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Identification of the Optimal Distillation Sequence Based on the Integration of Reaction-Distillation-Recycle System

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A general method is proposed to target the optimal N-component distillation sequence with the integration of the reaction-distillation-recycle (RDR) system considered. Considering the product distribution of each column and the composition of recycle, a universal logical algorithm is deduced to identify the distillation sequence by the partition method. With the reaction kinetics integrated into this algorithm, a model is built to evaluate the effect of reaction/recycle parameters on the investment and operation cost of each distillation sequence, and the corresponding cost curve is plotted. The optimal one at different reaction and recycle parameters are identified with all distillation sequences compared intuitively. A case of styrene unit is studied and the results show that the method can provide important guidance for the initial process design and optimization.

1. Introduction

Distillation is a widely used and energy intensive separation process (Lucia and Mccallum, 2010). To separate a mixture with multiple components, multiple distillation columns are required, and different separation orders result in different distillation sequences with different investment and operation costs (Xu et al., 2015). It is of great significance to identify the optimal distillation sequence.

Reactor is the core of the chemical process. Its effluent is the feed of distillation system, and the unreacted feed separated by the latter usually needs to be recycled. Hence, the optimal distillation sequence might change along the reaction and recycle parameters. To design and optimize a process systematically, it is necessary to consider the interaction among them (Hentschel et al., 2014).

A lot of research has been done to optimize the distillation sequence. Baghmisheh et al. (2010) investigated the steady state and dynamic performances of quaternary distillation sequences, and proposed a method for choosing the best one with much less computational load. Torres-Ortega et al. (2015) studied the intensification of the distillation sequences separating an N-component mixture with more than N-1 columns, and deduced the configurations with design and optimization considered simultaneously. Vazquez-Castillo et al. (2015) introduced a multi-objective optimization approach to integrate the design and control of distillation sequences with the environmental impacts considered. Besides, the design of distillation sequence is closely related to heat transfer optimization. Long and Lee (2015) reported the results of a techno-economic feasibility study to debottleneck the distillation column using a hybrid process combining a heat pump and thermally coupled distillation sequence. Chew et al. (2015) developed a systematic methodology considering pressure drops in Total Site Heat Integration (TSHI) utility targeting, and extended it to consider the pressure drop factor during the targeting stage of the minimum energy requirement. Leeson et al. (2017) proposed a novel methodology for the optimization of the preliminary design of heat-integrated multicomponent distillation sequences. Compared to the heuristic-based design, the obtained distillation sequence has significant cost reduction. Based on the thermodynamic balance for processes that use mechanical and heat energy, Tsirlin et al. (2016) proposed the preliminary calculation rules for the optimal separation order of multicomponent mixtures. However, the method introduced above only considered the optimization of distillation sequence, while ignored its interaction with the reactor and recycle streams.

In this paper, a systematic method will be proposed to identify the optimal distillation sequence with the integration of reaction-distillation-recycle (RDR) system considered. With the distribution of the key components and the composition of recycle stream considered, the influence of the reaction and recycle parameters on the

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distillation sequence will be analyzed first. Then, the investment and operation cost curves of each distillation sequence are plotted, and the optimal distillation sequence is identified. A case will be studied to illustrate the proposed method.

2. Identification of the optimal distillation sequence

2.1. RDR system and partition method

In a chemical production process, unreacted reactant separated by distillation usually needs to be recycled to the reactor, and contains some impurities. Figure 1 shows the simplified flowchart of a RDR system with four components, and components *A*, *B*, *C* and *D* are listed in the order of decreasing volatility. *B* is the reactant of reactor, and is taken as the basis reactant (BR), *A*, *C* and *D* are the products. The effluent of the reactor is a 4-component mixture, and 5 possible distillation sequences can be used to separate it. Unreacted *B* is recycled to the reactors, and might contain a bit of *A* and *C* because of the incomplete separation.

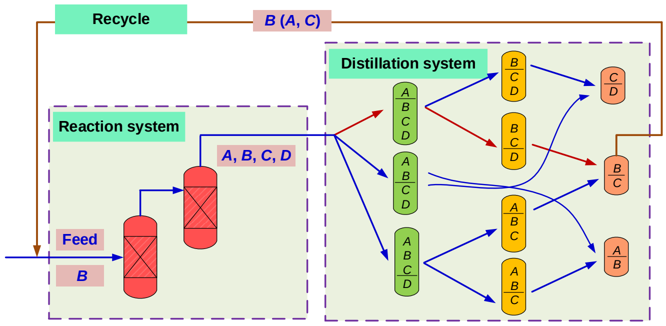


Figure 1: Simplified flow chart of 4-component RDR system

To separate an N-component mixture, N-1 simple columns are needed. The number of possible sequences is $\left[2(N\text{-}1)\right]!/\left[N!(N\text{-}1)!\right]$ (Thompson and King, 1972). Partition method can be used to identify the feasible distillation sequences. For a split between two key components neighbouring in volatility order, a partition is needed; N-1 partitions are required to obtain N products, and each partition corresponds a distillation column. For example, in the distillation sequence separating a 5-component mixture, there are 4 partitions. With *A, B, C, D* and *E* representing the components in the order of decreasing volatility, and 1, 2, 3 and 4 representing partitions, respectively, their positions are shown below:

Components *A* | *B* | *C* | *D* | *E*
Partitions 1 2 3 4

Figure 2: Partitions for separating a 5-component mixture.

Based on the permutation and combination of N-1 partitions, $(N\text{-}1)!$ partition sequences can be recorded in a full permutation matrix (FP matrix), whose size is $(N\text{-}1)!\times(N\text{-}1)$. In this matrix, each row represents a distillation sequence, each column corresponds a partition. The element denotes the position of the corresponding split in the sequence. The FP matrix for separating the 5-component mixture is shown by Figure 3.

$$\left.\begin{bmatrix} 4 & 3 & 2 & 1 \\ 4 & 3 & 1 & 2 \\ 4 & 2 & 3 & 1 \\ \vdots & \vdots & \vdots & \vdots \\ 1 & 2 & 3 & 4 \end{bmatrix}\right\}\text{24 lines}$$

Figure 3: FP matrix for separating a 5-component mixture

For simplification, all separations are assumed to be sharp splits performed by simple columns. For columns with BR as a key component, only key components distribute between overhead and bottom, lighter-than-light key components leave form the overhead and heavier-than-heavy key components form the bottom; for those without BR as key component, the distribution of key components between overhead and bottom is ignored.

The key component recovery matrix (KCR matrix), which is used to represent record the recovery of key components of the distillation column with BR as a key component, is employed in order to identify the distillation columns.

For a distillation sequence, the to be separated components ($A_1A_2\cdots A_N$) are numbered in the decreasing order of volatility, BR is A_{PN} and PN represents the order number of BR. If BR is the lightest or heaviest component in feed, the corresponding PN equals to 1 or N, the BR only can be treated as a light/heavy key component once in each distillation sequence, and the size of KCR matrix is 1×2. Otherwise, it will be treated once as a light key component in a column and once as a heavy key component in another column, and the size of KCR matrix is 2×2.

2.2. Procedure for identifying the optimal distillation sequence

The evaluation function, CDSV, shown by Eq(1), is proposed with the four heuristics for selecting simple distillation sequence (Stephanopoulos et al., 1982) considered systematically, and the coefficient of the difficulty of separation (CDS) (Nath and Motard, 1982) and the vapor rate (V) (Porter and Momoh, 1991) combined. It can be applied to evaluate both investment and operation cost, and is used to identify the optimal distillation sequence in this work.

$$\mathrm{CDSV} = 10^{-4} \times \frac{\log\left[\left(\dfrac{x_l}{x_h}\right)_D \cdot \left(\dfrac{x_h}{x_l}\right)_W\right]}{\log \alpha_{(\mathrm{LK,HK})}} \times \frac{1}{2}\left(\frac{D}{F} + \left|\frac{D-W}{F}\right|\right) \times \left(D + \frac{R_{\mathrm{F}}F}{\alpha_{(\mathrm{LK,HK})} - 1}\right) \qquad (1)$$

Where, $\left(\dfrac{x_l}{x_h}\right)_D$ is molar fraction ratio of light and heavy key components in the distillate product; $\left(\dfrac{x_h}{x_l}\right)_W$ is molar fraction ratio of heavy and light key components in the bottom product; D and W are the distillate flowrate and bottom flowrate, koml·h^{-1}; $\alpha_{(\mathrm{LK,HK})}$ is the relative volatility between the key components; V is the vapor rate of distillation column, koml·h^{-1}; F is the feed flowrate, koml·h^{-1}; R_F is the ratio between the operating reflux ratio (R_r) and the minimum reflux ratio ($R_{\min}$), and is typically taken as 1.1.

Since each row in FP matrix represents a distillation sequence and each element corresponds a partition (or a distillation column), all possible distillation sequences can be identified by analysing the FP matrix row by row, and calculating their CDSVs. Since the separation task of downstream distillation column is affected by the upstream one, the partition in each row of FP matrix is affected by that lies on its left. After identifying the corresponding element of an upstream controlling partition (distillation column), the feed condition of the column can be analysed further. If the value of a partition is greater than the upstream controlling element, its feed is the bottom product of the column which corresponds to the upstream controlling element; otherwise, its feed is its distillate product. Then, the distillate and bottom flowrate, and the CDSV of this distillation column can be calculated. Based on the identification of the element in the corresponding row of FP matrix from left to right, the CDSVs of all columns can be calculated. The total CDSV of a distillation sequence equals the sum of the CDSVs of all the columns in this sequence.

Based on this, the total CDSVs of (N-1)! distillation sequences separating an N-component mixture can be determined. However, it is necessary to screen the effective values since some of these sequences characterize the same separation structure. The optimal distillation sequence with the minimum total CDSV can be identified by sorting all the values of total CDSVs from small to large.

In a RDR system, the reactor's effluent is the feed of distillation system; its composition and flowrate can be calculated based on the feed and reaction kinetics. The total CDSV of each possible distillation sequence can be identified with the reaction, distillation, and recycle system integrated, and the corresponding mathematical model built. Based on this, the relation between the energy consumption of each distillation sequence and reaction/recycle parameters can be analysed, and the optimal distillation sequence at specific reaction/recycle parameters can be identified according to the procedure shown in Figure 4.

3. Case study

In a styrene production unit, styrene is produced through the dehydrogenation of ethylbenzene. The main reactions occurring in the ethylbenzene dehydrogenation reactor are shown by Eqs (2)~(4). Benzene (ben), toluene (tol), ethylbenzene (eb) and styrene (st) are products, and are separated by the distillation sequence.

$$R_1: \quad C_8H_{10} \rightarrow C_8H_8 + H_2 \qquad (2)$$

$$R_2: \quad C_8H_{10} + H_2 \rightarrow C_7H_8 + CH_4 \qquad (3)$$

$$R_3: \quad C_8H_{10} \rightarrow C_6H_6 + C_2H_4 \tag{4}$$

The reaction rates of ethylbenzene dehydrogenation (Li et al., 2017) are shown by Eqs (5)~(8).

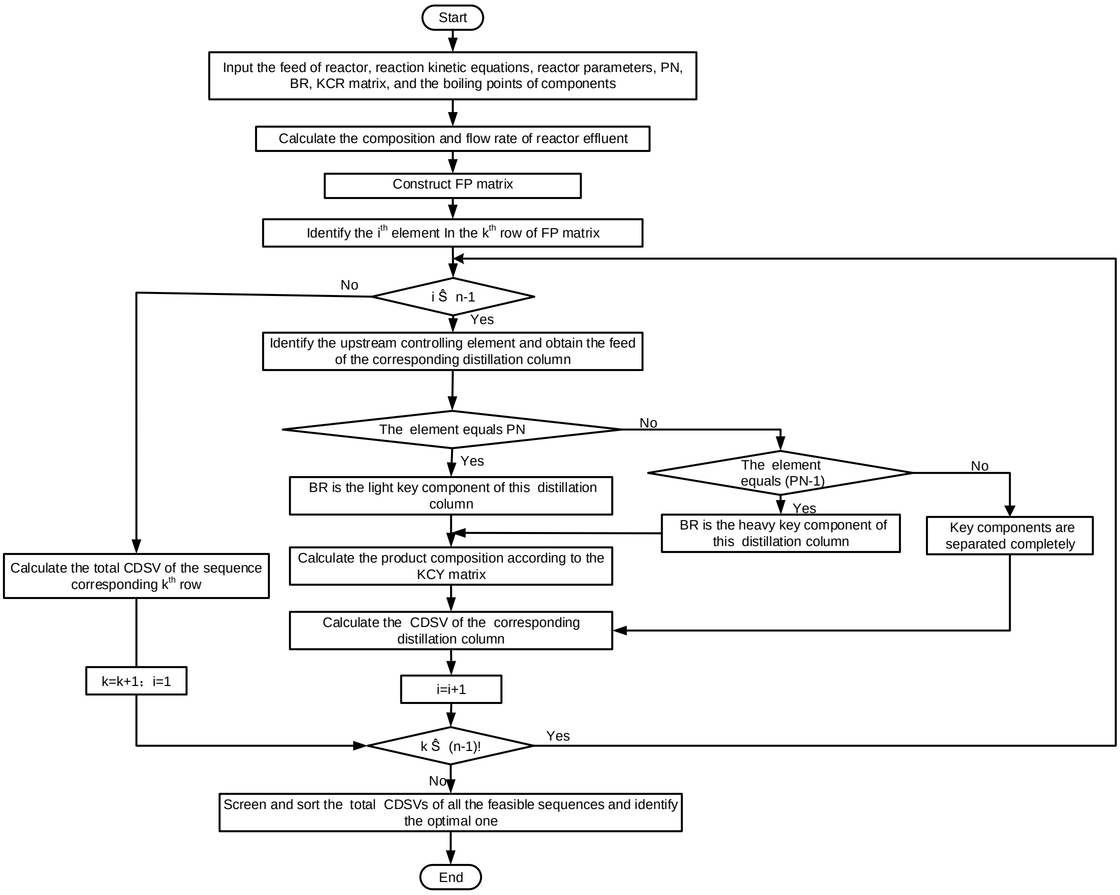


Figure 4: Procedure for identifying the optimal distillation of RDR system

$$r_{st} = \frac{k_1(p_{eb} - p_{st}p_{H_2} / K_p)}{p_{eb} + k_a p_{st}} \tag{5}$$

$$r_{tol} = \frac{k_2 p_{eb} p_{H_2}}{p_{eb} + k_a p_{st}} \tag{6}$$

$$r_{ben} = \frac{k_3 p_{eb}}{p_{eb} + k_a p_{st}} \tag{7}$$

$$r_{eb} = -r_{st} - r_{ben} - r_{tol} \tag{8}$$

Where, r represents reaction rate, mol·kg^{-1}·s^{-1}; p represents the partial pressure, kPa; k_j (j = 1, 2, 3) is the reaction rate constant, mol·kg^{-1}·s^{-1}; K_p is the thermodynamic equilibrium constant. k_j and K_p can be calculated according to Eqs(9)~(12), k_a is a kinetic parameter, and is taken as 4.36 mol·kg^{-1}·s^{-1}·kPa^{-1}.

$$k_1 = 1.59 \times 10^6 \exp[-146300 / (RT)] \tag{9}$$

$$k_2 = 9.89 \times 10^7 \exp[-169100 / (RT)] \tag{10}$$

$$k_3 = 2.97 \times 10^9 \exp[-229200 / (RT)] \tag{11}$$

$$\ln K_p = 19.67 - \frac{1.537 \times 104}{T} - 0.5223 \ln T \tag{12}$$

Where, R represents the molar gas constant, and equals 8.314 $J \cdot mol^{-1} \cdot K^{-1}$ and T denotes the temperature, K. The reaction heats of R_1~R_3 can be calculated according to Eqs(13)~(15), respectively.

$$-\Delta H_1 = -120679 - 4.56T \tag{13}$$

$$-\Delta H_2 = 53145 + 13.18T \tag{14}$$

$$-\Delta H_3 = -108750 + 7.95T \tag{15}$$

Where, ΔH_i (i=1,2,3) represents the of reaction heat of R_1~R_3, $J \cdot mol^{-1}$.

The dehydrogenation of ethylbenzene is carried out in two same reactors connected in series. The feed composition and the recovery of four components are shown in Table 1.

By the proposed method, five sequences are identified and their CDSVs are shown in Table 2. It is identified that the optimal distillation sequence at the present operating conditions is SQ_1 (ben, tol, eb / st $\rightarrow$ ben, tol / eb $\rightarrow$ ben / tol).

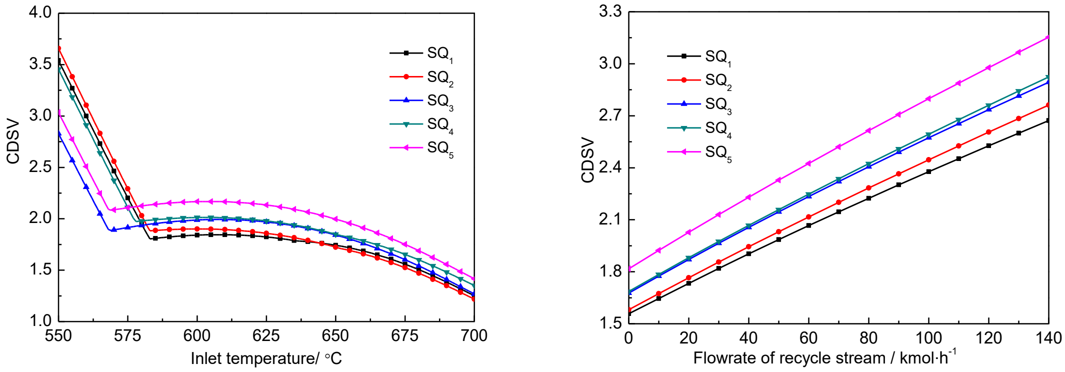
With other operating parameters kept unchanged, the total CDSVs of the five distillation sequences can be calculated automatically when the inlet temperature of the reactor increases from 550 °C to 700 °C, and are shown in Figure 5(a).

Table 1: Data of feed and recovery of the component

Components	benzene	toluene	ethylbenzene	styrene
Feed flowrate/ $kmol \cdot h^{-1}$	10	20	120	50
Mole fraction/ mol%	5	10	60	25
Relative volatility	1.96	1.80	1.24	1.00
recovery/ mol%	100	98	100	98

Table 2: The total CDSVs of five different and effective distillation sequences

Sequence number	Distillation sequence	CDSV
SQ_1	ben,tol,eb / st → ben,tol / eb → ben / tol	1.8268
SQ_2	ben,tol,eb / st → ben / tol,eb → tol / eb	1.8641
SQ_3	ben,tol / eb,st → ben / tol → eb / st	1.9732
SQ_4	ben / tol,eb,st → tol,eb / st → tol / eb	1.9839
SQ_5	ben / tol,eb,st → tol / eb,st → eb / st	2.1394



a: CDSV versus inlet temperature diagram

b: CDSV versus recycle flowrate diagram

Figure 5: The total CDSVs of five distillation sequences at different inlet temperature and recycle flowrate

In each sequence, the feed composition changes along the inlet temperature, and the inflection point of each curve in Figure 5a is caused by the term $\left|\frac{D-W}{F}\right|$ in Eq(1). From this figure, it can be seen that the vapor flowrates of these sequences have different order in different temperature intervals. When 550 °C < T< 580 °C, the optimal distillation sequence is SQ_3; when 580 °C < T < 643 °C, the optimal one is SQ_1; when 643 °C < T < 700 °C, the optimal one is SQ_2. Within the normal operating range (600 °C < T < 640 °C), the optimal distillation sequence identified by the method is consistent with the actual chemical plant. Similarly, Figure 5b shows the variation of the total CDSVs along the flowrate of recycle stream. It can be seen that the optimal distillation sequence is SQ_1. The reason is that the vapour rate has a significant effect on CDSV. In the mixture to be separated by the distillation sequence, the desired product, styrene, takes a large fraction, as well as the unreacted ethylbenzene. The indirect sequence (SQ_1) with styrene separated first and then ethylbenzene has the minimum vapour load, and hence the minimum CDSVs.

4. Conclusions

A general method is developed for identifying the optimal distillation sequence based on the integration of the reaction-distillation-recycle system. The investment and operation cost of each distillation sequence at different reaction/recycle parameters is quantitatively evaluated and analysed based on the proposed method, and the optimal distillation sequence is identified efficiently. The method can provide important guidance for the initial process design and optimization. Case study shows that the results identified by the proposed method are in good agreement with the actual chemical plant. In the proposed method, only sharp separation of key components is considered. This affects the difficulty of separation, the composition of recycle stream and the accuracy of the results to a certain extent. To solve this problem, sloppy separation should be incorporated into this method and a more rigorous model should be built. Furthermore, heat transfer optimization associated with changes in sequential operations, complex reaction system and the optimization of multiple reactor parameters should also be taken into consideration. This will be studied in the future work.

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