SEPARATION OF ETHANOL-WATER AZEOTROPE MIXTURES USING EXTRACTIVE DISTILLATION METHOD

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Abstract *Extractive distillation is a specialized distillation process that involves adding an additional component (extractive agent or solvent/entrainer) to the mixture in order to alter the relative volatilities of the components and enable their separation, even when they form azeotropes. This technique is commonly used to separate azeotropic mixtures, such as ethanol-water azeotropes. The ethanol-water azeotrope is a well-known example, where the mixture contains around 95.6 wt% ethanol and 4.4 wt% water. Traditional distillation methods cannot separate these components efficiently due to the azeotropic behavior. However, extractive distillation offers a solution by introducing a third component (entrainer) that forms a ternary azeotrope, which has different properties compared to the binary azeotrope (ethanol-water). This study presents the effect of the operating parameters (e.g., column configuration, pressure, entrainer type) on energy consumption while the purity of ethanol is set to 99.5 wt%. Appropriate entrainers (i.e., glycerol, ethylene glycol) are chosen to extract water from methanol at different compositions. The optimum design of ethanol-water azeotrope separation is obtained by using sensitivity analysis in Aspen Plus simulation. The results indicate the trade-off between solvent and reboiler duty consumption. An advanced comparison study is recommended, including the mixing of both solvents as entrainer.*

Keywords: Azeotrope separation, entrainer, ethanol-water, extractive distillation.

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1. INTRODUCTION

Water-ethanol separation, often referred to as ethanol dehydration or ethanol purification, is a crucial process in various industries, including the pharmaceutical, chemical, and beverage sectors, as well as in the production of biofuels. This separation involves the removal of water from an ethanol-water mixture to achieve the desired ethanol concentration or purity [1].

Ethanol, commonly known as alcohol, is a versatile and widely used solvent, fuel, and beverage ingredient. It is often produced through fermentation processes, which result in a mixture of ethanol and water [2]. However, for many applications, especially when high-purity ethanol is required, the removal of water is essential.

Separating azeotropes can be challenging due to their unique properties. Azeotropes are mixtures of two or more substances that have a constant boiling point and composition. This means that during traditional distillation processes, it's difficult to separate the components completely because they evaporate and condense together [3]. Therefore, special techniques are required to apply in the azeotrope separation.

The separation of water from ethanol as azeotrope mixture can be challenging because ethanol forms an azeotrope, a mixture with a constant boiling point composition, with water at approximately 95.6% ethanol by weight. This means that simple distillation cannot achieve ethanol concentrations greater than this value. To obtain anhydrous ethanol (ethanol with very low water content, typically less than 1% water by weight), more advanced separation techniques are necessary.

Several methods are employed for water-ethanol azeotrope separation, including distillation techniques (e.g., pressure swing distillation [4], extractive distillation [3]), molecular sieves solid materials with highly porous structures, membrane separation technologies (e.g., pervaporation [5], vapor permeation [6]), chemical looping [7], [8], and azeotropic distillation [9].

Extractive distillation offers several advantages compared to other separation techniques, particularly when dealing with challenging azeotropic or close-boiling mixtures. Extractive distillation is particularly effective at breaking azeotropes, which are mixtures with constant boiling points. By introducing an extractive agent (also known as a solvent or entrainer), it alters the vapor-liquid equilibrium, allowing for the separation of components that would otherwise form an azeotrope [10]. This capability is especially valuable in situations where other methods struggle to achieve separation.

Extractive distillation allows for highly selective separation. The choice of the extractive agent can be tailored to the specific components being separated, ensuring that one component is preferentially absorbed by the solvent while the other is distilled overhead. This selectivity can lead to higher-purity products.

In some cases, extractive distillation can be more energy-efficient than other separation techniques. By using an extractive agent, it's possible to reduce the number of theoretical trays or stages required for separation, which can result in energy savings [11], [12].

Extractive distillation systems are flexible and adaptable. Engineers can design systems with varying levels of complexity, depending on the desired separation goals and constraints. This flexibility makes it suitable for a wide range of applications.

2. METHODOLOGY

2.1. Aspen plus simulation

Simulating the separation of methanol and water using Aspen Plus involves setting up a process flow diagram, specifying components, choosing appropriate thermodynamic models, and defining operating conditions (Table 1).

Ethanol and water form an azeotrope at approximately 95.6% ethanol by weight (Fig. 1). It means that when a mixture of ethanol and water containing about 95.6% ethanol and 4.4% water is heated and distilled, the vapor that comes off has the same composition as the liquid mixture. In other words, the ethanol and water in this mixture are so strongly bonded that it's difficult to separate by simple distillation.

Tabel 1. Initial operating parameters [13]

Parameter	Value
Colum pressure (atm)	1
Feed flow (kmol/h)	12.461
Feed composition	EtOH/H_2O (0.47/0.53)
Target EtOH purity	0.995
Entrainer flow (kmol/h)	5
Entrainer composition (mole fraction)	EG (1) GLY (1) GLY/EG (0.5/0.5)
Number of stage	EDC (26 stages) RGC (10 stages)
Feed stage	Ent. (2nd stage) EDC (17th stage) RGC (5th stage)

EtOH-H_2O azeotrope poses a challenge in industries where the separation of ethanol and water with high purity is necessary, such as in the production of anhydrous (water-free) ethanol for fuel or pharmaceutical applications. To separate ethanol and water beyond this azeotrope composition, more advanced separation techniques like extractive distillation, pressure swing distillation, or the addition of specialized entrainers are often used to break the azeotrope and achieve the desired separation.

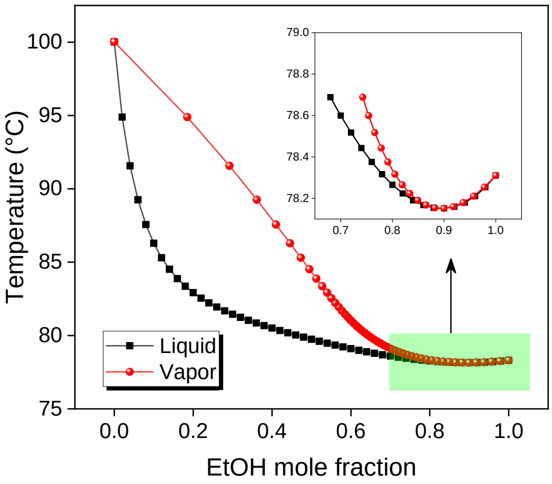

Figure 1. Txy diagram of ethanol-water at 1 atm.

The extractive distillation design for ethanol-water azeotrope separation is shown in Fig. 2. The entrainer is introduced at the top and ethanol-water azeotrope mixture is fed at the bottom of the extractive distillation column (EDC). The bottom product of EDC is then fed into the entrainer regeneration column (RGC) in order to regenerate entrainer and further recycled into EDC.

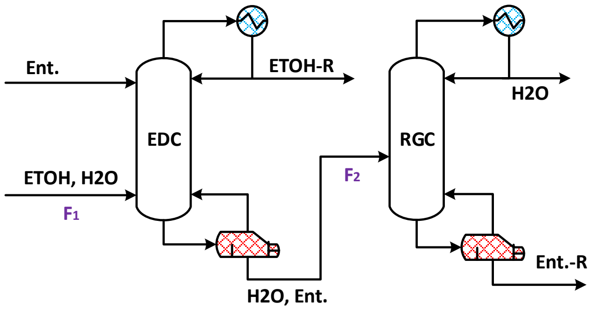

Figure 2. Extractive distillation design for EtOH-H_2O azeotrope separation

2.2. Sensitivity analysis strategy

Sensitivity analysis in the context of extractive distillation refers to evaluating how changes in various parameters or factors affect the performance and efficiency of the distillation process. This analysis is crucial for optimizing the design and operation of extractive distillation systems.

The sensitivity analysis of the EtOH-H_2O azeotrope separation is started from the EDC as the main process of azeotrope separation by extraction method. The sensitivity analysis of RGC is not considered in this study. However, the optimum parameter in RGC can be easily discussed once the optimum parameter of EDC is presented. The operating parameters in the sensitivity analysis of EDC include entrainer flowrate, reflux ratio, and feed stages (Table 2), with respect to the reboiler duty as well as EtOH purity. The prior target of the sensitivity analysis is preferred to high EtOH and with lower reboiler duty.

Table 2. Parameter range of sensitivity

Parameter	Range
Entrainer flow rate (kmol/h)	1-10
Reflux ratio	0.8-1.8
Feed stage	14-24

3. RESULTS AND DISCUSSION

3.1. Sensitivity analysis of EDC using EG

The effect of EG flow rate and reflux ratio on the purity and reboiler duty are presented in Figure 3.

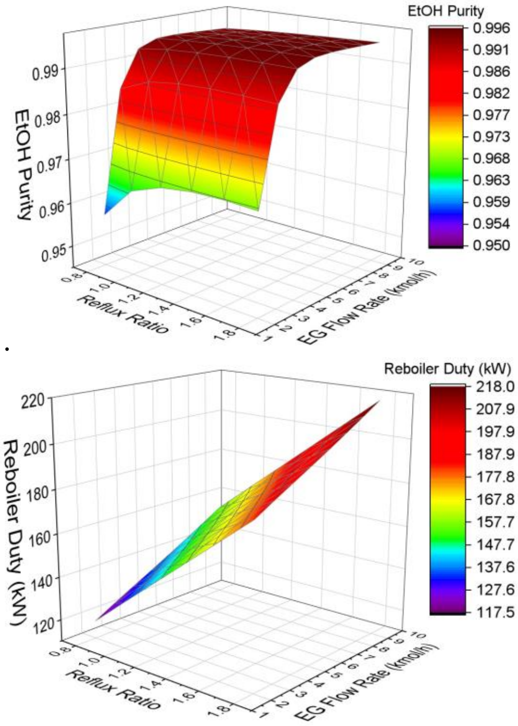

Figure 3. Effect of EG flow rate and reflux ratio to the purity and reboiler duty

At a lower EG flow rate and low reflux ratio, the maximum purity is about 0.955. When the reflux ratio inrease to 1.4, the purity is significantly increases to 0.970 which presents the optimum point for reflux ratio at EG flow rate of 2 kmol/h. Once the EG flow rate is increased to 5.5 kmol/h, the EtOH purity enhances to 0.995. It means that the minimum EG consumption is 5.5 kmol/h to achieve the purity of 0.995 with a reboiler duty of 204 kW.

In Figure 4, the influence of the reflux ratio and feed stage to the purity and reboiler duty are shown. The feed stage does not significantly influence the

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EtOH purity as well as reflux ratio but the reboiler duty increase by increasing of reflux ratio.

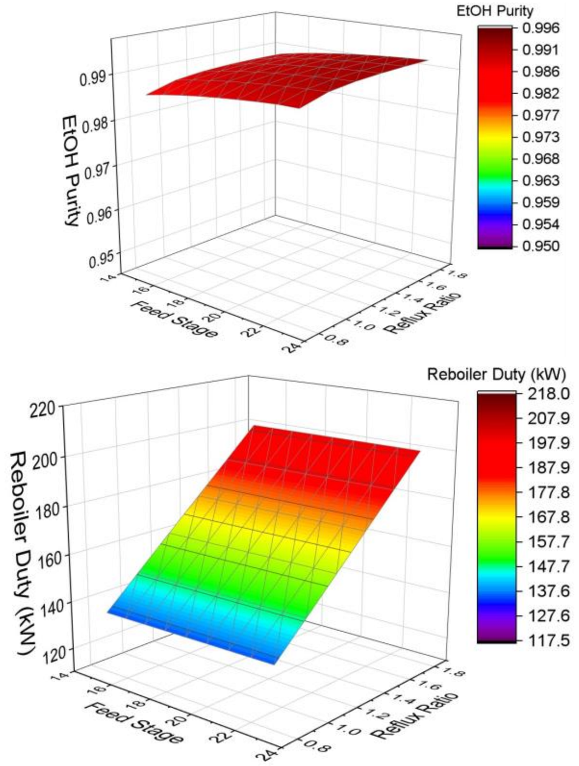

Figure 4. Effect of reflux ratio and feed stage to the purity and reboiler duty with EG=5 kmol/h

3.2. Sensitivity analysis of EDC using GLY

Because of the differences in the physical and chemical properties, GLY solvent is considered as the comparison to the EG solvent. Different properties of the solvent impact the extraction performance [14].

Figure 5 shows the influence of GLY flow rate and reflux ratio on the purity and reboiler duty. Although the optimum point is shown at reflux ratio of about 1.0, it does not really impact when the when GLY flow rate increases over 3 kmol/h. The result indicates the purity of 0.995 can be achieved at 3 kmol/h and even up to 0.999 purity at the same flow rate in EG case (5.5 kmol/h). It can be proven that the solvent consumption is less by using GLY. In the economical point of view, less solvent used resulting the less material cost [15]. Furthermore, reducing the solvent consumption can reduce the reboiler duty in the RGC and reduce the operating cost in advance [16].

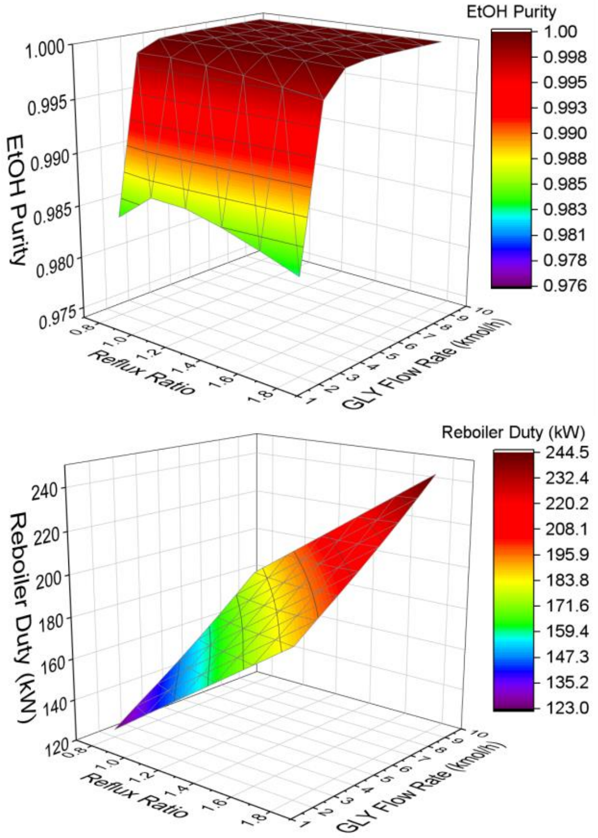

Figure 5. Effect of GLY flow rate and reflux ratio to the purity and reboiler duty

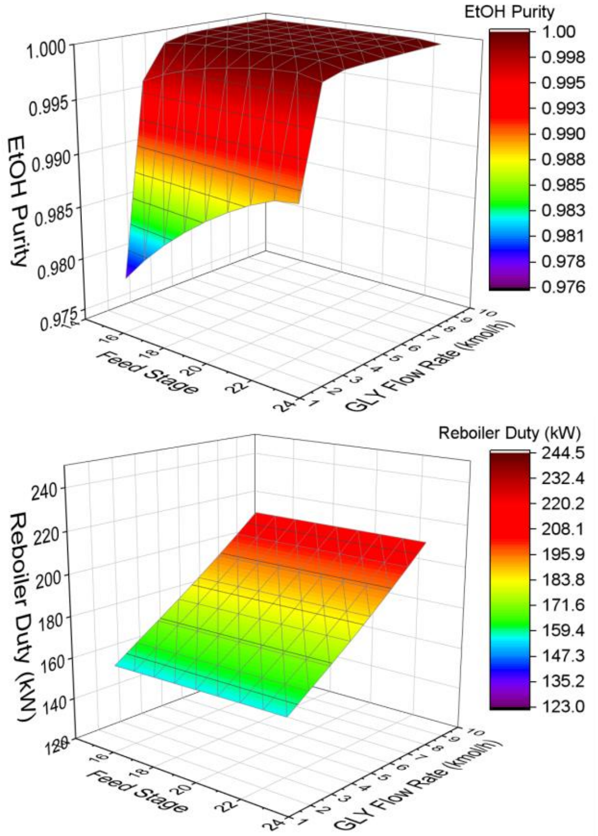

Figure 6. Effect of reflux ratio and feed stage to the purity and reboiler duty with GLY=5 kmol/h

By Figure 6, the the feed stage impact the purity if the GLY flow rate is set at lower bond and is less impact when the its flow rate increased over 3 kmol/h. At the low solvent flow rate, the extraction performance of the solvent to extract the water from EtOH is less. Therefore, the feed stage need to be fed at the lower part of the column or far away from the solvent feed stage of at high number of stage in order to maximaze the contact time between the solvent and the mixture.

The comparison of the optimum solvent is presented in Figure 7. At the same EtOH purity (0.995), the optimum solvent consumption are obtained at 5 kmol/h and 3 kmol/h, respectively. In addition, the energy consumption or reboiler duty of EDC using EG solvent is 204 kW, less than GLY solvent, which is about 233 kW. This result is influenced by the boiling point of each component (Boiling point EG = 197°C, GLY = 290°C). This comparison shows the trade-off between the solvent and the reboiler duty consumption for both solvents. Mixing of both solvents as an entrainer is also recommended by previous studies to maximize the advantage from these solvents. An advance comparison study is necessary especially in the RGC due to the high energy consumption taken by RGC rather than EDC.

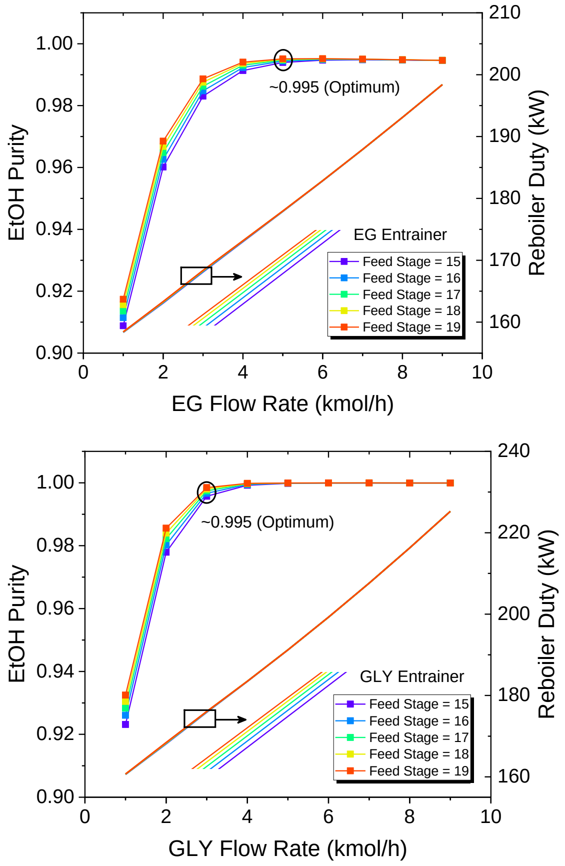

Figure 7. Comparison of the optimum solvent.

4. CONCLUSION

This study presents the effect of the operating parameters on energy consumption while the purity of ethanol is set to 99.5 wt%. Two entrainers (GLY, EG) are chosen. The optimum design of ethanol-water azeotrope separation is obtained by using sensitivity analysis in Aspen Plus simulation. At the same EtOH purity (0.995), the optimum solvent consumption are obtained at 5 kmol/h and 3 kmol/h, respectively. The reboiler duty of EDC using EG solvent is 204 kW, less than GLY solvent (233 kW). The results indicate the trade-off between solvent and reboiler duty consumption. This comparison illustrates the compromise between the solvent and the amount of reboiler duty required for each solvent. An advanced comparison study is particularly imperative in the RGC context, given that the RGC consumes significantly more energy than the EDC. Additionally, prior research suggests utilizing a mixture of both solvents as an entrainer in order to optimize the benefits of these solvents.

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