Optimal operating conditions for reactor-separator-recycle system

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Characteristic equation (CE) for the Reactor-Seperator-Recycle (RSR) system is obtained using geometrical methods. Total yield is selected as the objective function of the complex reaction in two-dimensional concentration space. CE for RSR system can be separated into Plug Flow Reactor (PFR) and Continuous Stirred-Tank Reactor (CSTR) based CEs. By combining CE curves of RSR system with the attainable region boundary curves, optimal operating conditions of RSR system for maximal total yield can be conveniently determined. Besides consecutive reaction, application of CE for RSR system can also be extended to other kinds of complex reaction processes.

Keywords: Optimal operating condition, Characteristic equation (CE), Reactor networks, Process synthesis, Reactor-Seperator-Recycle (RSR) system, Attainable region partition

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Introduction

Reactor-Seperator-Recycle (RSR) system is the key of chemical engineering process. The successful selections (selections of reactor, flow configuration and operation parameters of RSR system) determine advancement and rationality of whole chemical engineering process. In industry process, reactants are usually controlled at certain appropriate conversion ratio in RSR system, especially in complex reaction process. Otherwise, if conversion ratio of the reactants is unduly low, it will result in extremely high physics loss and recycle of the reactants, and if conversion ratio of the reactants is unduly high, it will result in large quantities of byproducts, which means a large chemical loss and low total yield of target product. Therefore, an optimal operating point exists in RSR system with total yielding as the objective function.

Optimizing calculation method 1,2 for complex reaction process cannot ensure that the flow configuration obtained by the reported method is optimal. It did not clear that whether the presented technology condition constraint equations are suitable for others reaction process except the consecutive reaction process. Superstructure-based approach 3,7 and theory of attainable region 8,10 are the main methods to research the reactor network synthesis problems at present. Choosing gross profit as the target, Pahor et al combined superstructure and attainable region method to discuss the mixed-integer nonlinear programming synthesis of reactor networks 3-6. Kauchali et al 10 used attainable region technique to generate reactor network synthesis solutions for water/gas shift reaction system that is overall adiabatic. In this paper, characteristic equation (CE) for the maximal total yield of RSR system is presented. The total yield is selected as the objective function of the complex reaction in two-dimensional concentration space, and CE is derived by geometrical methods based on the principles of reaction and mixing. The reactor system is assumed a steady, isothermal, homogenous phase and constant volume process.

Characteristic Equation for RSR System

In RSR system (Fig. 1), input stream of reactor subsystem is the mixture of fresh stream and recycle stream separated from separator subsystem. Output stream of the reactor subsystem is separated in the separator subsystem. Type and connecting mode of reactor subsystem are arbitrary, and the flow configuration and separating mode of separator
subsystem are arbitrary too. Where, m is the recycle ratio of A in products, F means flow rate (mol/min), subscript R and A refer to the components A and R respectively.

According to material balance of RSR system (Fig. 1), total yield of production R \( (Y_R) \) is defined as:

\[
Y_R = \frac{F_{R2}}{F_{A0}} - \frac{F_{R2}}{F_{A1}} = mF_{A2}
\]  \( \ldots(1) \)

To express the mole flow speed of materials using relative concentration, Eq. 1 can be simplified as:

\[
y = Y_R(1-mx)
\]  \( \ldots(2) \)

where, \( x \) and \( y \) are the relative concentration of A and R respectively, \( x = C_{A2}/C_{A1} \), and \( y = C_{A2}/C_{A1} \).

In the space of \( (x, y) \), the equal total yield lines are a group of straight lines (Fig. 2), where \( Y_R \) and \( m \) are parameters. According to the characteristic that a protruding area in concentration field could be obtained by combining the process of reacting and mixing\(^{11} \), tangent point of the equal total yield line and the protruding area should meet the following equation,

\[
\frac{dy}{dx} = \frac{\partial Y_R}{\partial x} + \frac{\partial Y_R}{\partial y} \frac{dy}{dx} = 0
\]  \( \ldots(3) \)

By substituting Eq. 2 into Eq. 3, the following formulation was obtained,

\[
(m-1) \frac{dy}{dx} - my = 0
\]  \( \ldots(4) \)

Eq. 4 is the same as the equation in literature\(^{1} \) in expression, which deduced based on the consecutive reaction process. But in this paper, it is not limited in the consecutive reaction and certain given flow configurations. Because it is based on the condition that the contour lines of total yield and the boundary curves of attainable region are tangent, so the results can be used to a more universal range.

Choosing total yield of RSR system as optimizing object, Eq. 4 presents quantitative relationships among \( x \), \( y \) and \( m \). If \( dx/dy \) is known, a line can be figured out based on Eq. 4 in the space of \( (x, y) \), which was named the characteristic line of RSR system, and the equation was named CE of the RSR system.

**Results and Discussion**

From deducing process of CE of the RSR system, following conclusions can be drawn:

1. When the value of \( m \) and the kinetics conditions are given, every condition point on CE curves of the RSR system are correspond to the maximum of total yield. According to the definition of attainable region\(^{11} \), total yield at the intersection point of CE line and the boundary curve of attainable region is the maximum, which is influenced by the value of \( m \). Beyond the boundary of attainable region, CE curves of the RSR system become practically useless.

2. \( m \in [0,1] \), it means that \( x \) is limited within a certain range, out of the range, the optimal point of technical condition is unavailable. If \( m = 0 \), Eq. 4 can be expressed as,

\[
\frac{dy}{dx} = 0
\]  \( \ldots(5) \)

Eq. 5 is corresponding to the condition point where the single yield of reactor subsystem is maximal. If \( m = 1 \), Eq. 4 can be rewritten as:

\[
\frac{dy}{dx} = \frac{-y}{1-x}
\]  \( \ldots(6) \)
Eq. 6 coincides with the trace equation of CSTR when the material was input at the condition point of A (1, 0). So if all the unconverted reactant is recycled and reused, the optimal point of technical condition \((x^*, y^*)\) must be on the trace of CSTR.

3 Eq. 4 can be rewritten as:

\[
\frac{dy}{dx} = \frac{y}{x - \frac{1}{m}} \quad \cdots (7)
\]

Eq. 7 indicates that CE of the RSR system is the tangent equation of the total yield line and protruding area. The right of Eq. 7 is the slope of the tangent, and the left is the changing rate of \(y\) to \(x\) at the tangent point. Therefore, when the contour lines of total yield are tangent to the trace of PFR, CE of the RSR system based on PFR can be obtained directly by substituting the tangent equation into dynamic equation. But when the Contour lines of total yield are tangent with the traces of CSTR, \(\frac{dy}{dx}\) should be obtained based on CE of the RSR system of CSTR. According to the characteristic that the boundary curves of attainable region consist of both the trace of CSTR and straight lines\(^{12}\), the optimal flow configuration and operating conditions can be obtained only based on the intersection, which CE of the RSR system (based on PFR) inter-sects with the boundary curves of attainable region.

Applications of RSR System

The following examples illustrate the application of CE of the RSR system:

Example 1

Trambouze reaction model is as:

\[
A \overset{k_1}{\rightarrow} B , \ A \overset{k_2}{\rightarrow} R , \ A \overset{k_3}{\rightarrow} D
\]

where R is desired production, B and D are byproducts. Then the producing rates of A \((r_A)\) and R \((r_R)\) can be expressed respectively as,

\[
r_A = -k_1 - k_2 C_A - k_3 C_A^2 \quad \cdots (8a)
\]

\[
r_R = k_2 C_A \quad \cdots (8b)
\]

\[
x = \frac{C_A}{C_{A0}}, \ y = \frac{C_R}{C_{A0}} \quad \cdots (9)
\]

where \(C_{A0}\) is the feed-in concentration of A, and \(k\) is reaction rate constant. It is supposed that \(C_{A0} = 1\text{mol.l}^{-1}\text{min}^{-1}\), \(k_1 = 0.025\ \text{mol.l}^{-1}\text{min}^{-1}\), \(k_2 = 0.2\ \text{min}^{-1}\) and \(k_3 = 0.4\ \text{mol.l}^{-1}\text{min}^{-1}\).

Above reactions are parallel. According Eqs 8a and 8b, trace equation of PFR can be written as,

\[
\frac{dy}{dx} = -\frac{x}{a_1 + x + a_2 x^2} \quad \cdots (10)
\]

Combining Eqs 8a, 8b and Eqs of material balance, trace equation of CSTR can be written as,

\[
y = -\frac{x^2 + x}{a_1 + x + a_2 x^2} \quad \cdots (11)
\]

where, \(a_1 = \frac{k_1}{k_2 C_{A0}}\), \(a_2 = \frac{k_4 C_{A0}}{k_2}\) \cdots (12)

The attainable region of the reaction system (Fig. 3) can be obtained according to the method presented in literature\(^{11}\). The curve AD is the trace of PFR, and ABO is the trace of CSTR. Similarly, the curve BC is the trace of PFR, which is feed-in at point B. And the beeline AB means the mixture trace of feed-in point A and B. Then the protruding area surrounded by ABCOA is the attainable region.

Combining Eq.10 and Eq. 4, CE of the RSR system based on PFR can be obtained as,

\[
y = \left[ x \left( x - \frac{1}{m} \right) \right] \frac{x}{a_1 + x + a_2 x^2} \quad \cdots (13)
\]

The characteristic curves of the RSR system are plotted according to Eq. 13 with different values of \(m\), and the boundary curves of attainable region are plotted too (Fig. 4). Intersection point \((x^*, y^*)\) is just the operation point, which is the intersection point of CE curve and the boundary curve of attainable region.
Where the total yield is maximum at given $m$ corresponding to the combining operation of CSTR and PFR.

Substituting a series of values of $x^*, y^*$ into Eq. 2, quantitative relationship among $m, x^*, y^*, Y_R$ can be obtained (Table 1).

### Example 2
Van de Vusse reaction model is as:

$$A \xrightarrow{k_1} R \xrightarrow{k_3} S$$

$$2A \xrightarrow{k_1} D$$

Equations of reaction rate can be expressed as follows,

$$-r_A = -\frac{dC_A}{dt} = k_1C_A + k_3C_A^2 \quad \ldots(14a)$$

$$r_R = \frac{dC_R}{dt} = k_1C_A - k_2C_R \quad \ldots(14b)$$

where, $\alpha_1 = k_3C_{A0}/k_1, \alpha_2 = k_2/k_1 \quad \ldots(15a)$

and $x = C_A / C_{A0}, y = C_R / C_{A0} \quad \ldots(15b)$

Assuming that $\alpha_1 = 20, \alpha_2 = 2, x = 1, y = 0$.

Above reactions are also parallel reactions, so the similar method as in Example 1 is used and the following equations are obtained:

Trace equation for PFR,

$$\frac{dy}{dx} = \frac{x - \alpha_2 y}{-x - \alpha_1 x^2} \quad \ldots(16)$$

Trace equation for CSTR,

$$y = \frac{x(1-x)}{\alpha_1 x^2 + (1-\alpha_2 x)\alpha_2} \quad \ldots(17)$$

Combining Eq.16 and Eq. 4, CE based on PFR can be written as:

$$y = \frac{x - mx^2}{a_1 mx^2 - mx + a_2} \quad \ldots(18)$$

The attainable region boundary curves of Van de Vusse reaction model (Fig. 5) and the characteristic curves of the RSR system (Fig. 6) in two-dimensional concentration space are plotted. The curve ABO represents the trace of PFR, while the curve ACO is the trace line of CSTR (Fig. 5). The feed-in point of both curves is A. CDO is the trace line of PFR, and the feed-in point is C. The beeline AC means the mixture trace of point A and C. The protruding area surrounded by ACDOA is the attainable region.

For the correlation between the characteristic of reaction system and characteristic of the RSR system, the single reactor system is studied for its simpleness and clarity. Research is focused on the relationship between the Contour lines of total yield and the protruding area (it need not meet the necessary condition of attainable region), later is constructed by the exiting concentration of single reactor.

### Table 1 — Relationship of $m, x^*, y^*, Y_R$ for Trambouze reaction

<table>
<thead>
<tr>
<th>$m$</th>
<th>0.000</th>
<th>0.500</th>
<th>0.850</th>
<th>0.950</th>
<th>1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x^*$</td>
<td>0.000</td>
<td>0.040</td>
<td>0.104</td>
<td>0.151</td>
<td>0.250</td>
</tr>
<tr>
<td>$y^*$</td>
<td>0.471</td>
<td>0.466</td>
<td>0.445</td>
<td>0.424</td>
<td>0.375</td>
</tr>
<tr>
<td>$Y_R$</td>
<td>0.471</td>
<td>0.476</td>
<td>0.488</td>
<td>0.495</td>
<td>0.500</td>
</tr>
</tbody>
</table>
For Van de Vusse reaction model, traces of PFR (Fig. 7) and CSTR (Fig. 8) are plotted. The area, surrounded by trace of PFR, the trace of CSTR and the x-axes, is a non-protruding area, so it can be filled with beeline. Protruding area is the largest available protruding area of single PFR (or CSTR) process or the mixing operation of them, which is enclosed by the beeline, the trace of PFR (or CSTR) and the x-axes.

Combining Eq. 17 with Eq. 4, CE based on CSTR can be written as,

$$y = \frac{(a_2 - a_1 - 1)x^2 - 2a_1 x + a_2}{a_2 x^2 + (1 - a_2)x + a_2^2} \left( x - \frac{1}{m} \right) \quad \text{...}(19)$$

In Figs 5-8, largest total yield and the optimal non-conversion ratio can be determined in terms of the intersections of the trace of PFR, the trace CSTR and the corresponding characteristic curves of the RSR system. Quantitative relationships of $m \sim x \sim y \sim Y_R$ (Table 2) for different operating modes indicates that, for a given value of $m$, the largest total yield of PFR is less than that of CSTR at the same feed-in condition, and CSTR is better than PFR in single reactor system. However, from the viewpoint of process synthesis, largest total yield can be obtained by the series operation of CSTR and PFR, so the operation point with the largest total yield should lie on the PFR trace of the boundary curves of attainable region.

There are common characters between Trambouse reaction (parallel reaction) and Van de Vusse reaction (series reaction). In both cases, total yields are influenced by $m$. Largest total yield operation point of the reaction system can be determined by choosing the operation point with largest selectivity in CSTR [feed-in at the point A (1, 0)], then connecting CSTR with a PFR. Along the trace of PFR, corresponding optimal non-conversion ratio $(1 - x^*)$ increases and total yield $Y_R$ decreases with the decrease of $m$.

The characteristic of reaction system can be indicated by the boundary curves characteristic of the attainable region, and the characteristic of the RSR system is determined by its characteristic equation curves. The reaction system has its own characteristic, which is independent of the characteristic of RSR system. In addition, the intrinsic characteristic of RSR system is also independent of the characteristic of reaction system. Once both of them are plotted together, the intersection point is just the operation point of the reaction system.
From the view of process synthesis, once the optimal reactor flow configuration and reactor style is certain, the optimal technical operating point of RSR system can be obtained conveniently by combining the characteristic curves of the RSR system with the boundary curves of attainable region. The characteristic curves of the RSR system is based on the PFR.

Conclusions

Based on the theory of process synthesis of Reactor network, CE of RSR system is deduced in two-dimensional concentration space. Quantitative relationships among $m \sim x^* \sim y^* \sim Y_R$ in RSR system are presented, and the total yield is selected as the optimizing objective function. By combining CE curves (based on PFR) of RSR system with the attainable region boundary curves (the flow configuration of reactor need not given in advance), the optimal operating conditions of RSR system for the maximal total yield can be conveniently determined. Besides the consecutive reaction, CE for the RSR system can also be extended to other complex types of reaction process.

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References


