

MODELING AND SIMULATION OF A SULFOLANE EXTRACTION PROCESS

Jae-Ouk Choo, Yeong-Koo Yeo[†], Myung-Kil Kim*, Ki-Sung Kim* and Kun-Soo Chang**

Dept. of Chem. Eng., Hanyang University, Seoul 133-791, Korea

*Yeochoon Plant, Daelim Industrial Co., Yeochoon, Chonnam, Korea

**Dept. of Chem. Eng., Pohang Univ. of Sci. & Tech., Pohang, Korea

(Received 29 July 1997 • accepted 5 January 1998)

Abstract – Modeling and simulation for a sulfolane extraction process were performed. The process investigated in the present work consists of two tray columns, one of which is used for extraction and the other one for washing. The modified θ -method was employed for the modeling of the process. The computation of the equilibrium state of a two-phase system is one of the key issues in the modeling and simulation of extraction processes. In the present work the UNIFAC method was used for the computation of related thermodynamic properties and equilibrium states. Results of simulations showed good agreement with actual plant operation data.

Key words: Extraction, Sulfolane, Simulation, Theta-Method, UNIFAC

INTRODUCTION

Many extraction processes have been developed to separate aromatics from hydrotreated petroleum resources. The sulfolane process, which was developed by the Shell company, is one of the most promising extraction processes used widely in the world [Mcketta, 1977]. Sulfolane (Tetra-Hydro-Thiophene 1-1 Dioxide, $(\text{CH}_3)_4\text{SO}_2$), which is used as a solvent in the process, has good selectivity to aromatics, good solubility to water and a boiling point higher than that of the involved hydrocarbons [Bailes et al., 1976].

In the modeling and simulation of sulfolane extraction processes, only few research results have been reported so far. Difficulty in the estimation of thermodynamic properties of sulfolane is one of the major stumbling blocks in the modeling and simulation of the sulfolane process. In the present work, the well-known UNIFAC method was found to be useful in estimating the thermodynamical properties of sulfolane.

In the modeling of a tray-type extractor, the conventional methods such as the ISR method [Tsuboka and Katayama, 1976], the direct iteration method [Holland, 1975] and the θ -method [Holland, 1975] can be used. The inside-out method [Trevino-Lozano and Kisala, 1984; Boston, 1979], the Global Newton based method [Brett and Ian, 1990] and Homotopy method [Kovach and Seider, 1987] can be used especially in the computations of absorption processes and three phases distillation processes. The ISR method requires long computing time and large computer memory, and sometimes does not converge. The direct iteration method and the θ -method have better convergence characteristics than the ISR method. The direct iteration method is simple compared to other methods but needs more computing time. In the present work, the modified θ -method was used in the modeling of the sulfolane process. Results of simulations were compared

with actual operation data to demonstrate the effectiveness of the model developed.

MODELING OF SULFOLANE EXTRACTION PROCESS

The sulfolane extraction process to be modeled is operated adiabatically. The equilibrium state of the process is mainly determined by concentrations of two immiscible phases. Thus we assumed isothermal operation, steady-state and no chemical reaction. With these assumptions we can set up material balances, equilibrium relations and molal flow summations.

1. Mathematical Formulation

In the extraction process considered in this study, there is no phase separation except at the top and bottom stages and no sidecuts. Considering multiple feed inlets in the process, we can represent the material balances as

$$A_{j-1,j} v_{j-1,j} - (A_{j,j} + 1)v_{j,j} + v_{j+1,j} = -F_j X_{j,j} \quad (1)$$

$$\text{where } A_{j,j} = \frac{L_j}{V_j K_{j,j}}$$

Equilibrium relations for each component are given by

$$E_{j,j} \equiv l_{j,j} - A_{j,j} v_{j,j} = 0 \quad (2)$$

Finally, molal flow summations are given by

$$(S_y)_j \equiv \sum_{i=1}^{NC} v_{j,i} - V_j = 0 \quad (3)$$

$$(S_x)_j \equiv \sum_{i=1}^{NC} l_{j,i} - L_j = 0 \quad (4)$$

The material balance relation (1) can be rearranged in tri-diagonal matrix form and the Thomas algorithm can be used to solve the equations with given initial estimates of vapor and liquid flow rates.

2. Thermodynamic Properties

An equation of state model and an activity coefficient meth-

[†]To whom all correspondence should be addressed.

E-mail: ykyeo@email.hanyang.ac.kr

od can be used to estimate the phase equilibrium in extraction calculations. The activity coefficient method gives better results than the equation of state model for mixtures showing ideal behavior and containing light interaction molecules (for example water, alcohol, etc.) under low pressure. The distribution coefficients in the activity coefficient method are given by

$$K_{j,i} \equiv \frac{y_{j,i}}{x_{j,i}} = \frac{\gamma'_j}{\gamma'_i} \quad (5)$$

The well-known UNIFAC method was used to compute activity coefficients. The UNIFAC method is one of the most useful method for multi-component multi-stage separation process simulation, especially when there are not enough experimental or operation data.

One of the difficulties in using the UNIFAC method for the sulfolane process is that there are no molecular subgroups available in UNIFAC. However, the solvent with the same solvation properties with sulfolane is acetone [Marcus, 1985] and so sulfolane can be represented by two methylene-carbonyl groups (-CH₂CO-). The UNIFAC group parameters used to compute activity coefficients of sulfolane are shown in Table 1 [Reid et al., 1988]. Calculated activity coefficients showed good agreement with experimental results which are quoted from Panneman's paper [1992]. The comparison is shown in Table 2.

3. Operating Conditions

The sulfolane process considered in the present study consists of two columns: main extractor and washing column. The operating conditions of each column are shown in Table 3 and Figs. 1 and 2 show schematics of these columns. Table 4 shows feed compositions.

Table 1. UNIFAC group volume and surface-area parameters

Main group	Subgroup	no.	R _k	Q _k
9	-CH ₂ CO-	20	1.4457	1.180

Table 2. K-values in the tertiary system of sulfolane, water and cyclo hexane

Temperature (K)	Composition (mol)			K-value (γ^H / γ^L)	
	Sulfolane	Water	Cyclohexene	Experiments	UNIFAC
313	0.40	0.60	0.15	0.150	0.1521
	0.90	0.10	1.00	0.130	0.1299
373	0.40	0.60	0.15	0.274	0.2794
	0.90	0.10	1.00	0.291	0.3010

Table 3. Operating conditions of the extractor and the washing column

	Main extractor	Washing column
Feed rate (kg/hr)	28700 (stage 47) 14466 (stage 105)	9838 (stage 40)
Solvent rate (kg/hr)	109240 (stage 1, sulfolane)	1698 (stage 1, water)
Temperature (°C)	75 (top)-56 (bottom)	40.2 (overall)
Pressure (kg/cm ²)	6.33 (top)-9.53 (bottom)	3.03 (top)-4.53 (bottom)

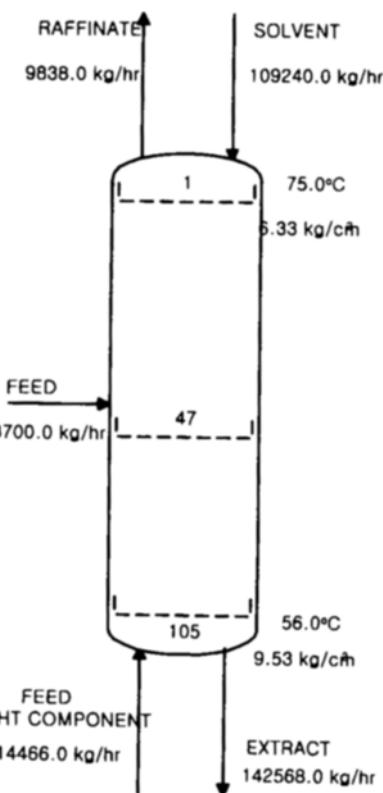


Fig. 1. Operating condition of main extractor.

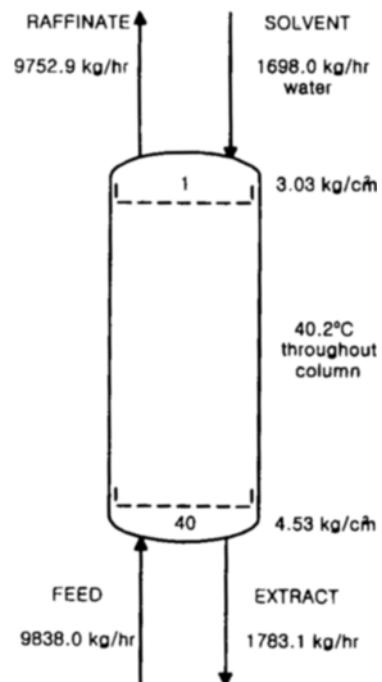


Fig. 2. Operating condition of washing column.

RESULTS OF SIMULATION

In the simulations of distillation columns, the flow rates, temperatures, compositions which satisfy material balances, equilibrium relations and enthalpy balances of each stage are obtained with initial estimates of temperatures and flow rates

Table 4. Feed compositions (weight %) of the extractor and the washing column

Component	Main extractor (wt%)	Washing column (wt%)
Cyclo-hexane	1.53	4.47
n-Hexane	7.38	21.55
Methyl cyclo pentane	9.76	28.52
Benzene	33.28	0.02
3-Methyl-hexane	4.08	11.89
Methyl-cyclo hexane	7.14	20.84
Toluene	19.65	0.09
n-Octane	1.25	3.65
di-Methyl cyclo hexane	2.61	7.52
Ethyl benzene	6.38	0.27
p-Xylene	1.43	0.06
m-Xylene	4.03	0.17
o-Xylene	1.48	0.06
Sulfolane	0.00	0.88
Water	0.00	0.01
Sum (100 %)	100.00	100.00

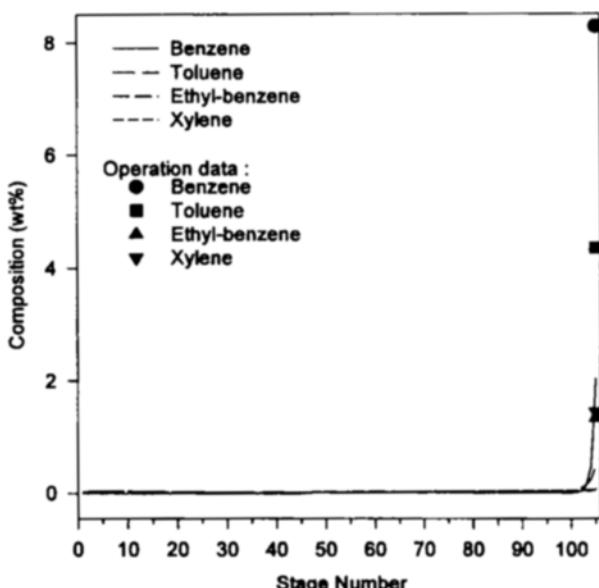
which are iteration variables. But in the case of extraction columns, the temperatures of each stage have little effect on other variables. The sulfolane plant considered in the present study is located in Yeocheon, Chonnam and the main extractor consists of 105 trays.

The single θ -method, which was used in modeling and simulation, showed good convergence. Computational results showed convergence after 31 iterations in the main extractor and after 5 iterations in the washing column.

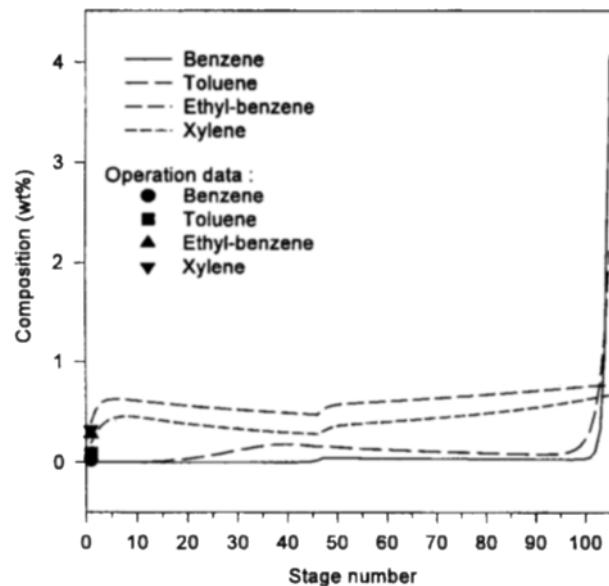
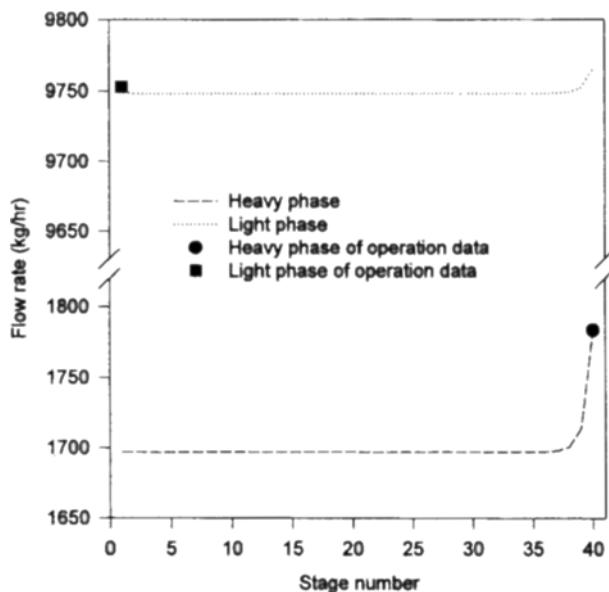
The criterion used in the convergence test is given by

$$\sum_{j=1}^{NS} \left(\frac{V_j^a - V_j^c}{V_j^a} \right)^2 \leq \varepsilon * NS$$

where $\varepsilon = 1.0 * e^{-3}$

**Fig. 3. Compositions of heavy stream in the main extractor.**

January, 1998

**Fig. 4. Compositions of light steram in the main extractor.****Fig. 5. Flow rate in the washing column.**

The results of simulations as well as related operation data are given in Figs. 3-6.

Due to the lack of operating data at each stage accurate comparisons between simulation results and plant data were not possible. Operating data were available only at the top and bottom plates.

Fig. 3 shows compositions of the heavy stream in the main extractor. The measured values of benzene and toluene show some discrepancies from the simulation results. But, as can be seen from Fig. 4, the measured compositions of the light stream in the main extractor showed good agreement with simulation results. Fig. 5 shows flow rates of heavy and light phases at each stage of the washing column. Only one set of operating data was available and comparisons were possible only at the top and bottom stages. Fig. 6 shows compositions of sulfolane and water at each stage of the washing

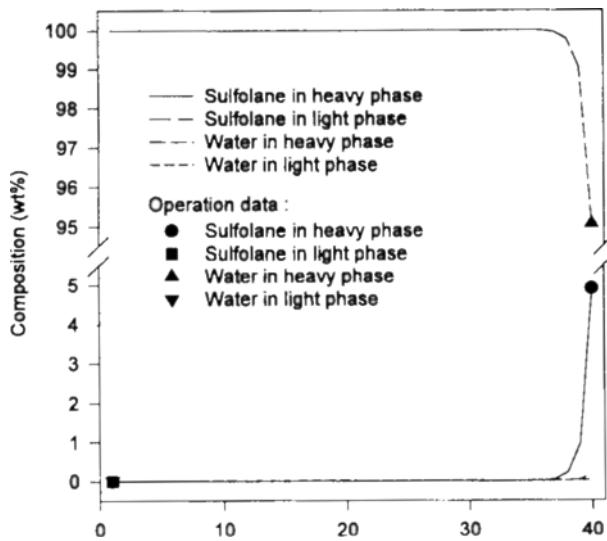


Fig. 6. Composition profiles of sulfolane and water in the washing column.

column. Again simulation results show good agreement with operating data.

CONCLUSIONS

The actual sulfolane extraction process was modeled and simulated. To obtain thermodynamic properties required in the composition of phase equilibria, the well-known UNIFAC method was employed. In contrast to the ISR and direct iteration methods, which failed to converge, the modified single θ -method used in the present work showed good convergence.

Results of simulations showed good agreement with actual operation data especially in the washing column, but some discrepancy in the compositions appeared in the main extractor. The overall error range was acceptable considering the accuracy of the operation data.

ACKNOWLEDGEMENT

This work was supported in part by the Korea Science and Engineering Foundation (KOSEF) through the Automation Research Center at POSTECH.

NOMENCLATURE

$A_{j,i}$: absorption factor of each stage j and each component i
 $E_{j,i}$: phase equilibria function of stage j and component i , defined by (2)
 F^{act} : actual operating data of flow rate [kg/hr]
 F^{calc} : calculated data of flow rate by simulation [kg/hr]
 F_j : feed flow rate of each stage j [kg/hr]
 $K_{j,i}$: equilibrium constant, K-value, stage j , component i
 L_j : heavy phase flow rate of each stage j [kg/hr]
 $l_{j,i}$: component flow rate of heavy phase, stage j , component i [kg/hr]
 NC : number of components

NS : number of stages

$(S_x)_j$: mole fraction summation function of heavy phase, stage j , defined by (4)

$(S_y)_j$: mole fraction summation function of light phase, stage j , defined by (3)

V_j : light phase flow rate of each stage j [kg/hr]

V_j^a : assumed light phase flow rate of each stage j [kg/hr]

V_j^c : calculated light phase flow rate of each stage j [kg/hr]

$v_{j,i}$: component flow rate of light phase, stage j , component i [kg/hr]

$X_{j,i}$: total feed composition of each stage j , component i

$x_{j,i}$: mole fraction in heavy phase, stage j , component i

$y_{j,i}$: mole fraction in light phase, stage j , component i

Greek Letters

ϵ : convergence tolerance

$\gamma_{j,i}^h$: activity coefficient of heavy phase, stage j , component i

$\gamma_{j,i}^l$: activity coefficient of light phase, stage j , component i

Superscripts

a : assumed value

act : actual operating data

c : calculated value

$calc$: calculated data by simulation

H : heavy phase

L : light phase

Subscripts

i : component number

j : stage number

x : heavy phase

y : light phase

REFERENCES

Bailes, P. J., Hanson, C. and Hughes, M. A., "Liquid-Liquid Extraction: Nonmetallic Materials", *Chem. Eng.*, 115 (1976).

Boston, J. F. and Shah, V. B., "An Algorithm for Rigorous Distillation Calculations with Two Liquid Phase", *AICHE Meeting*, Huston, TX, April 1979.

Brett, P. C. and Ian, A. F., "Multicomponent Three-Phase Azeotropic Distillation. 2. Phase-Stability and Phase-Splitting Algorithms", *Ind. Eng. Chem. Res.*, 29(7), 1364 (1990).

Holland, C. D., "Fundamentals and Modeling of Separation Processes", Prentice-Hall, New Jersey, 1975.

Kovach, J. W. and Seider, W. D., "Heterogeneous Azeotropic Distillation Experimental and Simulation Results", *AICHE J.*, 33(8), 1300 (1987).

Marcus, Y., "Ion Solvation", John Wiley & Sons, Chichester, U. K., 190 (1985).

Mcketta, J. J., "Benzene from Petroleum", Encyclopedia of Chemical Processing and Design, Dekker, New York, 1977.

Panneman, H. J. and Beenackers, A. A. C. M., "Solvent Effects on the Hydration of Cyclohexane Catalyzed by a Strong Acid Ion Exchange Resin. 1. Solubility of Cyclohexane in Aqueous Sulfolane Mixture", *Ind. Eng. Chem. Res.*, 31(4), 1227 (1992).

Reid, C. R., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids", 4th ed., McGraw-Hill, 1988.

Trevino-Lozano, R. A., Kisala, T. P. and Boston, J. F., "A Simplified Absorber Model for Nonlinear Simultaneous Modular Flowsheet Calculations", *Comput. Chem. Eng.*, **8**(2), 105 (1984).

Tsuboka, T. and Katayama, T., "General Design Algorithm Based on Pseudo Equilibrium Concept for Multistage Multicomponent Liquid-Liquid Separation Process", *J. Chem. Eng. Japan*, **9**, 40 (1976).