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Efficient separation method for *tert*-butanol dehydration via extractive distillation

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ABSTRACT

Separation of *tert*-butanol and water is an important task in the co-oxidation process of propylene/isobutane. These two compounds form minimum-boiling azeotrope which cannot be separated by simple distillation. In this paper, an efficient separation method for *tert*-butanol dehydration via extractive distillation is investigated. The heavy entrainer used is glycerol, a non-toxic byproduct in the production of biodiesel, is less expensive and more environmentally friendly than other conventional entrainers. By comparing the optimized design of this extractive distillation system with a recently published heterogeneous azeotropic design, significant reductions of 57.5% in the steam cost and 43.7% in the total annual cost can be obtained. In order to further save energy, a feed-effluent heat exchanger can be added in the proposed extractive distillation system. With this simple heat-integration design, a further 15.9% reduction in steam cost and 11.7% in total annual cost can be made as compared to the original one.

1. Introduction

tert-Butanol (TBA) is widely used as a solvent, paint remover ingredient, gasoline octane booster [1] and can react with methanol to produce methyl tertiary butyl ether (MTBE) [2]. It is derived commercially from isobutane as a co-product of propylene oxide production [3]. This process gives water-containing TBA. This mixture can be concentrated by simple distillation into a TBA/H_2O minimum-boiling azeotrope. Because of its still high water content, it is not suitable for all uses of TBA. Therefore, separation of TBA/water azeotrope is an important research topic worthy of detail study.

Extractive distillation is a commonly used method for the separation of azeotropic mixture. In this method, a third component is added into the system as entrainer to alter the relative volatility of the components to be separated. With the presence of the suitable entrainer, the relative volatility of the original two components can be greatly enhanced. Arifin and Chien [4] studied an extractive distillation system for separating isopropanol and water using dimethyl sulfoxide as an entrainer. The result showed that the separation by extractive distillation is more promising than heterogeneous azeotropic distillation. The energy requirement of the former was cut by 30.3% as compared to the latter. You et al. [5] investigated how the reduction of operating pressure improving the extractive distillation process for the separation of the diisopropyl ether and isopropanol minimum boiling azeotrope with heavy entrainer 2-methoxyethanol. The result shows that the reduction of the pressure is beneficial to the separating case. Liu et al. [6] studied the effect of mass transfer on the design of an extractive distillation process for the separation of dimethyl carbonate and methanol. The above three references are just few examples of many papers in open literature studied various topics of using extractive distillation for the separation of azeotropic mixtures. To the best of our knowledge, none of the papers in open literature have studied the detailed design flowsheet for the separation of TBA/water azeotrope via extractive distillation.

Alternative way for the separation of the azeotropic mixture is the heterogeneous azeotropic distillation (HAD). By adding a light entrainer to introduce heterogeneous low-boiling azeotropes, the nature liquid–liquid separation in the decanter occurs. Industrial applications include organic alcohol and acetic acid dehydration systems [7–9]. However, large recirculation rate may occur in the HAD system resulting in higher operating cost as well as total annual cost (TAC). Therefore, for the purpose of further saving of energy via process intensification, azeotropic dividing wall column (A-DWC) is commonly incorporated into the HAD process to combine the heterogeneous azeotropic column with the recovery column [10,11]. It was shown that there is a high potential of significant savings in energy consumption. Recently, Yu et al. [12] demonstrated the design of A-DWC for the TBA dehydration using cyclohexane as entrainer. The result showed that A-DWC can lead to 23.8% of reduction in energy consumption savings as compared to the conventional two-column design of the HAD process.

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Table 1
NRTL model parameters for the extractive distillation system.

Comp. i	TBA	H_2O	TBA	H_2O	TBA
Comp. j	H_2O	GLY	GLY	TEG	TEG
aij	−0.687	−1.252	0	0	0
aji	7.089	−0.732	0	0	0
bij (K)	203.419	272.608	408.595	1871.136	325.101
bji (K)	−1372.384	170.917	−6.511	−691.461	−160.862
cij	0.3	0.3	0.3	0.300	0.300

Comp. i	H_2O	TBA
Comp. j	1,3-BDO	1,3-BDO
aij	0	0
aji	0	0
bij (K)	989.684	192.583
bji (K)	−226.910	−89.726
cij	0.3	0.3

Table 2
NRTL model parameters for the duplicated HAD case and A-DWC case.

Comp. i	TBA	H_2O	TBA
Comp. j	H_2O	CYC	CYC
aij	−0.687	13.143	−1.374
aji	7.089	−10.459	1.069
bij (K)	203.419	−1066.976	559.521
bji (K)	−1372.384	4954.897	245.107
cij	0.3	0.2	0.47

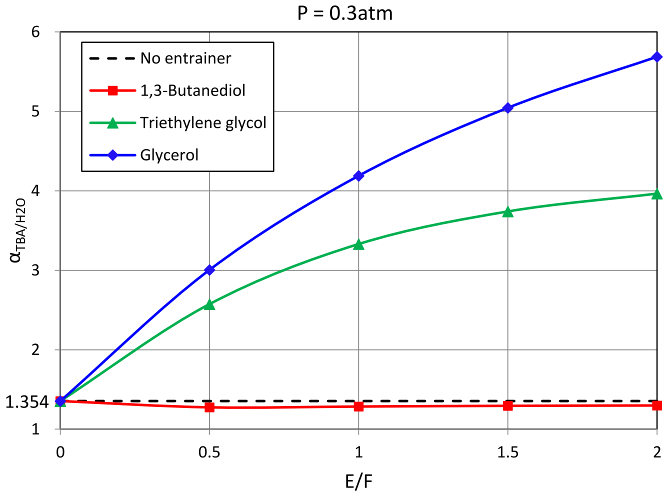

Fig. 1. Enhancement of relative volatility at 0.3 atm for the studied system by adding several heavy entrainers.

In this study, the separation of TBA/water via extractive distillation is investigated. Extractive distillation method is promising if a suitable entrainer for the system can be found. To the best of our knowledge, there is only one U.S. patent [13] listed 44 potential entrainers to aid the dehydration of TBA via azeotropic separation. It mentioned that typical examples of effective entrainers are 1,3-butanediol (1,3-BDO) and triethylene glycol (TEG). In this paper, glycerol (GLY) will be proposed as entrainer in the extractive distillation system for this separation task. Glycerol is becoming more important into separation process recently due to the low price and its nontoxic and environmental friendly nature. [14,15] These characteristics have encouraged the use of it as an entrainer for the extractive distillation system. Gil et al. [16] investigated the design and control of an extractive distillation process to produce anhydrous ethanol using glycerol as entrainer. Raeva and Sazonova [17] studied the separation of ternary mixtures via extractive distillation process using glycerol as the entrainer. To the best of our knowledge, no application of using glycerol as entrainer for TBA dehydration was found in open literature.

2. Thermodynamics model

According to Hahn et al. [18], TBA (normal boiling point 82.6 °C) forms a minimum-boiling azeotrope with water (normal boiling point 100 °C) at 1 atm with an azeotropic temperature of 79.9 °C and azeotropic composition of 88.24 wt% of TBA. Thus, these two components cannot be separated in a single distillation column.

For the overall three-component extractive distillation system studied in this paper, NRTL model will be used to describe the non-ideality of the liquid phase while the vapor phase is assumed to be ideal. The NRTL model parameters of the TBA–H_2O pair and H_2O–GLY pair are taken from the built-in values in Aspen Plus. For the other binary pairs in the following studies with no Aspen built-in parameters, the NRTL model parameters will be estimated via UNIFAC group contribution method. All model parameters used in the following studies are given in Table 1. For the HAD case and A-DWC case in Section 4.2 for the purpose of duplicating simulation results in Yu et al. [12] via heterogeneous azeotropic distillation, the NRTL model parameters are given in Table 2.

3. Entrainer selection

Entrainer selection is the most important step before the extractive distillation sequence is designed. Relative volatility is the main evaluation index of the separation effect, which is defined as Eq. (1) below.

$$\alpha_{i/j} = \frac{y_i/x_i}{y_j/x_j} \tag{1}$$

where y_i, y_j are the mole fraction of component i and j in the vapor phase, x_i, x_j are the mole fraction of component i and j in the liquid phase.

According to Hsu et al. [19], we can generate a plot to compare candidate entrainers which is shown in Fig. 1. In the figure, the x-axis is the entrainer to feed ratio. The y-axis is the relative volatility of TBA to water with addition of the entrainer into the system. The data can easily be collected by just performing a flash calculation using FLASH2 module in Aspen Plus. The fresh feed flowrate is 100 kmol/h with composition of 50 mol% of TBA and 50 mol% of water, the entrainer feed flowrate is from 10 kmol/h to 200 kmol/h. The flash is operated at 0.3 atm (which is the operating pressure of extractive distillation column shown later) and the vapor fraction equals to 0.001 to mimic the bubble-point condition. After running the simulation, the relative volatility of TBA to water can be calculated by Eq. (1). In this study, the entrainer candidates are 1,3-butanediol and triethylene glycol, as suggested in [13], and glycerol, as proposed in this paper.

Without adding any entrainer, the original $\alpha_{TBA/H2O}$ is at 1.354. Since it is quite close to unity, which means the separation is difficult. By gradually adding entrainer into the system, the enhancement of the relative volatility of TBA to water is calculated at different entrainer to feed ratios (E/F). By adding glycerol to the feed ratio at 0.5, the relative volatility of TBA to water can greatly be enhanced to 3.0. It is noticed that another entrainer (1,3-butanediol) did a poor job to enhance the relative volatility of TBA over water. From Fig. 1, it is quite clear that the enhancement of relative volatility by using triethylene glycol as entrainer is not as

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