Extractive distillation simulation of tert-butanol/water using TRIS as entrainer

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Abstract. The mixture of tert-butanol and water cannot be separated by conventional distillation methods. The distillate composition will always be the same until all of the liquid is evaporated. The separation is difficult because the tert-butanol and water systems have azeotropic behaviour. The azeotrope occurs at a mole fraction of 0.643 and temperature of 353 K. Extractive distillation is one of the methods which can be used to separate the azeotropic behaviour effectively. The system uses two columns namely extractive distillation column and recovery distillation column. The extractive distillation column requires a third component called entrainer. The novel, environmentally friendly and non-corrosive entrainers is Tris (hydroxymethyl) aminomethane (TRIS). In this study a simulation of extractive distillation of the tert-butanol / water system was carried out using a TRIS entrainer. The optimization results show that the extractive column design configuration is the number of stages 19, binary feed stage 11, entrainer feed stage 4, reflux ratio 0.5, mixed feed temperature 78°C, and entrainer feed temperature 25°C. This configuration is capable of producing 0.996 tert-butanol purity with a reboiler load of 1255.95 kW and a condenser load of -327.29 kW.

1. Introduction

tert-Butanol is an organic compound with the formula of $C_4H_{10}O$. tert-Butanol is widely applied in various industrial sector. tert-Butanol is used as a solvent in pharmaceutical and paint industries, as a raw material for making isobutylene, methyl tertiary butyl ether (MTBE), and butyl elastomer [1], as a separating agent in the polyolefin industry and also as a blowing agent in the foam industry made from metacreylonitrile and metacrylic acid [2], and can be added to gasoline to increase the octane numbers [3].

tert-Butanol can be obtained from homogeneous reaction between isobutene containing a mixture of hydrocarbons in addition to acetylene, water and tert-butanol derivatives by adding an acidic ion-exchange catalyst. The process is carried out at a temperature of 30-120°C and the initial composition of 10% of isobutene and 30-80% of water. The formation of tert-butanol from the mixture occurred in

four reactors arranged in series. The isobutene conversion ranges from 70-90% so the product that comes out from the fourth reactor still contains a mixture of hydrocarbons and tert-butanol solution. Then the product is fed into a distillation column at a pressure of 1 bar to separate the mixture into hydrocarbons as a top product and tert-butanol as a bottom product [4].

However, the mixture of tert-butanol and water cannot be separated by conventional distillation. The distillate composition will always be the same until the water is evaporated because the systems have azeotropic point. Azeotropic point of the mixture of tert-butanol and water occurs at the mole fraction of 0.643 at 353 K [5].

Various modifications to the distillation system have been carried out to overcome the azeotropic problem such as pressure-swing distillation [6], azeotropic distillation [7] and extractive distillation [8]. Pressure-swing distillation uses two different columns of pressure to separate the azeotropic point. Azeotropic distillation and extractive distillation both use a third component called an entrainer. Azeotropic distillation uses a light entrainer so the impurities and entrainer components will be at the top product. However, the system requires a large amount of additional energy to vaporize the mixture [9]. Extractive distillation uses a heavy entrainer that is able to change the relative volatility of components. Pure components are obtained in the top column and without solvent evaporation process as in azeotropic distillation so extractive distillation is more beneficial than azeotropic distillation [10].

 Extractive distillation can be used as an alternative for separating a mixture that have azeotropic point. Entrainers are fed at the top of the distillation column. The selected entrainer must be able to break the azeotropic point in the mixtures. In addition, entrainers must have stable properties, high selectivity, and low toxicity [11]. Some examples of entrainers for extractive distillation such as water [12], dimethyl sulfoxide [13], glycerol [14], mixtures of organic solvents and ionic liquid [15], biological buffer tris (hydroxymethyl) aminomethane (TRIS) [5], 1,2-propanediol [16], butyl acetate [17] and ethylene glycol [18].

Several studies have been carried out to remove the azeotrope of the tert-butanol / water system with entrainers. Aniya et al. (2018) [19] used ionic liquid (IL), 1-ethyl-3-methylimidazolium chloride [emim] [Cl] and magnesium chloride (MgCl2) as entrainers. The azeotrope of tert-butanol / water was eliminated with the addition of IL of 0.1667 mole fraction. However, the use of salt can cause corrosion in process equipment [5]. Lo and Chien [20] used glycerol as an entrainer with a solvent to feed mole ratio of 0.5. Another research conducted by Hartanto et al (2016) succeeded in using an alternative entrainer that is environmentally friendly, non-corrosive and not at risk of damaging the equipment namely Tris (hydroxymethyl) aminomethane (TRIS). The addition of TRIS by 0.2 mass fraction was able to remove the azeotrope of tert-butanol / water system [5]. The use of environmentally friendly entrainer for the azeotropic system separation needs to be investigated next to the process simulation. The extractive distillation will be simulated using Process Simulation Software. In this work, distillation purity and energy consumption which are affected by the number of stages, stage feed, feed temperature, and reflux ratio were investigated. The research is intended to to make contributions to the literature on designing extractive distillation column in tert-butanol industry.

2. Methods

Property data of tert-butanol, water and TRIS components which used in calculation are obtained from the Aspen Plus database which are listed in the table 1,2, and 3.

Table 1. Properties of *tert*-Butanol, Water and TRIS: critical temperature (T_c), critical pressure (P_c), critical volume (V_c), critical compresibility factor (Z_c), acentric factor (Ω)

Components	P_c (kPa)	T_c (K)	Z_c	V_c (cm^3/mol)	Ω
tert-Butanol	3972	506.2	0.26	275	0.6152
Water	22064	647.09	0.229	55.9	0.3449
TRIS	6400	835	0.304	330.1	1.2574

**Table 2.** Extended Antoine Equation (A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, and A_9)

Components	A_1	A_2	A_3	A_4	A_5	$A_6\ 10^{-6}$	A_7	A_8	A_9
tert-Butanol	62.1361	-7258.2	0	0	-7.3037	4.16	2	0.01	373.95
Water	165.362	-11589	0	0	-22.113	1.37	2	25.82	233.05

However, the interaction parameters between components are not available in the process Aspen Plus databases. Thus, the interaction parameters are taken from Hartanto et al (2016) as follows.

Table 3. Components Interaction Parameters (M_{ii}, M_{ij}, N_{ij}, N_{ji}, and α) (Hartanto *et al*., 2016) [5]

Components i	Components j	M_{ii}	M_{ji}	N_{ij}/K	N_{ji}/K	A
tert-Butanol	Water	5.82	17.73	-2058.35	-5175.75	0.3
Water	TRIS	11.22	0.6	-1868.87	-1141.98	0.3
tert-Butanol	TRIS	-16.80	41.34	8485.53	-16904.5	0.3

The flowsheet used in this simulation study is shown in figure 1. The two distillation columns were used namely extractive distillation column and recovery distillation column. The extractive distillation column had two feeds for binary feed stage (BFS) and entrainer feed stage (EFS). BFS was placed above the EFS so that there is good contact between the azeotropic mixture and the entrainer. The product of extractive distillation column distillate was ethanol while the bottom product contained water and entrainer. The recovery distillation column only needs one feed for the mixture of entrainer and water. The mixture was fed to the recovery distillation column to be separated between water as the top product and entrainer as the bottom product.
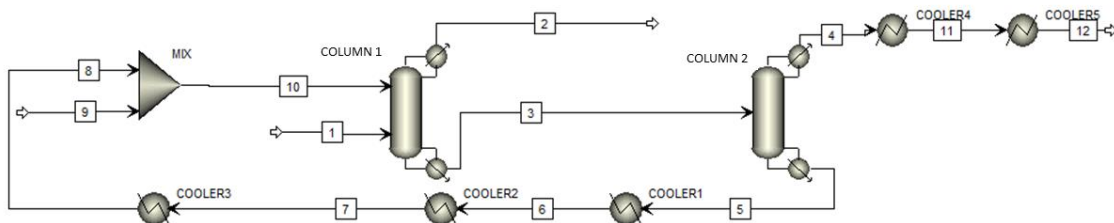
Figure 1. Process flow diagram for the extractive distillation using TRIS as an entrainer.

Feed composition, configuration of extractive column and recovery column are shown in table 4.

Table 4. Process Design Parameters

| Parameters	Value
tert-Butanol feed mole fraction	0.4
Theoritical stage numbers	16
Entrainer mole fraction	0.2
Feed temperature (^{o}C)	25
Entrainer temperature (^{o}C)	25
Binary feed stage	10
Entrainer feed stage	3
Pressure (*kPa*)	101.3

3. Results and discussions

The extractive distillation column consists of 16 stages with two inlets namely azeotropic tert-butanol/water mixture and TRIS entrainers. Azeotropic mixture entered at stage 10 while entrainer entered at stage 3. Azeotropic mixture entered with a composition of 0.4 mole fraction of tert-butanol at 25°C. Distillation products consist of top products and bottom products. The top product contained tert-butanol anhydrous. The top product was partially recycled to the distillation column as reflux. The bottom product contained a mixture of water and TRIS. The bottom product then flowed to the second distillation column for recovery. Therefore, the TRIS entrainer could be circulated to the first column. The simulation results of each column is shown in table 5 as follows.:

Table 5. Simulation Results of Extractive Distillation Column and Recovery Distillation Column

Parameters	Distillation Column	
	Extractive	Recovery
Condenser temperature	81.96 $^{\circ}$C	208.143 $^{\circ}$C
Heat duty	-327.359 kW	-603.609 kW
Distillate rate	60 kmol/h	90 kmol/h
Reboiler temperature	81.88 $^{\circ}$C	345.592 $^{\circ}$C
Heat duty	1915.8 kW	2233.1 kW
Bottom rate	102.913 kmol/h	12.5 kmo/h
Boil up rate	131.292 kmol/h	99.7305 kmol/h
Boil up ratio	1.275	7.97

The extractive distillation results are shown in stream number 3. The purity of the tert-butanol achieved until 0.99627 mass fractions which is to fulfil the standard purity used in the industry [21]. The bottom product of the extractive distillation column consists of a mixture of water and TRIS which was then recovered in the second column. TRIS would be at the bottom product while water would be at the top product. After the recovery process, 12.5 kmol/hour TRIS generated in the lower column of the second column, was flowed again to break the azeotropic point in the first column.

The sensitivity results of the number of stages to the distillation of the distillate product at binary feed stage (BFS) of 10 and entrainer feed stage (EFS) of 3 are shown in figure 2.
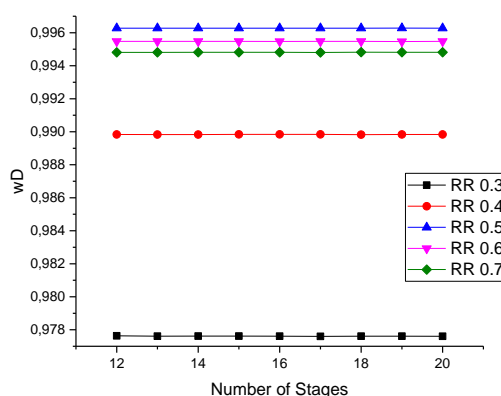
**Figure 2.** Effect of Stage Number and Reflux Ratio on Distillate Purity (BFS 10, EFS 3)

The increasing number of stages (NS) from 12-20 with BFS 10 and EFS 3 configurations had no effect on the purity of the distillate (wD). The number of stages needed to obtain a purity of 0.995 mass fraction varies with each reflux ratio. The reflux ratio (RR) that can be used to obtain the purity

is 0.5, 0.6, and 0.7. The highest purity of the distillate was obtained at a reflux ratio of 0.5. In this simulation, the reflux ratio increases from 0.3 to 0.5 occurred when the reflux ratio was 0.6 and 0.7. An increase in reflux ratio will increase the purity of the distillate product at the same number of stages. In the case of an increase in reflux from 0.5 to 0.6 and 0.7 the purity of the product in the same number of stages decreases. This phenomenon occurred because at that point an excess amount of reflux causes dilution of the solvent in the liquid phase [12]. Thus, the increase in relative volatility of the mixture is smaller.
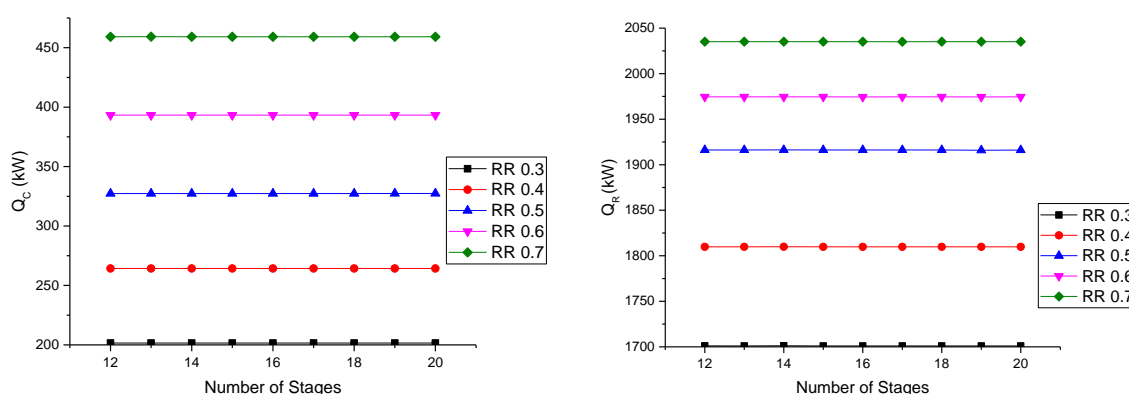
**Figure 3**. Effects of number of stages on (a) Condenser Load, and (b) Reboiler Load

In figure 3,(a) and (b) it showed that there was an increase in reboiler load by increasing the number of stages. The reflux ratio in this case had a significant effect. The greater the reflux ratio, the greater the reboiler load. Likewise with the condenser load which was only significantly affected by the reflux ratio. Increasing reflux ratio means more vapor flow in the column so the reboiler and condenser duty will increase to vaporize and condense the mixture. Energy requirements for heating and cooling processes had a linear relation to the reflux ratio.
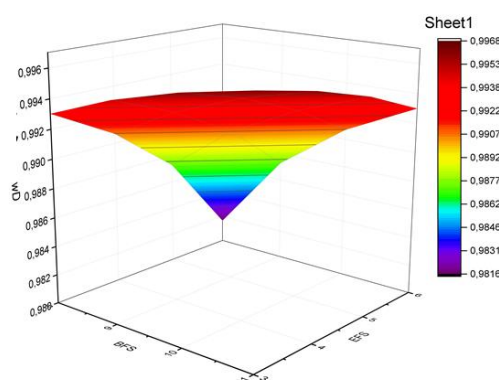
Figure 4. Feed stage and Entrainer feed stage sensitivity results to Purity (NS 16, RR 0.5)

Figure 4 showed the results of sensitivity between feed stage and entrainer feed stage on the concentration of tert-butanol in the distillate. The location of the BFS downward will increase the purity of the distillate. The placement of EFSs that were increasingly downward tends to reduce purity for the same BFS. Based on the simulation results, it can be seen that the purity of tert-butanol of

0.995 mass fraction varies each location of BFS and EFS. Purity above 0.995 mass fraction was obtained by BFS and EFS configurations, 10 and 3; 11 and 3; 11 and 4. The purity of the distillate did not reach 0.995 when EFS 6 was used. The best combination of BFS and EFS need to be investigated also in terms of reboiler energy consumption. The results of feed stage sensitivity to reboiler energy consumption are shown in Figure 5.

(a)   (b)
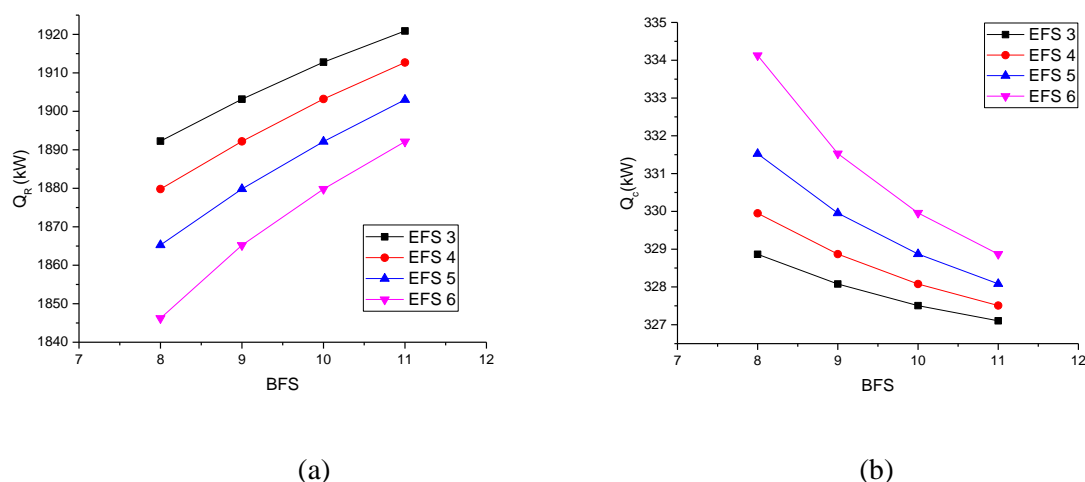
Figure 5. Effects of EFS on Energy: (a) Reboiler Load (b) Condenser Load

Figure 5 showed that EFS position affects the energy consumption. The higher the EFS position, the reboiler energy consumption increases. This means that the amount of energy needed per kilogram of pure tert-butanol increases. This is due to the water transfer from vapor phase to liquid phase increases. The condenser duty have more energy when the entrainer is fed at stages near to the bottom column. This could be owed to the higher vapor flow be condensed in the first stage [22].

4. Conclusions

The extractive distillation of tert-butanol/water mixture contains TRIS as an entrainer has been simulated using Aspen Plus. The number of stages and reflux ratio was studied. From the sensitivity analysis, it can be seen that if a reflux ratio of 0.5 and the number of stages ranging from 12 to 20 were used, the purity of the distillate meets the target. The selection of the number of stages is based on its energy consumption. The simulation results show that the smallest energy load is the number of stage 19 with a total of 2243.246 kW. Then, a combination of BFS and EFS has been investigated. Minimum purity of tert-butanol has been achieved in a combination of BFS and EFS: 10 and 3, 11 and 3, 11 and 4. BFS 11 and EFS 4 provide the lowest energy load, which is 2240.188 kW.

References

[1]   Clark J 2001 *tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards* (Los Angeles: American Chemical Society) 92-106

[2]   INCHEM. 1987 Retrieved October 20, 2018, from http://www.inchem.org/documents/ehc/ehc/ehc65.htm

[3]   Zheng Z, Li C, Liu H, Zhang Y, Zhong X and Yao M 2015 *J. Fuel*, **141** 109–119.

[4]   BeckmannWilfried A, KaizikFranz B, Scholz N. R and Santiago-FernandezBernhard 2002 EP1431264A1 Germany

[5]   Hartanto D, Gupta B S, Taha M and Lee M J 2016 *J. Chem. Thermodyn*. **98** 159–164

[6]   Luyben W L 2012 *Ind. Eng. Chem. Res.* **51(33)** 10881–10886

[7]   Widagdo S and Seider W D 1996 *J.AIChE* **42(1)** 1–35
[8]   Lei Z, Li C, and Chen B 2003 *Sep. Purif. Rev*. **32(2)** 121–213
[9]   Ma S, Hou Y, Sun Y, Li J, Li Y and Sun L 2017 *Chem. Eng. Process*. **121** 71–80
[10]   Meirelles A 1992 *Chem. Technol. Biotechnol*. **53** 181–188
[11]   Lladosa E, Montón J B, Burguet M C and Muñoz R 2007 *Fluid Ph. Equilibria* **255(1)** 62–69
[12]   Gil I D, Botía D C, Ortiz P and Sánchez O F 2009 *Ind. Eng. Chem. Res*. **48** 4858–4865
[13]   Zhang Z, Lv M, Huang D, Jia P, Sun D and Li W 2013 *J. Chem. Eng. Data* **58(12)** 3364–3369
[14]   Zhang Z, Huang D, Lv M, Jia P, Sun D and Li W 2014 *Sep. Purif. Technol*. **122** 73–77
[15]   Dai C, Lei Z, Xi X, Zhu J and Chen B 2014 *Ind. Eng. Chem. Res*. **53(40)** 15786–15791
[16]   Xu S and Wang H 2006 *Chem. Eng. and Process*. **45(11)** 954–958
[17]   Acosta J, Arce A, Rodil E and Soto A 2002 *J.Fluid Ph. Equilibria* **203(1)** 83–98
[18]   Zhang L, Shen D, Zhang Z and Wu X 2017 *J. Chem. Eng. Data* **62(5)** 1725–1731
[19]   Aniya V, De D, Singh A and Satyavathi B 2018 *J.Energy* **144** 1013–1025
[20]   Lo K M and Chien I L 2017 *J. Taiwan. Inst. Chem. E* **73** 27–36
[21]   ThermoFisher 2018 Retrieved October 20, 2018, from
         https://www.fishersci.ca/shop/products/tert-butanol-99-5-extra-pure-acros-organics-3/p-
         3735808
[22]   Gomez P and Ivan G 2007 *J. Lat Am Appl Res* **39**

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