분자 시뮬레이션을 이용한 방향족 화합물 분리용제의 개발

김병철[1], 박진환[2], 김영한[2,*]
경남정보대학교 신소재화공계열[1]
부경대학교 도장방식융합기술사업단[2]
(yhkim2@pknu.ac.kr[*])

Development of aromatic separation solvent using molecular simulation

Byoung Chul Kim[1], Jin Whan Park[2], and Young Han Kim[2,*]
Sub. of Adv. Mater. & Chem. Eng, Kyungnam Coll. of Info. & Tech.[1]
Center for Advanced Painting, Pukyong National University[2]
(yhkim2@pknu.ac.kr[*])

1. Introduction

Though distillation has been being widely used in chemical processes, its application is limited in some cases, such as close-boiling or azeotropic mixture separation. Adsorption (e.g., Parex and Molex processes) and crystallization (e.g., Badger/Niro para-Xylene process) are alternatives to the difficult distillation processes requiring an excessive number of trays and a large amount of reflux flow. With appropriate solvents that improve the selectivity in the vapor-liquid equilibrium (VLE) or in crossing the distillation boundary of an azeotrope such as ethanol dehydration using ethylene glycol, well-developed distillation can be utilized in the separation with a moderate number of trays and a relatively small reflux flow. The extraction solvent is critical in the design of extractive distillation processes. An experimental database of solvent extraction is commonly used in searching for solvents, and even commercial solvent selection programs use the database. In that process, the selectivity improvement calculated with the activity coefficient at an infinitely diluted solution determines the best solvent. The limited solvent finding depending on the experimental database restricts the application of less costly, energy-efficient distillation in the separation of close-boiling mixtures.

This study proposes a generalized solvent searching procedure with the help of a molecular simulation. We found solvent that we applied to aromatics distillation process to examine its performance. The investigation includes technical achievement and economic improvement over conventional technique.

2. Solvent Selection

In the design of extractive distillation processes, the solvent determines the performance and economics. Because the solvent improves the selectivity of the extracted component from the feed mixture, a solvent with high selectivity is desired in the process design. An early classification of solvents for azeotropic distillation was in five groups by potential for forming hydrogen bonds. The classification was based on the strength of the hydrogen bond, and the solvent was selected by comparing the boiling point, water azeotrope temperature and water solubility. The first two classes, which had the strongest hydrogen bonds, were the best in most cases. A molecular simulation provides vapor-liquid equilibrium (VLE) compositions for mixtures of any chemical structure at a given condition. In other words, its computation does not require a database as the CAMD[1] and COSMO-RS[2] do. The selectivity computed from the VLE composition is more representative and

widely selected than that estimated with the activity coefficient. For molecular systems, the force field takes into account the intramolecular potential, such as bond stretching, angle bending and torsion, and intermolecular potential, such as van der Waals and Coulomb forces[3]. When a system of two species of close-boiling compounds is separated by distillation with the help of solvent-improving selectivity, the extracted compound and solvent that have a similar chemical structure minimize the total potential. The intermolecular potential needs to be minimized by selecting an adequate solvent. The intermolecular potential is small when two molecules have a similar chemical structure. Because the potential is computed between the comprising atoms in opposite molecules, the structural similarity helps orderly distribution of the molecules and results in the minimum potential. They can be placed in a more orderly fashion than molecules of different structures, which indicates that a solvent with a chemical structure similar to that of the extracted component places more of the extracted component in a liquid phase, where molecules are compactly present. As predicted with the potential formula, molecularly-similar solvent attracts more extracted molecules in the liquid phase which decreases the vapor phase at the vapor-liquid equilibrium. This improves selectivity of the extracted by distillation compared to conventional distillation without solvent. Therefore, molecular similarity has an important role in solvent selection. Moreover, as in the CAMD and COSMO-RS, the boiling point of the solvent is also a key factor in determining the solvent. The selected solvent attracts more in a liquid, which becomes the bottom product of the extracted and solvent mixture at an extractive distillation column. The solvent has to be recycled after it is separated from the extracted by distillation that requires a boiling point difference between them for distillation separation. The solvent boiling point needs to be sufficiently higher than either of feed components. After possible solvents are selected using the two qualitative selection guidelines, the selectivity of the extracted component is calculated using the VLE data computed from the molecular simulation, and the solvent with the highest selectivity is finally chosen.

3. Process Design

The process design was conducted with the commercial process design software HYSYS. The thermodynamic equilibrium was computed with a non-random two-liquid (NRTL) model, because the parameters for equation of state (EOS) models are not available for various solvents. Unlisted parameters of the NRTL model were estimated with the UNIQUAC functional-group activity coefficients (UNIFAC) method. Molecular simulation gives the numbers of constituent molecules at each boxes of liquid and vapor phases in equilibrium, and therefore component mole fractions are readily calculated from the molecules number in both phases. The relative volatility is the ratio of solute composition in vapor and liquid phases, and the selectivity is the ratio of the relative volatilities with solvent and without solvent. The selectivity is an indicator of how the solvent works. Because the molecular simulation directly computes the compositions of vapor-liquid equilibrium, no thermodynamic model is necessary.

Aromatics are the most important feedstock in both petroleum and petrochemical processes, which require a huge production and energy demand. Thus, a small improvement in the aromatics separation process significantly affects the production and economics in the aromatics process. Aromatics, also known as BTX (benzene, toluene and xylenes), are used as gasoline blends and feedstock for a variety

of petrochemical products, including styrene, cyclohexane and terephthalic anhydride. When naphtha reformate is derived from the naphtha reforming process, various aliphatic compounds are also present, and separating the aromatics is difficult due to the wide range of boiling points of their constituents with distillation.

A widely-used solvent sulfolane, which separates aromatics from the reformate, has been applied in many processes since its commercial development in the early 1950s. Various modifications of the sulfolane process were introduced for the reduction of energy demand and improved recovery and product purity. In fact sulfolane was initially developed as a purifying solvent by removing H_2S, CO_2, COS and mercaptans from natural gas. Examining the sulfolane molecule, which contains a sulfur atom and two oxygens with a cyclic C4 structure, does not indicate how it selectively dissolves aromatics only. However, its high boiling point, large ratio ofs olvent to feed, and high recycled feed rate require a large amount of steam at high temperature. Though its high boiling point is beneficial for solvent recovery, the recovery consumes high pressure, costly steam. The aromatic and aliphatic components are evenly distributed by their boiling points though larger amounts of aromatics are included in the feed. The boiling points of methylcyclopentane and benzene are too close to be separated by distillation that is repeated in the separation of toluene and xylenes mixed at same feed. As explained in the section on solvent selection, pyridazine was the extraction solvent in the process. The first extractive distillation column separates toluene and xylenes as the bottom product, which is separated at the following two distillation columns after the solvent is recovered. A minor amount of solvent loss was recovered by a make-up stream.

Benzene was derived from the overhead product of the first extractive distillation column. The overhead product contains most of components in the feed except toluene and xylenes, and therefore it was extracted as in the process diagram. The extractive distillation column separates most of aliphatic compounds as an overhead product, and its bottom product includes benzene, a small amount of aliphatic products and pyridazine as three groups of products. A divided wall column was used for the separation of the three products.

4. Design results

The selected solvent using the guidelines for the BTX process was pyridazine. The chemical structures of benzene and pyridazine show for their resemblance. Both have six-membered rings and π bonds. Two nitrogen atoms in pyridazine are different from benzene. Because the nitrogen atom has three free radicals while the carbon atom has four radicals, no hydrogen atom is bonded. Two nitrogen atoms are used for the higher boiling point considering xylenes separation. The relative volatility between methylcyclopentane and benzene was computed with VLE data by molecular simulation at the vapor composition of benzene between 0.23 and 0.32. In this process toluene and xylenes are also separated along with benzene, and a highly selective solvent is necessary. The pyridazine selectivity for benzene is significantly higher than the others for the separation. Pyridine was also a good solvent for the separation as expected from its chemical structure, but its boiling point was lower than those of xylenes.

The total heating duty was 21.8 MW, and the recovered heat duty was 10.7 MW. Because recycled solvent is supplied to extractor at room temperature and its temperature is the highest in the process, recovered heat from the solvent is sufficient for feed preheating at distillation columns. The preheating reduces reboiler heat duty, but the listed heat duty does not include the preheating. The cooling duty

was 10.3 MW. Though the product purity and recovery were lower than in this study, the conventional BTX separation process using sulfolane as a solvent for the same feed amount consumed 34.9 MW for heating and 22.5 MW for cooling. The sulfolane process was compiled for the process data given in reference based on field operation. Its large energy consumption comes from the difference of the extraction process. The proposed process of this study extracts all the products without recycling untreated products. In addition, the boiling point of pyridazine (208°C) is much lower than that of sulfolane (285°C). When the solvent is recovered at the recovery distillation column, the column bottom temperature is determined by the solvent boiling point. A high temperature solvent exhausts high-pressure, costly steam. The total cost was 7.26 million U.S. dollars. A commercial UOP sulfolane process that handled 54.5 ton/h of feed required an investment of 13.5 million U.S. dollars at the 2002 price. Compared to the 28.7 ton/h process of this study, the UOP process cost 10.33 million U.S. dollars at the 2017 price. The investment cost of the proposed BTX process was 30% less than the UOP process. The steam consumption in the UOP process was 27.5 ton/h, which is equivalent to 12.7 MW. The proposed process consumed 11.1 MW that is 13% less than the UOP process.

References

1. Gani R, Ng KM. Product design - Molecules, devices, functional products, and formulated products. *Comput chem Eng.* 2015, 81, 70-79.
2. Gutierrez JP, Meindersma GW, de Haan AB. COSMO-RS-Based Ionic-Liquid Selection for Extractive Distillation Processes. *Ind Eng Chem Res*. 2012, 51, 11518-11529.
3. Dubbeldam D, Calero S, Ellis DE, Snurr RQ. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. *Mol Simul*. 2016, 42, 81-101.
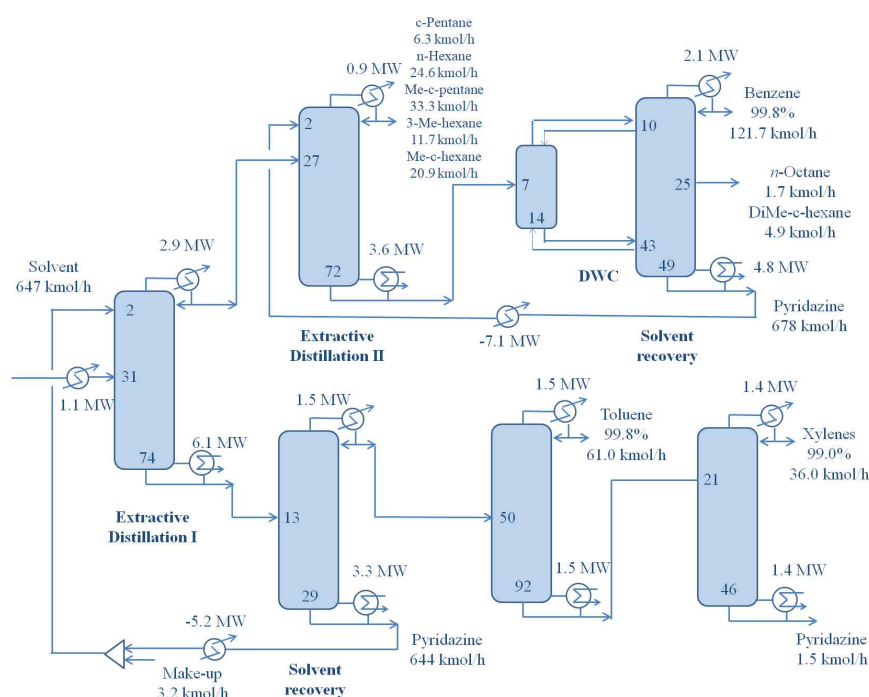

Figure 1. Process flow diagram of the benzene/toluene/xylene (BTX) process.