The Azeotropic Distillation for Bioethanol Purification: The Effects of Entrainer Solvents

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Abstract. Bioethanol is one of the most interesting biofuels in Indonesia. In the recent years, various research studies on bioethanol production have been reported. The main problem using bioethanol as alternative energy is the refining process. In this paper, we report on our effort to increase the purity of bioethanol. The effects of different entrainer combinations were investigated. Based on our study, we found that the double entrainers combination generated better ethanol purity compared to a single entrainer. Among the possible combinations of entrainer, the combination of 10% (v/v) n-Heptane on cyclohexane-n-heptane could increase ethanol purity up to 87.39%.

Keywords: bioethanol, entrainer, azeotropic distillation

1. Introduction

Until now and for the next few years, fossil fuels including natural gas, coal dan oil are still the primary energy sources in the world. But the present energy sources based on fossil fuel are being phased out due to some factors especially CO₂ emission. Renewable energy resources such as solar, wind and biofuel are the most promising candidates. Compared to other alternative energy sources, bioethanol is one of a stunning and promising energy sources[1]. Bioethanol is one source of alternative energy that has a magnificent potential to be developed in Indonesia. The main sources of bioethanol are corn, wheat, and sugarcane. However, there are new problems arising due to bioethanol production from corn and wheat which reduce their supply of food[2, 3]. To avoid that problem, some researchers have tried to develop bioethanol from various available types of lignocellulose biomass[2, 4, 5]. Compared to fossil fuel, bioethanol has several advantages including being a cleaner source of fuel, being able to increase the octane of fuel with small cost, being virtually usable in all vehicles, and easy to produce and store[6].

One major problem in bioethanol production is purification process since feedstock of fermentation process can only produce a final titre ethanol of 19-20% (v/v) ethanol[7, 8]. To get bioethanol with a higher purity that meets fuel specification, it is necessary to do a gradual distillation which requires higher cost. This is due to the fact that bioethanol (ethanol) and water proportions cannot be altered or changed by a simple distillation. Since their composition cannot be changed by distillation, it is called an azeotrope or constant boiling point mixture[9, 10]. A mixture of bioethanol and water can be economically separated using extractive distillation, distillation-adsorption, membrane pervaporation or azeotropic distillation.
Liquid mixtures containing azeotropes are easier to separate into their pure components with the aid of extraneous a separating agent or entrainer [11]. It plays an important role in altering the relative volatility of the key component without additional azeotrope formation and also makes a boiling point difference in the component[12]. Entrainer application is different for different behaviour of mixture and distillation[13]. Several simulation process of ethanol purifications with distillation columns have been carried out. By using Aspen plus simulation, it has been found that cyclohexane yielded maximum purity of ethanol (99.9%) closely followed by n-pentane (99.84%) and benzene (99.77%) as an entrainer[14]. Compared to experimental data, benzene can increase the purity of bioethanol better than n-heptane and cyclohexane[15]. In this research it was expected to increase bioethanol purity by applying a combination of double entrainer composition.

2. Materials and Method
A mixture of bioethanol + water 20% (v/v) was applied as the bioethanol product from fermented feedstock. The entrainers used were benzene, n-heptane and cyclohexane, which were obtained from Merck and had a nominal purity >99%. The differences between two entrainers were used with the total value being 40% (v/v)[15].

The experiment was conducted using the distillation method. The column operated at atmospheric pressure and the temperature was maintained at 338°K[16]. To determine the bioethanol content, a refractometer and density analysis test were performed.

3. Results and Discussion
Three candidate entrainers were studied in detailed distillation processes to demonstrate the best entrainer composition in the enhancement of bioethanol purification. The different compositions of entrainers were confirmed by refractive index and density analysis test. The various combinations of benzene and cyclohexane composition are shown in Table 1. From the table, it can be seen that the ethanol purity values determined using refractive index and density were similar. The ethanol purity increased proportionately to the value of benzene. The ethanol purity in 10, 20, 30% (v/v) benzene were found to be 64.48, 65.68, 65.79% respectively (based on density analysis). It can be seen that, an increase in the percentage volume of benzene increases the purity of ethanol.

| Composition (v/v) | Refractive Index | % Ethanol | Density | % Ethanol |
|------------------|-----------------|-----------|---------|-----------|
| Benze 10 | Cyclohexane 30 | 1.3544 | 63.75 | 0.90248 | 64.48 |
| Benze 20 | Cyclohexane 20 | 1.3549 | 65.03 | 0.89965 | 65.68 |
| Benze 30 | Cyclohexane 10 | 1.3553 | 65.98 | 0.89940 | 65.79 |

Benzene and cyclohexane are composed of six carbon and cyclic structures. In this case, cyclohexane has a strong effect in increasing the purity of ethanol better than benzene. This would be due to that fact that cyclohexane has a single bond thus it reacts faster with other compounds and has a more stable structure compared to benzene.
Table 2. The combination of benzene and n-Heptane composition for bioethanol purification.

| Composition (v/v) | Refractive Index | % Ethanol | Density   | % Ethanol |
|-------------------|------------------|-----------|-----------|-----------|
| Benzene           | n-Heptane        |           |           |           |
| 10                | 30               | 1.3629    | 85.04     | 0.84738   | 85.50     |
| 20                | 20               | 1.3581    | 72.97     | 0.88034   | 73.49     |
| 30                | 10               | 1.3593    | 75.13     | 0.87318   | 76.52     |

The combinations of different types of chemical structures of entrainers had a significant influence in increasing ethanol purity. The combination between the strain chain of n-Heptane and cyclic structure of cyclohexane had a better performance in increasing ethanol purity compared to cyclic-cyclic structure of an entrainer. It is due to the different entrainer characteristic resulting in a higher boiling point which was different from an azeotropic mixture. From Table 2, it can be seen that the purities of ethanol were 85.50, 73.49, and 76.52% for 10, 20, 30% (v/v) of benzene respectively. The 10% (v/v) of benzene increased ethanol purity to 85.50% and it decreased with increasing composition value of benzene.

Table 3. The combination of cyclohexane and n-Heptane for bioethanol purification.

| Composition (v/v) | Refractive Index | % Ethanol | Density   | % Ethanol |
|-------------------|------------------|-----------|-----------|-----------|
| Cyclohexane       | n-Heptane        |           |           |           |
| 10                | 30               | 1.3637    | 86.98     | 0.84119   | 87.39     |
| 20                | 20               | 1.3617    | 82.16     | 0.85529   | 82.73     |
| 30                | 10               | 1.3541    | 63.14     | 0.86458   | 62.86     |

Similarly to benzene-n-Heptane, the combination of cyclohexane-n-Heptane also increased ethanol purity better than benzene-cyclohexane. The ethanol purity in 10, 20, 30% (v/v) benzene were found to be 87.39, 82.73, 62.86% respectively as shown in Table 3. The combination with n-Heptane, cyclohexane resulted in higher ethanol purity values that were better than benzene. As previously explained, this might be because cyclohexane has a stable structure.

The computed ethanol purity values for cyclohexane-n-Heptane entrainer combination with 10% (v/v) of cyclohexane were found to be better than all of the other combinations of compositions and types of entrainers in this study (87.39%). It was also found that double entrainer combinations resulted in better alcohol purity compared to a single entrainer[15].

4. Conclusion

We proposed double entrainer combinations to increase ethanol purity. The refractive index and density result implied that cyclohexane-n-Heptane combination was able to increase ethanol purity up to 87.39%. We also found that double entrainers combination could improve ethanol purity better than a single entrainer.

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