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Short communication

Process improvement on separating C4 by extractive distillation

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Abstract

C4 mixtures are usually separated by extractive distillation with acetonitrile (ACN) and *N*,*N*-dimethylformamide (DMF) methods in industry. These two methods were modified to improve the extractive distillation process in this work. Vapor–liquid equilibrium (VLE) models for the ACN and DMF methods were established with the Wilson equation. In terms of the models the extractive distillation processes were improved by means of a computer simulation software. The improvement to the ACN method was such that liquid load in the second extractive distillation column was significantly decreased and there were few changes on the equipment. Improvement to the DMF method was also made by replacing tray configuration and decreasing the times of butadiene phase changes. Both improvements are closely connected with the C4 practical production and are easily accomplished. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: ACN/C4; DMF/C4; Extractive distillation; VLE; Process improvement

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1. Introduction

Extractive distillation is more and more commonly applied in industry, and becomes an important separation method in petrochemical engineering. It is mainly used in the following two cases. One is for separating hydrocarbons with close boiling point, such as C4 mixture, the other for separating mixtures which exhibit an azeotrope. In recent years, the continuous modification of ethylene plants has promoted the production of C4 compounds. Among C4 compounds, butadiene-1,3 which is an important basic organic raw material, can be separated by extractive distillation. However, it is well-known that the disadvantage of extractive distillation is its high solvent mass and feed mass ratio, which leads to difficulty in improving butadiene capacity.

In most cases the solvents for separating C4 are acetonitrile (ACN) and *N*,*N*-dimethylformamide (DMF) [1–5]. It is very important to know the operation conditions and production capacity of both the ACN and DMF methods in order to meet the needs of modification of ethylene plants. Since it is not economical to construct additional plants to separate C4 mixture, the simulation of the original processes is required. In this work the vapor–liquid equilibrium (VLE) models for the ACN/C4 and DMF/C4 systems are put forward. With these models it is easy to simulate and calculate the separation process, and to obtain necessary information of the extractive distillation column. As a result, the separation process can be improved.

2. Process improvement of the ACN method

The key in the simulation process of separating C4 by extractive distillation with the ACN method is the selection of an accurate VLE model to solve the traditional equilibrium stage model (MESH equation) of the column. The VLE model given in Ref. [6] is just a modified Margules equation, which cannot be directly used in some chemical engineering simulation softwares, such as ASPEN PLUS, PROII and so on. While using the equation without transformation much time is required to program the process again and study the algorithm to shorten the run time, which is not advisable.

Therefore, it is necessary to transform the modified Margules equation into other forms, and the interaction parameters of equations that we select can be directly input to chemical engineering simulation softwares in order to know the detailed state in the columns. For the ACN/C4 system it

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Nomenclature

i, j	C4 components
L	liquid flow rate ($\mathrm{kg\,m^{-3}}$)
R	gas constant
T	temperature
V	vapor flow rate ($\mathrm{kg\,m^{-3}}$)
x	mole fraction in liquid phase

Greek letters

γ	activity coefficients
Λ	interaction parameter of Wilson equation ($\mathrm{J\,mol^{-1}}$)
ρ_V	density of vapor phase ($\mathrm{kg\,m^{-3}}$)
ρ_L	density of liquid phase ($\mathrm{kg\,m^{-3}}$)
σ	surface tension ($\mathrm{N\,m^{-1}}$)

is wise to select the frequently used Wilson equation which is suitable for systems composed of many components and can deduce the multi-components system from binary system. So the interaction parameters of the modified Margules equation should be transformed into that of Wilson equation. The transformation procedure is as follows:

1. The activity coefficients for a system with two components at infinite dilution at temperatures 50 and 75 °C are deduced from the modified Margules equation. For instances, if $x_1 = 0$ and $x_2 = 1$, then γ_1 at infinite dilution is able to be solved by the modified Margules equation at a given temperature.
2. By virtue of the data of activity coefficients at infinite dilution, the interaction parameters of the Wilson equation are correlated, and this step is obviously reverse to the above.

For multi-components systems the Wilson equation is given [7] by:

$$\ln \gamma_i = 1 - \ln\left(\sum_j x_j \Lambda_{ij}\right) - \sum_k \left(\frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}\right),$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right), \qquad \Lambda_{ii} = \Lambda_{jj} = 1$$

It is thought that $\Lambda_{ij} = 1$ for C4 hydrocarbons. C4 hydrocarbons are generally assumed to be ideal solution because they have similar molecular structure, molecular volume and molecular polarity. By simulation it found that this assumption has nearly no influence on the results.

In the range of normal temperature $\lambda_{ij} - \lambda_{ii}$ can be taken on as unchanging with temperature. The Wilson parameters of 15 components for the ACN/C4 system, which are correlated by the Marquardt method, are listed in Tables 1 and 2. The used molar volumes ($\mathrm{cm^3\,mol^{-1}}$) of 15 components are

Table 1
Interaction parameters of Wilson equation (unit: $\mathrm{J\,mol^{-1}}$)[a]

Number	1	2	3	4	5	6	7	8
1	0	74.34	330.12	328.04	253.49	257.22	260.42	152.49
2	314.44	0	759.92	781.72	679.85	661.75	665.67	459.03
3	118.93	361.78	0	0	0	0	0	0
4	97.12	367.88	0	0	0	0	0	0
5	57.55	271.82	0	0	0	0	0	0
6	61.72	249.53	0	0	0	0	0	0
7	72.28	262.02	0	0	0	0	0	0
8	35.62	98.40	0	0	0	0	0	0
9	67.96	246.04	0	0	0	0	0	0
10	8.09	136.34	0	0	0	0	0	0
11	49.45	194.57	0	0	0	0	0	0
12	−48.77	16.11	0	0	0	0	0	0
13	−39.90	68.63	0	0	0	0	0	0
14	−11.48	64.04	0	0	0	0	0	0
15	−26.59	80.28	0	0	0	0	0	0

[a] Number and corresponding components: (1) ACN; (2) water; (3) butane; (4) isobutane; (5) isobutene; (6) butene-1; (7) *trans*-2-butene; (8) propadiene; (9) *cis*-2-butene; (10) butadiene-1,3; (11) butadiene-1,2; (12) methyl acetylene; (13) butyne-1; (14) butyne-2; (15) VAC.

Table 2
Interaction parameters of Wilson equation (unit: $\mathrm{J\,mol^{-1}}$)[a]

Number	9	10	11	12	13	14	15
1	246.68	190.71	208.00	147.50	138.77	152.51	118.64
2	643.54	551.49	582.35	453.70	488.56	472.15	467.68
3–15	0	0	0	0	0	0	0

[a] Number and corresponding components: (1) ACN; (2) water; (3) butane; (4) isobutane; (5) isobutene; (6) butene-1; (7) *trans*-2-butene; (8) propadiene; (9) *cis*-2-butene; (10) butadiene-1,3; (11) butadiene-1,2; (12) methyl acetylene; (13) butyne-1; (14) butyne-2; (15) VAC.

Table 3
Operation parameter of the columns

	The first extractive distillation column	The second extractive distillation column
Theoretical plates	75	60
Top pressure (MPa)	0.60	0.52
Bottom pressure (MPa)	0.62	0.55
Top temperature (°C)	45.6	40.1
Bottom temperature (°C)	115.9	137.5
Solvent rate ($\mathrm{kg\,h^{-1}}$)	37947	7000
C4 rate ($\mathrm{kg\,h^{-1}}$)	5421	5000
Reflux ratio ($\mathrm{kg\,kg^{-1}}$)	3	2.5

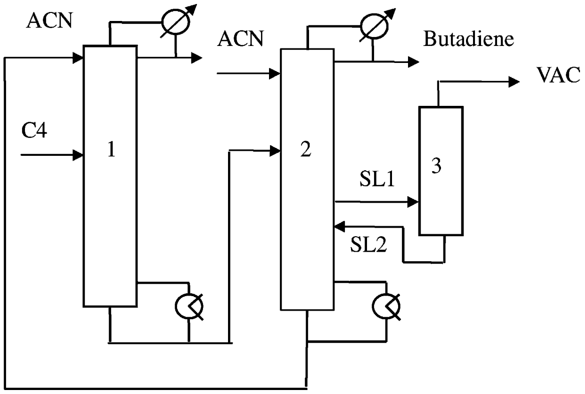

Fig. 1. The original process of extractive distillation with ACN method for separating C4: (1) the first extractive distillation column; (2) the second extractive distillation column; (3) flash column.

57.01, 18.00, 113.52, 121.08, 107.88, 107.88, 105.45, 79.64, 102.0, 98.35, 93.26, 100.15, 92.46, and 86.68, respectively.

The above Wilson parameters were put into the PROII (version 4.15) simulation software to calculate the key section of the process for separating C4, the extractive distillation column. We know that in the process simulation the enthalpy data of vapor and liquid phases are also important. Here the vapor enthalpy of each component is calculated by the modified Peng–Robinson (MPR) equation, and the addition of the each vapor enthalpy multiplied by mole fractions is the total vapor enthalpy. The liquid phase enthalpy is deduced from vapor phase enthalpy and evaporation heat.

The operation parameters of the columns are from the plant and are listed in Table 3 where theoretical plates include reboiler and condenser of the column and are numbered from the bottom. The C4 mixture are composed of butane, butene-1, *trans*-2-butene, *cis*-2-butene, butadiene-1,3 and vinylacetylene (VAC), the weight fractions of which are 0.0174, 0.3592, 0.0496, 0.0375, 0.5272 and 0.0091, respectively.

The comparisons of temperature and composition between the calculated and measured values from the plant are given in Tables 4 and 5, where the calculated values are in good agreement with those of the measured ones except the great deviation for *trans*-2-butene in Table 5 that may be due to its too low concentration and analysis error of gas chromatogram (GC). Anyway, it is shown that the present VLE model is accurate in some degrees. Thus, the process simulation and calculation of different operation conditions can be safely carried out.

The original process for separating C4 with ACN is shown in Fig. 1. We see that in Fig. 1 the feedstock is flowed into extractive distillation column 1. The solvent ACN enters the top sections of columns 1 and 2. The mixtures of butane and butene are discharged from the top of column 1. The product, butadiene-1,3 is obtained from the top of column 2. Alkyne hydrocarbons mainly containing VAC and drawn out through stream SL1, are removed from flash column 3. But SL2 stream is also returned into column 2. This is to say that column 2 and column 3 are thermally coupled.

Table 4
Comparison of temperature between the calculated values and measured values

	T (°C), the first extractive distillation column		T (°C), the second extractive distillation column	
	At the top	At the bottom	At the top	At the bottom
Measured values	45.6	115.9	40.1	137.5
Calculated values	47.8	123.8	41.5	138.8

Table 5
Comparison of composition between the calculated values and measured values

	Composition (wt.%), top of the first extractive distillation column		Composition (wt.%), top of the second extractive distillation column	
	Measured values	Calculated values	Measured values	Calculated values
Butane	6.16	5.84	0	0
Butene-1	79.24	79.27	0	0.02
trans-2-Butene	10.38	9.20	0.04	0.35
cis-2-Butene	4.15	3.72	2.18	2.52
Butadiene-1,3	0.07	1.22	97.78	96.98
VAC	0.0	0.0	<5 ppm	<5 ppm

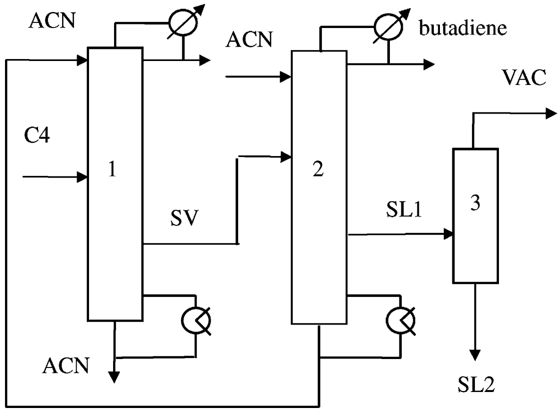

Fig. 2. The optimum process of extractive distillation with ACN method for separating C4: (1) the first extractive distillation column; (2) the second extractive distillation column; (3) flash column.

In the above original process there exists an obvious disadvantage, that is, the liquid load is very high in the lower section of the second extractive distillation column 2, which has negative influence on the tray efficiency and decreasing production capacity of butadiene-1,3. It is the current case that the demand for butadiene goes up gradually year by year. Moreover, the thermal coupling between columns 2 and 3 leads to the difficulty in operation and control. To solve this problem, a new optimization process was put forward as shown in Fig. 2. The vapor stream SV is drawn from the lower section of the first extractive distillation column 1 into the second extractive distillation column 2. SL1 mainly containing ACN and alkyne hydrocarbons is flashed in column 3. It can be seen that the thermal coupling in the optimization process is eliminated and operation and control would be more convenient.

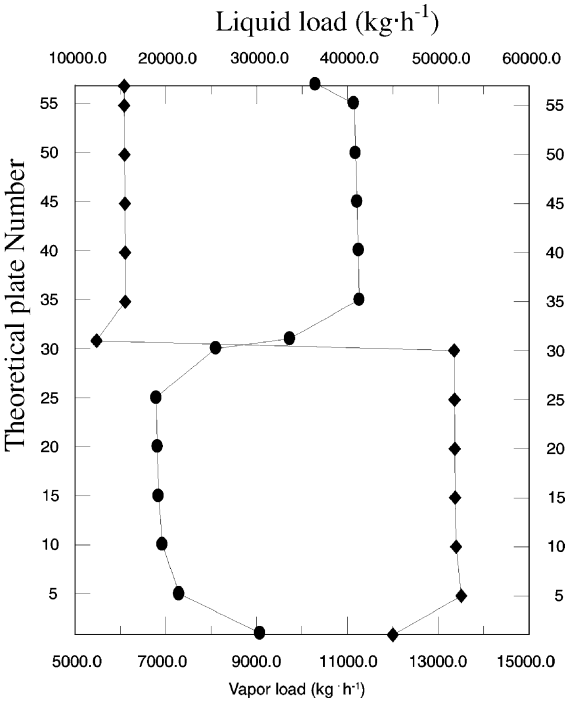

Fig. 3. The vapor and liquid load distribution diagram of the second extractive distillation column for the original process: (◆) liquid load in the column; (●) vapor load in the column.

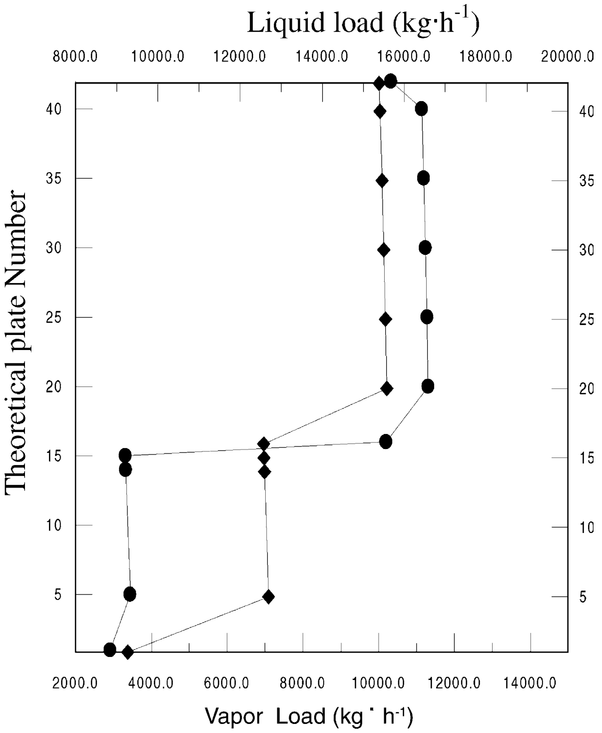

Fig. 4. The vapor and liquid load distribution diagram of the second extractive distillation column for the optimized process: (◆) liquid load in the column; (●) vapor load in the column.

By simulation it is found that the liquid load in the lower section of the second extractive distillation column 2 is effectively decreased from 51943 to 12584 kg h^{-1}, about 75.8% of the original process. This demonstrates that it is possible to further increase the yield of butadiene on the basis of old equipment. The vapor and liquid loads of the old and new processes are respectively illustrated in Figs. 3 and 4.

3. Process improvement of the DMF method

The separation process of DMF method is divided into two parts: the extractive distillation process and the butadiene refining process. These two parts are respectively improved in this work. Due to the high liquid load of the first extractive distillation column, the original double overflow valve trays cannot meet the needs of increasing capacity. Because both the columns and pipings are not easy to be altered in the extractive distillation process, the improvement strategy is to replace the double overflow valve trays with double overflow slant-hole trays [8,9] so as to raise the capacity. The double overflow slant-hole trays have ever been applied in a column

Table 6
Interaction parameters of the Wilson equation (unit: $J\,mol^{-1}$)[a]

Number	1	2	3	4	5	6	7
1	0.00	9148.42	6563.09	7043.26	6953.99	4950.44	2368.68
2	2692.47	0.00	0.00	0.00	0.00	0.00	0.00
3	835.84	0.00	0.00	0.00	0.00	0.00	0.00
4	1244.48	0.00	0.00	0.00	0.00	0.00	0.00
5	1333.81	0.00	0.00	0.00	0.00	0.00	0.00
6	−463.50	0.00	0.00	0.00	0.00	0.00	0.00
7	−2146.34	0.00	0.00	0.00	0.00	0.00	0.00

[a] Number and corresponding components: (1) DMF; (2) butane; (3) butene-1; (4) *trans*-2-butene; (5) *cis*-2-butene; (6) butadiene-1,3; (7) VAC.

for separating propane and propylene. In that case the feeds to be treated are raised above 50% with a tray efficiency similar to or higher than that of the valve trays and an energy save of 10% by decreasing pressure drop to about 1/3 of the original.

In the extractive distillation process the Wilson equation is selected as the activity coefficient model. The same treatment as the ACN/C4 system was made to deal with the experimental data was reported in Ref. [10]. However, in this reference only two systems, 1,3-butadiene/DMF and 1-butene/DMF, are investigated. Therefore, in the first step the data on these two systems are used to deduce the UNIFAC interaction parameters because the concerned UNIFAC groups are a few for DMF/C4 system. Then, the UNIFAC equation is transformed into Wilson equation. The interaction parameters of Wilson equation are given in Table 6.

The key equipment of the first part, the first extractive distillation column, was calculated. The feed compositions of C4 mixture are the same as those of the ACN method. The operational parameters of the first extractive distillation column are given in Table 7 where theoretical plates include reboiler and condenser of the column and are numbered from the bottom. The calculated values and those measured from the plant are listed in Table 8 where *cis*-2-butene and *trans*-2-butene are regarded as a whole, 2-butene. Comparison shows that the calculated results are reliable. The vapor and liquid load, which will provide the important information for the tray design of the columns are listed in Table 9.

Table 7
Operation parameters of the first extractive distillation column

	The first extractive distillation column
Theoretical plates	70
Top pressure (MPa)	0.54
Bottom pressure (MPa)	0.56
Top temperature (°C)	42.1
Bottom temperature (°C)	130.0
Solvent rate ($kg\,h^{-1}$)	136000
C4 rate ($kg\,h^{-1}$)	17000
Reflux ratio ($kg\,kg^{-1}$)	2.5

C4 mixture is usually separated under middle pressure by extractive distillation. In general the plate trays, especially double overflow trays, are used as internal fittings. However, slant-hole trays are selected in the design of the first extractive distillation column, which are very excellent and extensively applied in the industry. The slant-hole tray has opposite stagger arrangement of slant-holes, which causes rational flowing of vapor–liquid, level blowing of vapor, permission of a large vapor speed, no mutual interference, steady liquid level and high efficiency of trays. On the basis of slant-hole trays, after studying and analyzing the columns with multiple downcomer (MD) trays, we invent a new-type multi-overflow compound slant-hole trays [11], which adopt the downcomer similar to MD trays. The number of downcomers used is not too many, but only two.

Table 8
Comparison of the calculated and measured values

	T (°C)		The top composition (wt.%)			
	The top	The bottom	Butane	Butene-1	2-Butene	Butadiene-1,3
Measured values	42.1	130.0	5.00	80.00	15.00	≤0.3
Calculated Values	44.9	129.4	6.98	76.87	16.14	≤0.3

Table 9
Load of vapor and liquid phases in the first extractive distillation column

Plate number	V ($m^3\,h^{-1}$)	L ($m^3\,h^{-1}$)	ρ_V ($kg\,m^{-3}$)	ρ_L ($kg\,m^{-3}$)	σ ($N\,m^{-1}$)
6–44	3448	212.9	11.76	794.0	0.02430
45–74	3765	259.6	13.16	748.3	0.02076

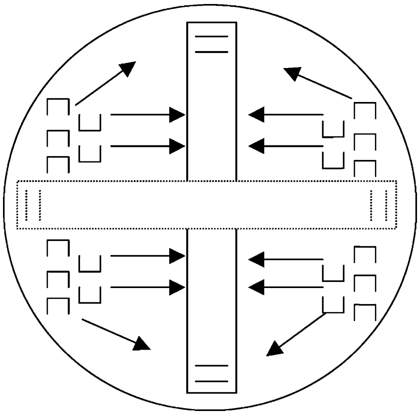

Fig. 5. Configuration of multi-overflow (double flow) slant-hole tray.

Table 10
Design results of the first extractive distillation column

	Plate number	
	6–44	45–74
Column diameter (m)	2.5	2.5
Tray spacing (m)	0.38	0.38
Slant-hole area ratio (%)	6	6
Overflow type	Double overflow	Double overflow
Weir length (m)	4.8	4.8
Weir width (m)	0.4	0.5
Weir height (m)	0.03	0.03
Downcomer gap (m)	0.1	0.1
Downcomer area (m^2)	0.96	1.2
Overflow intensity ($m^3\,m^{-1}\,h^{-1}$)	44.35	54.08
Vapor velocity for diameter ($m\,s^{-1}$)	0.195	0.213
Hole *F*-factor	11.16	12.89
Liquid height in the tray (mm)	67.21	72.47
Tray pressure drop (mm H_2O)	50.41	60.02
Downcomer pressure drop (mm H_2O)	22.07	32.82
Liquid height in the downcomer (mm H_2O)	72.48	92.84
Residence time (s)	5.03	5.16
Vapor entrainment	0.005	0.010

The downcomer has the features of simple structure, longer flowing distance of liquid, higher capacity of column and high efficiency of trays. The configuration of the double overflow slant-hole trays is diagrammed in Fig. 5. In terms of the vapor and liquid load of the first extractive distillation column, the tray parameters were obtained by a tray software that we programmed for modification. The character of the tray software is presented in detail in Ref. [12]. The parameters listed in Table 10 are valid because the designed values are within the range of normal operation condition.

For the butadiene refining process, the original process is drawn in Fig. 6. In the original process butadiene containing alkyne hydrocarbons is first removed from the top of the second extractive distillation column 1, and then is condensed and enters into the first distillation column 2 for removal of low-boiling point components. Afterwards the high-pure butadiene is obtained at the top of the second distillation column 3. By analyzing this process, it can be seen that butadiene experiences evaporation and condensation repeatedly, having phase change many times in the butadiene refining section. The whole procedure of phase change is given below:

$$\text{liquid} \rightarrow \text{vapor} \rightarrow \text{liquid} \rightarrow \text{liquid} \rightarrow \text{vapor} \rightarrow \text{liquid}$$

Butadiene goes through twice evaporation and twice condensation altogether.

With a view to decrease phase change of butadiene, the main modification shown in Fig. 7 is that the first distillation column 2 and the second distillation column 3 are exchanged with each other. The vapor V_1 at the top of the second extractive distillation column 1 is directly fed into the second distillation column 3 by pressure difference between two columns. Then butadiene is drawn from the top of the former second distillation column 3 and enters into the former first distillation column 2. The whole procedure of phase change

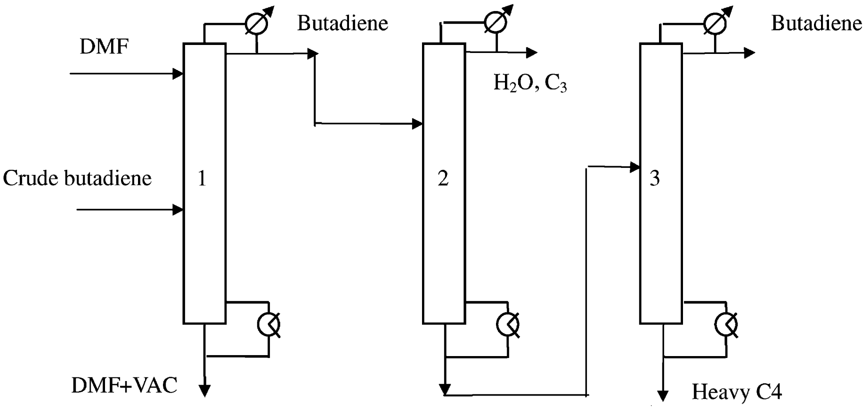

Fig. 6. The original process of butadiene refining: (1) the second extractive distillation column; (2) the first distillation column; (3) the second distillation column.

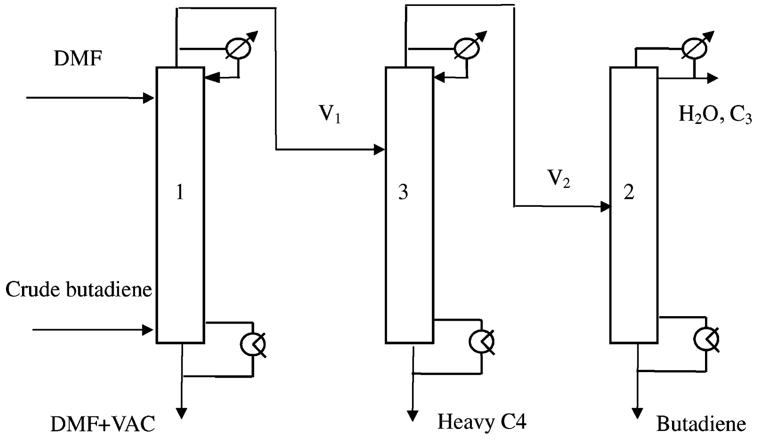

Fig. 7. The improved process of butadiene refining section: (1) the second extractive distillation column; (2) the first distillation column; (3) the second distillation column.

Table 11
Results of the existing and improved processes

	Original process		Optimum process	
	Q_C (kW)	Q_R (kW)	Q_C (kW)	Q_R (kW)
The second extractive distillation column	1969.6	2636.3	1116.9	2636.4
The first distillation column	1394.2	1405.8	1349.1	502.4
The second distillation column	3958.7	3947.2	738.3	3077.0
Total duty	7322.5	7989.3	3204.3	6215.8
Percent of saved energy (%)	–	–	56.2	22.2

is given as follows:

liquid → vapor → vapor → liquid

Thus, butadiene goes through condensation only once altogether. As a result, the improved process is evidently more advantageous than the original process.

Assuming that the flow rate of streams and reflux ratio of columns remain constant, three columns of the original and improved processes are simulated by PROII software. In the simulation of the first distillation column, Soave–Redlich–Kwong (SRK) equation which is especially suitable for the systems with water and hydrocarbons is used. The results are listed in Table 11.

From the above it can be found that the total heat duty of condensers in the improved process is saved by 56.2%, with the total heat duty on reboilers 22.2% of the original. In addition, there is no new equipment added. Because of the reduction of vaporization and condensation times in the improved process, heat polymerization of butadiene is also relieved in some degrees. The way of improving the butadiene refining part of the DMF method is also applied to the ACN and NMP methods because the their processes in this part are almost identical [13].

4. Conclusion

The extractive distillation processes for separating C4 mixture with solvents ACN and DMF were thoroughly analyzed and improved. The Wilson equation, which can be extended from binary components to multi-components, was selected to simulate the processes of the ACN and DMF methods. The parameters of the VLE model were correlated by the Marquardt method. The correlated parameters were convenient to be put into the simulation software. It was found that the calculated and measured values showed good consistency, and this proved that the VLE model was reliable.

The ACN method was improved, with liquid load decrease of 75.8% in the second extractive distillation column compared with the existing process. The improvement will promote the increase of butadiene capacity. At the same time the way to draw alkyne hydrocarbons from the column was changed. The thermally coupling was eliminated, and operation and control were more convenient.

On the other hand, for the DMF method the double overflow valve trays were replaced by novel slant-hole trays in the first extractive distillation column. The slant-hole trays were designed with the help of a programmed tray software. In the butadiene refining part, the times of butadiene phase change were decreased, and the heat duties of condensers and reboilers were reduced accordingly. All the improvements are easily accomplished in industrial practice.

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