State Multiplicity in Multi-reaction Reactor-Separator-Recycle Systems

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Abstract

This study deals with nonlinear phenomena, such as state multiplicity and instability, in Reactor-Separator-Recycle (RSR) systems involving multi-reactions, as well as with reactor design and plantwide control issues. One typical scheme is studied, the parallel / consecutive reaction: \( A + B \rightarrow P; A + P \rightarrow R \), both reactants being recycled. The analysis is presented in term of dimensionless numbers, as plant Damköhler number and ratio of kinetic constants. A set of design guidelines that should be considered during the conceptual stage of recycle systems has been formulated. An industrial case study confirms the theoretical analysis.

1. Introduction

Plants with recycles could manifest strong nonlinearities by unwanted dynamic phenomena such as unstable steady, oscillations or even chaotic behaviour. The study of generic RSR systems, by non-linear analysis, allows getting valuable insights into the behaviour of complex real plants. Of particular attention is the problem of stability, namely the occurrence of multiple steady states and their assessment.

In previous studies we investigated the state multiplicity in RSR systems involving complex reactions such as polymerization, where only one reactant was recycled (Kiss et al., 2003). We demonstrated that multiple steady states are possible and the low branch conversion is typically unstable. A minimum reactor volume is necessary for feasible steady states. It is remarkable that the behaviour of CSTR- and PFR-Separator-Recycle systems shows similarity, demonstrating the essential role of the mass recycle. This article addresses the design and plantwide control of RSR systems implying complex stoichiometry. The non-linear analysis is conducted in terms of dimensionless numbers. Important issues are feed policy and reactor design for desired selectivity. In this study we use the concept of self-regulation for the component inventory control. The inventory is self-regulating if it is not measured and no attempt is made to regulate it by manipulating streams or process conditions. On the contrary, in controlled-regulation the inventory of each reactant is measured or evaluated by indirect measurements. The approach based on self-regulation has the advantage of setting directly the production rate by adjusting the flow rate of self-regulating reactants. In case of complex reactions an additional benefit is the fixed products distribution. Due to space restrictions, we limit the discussion to RSR systems involving CSTRs but the results are equally applicable to PFRs (Kiss et al., 2003). In general, \( f_i \) and \( z_{k,i} \) are dimensionless flow rates and concentrations, respectively, where the subscripts \( i \) and \( k \)
define streams and components, respectively. The plant input flow rate and concentration of reactant $A$ is used as reference values.

2. **Self-regulation condition for complex stoichiometry**

Unlike for the simple $A + B \rightarrow P$ reaction, in case of parallel/consecutive reactions it is possible to put all feeds on flow control. This is because the system can rely on self-regulation to reject disturbances in the feed flow rate. Due to more complex stoichiometry, the ‘generation’ and ‘consumption’ for each component are adjusting according to the reactants ratio. As a rule, it is possible to put all feed flow rates on flow control, only if the rank of the stoichiometric matrix is higher than or equal to the number of reactants. Let us consider a Reactor – Separator – Recycle system where $N$ reactants $A_j$ gives $M$ products and intermediates $P_k$. Assuming that reactants $A_j$ do not leave the process, the network of $R$ reactions and the overall mass balance can be written as:

$$
\nu_A^T \cdot A = \nu_P^T \cdot P \\
\nu_A \cdot \xi = F_0
$$

where $\nu_A^T$ and $\nu_P^T$ are matrices of stoichiometric coefficients, $\xi$ is the vector of reaction extents and $F_0$ is the vector of fresh reactant flow rates. Obviously, this linear system has at least one solution $\xi$ for any vector $F_0$, only if:

$$
\text{rank} (\nu_A) = N \leq R
$$

When $N = R$, this equation has a unique solution. This denote that kinetics or reactor volume do not influence the selectivity or the production rate (Bildea & Dimian, 2003).

3. **One reactant on self-regulation**

This section analyses reactions: $A + B \xrightarrow{b} P$; $A + P \xrightarrow{b} R$, taking place in an isothermal RSR system. Such chemistry is common in important industrial processes. We consider the case when reactants have adjacent volatilities and they are recycled together (Figure 1). One reactant feed is on flow control ($f_{A,0}$=1) – self-regulation, while the feed flow rate of the second reactant ($f_{B,0}$) is used to control its inventory. We assume good separation such that reactants are completely recycled. The model includes reactor, separation and control structure equations:

$$
1 + f_1 \cdot z_{A,3} - f_2 \cdot z_{A,2} - Da \cdot (z_{A,2} \cdot z_{B,2} + \alpha \cdot z_{A,2} \cdot z_{P,2}) = 0 \\
f_{r,0} + f_2 \cdot z_{B,3} - (f_2 \cdot z_{B,3} + Da \cdot z_{A,2} \cdot z_{B,2}) = 0 \\
f_2 \cdot z_{P,2} - Da \cdot (z_{A,2} \cdot z_{B,2} - \alpha \cdot z_{A,2} \cdot z_{P,2}) = 0 \\
1 + f_1 = f_2 = 0 \\
f_2 z_{A,2} - f_1 z_{A,3} = 0 \\
f_2 z_{B,2} - f_3 z_{B,3} = 0 \\
z_{A,3} + z_{B,3} + z_{D,3} = 1
$$
\[ f_R - f_1 - f_{R,0} = 0 \]  
(11)

Plant Damköhler number:  
\[ Da = k_i \left( V / F_0 \right) \cdot C_{A,0} \]  
(12)

Kinetic constants ratio:  
\[ \alpha = k_2 / k_1 \]  
(13)

We consider the feed flow \( (F_{A,0}) \) and the recycle \( (F_R) \) as the two flow rates that must be controlled. When product P is absent from recycle \( (z_{P,3} = 0) \), the Damköhler number and the conversion of reactant A can be expressed as:

\[
Da = \frac{\left(1 - f_{R,0}\right)^2 \left(1 + f_R\right)^2}{\alpha \cdot \left(2f_{R,0} - 1\right) \cdot \left(\alpha \cdot f_{R,0} \left(2f_{R,0} - 1\right) - \left(f_{R,0} - f_R\right) \left(1 - f_{R,0}\right)\right)}
\]  
(14)

\[
X = \frac{1 - f_{R,0}}{1 + f_R \left(1 - f_{R,0}\right) - f_{R,0} \left(2 - f_{R,0}\right) + \alpha \left(2f_{R,0} - 1\right)}
\]  
(15)

The product distribution is dependent on the fresh feed flow rates ratio:

\[
\frac{f_{P,A}}{f_{R,A}} = \frac{S_{P,A}}{S_{R,A}} = \frac{2f_{R,0} - 1}{1 - f_{R,0}}
\]  
(16)

The fold value \( Da_i \) is the minimum Damköhler number for which feasible steady state exists. From control viewpoint, designs close to \( Da_i \) should be avoided. High sensitivity and uncertainty of the design parameters may shift the operating point to another region, where undesired behavior is likely to occur, as loss of stability or even inexistence of feasible steady states. The following feasibility conditions (i.e. existence of steady states) can be derived:

\[
Da_i = \frac{4(1 + f_R)^2}{\left(1 - z_{P,3}\right)^2 (f_R - 1)^2}; \quad Da > Da_i
\]  
(17)
The selectivity of product $P$, $S_{P/A}$ is given in Figure 2 as a function of Damköhler. Selectivity becomes higher at low values of the reaction constants ratio and exhibits a high sensitivity. Figures 3 and 4 show the conversion of the key component, $X_\alpha$, for different values of the separation performance ($z_{P,3}$) and recycle flow rate ($f_R$). All diagrams exhibit state multiplicity, with unfeasibility region at low Damköhler values. When $Da$ exceeds the critical value two feasible steady states exist. A higher recycle rate (Figure 3) shifts the limit point to lower conversion and Damköhler number values and enlarges the region of feasible steady states and the range of achievable conversions. In addition, at given recycle rate, a poorer separation (higher molar fraction of product in recycle, $z_{P,3}$) shifts the fold to higher conversions and $Da$ (Figure 4). In this case, the presence of products in recycle leads to a smaller range of stable operating points. Minimizing the effect of recycle purity on state multiplicity can be achieved by designing the separation section such that pure products are obtained.

An interesting aspect, highlighted by Figures 2, 3 and 4, is the insignificant variation of selectivity at higher Damköhler numbers. In conclusion neither the volume nor the type of reactor can be used to improve the selectivity.

4. All reactants on self-regulation

Let us consider the case when both reactants are self-regulating. This means that both feeds ($f_{A,0}, f_{B,0}$) from Figure 1 are set on flow control. Figures 5 and 6 shows that the non-linear behaviour is still present. Moreover the variation of conversion with other parameters exhibits a similar trend with previous figures. However, one important difference exists: selectivity does not depend on the Damköhler number, only on $f_{B,0}$.
This dependence is given by the simple linear relationship: \( S_{P/A} = 2f_{B,0} - 1 \). Therefore the feasible range of values for \( f_{B,0} \) is limited to 0.5 ... 1.

Considering the results obtained for this RSR system, the following guidelines can be derived for screening feasible designs in case of parallel/consecutive reactions:

1. Work at high recycle rates, considering the economical trade-off between selectivity gain versus cost of recycling;
2. Use high purity recycles, preferable free of product (\( z_{P,3} = 0 \));
3. Optimise the kinetic ratio \( \alpha \), according to the desired product – \( P \) or \( R \).

5. Case study – butene/butane alkylation

This system corresponds to the stoichiometry analysed in the previous section. Physical properties of \( A, B, P, \) and \( R \) correspond to butene, butane, iso-octane and \( C_{12}H_{26} \), respectively. The main reactions are:

\[
\begin{align*}
C_4H_8 + C_8H_{10} & \xrightarrow{k_0,1} C_{18}H_{18} & k_{0,1} = 1.735 \times 10^{10} \text{ mol}^3/\text{kmol} \cdot \text{s}; E_{a,1} = 15.55 \text{ kcal/mol} \\
C_4H_8 + C_8H_{18} & \xrightarrow{k_0,2} C_{12}H_{26} & k_{0,2} = 4.342 \times 10^{13} \text{ mol}^3/\text{kmol} \cdot \text{s}; E_{a,2} = 19.45 \text{ kcal/mol}
\end{align*}
\]

Secondary reactions are possible but not essential in this case. The product of interest is iso-octane, while n-dodecane (\( C_{12}H_{26} \)) is the by-product. The unconverted reactants are separated from the products and recycled to the reactor. Main and by-product are separated in a secondary column. The design of this plant is based solely on the rules formulated in the previous section. Since \( P \) (iso-octane) is the product of interest, the kinetic ratio \( \alpha \) should be minimized. Therefore, it is better to work at the lowest feasible temperature (Figure 7), taking into account the cooling requirements constraints. Due to the easy separation \( C_4 / C_8-C_{12} \), a safe assumption is that no products are recycled. In order to keep a high selectivity higher recycle rates should be used (Figure 8).

The rigorous models were simulated in AspenTech AspenPlus™ and AspenDynamics™ (AspenTech, 2001). Three cases, for two different control structures, were considered:

1. Case A: one reactant \( (A) \) on flow control (Fig.1); \( V_R = 3 \text{ m}^3; Da = 12 \) (optimisation).
2. Case B: one reactant \( (A) \) on self-regulation; \( V_R = 5 \text{ m}^3; Da = 20 \) (guidelines design).
3. Case C: both reactants \( (A,B) \) on self-regulation; \( V_R = 5 \text{ m}^3; Da = 20 \) (guidelines).
Figure 9 presents the results of the dynamic simulation results. At time $t = 1 \text{ hr}$, a disturbance of $+100\%$ in the feed is applied. The inability of the small reactor to reject such a huge disturbance is visible from Case A. After two hours the system can no longer be controlled because of overflow. In Case B the increase of production rate is accompanied by a decrease of purity and selectivity. No difficulties were expected in this case because this control structure obeys Luyben’s rule keeping a recycle loop on flow control. Case C shows the dynamic response when both reactants are self-regulating. The decrease in purity is not as large as in previous case, but the system reaches the new steady state after a longer time.

Although this control structure does not obey Luyben’s rule, there are no control difficulties. The explanation is given by the self-regulation condition (Eq.3), which correctly predicts that for this stoichiometry both reactants can be set on flow control.

6. Conclusions
- If the control structure implies self-regulation of the mass balance for one or more reactants, multiple steady states are possible, the low-conversion one being unstable.
- Control structures involving self-regulation are feasible only if there are sufficient reactions to adjust the consumption rate of each reactant such that no accumulation occurs. All feed flow rates can be set on flow control only if the rank of the stoichiometric matrix is higher than or equal to the number of reactants.
- Design guidelines that enlarge the feasibility region and avoid unstable states or regions where no steady states exist were formulated. These are:
  1. The recycles should have low concentration or be free of component products.
  2. The recycle flow rate should be set at the highest value acceptable economically.
  3. The operating parameters should be adapted to maximise the selectivity.
For example, the kinetic ratio can be adjusted by changing the reaction temperature or by using a different catalyst.

References