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# Effect of Relative Volatility on the Design of Reactive Distillation with Side Reactors using MINLP Optimization

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A mixed integer non-linear programming (MINLP) model for distillation column with side reactors (DCSR) process of a general consecutive reaction was established firstly. Then, the method based upon outer-approximation/equality-relaxation/augmented-penalty (OA/ER/AP) algorithm is proposed as MINLP solver for the optimization calculation of discrete and continuous variables. The effect of relative volatilities between adjacent components on optimal discrete and continuous variables including the number of stripping stages (NS), the number of stages between reactors (NSR), the number of side reactors (NR) and reaction amounts in each reactor was explored. Results show that when relatively volatility between components of consecutive reaction is larger, it requires less NS, NSR and NR. Besides, the reaction amount in side reactors decreases gradually from top to bottom. These results are of guiding significance to the rapid design of DCSR process for consecutive reactions.

## 1. Introduction

As a significant instance of process intensification, reactive distillation (RD) that integrates reaction and separation in a single unit can facilitate reaction conversion or product selectivity with low energy consumption (Chen et al., 2015). However, RD is limited by some constraints such as the proper match between the temperatures and pressures required for distillation and reaction (Kaymak et al., 2004). Distillation column with side reactors (DCSR) coupling of a nonreactive distillation column with side reactors is widely believed to circumvent above-mentioned drawbacks. For example, DCSR can provide better economics than conventional RD in the hydration of cyclohexene to cyclohexane (Ye et al., 2014) and cyclohexyl formate production (Wang et al., 2016) when there is a temperature mismatch between reaction and distillation.

It is of note that both equipment and process operating parameters should be optimized in order to take full advantages of RD or DCSR process. Gangadwala and Kienle (2007) presented a MINLP technique to minimize the reboiler heat duty in the design of butyl acetate synthesis in RD and DCSR process. This MINLP optimization was solved using a commercially available optimization tool and its name is GAMS. Besides, another MINLP optimization of MTBE process which is a kinetically controlled RD process was proposed based on the concepts of equilibrium stage and tray efficiencies (Poth et al., 2001). The outer-approximation/equality-relaxation/augmented-penalty (OA/ER/AP) algorithm was applied in this MINLP optimization. The OA/ER/AP algorithm is an improved outer-approximation algorithm which features an exact penalty function that allows violations of linearization of nonconvex constraints.

Cheng-Ching Yu (2007) investigated the effect of relative volatility between reactants and products on the structure and cost of production in traditional RD column. It was pointed out that the location of the reaction zone is determined by the relative volatility between reactants and products and the principle of determining the position of the raw material feed tray was given. Moritz (2016) has explored the influence of relative volatility of the reaction system on the energy saving potential for the reactive dividing-wall column. However, there is almost no such research about the effect of relative volatility in DCSR process. In this work, a MINLP model for DCSR process of a general consecutive reaction ( $A \xrightarrow{B} C \xrightarrow{B} D$ ) in gPROMS software based

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on the concept of independent reaction amount (Ding et al., 2011) was established initially. Then, OA/ER/AP algorithm within gPROMS was selected as MINLP solver for the optimization calculation of discrete and continuous variables. The effect of different relative volatilities between components on optimal discrete variables including the number of stripping stages (NS), the number of stages between each reactor (NSR) and the number of side reactors (NR) and continuous variable including total feed flow rate of B ($F_B$) and distribution ratio of B in each reactor ($f_k$) was explored with fixed vapor boilup and product purity. Results show that there exist corresponding relations between relative volatility and design variables. This can be applied in rapid design process in DCSR process of consecutive reactions according to inductive corresponding relations.

## 2. Methodology

### 2.1 Flowsheet Configuration for DCSR

Figure 1 presents the diagram of DCSR process for a general consecutive reaction. The column is divided into a reactive distillation zone with an external side reactor and a stripping zone. The liquid reactant A is pumped into the first reactor from the top while the reactant B is divided into multiple streams and then introduced into all of side reactors. Each reactor is assumed to be a stirred tank reactor and reaction only occurs in the external reactors rather than in the column. Total liquid is transferred from distillation tray into the side reactors. Reactors liquid effluents are pumped back to the column on the tray below the trap-out tray from which they are withdrawn. Target product C and by-product D are withdrawn from the column bottom. In order to avoid the negative influence of difference between side reactor outlet temperature and the relevant tray temperature on smooth operation of column, a heat exchanger is set between the column and each side reactor. The stage of column, side reactors and heat exchanges are counting from top to bottom.

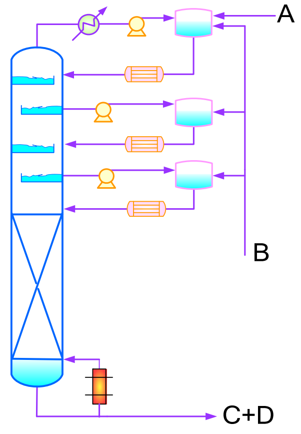

*Figure 1: Diagram of DCSR process*

*Table 1: Physical and chemical parameters*

| Parameters | Values |
|---|---|
| reaction characteristic factor, Φ | 10 |
| heat of main/side reaction (kJ/mol) | -50.0/-50.0 |
| heat of vaporization of A/C/D (kJ/mol) | 34/38/42 |
| molecular weight of A/C/D (g/mol) | 92/126/161 |
| liquid density of A/C/D (kg/m$^3$) | 771.5/1,003.6/1,144.5 |
| heat-transfer coefficient of condenser(W·K·m$^2$) | 250 |
| heat-transfer coefficient of reboiler (W·K·m$^2$)) | 1,000 |
| ideal gas constant (J·mol$^{-1}$·K$^{-1}$) | 8.314 |

### 2.2 Process studied

Reaction scheme and the kinetics are given as follows:

$$A\xrightarrow{B}C\xrightarrow{B}D \tag{1}$$

$$r_1=k_1x_Ax_B \tag{2}$$

$$r_2=k_2x_Cx_B \tag{3}$$

This is an exothermic consecutive reaction and the sequence of the boiling point is B＜A＜C＜D. In Eq(2) and Eq(3), $r_1$ and $r_2$ are reaction rate of main and side reaction respectively while $k_1$ and $k_2$ are their reaction rate constant. The ratio of $k_1/k_2$ is defined as reaction characteristic factor Φ.

In this work, $\alpha_{A,C}$ and $\alpha_{C,D}$ are assumed to be equal so that α can used to represent them. Besides, seven different systems with α=1.25, 1.5, 1.75, 2.0, 3.0, 5.0 and 8.0 were studied and the effect of temperature on relative volatility is ignored. Table 1 gives physical and chemical parameter values of this system.

### 2.3 MINLP Model for DCSR

DCSR process mainly contains two kinds of unit operation equipment that are distillation column and reactors. MINLP model for DCSR can be an integral whole coupling the column and reactor model established respectively. This MINLP model is based on the concept of independent reaction amount which was put forward previously (Ding et al., 2011). The reaction space in side reactor is assumed to be big enough so that the reactant B entering the reactor can be consumed completely. Both product selectivity of C and reactor volume can be calculated combined with reaction kinetics.

**Model for side reactor**

The temperature of reaction is assumed to be constant (373.15 K). The gasification in the side reactor is assumed to be ignored. $I_j$ was 0-1 variable and it was introduced to indicate whether the reactor j is connected to the column. If $I_j$ is 1, it means a connection. If $I_j$ is 0, it means no connection.

Material balances:

$$\begin{aligned}&RL_j=D+F_A,\ \frac{R_{k,C}}{R_{k,D}}=\frac{k_1RX_{j,A}-k_2RX_{j,C}}{k_2RX_{j,C}}=\frac{\Phi RX_{j,A}}{RX_{j,C}}-1\\&F_A+DX_{D,A}=RL_jRX_{j,A}+F_Bf_k(p_k+\frac{q_k}{2})\ ,DX_{D,C}+F_Bf_kp_k=RL_jRX_{j,C}\ ,DX_{D,D}+F_Bf_k\frac{q_k}{2}=RL_jRX_{j,D}\end{aligned}\quad ,\ j=1 \tag{4}$$

Second and below reactors (2≤j≤N-1):

$$\begin{aligned}&RL_j=I_jL_{j-1}\ ,\ \frac{R_{k,C}}{R_{k,D}}=\frac{k_1RX_{j,A}-k_2RX_{j,C}}{k_2RX_{j,C}}=\frac{\Phi RX_{j,A}}{RX_{j,C}}-1\\&I_jL_{j-1}X_{j-1,A}=RL_jRX_{j,A}+F_Bf_k(p_k+\frac{q_k}{2}),\ I_jL_{j-1}X_{j-1,C}+F_Bf_kp_k=RL_jRX_{j,C},\ I_jL_{j-1}X_{j-1,D}+F_Bf_k\frac{q_k}{2}=RL_jRX_{j,D}\end{aligned} \tag{5}$$

$$\sum f_k=1,\ f_k>0 \tag{6}$$

$$p_k+q_k=1,\ p_k>0,q_k>0 \tag{7}$$

Energy balances:

$$F_Ah_A^L+F_Bf_kh_B^V+DH_D+Q_{input,k}+Q_{heat,k}=RL_jHR_j^L+RV_jHR_j^V\ ,\ j=1 \tag{8}$$

$$I_jL_{j-1}H_{j-1}^L+F_Bf_kh_B^V+Q_{input,k}+Q_{heat,k}=I_j(RL_jHR_j^L+RV_jHR_j^V)\ ,\ 2\le j\le N-1 \tag{9}$$

**Model for distillation column**

An equilibrium stage column model is used for a nonreactive distillation column. The vapour-liquid equilibrium is assumed to be idea. $Z_j$ was 0-1 variable and it was introduced to indicate whether the tray j is a real tray or a virtual tray. If $Z_j$ is 1, it means a real tray. If $Z_j$ is 0, it means a virtual tray.

Material balances:

$$\text{Reflux Drum：}\ D=V_1,X_{T,i}=Y_{1,i} \tag{10}$$

$$M_{j,i}=V_{j+1}Y_{j+1,i}+I_jRL_jRX_{j,i}-L_jX_{j,i}-V_jY_{j,i}\ ,\ j=1 \tag{11}$$

$$\text{If } Z_j=1,\text{ Then: } M_{j,i}=V_{j+1}Y_{j+1,i}+I_jRL_jRX_{j,i}+(1-I_j)L_{j-1}X_{j-1,i}-L_jX_{j,i}-V_jY_{j,i}\ ,\ 2\le j\le N-1 \tag{12}$$

$$\text{If } Z_j=0,\text{ Then: } X_{j,i}=X_{j-1,i},Y_{j,i}=Y_{j+1,i},L_j=L_{j-1},V_j=V_{j+1}\ ,\ 2\le j\le N-1 \tag{13}$$

$$\text{Column bottom: } M_{j,i}=L_{j-1}X_{j-1,i}-V_jY_{j,i}-L_jX_{j,i}\ ,\ j=N \tag{14}$$

Phase equilibrium:

$$Y_{j,i}=\alpha_{i,D}X_{j,i}/\sum_{i=1}^{C}\alpha_{i,D}X_{j,i}\ ,\ j=1 \text{ or } N \qquad (15)$$

$$\text{If } Z_j=1, \text{ Then: } Y_{j,i}=\alpha_{i,D}X_{j,i}/\sum_{i=1}^{C}\alpha_{i,D}X_{j,i}\ ;\ \text{If } Z_j=0, \text{ Then: } X_{j,i}=X_{j-1,i}, Y_{j,i}=Y_{j+1,i}\ ,\ 2\le j\le N-1 \qquad (16)$$

Summation equations: $S_j=\sum_{i=1}^{c}X_{j,i}-1$ (17)

Energy balances:

Condenser: $H_j=DH^D-V_1H_1^V-Q_C$ (18)

$$H_j=I_jRL_jHR_j^L+V_{j+1}H_{j+1}^V-L_jH_j^L-V_jH_j^V\ ,\ j=1 \qquad (19)$$

$$\text{If } Z_j=1, \text{ Then: } H_j=I_jRL_jHR_j^L+(1-I_j)L_{j-1}H_{j-1}^L+V_{j+1}H_{j+1}^V-L_jH_j^L-V_jH_j^V\ ,\ \text{If } Z_j=0, \text{ Then: } T_j=T_{j-1}\ ,\ 2\le j\le N-1 \qquad (20)$$

Reboiler: $H_j=Q_b+L_{j-1}H_{j-1}^L-L_jH_j^L-V_jH_j^V$ , $j=N$ (21)

### 2.4 Optimization method and procedure

Optimized objective function is total unit cost (TUC) which is the ratio of total annual cost (TAC) to annual production (AP). TAC is composed of total capital cost and operation cost. A payback period of 7 years and annual operating time of 8,000 h are assumed.

TAC = (Capital cost/Payback period) + Operation cost (22)

Total Capital cost = Column cost + Reactor cost + Heat exchanger cost + Pump cost (23)

The calculation formula of column cost, reactor cost, heat exchanger cost and pump cost in Eq(23) comes from Douglas (1988) and Seider (2004). Operation cost mainly contains steam cost and condensate water cost. NSR is assumed to be the same. Optimization procedure for DCSR is shown in Figure 2.

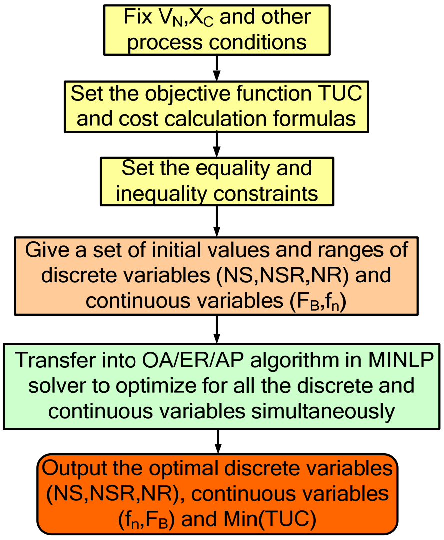

*Figure 2: Optimization procedure for DCSR*

## 3. Results and discussion

The selectivity of the target product C was specified to be 0.98 and flow rate of steam for the reboiler was fixed at 20 kmol/h. The effect of different relative volatilities on optimal NS, NSR, NR, $F_B$, $f_k$ is shown in Figure 3. It can be seen in Figure 3 (a), optimal NS decreases from 78 to 9 as α rises from 1.25 to 8.0. Reasonable explanation is that components are easier to separate when the system has larger relative volatility so that less stripping stages are needed for the separation with fixed flow rate of rising steam from rebolier. In addition, the reduction of optimal NS is not significant as the relative volatility increases in the larger range and it is obvious to understand. Similar to the change trend of optimal NS, optimal NSR declines from 12 to 1 as α rises from 1.25 to 8.0. The reason of this phenomenon is also the same to that of optimal NS because the main roles of the stages between each reactor and the stripping section stages both are promoting the removal of product C by separation. Increasing the number of side reactors can enhance the reaction capacity of the DCSR process. As α rises from 1.25 to 8.0, optimal NR decreases from 5 to 2. Specifically, there are some constant trends in the process of changes of optimal NR and it may due to that NR is discrete variable. It is found out that it is reasonable to select optimal NR as 4 when α is located in a smaller range (less than 2.0) while three side reactors can be chosen when α is greater than 2.0 in the design of the DCSR process. The level of production capacity for the DCSR process can be expressed by total feed flow rate of B ($F_B$). As shown in Figure 3 (b), optimal $F_B$ increased gradually when α rises from 1.25 to 8.0. It is obvious that optimal $F_B$ is growing fast when α is less than 3.0 while the growth trend is slowing down rapidly when α is over 3.0. The separation of components becomes easier as α rises so that product C is more easily removed from the reactive distillation zone and this will cause more consumption of reactant B. It's worth noting that the separation is much easier when α lies in a smaller range compared with a larger one. Distribution ratio of reaction amounts in each reactor is shown in Figure 3 (c). Distribution ratio of reaction amounts decreases gradually as reactor number is in an increasing order and that is to say the lower the reactor position, the smaller the amount of reaction. What's more, distribution ratios of reactant B are almost the same when optimal NR is the same as well and this is a piece of valuable principle during primary design of DCSR. Table 2 gives the optimization results of design and operating parameters for DCSR process.

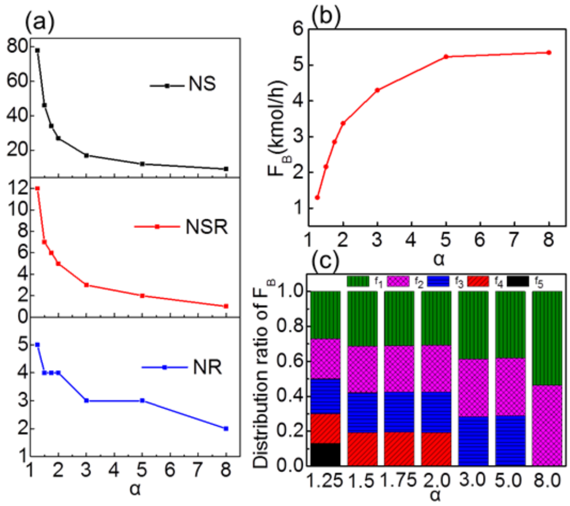

*Figure 3: Effect of α on optimal NS, NSR, NR (a), $F_B$ (b) and $f_k$ (c)*

*Table 2: Optimization results of DCSR process*

| α | 1.25 | 1.50 | 1.75 | 2.00 | 3.00 | 5.00 | 8.00 |
|---|---|---|---|---|---|---|---|
| NS | 78 | 46 | 34 | 27 | 17 | 12 | 9 |
| NSR | 12 | 7 | 6 | 5 | 3 | 2 | 1 |
| NR | 5 | 4 | 4 | 4 | 3 | 3 | 2 |
| $F_B$(kmol/h) | 1.298 | 2.158 | 2.854 | 3.374 | 4.299 | 5.234 | 5.353 |
| $f_k$ | 0.27/0.23/0.20/0.17/0.13 | 0.31/0.27/0.22/0.19 | 0.31/0.27/0.23/0.20 | 0.31/0.27/0.23/0.19 | 0.39/0.33/0.28 | 0.38/0.33/0.29 | 0.54/0.46 |
| TAC ($10^3\$$) | 198.7 | 174.6 | 172.5 | 171.9 | 163.2 | 173.4 | 172.1 |
| AP (t/y) | 1,289 | 2,142 | 2,833 | 3,350 | 4,268 | 5,196 | 5,344 |
| TUC($/t) | 154.1 | 81.5 | 60.9 | 51.3 | 38.2 | 33.4 | 32.2 |

## 4. Conclusions

In this paper, a distillation column with side reactors process for a general consecutive reaction was optimized using MINLP model. When vapor boilup and product purity are fixed, relative volatilities between components can exert significant impact on the optimization of discrete structural variables and continuous operation variables in the DCSR process. The appropriate variables (NS < 20, NSR ~2 and NR = 3) is obtained when relative volatilities are larger than 3.00. In addition, lower reactor position can give rise to the reduced reaction amount in each reactor. These results are likely to provide the blueprint for preliminary design of DCSR process in the context of consecutive reactions.

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## Nomenclature

$\alpha$ = relative volatility between adjacent components, dimensionless quantity
$\alpha_{i,D}$ = relative volatility between i and D
D = distillate flow rate in the column (kmol/h)
$F_B$ = total feed flow rate of B (kmol/h)
$F_i$ = total flow rate of component i (kmol/h)
$f_k$ = distribution ratio of B in reactor k
$HR_j^L$ = enthalpy of the liquid stream back to tray j (kJ/mol)
$HR_j^V$ = enthalpy of the vapor stream back to tray j (kJ/mol)
$H_j^L$ = enthalpy of the liquid mixture to tray j (kJ/mol)
$H_j^V$ = enthalpy of the vapor mixture to tray j (kJ/mol)
$H_D$ = distillate enthalpy in the column (kJ/mol)
$h_A^L$ = liquid enthalpy of A (kJ/mol)
$h_B^V$ = vapor enthalpy of B (kJ/mol)
$I_j$ = connection parameter between tray j and reactor
$L_j$ = liquid flow rate from tray j (kmol/h)
$Q_b$ = heat duty of reboiler (MJ/h)
$Q_C$ = heat duty of condenser (MJ/h)
$Q_{heat,k}$ = the sum of reaction heat in reactor k (MJ/h)
$Q_{input,k}$ = external heat supplied to the reactor k (MJ/h)
$p_k$ = distribution coefficient of B to C in reactor k
$q_k$ = distribution coefficient of B to D in reactor k
$RL_j$ = liquid flow rate of stream fed back to tray j (kmol/h)
$RX_{j,i}$ = mole fraction of i in stream fed back to tray j
$T_j$ = temperature on tray j (K)
$V_j$ = vapor flow rate from tray j (kmol/h)
$X_{D,i}$ = distillate mole fraction of component i in liquid
$X_{j,i}$ = liquid mole fraction of component i on tray j
$Y_{j,i}$ = vapor mole fraction of component i on tray j
$Z_j$ = Boolean variable for real/virtual tray j
$\Phi$ = reaction characteristic factor, dimensionless quantity

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