIQUAC) models with absolute average deviation in temperatures (AADT) and that in vapor compositions (AADy) smaller than 0.3% and 0.2%, respectively. The Universal Chemical Functional Group Activity Coefficient (UNIFAC) in predicting VLE the system studied showed good performance giving AADT and AADy smaller than 7.4% and 0.04%, respectively.

1 Introduction

The increase in population has resulted an increase of petroleum which is expected to continue continuously so that energy reserves are increasingly depleted and petroleum fuel is increasingly scarce. This has led to the development of various alternative energy sources such as solar energy, geothermal energy, water energy and various other energies [1]. Indonesia has the ability to create biodiesel as one alternative energy source. As an alternative fuel for diesel engines, biodiesel is a fuel generated from renewable resources like vegetable and animal oils. It is composed of a blend of mono-alkyl esters from long chain fatty acids [2]. Blending, microemulsion, pyrolysis, and transesterification are the four primary processes used to produce biodiesel. The most popular technique uses alcohol as a catalyst to transesterify triglycerides (plant oils and animal fats). The alcohols that commonly used are methanol, ethanol, propanol, butanol and amyl alcohol [3].

Biodiesel resulting from transesterification still contains water components and other impurities, so a separation process needs to be carried out. Separation is intended to separate biodiesel from its by-product (crude glycerol) and is also used to recover methanol/alcohol contained in biodiesel. The chemical process that is often used to purify crude glycerol is the distillation process. In designing the distillation process, it is

necessary to have vapor-liquid equilibrium (VLE) data between the components [4].

Some previous research was researched the vapor-liquid equilibrium for binary systems of water + glycerol and ethanol + glycerol, ethyl stearate, and ethyl palmitate at low pressure using an Othmer-type ebulliometer at 14 kPa to 96 kPa [5]. Wibawa et al. [6] conducted experiments using a modified ebulliometer to find the vapor-liquid equilibrium of the binary systems ethanol + glycerol and 2-propanol + glycerol at temperatures of 323.15 K, 333.15 K, 343.15 K. Wiguno et al. [7] carried out vapor-liquid equilibrium measurements of the binary systems methanol + glycerol and 1-propanol + glycerol under isothermal conditions with a temperature range of 313.15 K – 363.15 K using modified Othmer type Ebulliometer. Batutah et al. [8] carried out isobaric vapor-liquid equilibrium measurements of binary systems ethanol + glycerol, 1-propanol + glycerol at 16 and 101.3 kPa. Mustain et al. [9] examined vapor-liquid equilibrium under isothermal conditions of 1-butanol + glycerol and 2-methyl-1-propanol + glycerol systems.

This research was conducted to experiment and predict the vapor-liquid equilibrium in isobaric conditions of methanol + glycerol binary system at 31.3, 61.3, and 100.8 kPa using a modified Othmer-still type glass ebulliometer, refractometer index type Bausch and Lomb ABBE was used to analyse the equilibrium

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composition of the vapor and liquid phases based on experimental data, experimental data were correlated with the Wilson [10], NRTL (*Non-Random Two Liquid*) [11], UNIQUAC (*Universal Quasi-Chemical*) [12] models and UNIFAC (*Universal Chemical Functional Group Activity Coefficient*) predictions and presented in the form of T-x-y.

The knowledge obtained from this research is in the form of experimental data and thermodynamic model parameters, which are very useful in increasing the content/purification of glycerol for biodiesel development in Indonesia. Biodiesel as a fuel has several advantages, including being renewable and environmentally friendly. With the knowledge developed, it can reduce glycerol imports or save the country's foreign exchange.

2 Experimental Section

2.1 Material

The glycerol and methanol utilised in this experiment were obtained from MERCK and were not subjected to any additional purification procedures. Pure component data from the system used is presented in **Table 1** as follows:

Table 1. Properties of Chemicals used in Research

Component	Purity*	MW** g.mol ⁻¹	Boiling Point /K	Density g.cm ⁻³
Methanol	0.999	32.04	337.93	0.78659
Glycerol	0.995	92.09	563.00	1.25780

*Purity from supplier without additives

**MW = Molecular Weight

2.2 Apparatus and Procedures

Modified Othmer-Still Distillation was utilised as the primary apparatus for measuring the vapor-liquid equilibrium data, this equipment consist of (RV 1 and RV 2) Heating source, (BC) Boiling Chamber, (CON) Condensor, (SP X) Sample Ports Liquid, (SP Y) Condensate chamber, (EH) Heater, (TI 1 and TI 2) Temperature Indicator liquid and vapor, (S) Magnetic stirrer, (PI) Pressure Indicator, (V) Control valve, (P) Vacuum pump as depicted in **Figure 1**.

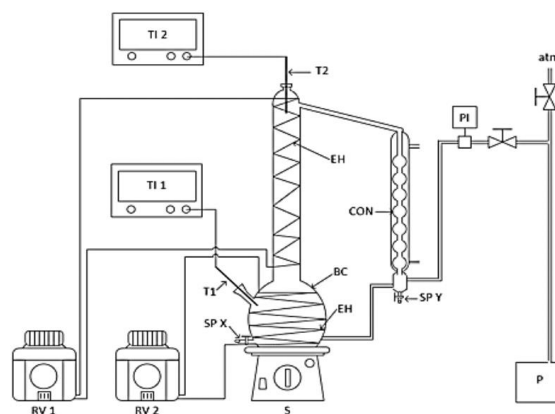


Fig. 1. Schematic of Modified Othmer Still Distillation Equipment

This research began by validating equipment using pure methanol. After validating the equipment, carried out research on vapor-liquid equilibrium of a mixture 200 mL of methanol + glycerol for various compositions (binary system) and put it into the boiling chamber (BC) of the othmer still distillation. Determine the atmospheric or vacuum experimental pressure by turning on the vacuum pump (P) and adjusting the pressure precision so that it accurately matches the specified pressure (31.3 kPa, 61.3 kPa or 100.8 kPa) by adjusting the needle valve (V). Next, the magnetic stirrer (S) was turned on to stir the solution until it becomes homogeneous. Then, SRR (RV 1, RV 2) as a heating source was turned on. Heating by SRR (RV 1, RV 2) which was delivered via the heating cable (EH) causes some of the liquid to evaporate and the steam from the heating will enter the condenser (CON) to condense the resulting steam into the liquid sample port (SP X). The system temperature was read by the temperature indicator (TI 1 and TI 2), and the pressure reading was read by the pressure indicator (PI). The system was run and left for approximately 3-4 hours until it reaches equilibrium. The equilibrium state was indicated by the temperature of the liquid (TI 1) and vapor (TI 2) being the same and stable and not experiencing changes in temperature. Once it balanced, the heating system (RV 1, RV 2) was turned off and wait for the solution temperature same with room temperature. The liquid phase samples in sample port (SP X) and vapor phase samples in sample port (SP Y) were analysis by refractometer index type Bausch and Lomb ABBE. The experiment was repeated for different compositions with a composition ratio of 10- 90% alcohol and glycerol. The equilibrium data obtained will be correlated using the Wilson, NRTL, and UNIQUAC equations as well as UNIFAC predictions.

3 Result and Discussion

Table 2. VLE Data for Binary System of Methanol + Glycerol at 31.3 kPa, 61.3 kPa and 100.8 kPa

P = 31.3 kPa			P = 61.3 kPa			P = 100.8 kPa		
T/K	x ₁	y ₁	T/K	x ₁	y ₁	T/K	x ₁	y ₁
312.48	0.7806	0.9999	328.65	0.8896	0.9999	340.15	0.8996	1
313.11	0.7298	0.9999	332.25	0.7618	0.9999	343.95	0.8006	0.9999
314.76	0.6198	0.9999	334.25	0.6953	0.9999	346.85	0.7003	0.9999

317.00	0.5089	0.9999	338.15	0.5937	0.9999	352.35	0.5993	0.9999
320.11	0.4010	0.9999	341.95	0.5120	0.9999	355.75	0.5174	0.9999
324.15	0.3058	0.9999	351.25	0.3759	0.9999	364.35	0.4009	0.9999
331.48	0.2007	0.9999	355.65	0.3214	0.9999	373.15	0.3020	0.9999
344.19	0.1095	0.9999	369.25	0.2015	0.9999	382.75	0.2369	0.9999
			391.55	0.1054	0.9999	410.25	0.1095	0.9999

uncertainty $u(T) = 1.5$ K, $u(x) = 0.002$, $u(y) = 0.002$ and $u(P) = 0.2$ kPa, where $u(T)$, $u(x)$, $u(y)$ dan $u(P)$ is uncertainty temperature, liquid mole fraction, vapor mole fraction and pressure.

The VLE data for the binary system of methanol and glycerol at 31.3 kPa, 61.3 kPa, and 100.8 kPa is listed in **Table 2**. In this study, equilibrium measurements of the binary system were not carried out for fractions close to zero ($x_1 \rightarrow 0$). This is caused by very high temperature of the glycerol vapor.

Using the *L-W test* method, which Wisniak devised, the consistency of the generated experimental data was examined [13], by plotting the experimental G^E/RT against the liquid composition (x_i). According to Wisniak, the Redlich-Kister expansion trend line is arranged so that it matches or represents the experimental G^E/RT distribution data. The following equation was used to analyse the thermodynamic consistency data test

$$G^E = RT \sum x_i \ln \frac{y_i}{x_i} + \sum x_i \Delta S_i^{\text{sat}} (T_i^{\text{sat}} - T) \quad (1)$$

$$L_i = \left[\sum x_i \frac{\Delta S_i^{\text{sat}}}{\Delta S} T_i^{\text{sat}} - T \right] = \left[\frac{g^E}{\Delta S} - \frac{RT}{\Delta S} \omega \right] = w_i \quad (2)$$

where $\Delta S = \sum x_i \Delta S_i^{\text{sat}}$ and $\omega = \sum x_i \ln y_i / x_i$. This method involved analysing the parameters L_i and W_i using the entropy of vaporisation. The consistency of the data was demonstrated by the deviation, which could be computed after both parameters were obtained. According to Batutah [8], if the requirement $0.92 < L_i/W_i < 1.08$ is met, the experimental data are thermodynamically consistent or adhere to the Gibbs-Duhem equation. **Table 3** displays the thermodynamic consistency results. The experimental data were found to be thermodynamically consistent, as indicated by the table.

Table 3. Thermodynamic Consistency Test with the L-W Test of Wisniak

System	Pressure, kPa	$0.9 < \frac{L_i}{W_i} < 1.08$	Consistance
Methanol + Glycerol	31.3	0.9834	Consistent
	61.3	1.0048	Consistent
	100.8	0.9866	Consistent

Experimental data from **Table 3** can be processed further to obtain the interaction parameters of the Wilson, NRTL, and UNIQUAC equations. This data can be used for designing distillation processes and the basis for purifying alcohol and glycerol as a by-product of the biodiesel industry [14].

The experimental data that has been obtained and tested for consistency is then correlated with Wilson, NRTL, and UNIQUAC equations. Correlation of experimental data using the three models aims to obtain optimal parameter values for each type of model, to obtain interaction parameters by carrying out an Objective Function with the NRG-Nonlinear method with the minimum possible difference values as shown in the equation

$$OF = \sum_{i=1}^N \left(\frac{y_1^{\text{exp}} - y_1^{\text{cal}}}{y_1^{\text{exp}}} \right)^2 + \left(\frac{y_2^{\text{exp}} - y_2^{\text{cal}}}{y_2^{\text{exp}}} \right)^2 \quad (3)$$

N denotes the total number of data points and subscripts, while the exp and cal stand for experimental and calculated values, respectively.

Wilson and UNIQUAC equations contain two parameters, while NRTL contains three parameters. Form the experimental and modelling data, the Absolute Average Deviation (AAD) of each model can be calculated from the experimental results. AAD T and AAD y were calculated based on the following equation

$$AADT = \frac{1}{n} \sum_{i=1}^n \left| \frac{T_{\text{cal}} - T_{\text{exp}}}{T_{\text{exp}}} \right| \times 100\% \quad (4)$$

$$AADy = \frac{1}{n} \sum_{i=1}^n \left| \frac{y_{\text{cal}} - y_{\text{exp}}}{y_{\text{exp}}} \right| \times 100\% \quad (5)$$

Equilibrium conditions were conditions when a system does not experience a tendency to change macroscopically. This is indicated by the absence of changes in pressure, temperature or composition of the system. Under equilibrium conditions, the fugacity of the vapor phase was the same as the fugacity of the liquid phase in component i (isofugacity). After the parameters were obtained for each system, Wilson, NRTL, and UNIQUAC correlation parameters were further obtained by processing the data, and the outcomes are displayed in **Table 4**.

Table 4. Binary Interaction Parameters of Wilson, NRTL, UNIQUAC and UNIFAC Equations

Correlation model	Interaction parameter			AAD T (%)	AAD y (%)
	A_{12}^*	A_{21}^*	α		
$P = 31.3$ kPa					
Wilson	530.80	786.24	0.3	0.12	0.15
UNIQUAC	-16.12	611.45		0.27	0.01
NRTL	1104.56	-94.97		0.19	0.01
UNIFAC	-	-		7.40	0.01
$P = 61.3$ kPa					
Wilson	-4.98	239.76	0.3	0.09	0.01
NRTL	-375.20	-281.21		0.09	0.02
UNIQUAC	-181.65	424.91		0.13	0.02
UNIFAC	-	-		6.30	0.02
$P = 100.8$ kPa					
Wilson	387.12	-479.77	0.3	0.12	0.25
NRTL	-299.75	-233.62		0.11	0.03
UNIQUAC	-230.50	461.79		0.21	0.04
UNIFAC	-	-		5.70	0.04

* A_{12}, A_{21} were the interaction parameters :

Wilson ; $\Lambda_{12}, \Lambda_{21}$
 NRTL ; $\Delta g_{12}, \Delta g_{21}, a_{12}$
 UNIQUAC ; $\Delta u_{12}, \Delta u_{21}$

According to the **Table 4**, AAD T and AAD y were less than 0.5% after the experimental data were satisfactorily fitted by three correlated equations. The comparison of the T-x-y data with the associated ones is shown in **Figure 2, 3, and 4**, respectively. T-x data modelling the Wilson, NRTL and UNIQUAC equation were close to

the experimental results. This shows that Wilson, NRTL and UNIQUAC modelling have accurate results. The vapor phase composition was found to be near to 1, as the differences in boiling temperatures between glycerol and methanol were sufficiently large.

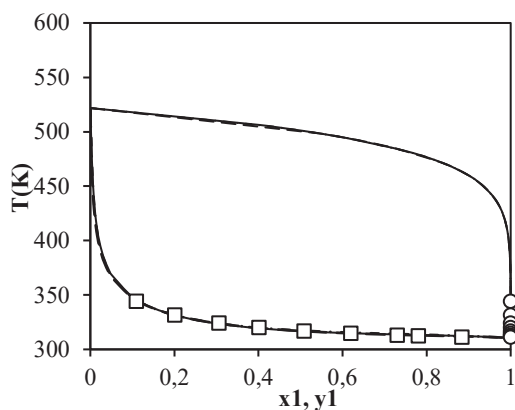


Fig. 2. The methanol + glycerol system at 31.3 kPa, the binary VLE (T-x-y) graph shown: (□), T-x, for experimental data; (○) T-y for experimental data; (---), Wilson equation; (- · -), NRTL equation; (—), UNIQUAC equation.

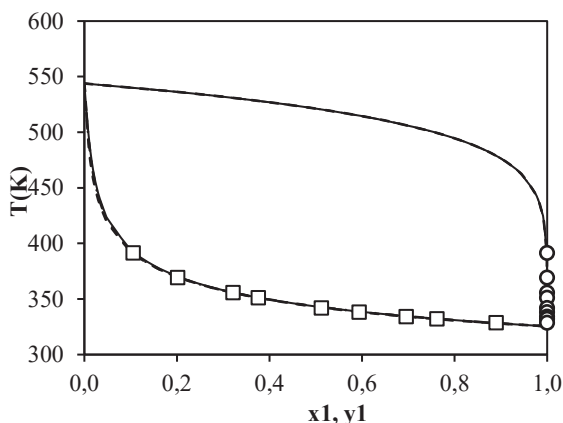


Fig. 3. The methanol + glycerol system at 61.3 kPa, the binary VLE (T-x-y) graph shown: (□), T-x, for experimental data; (○) T-y for experimental data; (---), Wilson equation; (- · -), NRTL equation; (—), UNIQUAC equation.

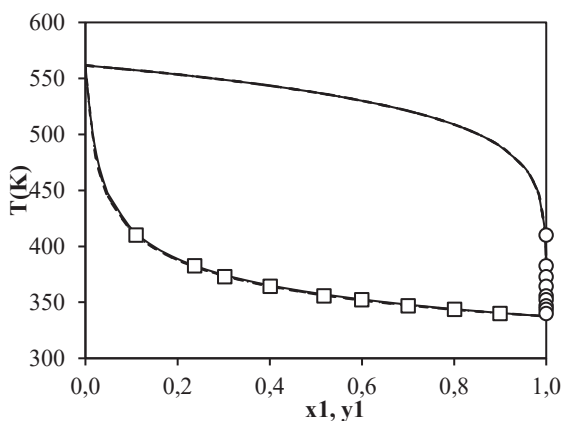


Fig. 4. The methanol + glycerol system at 100.8 kPa, the binary VLE (T-x-y) graph shown: (□), T-x, for experimental

data; (○) T-y for experimental data; (---), Wilson equation; (- · -), NRTL equation; (—), UNIQUAC equation.

In this study, it was noted that the UNIFAC equation performed well at predicting data. The liquid phase activity coefficient at moderate pressure and temperature can be predicted using the simplest vapor-liquid equilibrium prediction method, UNIFAC [15]. The group volume, area parameters, and group interaction data from the UNIFAC equation that were employed in this investigation are displayed in **Table 5**.

Table 5. UNIFAC Group Identification

Molecule	Group Identification			V _k	R _k	Q _k
	Group	Main	Secondary			
Methanol	CH ₃ OH	6	15	1	1.4311	1.432
Glycerol	CH ₂	1	2	2	0.6744	0.540
	CH	1	3	1	0.4469	0.228
	OH	5	14	3	1.0000	1.200

Information:

V_k = the number of species that belong to the same group

R_k = Parameter of volume

Q_k = Parameter of area

As shown in **Table 4**, the prediction results were compared with the experimental data. Based on these data, the prediction results using UNIFAC equation gave quite good results because they were still below <10%. UNIFAC equation on average provides an accuracy of less than 20% when compared with experimental data and can be used as an extension of data for mixtures. Apart from that, UNIFAC equation also good for nonelectrolyte solutions and mixtures with different types of distribution groups. Results from the UNIFAC approach are displayed on a T-x-y graph are shown in **Figure 5**. The resulting values of AADT and AADy were 7.4% and 0.01% for pressure 31.3 kPa, 6.3% and 0.02% for pressure 61.3kPa, and 5.7% and 0.04% for pressure 100.8 kPa.

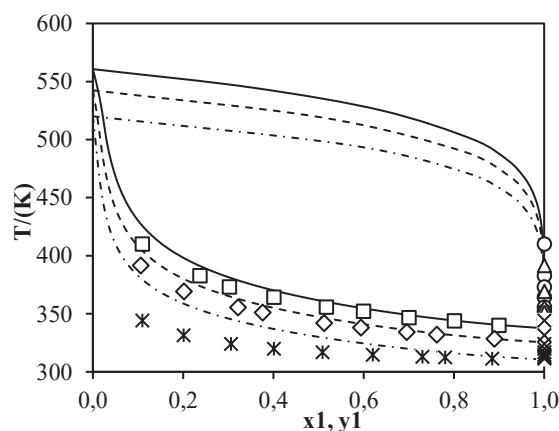


Fig. 5. T-x-y graph of the binary system methanol + glycerol at 31.3, 61.3 and 100.8 kPa; (*), T-x experimental data at 31.3 kPa; (x), T-y experimental data at 31.3 kPa; (◇), T-x experimental data at 61.3 kPa; (△), T-y experimental data at 61.3 kPa; (□), T-x experimental data at 100.8 kPa; (○), T-y

experimental data at 100.8 kPa; (-·-·), T-x-y UNIFAC method at 31.3 kPa; (---), T-x-y UNIFAC method at 61.3 kPa; and (—), T-x-y UNIFAC method at 100.8 kPa.

The results obtained were differences between the predicted results and the experimental results of T-x, but they were still below AAD 10%, while for T-y below 1%, this shows that the experimental data predicted with UNIFAC equation was acceptable but the average absolute deviation (AAD) higher compared to Wilson, NRTL and UNIQUAC equations. The relationship between glycerol by-products and energy reduction in the biodiesel distillation process can occur based on glycerol composition. This is because the purity level of the glycerol produced varies depending on the production method used, such as the efficiency of the distillation process. Understanding how this relationship can occur in a particular research or industry context requires further study and analysis.

4 Conclusion

Based on the *L-W test* method, the experiment of vapor-liquid equilibrium under isobaric circumstances of the binary system of methanol + glycerol at 31.3, 61.3, and 100.8 kPa using a modified Othmer-Still was shown to be thermodynamically consistent. Absolute average deviation in temperatures (AADT) and that in vapor compositions (AADy) were less than 0.3% and 0.2%, respectively, in Wilson, NRTL (*Non-Random Two Liquid*), and UNIQUAC (*Universal Quasi-Chemical*) models the experimental results showed well correlations with these models. The UNIFAC (*Universal Chemical Functional Group Activity Coefficient*) in predicting VLE of the system studied showed a good performance with AADT and AADy smaller than 7.4% and 0.04%, respectively.

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