Korean J. Chem. Eng., 17(6), 712-718 (2000)

Optimization of the Sulfolane Extraction Plant Based on Modeling and Simulation

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(*Received 14 August 2000 • accepted 24 October 2000*)

Abstract–An optimization system, based on modeling and simulation, was developed for a sulfolane extraction plant. The primary objective of the operation of this plant is to increase benzene composition, which is mostly affected by the recycle streams in the plant. In this work the optimal recycle streams were identified and resulting product compositions were evaluated. In the optimization, suitable parametric models for each process unit were obtained first from the steady-state rigorous modeling and simulation of the sulfolane extraction plant. The parametric models were then employed to develop the optimization system based on the SQP scheme. Results of simulations show promise for further economic improvements over present operation states.

Key words: Sulfolane, Extraction Plant, Simulation, SQP, Optimization

INTRODUCTION

A BTX (Benzene-Toluene-Xylene) plant consists of four unit plants including a sulfolane extraction plant. In this plant, aromatics including BTX and non-aromatics are extracted from hydrogenated crude oils by using sulfolane as the solvent. The sulfolane has an outstanding selectivity to aromatics, a high solubility to water and a high boiling point [Balies et al., 1976]. The sulfolane extraction plant consists of an extraction unit, distillation units and other related units such as strippers and settlers. The extraction plant includes critical unit operations such as extraction, distillation and absorption [Cho et al., 1999]. Fig. 1 shows a schematic diagram of the sulfolane extraction plant.

As can be seen, the plant consists of six major process units. In the extraction column (extractor), desulfurized hydrocarbons from crude oil including naphtha, aromatics, heavy polymers and tars are fed into the middle of the column and are extracted by the mixture of solvent and sulfolane. The extract contains heavy components such as aromatics, polymers and tars, and the raffinate contains light hydrocarbons less than C5. The column is generally operated at 120 °C, but the modified process is operated at 60 °C, resulting in lower energy consumption. In the wash column the solvent and hydrocarbons are separated from the raffinates. The column is operated at 40 °C and non-aromatics (below C5) are obtained as the overhead product.

Very small amounts of light hydrocarbons and water are contained in the bottom product of the extractor. To remove these components, extractive distillation under vacuum is performed in the extract-distillation column. From the column, light non-aromatics and the solvent are obtained as overhead product and heavy components are produced as the bottom product. The column is operated in the temperature range of 40-200 °C. Use of the additive water stripper instead of the distillation under vacuum is quite popular in most of the modified processes.

The bottom products of the wash column and the extract-distillation column are fed into the solvent recovery column which is operated in the range of 40-200 °C. Water and aromatics are obtained as the overhead product, which in turn is separated by density difference, and the resulting water is recycled to the wash column and aromatics are obtained as the products. The solvent and heavy components such as tars are obtained as the bottom product of the column and the solvent is recycled to the extractor. It is not uncommon to add a solvent regenerator or vacuum distillation equipment operated under high temperature to remove tars and impurities.

The optimization of the extraction plant is by far the most important to improve economics of the BTX plant. In this work, optimal recycle streams in the sulfolane extraction plant were identified based on modeling and simulation of the actual plant. Optimization of the fractionation process in the BTX plant has been reported [Chung et al., 1997], but the sulfolane extraction process is one of the few processes that can hardly be modeled by commercial packages such as ASPEN Plus or HYSYS. As far as the authors know, no published results on the modeling and simulation of the sulfolane extraction process have been found for the last two decades. In the present study a rigorous model of the sulfolane extraction process was established and used in the optimization in conjunction with HYSYS. Many useful optimization techniques for chemical processes have been investigated. Among them, the global optimization technique based on the interval analysis might be effectively used for our purpose [Han et al., 1997]. For the estimation of the sulfolane extraction plant, the nonlinear static composition estimator may be used in the present study [Shin et al., 1998]. From the results of simulations based on rigorous process models, parametric models for each plant unit were developed, which in turn were employed in the SQP method to identify recycle streams of the extraction plant.

MODELING OF THE EXTRACTION PLANT

Fig. 2 shows the flow diagram of the sulfolane extraction plant

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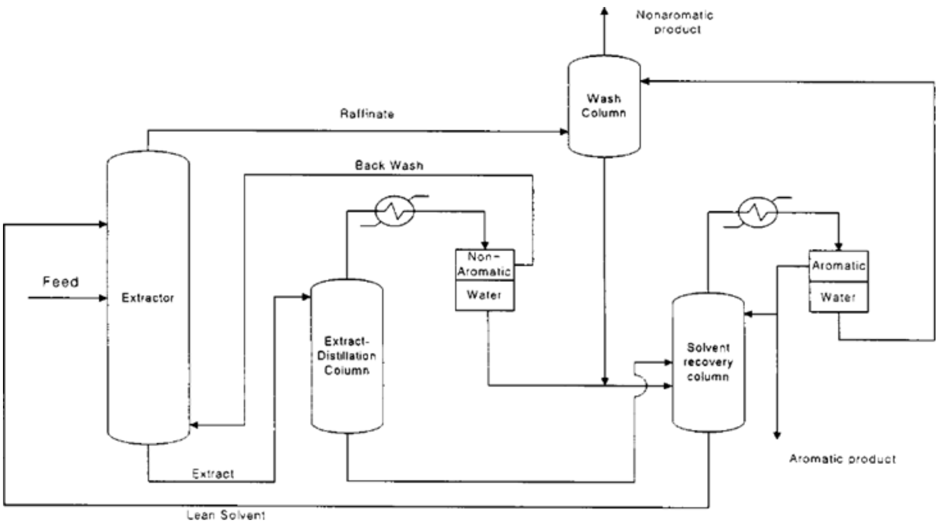

Fig. 1. Schematic of sulfolane extraction plant.

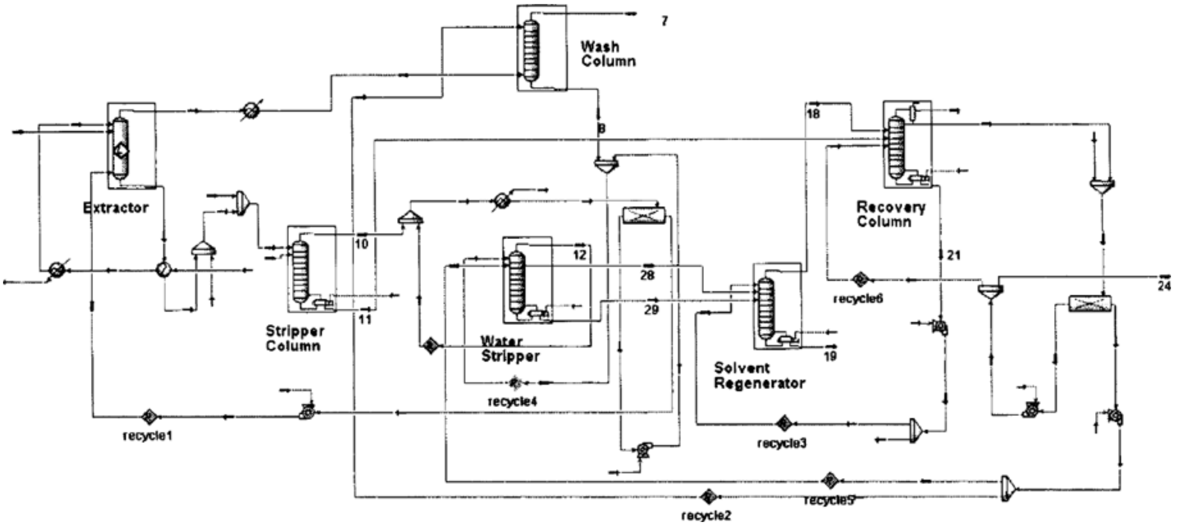

Fig. 2. Flow diagram of the extraction plant.

Table 1. Operating conditions

Unit	Number of stage	Temperature (°C)	Pressure (atm)	Feed (ton/hr)		
				Feed 1	Feed 2	Feed 3
Extractor	105	73.3-58.9	6.3-9.14	28.7(47)	14.5(105)	
Wash column	40	30.6-34.2	3.0-4.5	9.8(40)		
Stripper column	44	101.4-170.8	2.08-2.54	18.9(1)		
Solvent recovery column	27	76.0-170.7	0.4-0.6	0.066(C)	174.0(9)	6.5(27)
Water stripper	Absorb	117.0-117.3	2.84	2.3(T)	2.0(R)	
Solvent regenerator	4	168.5-172.1	1.81	2.2(1)	1.4(4)	1.7(R)

( ); stage number, (c); condenser, (T); top, (R); reboiler.

considered in the present study, and Table 1 shows typical operating conditions of the extraction plant. HYSYS was used to model the extraction process, except the extractor. Because of the high nonlinearity of the complicated operating constraints and of the unknown physical properties of the key components, the extractor could not be modeled by commercial simulation packages such as HYSYS and ASPEN. In the present study a rigorous model of the extractor was developed and coupled with other process units through the HYSYS system. From the actual operation data, it was found that the feed stream to the extractor consisted of 13 compo-

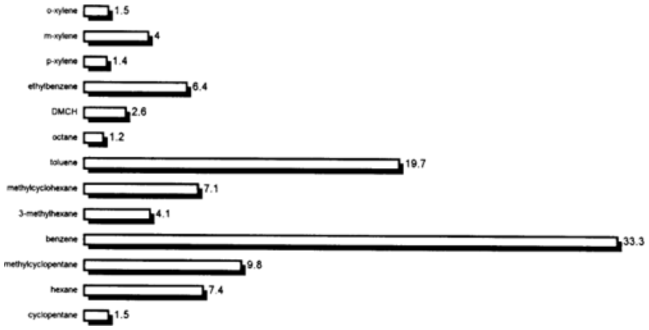

Fig. 3. Feed composition (wt%).

nents as shown in Fig. 3.

For the modeling of the extraction process, it is imperative to choose an appropriate thermodynamic model. Although equations of state models have been proven to be very reliable in the prediction of properties of most hydrocarbon fluids over a large range of operation conditions, their applications have been limited to primarily non-polar or slightly polar components. Because of the high polarity of sulfolane and water contained in virtually all the streams of the extraction plant, we can see that equations of state are not suitable for the modeling of the extraction unit. In the computation of the extraction column, we tried various equations of state and found that the UNIFAC model gives the best results. In the modeling of process units except the extraction column, the equation of state embedded in HYSYS can be effectively used. In the present study, an activity model was employed in the modeling. Characteristics of various activity models are summarized in Table 2 [HYSYS Reference Manual, 1997]. From Table 2, we can see that NRTL and UNIQUAC are possible candidates. We picked UNIQUAC for the computations of related thermodynamic properties in relation to UNIFAC used in the extraction column. The UNIQUAC equation can be summarized as [Bruce et al., 1988]

$$\ln\gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 0.5Zq_i\ln\left(\frac{\theta_i}{\Phi_i}\right) + L_i - \left(\frac{\theta_i}{\Phi_i}\right)\sum_{j=1}^{n}L_j x_j + q_i\left(1.0 - \ln\sum_{j=1}^{n}\theta_j\tau_{ji}\right) - q_i\sum_{j=1}^{n}\left(\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{n}\theta_k\tau_{kj}}\right)$$

where

$$L_j = 0.5Z(r_j - q_j) - r_j + 1$$

Table 2. Comparisons of activity models

Application	Margules	van Laar	Wilson	NRTL	UNIQUAC
Binary systems	A	A	A	A	A
Multicomponent systems	LA	LA	A	A	A
Azeotropic systems	A	A	A	A	A
Liquid-liquid equilibria	A	A	N/A	A	A
Dilute systems	?	?	A	A	A
Self-associating systems	?	?	A	A	A
Polymers	N/A	N/A	N/A	N/A	A
Extrapolation	?	?	G	G	G

(A=Applicable; N/A=Not Applicable; ?=Questionable; G=Good; LA=Limited Application)

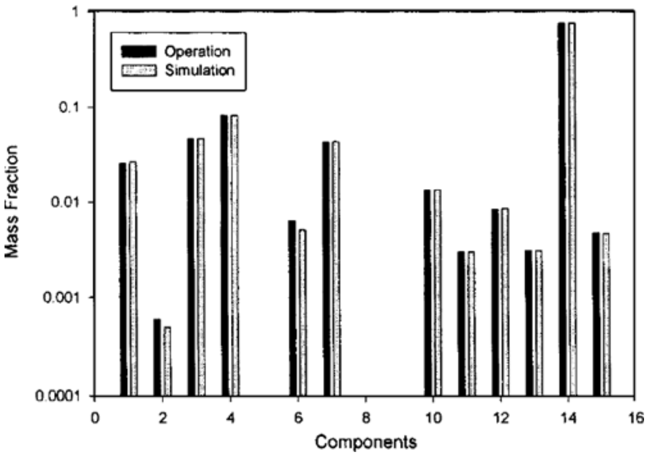

Fig. 4. Results of simulations and operation data of the extractor.

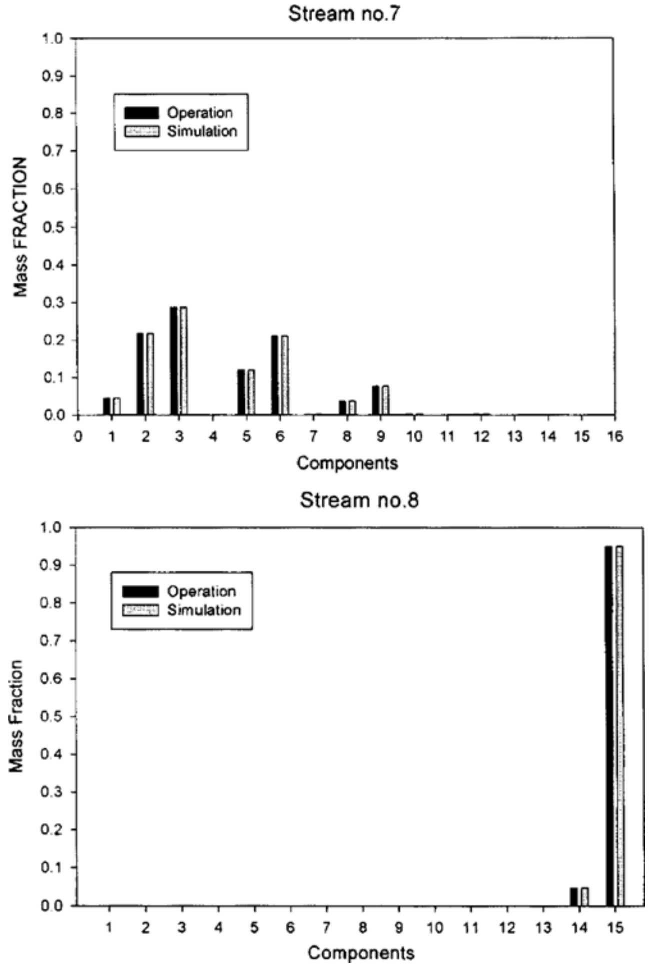

Fig. 5. Results of simulations for the wash column.

$$\theta_i = \frac{q_i x_i}{\sum q_j x_j}$$

$$\tau_{ij} = \exp -\left[\frac{a_{ij} + b_{ij} T}{RT}\right]$$

As stated before, the model of the extractor was developed in the present study and all the other units extraction plant were modeled by using HYSYS. The extractor model was linked to the HYSYS by a suitable method.

Results of simulations for the extractor are shown in Fig. 4. In the figures, numbers in the components axis denote the following: 1=Cyclopentane, 2=Hexane, 3=Methylcyclopentane, 4=Benzene, 5=3-Methylhexane, 6=methylcyclohexane, 7=toluene, 8=N-octane, 9=DMCH, 10=Ethylbenzene, 11=p-Xylene, 12=m-Xylene, 13=o-xylene, 14=sulfolane, 15=Water.

Results of simulations of all the other units of the extraction plant except the extractor are summarized in Fig. 5~Fig. 8. As can be seen, results of simulations show good agreement with actual operation data. Results for stream 24 in Fig. 8 are the final product stream in the sulfolane extraction plant. Stream 24 is fed to the fractionation plants to give high purity benzene.

OPTIMIZATION OF THE EXTRACTION PLANT

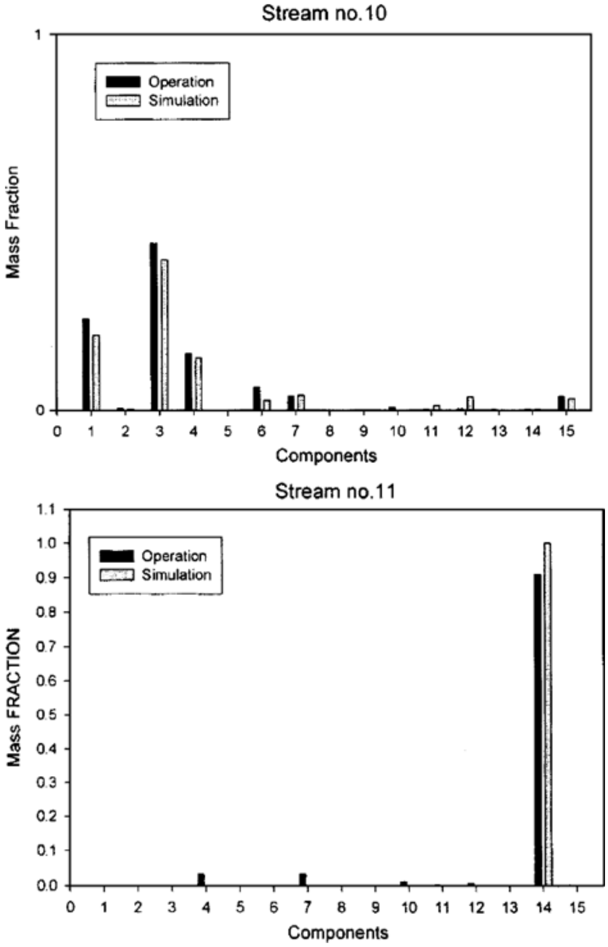

Fig. 6. Results of simulations for the stripper.

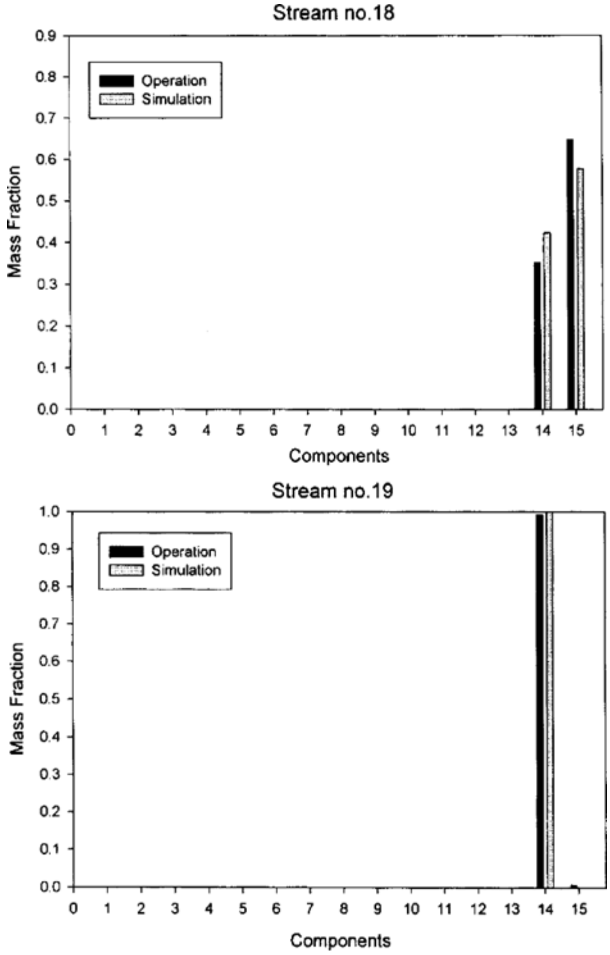

Fig. 7. Results of simulation for the solvent regenerator.

The purity of the benzene in final product streams is severely influenced by the recycle streams within the plant. Therefore, the primary task in the operation is to maintain the optimal levels of flow rates of recycle streams. For this reason, the major effort in the optimization should be given to identifying the optimal recycle flow rates in the plant.

In the present study, the effects of recycle flow rates on the benzene fraction in the product stream were represented in the parametric model forms. The general form of the parametric model can be written as

$$f_j(s_j) = \sum_{i=0}^{n} b_j[i] s_j^i$$

where $f_j(s_j)$ is the mass fraction of benzene of the recycle stream j and $b_j[i]$ is coefficients of the model. Values of $b_j[i]$ for each recycle stream j (see Fig. 2) are given in Table 3. Fig. 9 shows outputs from rigorous computations and from parametric models. In Fig. 9, dots ('●') represent data from rigorous plant models and solid lines represent parametric models identified. The parametric models are employed in the SQP optimization method [Edgar et al., 1988] to give optimal recycle rates. The objective function to be maximized mainly consists of the values of benzene, toluene and xylene as given by

$$J(x) = (14.76)(c_1 x_1 + c_2 x_2 + c_3 x_3) - (p_1 s_1 + p_2 s_2 + p_3 s_3 + p_5 s_5 + p_6 s_6)10^{-3}$$

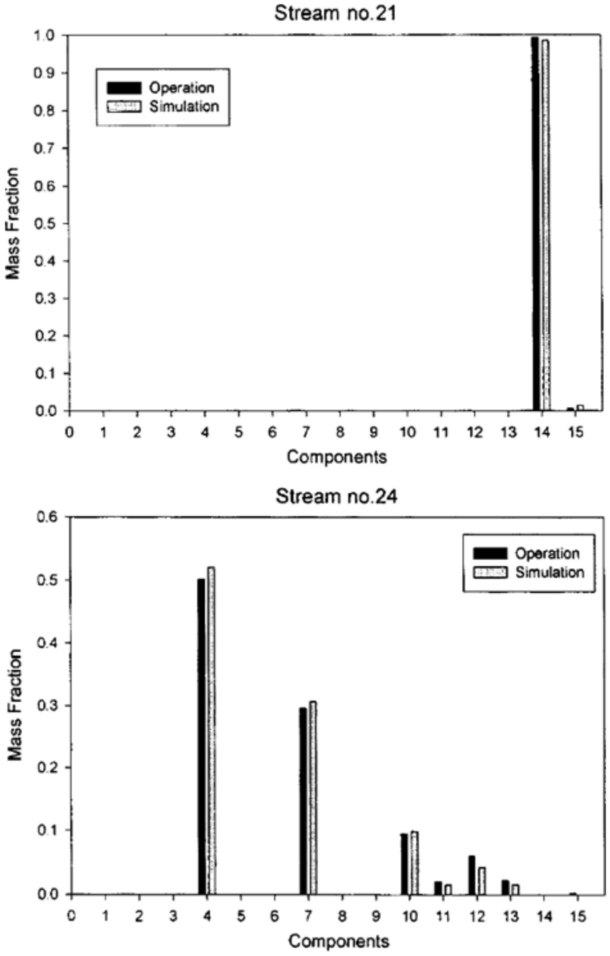

Fig. 8. Results of simulations for the solvent recovery column.

Constraints can be summarized as

$$s_1 \geq 0,\ s_2 \geq 0,\ s_3 \geq 0,\ s_4 \geq 0,\ s_5 \geq 0,\ s_6 \geq 0$$

$$0.5 \leq f_1(s_1) \leq 1.0,\ 0.5 \leq f_2(s_2) \leq 1.0,\ 0.5 \leq f_3(s_3) \leq 1.0$$

$$0.5 \leq f_4(s_4) \leq 1.0,\ 0.5 \leq f_5(s_5) \leq 1.0,\ 0.5 \leq f_6(s_6) \leq 1.0$$

where s_j represents the mass flow rate of recycle stream j.

Results of optimization computations are summarized in Tables 4 and 5 where the optimal results are compared with operating conditions. The optimal recycle rates are given in Table 4, and Table 5 shows optimal component fractions. From Table 4 we can see that almost 10% increase of the purity of the benzene is achieved by the optimization.

CONCLUSIONS

In the modeling of the sulfolane extraction plant, it is well known that commercial process software packages do not give an adequate model for the sulfolane extraction unit. In the present study a steady-state model for the sulfolane extraction column was developed and coupled with other models of extraction plant units obtained by using HYSYS.

The purity of the products from the sulfolane extraction plant is highly dependent upon the rates of recycle streams, which can be manipulated during the operation. To identify the optimum values of rates of recycle streams, parametric models relating recycle stream with the product quality were obtained first based on rigorous steady-state models mentioned earlier. Optimum recycle rates were found by using SQP algorithm. Extension to the dynamic modeling and optimization is yet to be investigated.

ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundation (No. 98-0502-06-01-3) and in part by Hanyang University, made in the program year of 2000.

NOMENCLATURE

A_ω : van der Waals area
a_{ij} : temperature independent energy parameter between components i and j [cal/gmol]
b_{ij} : temperature dependent energy parameter between components i and j [cal/(gmol-K)]
c_i : cost of material i [\$/ton]
L_j : $0.5Z(\gamma_j - q_j) - \gamma_j + 1$
n : total number of components
p_i : pumping cost for each stream [\$/ton]

Table 3. Coefficients of parametric models

Recycle stream	n	B[i] (i=0, 1, ..., n)
Recycle 1	10	b[0]=0.4687, b[1]=4.8043e−6, b[2]=−1.7275e−10, b[3]=3.2146e−15, b[4]=−3.5042e−20, b[5]=2.3836e−25, b[6]=−1.0406e−30, b[7]=2.9145e−36 ,b[8]=−5.0610e−42, b[9]=4.9582e−48, b[10]=−2.0941e−54
Recycle 2	10	b[0]=0.4398, b[1]=6.9078e−5, b[2]=−2.0409e−8, b[3]=2.6759e−12, b[4]=−1.5549e−16, b[5]=1.0691e−21, b[6]=3.6284e−2, b[7]=−2.1183e−29, b[8]=5.4800e−34, b[9]=−7.0043e−39, b[10]=3.5915e−44
Recycle 3	7	b[0]=0.4852, b[1]=2.0146e−5, b[2]=−4.5018e−9, b[3]=5.1123e−13, b[4]=−3.2269e−17, b[5]=1.1459e−21, b[6]=−2.1418e−26, b[7]=1.6387e−31
Recycle 4	7	b[0]=0.4956, b[1]=7.4640e−6, b[2]=−7.7213e−10, b[3]=3.5426e−14, b[4]=−8.5556e−19, b[5]=1.1340e−23, b[6]=−7.8100e−29, b[7]=2.1854e−34
Recycle 5	1	b[0]=0.5090, b[1]=2.0053e−6
Recycle 6	10	b[0]=1.1493, b[1]=−5.3256e−5, b[2]=1.7662e−9, b[3]=−3.0459e−14, b[4]=3.1266e−19, b[5]=−2.0364e−24, b[6]=8.6357e−30, b[7]=−2.3769e−35, b[8]=4.0937e−41, b[9]=−4.0077e−47, b[10]=1.7018e−53

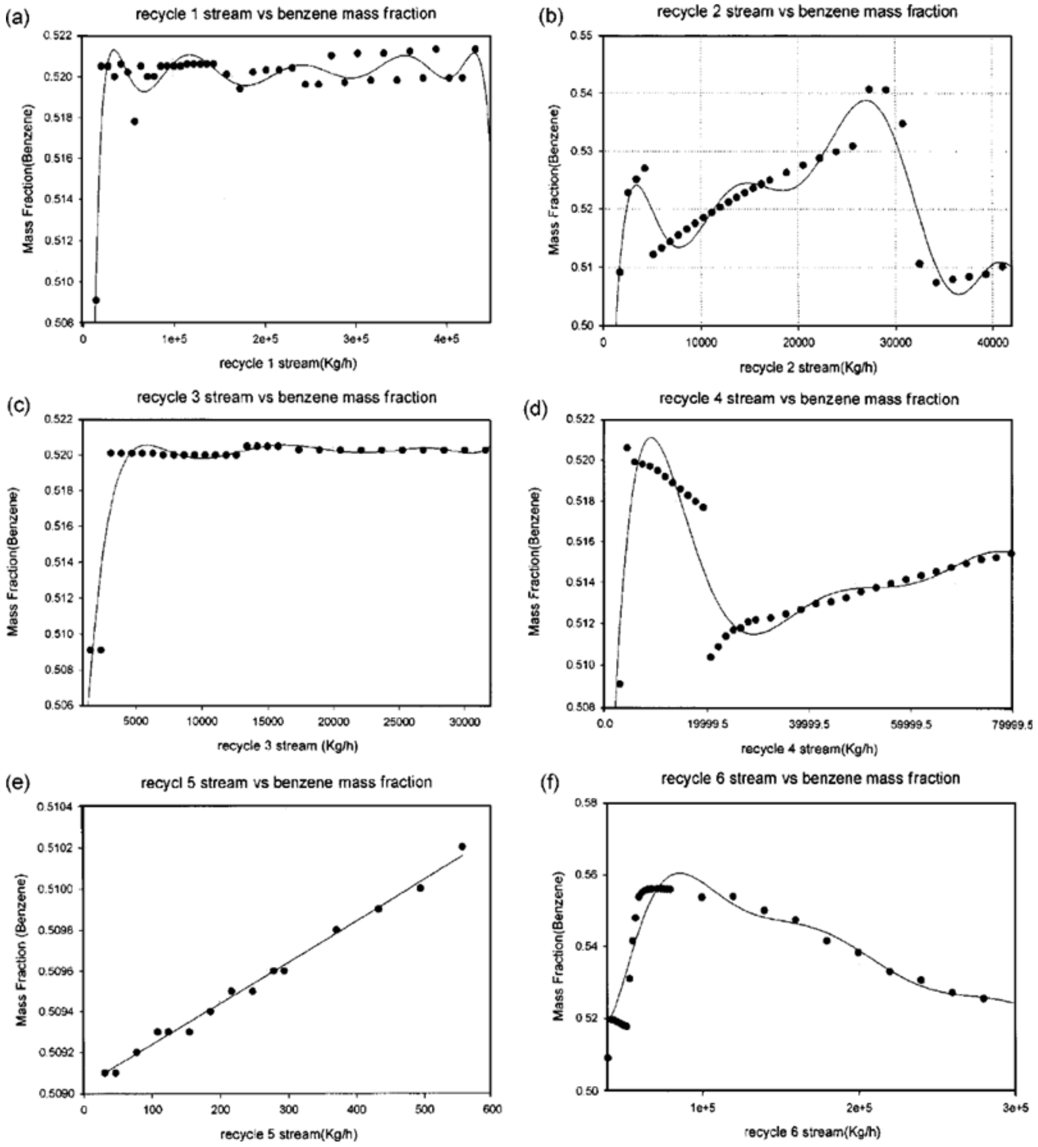

Fig. 9. Effects of recycle rates on the benzene composition in the final product.

Table 4. Results of optimizations-recycle rates

Stream \ Case	Operation	Optimization
Recycle 1 (kg/h)	4.750e+04	3.376e+04
Recycle 2 (kg/h)	1709	1709
Recycle 3 (kg/h)	1580	1576
Recycle 4 (kg/h)	2954	2728
Recycle 5 (kg/h)	30.85	44.73
Recycle 6 (kg/h)	3.997e+04	5.796e+04

q_i : van der Waals area parameter - $A\omega_i/(2.5e9)$
r_i : van der Waals volume parameter - $V\omega_i/(15.17)$
s_i : flow rate of recycle stream i [kg/hr]
T : temperature [K]
V_ω : van der Waals volume
x_i : mole fraction of component i
Z : the coordination number in the UNIQUAC equation (=10)

Table 5. Results of optimizations-Component fractions

	Operation	Optimization
Cyclopentane	0.0000	0.0000
n-Hexane	0.0000	0.0000
Methyl-cyclo-pentane	0.0000	0.0000
Benzene	0.5091	0.5560
3-Methylhexane	0.0000	0.0000
Methyl-cyclo-hexane	0.0000	0.0000
Toluene	0.3003	0.3304
n-Octane	0.0000	0.0000
Dimethyl cyclohexane	0.0004	0.0000
E-benzene	0.0963	0.1094
p-Xylene	0.0192	0.0008
m-Xylene	0.0545	0.0024
o-Xylene	0.0199	0.0008
Sulfolane	0.0000	0.0000
Water	0.0003	0.0002

Greek Letters

γ_i : activity coefficient of component i

θ_i : $\frac{q_i x_i}{\sum q_j x_j}$

τ_{ij} : $\exp - \left[\frac{a_{ij} + b_{ij} T}{RT}\right]$

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