추출용제 선정을 위한 분자 시뮬레이션의 응용

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Application of molecular simulation for selection of extraction solvents

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1. Introduction

A mixture comprised of close-boiling components is difficult to be separated by distillation, because their relative volatilities are not favorable to collect more volatile components in vapor phase compared to in liquid phase. A solvent (entrainer) holds it in its phase to help the distribution of the target between vapor and liquid phases for the separation. In the selection of the solvent the closeness of molecular structure to the target material answers what the preferred choice is. The reduced pair potentials of the target and solvent place the two molecules in the same phase enhancing the separation of the target material unless the solvent is evenly distributed into vapor and liquid phases.

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 were available for all components, 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 otho, 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.

In this study, the solvent selection for extraction adopted the procedure of molecular simulation in finding possible candidates of solvents, and its process was applied to trimethylbenzene separation process.

2. Molecular Simulation

In molecular simulation the distribution of comprising molecules in a space is optimized making the sum of combined potentials the minimum [1]. And intermolecular potentials are composed of the Lennard-Jones potential and Coulomb potential.

By positioning molecules in a box at their optimized coordinate, the total potential energy of the molecules becomes the minimum, equilibrium. The Monte Carlo simulation places the molecules toward the minimum energy in statistical way. In the canonical ensemble, the partition function is given by [2]

$$곿 \quad ᆳ \quad 강갌 \tag{1}$$

where *U* is the potential of molecules at position vector **r**, and the integration ranges at the number of molecules *N*. The potential includes bonded and intermolecular unbonded forces such as Lennard-Jones potential. The de Broglie wavelength *Λ* is the length at which intermolecular interactions are neglected. When the integrand in Eq. (1) is proportional to the probability of the desired configuration **r** of all the molecules, the average probability is found as

$$갌 \quad \frac{갌 \quad 곿 \quad ᆳ \quad 강갌}{곿 \quad ᆳ \quad 강갌} \tag{2}$$

In the Monte Carlo simulation the positions of molecules are not deterministically calculated but stochastically sought, where a random number is generated to find the new position of each molecule. The newly computed potential at the position gives the average probability in Eq. (2). Here Metropolis criterion is applied to determine if the newly suggested positions of molecules are accepted.

In this study the Monte Carlo simulation in NVT ensemble was conducted using the open program RASPA that includes the procedures explained above. The molecular structure and bond and bend stretches were from the transferable potentials for phase equilibria (TraPPE) potentials [3]. The box size in liquid phase was 40 angstrom cubic, and that of vapor was 150 angstrom. The input data in the simulation were referenced to the result of the HYSYS VLE simulation for fast settlement at equilibrium. The numbers of molecules were about 250 and 50 for liquid and vapor, respectively. The numbers were adjusted for the density calculated in the HYSYS.

3. Process Design

The proposed process is composed of three distillation columns with a recycled stream. The process was designed with a commercial program HYSYS. The process flow diagram with the detailed column and stream information is illustrated. The first was the extractive distillation column separating lighter components than the 1,2,4-trimethylbenzene as an overhead product. The components boiling points are high enough to be processed at an atmospheric pressure. Therefore, the column operating pressures was set near the pressure. The thermodynamic model for vapor-liquid equilibrium was the non-random two liquid (NRTL) model for liquid phase activity computation and the Redlich-Kwong (RK) model for vapor phase computation. The unknown binary parameters of the NRTL model were estimated using the universal functional-g activitycoefficients(UNIFAC) group contribution method included in the HYSYS. The amount of solvent was set at 5 times the feed flow after considering the solvent/feed ratio in the sulfolane process and the experimental study of extractive distillation for the p-xylene/ethylbenzene separation.

Because the number of trays in a distillation column is inversely proportional to reflux flow for a given separation, the number was optimized for the total annual cost (TAC) including investment and operating cost. The differential evolution technique was used in the optimization. The bounds of three tray numbers in search were set at different values for fast convergence. The computation of investment cost was conducted by the equations with the Marshall & Swift cost index of 1593.7 in 2017. Payout time of the investment was 3 years, and annual operating day was 300. Steam and cooling water prices

for operating cost were taken from Douglas. With the column operating pressure and the tray numbers being set, the operating condition the reflux flow rates were iteratively adjusted for the given specifications of products.

4. VLE computation with molecular simulation

Only 5% of binary NRTL parameters used in the process simulation were provided in the HYSYS database, and remainder was estimated using the UNIFAC method. For the examination of the estimated parameters, two typical ternary systems, 1-methyl-2-ethylbenzene/ 1,2,4-trimethylbenzene/ 1,2,4-trichloro-benzene and 1,2,4-trimethylbenzene/1-methyl-3-ethyl-benzene/1,2,4-trichloro-benzene, were used for the comparison of computed VLE data.

The molecular simulation yields the optimized potential, the sum of Eqs. (1) and (2) by placing the comprising molecules at their equilibrium locations. Practically the results show the locations of the molecules in two boxes, one for liquid measured 30 angstrom cubic and the other for vapor of 150 angstrom cubic. The numbers of molecules in a box lead to their mole fractions in either phase. The optimization was conducted with the Monte Carlo simulation, and the open package of molecular simulation RASPA [2] was utilized in this study. The parameters used in the simulation are summarized in Tab. 5. While the volumes of vapor and liquid phases were fixed, a small number of molecules were relocated between the phases to reduce the total potential. The comparison of VLE computation results is demonstrated in Fig. 3. Top figure displays the compositions in equilibrium between liquid and vapor for 6 sets in the system of 1-methyl-2-ethylbenzene/ 1,2,4-trimethylbenzene /1,2,4-trichlorobenzene. The circles are in vapor, and pluses are of liquid. The dotted lines connect the computed equilibrium with the HYSYS. Those of dash-dotted lines are of the molecular simulation. The same comparison is given in the bottom figure for the ternary system of 1,2,4-trimethylbenzene/ 1-methyl-3-ethylbenzene/1,2,4-trichlorobenzene. The average difference between the computed mole fractions in absolute values was 0.014 for the first system and 0.019 for the second. The small difference indicates that two estimation techniques give reliable VLE data. The distillation design results of the HYSYS using the UNIFAC estimation have been accepted in most of field application.

5. Design results

When the column operating pressure is set, the tray number and reflux flow in a distillation column are inversely proportional for a given product specification. Because the former determines investment cost and the latter does utility cost, an optimum number of trays has to be found. The number of trays was determined by minimizing the total annual cost including investment and operating costs as explained above in detail. The optimization applied to two columns in a conventional process and three columns in the proposed extractive distillation process. While the total number of trays in the proposed process was 15% less than the conventional process, its total heating duty was 22% less than the conventional. Utilizing the solvent is responsible for the differences. A 99% 1,2,4-trimethylbenzene was yielded with 93% recovery from either process.

At the extractive distillation column a solvent was supplied to selectively separate the objective material, 1,2,4-trimethylbenzene, and Tab. 2 demonstrates how the solvent worked in the separation. The column produced the overhead product with 5.45 kmol/h without the solvent, 1,2,4-trichlorobenzene, while the product with 1.45 kmol/h with the solvent at the same operating conditions. The components of close-boiling to the target are listed in the table for better comparison. While other close-boiling components were not much affected by the solvent introduction, the target was significantly reduced

with the solvent. It indicates that the solvent helps to move the target to the bottom of the column along with the solvent.

The investment and operating costs of the proposed extractive distillation process were compared to those of the conventional two-column process. The investment cost includes column shell construction, internal and heat exchanger expenses, and the operating costs are of steam and cooling water. The investment cost of the proposed process was 16% less than that of the conventional, while the operating cost saving was 22%. These cost savings come from the separation improvement by the solvent, 1,2,4-trichlorobenzene. Though a third column was installed for recycling the solvent, the cost was lowered even with the additional expenses of the solvent recovery.

References

1. M.P. Allen, NIC Series, John von Neumann Institute for Computing, Julich, Germany **2004**, *23*, 1-28.
2. D. Dubbeldam, A. Torres-Knoop, K.S. Walton, *Mol. Simul.* **2013**, *39,* 1253-1292.
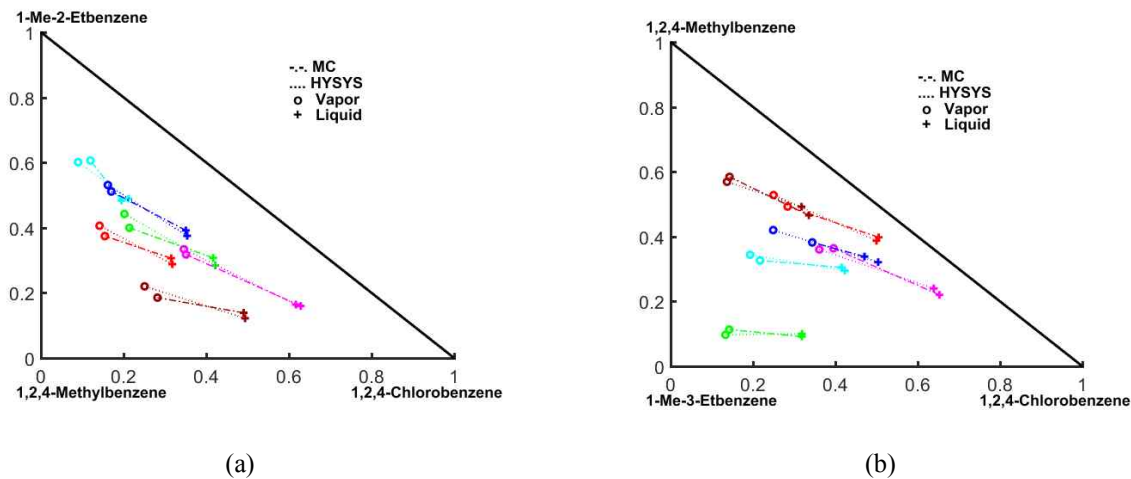3. N. Rai, J.I. Siepmann, *J.Phys.Chem.B* **2013**, *117,* 273-288.

(a)   (b)

Figure 1. Ternary diagrams of vapor-liquid equilibrium: (a) 1-methyl-2-ethylbenzene/1,2,4-trimethyl-benzene/1,2,4-trichlorobenzene system, and (b) 1,2,4-trimethylbenzene/1-methyl-3-ethylbenzene/1,2,4-trichloro-benzene system.