

추출증류를 이용한 에틸벤젠과 *p*-자일렌의 분리

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Separation of ethylbenzene and *p*-xylene using extractive distillation

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1. Introduction

Xylene isomers and ethylbenzene are contained in naphtha reformat processed with a naphtha reformer. The C8 compounds are separated along with other aromatic compounds, such as benzene and toluene, by the extractive distillation using sulfolane. Further distillation produces the C8 components of close boiling points in a group. Among the mixture *p*-xylene has high demand to produce terephthalic acid, a raw material in the production of polyesters and polyethylene terephthalates (PETs). The separation processes of *p*-xylene based on solvent extraction or crystallization were not efficient with only 60–65% recovery rate. In 1971, the Universal Oil Products (UOP) commercialized a new separation method, an adsorption process, called Parex process with a 95% recovery rate. Though the adsorption process is largely effective and efficient in the separation of a specific component from a mixture with high recovery and high purity, it requires a large volume of high-cost adsorbent. Moreover the next stage of the separation process includes a desorption process to recover the adsorbed product from the adsorbent using a desorbent. The recovery and recycling of the desorbent accommodates a distillation column separating the targeted adsorbate, final product, and desorbent.

For a large throughput of chemical production a continuous processing is desired, and distillation and extraction are suitable for the continuous process of large production. Because the adsorption is a batch process, a simulated moving bed (SMB) operation, a quasi-continuous process, requiring multiple beds of adsorbents was introduced and the Parex process utilized the SMB operation. While one of the beds releases the adsorbate, the product, other three beds are preparing for the next production of product in sequence. However, the SMB operation necessitates a large volume of high-cost adsorbents. The extractive distillation of ethylbenzene and *p*-xylene has been studied for many years, but no commercial process was developed due to the failure finding an effective extractant.

In this study, an efficient solvent nitrobenzene for the separation of *p*-xylene from the mixture of ethylbenzene and *p*-xylene, two main components in the naphtha reformat is proposed, and the separation process of *p*-xylene is designed for 99% recovery and 99% purity of *p*-xylene using the proposed extractive distillation. The design procedure is explained to present the performance of the proposed separation process.

2. Process Overview

p-Xylene and ethylbenzene are isomers having close boiling points, difficult to be separated by common distillation. To assist the distillation separation of the mixture, *p*-dinitrobenzene was added to the distillation as an extractant, which is separated from the product at the subsequent distillation and recycled as shown in Fig. 1. The sequence of extractive distillation used here is the same as applied in the conventional processes. Solvent introduced in the extractive distillation column was recovered at the

solvent recovery column by separating the product.

The process proposed here was designed with the commercial software HYSYS using the thermodynamic model NRTL for vapor-liquid equilibrium (VLE). Because no experimental binary VLE data with p-dinitrobenzene were available, the NRTL parameters were calculated with the group contribution technique UNIFAC. However, the technique considers the type and number of the comprising groups in a molecule for the parameter estimation. In other words, the UNIFAC does not distinguish the difference among the location of nitro group at the dinitrobenzene molecules, such as ortho, meta and para locations. For the verification of the parameters used in the HYSYS design, a molecular simulation procedure was applied to examine the UNIFAC estimated NRTL parameters by computing the vapor compositions for given liquid compositions.

3. Process Design

Because the designs of extraction and distillation utilize the equilibrium-stage design procedures, the column design in this study followed a common procedure using the commercial program HYSYS. The NRTL model with parameters in the program was used for the computation of vapor-liquid equilibrium. A well-known extraction process, sulfolane process separating aromatic compounds from naphtha reformat utilizes solvent at a rate of 5 times feed flow rate. An experimental study of extractive distillation of ethylbenzene and p-xylene suggested 5 times the flow rate of solvent gives the best performance. In this study the solvent was supplied at a rate of 5 times the feed rate.

The number of trays in the extractive distillation is inversely proportional to reflux flow rate. While the former increases the investment cost, the latter raises the operating cost. For the optimum of the total annual cost (TAC), an optimization procedure, differential evolution method, was used to determine the number of trays. The cost equations are listed in reference, and the cost index, Chemical Engineering Cost of 2016, 541.7, was used here. Payback time of the investment was 5 years, and annual operation day was 330.

After the column tray number and reflux flow were calculated, minor numbers of feed location was iteratively adjusted for minimum reflux. The design results are listed in Table 1.

4. Results and Discussion

For the separation of ethylbenzene and p-xylene consisted of close boiling compounds, an effective solvent was proposed and its performance was examined to explain below.

3.1 Solvent selection

There were many studies of extractive distillation, but none of the proposed solvent worked as efficient as nitrobenzene. Berg (Berg, 1995) introduced methyl formate, n-butanol and c-pentanol as solvents in the extractive distillation. He has published the experimental data of ethylbenzene separation using polychloro organic compounds as solvents (Berg and Kober, 1980). A variety of solvents were experimentally examined for possible utilization as solvents in the extractive distillation (Jeon et al., 2014). These previously introduced solvents were not efficient as nitrobenzene proposed here. Applying large amount of reflux flow in a tall distillation column separates close boiling mixtures, which cannot be commercialize due to high operating cost with large investment. Various solvents introduced in the previous studies were tested to determine nitrobenzene the most efficient. In terms of separation nitrobenzene was more effective, but solvent recovery was difficult because it had high boiling point requiring high-cost utility.

3.2 Design results

The proposed extractive distillation process was designed using a commercial design program HYSYS (Aspen and Guide, 2007). Because varying pressure does not improve the separation, the column pressure at the top trays was set at 120 kPa. The number of trays was determined using differential evolution method for the minimum total annual cost consisted of investment and operating

cost. The locations of feed and solvent were adjusted after the number of trays and reflux flow rate were set. The amount of solvent was also adjusted for the product specification. Table 1 lists the design results of the structural and operating variables of the extractive distillation along with product specification. Because no phase separation in liquid was observed in the ternary system, the distillation simulation was not complex as in the design of an azeotropic distillation.

References

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Table 1. Structural information and operating conditions in the proposed process. Tray numbers are counted from the top.

Variable	Extractive	Distillation	Recovery
Structural			
Tray No.	42		12
Feed	23		6
Solvent	2		
Operating			
Pressure (MPa)- top	0.12		0.12
Temperature (°C)			
Overhead	143		150
Bottom	188		310
Feed (kmol/h)	100		580
Solvent (kmol/h)	500		
Make-up/Purge	0.8		0.8
Product (kmol/h)			
Overhead	20		80
Bottom	580		499
Reflux (kmol/h)	184		61
Vap. boilup(kmol/h)	255		248
Cooling duty (MW)	2.0		1.4
Reboiler duty (MW)	5.8		4.2
Comp. (mole frac.)			
Feed			
p-Xylene	0.8		0.138
Product			
p-Xylene	0.012	Ovhd.	Ovhd.

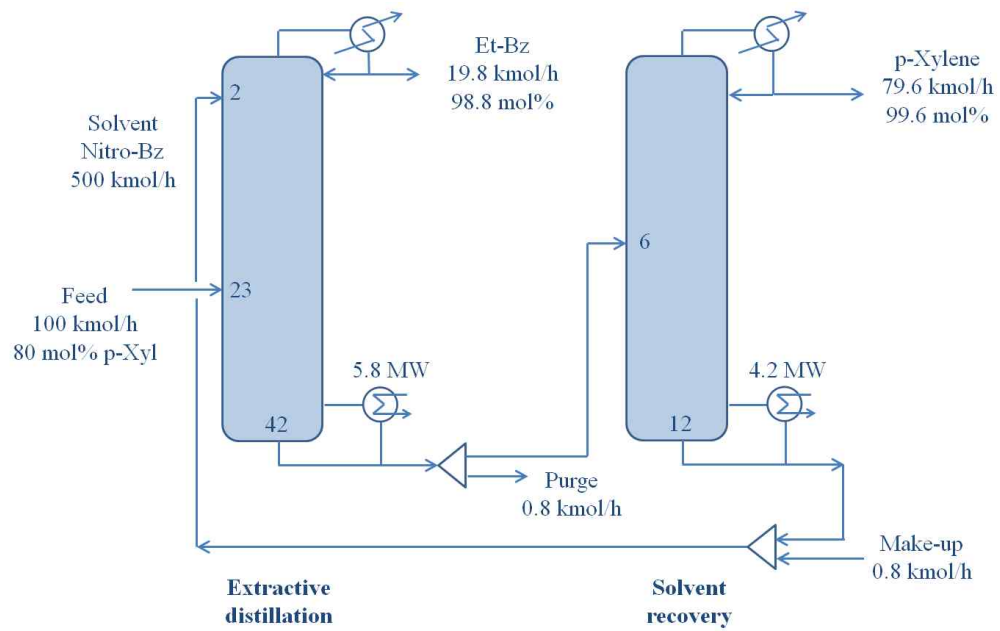


Fig. 1. Schematic diagram of the proposed extractive distillation process.