

## 클로로벤젠을 이용한 1,2,4-메틸벤젠의 분리

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### Separation of 1,2,4-methylbenzene using 1,2,4-chlorobenzene

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#### 1. Introduction

The chemical 1,2,4-trimethylbenzene, also known as pseudocumene, is widely used in the production of fine chemicals, such as hydrogen peroxide, mellitic anhydride, and vitamin E. It is also used as a coating solvent and stabilizer. With increase in the demand for *p*-xylene, the transalkylations of 1,2,4-trimethylbenzene and toluene have been examined as an alternative route for the production of *p*-xylene. Though the total consumption of 1,2,4-trimethylbenzene is small, it has wide applications in fine chemical processing. The best way to produce it is by separation from the C<sub>9</sub> aromatic fraction derived from petroleum refinery cuttings rather than from direct synthesis. However, many isomers of close-boiling components present in its feed make distillation separation very difficult, requiring tall columns equipped with over 300 trays and large amount of reflux flows. Extractive distillation is a solution for difficult separation by common distillation, and recent studies have examined its process control and energy saving aspects.

In molecular simulation, the total potential energy among molecules is minimized to find the equilibrium distribution of the constituent molecules in a given space. The computation of potential energy includes potentials of intramolecular bonding and intermolecular interactions, such as van der Waals and Coulombic forces. The Lennard-Jones potential is the most common potential for the van der Waals pair interactions. In molecular based computation of pair potentials, the interactions among the constituent atoms in the molecules are computed, though sometimes groups of atoms are counted as in transferable potentials for phase equilibria (TraPPE) [1]. When the sum of the pair potentials is minimized to find the spatial distribution of the molecules, a solvent having a molecular structure similar to that of the target material (to be separated from a mixture) can attract the target more than other molecules in the mixture. In other words, when the solvent and the target material are close together, the pair potential is low. Structurally similar molecules produce a lower pair potential than structurally different molecules. Though molecular simulation studies have been widely used in computing vapor-liquid equilibrium (VLE) [2-3], there are no reports on the use of molecular simulation for the selection of solvents for extractive distillation. A recent study utilized a molecular modeling based thermodynamic model in the development of an extractive distillation process for the separation of aromatic-aliphatic compounds in naphtha.

In this study, the solvent 1,2,4-trichlorobenzene is proposed for the separation of 1,2,4-trimethylbenzene from a mixture of various C<sub>9</sub> components by considering their structural similarity. The details of the solvent selection are demonstrated with molecular simulation and separation performance evaluation. The separation performance of the proposed extractive distillation is compared to that of conventional distillation. The economics of the proposed process is also compared to that of a conventional two-column process.

## **2. Process Overview**

A conventional two-column process was modified by adding a solvent recovery column in the proposed extractive distillation process. The first two columns are same as those in conventional two-column processes separating the middle component. The solvent aids collection of the target component 1,2,4-trimethylbenzene in the bottom product of the first column and separating it at the second column. Much less amount of 1,2,4-trimethylbenzene was incorporated in the overhead without the use of the solvent. The second column separates the target component as the overhead product, and the last column recovers the solvent which is recycled to the first. A heavy component, naphthalene, having a higher boiling point than the solvent was purged from the recycled solvent to avoid its accumulation during recycling, and the solvent loss with the purge was recovered by a solvent make-up.

## **3. Solvent Selection**

When a solvent is used in extractive distillation, it carries the target molecules with it at an optimum distance, reducing the intermolecular potential. The intermolecular potential is minimized when the molecular structures of the target and the solvent molecules are similar. The reason to choose 1,2,4-trichlorobenzene as the solvent for extractive distillation of 1,2,4-trimethylbenzene is the similarity in their molecular structures. The role of the solvent is evident from the comparison of the product compositions in extractive distillation with and without the use of the solvent.

Among the three species of molecules, namely 1,2,4-trimethylbenzene, 1-methyl-2-ethylbenzene, and 1,2,4-trichlorobenzene, the first is more structurally closer to the third than the second. Molecular simulation predicts that two molecules of similar structure are closely present in a liquid cell. A high-pressure vapor-liquid system in equilibrium at 3 MPa and 397 °C was used for the molecular simulation. In a liquid cell, 19 molecules of 1-methyl-2-ethylbenzene, 21 of 1,2,4-trimethylbenzene, and 32 of 1,2,4-trichlorobenzene were supplied, and 31 molecules of 1-methyl-2-ethylbenzene, 31 of 1,2,4-trimethylbenzene, and 41 of 1,2,4-trichlorobenzene were placed in a vapor cell. The liquid cell was a rectangular box of dimensions 40 × 40 × 20 angstroms, and the dimensions of the vapor cell was 90 × 90 × 20 angstroms. The picture does not demonstrate a 3D illustration; however, examination of the picture by graphical rotation indicates that 9 molecules of 1-methyl-2-ethylbenzene are present at the cell boundary and are isolated because of the structural difference with the solvent 1,2,4-trichlorobenzene. The structural similarity of the target molecule and the solvent helps in their aggregation in the liquid phase. This results in less number of molecules of the target in the vapor phase, thus improving the separation of the target component by distillation. The utilization of 1,2,4-trichlorobenzene as a solvent for the separation of 1,2,4-trimethylbenzene from the C9 aromatic mixture was proposed considering the molecular interactions computed by molecular simulation.

## **4. Results and Discussion**

The design results of the proposed process of 1,2,4-trimethylbenzene separation from C9 mixture, VLE equilibrium computation using molecular simulation, and economics of the proposed design are described in the following sections.

### **4.1 VLE computation with molecular simulation**

For the examination of the estimated parameters, two typical ternary systems, namely 1-methyl-2-ethylbenzene/ 1,2,4-trimethylbenzene/1,2,4-trichlorobenzene and 1,2,4-trimethylbenzene/ 1-methyl-3-ethylbenzene/ 1,2,4-trichlorobenzene, were used for the comparison of the computed VLE data.

The molecular simulation yields the optimized potential by placing the constituent molecules at their equilibrium locations. Practically, the results show the locations of the molecules in two boxes, one for liquid, measuring 30 angstrom cubic, and the other for vapor, measuring 150 angstrom cubic. The number of molecules in a box gives the mole fraction in each phase. The optimization was

conducted with Monte Carlo simulation, and the open package of molecular simulation RASPA was utilized in this study. The parameters used in the simulation are summarized in Tab. 5. While the volumes of the vapor and the liquid phases were fixed, a small number of molecules were relocated between the phases to reduce the total potential. The top figure displays the compositions in equilibrium between liquid and vapor phases for 6 sets in the system of 1-methyl-2-ethylbenzene/1,2,4-trimethylbenzene/ 1,2,4-trichlorobenzene. The circles represent vapor, and the plus symbols represent liquid. The dotted lines connect the computed equilibrium with the HYSYS. The dash-dotted lines represent 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 is 0.014 for the first system and 0.019 for the second. The small difference in the mole fractions indicates that the two estimation techniques provide reliable VLE data. The distillation design results of the HYSYS program using the UNIFAC estimation have been accepted in most of the field applications.

#### 4.2 Design results

The details of the column design results and the operating conditions are summarized in Tab. 6. When the column operating pressure is set, the tray number and the reflux flow in a distillation column are inversely proportional for a given product specification. Because the former determines investment cost and the latter determines utility cost, the optimum number of trays needs to be estimated. The number of trays was determined by minimizing the total annual cost including investment and operating costs as explained in detail above. The optimization was applied to two columns in the conventional process and three columns in the proposed extractive distillation process. The total number of trays in the proposed process was 15% less than that in the conventional process and its total heating duty was 22% less than that of the conventional process; the use of the solvent contributes to the difference. A yield of 99% 1,2,4-trimethylbenzene with 93% recovery was obtained from both the conventional and new processes.

In the extractive distillation column, a solvent was supplied to selectively separate the target component 1,2,4-trimethylbenzene. 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 was obtained using the solvent at the same operating conditions. The components with boiling points close to that of the target are listed in the table for better comparison. While the boiling points of other close-boiling components were not much affected by the solvent introduction, the boiling point of the target was significantly reduced in the presence of the solvent. This indicates that the solvent helps to move the target to the bottom of the column along with it.

#### 5.3 Economic evaluation

The investment and the 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 include steam and cooling water costs. The investment cost of the proposed process is 16% less than that of the conventional process, while the operating cost saving is 22%. These cost savings come from the separation improvement provided by the solvent 1,2,4-trichlorobenzene. Though a third column was installed for recycling the solvent, the cost was low even with the additional expenses of solvent recovery.

#### References

1. N. Rai, J.I. Siepmann, *J.Phys.Chem.B* **2013**, *117*, 273-288.
2. H. Goel, Z.W. Windom, A.A. Jackson, N. Rai, *J.Comput.Chem.* **2018**, *39*, 397-406.
3. F.L. Cao, Z. Gong, Y.Z. Wu, H. Sun, *FluidPhaseEquilib.* **2017**, *452*, 58-68.

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

Variable	Conventional		Extractive distillation		
	Column 1	Column 2	Extractive	Distill.	Recovery
<b>Structural</b>					
Tray No.	248	152	149	156	36
Feed	124	74	48	78	25
Solvent			8		
<b>Operating</b>					
Pressure (MPa)- top	0.11	0.11	0.11	0.11	0.11
Temperature (°C)					
Overhead	165	173	165	173	180
Bottom	189	187	218	223	220
Feed (kmol/h)	83.4	40	83.4	461	219
Solvent (kmol/h)			422		
Product (kmol/h)					
Overhead	43.4	30.2	44.5	30.2	8.4
Bottom	40	9.8	461	431	423
Reflux (kmol/h)	874	544	291	465	301
Vap. Boilup(kmol/h)	995	565	784	470	288
Cooling duty (MW)	9.69	6.2	3.5	5.3	3.4
Reboiler duty (MW)	10.5	6.1	8.9	5.3	3.2
Recovered (MW)			4.4		
Comp. (mol frac.)					
Feed					
1,2,4-MeBz	0.385	0.787	0.385	0.067	0.229
Product					
1,2,4-MeBz	0.787	0.990	0.067	0.990	0.991

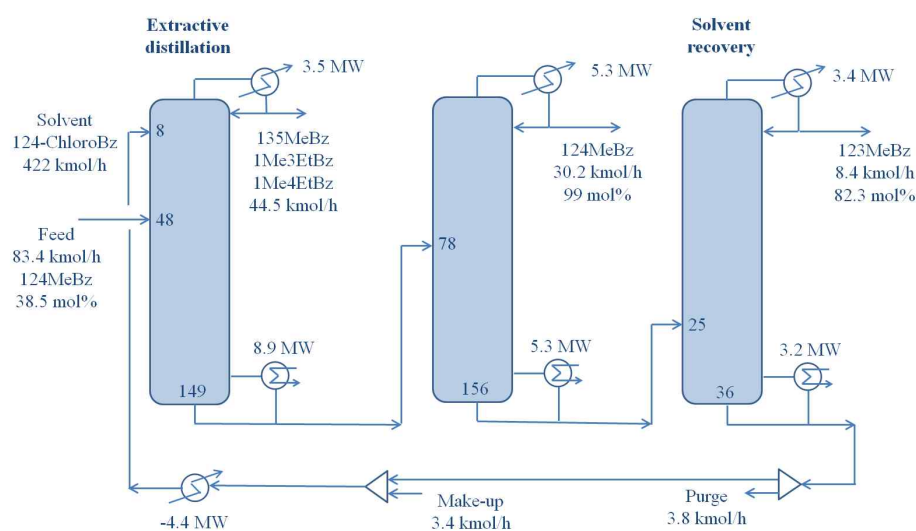


Fig. 1. Schematic diagram of the proposed extractive distillation process.