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Energy Evaluation of Ethanol Dehydration with Glycol Mixture as Entrainer

Extractive distillation of ethanol dehydration using glycols as entrainers is proposed. Specifically, ethanol dehydration of an azeotropic mixture in the presence of ethylene glycol + glycerol mixture is evaluated. Simulation is performed and the vapor-liquid equilibrium of ethanol + water + ethylene glycol + glycerol is predicted with the NRTL model. Minimization of energy consumption in both extractive and regeneration columns is attempted. Optimal operating parameters of the process including glycol concentration in the solvent mixture, main feed, and entrainer feed trays, total number of theoretical trays, and heat supplied to the reboiler are determined in order to achieve a specified distillate purity of 99.9 mol % ethanol.

**Keywords:** Ethanol dehydration, Extractive distillation, Glycol, NRTL model, Reflux ratio

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1 Introduction

Ethanol is widely used in the chemical industry as a raw material in the manufacturing process of esters and ethers as well as a solvent in the production of paint, cosmetics, and perfumery. It is a biofuel with high energy values and can be produced from renewable resources [1]. Currently, ethanol is added to gasoline as a substitute for methyl tert-butyl ether (MTBE) to increase the gasoline octane number and combustibility [2–4]. The most popular processes for ethanol dehydration are: heterogeneous azeotropic distillation using solvents such as benzene and cyclohexane, extractive distillation with solvents and salts as entrainers [5–7], adsorption with molecular sieves, and processes that employ pervaporation membranes [8–13]. Different alternative methods for ethanol dehydration, such as azeotropic distillation, adsorption with molecular sieves, or distillation with pervaporation, were industrially applied in the past but some are no longer in use due to high operating costs, operative problems, and high energy consumption. Meanwhile, extractive distillation proved as most interesting alternative of ethanol-water separation because of the low energy consumption [14].

Extractive distillation is the most common method for ethanol dehydration [15,16] which includes an entrainer to increase the relative volatility of the key components of the feed without forming a new azeotrope [17,18]. This process is applied to separate either low relative volatility systems or those including an azeotrope. The entrainer requires certain characteristics in order to make a process feasible [19,20]. In this process, entrainer feed flow rate and reflux ratio of the extractive column represent the crucial design degrees of freedom that govern feasibility and operating cost [21].

The solvent is fed into the upper section above the feed stream of the initial mixture and maintains a high concentration in the descending liquid phase. Then it is recovered as the bottom product of the column to be separated in the regeneration column. Commonly used solvents in extractive ethanol distillation are glycols [16–22], glycerol [23], and gasoline [24,25]. Lee and his team studied the extractive process using solvent mixtures and tried to achieve a balance between the solvent’s capacity (solvency) and selectivity, as in most cases solvents with high selectivity for the key components to be separated have a low capacity, and vice versa [17].

The separation of ethanol and water is complicated due to the existence of an azeotrope. The two traditional methods of high-purity ethanol separation are extractive distillation and azeotropic distillation. Other techniques include salt distillation, pressure swing distillation, or evaporation. Roth et al. [26] proposed a process analysis and optimization of hybrid processes for ethanol dehydration; however, five hybrid processes consisting of distillation, vapor permeation, and adsorption for the dehydration of bioethanol make the process rather complicated and provide low energy efficiency. Based on the different characteristics of these techniques, however, ethanol dehydration by extractive distillation proved to be a best choice in literature.

Extractive distillation uses a two-column system but the operation is simple. Ethylene glycol has been proposed in the literature as an extractive distillation solvent for separation of ethanol from its mixture with water. Here, extractive distillation is simulated as separation technique for an ethanol-water mixture.
system with glycols as separating agent. Optimal parameters of the extractive distillation process are determined to minimize energy consumption using a solvent mixture.

2 Problem Definition and Methodology

The process flow sheet of extractive distillation for the system ethanol + water is presented in Fig. 1. The azeotropic mixture and the entrainer streams are fed separately to the extractive distillation column, where the dehydration of the desired compound (ethanol) takes place. The bottom product of the extractive distillation column feeds the entrainer regeneration column, where the entrainer leaving from the reboiler is separated from water and is recycled to the extractive distillation column. Since part of the entrainer is missing in the process, the recycled stream is mixed with a make-up entrainer stream [27].

The process contains two columns, namely an extractive distillation column and an entrainer recovery column. The entrainer is continuously fed to one of the top stages of the extractive column while the azeotropic feed enters at a middle stage lower down the column. Ethanol is obtained at the top of the extractive distillation column and the water + entrainer mixture, removed at the bottoms, is sent to the second entrainer recovery column. At the top of the recovery column, water is withdrawn with some ethanol while at the bottom high-purity entrainer (ethylene glycol, glycerol) is recycled back to the extractive distillation column.

Ethanol + water mixture has a minimum-boiling homogeneous azeotrope of 89 mol% ethanol composition at atmospheric pressure and 78.1°C. The NRTL physical property model is used to describe the nonideality of the liquid phase, and the vapor phase is assumed to be ideal. All binary interaction parameters of the NRTL model are taken from the DECHEMA database (Tab. 1). The NRTL activity coefficient model is validated by calculating the vapor-liquid equilibrium of the azeotropic mixture in the presence of ethylene glycol and glycerol solvents. An equimolar azeotropic mixture of ethanol + water is the main feed, and the purity of the main product ethanol is desired to be higher than 99.5 mol%.

The two most important variables used to achieve the desired ethanol purity are the entrainer/feed ratio and reflux ratio. The former has a little effect on the energy consumption compared to the reflux ratio impact on the reboiler duty. Due to the foregoing reason, the reflux ratio in an extractive distillation column is fixed at a minimal optimization value. This work is carried out with the simulation tool Simulis Thermodynamic and ProSimPlus version 3.4.

The influences of parameters required for the separation process such as the reflux ratio \( R \), total column tray number \( N \), main feed tray \( N_E \), entrainer feed tray \( N_{FE} \), entrainer/feed ratio \( F_E/F \), and concentration of glycerol in the solvent mixture \( x_E \) were evaluated. The operating pressure of the column was set at 1 atm and the main feed state is considered as saturated liquid.

Sensitivity analysis was performed to visualize the effects of two variables on a specific design condition. The operating criteria considered were energy consumptions of the reboilers for extractive distillation and regeneration as well as the distillate purity of ethanol in the extractive column that should be above 99.5 mol%. Rigorous simulation of an extractive distillation column was conducted using the simulator Prosim Plus version 3.2 in order to determine the best operating conditions of the process flow sheet (Fig. 1). According to Serafimov’s classification scheme [28], the system ethanol + water + solvent belongs to class 1.0.1-a. Fig. 2a displays the corresponding univolatility curve \( a_{AB} = 1 \) and volatility order region. Knowledge of the residue curve map and the location of the univolatility curve can help to assess which product is removed in the distillate when using a light, intermediate, or heavy entrainer. With a heavy entrainer, A can be distilled using a direct sequence if the univolatility curve intersects the A-E edge [29].

3 Results and Discussion

3.1 Feasibility of the Extractive Distillation Process

The separation of ethanol from its mixture with water adding a heavy entrainer (ethylene glycol or glycerol) illustrates the case where the univolatility curve \( a_{AB} = 1 \) reaches the binary side ethanol-water (see Fig. 2b). The components of the main feed A (ethanol) and B (water) are saddle points (S) of the residue curves, the entrainer (E) is the stable node (SN), while the azeotrope at \( T_{min} \) is an unstable node (UN) (Fig. 2a). The univolatility curve \( a_{AB} = 1 \) goes from the azeotrope to its intersection with the AE side at the \( x_E \) point. Fig. 2a also indicates the essential features of residue curves, univolatility curve, and vol-
ability order region of class 1.0-1a, corresponding to the separation of the minimum-boiling azeotropic mixture AB by extractive distillation with a heavy entrainer E.

As Frits et al. [30] reported, the process feasibility is based on the study of operating parameter values like reflux ratio, entrainer/feed ratio, etc. to achieve the intersection of the composition profiles of different column sections (rectifying, extractive, and stripping sections; Fig. 2) joining the top and bottom products of the column, entrainer/feed ratio [30]. This intersection can be assessed geometrically, as demonstrated here, but a mathematical analysis can be employed as well. The profiles of the column sections are described by the general differential Lelkes model [31]:

\[
\frac{dx}{dh} = \pm \frac{V}{L} [y(x) - y^*]
\]  

(1)

Fig. 3 illustrates the evolution of the entrainer/feed ratio as function of reflux to achieve a 99.5 mol % purity of the distillate product in ethanol. The limitations of the feasibility of extractive distillation of the azeotropic mixture ethanol + water in the presence of ethylene glycol and glycerol are provided in Fig. 3.

Feasible regions for different conditions of entrainer/feed ratio and reflux ratio are plotted to include various feasible operating points (Fig. 4). The full triangle symbol represents an infeasible point, the open square a feasible point. It is found that the feasible region is limited by a minimum entrainer/feed ratio as function of the reflux ratio. Thus, due to a higher selectivity, the feasible region is larger in the case of glycerol than ethylene glycol. The addition of the solvent leads to the appearance of a UNextr point, A, and the disappearance of the azeotropic point which makes separation of the mixture easier (Fig. 4).

The optimal operating parameters for extractive distillation of the system ethanol-water in the presence of ethylene glycol and glycerol as entrainers are summarized in Tab. 2. The entrainer/feed flow ratio and energy consumed at the reboiler are lower with entrainer glycerol than with ethylene glycol at nearly the same reflux ratio. This also can be explained by the fact that glycerol has a better selectivity than ethylene glycol.

Figs. 5 and 6 illustrate that in order to obtain the desired purity of ethanol in the distillate, regardless the total number of

**Figure 2.** (a) Thermodynamic characteristic of a system of class 1.0-1-a; (b) residue curves map of ethanol-water with entrainer (ethylene glycol, glycerol).

**Figure 3.** Evolution of the entrainer feed ratio as function of reflux ratio to recover ethanol in distillate with entrainer: (a) ethylene glycol, (b) glycerol.
Table 2. Operating parameters of the extractive distillation column in the presence of ethylene glycol and glycerol as entrainers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ethylene glycol (EG)</th>
<th>Glycerol (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case study 1</td>
<td>Case study 2</td>
</tr>
<tr>
<td>$N$</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>$N_{FE}$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$N_{F}$</td>
<td>32</td>
<td>22</td>
</tr>
<tr>
<td>$F_{E}/F$</td>
<td>0.95</td>
<td>1.45</td>
</tr>
<tr>
<td>$R$</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>$x_D$</td>
<td>0.9952</td>
<td>0.9952</td>
</tr>
<tr>
<td>$Q_B$ [kJ h$^{-1}$]</td>
<td>68438.6</td>
<td>81287.2</td>
</tr>
</tbody>
</table>

Figure 4. Extractive profiles of the system ethanol-water with heavy entrainer: (a) ethylene glycol, (b) glycerol.

Figure 5. Temperature profiles of extractive distillation of the system ethanol-water using ethylene glycol and glycerol as entrainers.

Figure 6. Composition profiles of an extractive distillation column of the system ethanol-water with entrainer: (a) ethylene glycol; (b) glycerol.
stages, the separation of ethanol-water in the presence of glycol-glycerol entrainers requires more stages of extractive section than that of rectifying and stripping sections. Ethylene glycol and glycerol are less volatile due to their very high boiling temperatures compared to ethanol and water, therefore, most of them remain in the liquid phase without leaving for the column top during the vapor phase, resulting in very low mole fractions of these mixture entrainers in the rectifying section, but their concentration remains constant throughout the extractive section while increasing in the stripping section.

Moreover, it can be concluded from Tab. 2 that at nearly the same reflux ratio and same purity of ethanol in the distillate, along with the reduction of the total tray number of the extractive distillation column by ten stages, the amount of energy supplied to the reboiler increases by around 15.8% of ethylene glycol and 8.7% of glycerol.

### 3.2 Effect of Tray Number and Solvent Types on Entrainer/Feed Ratio

Rigorous simulation of extractive distillation with pure solvent (ethylene glycol and glycerol) indicates that the entrainer/feed ratio decreases when the total tray number of the extractive distillation column increases (Fig. 7 a). This decrease is more remarkable when the number of trays is reduced from 25 to 15. The amount of solvent used in the case of glycerol is lower than in the case of ethylene glycol. Therefore, a column with a number of trays between 35 and 25 is proposed since in this interval of total tray number the entrainer/feed ratio is slightly reduced.

Moreover, obviously the separation of the azeotropic mixture ethanol-water with glycerol requires a lower entrainer/feed ratio than that with ethylene glycol, due to the higher selectivity of glycerol compared to ethylene glycol. The mixture of glycerol and ethylene glycol reduces significantly the demand of entrainer/feed ratio (Fig. 7b). For the solvent mixture, the evolution of total tray number with entrainer/feed ratio follows the same trend as for pure entrainers. Consequently, a column with a total tray number between 25 and 35 stages is recommended.

### 3.3 Effect of Glycerol Concentration on Entrainer/Feed Ratio and Energy Consumed in the Reboiler

To determine the optimal operating parameters of the extractive distillation process including the regeneration column, several cases of rigorous calculations have been conducted. The optimized results are summarized in Tab. 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1 of column 1</th>
<th>Case 2 of column 1</th>
<th>Case 1 of column 2</th>
<th>Case 2 of column 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>35</td>
<td>25</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>$N_{FE}$</td>
<td>4</td>
<td>4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$N_F$</td>
<td>32</td>
<td>22</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$R$</td>
<td>1.6</td>
<td>1.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$F_E/F$</td>
<td>0.42</td>
<td>0.64</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$x_E$ (glycerol)</td>
<td>0.4</td>
<td>0.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$x_D$</td>
<td>0.9954</td>
<td>0.9955</td>
<td>0.9954</td>
<td>0.9955</td>
</tr>
<tr>
<td>$Q_B$ [kJ h$^{-1}$]</td>
<td>59 743.4</td>
<td>59 280.5</td>
<td>33 621.5</td>
<td>32 956.1</td>
</tr>
<tr>
<td>$Q_T$ [kJ h$^{-1}$]</td>
<td>93 364.9</td>
<td>92 236.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the same glycerol concentration in the solvent mixture (40 mol%), the entrainer/feed ratio increases while the reflux ratio reduces along with the total tray number. This means that there is a minor relationship among these three parameters in the case of mixed solvents (Tab. 3). The reflux ratio not only depends on the total tray number for the case of a pure solvent. The energy consumed in the extractive distillation column decreases very slightly by about 0.77% when the total tray number varies from 35 to 25 while the total energy of the whole process with the same parameters of the regeneration column reduces by about 1.2%.

In Figs. 8 a and b, at fixed reflux ratios of $R = 3.5$ and 1.6 the reboiler heat $Q_B$ is plotted against the mole fraction of glycerol with entrainer/feed ratio as parameter. The amount of reboiler heat demand $Q_B$ and entrainer/feed rate decrease with higher glycerol concentration in the solvent mixture. This decline is even more significant when the mole fraction of glycerol is between 0 and 10 mol % resulting from the positive effect of mixing glycerol with ethylene glycol to the ethanol dehydration process (Figs. 8a and b) whereas for

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**Figure 7.** (a) Effect of total tray number on $F_E/F$ value; (b) effect of glycerol concentration in entrainer mixture on $F_E/F$ value.
glycerol concentrations above 10%, the decrease in entrainer/feed ratio is less obvious. Accordingly, using a mixture of solvents containing less than 40 mol % of glycerol is recommended since the entrainer/feed ratio of the solvent mixture reduces slightly from a concentration of 50 mol % glycerol. This may be due to the balance between the solvency of glycerol and selectivity of ethylene glycol reached at the condition of 40 mol % of glycerol in the mixture.

The evolutions of the relative volatility and selectivity are plotted as function of the mole fraction of glycerol and entrainer/feed ratio in Figs. 8 c and 8 d, respectively. With higher mole fraction of glycerol the relative volatility and selectivity increase while the entrainer/feed ratio decreases. It is interpreted that the concentration of glycerol in the solvent mixture is inversely proportional to the aforementioned parameters. This means that the entrainer/feed ratio more sensibly influences the selectivity and relative volatility of the binary mixture compared to the effect of glycerol concentration on the behavior of the solvent mixture. Consequently, the selectivity of ethylene glycol is influenced by the ethylene glycol concentration in the solvent mixture.

The comparison between the total energy consumed by extractive distillation and regeneration columns in the case of pure entrainers (ethylene glycol or glycerol) and solvent mixture (ethylene glycol + glycerol) indicates that the process consumed minimal energy in the case of mixed entrainer (Tab. 4). Therefore, it is of great interest to investigate mixed solvents.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>EG</th>
<th>Glycerol</th>
<th>EG-glycerol</th>
<th>EG</th>
<th>Glycerol</th>
<th>EG-glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$Q_{\text{Total}}$ [kJ h⁻¹]</td>
<td>120 834.2</td>
<td>95 761.0</td>
<td>92 699.5</td>
<td>162 416.3</td>
<td>106 709.8</td>
<td>97 774.9</td>
</tr>
</tbody>
</table>
3.4 Evolution of Entrainer/Feed Ratio with Reflux Ratio and Solvent Concentration

The obtained results of rigorous simulation of the extractive distillation column demonstrate that the reflux ratio is closely related to the entrainer/feed ratio at different concentrations of solvent mixture in the extractive distillation process (Fig. 9). It should be pointed out that the entrainer/feed ratio decreases continuously with higher glycerol concentration in the solvent mixture when reflux ratio is between 3.5 and 1.6. When the reflux ratio ranges between 1.3 and 0.8, a minimum of entrainer/feed ratio occurs at a certain glycerol concentration, and the value of this minimum increases when the reflux ratio decreases.

Composition profiles of the ternary mixture along the extractive distillation column are given in Fig. 10. When the reflux ratio ranges between 1.6 and 0.8, the mole fraction of the mixed solvent in the ternary mixture remains constant along the extractive section stages. Its value depends on reflux ratio and entrainer/feed ratio. The solvent mixture is practically absent in the rectifying section. This minimum changes with the glycerol concentration in the mixed solvents when the reflux ratio decreases and disappears at a reflux ratio of 0.7 (Fig. 10). This evolution leads to determine the optimal setting of the operational parameters as summarized in Tab. 5.

![Figure 9. Composition profiles at different reflux ratios.](image1)

![Figure 10. Evolution of \( F_{E}/F \) as function of \( R \) and glycerol concentration in the solvent mixture.](image2)

### Table 5. Evolution of entrainer/feed ratio with mole fraction of glycerol and reflux ratio.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( F_{E}/F )</th>
<th>( x_{E} ) (glycerol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>0.305</td>
<td>0.56</td>
</tr>
<tr>
<td>1.2</td>
<td>0.358</td>
<td>0.44</td>
</tr>
<tr>
<td>1.1</td>
<td>0.426</td>
<td>0.32</td>
</tr>
<tr>
<td>1.0</td>
<td>0.510</td>
<td>0.20</td>
</tr>
<tr>
<td>0.9</td>
<td>0.610</td>
<td>0.10</td>
</tr>
<tr>
<td>0.8</td>
<td>0.722</td>
<td>0.04</td>
</tr>
</tbody>
</table>

### 4 Conclusions

A thermodynamic study was carried out based on the NRTL model to describe the behavior of ethanol-water mixture in the presence of an entrainer mixture consisting of ethylene glycol and glycerol. Process simulation allowed identifying extractive distillation with ethylene glycol and glycerol as the best option to dehydrate ethanol and to be implemented to the fuel ethanol production process.

This investigation allowed figuring out the relationship between process parameters in terms of entrainer/feed ratio, reflux ratio, total tray number, thermodynamic feature of entrainers, and concentration of the mixed solvent.

The presence of glycerol greatly improves the separation by exploiting its ability to retain water, and at the same time the presence of ethylene glycol is used to maintain the bottom temperature of the column at a moderate level. This leads to reduction of the required entrainer/feed ratio and energy demand in the process. The choice of the glycerol concentration in the solvent mixture is defined by the minimum rate of solvent reflux ratio; the reflux ratio is fixed between 0.8 and 1.3.

*The authors have declared no conflict of interest.*

### Symbols used

- \( F \) [kmol h\(^{-1}\)] feed flow rate
- \( F_{E}/F \) [-] entrainer/feed rate
- \( N \) [-] total tray number
- \( N_{F} \) [-] feed tray record number
- \( N_{FE} \) [-] entrainer/feed tray record number
- \( P \) [kPa] pressure
- \( Q \) [kJ h\(^{-1}\)] heat flow
- \( R \) [-] reflux ratio
- \( T \) [K] temperature
- \( x \) [-] component molar fraction in liquid
- \( x_{D} \) [-] component molar fraction of distillate
- \( x_{E} \) [-] component molar fraction of entrainer mixture
- \( y \) [-] component molar fraction in vapor
Sub- and superscripts
B reboiler
C condenser
E entrainer
I component i of the mixture
j distillation tray j

References