

Simulation of 1,3-butadiene extractive distillation process using N-methyl-2-pyrrolidone solvent

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(Received 24 October 2011 • accepted 24 May 2012)

Abstract—A computer simulation was performed using a commercial process simulator, Aspen Plus, for NMP (N-methyl-2-pyrrolidone) extractive distillation process to separate 1,3-butadiene from the C₄ hydrocarbon mixtures. The Redlich-Kwong equation of state and NRTL activity coefficient model were used to calculate thermodynamic properties in the simulation of the extractive distillation process. Binary parameters of the NRTL model not provided in the simulator were estimated using the UNIFAC method. The simulation results of the 1,3-butadiene recovery from the C₄ mixtures were in good agreement with the plant operation data. The process simulation showed that the material balances in the extractive distillation were successfully predicted for various NMP solvent flow rates. The results obtained in this work provided the optimum solvent rate and the reflux ratio for the NMP extractive distillation process to separate 1,3-butadiene from the C₄ mixtures.

Key words: Extractive Distillation, NMP Solvent, Aspen Plus, 1,3-Butadiene

INTRODUCTION

1,3-Butadiene is a major petrochemical product and an important feedstock in the production of rubbers and plastics, such as styrene butadiene rubber, polybutadiene rubber, and styrene butadiene latex [1]. It is contained in C₄ mixtures, which are a by-product from naphtha crackers. Before use in polymerization processes, 1,3-butadiene must be separated from C₄ mixtures. In general, C₄ mixtures include butanes, butenes, 1,2-butadiene, 1,3-butadiene and acetylenes, etc. The C₄ mixtures cannot be fractionated into each component using conventional distillation since many of the C₄ components have relative volatilities very similar to 1,3-butadiene [2]. To separate hydrocarbons which have similar boiling points using a conventional distillation process, the number of trays or the reflux ratio must be extremely increased [3]. 1,3-Butadiene can be separated by extractive distillation, because the other C₄ components have different solubility compared with 1,3-butadiene in some solvents such as acetonitrile (ACN), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP).

Many researchers have performed computer simulations of ACN and DMF extractive distillation processes to separate C₄ mixtures [2,4,5]. Liao et al. performed simulation of 1,3-butadiene extractive distillation process using ACN as an extraction solvent to investigate the operating conditions for effective separation [6]. Several solvents were evaluated for the recovery of 1,3-butadiene from crude C₄ fractions by extractive distillation [7]. The application of ACN method has been decreasing, since ACN is toxic to the environment [4]. DMF might be hydrolyzed into formic acid during the distillation process, which is corrosive to carbon steel [8]. Because of the high solubility and selectivity for unsaturated hydrocarbon,

NMP has been widely used in extractive distillation plants [9,10]. While NMP has been widely used as a solvent in extractive distillation for the separation of 1,3-butadiene from the C₄ mixtures, there are not sufficient studies about the operating conditions such as the solvent rates [9]. It has been reported that 1,3-butadiene extraction process, rather than the DMF extraction process, using NMP as a solvent can reduce the initial equipment cost [11,12]. In spite of the high solvent flow rates, the NMP extractive distillation process, rather than the DMF process, can reduce the heat duty by the low operating pressure and temperature due to properties of NMP solvent.

In this study, computer modeling and simulation of the BASF extractive distillation process to separate 1,3-butadiene from the C₄ mixtures using NMP as a solvent were performed. The 1,3-butadiene recovery from the C₄ mixtures and the reboiler duties in the distillation process were compared with the plant operation data [13]. The effects of the operating condition (reflux ratio of the 1,3-butadiene distillation column) and the NMP solvent flow rates on the performance of the extractive distillation process were investigated. The modeling and simulation of the extractive distillation process were performed using the commercial software Aspen Plus [14].

DESCRIPTION OF PROCESS

1. 1,3-Butadiene Extractive Distillation Process

The 1,3-butadiene extractive distillation process using NMP solvent was industrialized by the BASF company [9]. Fig. 1 shows the schematic flow diagram of the BASF NMP extraction process for separating C₄ mixtures [12]. The process consists of three main sections: extractive distillation section (first and second extractive distillation columns, rectifier), ordinary distillation section (propyne column, 1,3-butadiene distillation column) and degassing section (degasser, cooling column, water scrubber). The C₄ mixtures feed is fed into the first extractive distillation column, which produces

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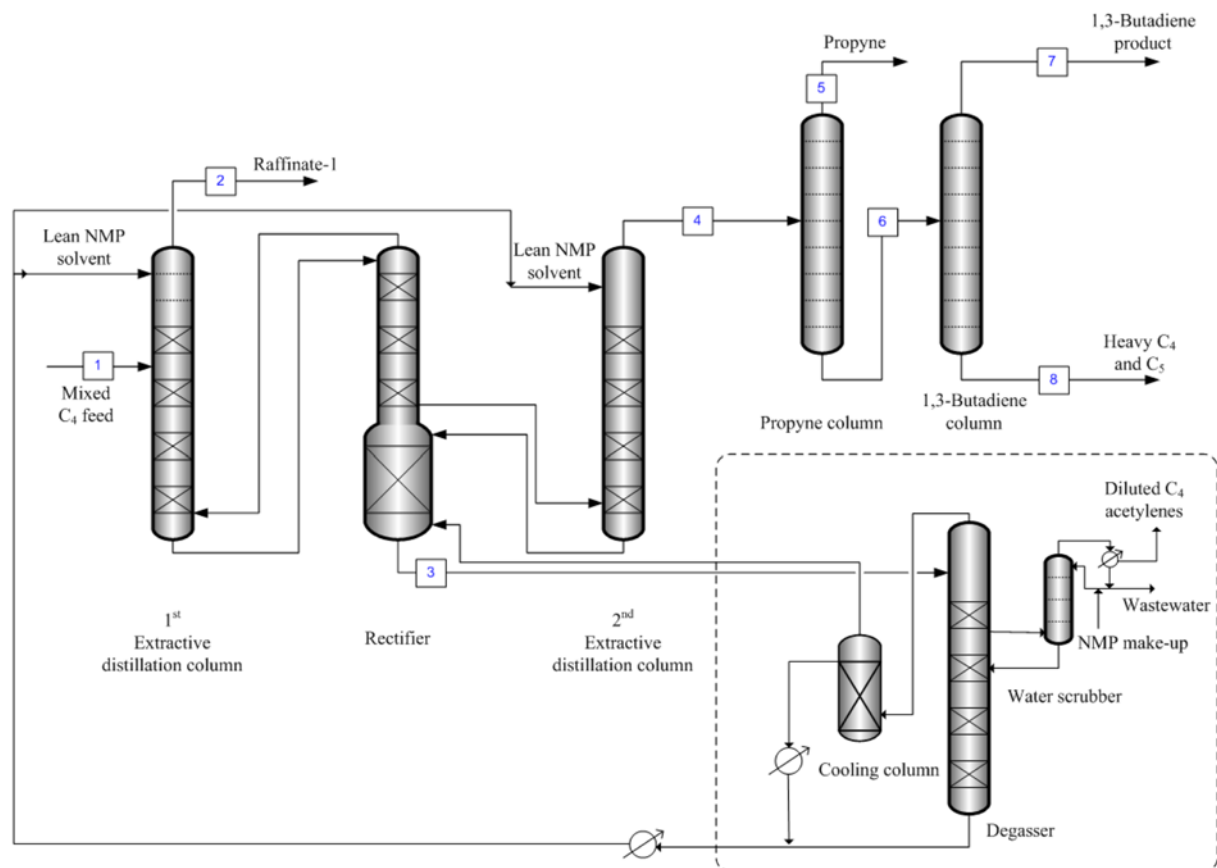


Fig. 1. Schematic of BASF NMP extraction process [12].

raffinate-1 mainly containing i-butene, 1-butene, n-butane and i-butane as an overhead product. The bottom product from the first extractive distillation column, containing 1,3-butadiene, the acetylene compounds (vinyl acetylene, ethyl acetylene) and some butenes dissolved in the solvent, is fed into the rectifier and stripped free of butenes in the top half of the rectifier. A side stream containing 1,3-butadiene and a small amount of acetylene compounds is withdrawn from the rectifier and fed into the second extractive distillation column. The solvent NMP is fed to the first and the second extractive distillation column, respectively. The bottom product of the rectifier, containing C₄ acetylenes, and C₅ hydrocarbons dissolved in NMP, is preheated and fed into the degasser (solvent stripping column). The hot-stripped solvent from the bottom of the degasser passes through a train of heat exchangers and is recycled to the extractive distillation columns. In the propyne column, propyne (methyl acetylene) is withdrawn with a small amount of 1,3-butadiene as an overhead product. In the 1,3-butadiene distillation column, a mixture containing 1,2-butadiene and heavy C₄-hydrocarbons is separated as the bottom product. The pure 1,3-butadiene product is withdrawn from the 1,3-butadiene distillation column as an overhead product.

2. Feed Composition

The composition of the C₄ mixtures and NMP solvent entering into the first extractive distillation column is shown in Table 1. A typical 1,3-butadiene content of the C₄ mixtures obtained in cracking naphtha to yield ethylene is between 40-55 wt%. The NMP solvent with approximately 8.3 wt% water is fed to the top of the first

Table 1. Composition of the C₄ mixtures and the NMP solvent into the 1st extractive distillation column [9]

C ₄ mixtures component	Mass fraction (%)
Propane	2.11×10^{-3}
Propene	1.00×10^{-2}
Methylacetylene	6.13×10^{-2}
Propadiene	4.83×10^{-2}
n-Butane	7.61
i-Butane	3.54
1-Butene	6.32
i-Butene	23.4
Trans-2-butene	3.27
Cis-2-butene	2.58
1,3-Butadiene	50.6
1,2-Butadiene	0.29
Ethylacetylene	0.36
Vinylacetylene	1.91
NMP solvent	
Mass fraction (%)	
NMP	91.7
Water	8.3

extractive distillation column because NMP-water mixtures have more selectivity for unsaturated hydrocarbon than pure NMP solvent [13]. To prevent 1,3-butadiene polymerization, tert-butyl cate-

chol (TBC) is added into the propyne column in the actual industrial process. However, addition of TBC is ignored in this study because the quantity of the entering TBC is negligible. A consideration of 1,3-butadiene polymerization is also ignored.

THERMODYNAMIC MODEL

In the computer modeling and simulation of 1,3-butadiene extraction process using NMP as a solvent, the equation of state and the activity coefficient model were used due to the properties of the polar solvent. For polar or non-ideal chemical systems, binary thermodynamic systems are employed. In this study, the Redlich-Kwong equation of state is used to predict the vapor fugacity coefficient, while the NRTL model of state is employed for the liquid phase in the extractive distillation process. The NRTL model is used as the main equation for the liquid phase with its binary interaction parameters [15]. Redlich-Kwong is applicable under moderate pressure in which the nonideality of the vapor phase is small. In the ordinary distillation column section, the Peng-Robinson equation of state is used as the thermodynamic model. Binary interaction parameters for the components in the liquid phase for NRTL model are not sufficiently provided in the commercial simulator. In this study, binary parameters not provided in Aspen Plus were estimated using the UNIFAC method. Thermodynamic calculations and the values of parameters used in the simulation are briefly described in the appendix.

PROCESS SIMULATION

As shown in Fig. 1, the extractive distillation section consists of the first extractive distillation column, the rectifier and the second extractive distillation column. The number of stages and the operating pressures of each column were decided referring to the plant operation data [12,13]. The decided theoretical number of stages, operating pressures, reflux ratios and feed trays of each column are described in Table 2. Reflux ratio of the first extractive distillation column was regulated to satisfy the plant operation data for the composition of 1,3-butadiene and i-butene in the top product. DMF solvent flow rate was required 7-8 times larger than C_4 mixtures feeding rate in order to satisfy both purity and recovery of the final 1,3-butadiene product. A larger amount of NMP solvent flow rate is needed compared to the DMF process.

The stage of the side stream from the rectifier was decided to satisfy the mass balance in the rectifier. The side stream from the rectifier containing 1,3-butadiene and a small amount of C_4 acetylenes is fed into the second extractive distillation column. Vinyl acety-

lene and ethyl acetylene dissolved in NMP solvent are withdrawn as a bottom product from the second extractive distillation column and recycled into the rectifier. 1,3-Butadiene with propyne and heavy C_4 , C_5 components is withdrawn as a top product from the second extractive distillation column and fed into the propyne column. The NMP solvent flow rate into the second extractive distillation column was decided 0.8-1.2 times larger than the feed rate (1,3-butadiene and a small amount of C_4 acetylenes).

The degassing section is to refine and to reuse the NMP solvent. There is only one column, degasser in this section, which is to separate out such material as waste water, diluted C_4 acetylenes and some hydrocarbons. The refined NMP is obtained at the bottom of the degasser.

As shown in Fig. 1, an ordinary distillation section consists of a propyne column and 1,3-butadiene distillation column. Methyl acetylene is removed as the top product of the propyne column. Bottom product containing 1,3-butadiene and a small amount of heavy C_4 and C_5 components from the propyne column is fed into the 1,3-butadiene distillation column. The final product of 1,3-butadiene is withdrawn as the top product, and components such as heavy C_4 and C_5 with lower volatility than 1,3-butadiene are withdrawn as the bottom product in the 1,3-butadiene distillation column. Distillate rates and reflux ratios of the propyne column and the 1,3-butadiene column were regulated to satisfy the plant operation data such as the purity and the recovery of the final 1,3-butadiene product.

RESULTS AND DISCUSSION

Calculations for the simulating process were based on equilibrium stage model. The actual number of trays can be estimated using the plate efficiency for tray towers. An estimate of overall plate efficiency can be made with the Lockett and Leggett version of the empirical O'Connell correlation [16]. In this correlation method, the overall plate efficiency depends on the product of the average liquid phase viscosity and a dimensionless volatility factor.

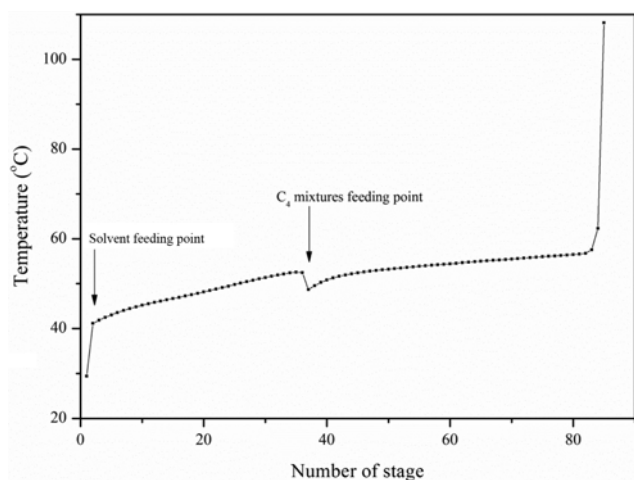
As can be seen in Fig. 1, the liquid phase side stream containing crude butadiene and solvent is withdrawn from the rectifier and fed into the second extractive distillation. In general, a liquid side stream is withdrawn from a distillation column in which the concentration of the light component in the liquid phase is smaller than the concentration of the light component in the vapor phase. The withdrawing of side stream from the rectifier in NMP extractive distillation process provides lower energy costs than does the DMF process [13]. All the simulation results such as the flow rates, temperatures, pressures and compositions for the main streams in Fig. 1

Table 2. Configurations of distillation columns

	1 st Extractive distillation column	Rectifier	2 nd Extractive distillation column	Propyne column	1,3-Butadiene column
No. of trays	85	12	21	25	70
Top pressure	3.27 bar	4.23 bar	3.95 bar	5.33 bar	3.07 bar
Bottom pressure	4.25 bar	4.37 bar	4.95 bar	5.82 bar	3.85 bar
Reflux ratio	1.85	26.7	5.95	23.8	3.85
Feed tray	37	-	8	12	35
Solvent feed tray	2	-	3	-	-

Table 3. Simulation results for the main streams in Fig. 1

	①	⑨	②	③	⑩	④	⑥	⑪
Temperature, °C	30	22.7	29.4	180	45	36.9	51.1	28.1
Pressure, bar	5.3	3.3	3.3	4.4	5.4	5.6	5.8	3.1
Flow rates, kg/s	6.34	63.89	2.96	71.61	7.64	3.30	3.30	3.21
Mass frac.								
1,3-Butadiene	0.506		0.001	-		0.971	0.972	0.997
n-Butane	0.076		0.163	-		-	-	-
i-Butane	0.035		0.076	-		-	-	-
1-Butene	0.063		0.135	-		-	-	-
i-Butene	0.234		0.502	-		-	-	-
trans-2-Butene	0.033		0.064	-		0.006	0.006	0.003
cis-2-Butene	0.026		0.055	-		-	-	-
1,2-Butadiene	0.003		-	-		-	-	-
Ethylacetylene	0.004		-	-		0.005	0.005	-
Vinylacetylene	0.019		-	-		0.016	0.016	-
NMP		0.917	-	0.916	0.917	-	-	-
Water		0.083	0.002	0.083	0.083	-	-	-

**Fig. 2. Temperature profile in the 1st extractive distillation column.**

are described in Table 3.

Fig. 2 presents the calculated temperature profile in the first extractive distillation column. The temperature changes most rapidly at the top and bottom of the column and in the vicinity of the solvent feeding point and the C₄ mixtures feeding point for the extractive distillation. Polymerization of C₄ hydrocarbons did not happen in the range of temperatures in the first extractive distillation column [17]. The temperature profile shows a similar tendency of the behavior of K-values of the main components obtained in the simulation on the each stage.

The influence of NMP solvent flow rate on the 1,3-butadiene production of the first extractive distillation column is illustrated in Fig. 3. The NMP solvent flow rate was chosen to satisfy the final 1,3-butadiene product purity. 1,3-Butadiene with purity of 99.7 wt% and recovery of 99.75% was presented in the plant operation data, when NMP solvent rate to C₄ mixtures feeding rate ratio was 10.1 times. The simulation results were compared with the butadiene extraction plant operation data of Amir Kabir Petrochemical Com-

Table 4. Comparison between simulated results and plant data in the 1st extractive distillation column [13]

Output section	Component	Simulated results (wt%)	Plant data (wt%)
Overhead	1,3-Butadiene	0.1	0.2
Overhead	i-Butene	50.2	50.0
Bottom	Trans-2-butene	0.06	0.02
Bottom	Cis-2-butene	0.0	0.1

Table 5. Comparison between simulated results and plant data in the 2nd extractive distillation column [13]

Output section	Component	Simulated results (wt%)	Plant data (wt%)
Overhead	1,3-Butadiene	97.07	99.08
Overhead	Ethylacetylene	0.5	0.0
Overhead	Vinylacetylene	1.4	0.0
Overhead	1,2-Butadiene	0.01	0.43
Overhead	Others	1.02	0.49

pany described in ref. [13]. Table 4 shows the comparison between the simulated results and the plant data at the top and bottom of the first extractive columns. The simulation results for the first extractive distillation column shown in Table 4 are in good agreement with the plant operation data.

Table 5 shows the comparison between the simulated results and the plant data of the second extractive distillation column. The quantity of vinyl acetylene at the top is very small, but vinyl acetylene is the main impurity leading to the operating instability such as fouling. For this reason, the vinyl acetylene pretreatment process has been proposed to develop 1,3-butadiene extractive distillation process [10]. The difference of the compositions between the plant data and the simulated results is due to the estimation errors of binary interaction parameters. To improve simulated results precisely, binary

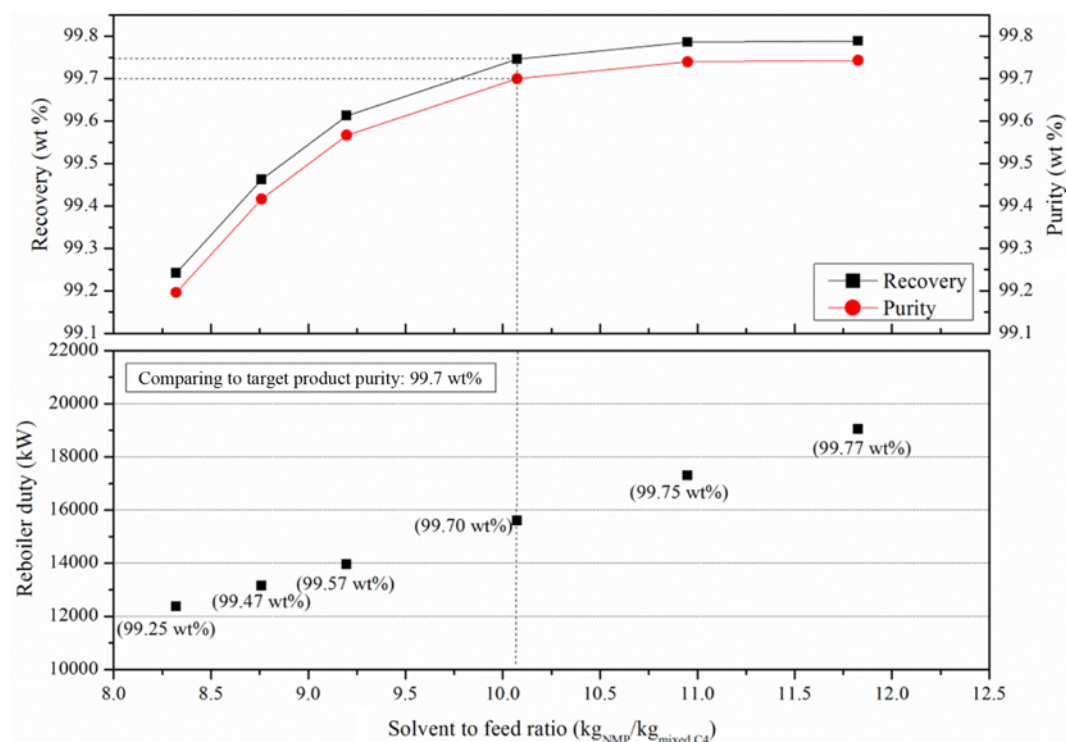


Fig. 3. Influence of solvent flow rate on the 1,3-butadiene production of 1st extractive distillation column.

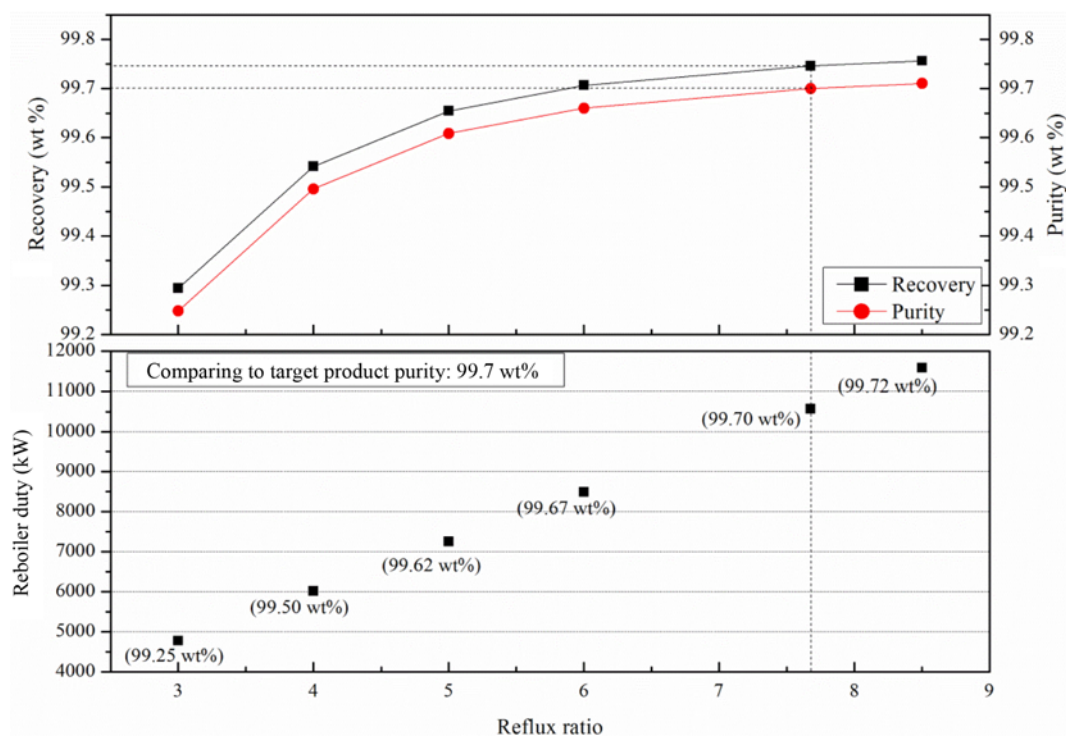


Fig. 4. Influence of reflux ratio on the 1,3-butadiene production of the 1,3-butadiene column.

interaction parameters obtained from UNIFAC method should be modified. Data regression method using phase equilibrium data would be suggested to modify binary interaction parameters.

As shown in Fig. 4, 1,3-butadiene purity and recovery was getting dramatically higher when the reflux ratio in the 1,3-butadiene

column was getting higher up to about 3-5. As against this, the heat duty (reboiler) in the 1,3-butadiene column was getting higher with increasing reflux ratio. The reflux ratio was decided as 7.7, which is sufficient for required 1,3-butadiene purity and minimal heat duty. Table 6 presents the composition of the final 1,3-butadiene product

Table 6. Comparison between simulated results and plant data in the 1,3-butadiene distillation column [13]

Output section	Component	Simulated results (wt%)	Plant data (wt%)
Overhead	1,3-Butadiene	99.7	99.7
Overhead	i-Butene	0.00	0.04
Overhead	Trans-2-butene	0.26	0.21
Overhead	Cis-2-butene	0.00	0.20
Overhead	Others	0.04	0.03

both of simulation result and plant data. 1,3-Butadiene specification obtained in the simulation is satisfied with the plant data. The commercial 1,3-butadiene product mostly guarantees 99.5 wt% purity. Considering the product purity and the utility cost, the solvent to feed ratio should be about 9.5-10 and the reflux ratio in the 1,3-butadiene column should be operated at about 5-6.

CONCLUSION

A simulation of the NMP extractive distillation process to separate 1,3-butadiene from the C₄ hydrocarbon mixtures was performed using Aspen Plus. Redlich-Kwong equation of state and NRTL activity coefficient model were used to calculate the thermodynamic properties. Binary parameters of NRTL model not provided in the simulator were estimated using the UNIFAC method. The results obtained provided the optimum solvent rate and the reflux ratio for the NMP extractive distillation process to separate 1,3-butadiene from the C₄ mixtures. NMP solvent rate to C₄ mixtures feeding rate ratio was decided 10.1 times in the 1st extractive distillation column. Reflux ratio in the 1,3-butadiene column was decided 7.7, which is sufficient for the required 1,3-butadiene purity. With the optimized operating condition, 1,3-butadiene product with a purity of 99.7 wt% and a recovery of 99.75% were in good agreement with the plant operation data. Simulation results of the 1,3-butadiene extractive distillation process could be useful for process improvement such as revamping.

NOMENCLATURE

a_{ij} , a_{ji} , b_{ij} , b_{ji} , α_{ij} : binary parameters in NRTL model
 g^E : excess Gibbs energy
 T : absolute temperature
 R : universal gas constant
 x : mole fraction
 G_{ij} : parameter for interaction between two components
 ACN : acetonitrile
 DMF : dimethylformamide
 NMP : N-methyl-2-pyrrolidone
 NRTL : Non-Random two liquid model
 TBC : tert-butyl catechol
 UNIFAC : UNiversal functional activity coefficient method
 τ_{ij} : parameter for interaction between two components

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APPENDIX

The most important part of simulation of the extractive distillation using solvent is how to obtain the binary parameters of two components. In general, the values of binary parameters are provided in the commercial simulator, and the values not provided in the simulator are estimated by the semi-empirical system to calculate the activity coefficients such as UNIFAC method. In this study, the NRTL-RK model was used in the simulation of the extractive distillation, which uses the NRTL equation as the main equation for the liquid phase with the binary interaction parameters and the Redlich-Kwong equation to predict the vapor fugacity coefficients. In an ordinary distillation column which does not include the solvent, the Peng-Robinson equation was used. The binary parameters not provided in the Aspen Plus were obtained from references

Table A.1. User-defined NRTL parameters for systems containing NMP (component j)

Parameter component i	a_{ij}	a_{ji}	b_{ij}	b_{ji}	α_{ij}
1,3-Butadiene	0	0	656.6	-176.9	0.3
n-Butane	0	0	634.9	145.1	0.3
i-Butane	0	0	635.2	143.8	0.3
1-Butene	0	0	448.8	-7.4	0.3
i-Butene	0	0	689.5	63.7	0.3
Trans-2-butene	0	0	495.1	13.7	0.3
Cis-2-butene	0	0	635.5	66.8	0.3
Water	7.2	-2.1	-2219	487.6	0.3

and estimated using UNIFAC method. The binary parameters have the temperature dependence function for NRTL model:

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (\text{A.1})$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\text{A.2})$$

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad (\text{A.3})$$

User-defined NRTL parameters of the major component and the solvent NMP are reported in Table A.1.