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Determination of an optimum entrainer for extractive distillation based on an isovolatility curve at different pressures

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ABSTRACT

The selection of a proper entrainer is a key factor affecting the feasibility of extractive distillation. Presently, we simply compare the relative volatility based on the same pressure to select the entrainer. In this work, we found that the separation effect on entrainers was impacted by pressure to a different extent. Two binary azeotropic systems, ethanol-benzene and ethanol-ethyl acetate, were used to demonstrate the entrainer selection based on an isovolatility curve at different pressures. The results indicated that ethanol-benzene with 1,2-propanediolas an entrainer can save 7.42% of the total annual cost compared to ethanol-benzene with p-xylene as an entrainer at atmospheric conditions, but after the pressure was considered, the ethanol-benzene-p-xylene system can save a 9.17% total annual cost compared to the ethanol-benzene-1,2-propanediol system. The relationship between pressure and total annual cost was nonlinear, and there was a minimum total annual cost at the corresponding pressure. Similar to the ethanol-benzene system, the above situation also existed in the ethanol-ethyl acetate system. The change in the isovolatility curve with the change in pressure shows different trends, and the change in pressure results in a change in the selection of the entrainer. The results provide more insight for the choice of an entrainer in extractive distillation.

1. Introduction

The separation of azeotrope and close boiling mixtures is a challenge in most chemical processes. For their separation, the use of a single conventional distillation column is impossible. In recent years, many special techniques have been used for separating the azeotropic systems such as azeotropic distillation [1–4], pressure-swing distillation [5–10], extractive distillation [11–16], and other new separation methods [17–20]. Of course, many studies [21–23] have been conducted on the dynamic characteristics of azeotrope separation, which has greatly promoted the progress of dynamic research. Pressure-swing distillation is a commonly used method in the separation of pressure-sensitive azeotropic mixtures. Fulgueras et al. [6] studied the separation of maximum-boiling azeotropic water-ethylenediamine by pressure-swing distillation. Zhu et al. [8] investigated the separation of multicomponent azeotrope and proposed triple column pressure-swing distillation for separating acetonitrile-methanol-benzene ternary azeotrope. For pressure-insensitive azeotropic mixtures, extractive distillation is the most widely used separation technique. Yu et al. [15] investigated the separation of ethylenediamine and water using extractive distillation. Modla et al. [16] presented two energy-saving methods, thermally integrated extractive distillation and extractive dividing-wall column distillation, for separating azeotrope toluene-methanol using triethylamine as the entrainer.

The choice of the separation technology cannot depend only on the type of the separated mixture. Luyben [24] compared two methods, pressure-swing distillation and extractive distillation, for the separation of acetone-methanol and found that the extractive distillation process could save 15% more than the pressure-swing distillation process in the economy. Lladosa et al. [25] studied the separation of di-n-propyl ether and n-propyl alcohol by extractive distillation and pressure-swing distillation, and the result showed that pressure-swing distillation is more attractive than extractive distillation. Li et al. [26] investigated new pressure-swing distillation for separating a pressure-insensitive maximum boiling azeotrope via combination of a heavy entrainer. You et al. [27] proposed a novel extractive distillation strategy by varying pressure for the separation of acetone–methanol and found that the extractive distillation with varying pressure could offer 33.9% and 30.1% reductions in energy consumption and total annual cost (TAC) compared with extractive distillation operated at atmosphere.

In the design process of extractive distillation, the choice of the entrainer is critical. Presently, there are many papers regarding the

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Nomenclature

TAC	total annual cost [$/y]
Feed	feed flow rate [kmol/h]
R_{rec}	solvent flow rate [kmol/h]
ID	diameter of the column [m]
N_F	number of feed locations
N_R	number of recycle location
N_T	number of stages
RR	reflux ratio
EDOS	Extractive Distillation Optimization Software
B	bottom flow rate [kmol/h]
D	distillate flow rate [kmol/h]
T_{azeo}	azeotropic point

selection of the entrainer [28–34]. Jongmans et al. [28] studied entrainer screening for the separation of dichloroacetic acid from monochloroacetic acid by investigating whether the entrainer can form complexes by hydrogen bonds/proton transfer, which may increase the relative volatility between dichloroacetic acid and monochloroacetic acid. Zhao et al. [31] investigated the separation of tetrahydrofuran-ethanol-water ternary azeotrope by optimizing the composition of a mixed entrainer that can be economically used. Tripodi et al. [32] studied $H_2O/CH_3CN/NH_3/HCN$ separation using a heterogeneous entrainer, dichloromethane, and homogeneous entrainers such as ethyl acetate, ethylene glycol and glycerol. The results showed that ethylene glycol, which has lower heat duties and lower total trays, is well posed to constitute a sustainable alternative to dichloromethane. One criterion for the selection of the entrainer is the relative volatility of the two key components. Normally, the greater the relative volatility between the two key components the easier the separation of the azeotrope. However, Raeva et al. [34] proposed a new method for selection of the entrainer based on the thermodynamic criterion-excess Gibbs energy and noted that the entrainer selection for the azeotropic mixture should not be limited to the relative volatility between the light and heavy component. We also found that the operational variable pressure has a great influence on the choice of the entrainer by the analysis of the isovolatility curve.

It is very easy to generate an isovolatility curve for a ternary system in Aspen [35]. The curve must be completed with knowledge of the location of the isovolatility curve $\alpha_{AB} = 1$ (relative volatility is equal to 1), which splits the composition triangle into regions with an explicit order of volatility of the A and B components. The isovolatility curve location is the core of a general feasibility criterion to infer which component is an attainable product and what the related column configuration is. To analyze the influence of pressure on the different entrainers, two binary azeotropic systems, ethanol-benzene and ethanol-ethyl acetate, are used as case studies for separation by extractive distillation by combining pressure. The change in pressure results in a significant change in the selection of the entrainer. This discovery provides more possibilities for the choice of the entrainer and indicates the importance of pressure in extractive distillation, especially the pressure-sensitive system.

2. Process design and economic analysis

Aspen Plus commercial software was used to simulate extractive distillation for separating ethanol-benzene and ethanol-ethyl acetate binary azeotropes. The thermodynamic models of the separation processes were validated using root mean square deviations [36] (Table 1). The predicted values using the thermodynamic model-UNIQUAC with built-in binary interaction parameters fit well with experimental vapor liquid equilibrium data [37–44] (Table 2).

The economics were evaluated in terms of the TAC, which was the sum of the capital costs and operating costs. The plant life time is assumed to be 3 years. The analytical expressions of the TAC are as follows:

$$\text{TAC}(\$/\text{year}) = \text{Annual operating costs} + \text{Captial costs/plant life time} \quad (1)$$

$$\text{Annual operating costs} = \text{Steam costs} + \text{Cooling water costs} \quad (2)$$

$$\text{Capital costs} = \text{Column vessel costs} + \text{Plate costs} + \text{Heat exchanger cost} \quad (3)$$

The capital costs include the costs of the column vessels, plates, and heat exchangers. The annual operating costs mainly include the steam costs for reboilers and cooling watercosts for condensers. The column parameters were calculated by the “Tray Sizing” function in Aspen Plus. Detailed information of the economics and calculated formulas [45] is shown in Table 3.

Due to the high equipment investment and high energy costs, optimization is necessary for most chemical engineering. There is a software that is based on the sequential iterative optimization procedures [8] (Fig. 1) and simulated annealing algorithms [46], named Extractive Distillation Optimization Software (EDOS) [47,48]. The EDOS optimization procedure consists of the following steps. First, some initial values and algorithm parameters are provided to the computer program, and then they are passed to simulation software as design variables for the process simulation. At the completion of the simulation, the results are transferred back to the computer program, which calculates the TAC, and the design variables are updated according to the optimization algorithm. The steps are repeated until a minimal TAC is obtained, and the optimal results can be found in the Microsoft Excel file that

Table 1
Results of correlation in two systems with three thermodynamic models.

system	Root mean square deviations		
	UNIQUAC	NRTL	WILSON
Ethanol-benzene	0.0157	0.0219	0.0244
Ethanol-1,2-propanediol	0.0081	0.0078	0.0079
Ethanol-p-xylene	0.0196	0.0203	0.0157
Benzene-p-xylene	0.0200	0.0202	0.0201
Ethanol-ethyl acetate	0.0131	0.0135	0.0947
Ethanol-EG	0.0334	0.0397	0.0357
Ethanol-furfural	0.0411	0.0429	0.0416
Ethyl acetate-furfural	0.0027	0.0045	0.0091