Influence of Ions and Temperatures on Water-Ethanol-Gasoline Liquid-Liquid Equilibrium

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Keywords: Water-Ethanol-Gasoline Equilibrium, Ions, KH_2PO_4, KCl, KOH.

Abstract: Water-ethanol-gasoline liquid-liquid equilibrium (LLE) was investigated. In this study, the LLE data was obtained gravimetrically and volumetrically by turbidity titration under influence of KH_2PO_4, KCl, and KOH. Effect of temperature was also evaluated at 30 and 50℃. Results suggest that presence of ions alter the LLE and different ions affect the LLE differently. At concentration of 20 mM, temperature had significant effect on the LLE. Increasing temperature reduced the heterogeneous region and allowed more water in gasoline phase.

1 INTRODUCTION

World energy demand is predicted to increase with Asian countries leading the trend (U.S. EIA, 2016). To meet the energy demand, alternative energy is currently being developed with lignocellulosic ethanol as one of the potential candidate. Cellulosic ethanol has gained popularity these recent years, but it is yet to be commercialized because it is too expensive and inefficient (Johnson, 2016; Olofsson et al., 2017; Klein-Marcuschamer et al., 2011). While many researches had been conducted emphasizing on different aspects of the production such as pretreatments (type and condition), hydrolysis (enzyme type and load), fermentation (microbes and condition), process scheme (SSF, SScF, CBP, and DMC), pre fermentation processing (hydrolysate detoxification, sugar pre concentration, additives), cell/enzyme immobilization, and so on (Li et al., 2017; Singh et al., 2017; Vohra et al., 2014; Hernawan et al., 2017; Xu and Wang, 2017; Kumar et al., 2016; Lam et al., 2014; Johnson, 2016; Ziolkowska, 2014), few focused on alternative purification step or its integration into the process scheme. One possible scheme is production of alcohol gasoline blend, known as gasohol, by extraction of fermentation broth (Leeper and Wankat, 1982; Lee and Pahl, 1985). Coupled with direct broth recycling using non-sterile fermentation (Chen and Wan, 2017), this method can reduce operation cost to overcome the economic barrier of cellulosic ethanol. Previous attempt on integration of purification step and direct broth recycling using biodiesel had shed some light on its viability, though extraction using gasoline might be more economically feasible (Bani, 2014). However, integrating extraction using gasoline into process scheme requires careful consideration due to possible enzyme and microbe inhibition, formation of emulsion, water infiltration into gasohol, etc. The interdependency of these factors also further complicates the analysis of such system. Therefore, this study aimed to collect water-ethanol-gasoline equilibrium data as foundation for the system analysis.

2 MATERIALS & METHODS

2.1 Materials Collection

Aquabidest, ethanol, KOH, KCl, and KH2PO4 were purchased from local chemical store (CV. Rudang Jaya) while gasoline was purchased from local petrol station. All chemicals used were of technical grade and gasoline was Pertamax from PT. Pertamina. Specification of Pertamax gasoline is tabulated in Table 1.

Bani, O., Sukeksi, L., Taslim, ., Iriany, . and Anggreawan, M.
Influence of Ions and Temperatures on Water-Ethanol-Gasoline Liquid-Liquid Equilibrium.
DOI: 10.5220/0008525601000103
In *Proceedings of the International Conference on Natural Resources and Technology (ICONART 2019)*, pages 100-103
ISBN: 978-989-758-404-6

Table 1: Some Specification of Pertamax Gasoline (Pertamina 2017).

Characteristics	Unit	Value
Octane number	RON	>92
Oxidation stability	min	>480
Sulfur content	% m/m	0.05
Lead content	g/L	0.013
Oxygen content	% m/m	<2.7
Aromatic content	% v/v	<50
Benzene content	% v/v	<5
Sediment	mg/L	<1
Colour		Blue
Die content	g/100 L	<0.13

2.2 Liquid Liquid Equilibrium Data Collection

Water-ethanol-gasoline equilibrium data was obtained by turbidity titration. The procedure began by preparing a water-ethanol mixture in a 100-ml flask. The mixture was titrated with gasoline using a 5-ml burette until it became turbid, then added again with gasoline. Afterwards, it was titrated with ethanol to clarity, then added again with ethanol. Each phase change and liquid addition was recorded. The titration was repeated until the flask was full. Initial mixture composition was adjusted with each procedure iteration to obtain enough data for construction of ternary phase diagram. The experiment was repeated under influence of potassium ions (KOH, KCl, and KH_2PO_4) and temperature of 30 and 50°C. Ion influence was investigated by replacing aquabidest with ionic solution at concentration of 20 mM. Temperature variation was maintained within ±2°C by immersing the flask in water bath during titration.

2.3 Ternary Phase Diagram Construction

LLE Data was plotted in R using ggtern library using gg_smooth_tern plotting (Hamilton, 2017). LLE composition was calculated as mass fraction by adding up each component during each phase change. For gravimetric data, the mass change during each addition of liquid was treated as added mass of said liquid. For volumetric data, the titer volume was converted to mass using the liquid density at the room temperature during experiment.

3 RESULTS AND DISCUSSIONS

3.1 Effect of Potassium Ions

Ternary phase diagrams for water-ethanol-gasoline system without presence of ions and under influence of KOH, KCl, and KH_2PO_4 are shown in Figure 1-4.

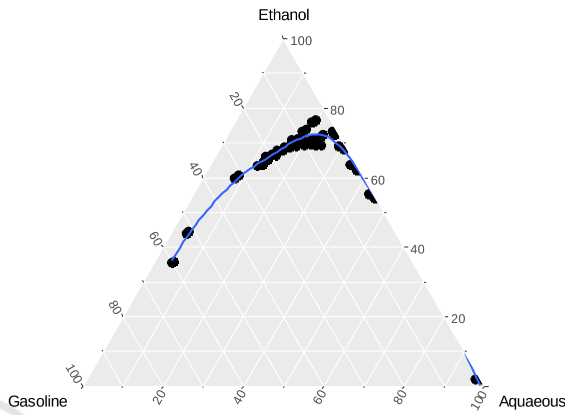

Figure 1: Water-Ethanol-Gasoline LLE System.

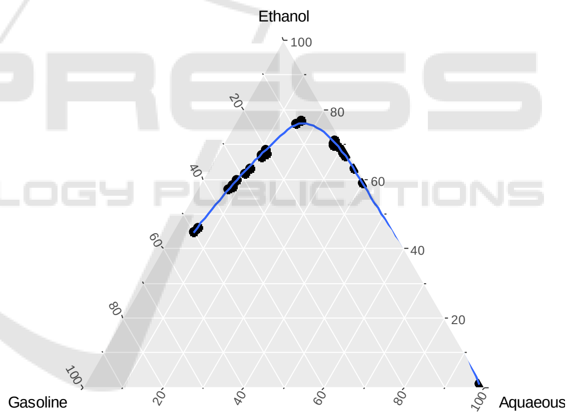

Figure 2: Effect of KOH on Water-Ethanol-Gasoline LLE System.

Addition of KH_2PO_4 increased the heterogeneous region of the diagram, indicating that the system had more separation. However, it is worth noting that KH_2PO_4 was emulsified in this system and as such, require a more thorough investigation to reach better conclusion. For KOH, the shape of heterogeneous region became rounder. This resulted in less water in the gasoline phase at low ethanol concentration region but more water in gasoline phase at high ethanol concentration region, which means that KOH promote both separation and homogeneity. A more sophisticated method is required to ascertain this result. For KCl, its addition seemed to promote homogeneity as evidenced from the shrinking heterogeneous region.

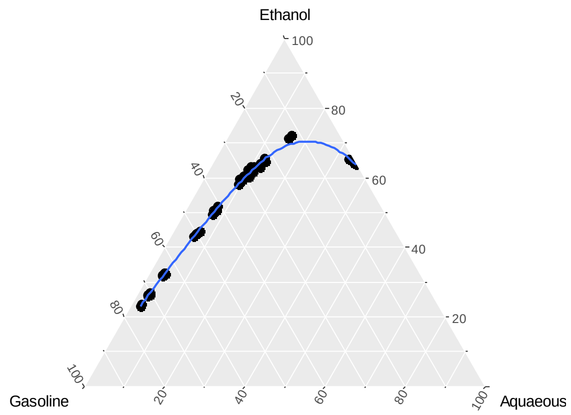

Figure 3: Effect of KCl on Water-Ethanol-Gasoline LLE System.

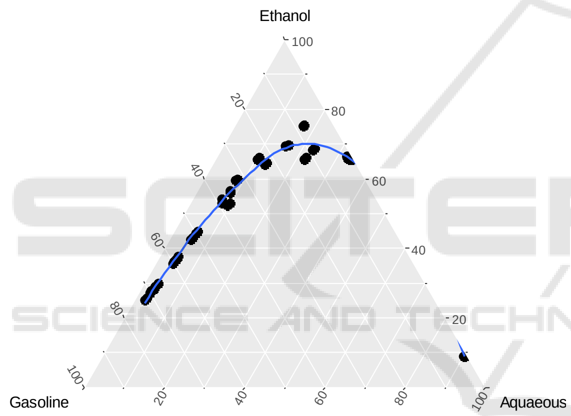

Figure 4: Effect of KH_2PO_4 on Water-Ethanol-Gasoline LLE System.

3.2 Effect of Temperature

Ternary phase diagrams for water-ethanol-gasoline system at 30°C and at 50°C are shown in Figure 5. It is apparent that temperature has significant effects on the LLE as the heterogeneous region shrank significantly, which suggests that more water will present in gasoline and more gasoline will present in water. Similar finding at different temperature range was also reported (Cerempei, 2011)

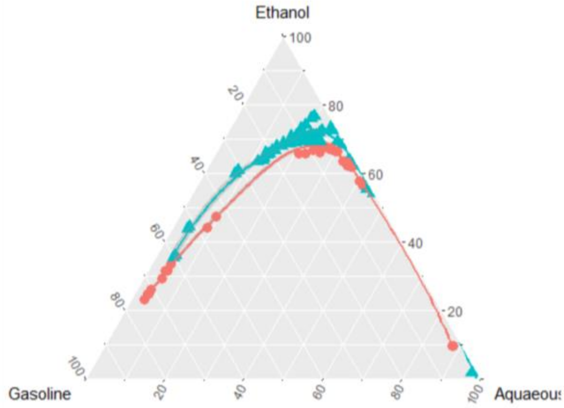

Figure 5: Effect of Temperature on Water-Ethanol-Gasoline LLE System. ▲: 30℃, ●: 50℃

4 CONCLUSIONS

Water-ethanol-gasoline LLE is influenced by presence of ions and temperature. The most pronounced of these two is temperature. Different ions bode different effects on the system, although more data are required to ascertain these results.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Higher Education of Indonesia for the funding through TALENTA USU 2017.

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