Anhydrous tert-butanol production via extractive distillation using glycerol as an entrainer: technical performances simulation

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Abstract. tert-Butanol is widely used as a main solvent in the industries. The high purity of tert-butanol is required to fulfil the industrial standard for the solvent. Unfortunately, tert-butanol separation from water required a special distillation named extractive distillation due to the azeotropic point in the mixture. Thus, entrainer as a third component should be used to break the azeotropic point. Glycerol is one of the potential green entrainer used in the extractive distillation. The simulation of the extractive distillation using glycerol as entrainer for the separation of tert-butanol/water mixture was conducted in this study. The Aspen Plus Process Simulator V.10 was used to simulate the feasibility of the glycerol as an entrainer and determine the optimum operating condition of the extractive distillation and recovery column in the anhydrous tert-butanol production. The results show that the optimum configuration for the extractive distillation column design consists of the number of stages of 25, binary feed stage of 21, entrainer feed stage of 3, reflux ratio of 0.6, mixed feed temperature of 25°C, and an entrainer feed temperature of 45°C. The condenser and reboiler duties are -1171.04 kW and 1744.48 kW, respectively. Moreover, the tert-butanol purity with this configuration can be achieved up to 0.996 of mole fraction.

1. Introduction

One of the most used chemicals in the industries is tert-butanol, which commonly act as a solvent and paint remover ingredient in the pharmaceutical and cosmetic industries, respectively; as raw material and chemical intermediate in isobutylene, methyl tertiary butyl ether (MTBE), and butyl elastomer production; and as a fuel oxygenate/gasoline octane booster in the energy sector [1].

The commercial production of tert-butanol comes as a by-product from the derivation of the isobutane oxidation process in the propylene oxide production. A by-product formed as a tert-butanol aqueous solution. The tert-butanol need to be further separated from the water to meet the industrial standard purity [2]. Unfortunately, this separation cannot be processed using ordinary distillation.
column due to the azeotrope behavior in the mixture. The tert-butanol and water mixture produce azeotropic point at mole fraction and temperature of 0.643 and 353 K, respectively [3]. Therefore, the promising method needs to be performed to overcome the difficulty of the azeotropic separation. The use of a heavy mass separating agent named entrainer via extractive distillation is one of the most potential methods to remove the azeotropic point in the mixture. Extractive distillation gives more advantages compared to the heterogeneous azeotropic distillation, which can save up to 30.3% of the energy requirement [4].

Several studies of removing the azeotropic point in the tert-butanol aqueous solution using entrainer have been conducted. The use of 0.1667 of mole fraction of 1-ethyl-3-methylimidazolium chloride and magnesium chloride ionic liquid could successfully remove the azeotrope behaviour [5]. But, the ionic liquids have the drawbacks such as high price and only some of the ionic liquids meet the green chemical criteria depend on the cation and its anion. Salt also can be used as an entrainer. But, the use of salt can bring the corrosion issue to the equipment. The use of a new green entrainer becomes an important issue in the current and future industries. The use of a biological buffer of Tris (hydroxymethyl) aminomethane (TRIS), which is eco-friendly and low-price, in the tert-butanol separation from the water have been successfully evaluated using the vapour-liquid equilibrium data and the simulation of the extractive distillation with the addition of 0.2 entrainer mass fraction [3][6]. More green chemicals need to be evaluated as a potential entrainer. Glycerol is one of the promising green chemicals which can break the azeotropic point in the alcohol + water system. Glycerol can be obtained as a by-product in the biodiesel production which is eco-friendly, non-toxic, and low price [7] [8]. In the removing of the azeotropic point, glycerol has been evaluated as an entrainer through the simulation of the extractive distillation in the isopropyl alcohol separation from water. The simulation results show that glycerol can break the azeotrope point and produce a high purity of alcohol up to 99.27% mole fraction [9]. Lo and Chien studied the energy-saving and total annual cost of the extractive distillation using glycerol as an entrainer compared to the heterogeneous azeotropic distillation in tert-butanol-water separation. The results show that the extractive distillation gives better performances compared to the heterogeneous azeotropic distillation [10].

To gain a deeper understanding of the extractive distillation in tert-butanol-water separation using glycerol as an entrainer, the techno-performances analysis should be explored. To the best our knowledge, the simulation for the techno-performances of the extractive distillation using glycerol in tert-butanol purification was not provided in the open literature. Therefore, the present study investigated the separation of tert-butanol-water via extractive distillation using glycerol as an entrainer from the techno-performances insight.

2. Methods

2.1 Thermodynamic Model
The Aspen Plus software package using rigorous methods was equipped in this work. The Non-Random Two-Liquid (NRTL) thermodynamic model was used to calculate the liquid phase nonideality with the assumption of the vapour phase is in an ideal condition. The optimum parameters used in the simulation are provided in Table 1.

| Component i | Component j | Aij       | Aji       | Bij (K)   | Bji (K)   | Cij |
|-------------|-------------|-----------|-----------|-----------|-----------|-----|
| tert-Butanol| Water       | -0.687    | 7.089     | 203.419   | -1372.38  | 0.3 |
| Water       | Glycerol    | -1.252    | -0.732    | 272.608   | 170.917   | 0.3 |
| tert-Butanol| Glycerol    | 0         | 0         | 408.595   | -6.511    | 0.3 |

The extended Antoine equation was used to calculate the total and partial pressure in the system, which provided in the Eq. 1.
\[ \ln(P^s) = A_1 + \frac{A_2}{T + A_3} + A_4 T + A_5 \ln T + A_6 T^{A_7}, \text{ for } A_8 < T < A_9 \] (1)

where \( P^s \) in kPa and \( T \) in K

The parameters used in the calculation of the extended Antoine equation, which taken from the Aspen Plus physical property databank, are listed in Table 2.

**Table 2.** The extended Antoine equation parameters

| Components    | \( A_1 \)   | \( A_2 \)   | \( A_3 \) | \( A_4 \) | \( A_5 \) | \( A_6 \times 10^8 \) | \( A_7 \) | \( A_8 \) | \( A_9 \) |
|---------------|-------------|-------------|-----------|-----------|-----------|-----------------|--------|--------|--------|
| tert-Butanol  | 165.362     | -11589      | 0         | 0         | -22.113   | 1.37            | 2      | 298.97 | 506.2  |
| Water         | 66.7412     | -7258.2     | 0         | 0         | -7.3037   | 4.17            | 2      | 273.16 | 647.1  |
| Glycerol      | 93.0782     | -13808      | 0         | 0         | -10.088   | 3.57 \times 10^{-13} | 6      | 291.33 | 850    |

2.2 Conceptual Process Design and Preliminary simulation

In this work, conceptual process design of the extractive distillation process uses the extractive distillation column and entrainer recovery column as a first and a second column, respectively. The tert-butanol aqueous solution and glycerol were fed into the extractive distillation column. In this column, tert-butanol is separated from the water using glycerol which acted as an entrainer. High purity tert-butanol was collected from the top column, while the water and glycerol were obtained from the bottom column. In the second column, glycerol and water were separated. Water was obtained in the top column and glycerol was recovered in the bottom column. Glycerol was recycled and mixed with the make-up glycerol to maintain the amount of the entrainer in the extractive distillation column. Furthermore, the preliminary simulation was conducted to validate the simulation method. The system, conceptual process design, and configuration used as provided from the literature without any changing or modification. Then, the results of the preliminary simulation were compared with the simulation results from the open literature.

2.3 Configuration and Sensitivity analysis

In this study, the initial process design parameters were determined as a simulation basis. The several parameters as initial configuration were listed in Table 3. The operating condition was set in the atmospheric condition. Moreover, the concentration of the tert-butanol in the feed stream was determined as 0.6 of mole fraction, which is below the azeotropic point of tert-butanol and water mixture.

**Table 3.** Initial process design parameter

| Parameters                          | Value   |
|-------------------------------------|---------|
| tert-Butanol feed mole fraction     | 0.6     |
| Theorical stage numbers             | 25      |
| Entrainer mole fraction             | 0.8     |
| Feed temperature (°C)               | 25      |
| Entrainer temperature (°C)          | 45      |
| Binary feed stage                   | 21      |
| Entrainer feed stage                | 2       |
| Pressure (atm)                      | 1       |

Sensitivity analysis was used to identify the several parameters which can affect the purity of tert-butanol and the condenser and reboiler heat duties. The parameters studied consist of the number of stages, reflux ratio, and binary and entrainer feed stages.
3. Result and discussion

3.1 Preliminary simulation

The simulation method in this work was validated using preliminary simulation. The preliminary simulation results in this work were compared with the simulation results from the literature. The comparison was provided in the Table 4 and Table 5. The results from the preliminary simulation meet a good agreement with the results from the literature. Hence, the simulation method can be used to simulate the extractive distillation of other alcohol aqueous solution and an entrainer. The process flow diagram of the simulation is provided in Figure 1.

Table 4. Preliminary simulation results for the extractive distillation in the ethanol-water separation using ethylene glycol and glycerol mixture as an entrainer (from this work)

| Stream | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Flowrate (kmol/hr) | 100 | 100 | 86.8| 93.4| 13.5| 79.9| 79.9| 79.9| 0.1 | 80  |
| M.F. ethanol       | 0.88| 0.88| 0.998| 0.014| 0.1 | 0   | 0   | 0   | 0   | 0   |
| M.F. water         | 0.12| 0.12| 0.0019| 0.129| 0.875| 0.003| 0.003| 0.003| 0   | 0   |
| M.F. ethylene glycol| 0  | 0   | 0.0001| 0.513| 0.02 | 0.596| 0.596| 0.596| 1   | 0.6 |
| M.F. glycerol      | 0   | 0   | 0    | 0.343| 0   | 0.4 | 0   | 0.4 | 0   | 0   |
| Temperatur (℃)     | 20  | 78.1| 78.3| 152.6| 49.6| 152.9| 164 | 60  | 60  | 60  |
| Vapor fraction     | 0   | 0.214| 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |

Table 5. Simulation results for the extractive distillation in ethanol-water separation using ethylene glycol and glycerol mixture as an entrainer [11]

| Stream | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Flowrate (kmol/hr) | 100 | 100 | 86.8| 93.2| 13.3| 79.9| 79.9| 79.9| 0.1 | 80  |
| M.F. ethanol       | 0.88| 0.88| 0.999| 0.013| 0.091| 0   | 0   | 0   | 0   | 0   |
| M.F. water         | 0.12| 0.12| 0.0002| 0.128| 0.889| 0.0004| 0.0004| 0.0004| 0   | 0   |
| M.F. ethylene glycol| 0  | 0   | 0.0001| 0.514| 0.009| 0.599| 0.599| 0.599| 1   | 0.6 |
| M.F. glycerol      | 0   | 0   | 0    | 0.343| 0   | 0.4 | 0   | 0.4 | 0   | 0.4 |
| Temperatur (℃)     | 20  | 78.1| 78.3| 156.7| 49.8| 163.9| 164.05| 60  | 60  | 60  |
| Vapor fraction     | 0   | 0.214| 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |

Figure 1. Process flow diagram for the extractive distillation in ethanol-water separation using ethylene glycol and glycerol mixture as an entrainer.
The process flow diagram of the extractive distillation was provided in Figure 2. Theoretical stages used in the extractive distillation column (EDC) is 25 with the EDC column inlets are azeotropic mixture of tert-butanol-water and glycerol as entrainer named as FEED and SOLVENT, respectively. The azeotropic mixtures and entrainer were fed to the EDC column at the stage of 21 and 2, respectively. The concentration of tert-butanol in the azeotropic mixture was set at 0.6 of mole fraction which is below the azeotropic point of the tert-butanol-water mixture. Anhydrous tert-butanol (TBA stream) was obtained at the top column, while the bottom product was the glycerol and water (RICH-SOL). Glycerol and water then separated in the second column which called entrainer recovery column (ERC). Water will be collected at the top column and glycerol will be obtained at the bottom column which then recycled and mixed with the glycerol from the MAKE-UP stream to maintain the composition of the glycerol in the extractive distillation column. The results of the extractive distillation and recovery column simulation were listed in Table 6.

![Figure 2. Process flow diagram for the extractive distillation in tert-butanol-water separation using glycerol as an entrainer.](image)

The results of the extractive distillation were shown in the EDC. The top product of the column was anhydrous tert-butanol with the purity of 0.9960 of mole fraction. In the extractive distillation column, feed molar flow was 100 kmol/hr, while glycerol molar flow was 30 kmol/hr. The sensitivity analysis results of the stage number (N-stage) and reflux ratio to the top product or distillate purity (w_d) in the extractive distillation column are the binary feed stage (BFS) of 21 and entrainer feed stage at 2 as provided in Figure 3.

| Parameters                  | Distillation Column |
|-----------------------------|---------------------|
|                            | Extractive | Recovery |
| Pressure (atm)              | 1          | 0.02     |
| Condenser temperature (°C)  | 82.43      | 21.85    |
| Condenser heat duty (kW)    | -1205.02   | -1254.34 |
| Reboiler heat duty (kW)     | 1779.31    | 1159.03  |
| Distillate rate (kmol/h)    | 60         | 52.5     |
| Reboiler temperature ()     | 128.35     | 175.54   |
| Bottom rate (kmol/h)        | 82.5       | 30       |
| Boil up rate (kmol/h)       | 144.395    | 53.97    |
| Molar boil up ratio         | 1.75       | 1.79     |
As the increasing of the stage number from 20-21 with the configuration of BFS and EFS are 21 and 2, respectively, give no effect to the distillate purity. But, the distillate purity has increased as the increasing of the stage number from 21 to 25. The highest distillate purity obtained in the stage number of 25. The distillate purity also affected by the reflux ratio (RR). Reflux ratio studied were in a range of 0.4 to 0.8. Figure 3 illustrates that the higher the reflux ratio, the higher distillate purity. The highest purity obtained when the reflux ratio was 0.8 which produce the distillate purity of 0.9969 of mole fraction. But, the reflux ratio of 0.6 and 0.7 also produce satisfactory purities which are 0.9960 and 0.9969 of mole fraction, respectively. As the increasing of the reflux ratio, the contact between vapour and liquid in the column also increase. Thus, higher reflux ratio will produce higher purity of the distillate product.

**Figure 3.** Effect of Stage Number and Reflux Ratio on Top Product Purity (BFS 21, EFS 2).

![Figure 3](image_url)

**Figure 4.** Stage number effect on (a) Condenser heat duty ($Q_C$) and (b) Reboiler heat duty ($Q_R$).

![Figure 4](image_url)
Figure 4 illustrates the increasing of the reflux ratio increases the heat duties both in condenser and reboiler. This phenomenon occurred because the higher the reflux ratio means more vapour flow in the extractive distillation column, which caused the increase of the heat duties in the reboiler and condenser to vaporize the product and condense the distillate, respectively. The stage number did not affect significantly to the condenser and reboiler duties. According to the purity and the heat duties sensitivity analysis, the reflux ratio of 0.6 was selected because the distillate purity and the energy consumption are in the best condition.

![Figure 5](image.png)

**Figure 5.** Sensitivity analysis of the binary feed stage (BFS) and entrainer feed stage (EFS) on the distillate purity (stage number of 25, RR 0.6).

The effect of the binary and entrainer feed stage on the distillate purity in the fixed extractive distillation stage number of 25 and reflux ratio of 0.6, which provided in Figure 5. The results illustrate that the increase of the distillate purity occurred in BFS number of 20, 21 and 22, which produced the purity of 0.995, 0.996, and 0.997, respectively. The distillate purity was decreasing in BFS number of 23 to 24, which is less than 0.995. The purity of the distillate also affected by the EFS number. The increase of the EFS number will decrease the purity. The energy consumption was investigated to obtain the minimum energy requirements in a certain BFS and EFS configuration. The sensitivity analysis of the BFS and EFS on the condenser and reboiler heat duties were shown in Figure 6.
Figure 6. Effect of binary feed stage (BFS) and entrainer feed stage (EFS) on energy consumption: (a) Condenser heat duty \(Q_C\) and (b) Reboiler heat duty \(Q_R\).

Figure 6 illustrates the effect of the BFS and EFS number on energy consumption in the condenser and reboiler heat duties. The BFS did not affect significantly on the condenser heat duty, but give effect on the reboiler duty, which increase from BFS 15 to 22 and start to decrease from 22 to 24. According to the profile, EFS of 2 gives the highest energy consumption both in the condenser and reboiler. As shown in Figure 5, the distillate purity of the EFS 2 and 3 are not significantly different. Each produces the distillate purity of 0.996, while EFS of 3 has a lower energy consumption compared to the EFS of 2. Thus, the satisfied configuration was BFS and EFS number of 21 and 3, respectively.

4. Conclusions
The separation of tert-butanol from the water via the extractive distillation using glycerol as an entrainer has been investigated in this study. The Aspen Plus software package V.10 was used to simulate the process. Sensitivity analysis has been conducted to understand the effect of the stage number; reflux ratio; and binary and entrainer feed stages to the distillate purity and energy consumption. The stage number and reflux ratio were in a range of 20 to 25 and 0.4 to 0.8, respectively. The binary feed stage and entrainer feed stage were in a range of 15 to 24 and 2 to 5, respectively. The stage number did not affect significantly on energy consumption but affect to the purity of the distillate. The best stage number was 25, which produce the highest purity. Moreover, the reflux ratio affects to the distillate purity and energy consumptions, the best reflux ratio is 0.6. The BFS and EFS were evaluated to determine the best configuration based on the distillate purity and the energy consumption with the fixed stage number of 25 and the reflux ratio of 0.6. The result shows that BFS gives the best results at 20, 21 and 22. Moreover, the BFS did not affect significantly on energy consumption, but the EFS does. EFS of 2 gives the highest energy consumption compared to EFS 3, 4, and 5. On the other hand, EFS 3 gives lower energy consumption, but it has the same purity as EFS 2. Thus, EFS 3 was selected as the best configuration.

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