Prediction of Ternary Vapor-Liquid Equilibria for Alcohols + Glycerol + Water Systems to Enhance the Quality of Glycerol as Biodiesel Side Product

Eviana D. Setiawati[1], Asalil Mustain[1], Gede Wibawa[1]

Abstract – Fossil fuels as the primary energy resources around the world cause significant negative effect on atmosphere. Recently, biodiesel, which primarily produced from renewable resources, has received great attention because of its environmental benefits. Higher chain of alcohols, such as butanol, may be used as solvent to produce biodiesel with glycerol as byproduct. In order to enhance the quality of glycerol as biodiesel side product which meets food and pharmaceutical standards, vapor-liquid equilibria (VLE) data for ternary systems consisting of 1-butanol, 2-methyl-1-propanol, glycerol and water are required to design and optimize the separation process of glycerol. In this work, the prediction of ternary VLE for (1-butanol / 2-methyl-1-propanol + glycerol + water) using UNIFAC model were determined at various temperatures and compositions and compared with the experimental data giving Average Absolute Deviations (AAD) less than 5.7%. The results indicated that UNIFAC was a reliable model for phase equilibria predictions in the mixtures containing of glycerol.

Index Terms – Vapor-liquid equilibria, 1-butanol, 2-methyl-1-propanol, glycerol, water.

INTRODUCTION

Biodiesel, which produced from vegetable oil, is considered to be a possible fuel for the future. It has received a great attention recently because of its environmental benefits, such as biodegradable, non-toxic, renewable and has reduced emission of CO, SO2, particulate matter [1].

Biodiesel fuel is mainly derived from transesterification process by alcohols and produced glycerol as a side product. Glycerol has several different potential uses in medical, pharmaceutical (drugs) and personal care preparations (cosmetics and toothpastes), tobacco and food processing (as a food additive, solvent, sweetener or a component of food packaging materials) and as a raw material in different chemical industries [2, 3].

Thus, distillation is an important process in related industries in order to separate glycerol which meets the food and pharmaceutical grade standards. Many data consisting of glycerol for binary and ternary VLE systems have been published, but there are just a few reports in the literature regarding to VLE data of related systems. For example, VLE data consisting of short-chain alcohols have been mostly reported in the literature.

VLE data were predicted by UNIQUAC Functional-group Activity Coefficients (UNIFAC) model [4] The calculated results were compared with the experimental data to observe the performance of UNIFAC model in predicting VLE for the systems consisting of glycerol as a side product in the biodiesel production.

MATERIAL AND METHOD

The materials used in this study, 1-butanol, 2-methyl-1-propanol, and glycerol, were supplied by Merck with minimum mass fraction purity of 0.995, 0.990, and 0.995, respectively. Table 1 shows the sources and the pure component properties used in the measurements. In this study, the vapor pressures were measured using a simple quasi-static ebulliometer as proposed previously in our previous work [5, 6].

RESULT AND DISCUSSION

The R_k and Q_k parameters of the UNIFAC groups for each component and interaction parameters between the existing UNIFAC main groups used in this study are taken from [7]. In this study, the VLE data (P-T-xi) for ternary systems of 1-butanol + glycerol + water at the temperatures of (303.15 to 343.15) K and 2-methyl-1-propanol + glycerol + water at the temperatures of (303.15 K to 333.15) K, respectively, have been measured. Before measured the VLE data, it is necessary to understand the region of total miscibility of such compounds to avoid the formation of two-layer phase. For this purpose, the concentrations of alcohols-water in binary liquid solutions reported by Fischer and Gmehling [8] were used as the basis to introduce the liquid mixtures of ternary systems.

Table 1 summarizes the comparison results between the experimental data with the prediction values of UNIFAC method. Considering the simplicity of the model, it is demonstrated that UNIFAC can describe very well the VLE consisting of alcohols, glycerol, and water mixtures as the average absolute deviation (AAD) in the vapor pressure less than 5.7%. The development of reliable predictive models would be useful for design, simulation and optimization of various separation processes in biodiesel or related compounds industries.

Both the experimental data and prediction values indicated that the vapor pressures increase with the

[1]Eviana D. Setiawati, Asalil Mustain, Gede Wibawa are with Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya. Email: eviana.setiawati@gmail.com; asalil89@polinema.ac.id; gwibawa@chem-eng.its.ac.id

increasing of alcohols alkyl chain length and temperatures.

Table 1. Absolute Average Deviation (AAD) in Vapor Pressures Resulting from the Prediction of VLE Using UNIFAC Method

System	*T* (K)	*n*[a]	AAD[a]
1-butanol + glycerol + water	(303.15 to 343.15)	90	4.3%
2-methyl-1-propanol + glycerol +water	(303.15 to 333.15)	98	5.7%

[a] $AAD = (1/n)\sum_{i=1}^{n}\left|\left(P_{cal} - P_{\exp}\right)/P_{\exp}\right|_i .100\%$, where n is the number of data points.

As illustration for several compositions, Figure 1 presents the comparison of VLE experimental data and UNIFAC predictions for the ternary systems of 1-butanol + glycerol + water and 2-methyl-1-propanol + glycerol + water, respectively. As presented, the UNIFAC predictions model is agree fairly well with the experimental data.

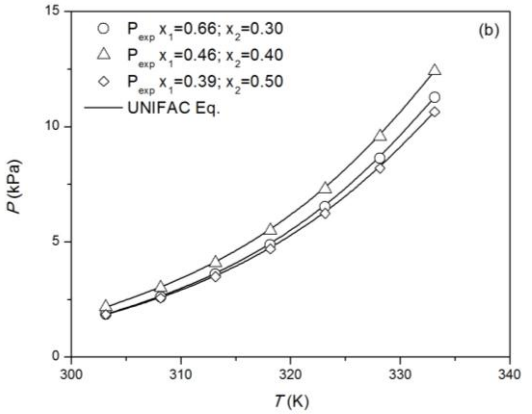

Figure 1. VLE Phase (P-T) Diagram for Ternary Systems:(a) 1-Butanol(1)+Glycerol(2)+Water(3); and(b) 2-Methyl-1-Propanol (1)+Glycerol(2)+Water (3)

CONCLUSION

The results indicated that the UNIFAC model was able to predict the VLE for the mixtures containing of glycerol with high accuracy to that obtained from experimental data. In the near future, group interaction parameters for UNIFAC structural groups in glycerol can be used to further extend the range of applicability of the UNIFAC model.

ACKNOWLEDGEMENTS

This research was supported by research grant of Institut Teknologi Sepuluh Nopember (ITS) under Contract No: 003246.53/IT2.11/PN.08/2015.

REFERENCES

[1] S. T. Keera, et al., "Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst," *Fuel*, vol. 90, pp. 42-47, 2011.

[2] M. B. Oliveira, et al., "Phase equilibria of glycerol containing systems and their description with the Cubic-Plus-Association (CPA) Equation of State," *Fluid Phase Equilibria*, vol. 280, pp. 22-29, 2009.

[3] C. A. G. Quispe, et al., "Glycerol: Production, consumption, prices, characterization and new trends in combustion," *Renewable and Sustainable Energy Reviews*, vol. 27, pp. 475-493, 2013.

[4] A. Fredenslund, et al., "Group-contribution estimation of activity coefficients in nonideal liquid mixtures," *AIChE Journal*, vol. 21, pp. 1086-1099, 1975.

[5] R. Oktavian, et al., "Vapor pressure measurements of ethanol–isooctane and 1-butanol–isooctane systems using a new ebulliometer," *Fuel*, vol. 107, pp. 47-51, 2013.

[6] G. Wibawa, et al., "Isothermal vapor–liquid equilibrium of ethanol + glycerol and 2-propanol + glycerol at different temperatures," *Journal of Chemical & Engineering Data*, vol. 60, pp. 955-959, 2015.

[7] H. K. Hansen, et al., "Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension," *Industrial & Engineering Chemistry Research*, vol. 30, pp. 2352-2355, 1991.

[8] K. FischerJ. Gmehling, "P-x and gamma infin. data for the different binary butanol-water systems at 50 degree.C," *Journal of Chemical & Engineering Data*, vol. 39, pp. 309-315, 1994 (GSTAR) Model and Its Properties," The 5th International Conference on Research and Education in Mathematics, 2008.