

Simulation of the Aromatic Recovery Process by Extractive Distillation

Min Su Ko, Sangyup Na, Jungho Cho* and Hwayong Kim†

School of Chemical Engineering & Institute of Chemical Processes, Seoul National University, Seoul 151-742, Korea

*Department of Chemical Engineering, Dongyang University, Youngju, Kyoungbuk 750-711, Korea

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Abstract—The NFM (*N*-formylmorpholine) extractive distillation process is used for the purpose of recovering aromatics, such as benzene, toluene, and xylene. The thermodynamic equation used in the simulation is the NRTL equation, and NRTL interaction binary parameters were obtained by experimental data. The missing thermodynamic properties are predicted by group contribution method. Simulation results of the extractive distillation column were in good agreement with the operation data.

Key words: *N*-formylmorpholine (NFM), Extractive Distillation, Process Simulation, NRTL, Liquid-Liquid Equilibria

INTRODUCTION

There has been an ever-increasing demand for a higher purity of aromatics as a feedstock for chemical synthesis. Many solvents such as sulfolane [Lee and Kim, 1995, 1998], *N*-methylpyrrolidone (NMP) [Muller, 1973], glycol [Symoniak et al., 1959; Taher and Emina, 1996], and *N*-formylmorpholine (NFM) [Cinelli et al., 1972; Park and Gmehling, 1989; Mohamed et al., 1995; Manoranjan et al., 1998] are used to extract aromatics such as benzene, toluene and xylene from hydrocarbon mixtures [Muller and Hoehfeld, 1963].

The NFM extractive distillation process separates aromatics from the reformat [Morrison and Brown, 1996; Taher and Emina, 1996]. It minimizes aromatic content in gasoline and refines the extracted aromatics, which are used as raw materials of petrochemical processes. The operating cost and the initial equipment cost for the overall plant can be reduced by the decision of its optimum value. Commercial process simulators such as PRO II (SimSci), HYSYS (Hyprotech) and ASPEN-PLUS (Aspentech) [Oonk, 1981] have been used to determine the optimum solvent rate. However, LLE data are not available for these mixtures.

The purpose of this work was to obtain LLE data for each binary system at the operating temperature range of the NFM extractive distillation process, and simulate the NFM extractive distillation process. LLE data for the binary systems were measured at the temperature range from 298.15 K to 413.15 K, and correlated with the NRTL [Renon and Prausnitz, 1968] model.

SIMULATION

1. Flowsheet for the NFM Extractive Distillation Process

Fig. 1 shows the flowsheet for the NFM process. The extractive distillation process separates aromatics from reformat produced by reformer. It minimizes aromatic content in gasoline and refines extracted aromatics to be used as raw materials of petrochemical

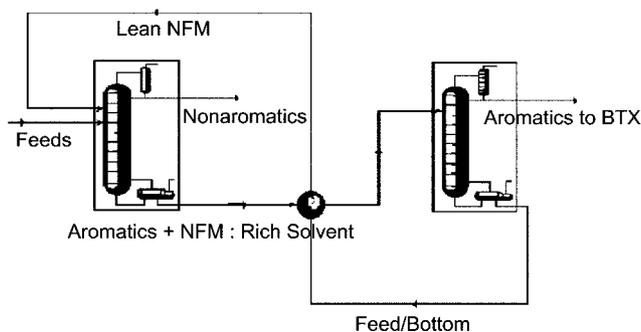


Fig. 1. Schematic flowsheet for simulation of NFM extractive distillation process.

products. A solvent, named NFM, is used to extract aromatics. The NFM process is appropriate for separating aromatics by the extractive distillation process because NFM has selective affinity with aromatics.

Injection of solvents that have good affinity with aromatics and less affinity with non-aromatics reduces the relative volatility of aromatics. This causes the collection of aromatics and solvents at the bottom of extractive distillation column. At the first column, extractive distillation occurs. Aromatics gather at the top and NFM at the bottom in subsequent stripper column, which is connected with the bottom of the first column. Then NFM is recycled to the extractive distillation column.

2. Simulation Input Data

Simulation of the extractive distillation column is performed by using the rigorous distillation model RADFRAC from the ASPEN PLUS simulator. NFM is not built in simulator library and then the user defined component wizard is used. The simulator required physical properties data and property parameters for non-databank components, such as normal boiling point, molecular weight, standard liquid density, critical temperature, critical pressure, acentric factor, Rackett parameter, vapor pressure, and heat capacity. We supplied the missing thermodynamic properties with both methods of the following: property estimation method to estimate the required properties data and data regression method to regress experimental data to obtain the parameters. The critical properties (T_c and P_c) are es-

†To whom correspondence should be addressed.

E-mail: hwayongk@snu.ac.kr

‡This paper is dedicated to Dr. Youn Yong Lee on the occasion of his retirement from Korea Institute of Science and Technology.

Table 1. Thermodynamic properties used in the simulation

Thermodynamic properties	Method using in the simulation
Critical properties	Joback method (molecular structure)
T _c	761.1 K
P _c	49.5 bar
ω	0.454
Pure vapor pressure of NFM	Experimental data [Park and Gmehling, 1989]
Binary parameters for LLE and VLE	Databanks, estimation, and experimental data Eight binary systems: pentane, hexane, heptane, octane, cyclopentane, cyclohexane, benzene, and toluene with NFM

timated with modified Joback method and experimental normal boiling point. The acentric factor is found from Eq. (1)

$$\ln(P_c/1.01325) = f^{(0)}(T_{br}) + \omega f^{(1)}(T_{br}) + \omega^2 f^{(2)}(T_{br}) \quad (1)$$

where P_c is critical pressure in bars, T_{br} is T_b/T_c in absolute temperature, K. Although a number of analytical expressions have been suggested for f⁽⁰⁾, f⁽¹⁾ and f⁽²⁾ [Brandani, 1993; Schreiber and Pitzer,

1989; Twu et al., 1994]. We used the analytical expressions developed by Ambrose and Walton (1989) [Poling et al., 2001] and the estimated critical properties for T_c and P_c. The results are shown in Table 1.

The thermodynamic equation used in the NFM process simulation is the NRTL equation, and the NRTL interaction binary parameters are obtained by experimental data, estimation, and databanks.

Table 2. Binary parameters for all components in the NFM extractive distillation process

	NC5	NC6	NC7	NC8	CP5	CH6	MCP	MCH	ECH	DMCH	BE	TOL	EBE	NFM
NC5														
NC6	A ¹													
NC7	B ²	A												
NC8	C ³	A	A											
CP5	C	C	C	C										
CH6	C	A	A	A	A									
MCP	A	A	C	C	C	A								
MCH	A	A	A	C	C	A	C							
ECH	C	C	C	A	C	C	C	C						
DMCH	C	C	C	C	C	C	C	C	C					
BE	A	A	A	A	A	A	A	A	C	C				
TOL	A	A	A	C	C	A	A	A	C	C	C			
EBE	C	C	A	A	C	A	C	C	A	C	A	C		
NFM	D ⁴	D	D	D	D	D	C	C	C	C	D	D	C	

¹The VLE-IG and VLE-LIT are databanks for vapor-liquid applications. A¹: The databank VLE_IG was developed by AspenTech using binary vapor liquid equilibrium data from the Dortmund databank. B²: The databank VLE_LIT contains binary parameters obtained from the literature. The both of VLE-IG and VLE-LIT are used with thermodynamic models, such as Wilson, NRTL, and UNIQUAC models and with ideal-gas model for vapor phase model. C³: R-PCES is obtained by UNIFAC model. D⁴: USER is obtained by regressing of experimental data.

²NC5: Pentane, NC6: Hexane, NC7: Heptane, NC8: Octane, CP5: Cyclopentane, CH6: Cyclohexane, MCP: Methylcyclopentane, MCH: Methylcyclohexane, DMCH: Dimethylcyclohexane, BZ: Benzene, TOL: Toluene, EBE: Ethylbenzene, NFM: *N*-Formylmorpholine.

³Total number of binary systems is 91 (=14C₂).

Table 3. User defined NRTL binary parameters for systems containing *N*-formylmorpholin

Component i	NC5	NC6	NC7	NC8	CP5	CH6	BE	TOL
Component j	NFM	NFM	NFM	NFM	NFM	NFM	NFM	NFM
a _{ij}	142.273778	-4.54662813	9.76074132	-95.8720696	52.2508155	178.9185	2.37871337	25.9668
a _{ji}	219.392189	35.2816182	-16.019515	-13.2889643	102.830391	174.840172	1.55606667	-12.5085029
b _{ij}	-6157.33676	1173.06664	1359.53594	6056.27081	-891.612371	-6567.53477	-433.899709	5225
b _{ji}	-9897.63006	-1381.77553	1917.75121	1739.02684	-3869.66766	-7658.69462	-960.692624	-2695
c _{ij}	0.3	0.3	0.3	0.3	0.3	0.3	0.300084047	0.030018311
d _{ij}	0.0001	0.0009	0.000536	0.000827	0.0001	0.0001	-0.000443	-0.000241
e _{ij}	-20.8054802	0.68991512	-1.87500939	13.8563414	-8.02588056	-26.8772204	-0.00011	-5.00536868
e _{ji}	-32.27468113	-4.91089597	2.24960645	1.90640856	-15.5077994	-25.853971	-0.000108	1.83778013

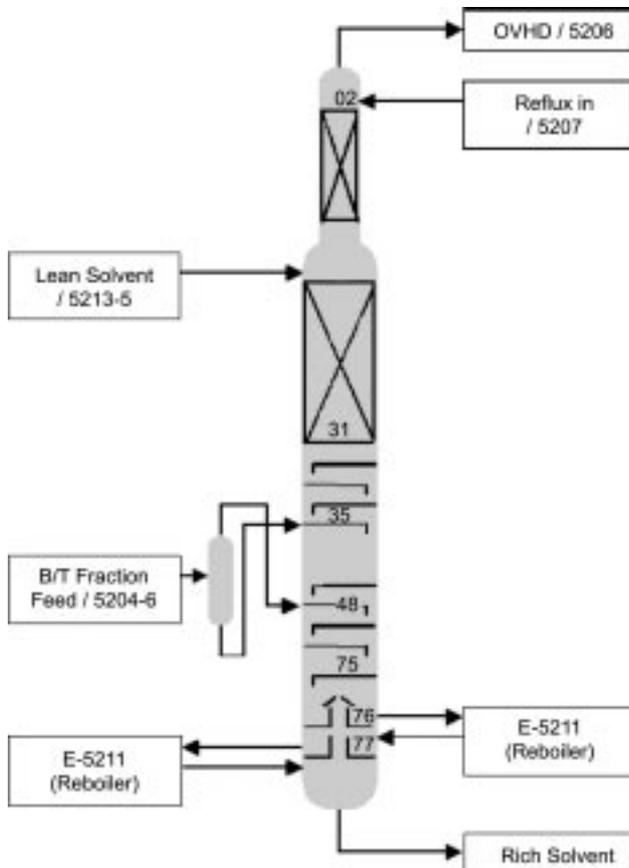


Fig. 2. Configuration of extractive distillation column.

The results of the existence of binary parameters for all components in the NFM extractive distillation process are shown Table 2. NRTL binary parameters of component i and j were calculated by means of the NRTL equation whose parameters are reported in Table 3.

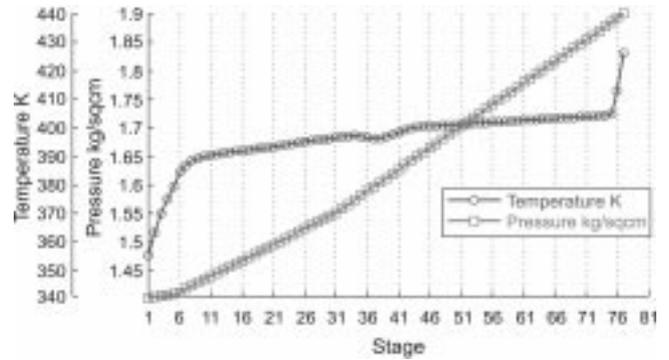


Fig. 3. Temperature and pressure profile in extractive distillation column.

The binary parameters have the temperature dependence function, for NRTL model:

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (2)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (3)$$

$$\tau_{ij} = \frac{g_{ij} - g_{ji}}{RT} \quad (4)$$

$$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij} \ln T \quad (5)$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15 \text{ K}) \quad (6)$$

Fig. 2 shows the column configuration for simulation of extractive distillation, and Table 4 shows simulation input data. For the extractive distillation column of this process, the number of practical stages is 77 (number of stages for packed section and tray section, 34 and 45, respectively). The extractive distillation column is composed of the packed section with structured packing, Gempack 2A of Glitsch Co., Ltd. and the tray section with sieve tray. The height equivalent of a theoretical plate (HETP) for the packed sec-

Table 4. Feed conditions and column specifications of Radfrac extractive distillation column

Column specification		Column specification	
Configuration		Pressure [kg/cm ²]	
Number of stages	77	Total pressure drop	1.4
Condenser	Partial-vapor	Section pressure drop	
Reboiler	Thermosyphon	2 to 6	0.01
Valid phases	Vapor-liquid-liquid	7 to 31	0.14
Convergence	Strongly non-ideal liquid	32 to 77	0.35
Distillation rate [kg/hr]	1031	Reboiler	
Reboiler duty [kcal/hr]	1769600	Outlet temperature [K]	162
Streams		Reboiler pressure [kg/cm ²]	1.9
5213-5	6	3-Phase	
vap-feed	48	Stages	8 to 18
liq-feed	35	Key components	Feed components
5207	2	Side duties	
5209-1	77	Stage	76
5206	1	Duty [kcal/hr]	1785000
Column type		Convergence	
2 to 31	Packed-column	Algorithm	Nonideal
32 to 77	Tray-column	Inside loop	Newton

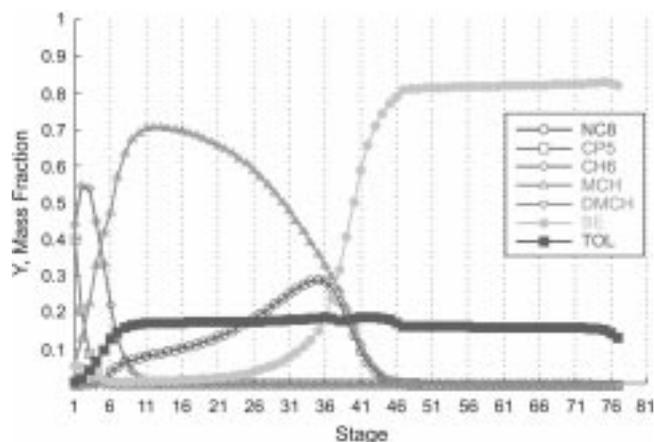


Fig. 4. Vapor-composition profile in extractive distillation of methylcyclohexane, benzene, with *N*-formylmorpholine as solvent.

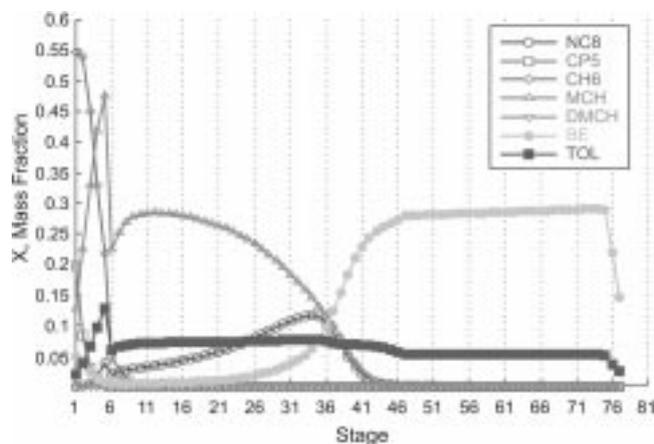


Fig. 5. Liquid-composition profile in extractive distillation of methylcyclohexane, benzene, with *N*-formylmorpholine as solvent.

tion of extractive distillation is found from the Strigle method [Strigle, 1994]. The valid phases from introduction stage of lean solvent, 6, to underneath stage of liquid feed, 36, are vapor-liquid-liquid phases. Condenser pressure is 1.4 kg/cm², and column pressure drop is 0.5 kg/cm². In extractive distillation, stage-to-stage [MESH] calculations start at the bottom since the feed species, such as methylcyclohexane and benzene are the keys for second liquid phase and the *N*-formylmorpholine (NFM) is a heavy nonkey.

RESULTS AND DISCUSSION

As shown in Fig. 3, the temperature changes most rapidly at the very top, at the bottom of the column, and in the vicinity of the lean solvent point and the feed point for the extractive distillation. The temperature profiles inside the column, the temperatures at the reboiler and condenser, are 425.98 and 355.05 K, respectively. The

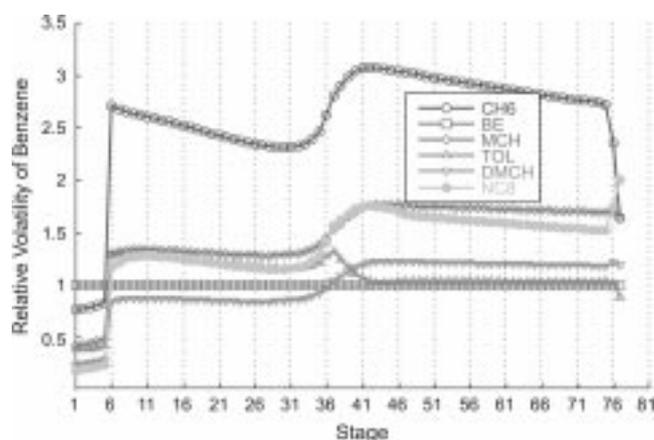


Fig. 6. Relative volatility profile in extractive distillation of methylcyclohexane, benzene, with *N*-formylmorpholine as solvent.

Table 5. Mass balance at the extractive distillation column

Stream number	Operation data				Simulation calculation			
	5207	5206	5209-1	5208-1	5207	5206	5209-1	5208-1
Pentane	2.5	3.0	0.0	0.5	2.5	3.0	0.0	0.5
Hexane	20.6	24.7	0.0	4.1	20.5	24.6	0.0	4.1
Heptane	11.0	13.3	0.0	2.2	11.0	13.2	0.0	2.2
Octane	0.0	0.1	7.2	0.0	0.1	0.1	7.3	0.0
Cyclopentane	341.8	410.1	0.0	68.4	342.0	410.4	0.0	68.4
Cyclohexane	378.6	454.3	0.0	75.7	378.5	454.2	0.0	75.7
Methylcyclopentane	4.2	5.0	0.0	0.8	4.0	4.8	0.0	0.8
Methylcyclohexane	56.5	67.8	1.5	11.3	48.6	58.3	3.1	9.7
Ethylcyclohexane	0.0	0.0	0.5	0.0	0.0	0.0	0.5	0.0
Dimethylcyclohexane	0.7	0.0	2.0	0.0	0.0	0.0	2.0	0.0
Benzene	42.9	51.5	13342	8.6	45.0	54.0	13341.6	9.0
Toluene	0.7	0.9	2392.9	0.1	7.0	8.4	2391.6	1.4
Ethylbenzene	0.0	0.0	5.0	0.0	0.0	0.0	5.0	0.0
<i>N</i> -formylmorpholine	0.0	0.0	75626	0.0	0.0	0.0	75626.0	0.0
Total flow (kg/hr)	859.5	1031	91377.1	171.7	859.2	1031.0	91377.1	171.8
Temperature (K)	345.15	355.15	424.15	345.15	346.29	355.05	425.98	346.29

pressure increases gradually toward bottom of the column.

Considering Figs. 4 and 5, above the feed the benzene in both liquid and vapor dies out rapidly. Because of low relative volatility with response to all the other components present, this component does not enter the up flowing vapor on the stages above the feed to any large extent. However, the benzene in both liquid and vapor increases on the stages above lean solvent point due to vapor-liquid phase region. While above the feed the methylcyclohexane in both liquid and vapor increases rapidly till feed stage of lean solvent. In 1 to 5 stages occurs vapor-2nd liquid phase, 6 to 36 vapor-1st liquid-2nd liquid phase and 37 to 77 stages vapor-1st liquid phase. The 1st liquid contains NFM and methylcyclohexane and aromatics to be highly soluble in NFM. The 2nd liquid contains paraffin and naphthene components.

Fig. 6. shows the relative volatility on the basis of the benzene. The relative volatility is less for the benzene than for the other components, because of the difference of the mutual solubility among aromatics, non-aromatics and NFM.

The results are presented in Table 5 for the mass balance, the total flow rate, and temperature of each stream. Simulation results of the extractive distillation column of the NFM process were in good agreement with the operation data.

CONCLUSIONS

The NFM process was simulated with ASPEN PLUS 10.1 a sequential modular simulation software package. The NRTL models were useful in simulating the NFM extractive distillation. The optimum solvent to feed ratio by mass of this process is around 3.5. The better optimum operation condition will require a good amount of experimental data, which are LLE data.

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NOMENCLATURE

g^E	: excess Gibbs energy [J/mol]
T	: absolute temperature [K]
T_b	: normal boiling point [K]
R	: universal gas constant [J/mol-K]
x	: mole fraction [-]
g_{ij}	: parameter for interaction between components [J/mol]
T_c	: critical temperature [K]
P_c	: critical pressure [bar]
$f^{(0)}, f^{(1)}, f^{(2)}$: functions in Pitzer's correlation for Pvp

Greek Letters

α_{ij}	: nonrandomness parameter [-]
ω	: acentric factor

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