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A Systematic Method for Integrating Reactor and Extractive Distillation Considering the Variation of Reactor Parameters

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A systematic method is proposed to integrate reactor and extractive distillation, and identify the optimal solvent, solvent to feed ratio and extractive distillation sequence. The relation among reactor parameters, the reactor effluent and the feed of extractive distillation is deduced, and the energy consumption of distillation is evaluated based on the marginal minimum vapour rate. Based on this, the influence of the reactor’s operating parameters is analyzed, and the optimal extractive distillation sequence and the optimal reactor parameters are identified. Furthermore, the energy consumption is evaluated to target the optimal solvent to feed ratio. A case is studied to illustrate the application of the proposed method.

1. Introduction

In extractive distillation, an additional solvent is used to increase the relative volatility of components to be separated. For a given separation task, increasing the solvent to feed ratio can increase the relative volatility of the components to be separated and decrease the required plates. However, the energy consumption of reboiler might increase correspondingly. At the same time, multiple distillation columns are required for separating multicomponent mixtures and form different distillation sequences, whose energy requirements are significantly different. The selection of appropriate solvent to feed ratio and extractive distillation sequence is significantly important for minimizing the energy consumption. Since the reaction system and the separation system interact with each other, in order to minimize the overall energy consumption, it is necessary to integrate them and optimize their operating parameters.

For extractive distillation, Van Dyk and Nieuwoudt (2000) proposed a computer-aided molecular design method of solvents. Souto et al. (2018) proposed an optimization method for targeting the operational conditions that result in the maximum thermodynamic efficiency. Considering the simultaneous optimization of the reaction-separation process, Recker et al. (2015) introduced a three–step design framework for the design of reaction–separation processes, and the results can be taken as the initial solution for the rigorous optimization models. All possible process variants are generated in the first step and evaluated with the help of shortcut calculations in the second step, then the results are used for an efficient initialization of the rigorous optimization model. Zhang et al. (2018) proposed a superstructure based optimization approach using generalized disjunctive programming (GDP) models for the rigorous and simultaneous design of reaction and separation processes. Although many published literatures have investigated the extractive distillation and reaction-separation process, there is no report on the integration of reaction system and extraction distillation.

This paper aims to propose a systematic integration method for the reaction–separation system with extractive distillation. The marginal minimum vapour rate will be calculated first, graphic is built to analyse the variation of vapour rate along the reactor’s conversion (*X*) for all possible distillation sequences. Based on this, the identification of the optimal solvent to feed ratio and extractive distillation sequence will be studied. A selective hydrogenation of benzene to cyclohexene process will be studied to illustrate the proposed method.

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2. Optimization of reaction-extractive distillation system

2.1 Relation among reactor parameters

The relation among the reactor temperature, conversion and selectivity will be analysed in this section. For the reactor with *n* components (A_1, A_2…A_n, ranked in the order of decreasing volatility) participating in *m* reactions, the reactions can be represented by Eq(1) in terms of the atomic balance.

$$\sum_{j=1}^{n} \nu_{jk} A_j = 0 \qquad (k = 1,2,3,...,m) \tag{1}$$

Where, ν_{jk} is the stoichiometric coefficient of component A_j in the *k*-th reaction. It is negative for the reactant and positive for the product.

The key component of the reaction, A_p , and its conversion, *X*, can be calculated by Eq(2). ξ_k (*k*=1, 2, ..., *m*) is the extent of reaction *k*, and is defined by Eq(3). The selectivity of A_p transfer into the target product (A_q) can be determined by Eq(4). In the reactor effluent, the flowrate of each component can be expressed by Eq(5).

$$X = \frac{F_{p0} - F_p}{F_{p0}} \tag{2}$$

$$\xi_k = \frac{F_{jk} - F_{jk0}}{\nu_{jk}} \tag{3}$$

$$S = \frac{F_{q0} + \sum_{k=1}^{m} \nu_{qk} \cdot \xi_k}{F_{p0} \cdot X} \tag{4}$$

$$F_j = F_{j0} + \sum_{k=1}^{m} \nu_{jk} \cdot \xi_k \tag{5}$$

Where, F_{p0} and F_p represent the flowrate of A_p before and after the reactions; F_{jk0} and F_{jk} represent the flowrate of A_j before and after the reaction *k*; F_{q0} represents the flowrate of the target product A_q before the reactions and ν_{qk} is the stoichiometric coefficient of component A_q in the *k*-th reaction. F_{j0} and F_j represent the flowrate of A_j before and after the reactions.

2.2 Extractive distillation

In extractive distillation, solvent is added to increase the relative volatility between the components to be separated, and the latter changes as the solvent and its flowrate change, as well as the performance and energy consumption. The amount of solvent can be expressed in terms of solvent to feed ratio, as shown by Eq(6).

$$F_S = q \cdot F_M \tag{6}$$

Where F_S and F_M represents the molar flow of solvent and the total molar flow of mixture to be separated, and *q* is the solvent to feed ratio.

Under normal or low pressure, the gas can be taken as ideal gas, while the liquid is taken as a non-ideal solution. The gas-liquid equilibrium constant can be calculated by Eq(7).

$$K_i = \gamma_i \cdot p_i^s / p \tag{7}$$

Where K_i is the gas-liquid equilibrium constant of species *i*, γ_i is the activity coefficient of species *i*, *p* is the pressure, and the saturated vapour pressure of species *i*, p_i^s can be calculated by the Antoine equation shown by Eq(8).

$$\lg p_i^s = A_i + B_i / T + C_i \times \lg T + D_i \times T + E_i \times T^2 \tag{8}$$

Where A_i , B_i , C_i , D_i and E_i are Antoine constants, *T* is the temperature.

The relative volatility of species *i* to species *j* is calculated by Eq(9).

$$\alpha_{ij} = \left[\frac{p_i^s}{p_j^s}\right]_T \left(\frac{\gamma_i}{\gamma_j}\right) \tag{9}$$

Where p_i^s and p_j^s are the saturated vapour pressures of species *i* and species *j* at temperature *T*, respectively.

The activity coefficient of species *i* and species *j*, γ_i and γ_j , can be calculated by the modified UNIFAC model (Gmehling et al., 1993; Gmehling et al., 2008).

The conversion (*X*) and the solvent to feed ratio (*q*) affect the relative volatility of components in the distillation system. Their influence can be determined based on the equations mentioned above, and can be illustrated by the three-dimensional diagram.

2.3 Optimization of the reaction-extractive distillation system

In the distillation sequence separating multicomponent mixture, assume that all the distillation columns are sharp split. Each column has two key components, which lie on either side of the corresponding separation point, and the other components are non-key components. For all distillation sequences, the total flowrates of key components are equal, but those of non-key components are different. For a distillation sequence, the high flowrate of non-key components will increase the heat load, total vapour rate and the temperature difference across columns, and the energy consumption of the distillation sequence will increase correspondingly. Therefore, the energy consumption of distillation sequences can be compared based on the flowrates of non-key components.

To calculate the flowrates of non-key components efficiently, the non-key component matrix NN_n can be used to illustrate the number of times a component appears as a non-key one, as shown by Eq(10). In this matrix, each row corresponds a distillation sequence, each column corresponds a component, and each element represent the number of times the corresponding component as non-key component in the corresponding distillation sequence, and there are a total of *n* components to be separated, and the corresponding number of distillation sequences is S_n.

$$NN_n = \begin{array}{c} \\ 1 \\ \vdots \\ i \\ \vdots \\ S_n \end{array}\!\!\begin{array}{c} \begin{array}{ccccc} A_1 & \cdots & A_j & \cdots & A_n \end{array} \\ \begin{bmatrix} \lambda_{11} & \cdots & \lambda_{1j} & \cdots & \lambda_{1n} \\ \vdots & & \vdots & & \vdots \\ \lambda_{i1} & \cdots & \lambda_{ij} & \cdots & \lambda_{in} \\ \vdots & & \vdots & & \vdots \\ \lambda_{S_n1} & \cdots & \lambda_{S_nj} & \cdots & \lambda_{S_nn} \end{bmatrix} \end{array} \tag{10}$$

Where λ_{ij} is the number of times of component A_j as a non-key component in the *i*-th distillation sequence.

For multi-component extractive distillation, the energy consumption changes along the reactor's conversion, solvent to feed ratio and the distillation sequence. On the premise of a saturated liquid feed to the distillation columns, the energy consumptions of distillation sequences can be compared based on the marginal minimum vapour rate (Modi and Westerberg, 1992), which can be calculated by Eq(11).

$$\sum MV_{\min}\left(l...lk/hk\ ...h\right)=\sum_{d=1}^{n-1}\left(\sum_{j=l_d}^{lk_d-1}\frac{\alpha_j\cdot F_j}{\alpha_j-\bar{\phi}_d}-\sum_{i=hk_d+1}^{h_d}\frac{\alpha_j\cdot F_j}{\alpha_j-\bar{\phi}_d}\right) \tag{11}$$

Where, subscript *d* denotes the split of the distillation sequence; l_d and k_d are the lightest and heaviest components of split *d*, l_{kd} and h_{kd} are the light and heavy key components of this split, respectively. α_j is the relative volatility of A_j relative to the heaviest component, $\bar{\phi}_d$ is the root of the equation and satisfies $\alpha_{l_{kd}} < \bar{\phi}_d < \alpha_{h_{kd}}$. To simplify the calculation, it is assumed that $\bar{\phi}_d = \left(\alpha_{l_{kd}} + \alpha_{h_{kd}}\right)/2$.

For the separation of *n*-component reactor effluent by the extractive distillation sequence, due to the addition of the solvent, the mixture to be separated by distillation sequence is a (*n*+1)-component mixture. When the solvent is the heaviest component, all possible distillation sequences can be generated based on the non-key component matrix. The non-key component matrix of *n*-component mixture is shown by Eq(10), and the procedure for identifying the optimal distillation sequence is shown by Figure 1. On the basis of the separation of the n-component mixture, it is only necessary to add a solvent to the non-key component matrix. And, Eq(11) should be modified into Eq(12) with the solvent considered. It is worth noting that this method only compares the energy consumption of extractive distillation column. The marginal minimum vapour rate of the distillation sequence, $\sum MV_{\min}$, is related to the conversion of the reactor and the solvent to feed ratio of the extractive distillation. Since the feed of extractive distillation sequence is the effluent of the reactor, the relationship between the conversion and the marginal minimum vapour rate of the distillation sequence ($\sum MV_{\min}$) can be deduced based on Eq(2), Eq(4), Eq(5) and Eq(12). Thereafter, the variation of the marginal minimum vapour rate of each extractive distillation sequence along reaction conversion and solvent to feed ratio can be analysed, and the optimal extractive distillation sequence can be identified simultaneously.

$$\sum MV_{\min}\left(l...lk/hk\ ...h\right)=\sum_{d=1}^{n-1}\left(\sum_{j=l_d}^{lk_d-1}\frac{\alpha_j\cdot F_j}{\alpha_j-\bar{\phi}_d}-\sum_{i=hk_d+1}^{h_d}\frac{\alpha_j\cdot F_j}{\alpha_j-\bar{\phi}_d}-\frac{\alpha_S\cdot F_S}{\alpha_S-\bar{\phi}_d}\right) \tag{12}$$

Where, α_S is the relative volatility of solvent relative to the heaviest component.

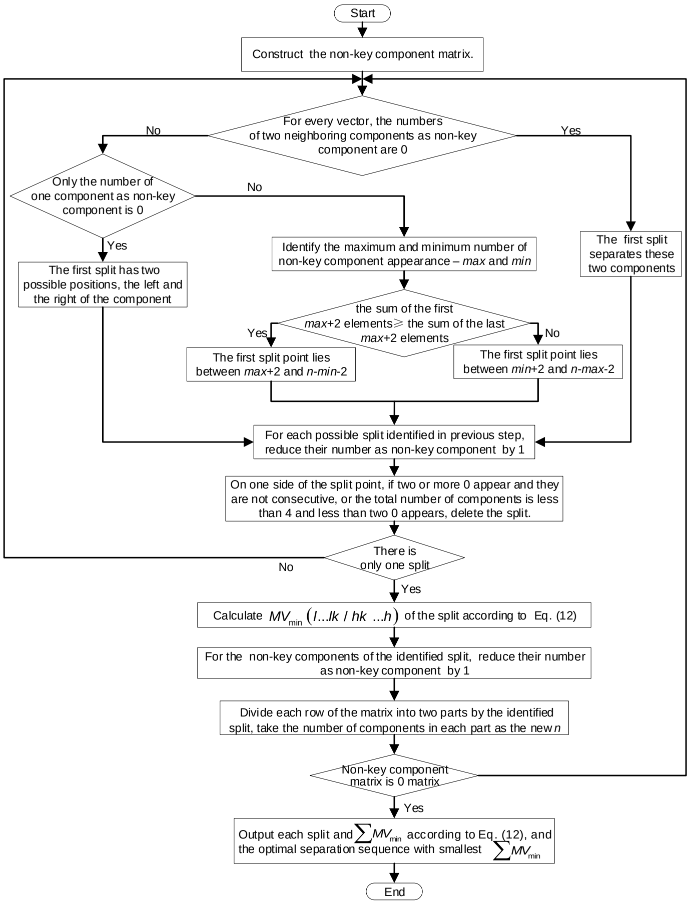


Figure 1: Procedure for identifying the optimal distillation sequence

3. Case study

Cyclohexene is generally produced by selective hydrogenation of benzene. The reaction is a series reaction in liquid-gas phase, as shown below (Struijk et al., 1992).

Primary reaction $BZ+H_2\xrightarrow{1}HE$

Side reaction $HE+H_2\xrightarrow{2}HA$

Where, BZ is benzene, HE is cyclohexene and HA is cyclohexane.

The feed flowrate of reactor, F_{BZ0}, is 1000 $\text{mol}\cdot\text{min}^{-1}$. When catalyst Ru-M-B/$ZrO_2$ is used, the selectivity of benzene hydrogenation process is about 40 % - 50 %, and the conversion changes in interval [0.3, 0.6]. The relationship between selectivity (S) and conversion (X) is shown by Eq(14) (Liu et al., 2003).

For the reactor with given volume, according to Eqs(2) ~ (5), the extent of reactions are shown by Eq(15), and Eq(16) is used to calculate the flowrates of each component in the reactor effluent.

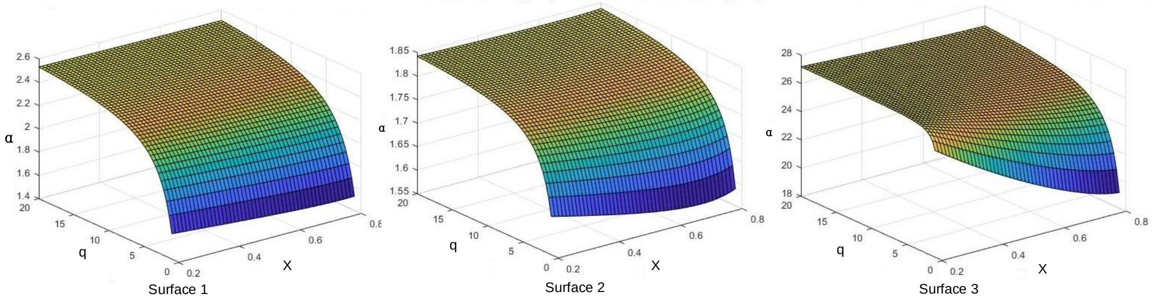
$$X = \frac{F_{BZ0} - F_{BZ}}{F_{BZ0}} \tag{13}$$

$$S = \frac{\left(1-X\right)\cdot\ln\left(1-X\right) + 92\exp\left\{\dfrac{0.65\ln\left[-\ln\left(1-X\right)\right]}{11024.5}\right\}}{\ln\left(1-X\right)\cdot\left(1-X\right)} \tag{14}$$

$$\xi_1 = F_{BZ0} - F_{BZ} \qquad \xi_2 = F_{HA} - F_{HA0} \tag{15}$$

$$F_{BZ} = F_{BZ0}\cdot\left(1-X\right) \qquad F_{HE} = F_{BZ0}\cdot X\cdot S \qquad F_{HA} = F_{BZ0}\cdot X\cdot\left(1-S\right) \tag{16}$$

In the reactor effluent, there are mainly three components: benzene, cyclohexene and cyclohexane. These three components will form azeotrope, and dimethylacetamide (DMAC) is usually used as a solvent to separate them. In the presence of solvent, their volatility order from high to low is cyclohexane (HA)> cyclohexene (HE) > benzene (BZ)> dimethylacetamide (DMAC). Figure 2 shows the variation trend of the relative volatility between every pair of adjacent components (*α*) along *X* and *q*. It can be seen that *q* has a significant effect on *α*. When *q*>5, its influence is gradually weakening. Since the energy consumption and cost of solvent increase along the amount of solvent, the optimal *q* is taken as 5.



Surface 1 Surface 2 Surface 3

Note: Surface 1, 2, 3 represent the relative volatility between HA and HE, HE and BZ, BZ and DMAC, respectively.

Figure 2: The X-q-α diagram

The three-component non-key component matrix is represented by Eq(17).

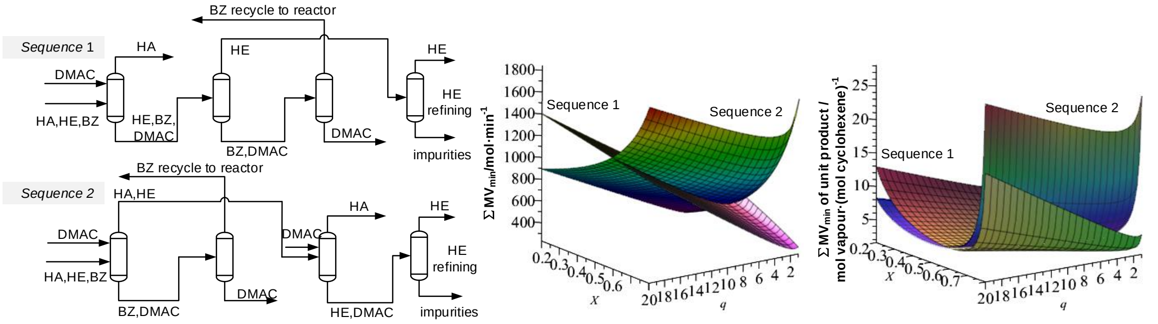
$$NN_3 = \begin{array}{c} \\ 1 \\ 2 \end{array}\begin{array}{c} \begin{matrix} HA & HE & BZ \end{matrix} \\ \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \end{array} \tag{17}$$

Based on this, two extractive distillation sequences can be identified and shown in Figure 3 (a). Since each distillation column is assumed to perform the sharp split, the unreacted benzene can be recycled to reactor in both sequence. The fresh feed inlet into the reactor can be identified with the recycle reduced from the stream inlet into the reactor, and the energy consumption of the distillation sequence does not change.

To minimize energy consumption and optimize the solvent to feed ratio and conversion, the variation of $\sum MV_{\min}$ is calculated according to the procedure shown in Figure 1 and plotted in Figure 3 (b). It can be seen that as *q*=1, when *X*<0.5 the marginal minimum vapour rate of the sequence 1 is greater than that of sequence 2; when *X*>0.5, the contrary is the case. The $\sum MV_{\min}$~*q*~*X* surfaces of two sequences intersect at a curve. On this surface, X will gradually increase along *q*; when *q*=20, it will increase to 0.61. In practical production process, the conversion is usually around 0.45, and the corresponding optimal extractive distillation sequence is sequence 2. This is in good agreement with that identified by the proposed method. When the conversion is constant, the marginal minimum vapour rate of sequence 2 decreases first and then increases along *q*, and the minimum value is obtained when *q*=3, while the marginal minimum vapour rate of sequence 1 increases monotonically along *q*.

In Figure 3 (c), the marginal minimum vapour rate of unit product is plotted for each distillation sequence, and can be applied to evaluate the distillation sequence with the variation of the desired product considered. For two sequences, it can be identified that the relative relationship among their marginal minimum vapour rates of unit product is same as that among their marginal minimum vapour rates. When the conversion of benzene increases gradually, the marginal minimum vapour rate of unit product for each distillation sequence decreases first and then increases along *X*; for sequence 1, the minimum value can be obtained when the conversion and *q* equal

0.63 and 1, respectively, while for sequence 2, they are 0.42 and 3. The variation trend of the marginal minimum vapour rate along the solvent to feed ratio is the same as that in Figure 3(b). Therefore, the model proposed in this work can effectively identify the optimal solvent to feed ratio and extractive distillation sequence.



(a) (b) Marginal minimum vapor rate (c) Marginal minimum vapor rate of unit product

Figure 3: The X-q-∑$MV_{\min}$ diagram

4. Conclusions

In this paper, a systematic method is proposed for integrating the reaction and the extractive distillation, and identifying the optimal solvent to feed ratio and sequence. The energy consumptions of extractive distillation sequences can be evaluated according to their marginal minimum vapour rates. The proposed method can automatically target the optimal sequence accurately based on the integration of the reaction and extractive distillation systems, and can be easily incorporated into the software. Case study shows that the proposed method can identify the optimal solvent to feed ratio and extractive distillation sequence efficiently. Furthermore, since the reaction and separation system are integrated, the downstream processes will be affected when the conditions of these two units change. This will be studied in the further work.

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