특별강연 3

# 석유화학공업에서의 투과증발분리

남 상 용
국립 경상대학교 공과대학 고분자공학과

# Pervaporation Separation in Petroleum Industry

Sang Yong Nam
Department of Polymer Science and Engineering,
Gyeongsang National University

## 1. Introduction

Petroleum refining is one of most energy intensive operation industry. For the separation of crude oil and petrochemicals, distillation process has been used. Distillation process needs a heating energy for increasing temperature to boil the petrochemical and eventually leads to higher energy cost. Membrane separation is emerging process to separate liquid and gas mixtures with lower energy cost. Especially pervaporation membrane separation is a good candidate to separate azctropic mixtures, liquid mixtures which has similar boiling point and chemical structure. Membrane process could replace some of the existing energy consuming distillation operations in the petroleum refining industry.

Specifically, the system investiaged consists of the ternary blend of styrene butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR), and polyvinylchloride. In pervaporation through the rubbery polymer membranes, solubility is more important factor for controlling permeability of the membrane. The solubility between permeant and membrane is measured by polymer-solvent interaction parameter and could be estimated by Flory-Huggins theory. An optimized blend membrane with controlled polar moiety content to tune solubility can

separate selectively aromatics from gasoline through pervaporation.

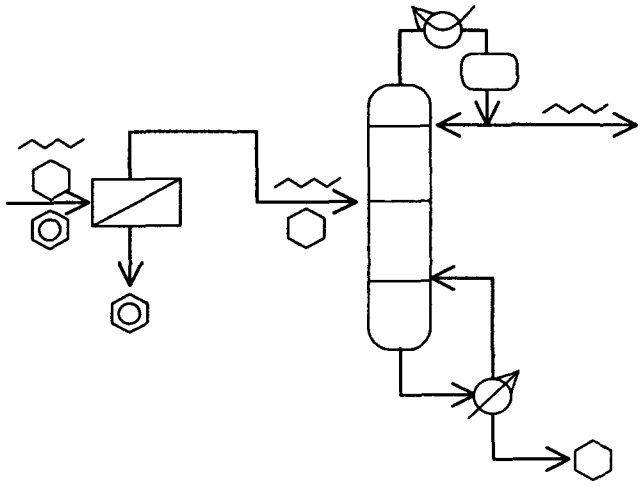

Figure 1. Schematic Diagram of Membrane-Distillation hybrid process to separate aromatic and aliphatic hydrocarbons.

## 2. Theory

In Table I, physical properties of benzene and cyclohexane were surmarized and interesting differences between two molecules are shown in solubility parameters. Many researchers have developed pervaporation and gas separation membranes and concluded overall selectivity of the system is divided into diffusion selectivity and sorption selectivity. Even though benzene has diffusion selectivity over cyclohexane through rubbery membrane because of small molar volume and collision diameter of benzene, diffusion selectivity might be mere for the rubbery blend membranes.

When using rubbery blend membranes for the benzene and cyclohexane mixtures, sorption selectivity is more important. Benzene and cyclohexane have big differences in solubility parameter of polar force and hydrogen bonding. This means that affinity between double bond of benzene molecules and the polar group of the polymer. In other words, phi electron of benzene have stronger affinity to polar groups.

Besides, benzene can also participate in hydrogen bonding with polar group.

Table I. Physical properties of benzene and cyclohexane

| | | Benzene | Cyclohexane |
|---|---|---|---|
| $f_p$(°C) | | 5.533 | 6.554 |
| $b_p$(°C) | | **80.1** | **80.7** |
| Density(g/cm3) | | 0.8737 | 0.7786 |
| Refractive Index, n25D | | 1.498 | 1.426 |
| Viscosity (cP) | | 0.65 | 0.98 |
| Surface Tension(dyn/cm) | | 28.2 | 25.3 |
| Molar Volume(cm3/mol) | | **89.4** | **108.7** |
| Collision diameter (nm) | | **0.53** | **0.61** |
| Solubility Parameter $(MPa)^{1/2}$ | $\delta$ | 18.5 | 16.8 |
| | $\delta_D$ | 18.4 | 16.8 |
| | $\delta_P$ | **0.0** | **0.0** |
| | $\delta_H$ | **2.0** | **0.2** |

Sorption selectivity was also investigated thermodynamically. UNIFAC-FV(UNIversal-QUAsi Chemical(UNIQUAC) Functional-group Activity Coefficient)-Free Volume) Model were used to calculate activity of the permeant in rubbery blend membranes. UNIFAC-FV model is considered as a good method for predicting swelling and permeation of benzene, because that UNIFAC-FV model shows activity of solvent to polymer by calculating functional group contribution. The activity is divided into three kinds of categories. First factor is the combinatorial entropy factor explains differences in size and shape of dissimilar molecules. Second one is residual, that is, interaction enthalpy factor represents the enthalpy exchange between two neighbor

molecules. And finally there is a free volume factor for solvents in polymer system. At first time, UNIFAC method is developed for liquid-liquid mixture system, but when it is expanded to polymer system, free volume factor should be added to exact calculation.

$$\ln \gamma_1 = \underset{Combinatorial}{\ln \gamma_1^C} + \underset{Residual}{\ln \gamma_1^R} + \underset{Free-Volume}{\ln \gamma_1^{FV}}$$

3. Results and Discussion

The activity of benzene and cyclohexane in the feed mixtures were calculated by iterative calculations using the UNIFAC model. Fig. 2 shows the relationship between the calculated solvent wt% and the swelling ratio each component (%). The swelling ratio of benzene and cyclohexane increase with increasing concentration of those components in membranes.

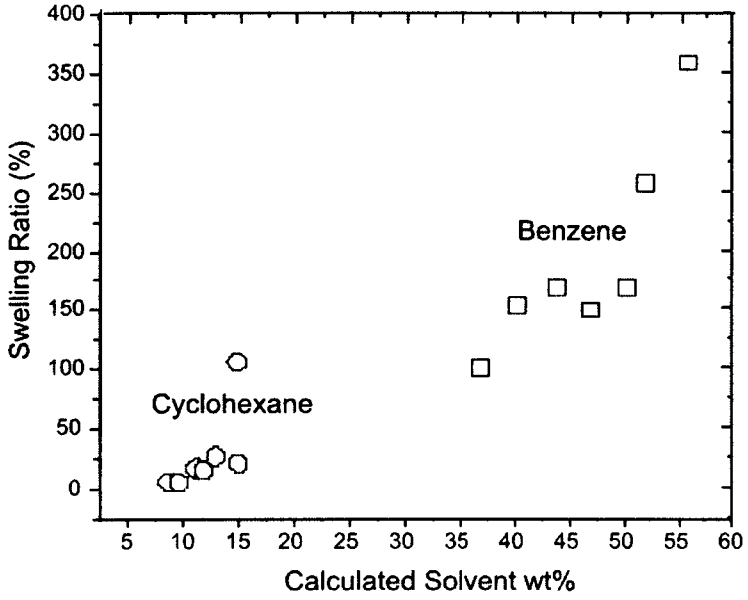


Fig 2. Relationship between calculated solvent wt% and swelling ratio(%) of benzene and cyclohexane

Fig. 3 shows prediction of selectivity using calculated ratio of benzene to cyclohexane. The calculated selectivity from the ratio of concentration of benzene to cyclohexane in membranes shows good accordance with the pervaporation selectivity.

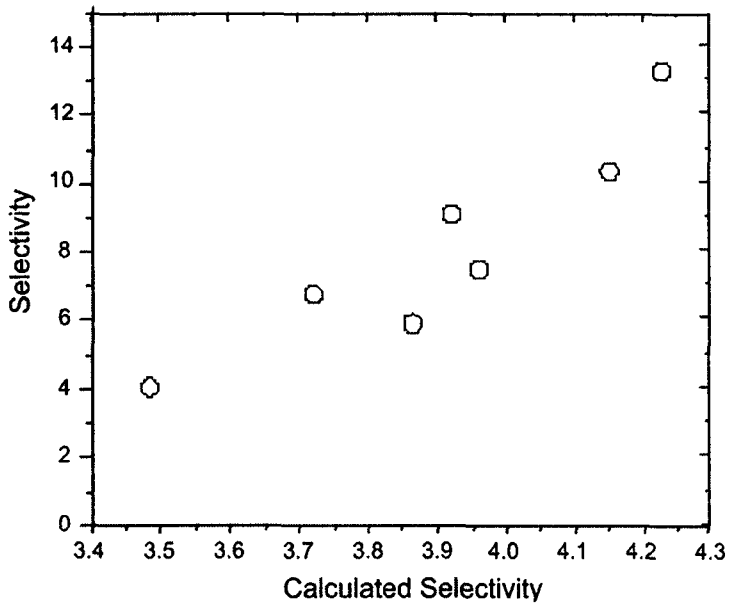


Fig 3. **Relationship between pervaporation selectivity and calculated selectivity.**

In order to evaluate and calculate economics of the membrane, the membrane performance with entire feed composition and operating temperatures should be investigated. A complete evaluation of membrane performance, therefore, requires knowledge of the variations of the permeation rate and the separation with respect to feed concentrations. Fig. 4 shows effect of feed concentration on pervaporation performance of benzene/cyclohexane mixtures through 316 membranes. For the entire feed concentration range of benzene, the benzene concentration in the permeate is higher than VLE(Vapor-Liquid Equilibrium) curves for benzene and cyclohexane mixtures, including the

azeotropic composition. This means the pervaporation membrane can separate benzene molecules from all range of concentration of benzene in the binary mixture feed, including the azeotrope. Permeation rate increases with increasing benzene concentration in feed.

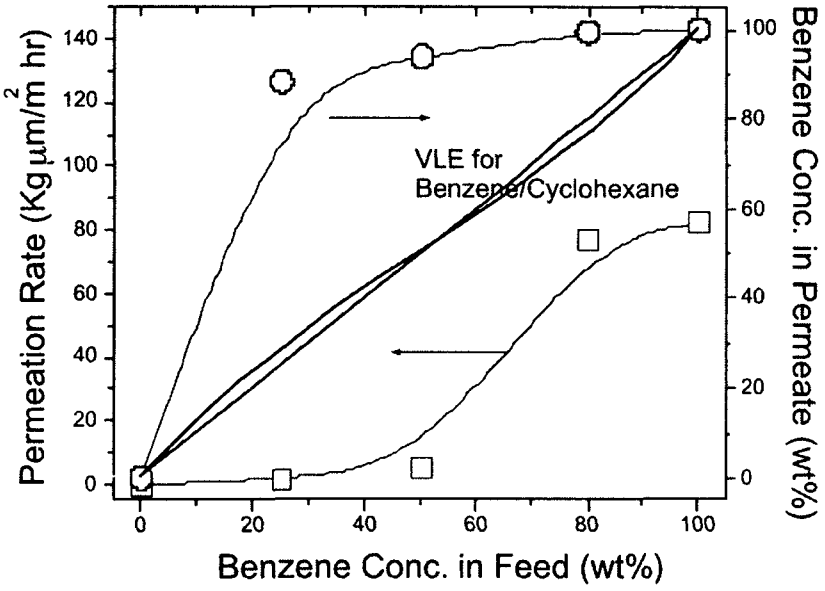


Fig 4. Effect of feed concentration on pervaporation performance of 316 membrane at room temperatur

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