Dehydration of Aqueous Ethanol Mixtures By Extractive Distillation

Thu Zar Thein
Chemical Engineering
Technological University
Ministry of Education
Thanlyin, Myanmar

Wai Mar Htway
Chemical Engineering
Technological University
Ministry of Education
Thanlyin, Myanmar

Win Ei Ei Tun
Chemical Engineering
Technological University
Ministry of Education
Thanlyin, Myanmar

Abstract: This paper investigate the dehydration of ethanol by extractive distillation process with salt in solvent and also without salt. There are many sources to produce ethanol. It can be obtained from plants and agricultural wastes as well as olefins from cracking units of petroleum refining. Because the methods of ethanol production are the hydration method and fermentation, water molecules are present in ethanol. It has to be dehydrated to use as a fuel in automobile engines and other applications. There are many methods to separate water from ethanol to improved concentration. In this paper, the dehydration of ethanol is carried out by extractive distillation process and use ethylene glycol as a separating agent with calcium chloride as salt in order to improve the concentration of ethanol. Different ratios of ethanol-water and ethylene glycol such as (1:1:0, 1:1:0.25, 1:1:0.25 (20% of solvent)) were tested to obtain the best result of concentration percent. The maximum ethanol concentration was 92 vol% which obtained from 52 vol% ethanol in feed mixture.

Keywords: anhydrous ethanol; ethylene glycol; calcium chloride; extractive distillation; concentration

1. INTRODUCTION

Ethanol or ethyl alcohol (C_2H_5OH) is a clear colorless liquid which is biodegradable, low in toxicity and causes little environmental pollution if split [1]. Ethanol burns to produce carbon dioxide and water. It is reduces pollution associated with petroleum products such as SO_x and NO_x. Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol [2]. Bioethanol and biodiesel are the alternative fuels that can be used. The production of alternative is due to the realization that crude oil stocks are limited, hence the swing towards more renewable sources of energy. Bioethanol and biodiesel have received increasing attention as excellent alternative fuels and have virtually limitless potential for growth [3].

Anhydrous ethanol is used as chemical reagent, organic solvent and raw materials for many important chemicals and intermediates for drugs, plastics, lacquers, polishes, plasticizers, cosmetics. It is also used in pharmaceutical formulations, production of biodiesel (fatty acid ethyl esters), electronic and military industries [3]. Anhydrous ethanol is considered to be an excellent alternative clean-burning fuel to gasoline. In properly designed automotive systems, ethanol has the potential to achieve very low emission levels. Pure 100% ethanol is not generally used as a motor fuel; instead, a percentage of ethanol is combined with unleaded gasoline. This is beneficial because the ethanol decreases the fuel's cost, increases the fuel's octane rating, and decreases gasoline's harmful emissions [4].

However the main challenge facing bioethanol production is the separation of high purity bioethanol, because bioethanol contains water. The separation of ethanol from water is difficult because of the existence of an azeotrope in the mixture. Since ethanol-water solution forms a minimum-boiling azeotropes of composition of 89.4 mol% ethanol and 10.6 mol% of water at 78.28℃ and standard atmospheric pressure, the dilute ethanol–water solutions produced by fermentation process can be continuously rectified to give at best solutions containing 89.4mol% ethanol at standard atmospheric pressure [5]. Therefore, special purpose for removal of the remaining water is required for manufacture of anhydrous ethanol. Various processes for producing anhydrous ethanol have been used. The two traditional methods of high purity ethanol separation are: Extractive distillation and Azeotropic distillation. Other three emerging techniques are: salt distillation, pressure swing distillation and pervaporation.

Extractive distillation is commonly applied in industry, and is becoming an important separation method in chemical engineering. Extractive distillation is a distillation in the presence of a miscible, high boiling, relatively non-volatile component, and the solvent that forms no azeotrope with the other components in the mixture. The method is used for mixtures having a low value of relative volatility, nearing unity. The method of extractive distillation uses a separation solvent, which is generally non-volatile, has a high boiling point and is miscible with the mixture, but doesn't form an azeotropic mixture. The solvent interacets differently with the components of the mixture, thereby causing their relative volatilities to change. This enables the new three-part mixture to be separated by normal distillation. The solvent should be easily separable from the bottom product, and should not react chemically with the components or the mixture, or cause corrosion in the equipment. The solvent plays an important role in design of extractive distillation and selection of suitable solvent/salt is fundamental to ensure an effective and economical design [5].

2. MATERIALS

2.1. Raw Materials

Ethanol was obtained from local market. The measured concentration of ethanol by alcohol-meter was 98 volume percent. Ethylene glycol was used as a solvent in this method. Calcium chloride was also used as a dissolved salt in solvent. And then, water was used as cooling water for condenser as well as solvent to get different concentrations of ethanol and it has the pH grade of 7. Ethylene glycol, calcium chloride and water can be obtained from local market.

3. EXPERIMENTAL PRODECURE

Three samples of experiment were tested in this paper. Experiment 1 was carried out by simple distillation method and 2, 3 were accomplished by extractive distillation method with solvent and then dissolved salt in solvent (20% of solvent). In these experiment were carried out by using simple batch distillation apparatus that operated bottom temperature in flask at 79℃, water flow rate of condenser 67.16 ml/sec, condenser water-in at 23℃ and condenser water-out at 32℃ The initial concentration of ethanol and the final concentration of ethanol were determined by using hydrometer**.**

Table-1. Operating Conditions for Experiment 1

Parameter	Experiment 1
Ethanol-water - ethylene glycol feed ratio	1:1:0
Volume of ethanol	200 ml
Volume of water	200 ml
Ethanol volume concentration in feed	52%

According to the Table-1, ethanol and water are fully mixed and stirred in beaker and then determined the ethanol concentration of feed using alcohol meter. It was heated on heating mantle at least 40 minutes and then simple bath distillation method was carried out. Finally, the volume concentration of the purified product was determined by using hydrometer.

Table-2. Operating Conditions for Experiment 2

Parameter	Experiment 2
Ethanol-water-ethylene glycol feed ratio	1:1:0.25
Volume of ethanol	200 ml
Volume of water	200 ml
Volume of ethylene glycol	50 ml
Mass of salt	-
Ethanol volume concentration in feed	52%

In experiment 2, ethylene glycol was used as a solvent and it was added to mixture of ethanol-water. That was heated on heating mantle at least 40 minutes. It was carried out extractive distillation process by using solvent.

Table-3. Operating Conditions for Experiment 3

Parameter	Experiment 3
Ethanol- water - ethylene glycol feed ratio	1:1:0.25
Mass of ethanol	200 ml
Mass of water	200 ml
Mass of ethylene glycol	50 ml
Mass of salt (20% of solvent)	11.1g
Ethanol volume concentration in feed	52%

In the experiment 3, 11.1 grams of calcium chloride was weighed and crushed with pestle to get the powder form. The powder of $CaCl_2$ was mixed with ethylene glycol in the beaker. The ratio of ethanol, water and ethylene glycol (1:1: 0.25) were completely mixed with stirrer. The final mixture was heated on a heating mantle at 79℃ for at least 2 hours. Finally, the ethanol concentration of product was measured by using alcohol meter. Each experiments were carried out at least three times and collected the data.

Figure 1 -Testing of simple bath distillation

4. RESULTS AND DISCUSSIONS

Table-4. Results of Experimental Testing

Test	Ethanol-water-ethylene glycol feed ratio	Mass of salt	Final Results of Ethanol (vol%)
Experiment 1	1:1:0	-	82%
Experiment 2	1:1:0.25	-	88%
Experiment 3	1:1:0.25	11.1g	92%

According to the experimental testing of Tabe-4, the result of experiment 1 was obtained the ethanol concentration of 82 vol% and it was simple distillation which separate ethanol and water based on their boiling point. Anhydrous ethanol could not be obtained in experiment 1.

In experiment 2, extractive distillation was carried out and ethylene glycol was used as a separating agent. The concentration of ethanol improved to 88 vol% was obtained in this experiment.

In the experiment 3, the resulting ethanol concentrations were more improved to 92 vol% in the top product from 52 vol% concentration of ethanol in the feed mixture. This experiment integrates the advantages of liquid solvent (easy solvent) and solid salt (high separation ability). It improves the performance of solvent. The amount of maximum ethanol concentration was obtained in this experiment because extractive distillation was carried out by using solvent in which $CaCl_2$ was used as salt.

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this paper, the main purpose is obtainable ethanol from the local market to be dehydrated by one of purifying processes. Among them, the extractive distillation with ethylene glycol solvent was used to purify ethanol-water mixtures in either with dissolved salt or without salt. According to the literature, a simple distillation process can produce maximum concentration of 95.6 vol% and the extractive distillation with dissolved salt in solvent enable to purify ethanol-water almost anhydrous (above 99.99 vol% ethanol). The extractive distillation with salt in solvent improves the performance of solvent, reduce the number of theoretical plates, the energy consumption and cost of equipment. This process has high efficiency and low solvent wastage.

The advantages of this process are (1) to complete nonvolatile, exist only in the liquid phase (2) the overhead product will be completed free of separating agent (3) require lesser energy (4) require lesser separating agent. The number of theoretical plates in liquid solvent extractive distillation is more than salt dissolved in liquid solvent extractive distillation. The most important parameters of the distillation such as the number of theoretical plates vary with the reflux ratio and the concentration of the desired component in the feed.

In the practical testing, the ethanol products were not pure because of some difficulties during the operation, such as controlling the temperature of the heating mental. However, ethanol concentration of 82 vol% was produced from the concentration of 52 vol% ethanol in feed mixture by a simple bath distillation method. That of about 88 vol% ethanol was accomplished from 52 vol% ethanol in feed mixture by an extractive distillation with ethylene glycol solvent. The ethanol concentration of 92 vol% was done from 52 vol% ethanol in feed mixture by extractive distillation with dissolved salt ($CaCl_2$) in solvent.

5.2 Recommendation

In this study, further experiment is needed to be done even though the experimental results of ethanol products are satisfied. The ethanol concentration will be more improved (1) if the heating mental can be controlled stable at the desired temperature and (2) if the distillation column with plates or trays can be used in extractive distillation.

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