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Fractional Freezing of Ethanol and Water Mixture

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Graphical abstract

Abstract

Fractional freezing was introduced to separate a mixture that contains a volatile organic compound in this case; ethanol and water. The mixture was separated by using freezing process since both ethanol and water have different freezing points. This method is an alternative method for fractional distillation as it does not consume high amount of energy to supply heat for vaporization purpose. Besides, this method is safer to our environment as it does not liberate any harmful vapor or gases since there is no heating process involved. In this study, the performance of the process in producing high purity ethanol was evaluated based on two parameters which are stirring rate and coolant temperature. It was found that the concentration of ethanol in liquid phase increased as the stirring rate increased. The ethanol concentration has increased by 52.2% when the stirring rate was at the highest rotating speed which is 500 rpm. When the coolant temperature was decreased to -14˚C, the ethanol concentration in liquid phase increased the most by 56.5%. Thus it can be concluded that the concentration of ethanol in liquid phase increased as the coolant temperature decreased.

Keywords: Fractional freezing; miscible liquid; ethanol and water

1.0 INTRODUCTION

There are many ways to separate various chemical compounds to its constituent components in a solution and one of them is fractional distillation process. The process is mostly used in industrial and lab process, while freeze concentration process is a new method process to be applied in this chemical compound separation process. The process involves evaporation process by heating the solution to its boiling point. Industrial distillation process is widely used in chemical plants, petroleum refineries, cryogenic air separation plants and natural gas processing. But, this process has disadvantages in terms of safety towards the environment and it does consume high energy to supply heat for the heating purposes. This problem could be handled by an introduction of a new method which is using fractional freezing method.

Fractional freezing process had been introduced from the application of a freeze concentration concept. Freeze concentration is a process involving of cooling process given to a solution until the water is frozen and gives the liquid left behind a higher concentration of solution. But, this method is for enhancing the concentration of a solution purposes only [1].

Fractional freezing, also known as freeze crystallization is a process that can separate two miscible organic compounds to its constituent's components. It has been used as a way to increase alcohol content of beverages like ice beer and making applejack out of hard apple cider. It may not achieve the same alcohol concentration with evaporative distillation method but the freezing method is much cheaper, easier and eco-friendly as it does not release dangerous and hazardous vapor when volatile organic compounds got engaged as in the evaporation method [2].

Besides, fractional freezing removes water from the alcohols instead of evaporating and condensing out the desired ethanol of everything else as in conventional distillation.

In fractional freezing process, energy consumption can be reduced to 70 to 90% instead of using distillation and evaporation processes. There are factors that reduce the energy consumption in this process. First, it is due to the phase change that is only required once in the freezing process. Besides, the latent heat of fusion is less than the heat of vaporization and the process operates at lower temperature, so the entropy of the separation is less. Moreover, the heat pump used in the fractional freezing process to transfer the heat to the melter is providing advantages similar to the vapor compression evaporator cycle [3].

2.0 EXPERIMENTAL

The aim of this study is to investigate the effect of stirring rate and coolant temperature of fractional freezing on ethanol concentration efficiency and effective partition constant. The experiment was executed by varying the stirring rate and coolant temperature. The investigation was done by:

i. Manipulating the stirring rate (100-500 rpm) at a fixed initial concentration of ethanol (2.3 mol), coolant temperature (-10˚C) and time 60 min.
ii. Manipulating the coolant temperature (-6˚C to -14˚C) at a fixed initial concentration of ethanol (2.3 mol), stirring rate (300 rpm) and 60 min.

2.1 Material

Ethanol mixed with water was used as the material in this study. Ethanol was obtained by purchasing it from the local supplier. Ethanol with an initial concentration of 2.3 mol was mixed with distilled water with a ratio of 2:3. A 50% (v/v) Ethylene Glycol solution was used as coolant.

2.2 Fractional Freezing Apparatus

A mixture of ethanol and water was mixed in a stainless steel vessel with a diameter and height of 11.5 cm. The vessel was immersed in a water bath with size of 26 cm×26 cm×26 cm as shown in Figure 1 and Ethylene Glycol at 50% volume with distilled water was used as coolant. A retort stand with clamp was used to hold the stainless steel vessel while immersing the vessel into the water bath. The temperature of the water bath was controlled by cooling temperature controller and a digital stirrer was used to stir the solution as shown in Figure 1. The minimum and maximum stirring rate was controlled in a range from 100 rpm until 500 rpm. A refractometer was used to observe and record the refractive index of the ethanol in liquid phase and ice after being thawed

2.3 Experimental Setup

Figure 1 shows the experimental set-up for fractional freezing that was conducted. The stainless steel vessel was contained with a mixture of ethanol and water and the vessel was partially immersed in the water bath at desired cooling temperature. A retort stand with a clamp on it was used to hold the vessel and a digital stirrer was used to stir the mixture at desired stirring rate.

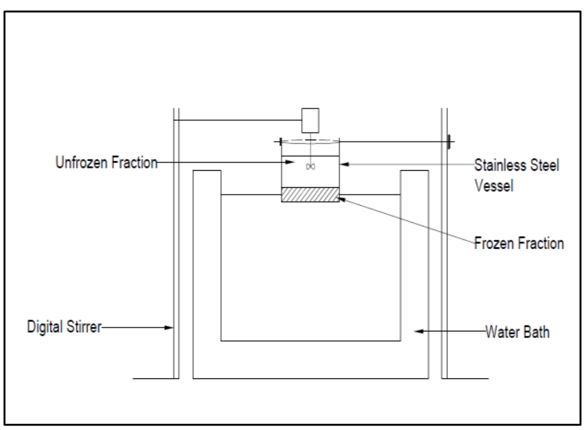

Figure 1 Schematic drawing for experimental set-up

2.4 Experimental Procedure

Ethanol was dissolved in distilled water and it was precooled at 2˚C in freezer for a day. The mixture was poured into a stainless steel vessel; fractional freezing vessel and fractional freezing process was started. Fractional freezing vessel was partially immersed in a precooled water bath at -10˚C.

The vessel was lowered into the water bath by 0.005 cm/min. The temperature of water bath was set to a desired cooling temperature and a digital stirrer was set to a desired stirring rate to stir the solution in the fractional freezing vessel. The solution then was left for one hour for freezing process takes places. After the designated time and the ice layer is formed as shown in Figure 2, the stirring process was stopped and the fractional freezing vessel was taken out from the water bath to be thawed. 10 ml of ethanol in the liquid phase and the ice after being thawed were collected as a sample to determine its concentration after fractional freezing process.

Figure 2 Ice layer formed

After the fractional freezing process was completed, the samples that had been taken were put in a refractometer to measure the refractive index of ethanol in liquid phase and ice after being thawed. The concentration for each sample was calculated to determine the increase in concentration of ethanol reached after the fractional freezing process. The procedure was repeated to investigate the effect of coolant temperature on fractional freezing process by varying the cooling temperature from -6˚C to -14˚C.

2.5 Data Analysis

Concentration efficiency (Eff). The concentration efficiency indicates the increase in concentration of the solution in liquid phase in relation to the initial concentration of mixture [4, 5, 6]. Concentration efficiency was calculated by Equation (1):

$$Eff = (C_L - C_0) / C_L * 100 \quad (1)$$

where Eff is the concentration efficiency (%), C_L is the concentration of ethanol in liquid phase after freezing process and C_0 is the initial concentration of mixture.

Effective partition constant. Effective partition constant indicates the efficiency of fractional freezing process. K is defined as follows:

$$K = C_S / C_L \quad (2)$$

where K is effective partition constant, C_S is the concentration of ice after being thawed and C_L is the concentration of ethanol in liquid phase after freezing process [7].

3.0 RESULTS AND DISCUSSION

3.1 Effect of Stirring Rate on the Concentration Efficiency of Ethanol and Effective Partition Constant

The experiment was conducted to study the effect of stirring rate on the effective partition constant, K and the concentration efficiency of the ethanol in liquid phase after fractional freezing process. In this experiment, the water bath was filled with a mixture of ethylene glycol and water and kept at -10ºC as a cooling medium. Because the only solution contacted with ethylene glycol become frozen, it is important to control the advance speed of the ice front (U), which is being kept constant at 0.0005 m/min in this experiment. A digital stirrer was used to stir the solution and equalize the whole concentration in the liquid phase. Thus, the stirring rate was being manipulated from 100 to 500 rpm.

Figure 3 displays the graph of concentration efficiency of ethanol versus the stirring rate. It can be seen that the concentration of ethanol increased as the stirring rate increased. In this study, U was fixed at 0.0005m/min and C_0 was fixed at 2.3 (%v/v). The highest increment of concentration was when the stirrer was rotated at 500 rpm which increased the concentration of ethanol by 52.2%. The result means the higher the rotational speed of the stirrer, the more pure ethanol obtained.

As the solution was being stirred, the solute had been washed away from the ice front leaving the ice in high purity. From the result obtained it is proven that stirring played an important role in lowering the concentration of the ice front thus enhancing the concentration of ethanol in liquid phase [7].

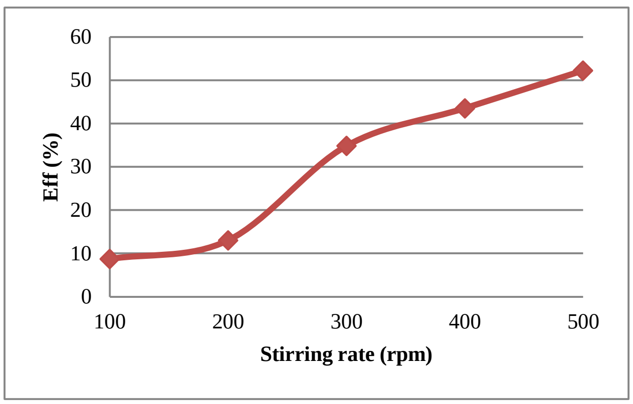

Figure 3 Effect of stirring rate on concentration efficiency at constant coolant temperature -10°C, time 60 min and concentration of ethanol 2.3 mol

Meanwhile, Figure 4 shows the effect of stirring rate on K. It is shown that increasing the stirring rate lowers the value of K which indicates the efficiency of the fractional freezing had increased as stirring rate increased. The lowest value of K was 0.2857 obtained when the stirring rate was at 500 rpm.

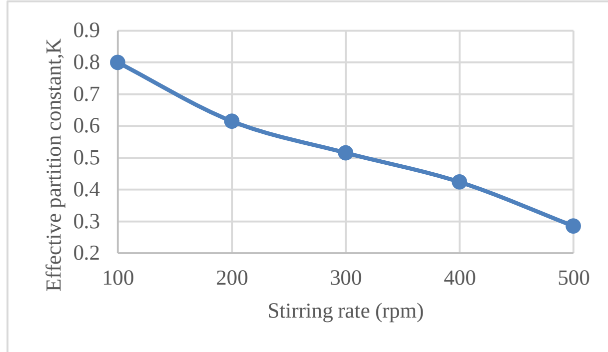

Figure 4 Effect of stirring rate on K value at constant coolant temperature -10°C, time 60 min and concentration of ethanol 2.3 mol

3.2 Effect of Coolant Temperature on the Concentration Efficiency of Ethanol and Effective Partition Constant

The experiment was conducted to study the effect of coolant temperature on concentration efficiency of ethanol in liquid phase and effective partition constant (K), after fractional freezing process. In this experiment, the advance speed of the ice front (U) and the stirring rate was kept constant at 0.0005 m/min and 300 rpm respectively. The coolant temperature was being manipulated from -6˚C to -14˚C.

Figure 5, the concentration efficiency of ethanol in liquid phase was found to increase as the coolant temperature decreased. Better outcomes were obtained at -14˚C where the concentration of the ethanol increased the most by 56.5% and it has the lowest value of K which is 0.3889 as shown in Figure 6.

It shows that the efficiency of the system also increased as the coolant temperature decreased. At higher cooling temperature, the ice crystals were able to grow in more ordered pattern since the heat transfer rate was slower [6]. Besides, the ice crystal size depends on the cooling rate, which can affect the level of occlusion [6, 8]. The result obtained can be explained by the relationship between the solutes mass transfer and the ice growth rate. It has been reported that the solutes mass transfer must be greater than the ice growth rate for the elution to occur [6, 9, 10]. Thus, it can be concluded that the advance speed of the ice front at 0.005m/min is very effective for an elution to occur at -14˚C resulting a high purity of ethanol in liquid phase.

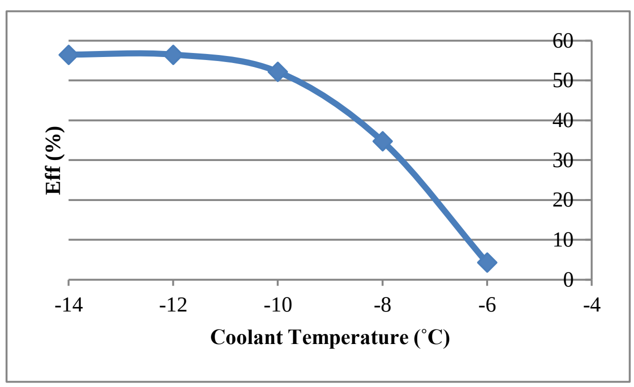

Figure 5 Effect of coolant temperature on concentration efficiency at constant stirring rate 300rpm, 60 min and concentration of ethanol 2.3 mol

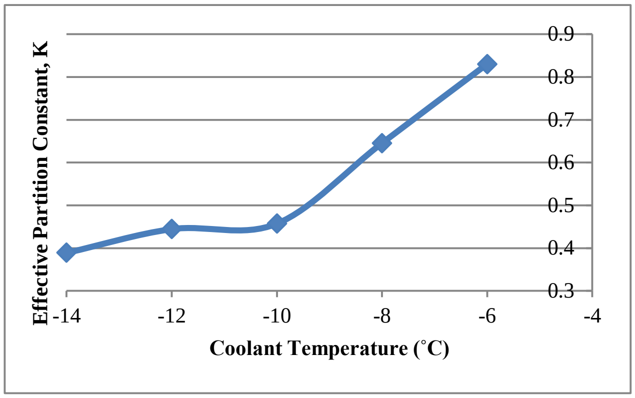

Figure 6 Effect of coolant temperature on K at constant stirring rate 300 rpm, 60 min and concentration of ethanol 2.3 mol

■4.0 CONCLUSION

This report is to draw attention to introduce fractional freezing method as an alternative method to separate a miscible liquid which contains volatile organic compound, in this case; ethanol and water. From this report, it can be concluded that fractional freezing efficiency was affected by stirring rate and coolant temperature.

The concentration of ethanol in liquid phase increased as stirring rate increased. The concentration of ethanol in liquid phase increased the most by 52.2% when the stirring rate at the highest rotating speed which is 500 rpm. The stirring is found necessary to equalize the whole concentration in the liquid phase and to wash away the impurities from the ice formed thus enhancing the concentration of ethanol in liquid phase.

Fractional freezing process was also affected by the coolant temperature used. It was found that as the coolant temperature decreased, the concentration efficiency of ethanol in liquid phase increased. The highest increment of ethanol concentration in liquid phase was when the coolant temperature was -14˚C where the concentration of ethanol increased by 56.5%. This is because the mass transfer is greater than the ice growth rate thus it gives high efficiency towards the process resulting high purity of ethanol in liquid phase.

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