Chapter 4: Plantwide Control of Recycle Systems with Multiple Reactions

Abstract

The design and plantwide control of Reactor-Separator-Recycle systems implying multi-reactions is addressed. This work presents results of the non-linear analysis for two reactor-separator-recycle systems involving consecutive/parallel reaction: S1. $A + B \rightarrow P; A + P \rightarrow R$ where both reactants are recycled together; and S2. $A + B \rightarrow 2P; 2A \rightarrow P + R$ where reactants are recycled separately.

The non-linear analysis, conducted in terms of dimensionless numbers, ensures a large range of applicability. Two case studies corresponding to each system are presented: butane alkylation and toluene trans-alkylation processes. It is demonstrated that plantwide control relying on self-regulation manifests regions of state multiplicity or unfeasibility. Ignoring the steady state multiplicity can lead to control difficulties or even un-operable plant. Nonlinear analysis is a way to identify and avoid such dangerous situations at an early stage of design. This study provides basic guidelines that are useful for the design and control of recycle systems involving multi-reactions.
Introduction

Today process plants have to be designed in such a way to be capable of handling large changes in throughput, product specifications and feedstock quality (flexibility). They should be capable to move between various operating points with smooth and short transitions (switch-ability). These issues are critical also in the case of plants with recycles where strong nonlinearities could manifest by unwanted dynamic phenomena such as unstable steady, oscillations or even chaotic behaviour. A good design should predict and avoid the occurrence of unstable behaviour when the process is faced with flexibility and switch-ability requirements.

This article investigates the problem of state multiplicity in generic system Reactor-Separator-Recycle systems dealing with complex stoichiometry from the perspective of the interaction between flowsheet design and plantwide control. Important issues are feed policy and reactor design, with regard to desired conversion and selectivity. These should comply with the requirement of a stable operating point faced to large disturbances.

State multiplicity has been intensively studied for stand-alone processes, mostly in chemical reaction engineering. Some works treated the effect of recycle but in the simplest manner as the split of the effluent without processing. Even in this case the interaction between energy and mass recycle can lead to complex behaviour. For instance, the dynamics of a fixed-bed reactor with reactant recycle may exhibit multiple and high-order periodic solutions (Recke and Jorgensen, 1999). However, in this study we are interested in the behaviour of a more generic system, when the effluent from the reactor is submitted to separation. This operation can be simple or more complex, depending on the thermodynamic properties, and purity specifications of products and recycled reactants. Accordingly, various designs of separators are possible. To avoid the combinatorial explosion of designs a systematic approach is necessary.

The systematic non-linear analysis of the Reactor-Separator-Recycle system is only recent. Tyreus & Luyben (1993) reported for the first time the occurrence of multiple steady states in a system dealing with a bimolecular reaction \( A + B \rightarrow \text{Products} \), as well as the connection between state multiplicity and reactant make-up control policy. However, they did not proceed to a fundamental analysis. A first theoretical investigation of the non-linear behaviour of the Reactor-Separator-Recycle systems has been published by Bildea, Dimian
and Iedema (2000). The dimensionless mole-balance equations have been parameterised in term of the plant Damköhler number ($Da$) and the specification of the separations. It was shown that reactant accumulation does not occur if the reactor volume exceeds a critical value. This condition can be expressed as $Da > Da^*$, in which $Da^*$ corresponds to a bifurcation point. Near the critical value of the plant Damköhler number the system manifests high sensitivity to disturbances. Only one reactant feed may be on flow control, while the other should be fed to exactly match the stoichiometry. These results have proved a generic significance in recycle systems. Further works of Kiss et al. (2002, 2003) have shown that state multiplicity and instability could occur also in systems with recycle, involving more complex kinetics such as polymerization. Although the stoichiometry is rather complex, only one recycle of one pure reactant was considered due to the relatively easy separation of monomer from polymer. It is remarkable that CSTR- and PFR-Separator-Recycle systems behave similarly, thus demonstrating the essential role of the mass recycle.

The above mentioned works assume perfect separation. The main limitation of this assumption is that the behaviour of the unstable states cannot be completely explored. Therefore, a dynamic model of the separation is necessary. In this respect a first attempt was done by Pushpavanam and Kienle (2001) and Waschler et al. (2003). They analysed a reactor-separator network housing a first-order exothermic reaction. The reactor was of CSTR type, adiabatic or non-isothermal, while the separator was a simple instantaneous single-stage flash. It was found that the nonlinear behaviour depends crucially on the control strategy. Fixing the feed flow rate was found to lead to unstable states.

The influence of complex reaction stoichiometry on the non-linear behaviour of the Reactor-Separator-Recycle system has not been investigated yet. Blagov et al. (2000) showed that state multiplicity is possible with consecutive-parallel reactions: $A + B \rightarrow P; A + P \rightarrow R$, but the reactants were fed together and no control structure was used. Nevertheless, the results presented in our article have an extensive character.

An important concept used in this article is the self-regulation. According to Larsson and Skogestad (2000) a plant is considered self-regulating "if with constant inputs the controlled outputs can be kept within acceptable bounds". Self-regulation implies that the expected disturbances can be rejected over the whole frequency range. In this study, we use the concept of self-regulation for the situation in which the component inventory is not measured. Consequently, there is no attempt to regulate the component inventory by manipulating
streams or process conditions. The implicit assumptions behind conventional control structures based on self-regulation of reactants inventory are: 1. the reactants are fed in the correct stoichiometric ratio, and 2. the reactor is large enough to transform into products the entire amount of components fed in the process. These assumptions are not always guaranteed, especially in systems involving complex reactions. In controlled-regulation the inventory of each reactant is measured or evaluated by indirect measurements and adjusted by manipulating the corresponding fresh feed flow rate. For controlled- and self-regulation examples, the reader is referred to work of Downs (1992) and Dimian and Bildea (2004).

The approach based on self-regulation has the advantage of setting directly the production rate by simple adjusting the feed flow rates of self-regulating reactants. In case of complex reactions an additional benefit is the fixed product distribution. This classical strategy is possible only if the reactor is large enough (i.e. high plant Damköhler number). In case of first-order reactions, this control structure could lead to snowballing if the conversion is low (Wu and Yu, 1996). However, the control structure relying on self-regulation works well at high conversion (Bildea and Dimian, 2003). Although the self-regulation strategy offers more advantages, one must be aware of the nonlinear behaviour when designing such systems. Additional constraints could arise because of undesired non-linear phenomena such as state multiplicity, high sensitivity to production rate changes or parameter uncertainty in design. Nevertheless, these constraints could be prevented by proper design decisions.

This study extends the analysis to more complex stoichiometry. The motivation for this study is given in the next topics. A general feasibility condition for self-regulation in multi-reactant/multi-reaction processes is presented in the next chapter. Then, the non-linear analysis starts with a one-recycle system implying parallel-consecutive reactions. It is demonstrated that state multiplicity occurs with unstable low conversion and selectivity branch. The results are confirmed by an industrial case-study, butane alkylation. The next topic is a two-recycle system involving parallel reactions. For this system, the selectivity shows a more complex pattern with regard to state multiplicity. The non-linear analysis is also supported by an illustrative example, the toluene trans-alkylation process. Guidelines of practical significance are provided in the conclusions. Although in the present paper we restrict the discussion to liquid-phase reactions and well-mixed reactor (CSTR), the results could be extended as well to recycle systems including PFRs. In Reactor-Separator-Recycle systems, CSTR and PFR exhibits similar non-linear behaviour (Kiss et al., 2003).
Self-regulation condition for complex stoichiometry

In case of the simple $A + B \rightarrow P$ reaction, the feed flow rates of reactants can not be set both on flow control. Because of inherit measurements errors, reactants can not be fed in the correct stoichiometric ratio if both feed flow rates are set on self-regulation. In case of parallel-consecutive reactions it can be possible to put all feed flow rates on flow control. This is because the system can rely on the self-regulating ability to reject disturbances in the feed flow rate. Due to the more complex stoichiometry, the ‘generation’ and ‘consumption’ terms from the mass balance for each component are adjusting according to the reactants ratio. The self-regulating behavior depends on the number of reactions and the stoichiometry of these reactions. 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 (Dimian and Bildea, 2004).

Let us consider a Reactor – Separator – Recycle system where $N$ reactants $A_j$ gives $M$ products and intermediates $P_k$. The network of $R$ reactions can be described by:

$$v_A^T \cdot A = v_P^T \cdot P$$  \hspace{1cm} (4.1)

where $v_A^T$ and $v_P^T$ are matrices of stoichiometric coefficients. Assuming that the separation section does not allow the reactants $A_j$ to leave the process, the overall mass balance can be written as:

$$v_A \cdot \xi = F_0$$  \hspace{1cm} (4.2)

where $\xi$ 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 $F_0$, if the following condition is fulfilled:

$$\text{rank}(v_A) = N \leq R$$  \hspace{1cm} (4.3)

For the second-order reaction: $A + B \rightarrow \text{Products}$, the rank of the stoichiometric matrix is one. According to Eq. 4.3 it is not possible to put both reactants on flow-control in such a system. This result has been also confirmed by previous studies reported in literature.
(Luyben, 1996). In Table 4.1 other examples are given. The self-regulation condition expressed by Eq. 4.3 is not always fulfilled for complex reactions. In other words the self-regulation condition could be expressed as: the maximum number of feed flows that can be put on flow control is equal with the minimum value between the rank of the stoichiometric matrix and the number of reactants.

**Table 4.1. Self-regulation condition for different stoichiometries.**

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Number of reactants</th>
<th>Number of reactions</th>
<th>Rank of stoichiometric matrix</th>
<th>Self-regulation condition fulfilled?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A \rightarrow P )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>( A \rightarrow P )</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>( A \rightarrow R )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>( A + B \rightarrow P )</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>( A + B \rightarrow P )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>Yes</td>
</tr>
<tr>
<td>( A + B \rightarrow P )</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>Yes</td>
</tr>
<tr>
<td>( A + B + C \rightarrow P )</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>( A + B \rightarrow R )</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>( B \rightarrow S )</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>( A + B + C \rightarrow P )</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>( A + B \rightarrow R )</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>( A + C \rightarrow S )</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>( A \rightarrow T )</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>Yes</td>
</tr>
</tbody>
</table>
In the following topics we show that complex stoichiometry helps enlarging the range of control structure that can be considered. The flow rates of fresh reactants can be set at arbitrary values, but within stoichiometric constraints. Then, the internal flow rates and concentrations adjust themselves in such a way that, for each reactant, the net consumption rate equals the feed flow rate. Therefore, the reactants' inventory is self-regulating. When $N=R$, equation 4.3 has a unique solution. This means that the reaction rate constants or reactor volume do not influence the selectivity or the production rate (Dimian and Bildea, 2004).

**Design by non-linear analysis**

In this section a brief description of the design methodology is presented. Some basic assumptions are considered: 1. isothermal reactors, this implies that temperature can be controlled and 2. 'black-box' separation models, this assumes that composition can be controlled. These assumptions allow writing a simplified balance in a dimensionless form that ensures a large range of applicability. The degree of freedom analysis for these equations will provide the number of variables that must be specified. Usually several sets of specifications are possible. Next step is choosing a control structure that satisfies one set of specifications. Then, bifurcation diagrams are plotted. Effect of different parameters is studied with regard to state multiplicity, stability and sensitivity. The instability of some states could be simply demonstrated by steady-state analysis. These unstable states must be avoided when the nominal design is selected. At this stage is also important to evaluate the behavioural sensitivity with Damköhler number. We have to ensure that no major changes in the non-linear behaviour are possible (e.g. disappearance of steady-states left to the fold) when Damköhler number fluctuates (e.g. change of production rate, catalyst deactivation or temperature changes). On top of everything, economic considerations must be taken into account: reasonable temperatures, realistic recycle rates, practical reactor volume, etc. The end result of this analysis is a nominal design. The approach described provides a fast method to find a feasible design. Steady state controllability of a design is a necessary condition for dynamic controllability.

After choosing the nominal operating point the model is detailed and developed using a traditional process simulator such as AspenTech Aspen Plus™ and Aspen Dynamics™. The full steady-state and dynamic model is used to validate the accuracy of the simple model.
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

One-recycle systems

Let us consider the following consecutive parallel reactions:

\[ \begin{align*}
A + B & \xrightarrow{k_1} P \\
A + P & \xrightarrow{k_2} R
\end{align*} \]

taking place in an isothermal CSTR-Separator-Recycle system. Such chemistry can be found in important processes, as olefins alkylation (butane/butene to iso-octane), or polyether synthesis (ethylene or propylene oxide and alcohols).

Usually, the intermediate product \( P \) is of interest. We consider here the case when the reactants have adjacent volatilities. The assumption is equivalent with this volatilities order: \( \alpha_A, \alpha_B > \alpha_P, \alpha_R \) (i.e. the reactants are lighter than the products). This volatilities order is important from a practical viewpoint since it is very reasonable that two moles of light components (reactants \( A \) and \( B \)) produce one mole of heavy/heaviest component. Since both reactants \( A \) and \( B \) are recycled together the flowsheet has only one recycle (Figure 4.1). We assume good separation, such that both reactants are completely recycled. However, cases when the recycle contains also product along with reactants are taken into account as well.

![Figure 4.1. Control structure relying on self-regulation for a one-recycle plant.](image)

The reactor effluent is processed by the separation section, and afterwards recycled.
Non-linear analysis

The analysis that follows is formulated in terms of dimensionless quantities. 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. The model assumptions are:

- Irreversible chemical reactions that follow the second-order reaction kinetics.
- The separation delivers pure product but not necessarily pure reactants.
- Constant mixture density.

The control structure consists of setting $A$ on flow control, and adding $B$ in the recycle on constant level control (Figure 4.1). The steady state mass balance can be described by the following equations:

**Reactor**

Component $A$: 
\[ 1 + f_1 \cdot z_{A,3} - f_2 \cdot z_{A,2} - Da \cdot \left( z_{A,2} \cdot z_{B,2} + \alpha \cdot z_{A,2} \cdot z_{P,2} \right) = 0 \]  
\[(4.4a)\]

Component $B$: 
\[ f_{B0} + f_3 \cdot z_{B,3} - \left( f_2 \cdot z_{B,2} + Da \cdot z_{A,2} \cdot z_{B,2} \right) = 0 \]  
\[(4.4b)\]

Component $P$: 
\[ f_2 \cdot z_{P,2} - Da \cdot \left( z_{A,2} \cdot z_{B,2} - \alpha \cdot z_{A,2} \cdot z_{P,2} \right) = 0 \]  
\[(4.4c)\]

Total balance: 
\[ 1 + f_R - f_2 = 0 \]  
\[(4.4d)\]

**Separation**

Component $A$: 
\[ f_2 z_{A,2} - f_3 z_{A,3} = 0 \]  
\[(4.4e)\]

Component $B$: 
\[ f_2 z_{B,2} - f_3 z_{B,3} = 0 \]  
\[(4.4f)\]

Component $P$: 
\[ z_{A,3} + z_{B,3} + z_{P,3} = 1 \]  
\[(4.4g)\]

**Reactant make-up**

Component $B$: 
\[ f_R - f_3 - f_{B0} = 0 \]  
\[(4.4h)\]

In the above relation the following dimensionless quantities are defined:

- Plant Damköhler number: 
  \[ Da = k_1 \frac{V}{F_0} \cdot C_{A,0} \]  
\[(4.5)\]

- Kinetic constants ratio: 
  \[ \alpha = \frac{k_2}{k_1} \]  
\[(4.6)\]
From the degree of freedom analysis results that five variables must be fixed \((DOF = 13\) variables – 8 equations). Several sets of specifications are possible. We consider two of them: 1. one reactant on self-regulation: \((Da, \alpha, z_{P,3}, f_{A,0}, f_R)\) or \((Da, \alpha, z_{P,3}, f_{B,0}, f_R)\), and 2. both reactants on self-regulation \((Da, \alpha, z_{P,3}, f_{A,0}, f_{B,0})\).

In case of the first set of specifications, for solving the system described by Eq. 4.4 we choose \(\alpha\) and \(f_R\) as parameters and \(f_{B,0}\) as variable. The separation of product \(R\) is perfect and there is no component \(R\) in recycle. When the product \(P\) is also absent from recycle \((z_{P,3}=0)\), the Damköhler number, conversion of reactant \(A\) and product distribution are given by:

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

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

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

where \(f_{B,0} = 0.5 \ldots 1\)

The value \(Da_r\) is the minimum Damköhler number for which feasible steady state exists and represents a limit point of the balance equations. At the limit point (fold):

\[
g(x, Da) = 0; \quad \det \frac{\partial g}{\partial x} = 0 \quad (4.10)
\]

where \(g\) is the model expressed by Eq. 4.4 and \(x\) represents all unknowns from \(g\).

Then, the following feasibility conditions (i.e. existence of steady states) can be derived, when no products are recycled \((z_{P,3}=0)\):

\[
Da_r = \frac{\left[ f_{B,0}^3 (4\alpha - 2) + 6f_{B,0}^2 (1-2\alpha) + f_{B,0} (7\alpha - 4) - \alpha \right]^2}{\alpha \cdot (f_{B,0} - 1) \left[ 1 - \alpha + f_{B,0} (4\alpha - 2) - f_{B,0}^2 (1-2\alpha) \right]}, \quad Da > Da_r 
\]

108
Figure 4.2. S1 – Influence of recycle flowrate ($f_R$) on conversion and selectivity.

A. $Da - X_A$ bifurcation diagram  
B. $Da - S_{PA}$ bifurcation diagram

Diagram A in Figure 4.2, shows the conversion of the key component $X_A$ for different values of the recycle flow rate ($f_R$). When the Damköhler number exceeds the critical value corresponding to the turning point of the $Da - X_A$ diagram, two feasible steady states exist. A higher recycle rate shifts the limit point to lower conversion and Damköhler number values. It is worth noting that increased recycle rates enlarge the region of feasible steady states and the
range of achievable conversions. Feasible low-conversion operating points are possible for large recycle rates. However, this might not be economically feasible due to the increased costs implied by higher recycle rates. Diagram B of Figure 4.2 shows the selectivity of product $P$ ($S_{P/A}$), as function of Damköhler number. Two steady state solutions are also possible. The shape of this diagram resembles a vertical flip of the $Da$–$X$ diagram. Again, a higher recycle rate increases the range of feasible selectivity.

Figure 4.3. S1 – Effect of separation performance ($z_{P,3}$) on conversion and selectivity.

A. $Da$–$X_A$ bifurcation diagram 
B. $Da$–$S_{P/A}$ bifurcation diagram
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

At a given recycle rate (Figure 4.3, diagram A), a higher molar fraction of product in recycle, \( z_{p,3} \), shifts the fold to higher conversions and larger Damköhler numbers. In consequence, due to the poorer separation, the critical (minimum) reactor volume increases. To minimize the effect of recycle purity on state multiplicity it is therefore recommended to design the separation section in such a way that pure products are obtained. In this case, the absence of product \( P \) in recycle – or its presence in very low concentrations – leads to larger range of stable operating points. Selectivity exhibits a similar trend, as shown in diagram B of the same figure. When the recycle contains only reactants \( (z_{p,3} = 0) \) the selectivity is much higher.

In diagram A of Figure 4.4, conversion is plotted versus Damköhler number for different values of the reaction rates ratio, \( \alpha \), for a fixed recycle rate and no product in recycle \((z_{p,3} = 0)\). Although the range of achievable conversion does not vary much with the reaction rates ratio, it is worth noting that a higher value of \( \alpha \) leads to a smaller reactor volume. As shown in diagram B, the selectivity becomes higher at low values of the reaction rates ratio, \( \alpha \). Unlike conversion, the selectivity exhibit a high sensitivity with the kinetic ratio \( \alpha \). If high selectivity is required one could decrease the reaction rates ratio by changing the reaction temperature, if the activation energies permit. An interesting aspect, highlighted by diagram B of Figures 4.3 and 4.4, 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.

At low Damköhler values all the diagrams from Figures 4.2, 4.3 and 4.4 exhibit an unfeasibility region. The turning point (fold) where a change in stability of states takes place plays an important role in the bifurcation diagrams, as shown in Figures 4.2-4.4. From a control viewpoint, designs close to this turning point should be avoided. The high sensitivity in this region and the uncertainty of the design parameters may shift the operating point to another region where undesired behavior, such as loss of stability or even inexistence of feasible steady states, is likely to occur. It is worth noting that in all figures exhibiting two steady states the low-conversion branch is unstable, as previously demonstrated by Kiss et al. (2002). A brief demonstration of the low-conversion branch instability, for all recycle systems considered in this study, is given in the appendix of this article.
Figure 4.4. S1 – Influence of kinetics ($\alpha = k_2 / k_1$) on conversion and selectivity.

A. $Da-X_A$ bifurcation diagram  \hspace{2cm} B. $Da-S_{P/A}$ bifurcation diagram

Let us consider now the second set of specifications $(Da, \alpha, z_p, f_{A,0}, f_{B,0})$ for Eq. 4.4. The control structure relies on self regulation of all reactants. This means that both feeds $(f_{A,0}, f_{B,0})$ from Figure 4.1 are set on flow control. Figure 4.5 shows that state multiplicity is still present in this case. Moreover the variation of conversion with other parameters exhibits a similar trend with previous figures (diagram A, Figures 4.2-4.4). However, a significant
difference exits with regard to variation of selectivity. In this case, the selectivity does not depend on the Damköhler number, only on $f_{B,0}$ and it is given by the simple linear relationship: $S_{PA} = 2f_{B,0} - 1$. Therefore the feasible range of values for $f_{B,0}$ is limited to the interval $f_{B,0} = 0.5 \ldots 1$. We remark that selectivity is constant for a given $f_{B,0}$.

![Diagram showing the influence of reactants feed ratio (A) and kinetics (B) on conversion.]

Figure 4.5. S1 – Influence of reactants feed ratio (A) and kinetics (B) on conversion.

Both feed flow rates of reactants are set on feed control (i.e. self-regulating).
Considering the results attained in this section the following guidelines can be derived for screening feasible designs in case of parallel/consecutive reactions:

- Work at highest recycle rate (e.g. $f_R > 10$) allowed by the economical trade-off between selectivity gain vs. cost of recycling;
- Use high purity recycles, preferable free of product ($z_{p,3} = 0$);
- Minimize or maximize the kinetic ratio $\alpha$, according to the desired product – $P$ or $R$.

**Case study – butane/butene alkylation**

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

$$C_4H_8 + C_4H_{10} \rightarrow C_8H_{18} \quad k_{0,1} = 1.735 \times 10^{10} \text{ m}^3/\text{kmol-s; } E_{a,1} = 15.55 \text{ kcal/mol}$$

$$C_4H_8 + C_8H_{18} \rightarrow C_{12}H_{26} \quad k_{0,2} = 4.342 \times 10^{11} \text{ m}^3/\text{kmol-s; } E_{a,2} = 19.45 \text{ kcal/mol}$$

Kinetic data and other parameters are available (Rama et al., 2001). 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 (mainly iso-butane) are separated from the products and recycled to the reactor. Main and by-product are separated in the last column. The product purity is minimum 99.8%.

The design of this plant is based solely on the rules formulated in the previous section. Because the product of interest is $P$ (iso-octanate), the kinetic ratio $\alpha$ should be minimized. In Figure 4.6, diagram A, the variation of the kinetic ratio $\alpha$ with the temperature is shown. As can be easily observed, in order to minimize the kinetic ratio it is better to work at the lowest temperature possible. However, cooling requirements constraints must be taken into account. Therefore a temperature of -6.5°C (266.5 K) is chosen. This corresponds to a kinetic ratio value of $\alpha = 1.55$. The next design decision concerns the purity of the recycle. Because of the easy separation $C_4 / C_8$=$C_{12}$, a safe assumption is that no products are recycled. This obeys the rules previously formulated.
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

Figure 4.6. Case study: butane alkylation – steady state design.

A. Variation of kinetic ratio $\alpha$ with temperature.

B. Variation of selectivity with recycle rate.

C. Effect of recycle rate on conversion.

D. Effect of recycle rate on selectivity.

In Figure 4.6, diagrams B, C and D, the variation of conversion and selectivity is presented at different recycle rates ($\alpha = 1.55$ and $z_{p,3} = 0$). According to the guidelines it is better to use higher recycle rates. Diagrams C and D will help us choose the proper recycle rate. Due to economical constrains (i.e. cost of the recycling) the recycle rate could not be extremely high. Therefore, in order to keep a high selectivity (>85%), while considering the economic constrains, we choose a recycle rate of twenty ($f_R = 20$). Any higher recycle rate will provide an irrelevant increase of selectivity, as illustrated in diagram B of the Figure 4.6.

A larger recycle means higher selectivity but also higher concentration of component $B$ in the recycle streams. That implies low sensitivity of the recycle with $Da$ or conversion. Hence an optimized design would suggest a design close to fold. If the activity of the catalyst is altered or temperature changes occur, then the design may fall left to the fold where no feasible states exist. Therefore, designs in the region near fold should be avoided. The last
design variable that must be set is the Damköhler number. According to Figure 4.6 there is no change in selectivity on the stable high-selectivity branch when $Da$ is increased. For that reason it is not required to use a large reactor (i.e. high $Da$). However, choosing a very small $Da$ leads to designs where no feasible states exist ($Da < Da^*$). A simple optimization procedure suggests $Da = 10$ as minimum value. Considering a classical 20% over-design of the reactor volume the chosen Damköhler number is $Da = 12$ (case A). This corresponds to a reactor volume of $3 \text{ m}^3$. However, such designs near fold that might be difficult to control. Therefore we choose a second design characterized by a higher Damköhler number, $Da = 20$ (case B). This relate with a reactor volume of $5 \text{ m}^3$. In this second case the Damköhler number was chosen taking into account that the minimum reactor volume corresponds to the maximum rejectable disturbance. Hence, a disturbance of +100% in the feed flow rate is equivalent with a decrease of $Da$ from 20 to 10. This value ($Da=10$) corresponds to the maximum disturbance and it is the minimum value suggested by the optimization procedure.

Finally, the designs based on these decisions have these parameters: isothermal CSTR (T=266.5 K); reactor pressure = 8.5 atm; recycle rate ratio = 20; products molar fraction in recycle = 0. The distillation columns are designed using the classical method: number of trays $N_{trays} = 2 \cdot N_{trays, \min}$ and reflux ratio $R = 1.3 \cdot R_{\min}$. The columns have 15 and 10 stages, respectively. Correspondingly, the reflux ratio is 0.1 and 1. Both columns have total condensers and 100% tray efficiency. The inlet pressure in the columns is the same as in the reactor and the total pressure drop is 0.7 and 0.35 atm, respectively. For each column, the reflux drum and the sump were dimensioned considering a residence time of 5 minutes. The same rule was applied for the design of the mixer. All controllers used are PI controllers with the following specifications:

- **LC:** Reactor, columns, mixer: $K_p = 10 \%/\%$ and $K_{p,mix} = 1 \%/\%$; $T_i = 6000 \text{ min}$; Range: 0...2-L
- **TC:** Columns: $K_p = 1 \%/\%$; $T_i = 20 \text{ min}$; Reactor: $K_p = 5 \%/\%$; $T_i = 6 \text{ min}$; Range: $T \pm 10 \text{ K}$
- **PC:** Columns: $K_p = 20 \%/\%$; $T_i = 12 \text{ min}$; Range: $P \pm 0.01 \text{ bar}$

The steady-state simulation was performed in AspenTech AspenPlus™. Afterwards, a rigorous dynamic model was built in AspenTech AspenDynamics™. Three cases, for two different control structures were considered:

1. **Case A:** only one reactant ($A$) on flow control, as shown in Figure 4.1 – optimized design;
2. **Case B:** only one reactant ($A$) on flow control (Figure 4.1) – guidelines design;
3. **Case C:** both reactants ($A,B$) on flow control – guidelines design.
Figure 4.7. Butane alkylation – dynamic response for a 100% increase of feed-flowrate.

Variation in time of product purity ($z_p$), production rate ($F_p$) and selectivity ($S_{PA}$).

Only one reactant is self-regulating: A. optimized design  B. guidelines design.

Both reactants are self-regulating: C. guidelines design

Figure 4.7 presents the results of the dynamic simulation results for all three cases considered. At time $t = 1$ hr, a disturbance of +100% in the feed flow-rate is applied. Diagram A shows the inability of the small reactor ($3 \, \text{m}^3, Da=12$) to reject such a huge disturbance. After two hours the system can no longer be controlled due to the overflow. Diagrams B show the dynamic response for the second case ($5 \, \text{m}^3, Da=20$) where only one reactant is self-regulating (i.e. reactant $A$ is on flow control). The increase of iso-octane production rate is accompanied by a decrease of purity and selectivity. The system reaches the new steady-state after approximately 8 hours. This control structure obeys Luyben’s rule to keep one of the
flow rates from recycle loop on flow control. Therefore, as expected, there are no difficulties
in this case. In diagram C, the dynamic response to the same disturbance is shown for the case
C (5 m$^3$, Da=20) where this time both reactants are self-regulating (i.e. both reactants A, B are
set on flow control). The production rate of iso-octane increases, being accompanied again by
a decrease of purity and selectivity. However, this decrease is not as large as in the previous
case thus offering a better performance, but the system reaches the new steady-state after a
longer time – approximately 17 hours. This control structure does not obey Luyben’s rule, as
there is no flow rate controlled in the recycle loop. However, as can be observed there are no
difficulties in this case. The explanation is simple given by the self-regulation condition (Eq.
4.3), which correctly predicts that both reactants can be set on flow control for this
stoichiometry. Luyben’s rule was established for simple stoichiometries and there is no
contradiction with the self-regulation condition (Eq. 4.3) deduced in the first part.

One predictable question is how the plant is able to reject such a large disturbance. At the
nominal operating point the reactor and columns must process the fresh feed and a recycle
flow rate that is 20 times larger than the feed. Any large increase of the fresh feed (e.g. 100%)
is rather small compared to the recycle rate. Therefore, all units involved in recycle are able to
reject the disturbance.

**Two-recycle systems**

In this section we consider another complex stoichiometry, namely the parallel reactions:

$$A + B \xrightarrow{k_1} 2P$$

$$2A \xrightarrow{k_2} P + R$$

Such chemistry can be found in the toluene trans-alkylation process presented as case study in
the next section. Depending on the physical properties of the species, several design
alternatives are possible. If the reactants A and B are lighter and heavier, respectively, than the
main product P, the flowsheet has two recycle streams. Figure 4.8 describes the flowsheet for
the case when volatilities are ordered as: $\alpha_R > \alpha_A > \alpha_P > \alpha_B$. The control loops regards
the reactor level and temperature, as well as the top and bottom purity of the distillation columns.
The feed of reactant A is on flow control, $f_A^0 = 1$, relying on self-regulation. The flow rate of
reactant B at the reactor inlet $f_{R,B}$ is fixed. Note that this includes recycle and make-up feed.
The feed rate of reactant $B, f_B^0$, is used to control its inventory.
Non-linear analysis - CSTR

Using the same assumptions as for the previous system, the following mass balance equations can be derived for this control structure:

**Reactor mass balance**

Component $A$: \[ 1 + f_3 \cdot z_{A,3} - f_2 \cdot z_{A,2} - Da \cdot (z_{A,3} \cdot z_{B,2} + \alpha \cdot z_{A,2}^2) = 0 \]  \hspace{1cm} (4.12a)

Component $B$: \[ f_{B,0} + f_5 \cdot z_{B,5} - (f_2 \cdot z_{B,2} + Da \cdot z_{A,2} \cdot z_{B,2}) = 0 \]  \hspace{1cm} (4.12b)

Total balance: \[ 1 + f_3 + f_5 + f_{B,0} - f_2 = 0 \]  \hspace{1cm} (4.12c)

**Separation mass balance**

Component $A$: \[ f_2 z_{A,2} - f_3 z_{A,3} = 0 \]  \hspace{1cm} (4.12d)

Component $B$: \[ f_2 z_{B,2} - f_3 z_{B,3} = 0 \]  \hspace{1cm} (4.12e)

Make-up of $B$: \[ f_{B,0} - f_5 - f_{B,0} = 0 \]  \hspace{1cm} (4.12f)

Selectivity: \[ S_{PA} = (1+3f_{B,0})/2; \quad S_{RA} = (1-f_{B,0})/2 \]  \hspace{1cm} (4.12g)

where: \[ Da = k_1 \frac{V}{F_0} \cdot C_{A,0}; \quad \alpha = \frac{k_2}{k_1} \]

Figure 4.8. Control structure relying on self – regulation for a two-recycle plant.
The degree of freedom for the model expressed by Eq. 4.12 is six (DOF = 12 variables – 6 equations). When the kinetic ratio $\alpha$ decreases to zero (first reaction dominates) or increases to infinite (second reaction dominates) the following limiting cases can be derived:

$$\lim_{\alpha \to 0} S_{PA} = 2$$  \hspace{1cm} (4.13)

$$\lim_{\alpha \to \infty} S_{PA} = 0.5 \ ; \ \lim_{\alpha \to \infty} Da = \frac{1}{\alpha \cdot z_{A,3}^2}$$  \hspace{1cm} (4.14)

![Figure 4.9. S2 – Effect of recycle flow rate ($f_R$) on conversion and selectivity](image)

**Figure 4.9. S2 – Effect of recycle flow rate ($f_R$) on conversion and selectivity**

A. $Da-X_A$ bifurcation diagram  \hspace{1cm} B. $Da-S_{PA}$ bifurcation diagram
Diagram A of Figure 4.9, shows the conversion of reactant A versus Damköhler number as bifurcation diagram for different recycle rates. State multiplicity is possible for Damköhler numbers exceeding the critical value. In addition, when the recycle rate increases too much ($f_R > 3$) the performance of the reactor (i.e. the conversion) drops down. This occurs due to the increased reactor inlet flow rate that leads to a smaller residence time.

Figure 4.10. S2 – Influence of recycle purity ($z_{BS}$) on conversion and selectivity.

A. $Da-X_A$ bifurcation diagram  
B. $Da-S_{PA}$ bifurcation diagram
In diagram B of Figure 4.9 the selectivity is plotted versus Damköhler number. The variation of selectivity with the Damköhler number is very low at high values of Damköhler number. However, around $Da = 5$ corresponding to the lowest selectivity, the sensitivity of selectivity is extremely high, signifying that any small change in the Damköhler number leads to a very large variation of selectivity.

Figure 4.11. S2 – Effect of kinetics ($\alpha = k_2 / k_1$) on conversion and selectivity.

A. $Da-X_A$ bifurcation diagram  B. $Da-S_{PA}$ bifurcation diagram
In Figure 4.10, diagram A, the $Da-X$ bifurcation diagram is plotted for different separation performances. When the purity of the recycle decreases the reactor performance also decreases. Therefore it is better to work with high purity recycles, considering of course the economic trade-off (i.e., purity vs. cost of separation). Diagram B shows the variation of selectivity with the Damköhler number for different recycle compositions ($z_{B,s}$). The selectivity exhibits low sensitivity at high Damköhler numbers, but very high sensitivity around the fold.

Figure 4.11, diagram A, shows the influence of kinetics on the conversion of reactant $A$ versus Damköhler number bifurcation diagram. For small kinetic ratios ($\alpha < 0.5$) multiple steady states are possible. However, for $\alpha > 0.5$ the second reaction dominates. As a result the system behaves similarly to a pseudo first-order reaction system ($A \rightarrow Products$). Therefore, only one steady state exists for these cases. Diagram B shows a similar transition for selectivity versus Damköhler number. For low $\alpha$ values the system behaves as pseudo first-order reaction, while for high $\alpha$ values the system follows a second-order reaction behaviour. The curves plotted in diagram B change from one steady state to two steady states.

It is interesting to remark that the guidelines to avoid the undesired effects of state multiplicity, formulated for the previous system, remain valid also for this case.

**Non-linear analysis - PFR**

Replacing the CSTR with a PFR leads to similar balance equations. The only difference is reactor mass balance:

_Reactor mass balance_

\[
\begin{align*}
\text{Component } A: \quad & \frac{dzc_A}{d\xi} = -\frac{1}{f_1} \cdot Da \cdot \left( z_{A,1} \cdot z_{B,1} + 2 \cdot \alpha \cdot z_{A,2}^2 \right) \\
\text{Component } B: \quad & \frac{dzc_B}{d\xi} = -\frac{1}{f_1} \cdot Da \cdot z_{A,1} \cdot z_{B,1} \\
\text{Total balance:} \quad & 1 + f_3 + f_5 + f_{B,0} - f_2 = 0
\end{align*}
\]

CSTR and PFR exhibit similar non-linear behaviour in recycle systems, as previously demonstrated (Kiss et al., 2003). In order to illustrate the similarities, Figure 4.12 shows the
non-linear behaviour of the PFR in the two recycle system. The similarity can be easily observed by comparing Figure 4.12 (PFR in recycle) with Figure 4.9 (CSTR in recycle). The non-linear analysis reveal the same qualitative behaviour. There are however some small quantitative differences.

Figure 4.12. S2 – The non-linear behaviour of the PFR-Separator-Recycle system is similar to the CSTR-Separator-Recycle system.
A. $Da-X_A$ bifurcation diagram  B. $Da-S_{p/A}$ bifurcation diagram
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

**Case study – toluene trans-alkylation**

In order to assess the stability of the steady states, a dynamic simulation was developed in Aspen Dynamics™. The physical properties of $A$, $B$, $P$, and $R$ species correspond to toluene, tri-methyl-benzene, xylene and benzene, respectively.

\[ C_6H_5-CH_3 + C_6H_4(CH_3)_2 \xrightarrow{k} 2C_6H_4(CH_3)_2 \quad k_{0,1} = 2 \cdot 10^{10} \text{m}^3/\text{kmol·s}; E_{a,1} = 20 \text{ kcal/mol} \]

\[ 2CH_3 \xrightarrow{k} C_6H_4(CH_3)_2 + C_6H_6 \quad k_{0,2} = 2.8 \cdot 10^9 \text{m}^3/\text{kmol·s}; E_{a,2} = 19 \text{ kcal/mol} \]

In this example both products are of interest. Setting the product distribution is the main challenge. As previously shown, several sets of specifications result after the degree of freedom analysis. These sets of specifications lead to different control structure. For this case study we consider the control structure based on one set of specifications: $(Da, \alpha, z_{A,3}, z_{B,5}, f_{A,0}, f_{k})$. Other control structures could be better but this is beyond the scope of this article.

The design of this plant is also based exclusively on the rules formulated in the previous section. According to Figure 4.11 it is preferable to work at a kinetic ratio $\alpha = 0.3$ because it offers a large range of achievable conversion and selectivity. Lower $\alpha$ values lead to state multiplicity and instability of one state and higher $\alpha$ values requires a large change of $Da$ for a small change of selectivity. In Figure 4.13, diagram A, the variation of the kinetic ratio $\alpha$ with the temperature is shown. The temperature of 380 °C (653 K) corresponds to the desired kinetic ratio $\alpha = 0.3$. The next design decision concerns the purity of the recycle. Because of the easy separation of products, a safe assumption is that no products are recycled. This obeys the rules previously formulated.

In Figure 4.13, diagrams B and C, the variation of conversion and selectivity is presented at different recycle rates ($\alpha = 0.3$ and $z_{A,3} = 1, z_{B,5} = 1$). According to the guidelines it is better to use higher recycle rates. Diagrams B and C facilitate choosing the proper recycle rate. Due to economical constrains the recycle rate could not be extremely high. Therefore, in order to keep a high selectivity, while considering the economic constrains, we choose the recycle rate $f_R = 5$. This value is enough to ensure a large range of achievable selectivity. Any larger recycle will offer an unimportant increase of the attainable selectivity range. The last design variable that must be set is the Damköhler number.
Chapter 4.  

Plantwide Control of Recycle Systems with Multiple Reactions

Figure 4.13. Case study: toluene trans-alkylation – steady state design.

A. Variation of kinetic ratio $\alpha$ with temperature  
B. Effect of recycle rate on conversion.  
C. Effect of recycle rate on selectivity.
Figure 4.14. Toluene trans-alkylation – products distribution and dynamic responses.

A. Variation of products distribution with plant Damköhler number.

B. Conversion and products distribution change when Damköhler increases with +100%.

C. Conversion and products distribution change when Damköhler decreases with -50%.
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

According to Figure 4.13 the sensitivity of selectivity is decreasing when $Da$ is increased. A smaller $Da$ offers a larger range of attainable selectivity. For that reason we choose $Da = 4$. This value let us manipulate the selectivity in a large range, by small changes of $Da$ (i.e. flow rate). Steady-state simulations were performed in AspenTech AspenPlus™. Afterwards, a rigorous dynamic model was built in AspenTech AspenDynamics™ (AspenTech, 2001). For each column, the reflux drum and the sump were dimensioned considering a residence time of 5 minutes. The same rule was applied for the design of the mixer. All controllers used are PI controllers with the following specifications:

- **LC**: Reactor, columns, mixer: $K_p = 10 \%$ and $K_{p,mix} = 1 \%$; $T_i = 6000$ min; Range: 0...2 L
- **TC**: Columns: $K_p = 1 \%$; $T_i = 20$ min; Reactor: $K_v = 5 \%$; $T_i = 5$ min; Range: $T \pm 10$ K
- **PC**: Columns: $K_p = 20 \%$; $T_i = 10$ min; Range: $P \pm 0.01$ bar

The reactor has a volume of 3 m$^3$ and is operated isothermal at $T=653$ K and $P=30$ atm. All distillation columns have 30 trays and are operated at normal pressure. The purity of products is 99.9%. The inlet pressure in all columns is 2 atm and the total pressure drop is 0.5 atm.

Diagram A of Figure 4.14 shows the product distribution at steady states. Unlike the previous case study, the stability is not the main concern here because the operating point was chosen in the region where only one steady-state exists. The most important issue in this case is the flexibility and products distribution. Any change of the nominal operating point ($Da=4$) shifts the distribution to a product or the other. Diagrams B and C of the same figure present the response of the system for +100% and -50% disturbance in the plant Damköhler number. These disturbances correspond to an increase from $Da=4$ to $Da=8$ and a decrease from $Da=4$ to $Da=2$, respectively. When Damköhler number is increased by 100% (i.e. feed flow rate is reduced to half of the nominal value) the distribution of the products change from 78% xylene and 22% benzene to 86% xylene and 14% benzene. The disturbance in opposite direction (Damköhler decreases by -50%, i.e. feed flow rate increases with half of the nominal value) shifts the distribution of products from 78% xylene and 22% benzene to 66% xylene and 34% benzene. Therefore, a reasonably large range of product distributions is feasible: 66%-86% for xylene and 14%-34% for benzene.

The flexibility of the production rate is associated with the flexibility of the products distribution. This important feature can be used in practice in a clever manner to change the production rate and product distribution according to market requirements.
Conclusions

This study deals with non-linear phenomena as state multiplicity and instability in Reactor-Separator-Recycle systems involving multi-reactions, as well as with reactor design and plantwide control issues. Two typical schemes are studied, as parallel/consecutive reaction S1: \( A + B \rightarrow P; \ A + P \rightarrow R \), and parallel reaction S2: \( A + B \rightarrow 2P; \ 2A \rightarrow P + R \), respectively, both considering bi-molecular kinetics. The analysis is presented in term of dimensionless numbers, as the plant Damköhler number and the ratio of kinetic constants. For each system a set of guidelines has been formulated. These guidelines should be considered during the conceptual stage of design and control of such systems. Two case studies consolidate the theoretical analysis of the studied systems.

When two or more reactants have adjacent volatilities, they are recycled together. Fixing partial flow rates would require composition measurements. In this case, designs achieving almost complete conversion of one reactant are recommended.

Although self-regulation works well for simple reactions, in the case of complex stoichiometry the situation is more complicated. Control structures involving self-regulation are feasible only if there are sufficient reactions to adjust the consumption rate of each reactant in such a way that no accumulation occurs. This condition is simple expressed by the equation 4.3, which states that it is possible to set 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.

State multiplicity could occur, some states being unstable, if the control structure implies self-regulation of one reactant. The low-conversion branch is always unstable. This instability sets a hard constraint on the selection of the operating point. The high sensitivity of selectivity around the turning point is an additional non-linear effect in the case of parallel reactions (two recycle system). Therefore, designs close to this area must be avoided.

Feasible steady states exist only if the reactor volume exceeds a critical value. This condition corresponds generally to a bifurcation point of the mass balance equations. For example, for first-order reactions with pure product and recycle the feasibility condition is simply \( Da > 1 \) (Bildea et al., 2000; Kiss et al., 2002). Similar expressions hold for complex stoichiometries (e.g. Eq. 4.11).

Ignoring the steady state multiplicity can lead to control difficulties. The nonlinear analysis is an appropriate tool to identify and avoid such dangerous situations at the
conceptual design stage. In order to enlarge the feasibility region and avoid unstable states or regions where no steady states exist, we provide some basic guidelines, as follows:

✓ The recycle should contain only a very small amount of product or no product at all.
✓ The recycle rate should be as high as possible, limited only by the economical trade-off.
✓ Depending on the product of interest the kinetic parameters could be changed in such a way that the selectivity is maximized. The kinetic ratio $\alpha$, used to manipulate the selectivity, can be adjusted by changing the reaction conditions (e.g. temperature) or using another catalyst.

**Notation**

\[ c_k \] = concentration of reactant $k$, mol/m$^3$
\[ Da \] = Damköhler number, dimensionless
\[ = k_i V F_0^{-1} C_A^{-1} \]
\[ E_{a1} \] = activation energy, kcal/mol
\[ F \] = flow rate, m$^3$/s
\[ f_k \] = flow rate, dimensionless
\[ = F_k / F_0 \]
\[ k_{0,1} \] = pre-exponential factor, m$^3$ kmol$^{-1}$ s$^{-1}$
\[ k_i \] = reaction rate constant, (mol/m$^3$) s$^{-1}$
\[ K_p \] = controller proportional gain, % / %
\[ n \] = reaction order, dimensionless
\[ S \] = selectivity, dimensionless
\[ T_i \] = controller integral time, minutes
\[ V \] = reactor volume, m$^3$
\[ X_k \] = conversion of reactant $k$, dimensionless
\[ z_k \] = concentration of reactant $k$, dimensionless
\[ = c_k / c_0 \]
\[ \alpha \] = reactions rate constants ratio, dimensionless
\[ = k_2 / k_1 \]
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

Subscripts

0 = fresh feed
1 = reactor inlet
2 = reactor outlet, separation inlet
3, 5 = recycle streams

Appendix

Instability of the low-conversion branch

When two steady states are born at a fold bifurcation point, at least one of them is unstable. In the following, we will prove the instability of the low-conversion steady state, using only the steady state model. Hence, this result is independent of the dynamic separation model. For a stand-alone reactor, the amount of reactant consumed depends on the reactor's feed flow rate. In a Reactor–Separator–Recycle system, the steady state values of the reactor-inlet flow rate or recycle rate are given by the intersections of this curve with the dimensionless amount of reactant fed in the process. We choose one example for each system discussed in the article.

For the case shown in diagram A of Figure 4.2 ($f_R=10$ and $Da = 10$) and the one presented in diagram A of Figure 4.9 ($f_R=10$ and $Da = 4$), two steady states exist. Both cases are shown in Figure 4.15. To analyse the stability of the low-conversion state B, let us consider a small, positive / negative deviation of the recycle and reactor inlet flow rate, respectively. At the right / left of point B, the amount of reactant fed in the process is larger / smaller than the amount of reactant consumed. Reactant accumulation / depletion occurs, which is reflected by a further increase / decrease of the recycle and reactor-inlet flow rates; hence the steady state B is unstable. Note that although these arguments are independent of the dynamic separation model, they give a necessary but not a sufficient stability condition. To prove the stability of the high-conversion steady state A, a dynamic model is needed. The results of the dynamic simulations for the case studies presented in the article confirm the stability of the high conversion branch.
Figure 4.15. Instability of the low-conversion branch for one- and two-recycle systems.
Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions

References


Chapter 4. Plantwide Control of Recycle Systems with Multiple Reactions


