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Isobaric Vapor-Liquid Equilibria for Binary and Ternary Systems Composed of Ethanol, Acetone, and 2-Butanol at Atmospheric Pressure

Putri Amalia Devianda, Surya Aji Prassetya, Annas Wiguno, Rizky Tetrisyanda, Kuswandi Kuswandi#

Department of Chemical Engineering, Faculty of Industrial Technology,
Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia.

ORCID: 0000-0003-1021-0055(Kuswandi)

Abstract

The isobaric vapor-liquid equilibrium (VLE) data for three binary systems of ethanol + 2-butanol, acetone + 2-butanol, and ethanol + acetone and for one ternary system of ethanol + acetone + 2-butanol were measured at atmospheric pressure. The VLE data were obtained in various compositions of the systems by using an ebulliometer. The system was heated until the equilibrium state was reached that indicated by steady temperature. The liquid samples for these systems were analyzed by using a Gas Chromatography to obtain the compositions of the liquid phase. The ebulliometer was validated by measuring the equilibrium temperatures of binary system of ethanol + water and comparing the result with literature data. All the experimental data were correlated using the Wilson, NRTL, and UNIQUAC models to get interaction parameters. The reliability of the models was tested by comparing the temperature result of correlation with that of experimental data in terms of Average Absolute Deviation (AAD). The AAD T of the Wilson, NRTL, and UNIQUAC models were 0.2008, 0.1660, 0.1483, for the system ethanol + 2-butanol, 0.2001, 0.1886, 0.1830, for the system acetone + 2-butanol, 0.1584, 0.1697, 0.1540, for the system ethanol + acetone, 0.3566, 0.3485, 03587, for the system ethanol + acetone + 2-butanol, respectively.

Keywords: 2-butanol; ethanol; acetone; Wilson; NRTL; UNIQUAC; vapor-liquid equilibria

I. INTRODUCTION

The increase in the population of Indonesia followed by the demand of engine vehicles as mobility equipment in facilitating human activities have an impact on the increase in fuel demand such as Solar, Premium, Pertalite, and Pertamax [1]. It raises concerns over the scarcity of fossil fuels, particularly essential oils for everyday life, transportation, development, industry, defense, and the military due to fossil fuel sources categorized as unrenewable energy. Thus, alternative energy is required as a substitute.

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Solar fuel is used in diesel engines. At this time, motor vehicles and industrial machinery are still many who use fuel oil in the form of diesel. The effort to overcome the depletion of the oil reserves to keep the solar needs fulfilled in regulation of the Minister of Energy and Mineral Resources No. 32 year 2008 on the provision, utilization, and administration of biofuels as an alternative fuel. In this regulation, the minimum obligation to use biofuel by 20% in the year 2025 [2].

Biodiesel is an alternative fuel for diesel engines made from renewable natural resources such as plant oils and animal fats. They are easy to unravel, are nontoxic, and have low emissions.

There are four main processes in making biodiesel, which are direct use and blending, microemulsions, thermal cracking, and transesterification (alcoholysis). The most widely used process is transesterification because it produces high yield, fast reacting, easy to do and reversible. Transesterification is the reaction of oil or a fat with an alcohol for the form of ester and glycerol. The alcohols that can be used for the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol [3].

As one of many kinds of alcohol, methanol can be used as a reactant, but it is toxic and corrosive that can cause the damaging of the reaction equipment. After that, a few researches have been conducted on ethanol as reactant, but ethanol has been used as drinks more often. This is because of its higher market value as a drink than it is as a reactant. While propanol can be used as rubbing alcohol that is commercially used as an antiseptic, so that its market value become higher. Based on those, this research is conducted to find another kind of alcohol that is more profitable to be used as a reactant, which is butanol.

Butanol has several advantages over methanol and ethanol, which produce highest yield up to more than 98% by using immobilized lipase adsorption method [4], stable ester conversion compared to secondary alcohols [5] and suggested for regenerating the activity of deactivated enzymes [6]. Butanol is mainly produced from carbohydrates fermentation by *Clostridium acetobutylicum* in a process known as the fermentation of acetone-butanol-ethanol (ABE) with a product

ratio of 3:6:1 [7]. These multicomponent mixtures need to be separated to obtain a high purity of biobutanol. The purification process widely used is distillation. In raising the levels of butanol, purification is necessary using the distillation column to be separated from its impurities. Therefore, the vapor-liquid equilibrium data are needed in the design of a distillation column.

Based on the study of literature, many conducted researches provide equilibrium data of butanol. However, the availability of equilibrium data for 2-butanol is still limited. Until now, there has not much conducted researches on an equilibrium data of a binary and ternary system of 2-butanol, for either ethanol + 2-butanol or acetone + 2-butanol. To overcome this condition, the experimental vapor-liquid equilibria for the systems have been conducted. The equilibrium data obtained were correlated with the Wilson, NRTL and UNIQUAC equations. These equilibrium data are expected to be the base for designing a distillation column.

These data are needed to find out the distribution of ethanol + acetone + 2-butanol that can be used as supporting data for separation process from fermentation product.

II. EXPERIMENTAL SECTION

A. Materials

Analytical grade of ethanol and 2-butanol used in this work were supplied by Merck. Acetone was supplied by Smart-Lab. The characteristics of the materials are presented in Table I.

TABLE I. MATERIAL DESCRIPTION OF PURE COMPONENTS

Components	Supplier	Purity[a]
Ethanol	Merck	99.8%
Acetone	Smart-Lab	99.8%
2-Butanol	Merck	99.0%

[a.] *Purity obtained from the supplier.*

B. Apparatus and Procedures

The experimental vapor-liquid equilibria were conducted by using an ebulliometer. The apparatus consists of an equilibrium cell connected to a reflux condenser with cooling system to condensate the vapor phase back to the equilibrium cell. A mixture containing a binary or a ternary system at certain compositions was prepared using an analytical balance and charged into the ebulliometer. A heating system used was a coil equipped with a magnetic stirrer to assure proper heating and mixing. The equilibrium temperatures of the cell were measured by a thermocouple and shown by a temperature indicator display. The system pressure was measured by a barometer. The equilibrium state of the system was achieved when its temperature was steady. The equilibrium temperature and pressure were then recorded. At the end, liquid samples were taken and analyzed by a Gas Chromatograph (GC).

C. Sample Analysis

The liquid samples collected were analyzed using the Shimadzu Plus 2010 Gas Chromatograph and injected by using a syringe. The samples were analyzed using Stabilwax Column (30 m, 0.32 mm ID, 0.25 μm) and flame ionization detector (FID). The method used in this work are presented in Table II. The FID used in the GC analysis was calibrated by plotting percent areas to mole fractions of components in calibration curves constructed for the system studied to obtain the mole fractions of each sample from the area fractions. Each mixture compositions with interval mole fraction 0.1 were used for calibration to ensure high level of confidence in GC analysis results.

The reliability of the experiment results was confirmed by plotting the percent area versus the mole fraction of the mixture. The four-degree polynomial was applied to find out the equation and a good consistency was shown by giving R^2 value of 1.

TABLE II. SPECIFICATION USED FOR ANALYSIS USING SHIMADZU PLUS 2010 GC

Carrier gas	High-purity Helium
Flow configuration:	
Total flow	28.1 mL/min
Pressure	101.2 kPa
Split ratio	20 : 1
Injector temperature	373.15 K
Detector temperature	373.15 K
Column temperature	373.15 K
Analysis period	3 minutes

III. RESULTS AND DISCUSSION

Before obtaining the experimental data, the ebulliometer was validated by comparing equilibrium temperatures of binary system of ethanol + water between experimental data and literatures of Wozny and Cremer [8] and Lai, et al [9]. The experimental data were correlated with the Wilson, NRTL, and UNIQUAC activity coefficient models to obtain the binary parameters as shown in Table III that will be used as comparison with literature data. Based on the correlation result, the smallest AAD obtained with the NRTL model. Thus, the results were compared with previous research using the

parameters of the binary system ethanol (1) + water (2) with the correlation NRTL model. The comparison results in Table IV show that the measured equilibrium temperatures were in good agreement with the literature data as the average deviations in temperature were less than 0.55.

The experimental data for binary systems of ethanol + 2-butanol, acetone + 2-butanol, and ethanol + acetone at atmospheric pressure are presented in Table V.

TABLE III. THERMODYNAMIC MODEL PARAMETERS FOR BINARY SYSTEM OF ETHANOL(1) + WATER(2) AT ATMOSPHERIC PRESSURE

Wilson			
a_{12} (cal/mol)	***a_{21} (cal/mol)***		***AAD T***
500.7332	867.1428		0.1790
NRTL			
b_{12} (cal/mol)	***b_{21} (cal/mol)***	***α***	***AAD T***
-565.3884	1889.2925	0.2	0.1153
UNIQUAC			
u_{12} (cal/mol)	***u_{21} (cal/mol)***		***AAD T***
172.2261	183.3834		0.1484

TABLE IV. COMPARISON BETWEEN CORRELATION RESULT AND LITERATURE DATA

Literatures	**AAD T**
Wozny and Cremer, 1981	0.1650
Lai, et al, 2014	0.5402

In the vapor-liquid equilibria, the experimental condition in this work was at atmospheric pressure so that the vapor phase could be assumed as ideal gas. Equation (1) could be used to calculate the vapor-liquid equilibrium data at low pressure condition.

$$y_i P = P_i^{sat} \gamma_i x_i \quad (1)$$

TABLE V. EXPERIMENTAL RESULTS OF BINARY SYSTEMS AT ATMOSPHERIC PRESSURE

x_1	x_2	T (°C)
Ethanol (1) + 2-Butanol (2)		
0.0000	1.0000	99.50
0.1124	0.8876	96.60
0.2090	0.7910	94.40
0.3059	0.6941	92.00
0.4026	0.5974	90.10
0.4989	0.5011	87.90
0.5936	0.4064	85.80
0.6969	0.3031	83.80
0.7971	0.2029	82.20
0.9045	0.0955	80.30
1.0000	0.0000	78.30
Acetone (1) + 2-Butanol (2)		
0.0000	1.0000	99.50
0.0969	0.9031	91.90
0.1938	0.8062	85.60
0.2923	0.7077	79.40
0.3925	0.6075	75.00
0.4965	0.5035	71.10
0.5933	0.4067	67.60
0.6934	0.3066	64.60
0.7968	0.2032	61.90
0.8995	0.1005	58.80
1.0000	0.0000	56.20
Ethanol (1) + Acetone (2)		
0.0000	1.0000	56.20
0.1045	0.8955	57.60
0.1943	0.8057	58.70
0.2866	0.7134	59.90
0.3771	0.6229	61.10
0.4703	0.5297	62.70
0.5749	0.4251	64.50
0.6949	0.3051	66.20
0.8093	0.1907	69.60
0.8964	0.1036	73.00
1.0000	0.0000	78.30

where x_i and y_i are mole fractions of component i in the liquid and the vapor phases respectively. γ_i is the activity coefficient of component i. P is the system pressure and P_i^{sat} is the vapor

pressure of the pure component *i,* calculated by (2) the Antoine equation [10]:

$$\ln P_i^{sat} = A_i - \frac{B_i}{T+C_i} \quad (2)$$

where P_i^{sat} is in kPa and T is in ºC. The constants of Antoine equation used in this work are presented in Table VI.

TABLE VI. PARAMETERS OF ANTOINE EQUATION FOR PURE COMPOUND USED IN THIS WORK

Components	A	B	C
Ethanol	16.6758	3674.49	226.45
Acetone	14.3916	2795.82	230
2-Butanol	15.1989	3026.03	186.5

The experimental data were correlated with the Wilson. NRTL and UNIQUAC equations to determine the binary interaction parameters for the systems of ethanol + 2-butanol, acetone + 2-butanol, and ethanol + acetone. For the UNIQUAC model, the volume, r and the surface area, q parameters of pure components are shown in Table VII [11]. The binary interaction parameter pairs were determined by minimizing the value of objective function using Average Absolute Deviation (AAD) defined as (3).

$$AAD\ T = \frac{1}{n}\sum_{i=1}^{n}\left|T_{exp} - T_{calc}\right| \quad (3)$$

TABLE VII. THE VOLUME AND SURFACE AREA PARAMETERS FOR THE UNIQUAC MODEL

Components	*r*	*q*
Ethanol	2.5755	2.588
Acetone	2.5735	2.336
2-butanol	3.9235	3.664

The correlation results are listed in Tables VIII-X, which consist of the best fitted binary interaction parameters and the Average Absolute Deviation (AAD) between the experimental and the calculated results.

TABLE VIII. INTERACTION PARAMETERS OF ACTIVITY COEFFICIENT MODELS FOR SYSTEM ETHANOL (1) + 2-BUTANOL (2)

Wilson			
a12 (cal/mol)	***a21 (cal/mol)***		***AAD T***
-35.7156	41.9764		0.2008
NRTL			
b12 (cal/mol)	***b21 (cal/mol)***	***α***	***AAD T***
590.7920	-602.0219	0.2	0.1660
UNIQUAC			
u12 (cal/mol)	***u21 (cal/mol)***		***AAD T***
64.3363	-87.2288		0.1483

TABLE IX. INTERACTION PARAMETERS OF ACTIVITY COEFFICIENT MODELS FOR SYSTEM ACETONE (1) + 2-BUTANOL (2)

Wilson			
a12 (cal/mol)	***a21 (cal/mol)***		***AAD T***
387.2434	-294.1691		0.2001
NRTL			
b12 (cal/mol)	***b21 (cal/mol)***	***α***	***AAD T***
-273.0136	408.1891	0.4	0.1886
UNIQUAC			
u12 (cal/mol)	***u21 (cal/mol)***		***AAD T***
-259.6679	372.4872		0.1830

TABLE X. INTERACTION PARAMETERS OF ACTIVITY COEFFICIENT MODELS FOR SYSTEM ETHANOL (1) + ACETONE (2)

Wilson			
a12 (cal/mol)	***a21 (cal/mol)***		***AAD T***
-68.4102	587.3968		0.1584
NRTL			
b12 (cal/mol)	***b21 (cal/mol)***	***α***	***AAD T***
795.1421	-378.2343	0.2	0.1697
UNIQUAC			
u12 (cal/mol)	***u21 (cal/mol)***		***AAD T***
518.5767	-284.5004		0.1540

The results show that the Wilson, NRTL, and UNIQUAC equations could correlated well the experimental data The best results are obtained by the UNIQUAC equation for all binary systems. The experimental and the correlated data with those

models for binary systems are also compared graphically with literature data as shown in Figs. 1-3.

The experimental data were also measured for ternary system ethanol (1) + acetone (2) + 2-butanol (3) at atmospheric pressure and the results are presented in Table XI. These experimental data were correlated by using the Wilson. NRTL and UNIQUAC equations to calculate the activity coefficients of the components using the binary interaction parameters. The calculated deviations from all those models were summarized in Table XII.

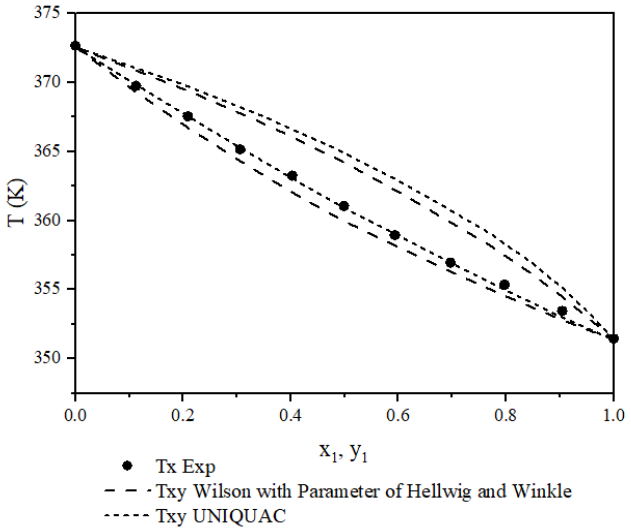

Fig. 1. Vapor-liquid equilibria for binary system ethanol (1) + 2-butanol (2) at atmospheric pressure with experimental and literature parameters [12]

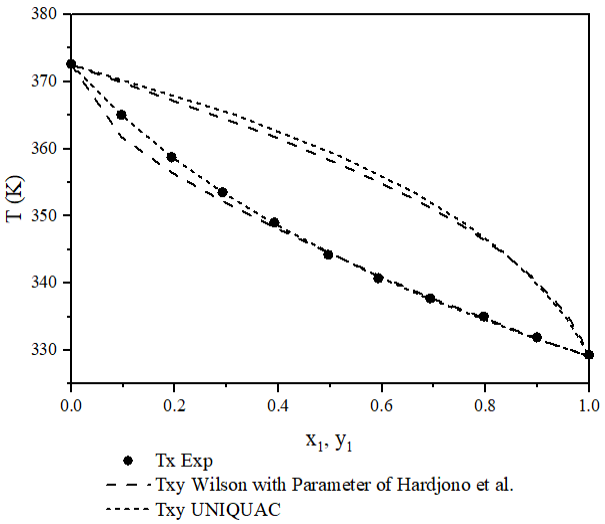

Fig. 2. Vapor-liquid equilibria for binary system acetone (1) + 2-butanol (2) at atmospheric pressure with experimental and literature parameters [13]

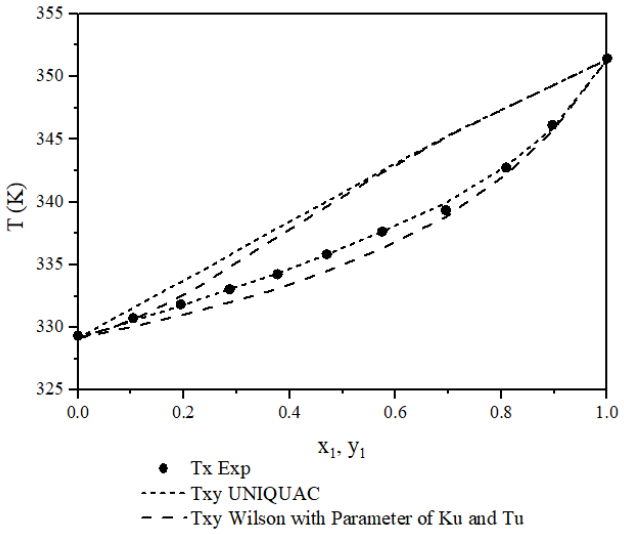

Fig. 3. Vapor-liquid equilibria for binary system ethanol (1) + acetone (2) at atmospheric pressure with experimental and literature parameters [14]

TABLE XI. EXPERIMENTAL RESULTS OF TERNARY SYSTEM ETHANOL (1) + ACETONE (2) + 2-BUTANOL (3)

x_1	x_2	x_3	T (°C)
0.6893	0.2592	0.0516	69.50
0.6338	0.2905	0.0757	69.80
0.5080	0.3041	0.1879	70.00
0.3653	0.3141	0.3206	71.80
0.2533	0.3013	0.4455	74.60
0.1648	0.2661	0.5691	78.00
0.1073	0.1972	0.6955	83.00
0.0933	0.1443	0.7625	86.40
0.0756	0.0708	0.8536	91.60
0.0636	0	0.9364	97.80

TABLE XII. AVERAGE DEVIATIONS FOR TERNARY SYSTEM ETHANOL (1) + ACETONE (2) + 2-BUTANOL (3) DETERMINED FROM BINARY PARAMETERS

Model	AAD T	
	This work	Literature
Wilson	0.3566	1.5142
NRTL	0.3485	1.0579
UNIQUAC	0.3587	1.1439

The experimental and the calculated data with those models for ternary system are also compared graphically with literature data then plotted as ternary diagrams presented in Figs. 4-6. As can be seen. all three models correlate well for the ternary

system. The NRTL model exhibits rather smaller deviation in equilibrium temperatures from experimental data than that of the Wilson and UNIQUAC models.

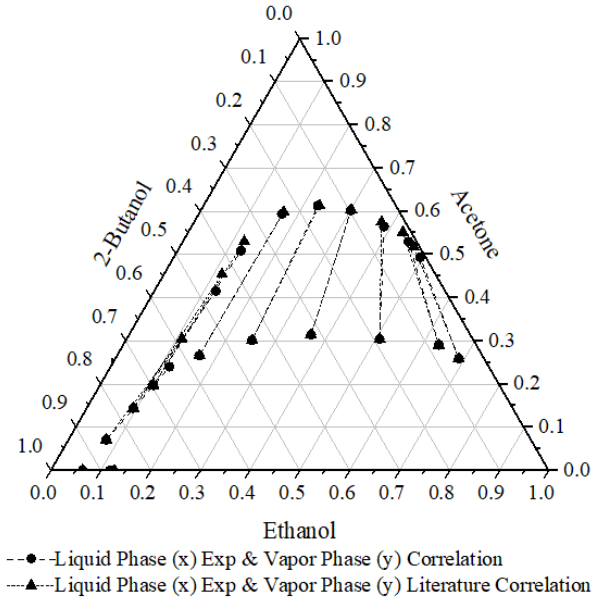

Fig. 4. Vapor-liquid equilibria for ternary system ethanol (1) + acetone (2) + 2-butanol (3) at atmospheric pressure with experimental and literature Wilson parameters

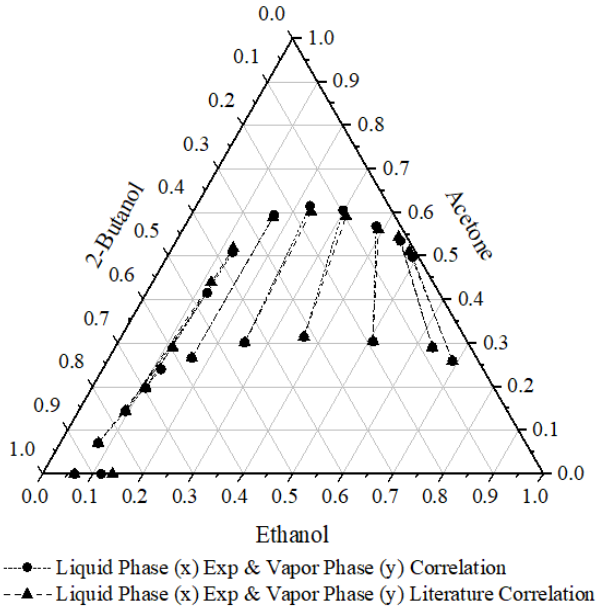

Fig. 5. Vapor-liquid equilibria for ternary system ethanol (1) + acetone (2) + 2-butanol (3) at atmospheric pressure with experimental and literature NRTL parameters

Each of the experimental data, the liquid phases were connected with tie-lines to the vapor phases obtained by the correlation. At certain temperature and pressure, the mixtures were in saturated between liquid and vapor phases.

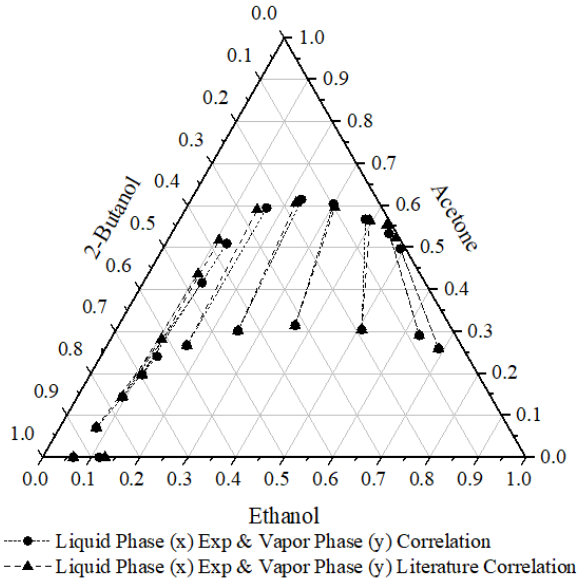

Fig. 6. Vapor-liquid equilibria for ternary system ethanol (1) + acetone (2) + 2-butanol (3) at atmospheric pressure with experimental and literature UNIQUAC parameters

IV. CONCLUSION

Vapor-liquid equilibrium data for binary systems of ethanol + 2-butanol, acetone + 2-butanol, and ethanol + acetone, also ternary system of ethanol + acetone + 2-butanol have been presented. The experimental apparatus validated by using binary system of ethanol + water shows that the measured equilibrium temperatures are in good agreement with low average absolute deviations in temperature. The experimental data were correlated well using the Wilson. NRTL and UNIQUAC equations wherein the deviations between experimental and calculated data were relatively small. The best results are obtained using the UNIQUAC model for all binary systems. The VLE data correlate equally well for the ternary system as shown by small deviations in all three models.

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REFERENCES

[1] D. Kusdiana, "Statistik EBTKE 2016," Jakarta: Direktorat Jenderal Energi Baru Terbarukan dan Konversi Energi, 2016.

[2] J. Winarno, "Study eksperimental pengaruh penambahan bioetanol pada bahan bakar pertamax terhadap unjuk kerja motor bensin," Jurnal Teknik, vol. 1, pp. 33-39, 2011.

[3] F. Ma and M.A. Hanna, "Biodiesel production: a review," Bioresource Technology 70, pp. 1-15, 1999.

[4] H. Fukuda, A. Kondo, and H. Noda, "Review: biodiesel fuel production by transesterification of oils," 92, 5, Journal of Bioscience and Bioengineering, pp. 405-416, 2001.

[5] H. Liu, S. Li, Z. Zheng, J. Xu, and M. Yao, "Effects of n-butanol, 2-butanol, and methyl octynoate addition to diesel fuel on combustion and emissions over a wide range of exhaust gas recirculation (EGR) rates," Applied Energy, 112, pp. 246-256, 2013.

[6] S.V. Ranganathan, S.L. Narasimhan, and K. Muthukumar, "Review: an overview of enzymatic production of biodiesel," Bioresource Technology, 99, pp. 3975-3981, 2008.

[7] Y. Arifin, E. Tanudjaja, A. Dimyati, and R. Pinontoan, "A second generation biofuel from cellulostic agricultural by-product fermentation using clostridium species for electricity generation," Energy Procidia, 47, pp. 310-315, 2014.

[8] G. Wozny and H. Cremer, "*Phasengleichgewichte binarer kohlenwasserstoff-gemische*," Chemie Ingenieur Technik, 53, 2, pp. 89-95, 1981.

[9] H.S. Lai, Y.F. Lin, and C.H. Tu, "Isobaric (vapor + liquid) equilibria for the ternary system of (ethanol + water + 1,3-propanediol) and three constituent binary system at P=101.3 kPa," The Journal of Chemical Thermodynamics, 68, pp. 13-19, 2014.

[10] J. M. Smith, H.C. Van Ness, and M.M. Abbott, "Introduction to Chemical Engineering Thermodynamics," 6th ed., McGraw-Hill, New York, 2001.

[11] B.E. Poling, R.C. Reid, J.M.. Prausnitz, and J.P. O'Connell, "The Properties of Gases and Liquids," 5th ed., Mc Graw-Hill, New York, 2001.

[12] L. R Hellwig and V.M. Winkle, "Vapor-liquid equilibria for ethyl alcohol binary system," Industial and Engineering Chemistry, 45, 3, pp. 624-629, 1953.

[13] H. Hardjono, A. Mustain, P.H. Suharti, D. Hartanto, and I. Khoiroh, "Isobaric vapor-liquid equilibrium of 2-propanone + 2-butanol system at 101,325 kPa," Experimental and Molecular Dynamics Simulation, Malang: Politeknik Negeri Malang Press, 2017

[14] H.C. Ku and C.H. Tu, "Isobaric vapor-liquid equilibria for mixtures of acetone, ethanol, and 2,2,4-trimethyl pentane at 101,3 kPa," Fluid Phase Equilibria, 231, pp. 99-108, 2005.