

A comparative study on the recovery of 1,2-dichloroethane and the removal of benzene contained in the byproducts of VCM process

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Abstract—A comparative study has been performed to compare initial investment costs and operation costs for two different process configurations. The two processes were used to recover 1,2-dichloroethane (EDC) and to remove benzene contained in the byproducts of the vinyl chloride monomer (VCM) process. The objectives of this process were to recover 70% of EDC contained in the byproducts and to reduce the benzene content below 0.7 wt%. The first process configuration for comparison is a conventional distillation column that consists of upper and lower columns. The other process configuration is an extractive distillation process that uses Normal Formyl Morpholine (NFM) as a solvent to remove benzene. The conventional distillation process which consists of upper and lower distillation columns was superior to the extractive distillation process, which used a solvent, in the aspects of the initial investment and annual operating cost.

Key words: Simulation, Extractive Distillation, Process Comparison, 1,2-Dichloroethane Recovery, Benzene Removal

INTRODUCTION

Among the byproducts in the manufacturing process of VCM, the residual component contains about 50% of EDC, which is one of the raw materials for producing VCM [1]. VCM and HCl can be formed by the decomposition reaction of EDC as shown in Eq. (1) [2].



Until recently, EDC was used for heat recovery by combustion. Since the recovery as a form of material is more valuable than heat recovery, a comparative study was performed to recover the EDC component from the byproducts of a separation process by distillation [3]. Table 1 shows feedstock compositions and total flow rate of each component contained in the byproducts of the VCM process. The boiling points of benzene and EDC are similar, 80.1 °C and 83.5 °C, respectively. Therefore, benzene is a light key component and EDC is a heavy key component. The relative volatility at atmospheric pressure is only 1.1166 since the boiling point difference between the two components is only 2.4 °C. This means that the separation by simple distillation requires many stages, and the distillation column needs to be split into the upper and lower columns as shown in Fig. 1. There are several examples using the upper and lower column configurations, such as an extractive distillation of 1,3-butadiene from mixed C4 components, xylene splitter separating p-xylene from mixed xylene components, the splitter between ethane and ethylene, and the splitter between propane and propylene [4]. According to Fig. 1, the feed stream exchanges heat with the bottom product of the lower column and is additionally heated by steam. The feed stream is then fed to the mid-stage of the upper

Table 1. Feedstock information

Component name	Chemical formula	Molecular weight	NBP (°C)	wt%
Vinyl chloride monomer	C ₂ H ₃ Cl	66.499	-13.70	0.191
Propane	C ₃ H ₈	58.124	-0.50	4.480
Ethyl chloride	C ₂ H ₅ Cl	64.515	12.27	0.198
Vinylidene chloride	C ₂ H ₂ Cl ₂	96.944	31.80	0.178
Isopropyl chloride	C ₃ H ₇ Cl	78.542	35.74	0.036
Normalpropyl chloride	C ₃ H ₇ Cl	78.543	46.60	0.055
Allyl chloride	C ₃ H ₅ Cl	96.944	47.70	0.155
t-1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	98.960	57.28	0.306
1,1-Dichloroethane	C ₂ H ₄ Cl ₂	88.537	59.40	10.850
1-Chloro-1,3-butadiene	C ₄ H ₅ Cl	96.944	60.30	5.529
c-1,2-Dichloroethane	C ₂ H ₂ Cl ₂	113.378	61.73	0.542
Chloroform	CHCl ₃	119.378	61.73	4.136
Chloroprene	C ₄ H ₅ Cl	88.537	68.00	9.228
CCl ₄	CCl ₄	153.823	76.54	1.733
Benzene	C ₆ H ₆	78.115	80.10	12.923
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	96.960	83.50	48.139
Tri-chloroethylene	C ₂ HCl ₃	131.389	86.95	1.321
Heptane	C ₇ H ₁₆	100.206	98.45	0.034

column. The liquid stream of the bottom product of the upper column is fed to the top of the lower column after being pressurized by a pump. The gas stream of the top of the lower column is fed to the bottom of the upper column through tubing. This is the first configuration for this comparative study.

The second configuration is an extractive distillation process used to remove the benzene selectively from the feed stream by NFM

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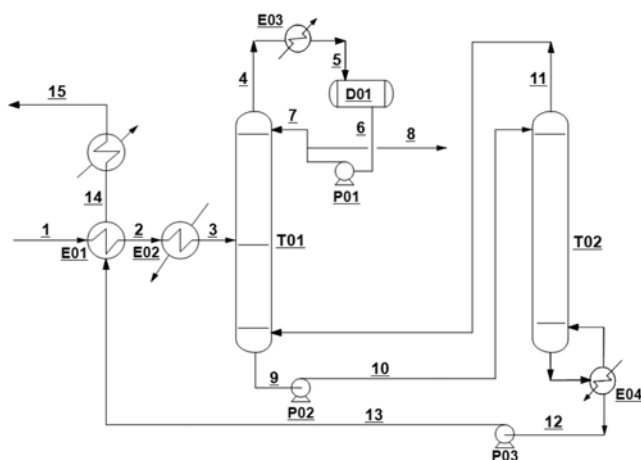


Fig. 1. Schematic diagram of the conventional distillation process using an upper and lower column configuration.

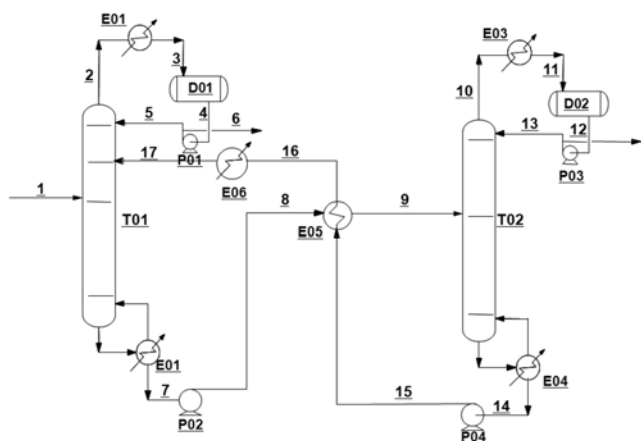


Fig. 2. A Schematic diagram for the extractive distillation process using NFM solvent.

as a solvent [5] as shown in Fig. 2. The feed stream is fed to the mid-stage of the first extractive distillation column, and the NFM solvent is fed to the top of the extractive distillation column. The solvent extracts benzene selectively as it flows down the column. The benzene-rich bottom solvent of the first column is called a 'rich solvent'. The first column is an extractive distillation column because it extracts the benzene selectively from the feed stream and also performs the role of a distillation column in that gas-liquid equilibrium is achieved within the column. In the top product stream of the extractive distillation column, the stream contains abundant EDC. The rich solvent of the bottom of the extractive distillation column exchanges heat with the bottom stream of the solvent recovery column and is fed to the solvent recovery column. Benzene is obtained at the top of the solvent recovery column. The lean solvent is obtained at the bottom of the solvent recovery column and refluxed to the extractive distillation column.

In this study, the minimum theoretical stage and minimum reflux ratio were determined by shortcut method to recover the EDC and remove the benzene by simple distillation column. The optimum theoretical stages which minimized the sum of capital cost and operating cost were determined by case study. The real stages were de-

cided from the efficiency of the distillation column as a function of the feedstock average viscosity of the feed liquid stream. The heat duty of the reboiler was minimized by the heat recovery through heat exchange between the feed stream and the bottom product and by optimization of the feed stage. The operation cost for the extractive distillation column was reduced by optimization of the solvent-to-feed steam ratio. The non random two liquid mixture (NRTL) liquid activity coefficient modeling equation was used to estimate the binary vapor-liquid phase equilibrium behavior between benzene and EDC and between benzene and NFM [6]. The NRTL model was also used to estimate the liquid-liquid phase equilibrium behavior between EDC and NFM. In this case, the distillation process and extractive distillation process were modeled rigorously.

THEORY

The thermodynamic modeling equation in this comparative study was the NRTL liquid activity coefficient model to simulate the distillation process between benzene, the light key component, and EDC, the heavy key component. The model was also used to simulate the extractive distillation column and solvent recovery column in which the NFM solvent removes benzene selectively. In this thermodynamic model suggested by Renon and Prausnitz, the liquid activity coefficient of the i^{th} component in the mixture can be represented as Eq. (2).

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right) \quad (2)$$

In Eq. (2), τ_{ij} and G_{ij} are the optimum binary interaction parameters to minimize the deviation from the experimental data and can be expressed as Eqs. (3) and (4).

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (3)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (4)$$

In Eq. (3), T is the absolute temperature and there are five interaction parameters a_{ij} , a_{ji} , b_{ij} , b_{ji} and α_{ij} for each binary component including a temperature-dependent term. The optimum NRTL binary interaction parameters are determined by pattern search method suggested by Nelder and Mead [7] to estimate the binary gas-liquid phase equilibrium between benzene and EDC as shown Table 2. The objective function for optimization is determined with the bubble point pressure and composition as shown in Eq. (5).

$$\text{Objective} = \sum_{j=1}^N \left(\frac{T_j^{\text{exp}} - T_j^{\text{cal}}}{T_j^{\text{cal}}} \right)^2 + \sum_{j=1}^N \left(\frac{x_j^{\text{exp}} - x_j^{\text{cal}}}{x_j^{\text{cal}}} \right)^2 \quad (5)$$

Table 2. NRTL binary parameters for the benzene/1,2-dichloroethane and benzene/NFM binary systems

Component i	Component j	a_{ij} and a_{ji}	b_{ij} and b_{ji}	α_{ij}
Benzene	EDC	0.0000	29.6038	0.3035
		0.0000	-19.9036	
Benzene	NFM	0.0000	327.9300	0.8000
		0.0000	-196.8231	

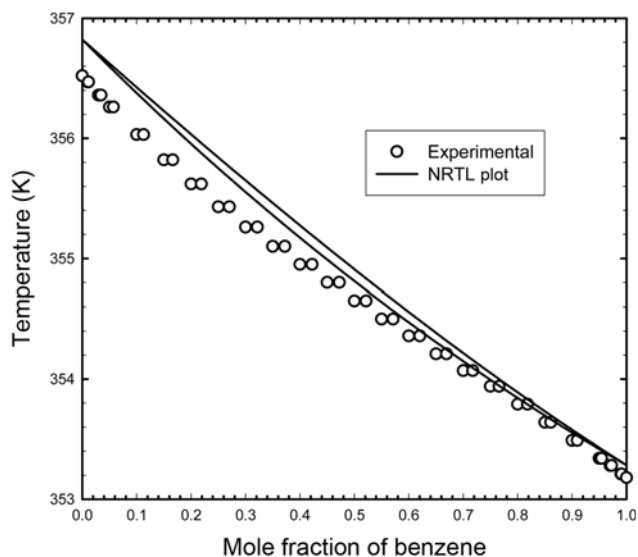


Fig. 3. Experimental isobaric vapor-liquid equilibria data for benzene and 1,2-dichloroethane at 101.325 kPa and its prediction with NRTL liquid activity coefficient model.

In Fig. 3, experimental data is compared with estimated results by NRTL liquid activity coefficient modeling equation for binary isothermal gas-liquid phase equilibrium between benzene and EDC. In Fig. 4, the temperature-composition diagram for the binary system of benzene and NFM at 101.325 kPa is depicted with the built-in NRTL parameter in Aspen Plus [8] and PRO/II with PROVISION.

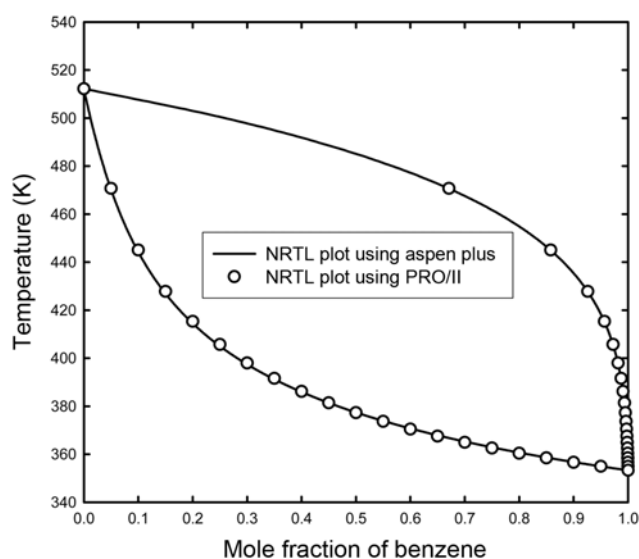


Fig. 4. Isobaric vapor-liquid equilibria prediction for benzene and NFM at 101.325 kPa using the NRTL model built-in aspen plus database and its prediction with the NRTL model built-in PRO/II database.

PROCESS SIMULATION

1. Simulation for the Simple Distillation Process

A comparative simulation was performed for the simple distillation process, which has upper and lower columns, and for the ex-

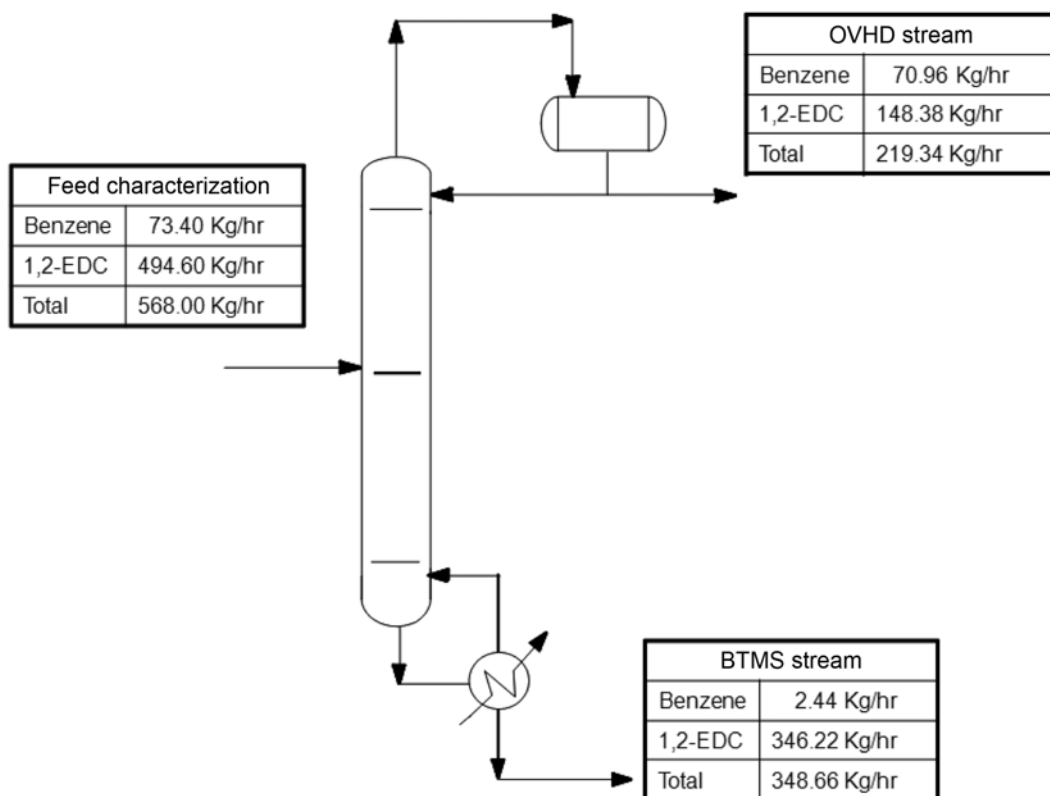


Fig. 5. Schematic diagram for binary shortcut modeling.

tractive distillation process by using NFM as a solvent. The minimum theoretical stages and minimum reflux ratio for the simple distillation column was determined by shortcut modeling and its optimum theoretical stages were determined by a case study for shortcut modeling. The efficiency of the stage was determined as a function of the average viscosity. The temperature and feed stage was determined to minimize the heat duty of the reboiler by optimization.

1-1. Shortcut Modeling

A simple binary shortcut model was used to determine the minimum theoretical stages and the minimum reflux ratio since the actual separation occurs between a light key component (benzene) and a heavy key component (EDC). Fig. 5 shows a schematic diagram of the shortcut modeling that determines the minimum theoretical stage and minimum reflux ratio in the distillation of the benzene and EDC binary system. The EDC recovery ratio at the bottom of the distillation column was fixed to 70% and the benzene content was set to 0.7 wt%. According to a shortcut modeling, the minimum theoretical stage for separation was 34.44 stages and the minimum reflux ratio was 11.72. Table 3 shows a material balance for the shortcut modeling between the binary benzene and EDC system. Since the EDC component mass flow rate in the bottom product was 346.22 kg/hr, the recovery ratio with respect to the feed was 70%, and benzene content of the bottom product was 0.7 wt%. Actually, the distillation column is operated above the minimum reflux ratio and minimum theoretical stages. Table 4 shows the relation between the theoretical stages and heat duty of the condenser and reboiler with the changes in the reflux ratio. The theoretical stages for separation at infinite reflux were 34.44 stages, which is the minimum number of stages. The heat duty of the condenser and reboiler

Table 3. Binary shortcut modeling result summary

Component (kg/hr)	Feed	Top	Bottom
Benzene	73.40	70.96	2.44
EDC	494.60	148.38	346.22
Total	568.00	219.34	348.66

Table 4. Case study results for binary shortcut modeling

N/N_{min}	Theoretical tray number	Reflux ratio	Condenser duty (10^6 kcal/hr)	Reboiler duty (10^6 kcal/hr)
1.00	34.44	∞	-	-
1.01	34.78	659.910	-12.0400	12.0500
1.05	36.16	136.270	-2.5010	2.5070
1.20	41.33	38.088	-0.7123	0.7177
1.30	44.77	27.586	-0.5209	0.5264
1.40	48.22	22.565	-0.4294	0.4349
1.60	55.10	17.316	-0.3338	0.3992
1.70	58.55	15.841	-0.3069	0.3123
1.80	61.99	15.072	-0.2929	0.2983
1.90	65.44	14.440	-0.2813	0.2868
2.50	86.10	12.329	-0.2429	0.2484
3.00	103.32	12.040	-0.2376	0.2431
4.00	137.76	11.926	-0.2355	0.2410
∞	∞	11.722	-	-

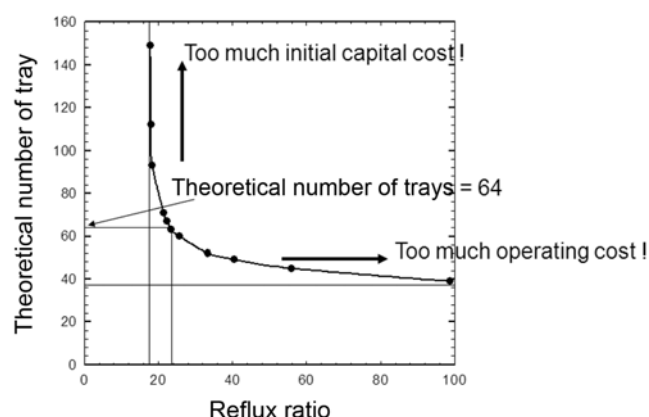


Fig. 6. Relationship between the reflux ratio and theoretical number of trays.

increased linearly with increasing reflux ratio. In addition, the theoretical stages for separation were infinite at the minimum reflux ratio of 11.722. In Fig. 6, the theoretical stages relative to the minimum reflux ratio are depicted. It includes the minimum theoretical stages and the minimum reflux ratio. The reflux ratio is inversely proportional to the theoretical stages. The operating cost increases with increasing reflux ratio, even though the initial equipment cost decreases due to a decrease in the necessary theoretical stages. On the other hand, when the reflux ratio decreases, it is the opposite. Therefore, the optimum reflux ratio to minimize the total investment cost, which includes the initial equipment and annual operating cost, is approximately 64 stages. This corresponds to the maximum curvature at the curve of the theoretical stage with respect to the reflux ratio. Therefore, the theoretical stages for separation were set to 66 stages, including the 64 stages, top condenser and bottom reboiler.

1-2. Rigorous Modeling

Rigorous modeling was performed with the result of shortcut modeling. The optimum position of the feed stage to minimize the heat duty of the reboiler was determined by a case study. In Fig. 7,

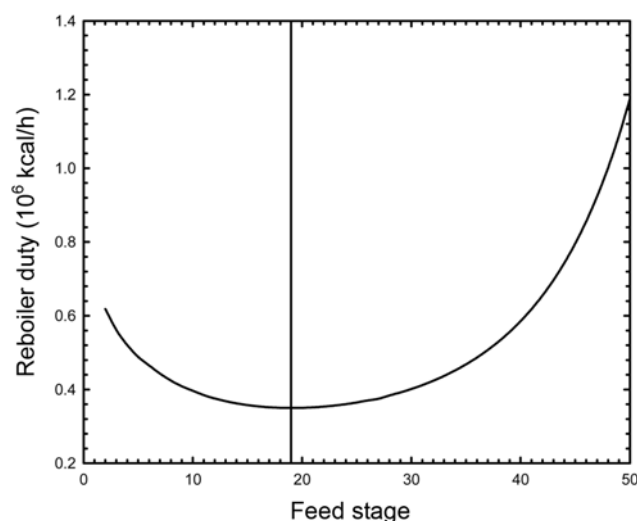


Fig. 7. Determination of the optimal location of the feed stage, which minimizes the heat duty of the reboiler for the conventional distillation process.

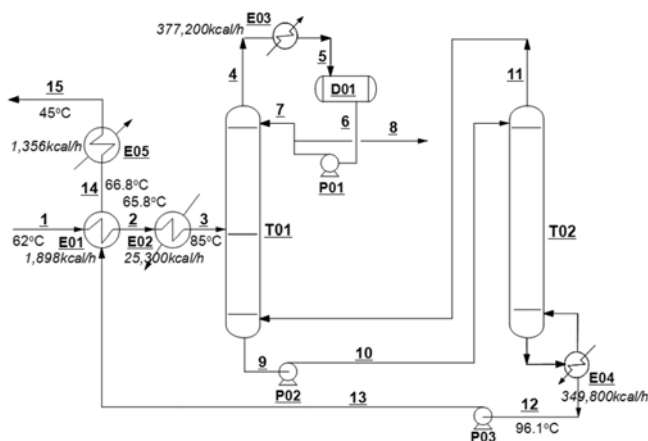


Fig. 8. Results summary of the process simulation for the conventional distillation process scheme.

the change in the heat duty of the reboiler with respect to the change in the feed stage is depicted. The optimum feed stage was 19 stages and the heat duty of the reboiler was 0.3498×10^6 kcal/hr. The simulation result is shown in Fig. 8 for the simple distillation process in Fig. 1. The feed mixture at 62 °C exchanges heat with the bottom stream of distillation via a heat exchanger, E01, and heats it up to 65.8 °C. Since the heat exchanger, E01, exchanges heat between the process streams and does not consume hot utility and cold utility, this recovers 1,898 kcal/hr corresponding to the heat duty of the heat exchanger E01. Moreover, heat exchanger E02 preheats the feed stream by steam before going into the distillation column. The downstream temperature of the heat exchanger, E02, was determined in order to minimize the heat duty of the reboiler through the optimization of the feed stage. The heat duty of the heat exchanger, E02, was 25,300 kcal/hr. The downstream temperature of heat exchanger, E02, was 85 °C. Through the optimization of the temperature of the feed stream and the position of the feed stage, the minimum heat duty of the reboiler was 0.3948 kcal/hr. In Fig. 9, the efficiency of the distillation column is depicted as a function of the relative volatility between the key components and the viscosity of the feed-

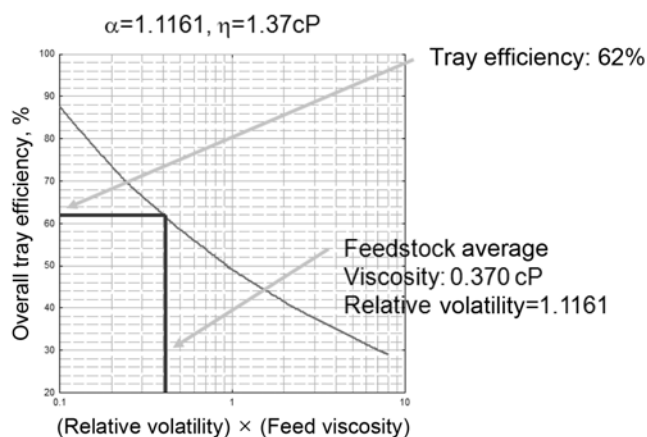


Fig. 9. Overall tray efficiency of the conventional distillation tower as a function of the feedstock liquid viscosity and relative volatility.

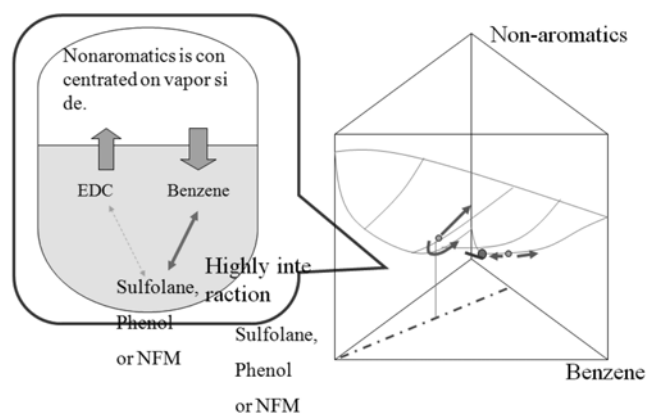


Fig. 10. The principle of extractive distillation.

stock at the mean temperature between the top and bottom of the column. The relative volatility between benzene and EDC is 1.1161 and the mean viscosity of the feedstock is 1.37 cP. The mean efficiency of the distillation column by the relationship in Fig. 9 is 62%. When the theoretical stages, 64 are divided by the stage efficiency, 0.62, the real stages are 103 stages.

2. Simulation of Extractive Distillation Process

The principle of extractive distillation is that the solvent with a relatively high boiling point, such as phenol, sulfolane or NFM, is used to separate components having a similar boiling point. A rich solvent of highly benzene dissolved is obtained at the bottom of the extractive distillation column and highly concentrated EDC is obtained at the top of the column, as shown in Fig. 10.

Phenol is an unsuitable solvent for the removal of benzene from an EDC mixture because its maximum permissible concentration in air is less than 10 ppm. Since the boiling point of NFM is lower than sulfolane, low temperature steam can be used for NFM. The NFM solvent can reduce steam consumption due to the relatively higher latent heat of low temperature steam than high temperature steam. The theoretical stages of the extractive distillation column were assumed to be 25 stages; the feed stage was the 14th stage. The feed stage of the lean solvent was the 4th stage. The recovery rate of EDC at the top of the extractive distillation column was above 70% with respect to the feedstock and the benzene content of the top recovery stream was below 0.7 wt%. The initial flow rate of the solvent was assumed to be 4,000 kg/hr, which corresponds to 7.04 of the solvent flow rate to the feed flow rate. To minimize utility consumption within the limits of maintaining the recovery rate of EDC and benzene content, the heat duty change of condenser and reboiler with respect to the solvent to feed ratio is shown in Fig. 11. According to Fig. 11, the solvent-to-feed ratio can be reduced from 7.04 to 2.04. When the solvent-to-feed ratio is 7.04, the heat duty of condenser is 0.6153 kcal/hr and the heat duty of the reboiler is 0.9484×10^6 kcal/hr. Therefore, the sum of the heat duty of the condenser and reboiler was 1.5637×10^6 kcal/hr. On the other hand, when the solvent-to-feed ratio was 2.4, the heat duty of the condenser was 0.1551×10^6 kcal/hr and the heat duty of the reboiler was 0.2413×10^6 kcal/hr. Hence, the sum is 0.3964×10^6 kcal/hr. If the solvent-to-feed ratio is reduced more, the distillation column does not converge and the minimum value is 2.4.

The theoretical stages of the solvent recovery column were as-

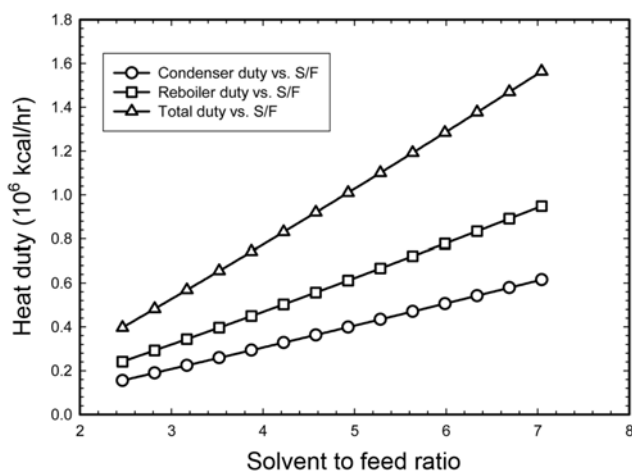


Fig. 11. Total heat duty versus the solvent-to-feed ratio for the case study of the condenser and reboiler.

sumed to be 20 stages. Feedstock was fed to the column at stage 10. The reflux ratio was set to 3.5 and the benzene content in the bottom products was set to the below 500 ppm.

RESULTS AND DISCUSSION

In Table 5, the simulation result of the conventional distillation process was compared with the extractive distillation process using NFM as a solvent. For convenience, the conventional distillation process is defined as scheme 1 and the extractive distillation process using NFM as scheme 2, respectively. According to Table 5, the number of distillation columns is two and both are the same. However, scheme 2 has one more heat exchanger than scheme 1. Moreover, the heat transfer area of scheme 2 will be bigger than that of scheme 1 because scheme 2 consumes more steam and cooling water than scheme 1. The diameter of the distillation column in scheme 2 is bigger than that of scheme 1. Scheme 2 is a little better than scheme 1 since scheme 2 has 30 stages for the stripper and 51 for the lower column, but scheme 1 has 52 stages for the upper column and 51 stages for the lower column. In scheme 1, the total heat duty of the reboiler is 349,800 kcal/hr for the lower column of scheme

1. On the other hand, the heat duty of scheme 2 is 963,500 kcal/hr, which is the sum of 857,300 kcal/hr for the reboiler and 106,200 kcal/hr for stripper. This means that the heat duty of scheme 2 is 2.75 times larger than that of scheme 1. Furthermore, the low pressure steam of 103 °C can be used because the temperature of the bottom product of the lower column in scheme 1 is 96.1 °C. Normally, the steam consumption of low pressure steam is lower than the high pressure steam because the latent heat of low pressure steam is higher than that of medium or high pressure steam. However, steam cannot be used in scheme 2 because the bottom temperature of the extractive distillation column is 210 °C and the bottom temperature of the stripper is 253.6 °C. This case requires the use of hot oil. If steam is to be used, the distillation column needs to be operated at reduced pressure. When the distillation column is operated at reduced pressure, extra vacuum system is necessary and the diameter of the distillation column will increase. In the case of the extractive distillation process, expensive solvents need to be purchased additionally. In conclusion, the process arrangement of the conventional distillation process (scheme 1) is superior to the extractive distillation process (scheme 2) in view of the initial investment and operation cost.

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NOMENCLATURE

T : absolute temperature [K]
 N : number of components
 γ_i : activity coefficient of component i
 x_j, x_k : liquid mole fraction of component j and k
 $a_{ij}, a_{ji}, b_{ij}, b_{ji}$ and α_{ij} : binary interaction parameter in NRTL model

Subscripts

i, j, k : component i, j and k

Superscripts

exp : experimental value

Table 5. A comparison of the conventional distillation process (scheme 1) and extractive distillation process (scheme 1) using NFM solvent

	Scheme 1	Scheme 2
Number of columns	2 (upper and lower column)	2 (extractive distillation column and stripper)
Number of heat exchangers	5	6
Number of actual stages	Upper column: 52 Lower column: 51	EDC: 52 Stripper: 30
Column diameter (valve tray, flooding: 85%)	Upper column: 761 mm Lower column: 761 mm	EDC: 1,200 mm Stripper: 900 mm
Steam consumptions	643 kg/hr (130 °C LP steam)	Hot oil required
Total reboiler duties	Lower column: 349,800 kcal/hr	EDC: 857,300 kcal/hr Stripper: 106,200 kcal/hr
Column bottom temperature	Lower column: 96.1 °C	EDC: 210.2 °C Stripper: 253.6 °C
Cooling water consumption	39 Ton/hr	968 Ton/hr

cal : calculated value

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