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Liquid-holdup regions research of novel reactive distillation column for C5 fraction separation

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ABSTRACT

Recent advances in technologies of reactive distillation (RD) offer various design concepts for chemical processes. For separation of cracking C5 fraction, one of the main challenges is improving the conversion of cyclopentadiene (CPD) and the recovery of isoprene (IP). In the current work, a novel reactive distillation column with several liquid-holdup regions was designed, since it allows long residence time and provides flexibility for narrowing the efficiency gap between reaction and distillation. By use of Aspen Plus, a corresponding mathematic model was established and verified to be accurate. Following that, comprehensive studies were carried out for the design of liquid-holdup regions position. Details and principles about the separation performance with the liquid-holdup regions were revealed and optimized parameters were determined with 100 theoretical plates, feed position of 35th plate, and four liquid-holdup regions at 25th, 60th, 75th and 90th plate. The designed RD column could well meet the technical requirement, and influence of other important factors including residence time, operating pressure and reflux ratio was further investigated.

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1. Introduction

The cracking C5 fraction is the byproduct in the steam cracking of the naphtha and other heavy hydrocarbon in ethylene plants, in which isoprene (IP), cyclopentadiene (CPD) and pentadiene are the main components and account for 40 wt%–60 wt% in total [1–6]. These dienes, especially IP, are important synthetic materials due to their high chemical activities. For the synthesis utilization, the purity requirement for IP is generally rigorous ($IP \geq 99.8\%$ and $CPD \leq 3 \times 10^{-6}\%$), so a good separation of IP and CPD is crucial [7–9].

As the boiling point of IP (34.1 °C) is close to that of CPD (41.5 °C), it is hard to separate them by conventional distillation. Instead, the thermal dimerization method has been widely employed in industry for better separation of the C5 fraction. In the thermal dimerization process, C5 fraction is heated for 1–3 h (< 130 °C) to convert CPD to dicyclopentadiene (DCPD) in the dimerization reactor. In the subsequent operation, DCPD and IP can be easily separated by conventional distillation because of the higher boiling point of DCPD (166.6 °C) [10,11]. However, besides the self-dimerization of CPD in the dimerization reactor, the self-dimerization of IP and dimerization of CPD with IP (or 1,3-butadiene (1,3-BD)) also occur, thus producing $(IP + IP)_{dimer}$ and $(CPD + IP)_{dimer}$ (or $(CPD + BD)_{dimer}$) byproduct, respectively [12]. Although the

conversion ratio of CPD can exceed 80%, the recovery of IP is only 88%–92% which is much lower than the requirement of 98% [13].

On the other hand, reactive distillation, a hybrid process where chemical reaction and distillative separation are performed simultaneously, was widely researched for esterification [14–16], etherification [17,18], transesterification [19,20], alkylation [21] and dimerization [22] process. In the 1990s, Hu *et al.* found that reactive distillation processes were very effective to separate CPD from the cracking C5 [4]. In the reactive distillation column, IP accumulates at the top whereas CPD flows towards the bottom due to their different boiling points. Meanwhile, CPD has a much higher dimerization activity and therefore is largely converted to DCPD on the feed plate. As a consequent result, the concentration of CPD decreases rapidly both upwards and downwards. The lower concentration of CPD along the column reduces the copolymerization of CPD with IP and thus improves the recovery of IP. In this sense, it is important to study the reactive distillation of C5 fraction for process intensification. In spite of some simulation studies on the C5 reactive distillation (RD) reported in the literatures [23–25], experimental researches are still limited. Even in the reported simulation studies, the effects of process parameters, such as the number of theoretical plates, feed position, reflux ratio and residence time, were not considered.

As is widely perceived, the coordination of distillation temperature and reaction temperature is extremely important in reactive distillation process. In C5 RD, however, limited by the distillation temperature, the self-dimerization of CPD is not efficient enough, while the side reactions, especially dimerization of CPD with IP, cannot be neglect. Hence

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in this work, a novel reactive distillation column with liquid-holdup regions was designed for the separation of cracking C5 fraction and a corresponding mathematic model was established in Aspen Plus. Using the model, the number of theoretical plates, feed position and liquid-holdup regions position were optimized in detail, and the influences of some important factors were also investigated.

2. Experimental

2.1. Reagents

The cracking C5 fraction used in this experiment is a by-product of the ethylene unit cracking with naphtha in a certain petrochemical corporation. Its composition is listed in Table 1. The mass fractions of IP, CPD and DCPD are 18.03%, 16.97% and 2.17%, respectively.

2.2. Apparatus

As shown in Fig. 1, the liquid phase flowing down from the packing bed 1 came into contact with the gas phase rising from the riser 2, and then flowed down from the overflow weir 5 to the packing bed below. The gas rising from the bottom of the lower packing bed flowed into the liquid phase in the liquid-holdup region to prevent the formation of dead zones. The RD column was 50 mm in diameter and packed with $\Phi 4$ mm $\times$ 4 mm stainless steel cannon rings. There were five packing sections connected with flanges in the column, the length of which were respectively 1, 1.5, 0.5, 1 and 1.5 m from top to bottom. Six thermocouple points were installed on the column, denoted as T1–T6. For ease of analysis, seven sampling ports were installed at the feed tank, at each hold-up region from top to bottom and at the reflux tank, respectively. The feed preheater, the reboiler and the thermal preservation of the column were all electrically heated while the cooler and the condenser were cooled with the cooling water.

A schematic diagram of the experimental apparatus is shown in Fig. 2. The apparatus can be divided into four parts. The first part is the feedstock part containing the feed tank 1, the feed pump 2, and the feed preheater 3. The cracking C5 fraction is pumped from tank 1 to the RD column after being heated to 60 °C by preheater 3. The second part is the reactive distillation 4 where the mass transfer and chemical reactions of C5 occurred. The third part consists of the condenser 5, the reflux tank 6, the reflux pump 7 and the overhead product tank 8. The reflux rate is controlled by a dosing pump. The last one is the bottom discharge part including the product cooler 9 and the product tank 10 at the column bottom.

3. Reaction Kinetics

In spite of the complex composition of the cracking C5 fraction, only three types of detected reactions, namely the self-dimerization, the co-dimerization and the multi-polymerization exist in the polymerization process of C5 fraction. Under the operating temperature, the dimerization of CPD producing DCPD is the main reaction, while other

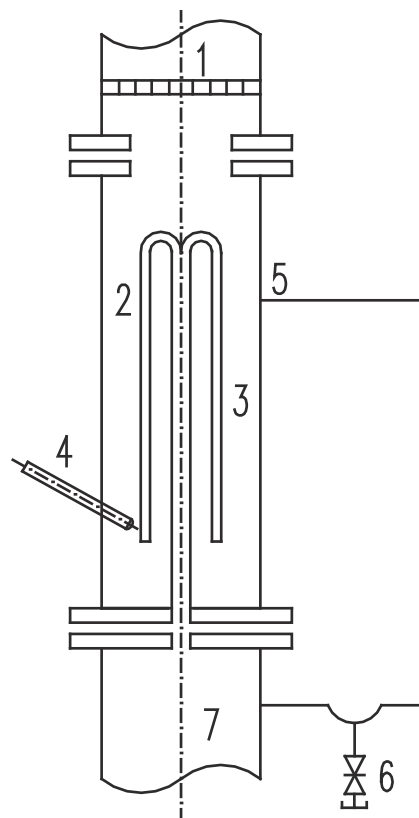


Fig. 1. The schematic diagram of the connection of holdup region and packing bed in RD. 1—upper packing bed; 2—gas riser; 3—holdup region; 4—thermocouple point; 5—overflow weir; 6—sample point; 7—lower packing bed.

reactions including the self-dimerization of IP, co-dimerization of CPD with IP and 1,3-BD are significant side reactions [23]. Though the multi-polymerization, which produces polymers, may cause serious implications, experiment studies and industrial productions show that it is negligible. Therefore only these two types of reactions were considered in this work.

- (1) Self-dimerization of CPD and its reverse reaction (main reaction)



- (2) Self-dimerization of IP



Table 1
Composition of steam cracking C5

Component	Composition/wt%	Component	Composition/wt%	Component	Composition/wt%
Isobutane + 1-butene	0.76	1,3-Butadiene	2.04	n-Butane	0.30
1-Butylene – 2-alkyne	0.00	trans-2-Butene	0.70	1-Butyne	0.00
cis-2-Butene	1.00	1,2-Butadiene	0.20	3-Methyl-1-butene	0.46
Isopentane	9.36	1,4-Pentadiene	1.96	2-Butyne	0.57
1-Pentene	3.08	2-Methyl-1-butene	4.65	n-Pentane	11.09
Isoprene(IP)	18.03	trans-2-Pentene	2.38	1-Pentyne	0.06
cis-2-Pentene	1.46	2-Methyl-2-butene	2.29	trans-1,3-Pentadiene	7.07
1-Pentene-3-alkyne	0.06	Cyclopentadiene(CPD)	16.97	cis-1,3-Pentadiene	3.58
Cyclopentene	2.78	Cyclopentane	1.15	Dicyclopentadiene (DCPD)	2.17
(CPD + BD) _{dimer}	1.64	(CPD + IP) _{dimer}	1.32	(IP + IP) _{dimer}	2.27

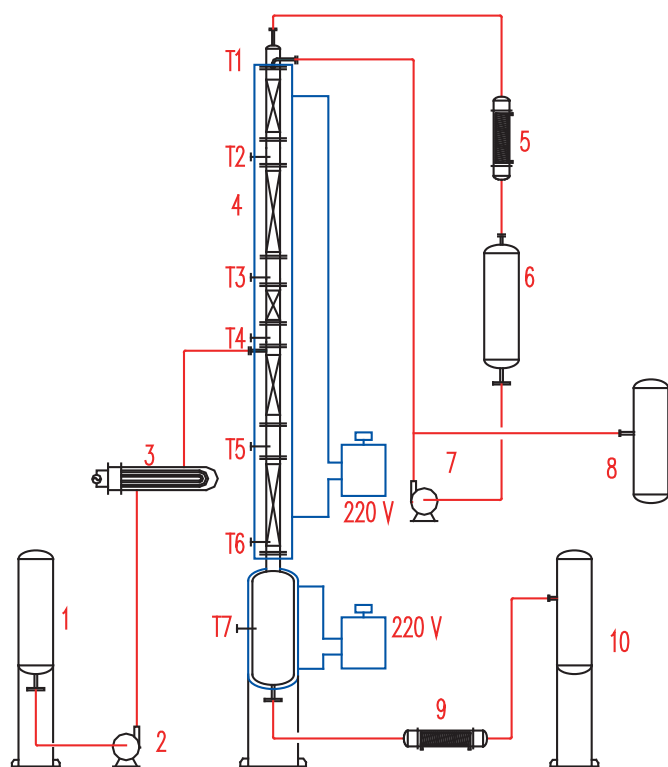


Fig. 2. Schematic diagram of the experimental apparatus. 1—Feed tank; 2—feed pump; 3—pre-heater of material; 4—RD; 5—cooler; 6—reflux accumulation; 7—reflux pump; 8—product tank at column top; 9—product cooler at column bottom; 10—product tank at column bottom; T1–T7: thermocouple points.

(3) Co-dimerization of CPD with IP



(4) Co-dimerization of CPD with 1,3-BD



The reverse reactions of (2)–(4) are weak and neglected in this work.

The reaction rate constant k of above Reactions (1)–(4) can be expressed as follows:

$$k = A \exp(-E/RT) \quad (5)$$

Some works have been carried out to study the kinetics of Reactions (1)–(4), but the temperature involved ranging from 80 to 130 °C was not in accordance with RD operation condition [25,26]. According to our previous work [27], the kinetics parameters of the reactions are listed in Table 2.

4. Mathematic Model

The reactive distillation is complex because the reaction and distillation take place simultaneously. To simplify the problem in this work, the balances of mass, phase and heat in the RD column were all studied in terms of the RADFRAC model in Aspen Plus with some reasonable assumptions: (1) only the dimerization reactions were considered; (2) the gas–liquid phase equilibrium was reached at every plate without

Table 2
Parameter values of the reaction kinetic model

$k/\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	A	$E/\text{J} \cdot \text{mol}^{-1}$
k_1	4.39×10^5	6.58×10^4
k_2	5.70×10^{12}	1.42×10^5
k_3	3.29×10^{14}	1.53×10^5
k_4	5.88×10^4	6.45×10^4
k_5	2.27×10^5	7.42×10^4

considering the disturbance of dimerizations; (3) all dimerizations were dominated by the reaction kinetics; (4) heat loss was negligible.

The RD diagram was shown in Fig. 3, in which the column plates were numbered as 1, 2, ..., N from the top to the bottom. The first stage represented the condenser and the N th stage was the reboiler. There was a feed inlet at every stage. Under the above assumptions, the balance equations for the j th stage are listed as follows:

(1) Mass balance:

$$L_{j-1}x_{ji} - V_jy_{ji} + V_{j+1}y_{j+1i} - L_jx_{ji} + F_jx_{ji} + r_{ji}t_j = 0 \quad (6)$$

$$1 \leq i \leq C, 2 \leq j \leq N-1 \quad (7)$$

when $j = 1$ (condenser), then:

$$-V_1y_{1i} + V_2y_{2i} - (L_1 + D)x_{1i} + r_{1i}t_1 = 0 \quad (8)$$

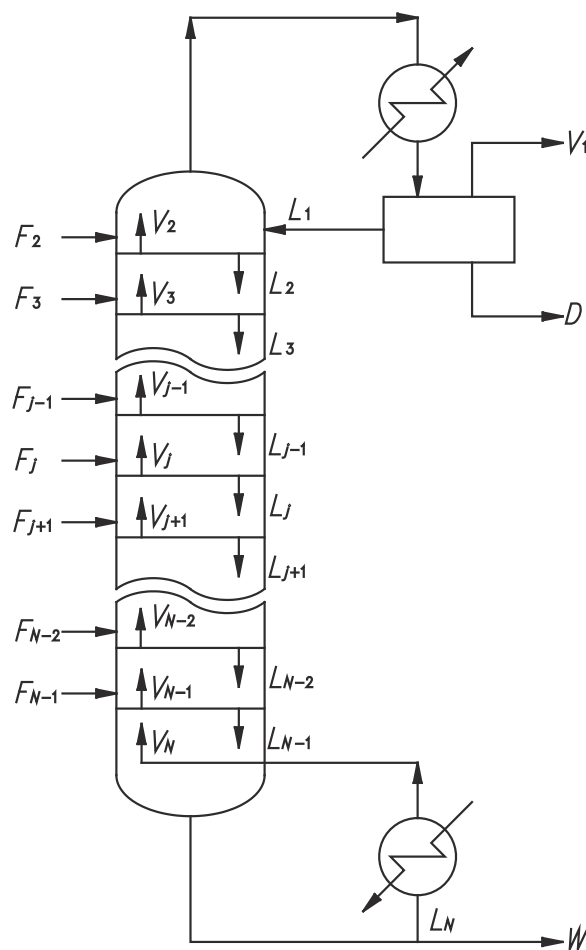


Fig. 3. The diagram of reactive distillation column of separation cracking C5 fraction.

when $j = N$ (reboiler), then

$$L_{N-1}x_{Ni} - V_N y_{Ni} - (L_N + W)x_{Ni} + r_{Ni}t_N = 0 \quad (9)$$

(2) Phase balance:

$$y_{ji} + k_{ji}x_{ji} = 0 \quad (10)$$

$$k_{ji} = \left[\frac{\gamma_{ji} \phi_{ji}^0 p_{ji}^0}{(\phi_{ji} p_{ji})} \right] \exp \left[\frac{V_{ji} (p_j - p_{ji}^0)}{RT_j} \right] \quad (11)$$

activity coefficient of liquid (γ) and fugacity coefficient of vapor (ϕ) are calculated in UNIFAC equation [28].

(3) Normalized equations:

$$\sum_{i=1}^C x_{ij} = 1 \quad (12)$$

$$\sum_{i=1}^C y_{ij} = 1 \quad (13)$$

(4) Enthalpy balance:

$$L_{j-1}h_{j-1}^L + V_{j+1}h_{j+1}^V - L_jh_j^L - V_jh_j^V + F_jh_j^F + \sum_{i=1}^C r_{ji}tQ_{ji}^r + Q_j = 0 \quad (14)$$

when $j = 1$ (condenser), then:

$$V_2h_2^V - (L_1 + D)h_1^L - V_1h_1^V + \sum_{i=1}^C r_{1i}tQ_{1i}^r + Q_1 = 0 \quad (15)$$

when $j = N$ (reboiler), then:

$$L_{N-1}h_{N-1}^L - V_Nh_N^V - (L_N + W)h_N^L + \sum_{i=1}^C r_{Ni}tQ_{Ni}^r + Q_N = 0 \quad (16)$$

(5) Reaction kinetic equations:

$$r_{im} = k_{im}C_iC_m \quad (17)$$

$$k_{im} = A \exp(-E_a/RT) \quad (18)$$

$$r_i = \sum_{i=1}^C r_{im} \quad (19)$$

$$1 \leq m \leq C$$

when $i = m$, Eqs. (17)–(19) represent the kinetic model of the self-dimerization of component i .

5. Results and Discussion

5.1. Experiment of reactive distillation

5.1.1. Number of theoretical plates

The number of theoretical plates is one of the major evaluating parameters affecting the separation efficiency in a distillation column. In this work, *N*-hexane and methyl cyclopentane were selected to determine the number of theoretical plates because of their easy separation. The mixture of *N*-hexane and methyl cyclopentane was rectified in the RD column (Fig. 2) with total reflux at the atmospheric pressure. After

the temperature profile was no longer changing, samples at both the top and the bottom were taken and analyzed (Table 3).

Table 3

Composition of top product and bottom product

	<i>N</i> -hexane/wt%	Methyl cyclopentane/wt%
Top product	85.19	14.81
Bottom product	17.35	82.65

Then the number of theoretical plates can be calculated by Fenske's correlation, *i.e.*

$$N_{\min} = \lg[(x_1/(1-x_1))_D/(x_1/(1-x_1))_W] / \lg \alpha_{12} \quad (20)$$

where the subscripts 1 and 2 respectively denote the light and heavy components, the subscripts D and W respectively represent the top and bottom products and α_{12} is the relative volatility between components 1 and 2 ($\alpha_{12} = 1.0897$ under the atmospheric pressure). The total number of theoretical plates was determined to be 38.5 and hence the number in each bed was obtained (see Table 4).

Table 4

Number of theoretical plates in each packing bed

No. of packing bed	Length/m	Theoretical plates
1	1	7
2	1.5	10.5
3	0.5	3.5
4	1	7
5	1.5	10.5

5.1.2. Measurement of liquid holdup

The liquid holdup is another critical parameter for the reactive distillation because it determines the residence time. In this work, the liquid holdup was defined as the total volume of the liquid at the pack surfaces as well as that in the pack pores, the holdup regions and the column bottom.

The liquid volume from each holdup region was 224 ml; therefore the sum for the four holdup regions is 896 ml. When the RD column was operated under the normal conditions given in Table 5, the feed and the reflux were shut down and the products drawing from the top and the bottom was stopped, and the liquid level was recorded. At this time, the liquid level in the bottom was 60% with the corresponding holdup of 2182 ml. After the column was cooled down, the volume of liquid at the bottom was 4657 ml with 2475 ml increases. Consequently, the liquid holdup of the RD column was 3371 ml.

Table 5

Operating conditions in experiments

	Experiment a	Experiment b
Feed plate	22	22
Feed flow/kg · h ⁻¹	0.76	0.93
Reflux rate/L · h ⁻¹	15	18
Top product/kg · h ⁻¹	0.39	0.48
Bottom product/kg · h ⁻¹	0.37	0.45
Top pressure/MPa	0.145	0.145
Bottom temperature/°C	85.4	85.4
Residence time/s	1333	1111

Note: Residence time = (Reflux rate / liquid holdup) × 3600 s.

5.1.3. Validation of mathematic model

To verify the accuracy of the mathematic model, the reactive distillation process was investigated by both experimental and simulated tests under the same conditions listed in Table 5. Slightly different from the

experiments, the calculated number of theoretical plates was 42, in which the first plate and the last one represented the condenser and the reboiler respectively. In addition, the liquid-holdup regions were not included in theoretical plates in the simulation. The liquid volume was 64 ml at one plate, 224 ml in every holdup regions and 2182 ml in the column bottom.

As shown in Fig. 4, the temperature profile in the column obtained by the simulation was close to that in experiments. The slight difference was probably caused by the heat loss of the column, which was not considered in the simulations. In addition, the temperature along the column ranged between 50 and 90 °C which was covered by the applicability region of the reaction kinetics parameters to ensure the model accuracy. According to the calculated reaction rate constant, co-dimerization of CPD with IP is the main side reaction in this temperature range.

Comparing the concentration distribution of IP, CPD and DCPD shown in Fig. 5, good agreement between the simulation and experiment was achieved. Moreover, the simulation results shown in Table 6 also matched well with the experiment results with a relative error less than 2%. On the other hand, it was found that a longer residence time was favorable to increase the conversion of CPD. As a consequence result, the separation efficiency of IP was also benefited. However, the recovery of IP was much lower than 98% and the concentration of IP in the bottom reached up to 4.65%. Such results suggested that 42 theoretical plates were inadequate and detailed optimization of process parameters was needed to ensure the recovery of IP larger than 98%.

5.2. Simulation of reactive distillation

In general, for the separation of C5 fraction, there are three main indexes should meet the requirement, namely, the recovery of IP is larger than 98%, the conversion of CPD is larger than 90% and the selectivity to DCPD is larger than 98%. Due to the constraints and limitations in the experimental study, some of the important RD design parameters could not be studied experimentally. The validated mathematic model was hence used for further research.

5.2.1. Preliminary determination of number of theoretical plates and feed position

For the original RD column, theoretical plates are far from adequacy. It should be note that, in this RD column, reactions mostly occur in the liquid-holdup regions, so the number of theoretical plates mainly affects the distillation efficiency. Therefore, the number of theoretical plates was firstly investigated without considering the liquid-holdup regions. As shown in Fig. 6(A), the recovery of IP increased rapidly with the increases of number of theoretical plates ranging from 50 to 100, but improved slightly when the number of theoretical plates was more than 100. On the other hand, the conversion of CPD increased with the increases of number of theoretical plates in the range of 50 to 120 due to the increasing of residence time, but the maximum CPD conversion with 120 theoretical plates was only 78.6%, which indicated that simply

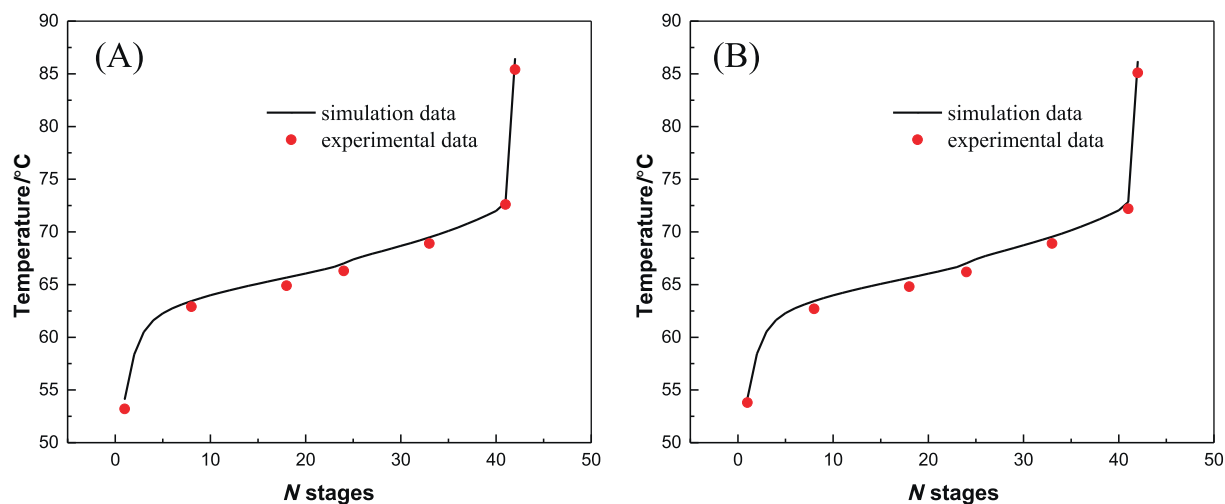


Fig. 4. Temperature profile in the RD column. (A) Feed flow: $0.76 \text{ kg} \cdot \text{h}^{-1}$, Reflux rate: $15 \text{ L} \cdot \text{h}^{-1}$. (B) Feed flow: $0.93 \text{ kg} \cdot \text{h}^{-1}$, Reflux rate: $18 \text{ L} \cdot \text{h}^{-1}$.

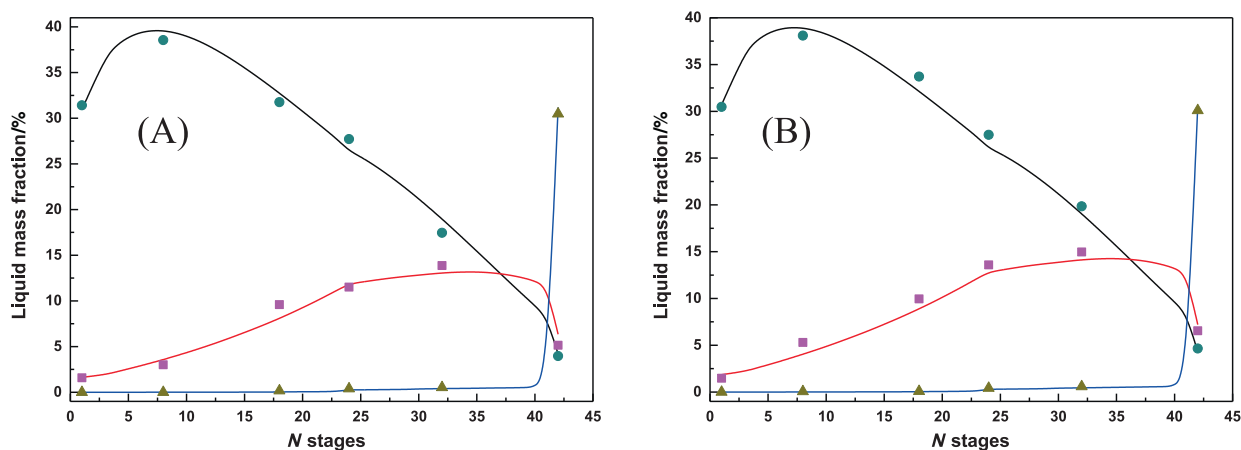


Fig. 5. Liquid concentration profiles in the RD column. (A) Feed flow: $0.76 \text{ kg} \cdot \text{h}^{-1}$, Reflux rate: $15 \text{ L} \cdot \text{h}^{-1}$. (B) Feed flow: $0.93 \text{ kg} \cdot \text{h}^{-1}$, Reflux rate: $18 \text{ L} \cdot \text{h}^{-1}$. — simulation data; ● IP experimental data; ■ CPD experimental data; ▲ DCPD experimental data.

Table 6

Comparison of the experimental and calculated results of the RD

	Experiment a			Experiment b		
	Experiment	Simulation	Relative error	Experiment	Simulation	Relative error
Conversion of CPD/%	80.05	79.31	0.92	76.88	75.81	1.39
Selectivity of DCPD/%	96.21	96.65	0.46	94.96	96.11	1.21
Recovery of IP/%	89.43	88.07	1.52	87.25	87.90	0.74

Note: Conversion of CPD = difference in mass flow of inlet and outlet of CPD/feed mass flow of CPD.

Selectivity of DCPD = difference in mass flow of inlet and outlet of DCPD/difference in mass flow of inlet and outlet of CPD.

Recovery of IP = top product mass flow of IP/ feed mass flow of IP.

adding the number of theoretical plates can hardly make the RD column meet the design requirement. As a practical remark, 100 theoretical plates were recommended to ensure the RD results.

The feed position determines the number of column plates in both the rectifying and stripping sections and hence has influence on the separation results. As for RD column, proper feed position is especially important, for it can minimize the contact of CPD with IP and hence reduce the side reaction. Shown in Fig. 6(B), the recovery of IP increased first and then decreased when the feed position moved downwards from the 10th plate to the 80th plate with the maximum IP recovery obtained between the 30th to 40th plates. Meanwhile, the selectivity to DCPD showed similar variation trend, so the feed stage was selected at the 35th plate.

5.2.2. Determine of liquid-holdup regions

The design of liquid-holdup regions is the core of this study. Replacing a theoretical plate with a liquid-holdup region will significantly increase the residence time, hence enhancing the CPD conversion. The side reactions, however, have also been improved somewhat, and consequently reduced the recovery of IP and selectivity to DCPD. Proper location of liquid-holdup regions is critical for the design of the RD column. So, the generation rate of DCPD as well as the ratio of the generation rate of DCPD and $(\text{CPD} + \text{IP})_{\text{dimer}}$ on each plate were taken into account as research objects (Fig. 7). The changes of recovery of IP, conversion of DCP and selectivity to DCPD with the increase of number of liquid-holdup regions are shown in Fig. 8. Residence time of all the liquid-holdup regions was preliminarily set as 200 s.

Shown in the curve without liquid-holdup region (Fig. 7(A)), the maximum selectivity occurring around 90th plate reached 330 due to the large concentration difference between CPD and IP in this area. Meanwhile, the generation rate of DCPD was also considerable. It is undoubtedly that the first liquid-holdup region installed in this area could

benefit the dimerization of CPD but also ensure the selectivity to DCPD. When the 90th plate was set as the first liquid-holdup region, the conversion of CPD enhanced significantly from 72.6% to 81.7%, causing generation rate of DCPD at the common plates between 80 and 100th reduced, while the selectivity around this area was still high (Fig. 7(B)). Taking both the rate and selectivity of DCPD generation into consideration, the second liquid-holdup region was set at 75th plate, and the conversion of CPD further increased to 84.3%. In addition, it can be seen that the generation rate of DCPD at the first liquid-holdup region reduced, because the second region is closer to the feed plate to convert more CPD. When considering the third liquid-holdup region, the low generation rate of $(\text{CPD} + \text{IP})_{\text{dimer}}$ should be given priority, for the conversion of CPD is pretty high. On the other hand, due to the low boiling point, there is a certain amount of CPD in the top product with low residence time. After some evaluation, the third liquid-holdup region was set at 25th plate, which is above the feed plate. From the view of the results, the design is reasonable, for the conversion rate of CPD reached 87.6%, while the recovery rate of IP remained unchanged. For further enhancing CPD conversion to 90%, the fourth and the fifth liquid-holdup regions could also be set. As shown in Fig. 7(D), the selectivity to DCPD is higher at the plates away from the feed position. In this way, the fourth and fifth liquid-holdup regions were set at 60th and 45th plate respectively to minimize the generation of $(\text{CPD} + \text{IP})_{\text{dimer}}$.

As shown in Fig. 8, with the number of liquid-holdup regions increasing from zero to four, the recovery of IP reduced slightly from 98.6% to 98.5%, while the conversion of CPD enhanced significantly from 72.6% to 89.2%. The results proved the importance of liquid-holdup regions and the rationality of the liquid-holdup regions position design. Further increase of the number of liquid-holdup regions to five didn't improved the CPD conversion obviously, but it improved the self-dimerization of IP and co-dimerization of IP and CPD, hence raising

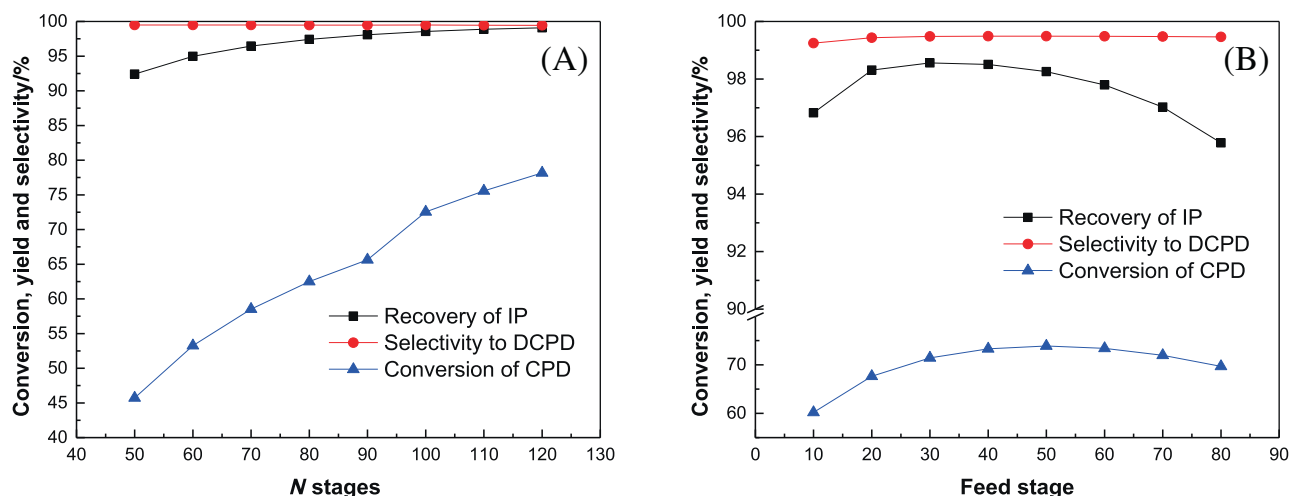


Fig. 6. Influence of (A) number of theoretical plates and (B) feed stage on separation performance. Conditions: Residence time in each plate = 5 s, reflux ratio = 8, operating pressure = 245 kPa.

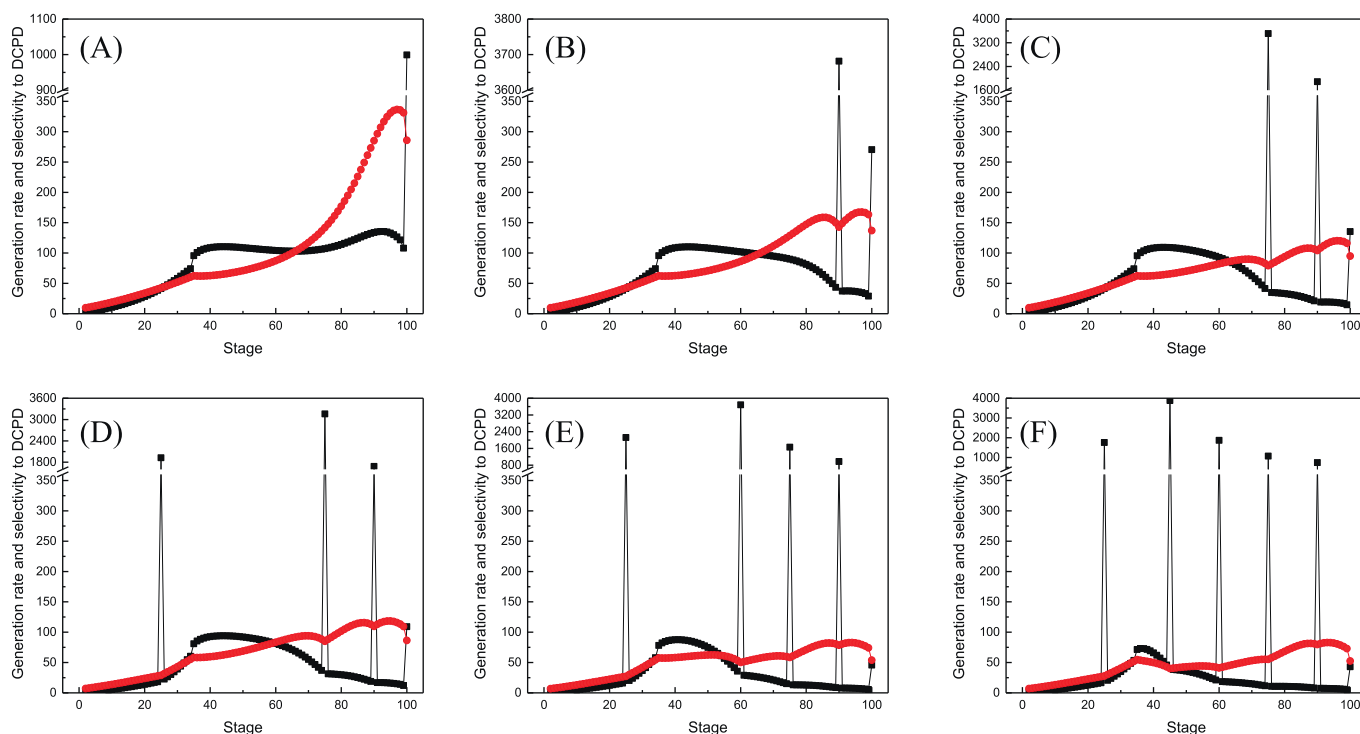


Fig. 7. Generation rate and selectivity to DCPD on each plate. —■— Generation rate of DCPD ($\text{mol}\cdot\text{h}^{-1}$) —●— Generation selectivity.

the conversion of IP and reducing both the recovery of IP and selectivity to DCPD. So the optimal number of liquid-holdup regions was four with the position of 25th, 60th, 75th and 90th plate.

Fig. 9 shows the mass fraction profiles of CPD and IP along the column. As indicated by the mass fraction of IP shown in Fig. 9(B), the distillation efficiency is almost not affected by the adding of liquid-holdup regions. The results suggested that the determination of the number of theoretical plates and feed position is correct. On the other hand, the adding of liquid-holdup regions mainly affects the CPD content in the plates nearby (Fig. 9(A)).

According to the calculation result previously, four liquid-holdup regions are suitable for design requirement. However, the design requirement was not well met, for the conversion of CPD is lower than 90%. Therefore the residence time should also be considered. It should

be noted that increases of the residence time may improve the CPD conversion as well as the side reactions according to analysis. As revealed in Fig. 10, only conversion of CPD is slightly sensitive to the changes of residence time, while the recovery of IP, selectivity to DCPD and conversion of IP are basically unchanged. The results further proved the rationality of liquid-holdup regions. On the other hand, the large range of residence time from 250 to 400 s merely increased the conversion of CPD from 89.9% to 91.5%, which means the design of residence time for this RD column is simple.

5.2.3. Influence of important operating parameters

For RD process, operation pressure, which determines the temperature distribution, is a key parameter to affect the dimerization reactions. As shown in Fig. 11, with the increases of operating pressure, the conversion of both CPD and IP enhanced, but the selectivity to DCPD and recovery of IP decreased. It is worth noting that the separation performance is very sensitive to the operating pressure. When the operating pressure was more than 300 kPa, IP recovery of less than 96% was obtained, which suggested that high operating pressure is very unfavorable for the separation. On the other hand, when the operating pressure is less than 230 kPa, the conversion of CPD cannot reach 90%. So the RD column could be operated in the range of 230 to 260 kPa.

In the distillation processes, the reflux ratio, an important operation parameter, affects both the separation performance and energy consumption. Fig. 12 shows the conversion of CPD, the selectivity to DCPD, and the recovery and conversion of IP as a function of the reflux ratio at a fixed residence time. As is well-known, the increasing of reflux ratio enhances the distillation separation efficiency. Hence, the recovery of IP increased with reflux ratio increasing. Moreover, the co-dimerization of IP with CPD, the major side reaction, was also inhibited due to the less contact of CPD and IP. However, when the reflux ratio increased above 12, IP recovery was improved slightly, but the dimerization of IP can be promoted. In spite the conversion of CPD kept increasing, the selectivity to DCPD slowly declined. Considering these changing trends as well as the high utilities consumption and even the appearance of flooding caused by large reflux ratio, the

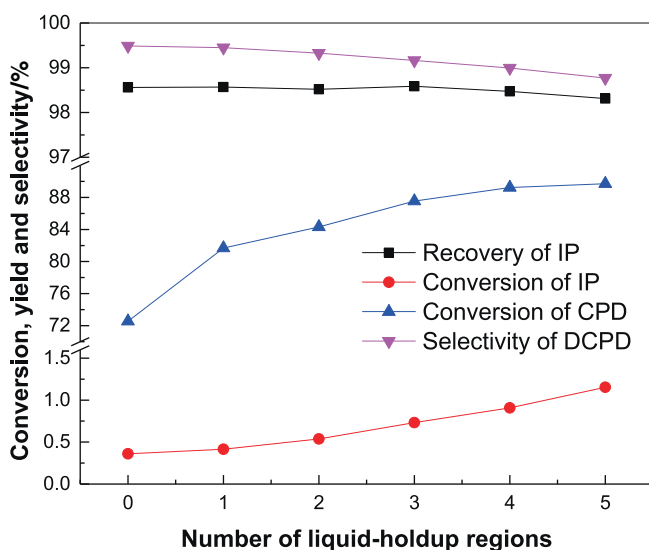


Fig. 8. Influence of number of liquid-holdup regions on RD performance.

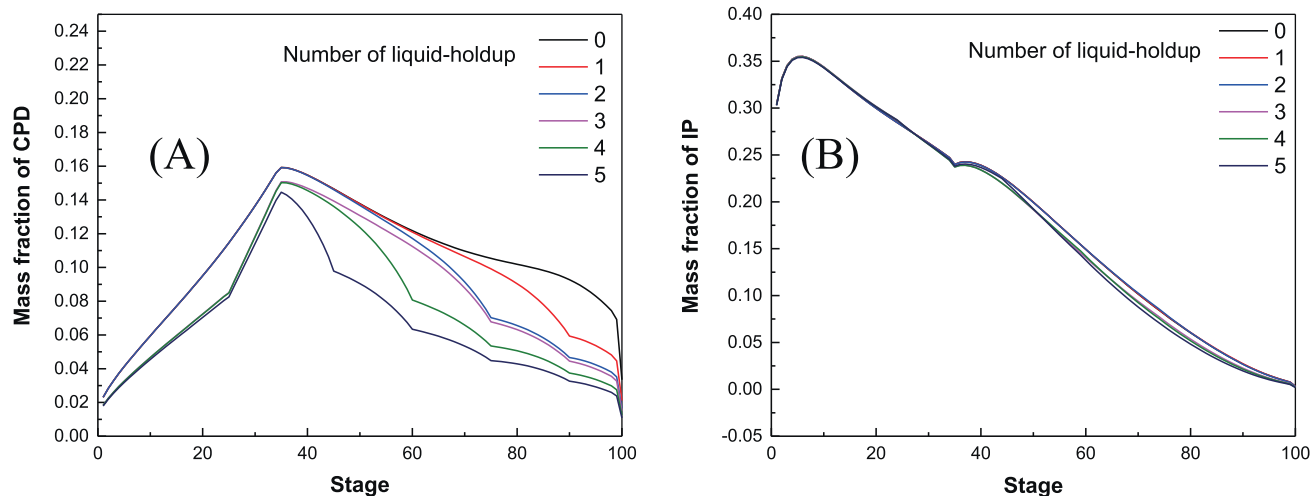


Fig. 9. Mass fraction distribution of (A) CPD and (B) IP on each plate.

appropriate reflux ratio could be selected as 8–12 to ensure the separation requirement.

6. Conclusions

In this work, a new type of reactive distillation column has been designed, in which the pack section and special liquid-holding areas were combined to make the distillation and the reactions work synergistically. The designed multiple liquid-holdup regions supply more residence time and provide flexibility for narrowing the efficiency gap between reaction and distillation. Thus a corresponding mathematic model was established and validated for the detailed research of the RD column. According to the DCPD generation rate and selectivity in each plate, five liquid-holdup regions were set at proper positions in sequences. The well-designed liquid-holdup regions enhance the CPD conversion significantly, while affect slightly on the CPD selectivity and IP recovery. Optimized process parameters were then determined: 100 theoretical plates, feed position of 35th plate, and four liquid-holdup regions at 25th, 60th, 75th and 90th plate respectively, with which the technical requirement of C5 separation can be well met. The synergistic effect between reaction and separation overcomes the equilibrium limitations and constrains the undesired side reaction.

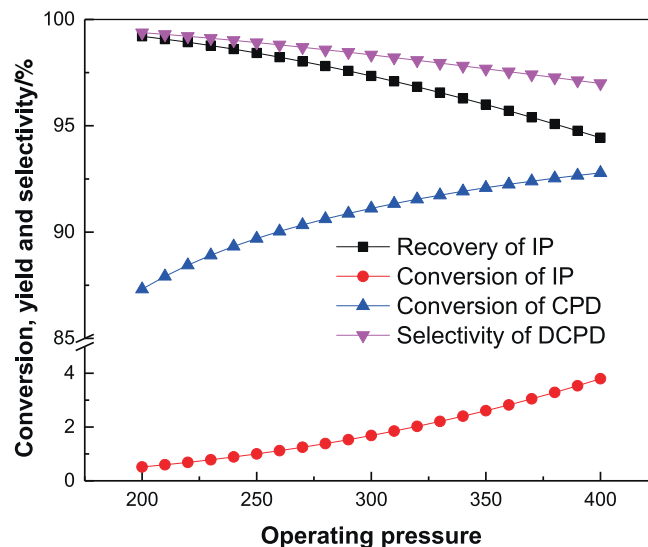


Fig. 11. Influence of operating pressure on RD performance.

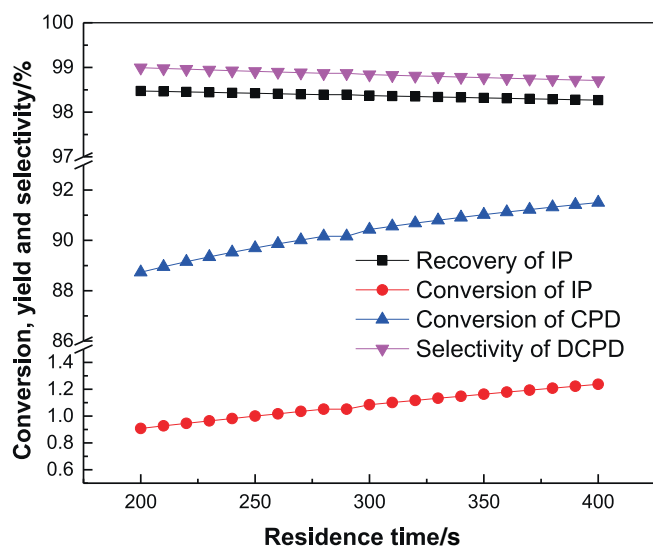


Fig. 10. Influence of residence time of liquid-holdup regions on RD performance.

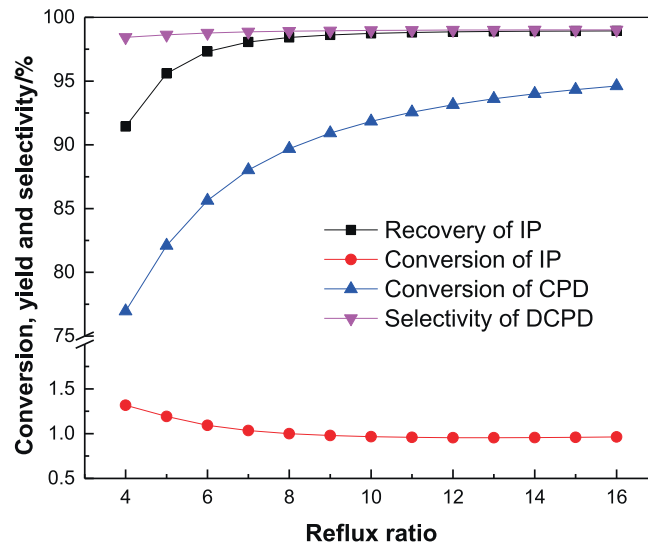


Fig. 12. Conversion of CPD and IP, recovery of IP and selectivity to DCPD at different reflux ratios.

Overall, the reactive distillation process is a promising technique for the cracking C5 fraction separation.

Nomenclature

A	pre-exponential factor
C	number of components
D	distillation flow rate of overhead, $\text{kmol} \cdot \text{s}^{-1}$
E	active energy, $\text{J} \cdot \text{mol}^{-1}$
F	feed flow rate, $\text{kmol} \cdot \text{s}^{-1}$
h^F	feed enthalpy, $\text{kJ} \cdot \text{mol}^{-1}$
h^L	liquid enthalpy, $\text{kJ} \cdot \text{mol}^{-1}$
h^V	vapor enthalpy, $\text{kJ} \cdot \text{mol}^{-1}$
k_{ij}	equilibrium constant
k_{im}	reaction rate constant, $\text{kmol} \cdot \text{s}^{-1}$
L	liquid flow rate, $\text{kmol} \cdot \text{s}^{-1}$
N	total number of stages
p	pressure, MPa
p^0	saturated vapor pressure of pure component under the system temperature, MPa
Q	heat removed or added, $\text{kJ} \cdot \text{s}^{-1}$
Q^r	heat of reaction, $\text{kJ} \cdot \text{mol}^{-1}$
R	gas constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
r_{im}	dimerization reaction rate constant of component i and m , $\text{kmol} \cdot \text{s}^{-1}$
r_i	total reaction rate constant of component i , $\text{kmol} \cdot \text{s}^{-1}$
T	temperature, K
t	residence time, s
V	vapor flow rate, $\text{kmol} \cdot \text{s}^{-1}$
W	bottom product flow rate, $\text{kmol} \cdot \text{s}^{-1}$
x	molar fraction of liquid component
y	molar fraction of vapor component
z	molar fraction of feed component
γ	activity coefficient of liquid
φ	fugacity coefficient of vapor
φ^0	fugacity coefficient of pure component under saturated vapor pressure
φ_{ij}	fugacity coefficient of mixture component

Subscripts

i, m	component, $i = 1, 2, \dots, C$
j	total number of stages or number of differential unit, $j = 1, 2, \dots, N$

References

- [1] L. Guo, D. Li, J. Wang, Progresses in the separation of steam cracking C5 fraction at home, *Petrochem. Technol.* 44 (2) (2015) 252–260.
- [2] L. Wang, J. Yang, J. Liu, Development and utilization of C5 distillate, *Sci. Technol. Chem. Ind.* 21 (5) (2013) 83–86.
- [3] L. Zhang, Development and application of steam cracking C5 fraction, *Petrochem. Ind. Appl.* 27 (4) (2008) 16–18.
- [4] J. Hu, X. Li, H. Xu, Y. Lu, P. Li, Study of co-dimerization in C5 reaction-distillation, *Petrochem. Technol.* 27 (4) (2001) 53–58.
- [5] R. Baur, A.P. Higler, R. Taylor, R. Krishna, Comparison of equilibrium stage and non-equilibrium stage models for reactive distillation, *Chem. Eng. J.* 76 (1) (2000) 33–47.
- [6] B. Zhang, M. Wang, Z. Luo, S. Wang, Q. Dai, Y. Hu, Z. Cheng, Development of etherification reaction for pyrolysis C5 olefins and application, *Petrol. Ref.* 45 (3) (2015) 30–35.
- [7] X. Chen, Z. Bao, Polymerization of dienes in C5 fraction by ionic liquid catalyst, *Petrochem. Technol.* 36 (3) (2007) 232–236.
- [8] J. Liu, X. Wang, Z. Zhang, J. Li, Formation of dicyclopentadiene by thermal dimerization from C5 fractions, *Petrochem. Technol.* 25 (4) (1996) 248–252.
- [9] S. Zhao, J. Huang, F. University, Fuzhou and Tianjin, Coupled reaction/distillation process for hydrolysis of methyl acetate, *Chin. J. Chem. Eng.* 18 (5) (2010) 755–760.
- [10] S. Sun, G. Huang, Simulation of reactive distillation process for monosilane production via redistribution of trichlorosilane, *Chin. J. Chem. Eng.* 22 (3) (2014) 287–293.
- [11] H. Tian, Z. Huang, T. Qiu, Reactive distillation for producing n-butyl acetate: experiment and simulation, *Chin. J. Chem. Eng.* 20 (5) (2012) 980–987.
- [12] H.-C. Hsu, S.-J. Wang, J.D.-Y. Ou, D.S.H. Wong, Simplification and intensification of a C5 separation process, *Ind. Eng. Chem. Res.* 54 (40) (2015) 9798–9804.
- [13] X. Wang, Z. Bao, Study on thermal dimerization of dienes in C5 fraction, *J. Nanj. Univ. Technol.* 21 (5) (2005) 737–742.
- [14] D. Singh, R.K. Gupta, V. Kumar, Simulation of a plant scale reactive distillation column for esterification of acetic acid, *Comput. Chem. Eng.* 73 (2015) 70–81.
- [15] R. Kumar, S.M. Mahajani, Esterification of Lactic Acid with n-Butanol by Reactive Distillation, *Ind. Eng. Chem. Res.* 46 (21) (2007) 6873–6882.
- [16] M.A. Santaella, A. Orjuela, P.C. Narváez, Comparison of different reactive distillation schemes for ethyl acetate production using sustainability indicators, *Chem. Eng. Process.* 96 (2015) 1–13.
- [17] Z. Qi, K. Sundmacher, E. Stein, A. Kienle, A. Kolah, Reactive separation of isobutene from C4 crack fractions by catalytic distillation processes, *Sep. Purif. Technol.* 26 (2002) 147–163.
- [18] A.M. Katariya, R.S. Kamath, K.M. Moudgalya, S.M. Mahajani, Non-equilibrium stage modeling and non-linear dynamic effects in the synthesis of TAME by reactive distillation, *Comput. Chem. Eng.* 32 (10) (2008) 2243–2255.
- [19] Y. Fang, W. Xiao, Experimental and modeling studies on a homogeneous reactive distillation system for dimethyl carbonate synthesis by transesterification, *Sep. Purif. Technol.* 34 (1–3) (2004) 255–263.
- [20] T. Keller, A. Górak, Modelling of homogeneously catalysed reactive distillation processes in packed columns: Experimental model validation, *Comput. Chem. Eng.* 48 (2013) 74–88.
- [21] B. Guo, Y. Li, Analysis and simulation of reactive distillation for gasoline alkylation desulfurization, *Wildl. Soc. Bull.* 38 (1) (2014) 43–50.
- [22] L. Tong, L. Chen, Y. Ye, Z. Qi, Kinetic studies on the dimerization of isobutene with $\text{Ni}/\text{Al}_2\text{O}_3$ as a catalyst for reactive distillation process, *Chin. J. Chem. Eng.* 23 (3) (2015) 520–527.
- [23] J. Cheng, X. Li, C. Du, L. Liao, D. Li, Study on C5 separation with reaction distillation, *Chem. Ind. Eng. Prog.* 28 (7) (2009) 1278–1281.
- [24] L. Guo, D. Li, J. Wang, Simulation of reactive distillation process for separation of steam cracking C5, *Petrochem. Technol.* 43 (12) (2014) 1394–1400.
- [25] B. Tian, G. Tang, Q. Zhang, C. Du, W. Dai, Simulations of thermal dimerization and reactive distillation processes in separation of cyclopentadiene from steam cracking C5, *Petrochem. Technol.* 37 (12) (2008) 1276–1281.
- [26] H.J. Flammersheim, J. Opfermann, The dimerization of cyclopentadiene – A test reaction for the kinetic analysis of DSC measurements and the performance of a kinetic evaluation program, *Thermochim. Acta* 337 (1–2) (1999) 149–153.
- [27] L. Guo, T. Wang, D. Li, W. Jinfu, Intrinsic kinetic modeling of thermal dimerization of C5 fraction, *Chin. Pet. Process Pe. Technol.* 18 (1) (2016) 92–99.
- [28] J. Seo, J. Lee, H. Kim, Isothermal vapor–liquid equilibria for ethanol and n-pentane system at the near critical region, *Fluid Phase Equilib.* 172 (2) (2000) 211–219.