Integration of design and control by nonlinear analysis
Bildea, C.S.

Citation for published version (APA):
Bildea, C. S. (2001). Integration of design and control by nonlinear analysis

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 7 Nonlinear behaviour of reactor-separator-recycle systems: Implications for integrating conceptual design and plantwide control

Abstract

This article studies the nonlinear behaviour of reactor-separator-recycle systems. The dimensionless mole-balance equations are parameterized by the plant Damköhler number \((Da)\) and the separation specifications. Reactant accumulation does not occur if \(Da > Da^c\). \(Da^c\) corresponds to a bifurcation point of the mole-balance equations and depends on separation performance. For one reactant recycle and high purity separation, \(Da^c = 1\). When two reactants are recycled, multiple steady states are possible. In this case, \(Da^c\) depends also on the control structure. Close to \(Da^c\), control structures must change the reaction conditions in order to reject effectively the disturbances. Reviewing several plantwide control studies that reported bad controllability, we found that the designs considered are close to the critical value of the plant Damköhler number.
Introduction

During the traditional design of chemical processes, many alternatives are generated. Early in the project development, economic criteria are used to discard unattractive designs. Later, when the flowsheet structure is established and the units are sized, controllability issues become more important. Often, the designer finds that the alternatives developed do not have the required operability properties. Hence, designs that have been rejected because of lower economic performance are re-evaluated. Because this approach may be time and effort consuming, the need of integrating process design and control is well recognized. Yet, a procedure to generate controllable design alternatives is not available.

Chemical plants are nonlinear systems. Today simulation software makes possible the development of detailed, nonlinear dynamic models. Nevertheless, for the purpose of controllability analysis (Skogestad and Postlethwaite, 1996), linear models are (frequently successfully) employed. This happens because the mathematical tools needed to analyze linear differential equations are well developed, while the theory of nonlinear differential equations is still an active field of research. However, many of the control problems originate from a bad design. Dynamic modeling requires equipment sizing, which is not available during conceptual design. Consequently, the designer relies upon steady state models. However, he still uses linear tools, although analysis of nonlinear algebraic equations is possible.

The nonlinearity of chemical processes can manifest as parametric sensitivity, state multiplicity, instability, or oscillatory behaviour (Seider and Brengel, 1991). These features can be predicted by singularity (Golubitsky and Schaeffer, 1985) and bifurcation (Guckenheimer and Holmes, 1983) theories, which have been extensively applied in the field of chemical reaction engineering. A classic example is the first-order, exothermic reaction in CSTR, axial dispersion reactor, or catalytic particle. Generally, bifurcation diagrams are used to represent the dependence of the system’s state vs. one distinguished operating variable (bifurcation parameter). Then, bifurcation varieties are computed. They divide the space of the remaining parameters into regions corresponding to qualitative-different bifurcation diagram. From the viewpoint of design and control, designs close to bifurcation varieties generally should be avoided. The reason is that the uncertainty of the design parameters and the disturbances affecting the process may shift the operating point to a region where the
qualitative behavior is different from the expected one. Then, undesirable phenomena may occur: loss of stability, reaction ignition or extinction, reverse sign of the gain in control loops, etc. Moreover, close to bifurcation points, high sensitivity to disturbances is expected.

Most of the previous studies considered the stand-alone reactor. Although the effect of recycling a fraction of the reactor effluent has been occasionally studied (Pareja and Reilly, 1969, Recke and Jorgensen, 1999), the systems considered are not good examples for chemical reactors in recycle plants. Typically, the reactor effluent is processed by the separation section. Hence, the composition and temperature of the recycle stream are different from the reactor effluent. Moreover, often temperature controllers keep constant reaction temperature, or, for adiabatic reactors, constant temperature of the reactor feed.

This article addresses the nonlinear behaviour of certain reactor-separator-recycle systems. Figure 7.1 presents the flowsheet considered. In a real plant, several feed, product, or recycle streams may exist. Hence, each general streams of Figure 7.1 (Plant feed; Reactor feed; Reactor effluent / Separation feed; Recycle; Products) represents an arbitrary number of real streams.

![Figure 7.1. General structure of Reactor-Separator-Recycle systems.](image-url)
Throughout this work, the molar flow rate of the streams enumerated above are denoted by \( F, R, S, Y, \) and \( P \), respectively. Symbols as \( F_A, S_B, \) are used for the components flow rates, where the subscript refers to chemical species. Dimensionless flow rates are obtained by division to the feed flow rate of a reference reactant (\( F_A \)). They are represented by lower-case symbols (for example, \( r = R/F_A, S_B = S_B/F_A \)). Greek letters are used for flow rate ratios (for example, \( \alpha_{YS} = Y_A/S_A, \phi_{RF} = R/F \)). \( c_{ik} \) and \( z_{ik} \) signify concentration and mole fraction, respectively, of the \( i^{th} \) component in the \( k^{th} \) stream.

The behaviour of reactor-separator-recycle systems is relevant for integrating conceptual design and plantwide control because, early during conceptual design, one reaches a stage when the recycle structure of the flowsheet is established. Then, the reactor is the first unit to be considered in detail because the chemical species present in the reactor effluent determine the separation section. Hence, reactor modeling, sizing, and control are considered before separation is addressed. In this work, we will treat the separation as a black box, and consider a kinetic model of the chemical reactor.

This article is organized as follows. In the next section, we study a first order reaction in a CSTR-separator-recycle system. The dimensionless mole-balance equations are parameterized by the plant Damköhler number (\( Da \)) and the separation specifications. It is demonstrated that reactant accumulation does not occur if \( Da > Da^C \), where the critical value \( Da^C \) depends on separation performance. For \( Da = Da^C \), a transcritical bifurcation of the mole balance equations takes place. For high purity of product and recycle streams, \( Da^C = 1 \). These conclusions also apply to the PFR, first-order consecutive, and \( n^{th} \)-order reactions. Further, we compare two different control structures and show that their relative performance depends on the design. Close to \( Da^C \) (small reactor or slow kinetics), it is necessary to change the reaction conditions when disturbances affect the process. In the last section, we discuss two different control structures for a second order reaction. In these cases, the critical value of the plant Damköhler number corresponds to a fold bifurcation of the mole balance equations. Reviewing several plantwide control studies that reported bad controllability, we found that the designs considered are close to the critical value of the plant Damköhler number.

**Plant Damköhler number**

In this section it will be shown that there is a minimum-volume constraint for a chemical reactor placed in a recycle plant.
Chapter 7. Reactor-Separator-Recycle Systems

We consider the first-order $A \rightarrow B$ reaction, taking place in a CSTR. Mole balance equations can be solved for consistent specifications. One possible choice is: flow rates of $A$ and $B$ in the feed stream ($F_A, F_B$); reactor volume ($V$); separation performance, for example as recoveries ($\alpha_{YS} = Y_A / S_A$ and $\beta_{PS} = P_B / S_B$). It must be pointed that often the reactant is completely recovered in the separation section ($\alpha_{YS}=1$).

The reactor feed is chosen as tear stream and the reaction conversion ($x_A = 1 - S_A / R_A$) is introduced as auxiliary variable. Then, the following dimensionless balance equations can be easily derived:

$$r_A = f_A + \alpha_{YS} \cdot r_A \cdot (1-x_A) \quad (7.1)$$
$$r_B = f_B + (1-\beta_{PS}) \cdot (r_A + r_A \cdot x_A) \quad (7.2)$$

If the product $B$ is not present in the feed stream ($f_B = 0$) and is completely recovered in the separation section ($\beta_{PS}=1$), then:

$$r_A = \frac{R_A}{F_A} = \frac{1}{1-\alpha_{YS} \cdot (1-x_A)} \quad (7.3)$$
$$r_B = \frac{R_B}{F_A} = 0 \quad (7.4)$$
$$z_{AS} = 1 - x_A \quad (7.5)$$

To find the conversion, the CSTR equation:

$$R_A - S_A = k \cdot V \cdot c_{AS} \quad (7.6)$$

is written in the following dimensionless form:

$$g(x_A, Da, \alpha_{YS}) = Da - \frac{x_A}{(1-x_A) \cdot (1-\alpha_{YS} \cdot (1-x_A))} = 0 \quad (7.7)$$

$$Da = \frac{k \cdot V}{F_A \cdot V_{mA}}$$

is the plant Damkohler number, which includes the reactor volume, the reaction kinetics, the reactant feed flow rate, and its molar volume at reactor temperature and pressure. Eq. 7.7 assumes that the molar volume does not depend on composition. This is true for gas-phase reactions. For liquid-phase reactions, an additional parameter, $v_B = V_{mB} / V_{mA}$, should be introduced in the balance equations. If $A$ and $B$ are isomers and have similar densities, then $v_B \approx 1$. 

163
Eq. 7.7 has two Damköhler-dependent solutions. They are presented in Figure 7.2a, for different values of the $\alpha_{y,s}$ parameter. For stand-alone CSTR ($\alpha_{y,s} = 0$) or incomplete reactant recycle ($\alpha_{y,s} < 1$), the feasible ($0 < x_A < 1$) and unfeasible ($x_A < 0$) solution branches do not intersect. When all the reactant is recycled ($\alpha_{y,s}=1$), one solution ($x_A = 0$) involves infinite recycle. The other solution has physical significance ($0 < x_A < 1$) if, and only if, $Da > 1$. Moreover, the two branches intersect at the point T having the coordinates $(x_A, Da) = (0, 1)$.

Figure 7.2. First-order reaction in CSTR-Separator-Recycle: conversion, yield and reactor outlet / separation inlet flow rate
In the framework of the bifurcation theory, the point T represents a transcritical bifurcation of the model equations. The defining condition for the transcritical bifurcation is (Guckenheimer and Holmes, 1983):

$$\frac{\partial g(x_A, Da, \alpha_{YS})}{\partial x_A} = -\frac{1-\alpha_{YS} + \alpha_{YS} \cdot x_A^2}{(1-x_A)^2 \cdot (1-\alpha_{YS} + \alpha_{YS} \cdot x_A)^2} = 0$$ (7.8)

The only feasible case ($0 < \alpha_{YS} \leq 1$) when the real root

$$x_A^{\alpha} = \pm \sqrt{\frac{(\alpha_{YS} - 1)}{\alpha_{YS}}}$$ (7.9)

exists is $\alpha_{YS}=1$. Substitution in Eq. 7.7 gives:

$$\lim_{x_A \to \alpha_{YS}} g(x_A^{\alpha}, Da, \alpha_{YS}) = Da - 1 = 0$$ (7.10)

Bifurcation theory states that an exchange of stability takes place at the transcritical bifurcation point. If the reactor volume is small or the reaction rate is slow, the reactant fed in the process can not be entirely transformed into products. Because the reactant can not leave the plant, it accumulates, and the recycle becomes infinite. Hence, for $Da < 1$, the trivial solution ($x_A = 0$, infinite recycle) is stable (solid line in Figure 7.2a). Increasing the Damkohler number $Da > 1$, the stable, feasible solution appears, while the infinite-recycle solution loses stability.

Figure 7.2b presents the yield, defined as $p_B = P_B/F_A$, of the CSTR – separator – recycle system, for different values of the reactant recycle ratio $\alpha_{YS}$. When the entire amount of unreacted A is recycled, the yield equals the maximum value, $p_B=1$. For the same feed, the yield of the stand-alone CSTR is the lowest.

In recycle systems, the yield enhancement is achieved through separation and increased flow rates. Figure 7.2c presents the flow rate of the stream entering the separation system. High values of the recycle ratio, small reactor volume or slow reaction rate lead to high flow rates. If the operating point is close to $Da=1$, then the flow rates exhibit extremely high sensitivity to change of reactant feed flow rate, reaction rate, or reactor volume, and severe control problems are expected.

The set of specifications ($\alpha_{YS} < 1, \beta_{PS}=1$) may represent a separation section that, after the A–B mixture is split into components, purges a fraction of A. This has a stabilising
effect. It should be remarked that systems where the purge flow rate is fixed are qualitatively identical with systems where the entire amount of reactant is recycled.

Often, the separation section is operated in such a way that the composition of the outlet streams are kept to required values \( z_{A,Y} < 1 \) and \( z_{B,P} < 1 \). Hence, a small quantity of reactant leaves the plant in the product stream, while some product is recycled. Such systems behave as systems with pure separation products (\( \alpha_{Y,S} = 1, \beta_{P,S} = 1 \)). To demonstrate this statement, we follow the procedure outlined above, using \( z_{A,Y} \) and \( z_{B,P} \) as specifications for the separation section. After some algebraic manipulations and cancellation of the trivial solution \( x_A = 0 \), the following equation is obtained:

\[
x_A = \frac{Da \cdot z_{A,Y} - z_{B,P}}{Da \cdot z_{A,Y} + z_{A,Y} - 1}
\]  

(7.11)

The solution of Eq. 7.11 is feasible \((0 < x_A < 1)\) if, and only if:

\[
Da > Da^c = \frac{z_{B,P}}{z_{A,Y}}
\]  

(7.12)

The conclusion of this section is that, if the reactant is not allowed to leave the plant due to the recycle or composition control of the product stream, then the internal flow rates are finite if, and only if, the plant Damköhler number exceeds a critical value. For complete reactant and product recovery in the separation section, the critical value of the Damköhler number is \( Da^c = 1 \). This result also applies for n-th order reactions, with the plant Damköhler number defined as:

\[
Da = k \cdot \frac{V}{F_A \cdot \frac{V}{V_{A}}} \left( \frac{1}{V_{A}} \right)^{n-1}
\]  

(7.13)

Interaction between design and control

The set of specifications used in the previous section \((F_A, V, z_{A,Y}, z_{B,P})\) can be viewed as a plantwide control structure (Figure 7.3a): the reactor volume is kept constant; the separation section is dual-composition controlled; and the plant throughput is set by the reactant feed. For this control structure, the feed disturbances affect the flow rate and composition of the reactor outlet. Hence, manipulated variables internal to separation section are used to reject the disturbances.

The CSTR-separator-recycle was previously analysed in several plantwide controllability studies. Luyben (1994) pointed out that the conventional control structure
exhibits high sensitivity to feed disturbances. He proposed (Figure 7.3b) to keep the reactor outlet on flow control and to modify the plant throughput by changing the reaction conditions (reactor volume or temperature). This control structure is equivalent to the following set of design specifications: $F_A$, $S$, $z_{A,Y}$, $z_{B,P}$. When disturbances affect the process, the load of the separation section changes only due to composition modification. Consequently, disturbances are rejected mainly by changing the reaction conditions.

Figure 7.3. CSTR-Separator-Recycle: controls structures.
In order to compare the conventional and Luyben’s control structures, we perform a steady state sensitivity analysis for different values of the design parameters. The equations are presented, for a more general case, in the Appendix.

Let $F_A^*$ and $V^*$ represent the nominal feed flow rate and reaction volume, respectively. Figure 7.4 presents, for the conventional control structure, the flow rate to separation vs. reactant feed flow rate, for different values of the nominal Damkohler number ($Da^* = k \cdot V^*/(F_A^* \cdot V_{inA})$) and recycle stream purity ($z_{A,Y}$). For Luyben’s control structure, reactor volume ($V \neq V^*$) vs. reactant feed flow rate is presented. In both cases, small changes mean that small effort is needed to reject disturbances.

**Figure 7.4. First-order reaction in CSTR-Separator-Recycle: sensitivity analysis for different control structures**
Results presented in Figure 7.4 demonstrate that systems with small reactor or slow reaction rate \((Da^* < 2)\) are better controlled by the Luyben’s structure. However, systems with large reactor or fast reaction rate \((Da > 3)\) are better controlled by the conventional control structure. To explain this, we recall that close to \(Da = 1\) the system is sensitive to \(Da\). For the conventional control structure, the plant \(Da\) number represents a disturbance (because it contains \(F_A\)). Because low sensitivity is required, designs with \(Da\) large perform better. For the Luyben control structure, the plant \(Da\) number is a manipulated variable (through the reaction volume \(V\)). Consequently, disturbances can be rejected with small effort if \(Da\) is small. It should be also remarked that high purity separation \((z_{A,Y} = 1)\) improves the performance of the conventional control structure. This is contrary to the Luyben’s structure. This observation is explained by Eq. 7.12: increasing \(z_{A,Y}\) shifts \(Da^*\) toward smaller values; then, the difference \(Da - Da^*\) becomes larger, with a beneficial effect for the conventional structure.

It is worthy to mention that the design analysed by Luyben (1994) had \(Da=1.8\). Hence, poor performance of the conventional control structure is expected. Larsson et al. (1999) pointed out that there is an economic penalty for fixing the reactor effluent and the conventional control structure works very well if the reaction volume is set to a larger value.

A closer look at the dimensionless mole-balance equations suggests a third control structure (Figure 7.3c). It is obvious that as long as the dimensionless model parameters do not change, all flow rates are proportional to feed. Moreover, stream compositions are constant. Hence, production change can be achieved by changing the feed and modifying the reaction conditions \((V\) or \(k)\) to keep constant Damkohler number. This control structure (Figure 7.3c) is similar to the alternatives proposed by Wu and Yu (1996). They called it “balanced control structure” because the disturbances are rejected changing both the reactor and the separation conditions.

**The Plug-Flow Reactor**

Considering a high-purity separation, the mole balance equations of the PFR-separator-recycle system can be reduced to:

\[
Da = \frac{k \cdot V}{V_{m_A} \cdot F_A} = \frac{1}{1-\alpha_x \cdot (1-x_A)} \cdot \ln \frac{1}{1-x_A}.
\]  

(7.14)
For given $Da$ and $\alpha_{Y,s}$, Eq. 7.14 is solved numerically to find the corresponding conversion. Then, flow rate and composition of various streams in the system can be calculated. Figure 7.5 presents the conversion, flow rate to separation, and production rate vs. plant Damkohler number. The behaviour of the PFR coupled with separation and recycle is similar to the behaviour of the CSTR. For complete reactant recycle, internal flow rates are finite if, and only if, the plant Damkohler number exceeds a critical value. For high purity separation, the critical value of the Damkohler number is $Da^{cr}=1$. Close to the critical value of the Damkohler number, high sensitivity to disturbances is expected.

Figure 7.5. First-order reaction in PFR-Separator-Recycle: conversion, yield and reactor outlet / separation inlet flow rate
Chapter 7. Reactor-Separator-Recycle Systems

Consecutive reactions

In this section, we consider the following first-order, consecutive reactions:

\[
\begin{align*}
A & \rightarrow B \rightarrow C \\
k_1 & k_2
\end{align*}
\]

B is the main product. \(k_1\) and \(k_2\) are the reaction constants. The flowsheet specifications are: flow rates of A and B in the feed stream \((F_A, F_B=0)\); reactor volume \((V)\); separation performance \((\alpha_{YS} = 1, \beta_{PS} = 1, \gamma_{PS} = 1)\).

Continuous Stirred Tank Reactor

The dimensionless reaction extents, \(\xi_{v,1} = \xi / F_A \alpha\), are given by:

\[
\xi_{v,1} = Da \cdot \frac{1 - \xi_{v,1}}{1 - \alpha_{YS} \cdot \xi_{v,1}}
\]  

with the solutions:

\[
\xi_{v,1} = \frac{Da + 1 \pm \sqrt{(Da + 1)^2 - 4 \cdot Da \cdot \alpha_{YS}}}{2 \cdot \alpha_{YS}}
\]  

and:

\[
\xi_{v,2} = \frac{Da \cdot \frac{k_2}{k_1} \cdot \frac{1 - \alpha_{YS}}{1 - \alpha_{YS} \cdot \xi_{v,1} \cdot \xi_{v,1}}}{1 + \frac{1 - \alpha_{YS}}{1 - \alpha_{YS} \cdot \xi_{v,1}}}
\]  

Then, the following expressions can be derived:

reactor outlet flow rate:

\[
s = \frac{1 - \alpha_{YS} \cdot \xi_{v,1}}{1 - \alpha_{YS}}
\]  

reactor outlet composition:

\[
z_{AS} = \frac{1 - \xi_{v,1}}{1 - \alpha_{YS} \cdot \xi_{v,2}}, \quad z_{BS} = \frac{(\xi_{v,1} - \xi_{v,2}) \cdot (1 - \alpha_{YS})}{1 - \alpha_{YS} \cdot \xi_{v,2}}
\]  

production rate:

\[
p_B = \xi_{v,1} - \xi_{v,2}
\]  

reaction selectivity:

\[
\sigma_{BA} = \frac{\xi_{v,1} - \xi_{v,2}}{1 - (1 - \alpha_{YS}) \cdot s_A}
\]

Results in Figure 7.6 demonstrate that the reactant recycle increases the production rate and improves selectivity, especially close to \(Da = 1\). However, the stream processed by
the separation section is more dilute in the B product and has higher flow rate (similar to Figure 7.2).

![Graphs showing consecutive, first-order reactions in CSTR-separator-recycle: yield, selectivity and main product concentration at reactor outlet / separation inlet.]

Figure 7.6. Consecutive, first-order reactions in CSTR-separator-recycle: yield, selectivity and main product concentration at reactor outlet / separation inlet.

Consecutive reactions in PFR

To solve the mole balance equations, the reactor feed is chosen as tear stream. Further, the mole balance equations of the reactant A can be reduced to:
Chapter 7. Reactor-Separator-Recycle Systems

\[ Da = r_A \cdot \ln \frac{\alpha_{YS} \cdot r_A}{r_A - 1} \]  
\hspace{1cm} \text{(7.22)}

Eq. 7.22 is solved numerically, and the following variables are computed:

reactor outlet component flow rates:

\[ s_A = r_A \cdot e^{-r_A}, \quad s_B = r_A \cdot \frac{r_A}{1 - k_2/k_1} \left( \frac{Da}{r_A} \right) \left( 1 - e^{-r_A} \right), \quad s_C = r_A - (s_A + s_B) \]  
\hspace{1cm} \text{(7.23)}

production: \[ p_B = s_B \]  
\hspace{1cm} \text{(7.24)}

selectivity: \[ \sigma_{BA} = \frac{P_B}{1 - (1 - \alpha_{YS}) \cdot s_A} \]  
\hspace{1cm} \text{(7.25)}

Figure 7.7. Consecutive, first-order reactions in PFR-separator-recycle: yield, selectivity and main product concentration at reactor outlet / separation inlet.
Chapter 7. Reactor-Separator-Recycle Systems

The dependence of production rate, selectivity and product concentration at reactor outlet vs. plant Damkohler number is presented in Figure 7.7. When placed in a recycle system, the PFR behaves very similar to the CSTR. However, higher product concentration at the reactor outlet can be obtained.

**Second order reaction in CSTR**

In this section we will analyse a process where the second-order reaction \(A + B \rightarrow C\) takes place in a solvent \(S\). The process consists of a temperature-controlled CSTR and a separation section. The process may be represented by the general reactor-separator-recycle flowsheet in Figure 7.1. It should be remarked that the second reactant (and the solvent) not only changes the reaction kinetics, but also adds more dimensionality to the problem.

We will consider two control structures, presented in Figure 7.8. They follow naturally when the degrees of freedom and consistent specifications of the mass balance equations are considered. Thus, for simultaneous, independent specification of the A and B feed flow rates \((F_A, F_B)\), the mass balance equations cannot be solved. The reason is that, in recycle systems, the ratio of reactants in feed must reflect the reaction stoichiometry. Hence, control structures in which both reactants are on flow control are unfeasible. Moreover, due to inherent measurement errors, ratio control cannot avoid the imbalance.

In control structure CS1, the A feed is flow-controlled (FC1). This stream is used to achieve production changes. The reactor effluent controls the reactor volume (LC1). We assume that in the separation section there are some locations reflecting species inventory. In Figure 7.8, they are denoted by A, B, C, S, respectively. The recycle of A and the product stream control species inventory (LC2 and LC4). The recycles of B and S are on flow control (FC2 and FC3). Reactant B is fed in the separation section in order to keep constant inventory (LC3). Solvent make-up may be necessary. This control structure corresponds to the following set of flowsheet specifications: feed \((F_A, F_C=0, F_S=0)\); reactor volume \((V)\); separation as recoveries \((\alpha_{A,S}=1, \beta_{B,S}=1, \gamma_{C,S}=1, \sigma_{V,S}=1)\); component recycles \((Y_B, Y_S)\).
Figure 7.8. Second-order reaction in CSTR-Separator-Recycle: control structures

To solve the mole-balance equations, the conversion of A is introduced as auxiliary variable. The flow rate of A, B, C and S at the reactor inlet are $F_A \cdot \frac{1-x_A}{x_A}$, $Y_B$, 0 and $Y_S$, respectively. Then, the volumetric flow rate is given by:

$$S^{\text{vol}} = F_A \cdot V_{V_{nA}} \left( \frac{1-x_A}{x_A} + v_B \cdot (y_B - 1) + v_S \cdot y_S + v_C \right)$$  \hspace{1cm} (7.26)

where $v_k = \frac{V_{nK}}{V_{nA}}$ is the dimensionless molar volume of the $k$ component.
Chapter 7. Reactor-Separator-Recycle Systems

The reactant concentrations:

\[ c_{AS} = \frac{1-x_A}{x_A} \frac{1-x_A}{\frac{1-x_A}{1-x_A} + v_B \cdot (y_B - 1) + v_s \cdot y_s + v_c} \]  (7.27)

\[ c_{BS} = \frac{y_B - 1}{x_A} \frac{1-x_A}{1-x_A} + v_B \cdot (y_B - 1) + v_s \cdot y_s + v_c \]  (7.28)

are introduced in the CSTR's equation. The following dimensionless form is obtained

\[ g(x_A, Da, y_B, v_B, v_s \cdot y_s, v_c) = Da - \frac{\left( \frac{1-x_A}{x_A} + v_B \cdot (y_B - 1) + v_s \cdot y_s + v_c \right)^2}{(y_B - 1) \cdot \frac{1-x_A}{x_A}} = 0 \]  (7.29)

where \( Da = \frac{k \cdot V}{F_A \cdot V_{\mu A} \cdot V_{\mu A}} \) is the plant Damkohler number for a second-order reaction.

Eq. 7.29 has two \( Da \)-dependent solution branches:

- \( Da < 0 \): the conversion is negative and has no physical significance.
- \( Da^c > Da > 0 \): the solutions are complex.
- \( Da > Da^c \): two meaningful solutions exist. They are presented in Figure 7.9, for different values of the model parameters.

The critical value of the Damkohler number corresponds to a fold bifurcation of the model equations. The defining condition for the fold bifurcation is (Guckenheimer and Holmes, 1983):

\[ \frac{\partial g(x_A, Da, y_B, v_B, v_s \cdot y_s, v_c)}{\partial x_A} = 0 \]  (7.30)

Solution of Eqs. 7.29 and 7.30 gives the location of fold points:

\[ Da^c = 4 \cdot \frac{v_B \cdot (y_B - 1) + v_s \cdot y_s + v_c}{y_B - 1} \]  (7.31)

\[ x_A^c = \frac{1}{1 + v_B \cdot (y_B - 1) + v_s \cdot y_s + v_c} \]  (7.32)

Generally, large \( B \) and small \( S \) recycles enlarge the region where the feasible solutions exist.
Bifurcation theory states that one stable and one unstable steady state emerge from the fold point. The unusual behaviour on the lower branch (larger reactor gives lower conversion) suggests that this steady state is unstable.

It is remarkable that near the fold bifurcation point, the system is very sensitive to disturbances. Consequently, from a control point of view, designs with $Da$ close to $Da^c$ should be avoided.

![Diagram](image)

**Figure 7.9.** Second-order reaction in CSTR-Separator-Recycle and CS1: multiple solutions of the mole-balance equations.
Chapter 7. Reactor-Separator-Recycle Systems

In the second control structure of Figure 7.8 (CS2), the A feed is flow-controlled (FC1). This stream is used to achieve production changes. The reactor effluent is on flow control (FC2). The recycles of A and B control species inventory in the separation section (LC2 and LC3). The recycle of S is on flow control (FC3). Reactant B is fed in order to keep constant reactor volume (LC1). This control structure corresponds to the following set of flowsheet specifications: feed \( F_A, F_C=0, F_S=0 \); reactor volume \( V \); separation as recoveries \( \alpha_{Y,S}=1, \beta_{Y,S}=1, \gamma_{S}=1, \sigma_{Y,S}=1 \); solvent recycle \( y_S \); reactor effluent volumetric flow rate \( S_{\text{vol}} \).

The following mole-balance equation can be derived:

\[
g(x_A, Da, s_{\text{vol}}, v_B, v_S, y_S, v_C) = Da \frac{(s_{\text{vol}})^2}{1-x_A \cdot \frac{1}{v_B} \cdot \left( \frac{1-x_A}{x_A} + v_C + v_S \cdot y_S \right)}
\]

Eq. 7.33 has two solutions \( 0 < x_A < 1 \) for \( Da > Da^{cr} \). The critical value of the plant Damkohler number corresponds to a fold bifurcation, and is given by:

\[
Da^{cr} = 4 \cdot v_B \cdot \left( \frac{s_{\text{vol}}}{s_{\text{vol}} - v_C - v_S \cdot y_S} \right)^2
\]

\[
x^{cr} = \frac{2}{2 + s_{\text{vol}} - v_C - v_S \cdot y_S}
\]

Figure 7.10 presents the physical-significant solutions of Eq. 7.33, for different values of the model parameters.

The analysis presented here is based on a black box model of the separation units. Nevertheless, the results apply when more detail is considered. Luyben and Luyben (1997) studied the controllability of the second-order reaction – separator – recycle system, with rigorous dynamic models for the separation section (distillation columns). For CS1 and a design having \( 29.7 = Da > Da^{cr} = 10.66 \), they could achieve large production changes. However, with CS2 they could not achieve production changes larger than 2%. This is not a surprise, because the design considered had \( Da = 29.7 > 28.4 = Da^{cr} \).
Figure 7.10. Second-order reaction in CSTR-Separator-Recycle and CS2: multiple solutions of the mole-balance equations.
Chapter 7. Reactor-Separator-Recycle Systems

Conclusions

When placed in recycle plants, chemical reactors behave different from the stand-alone reactors:

1. Production rate reflects the amount of reactants fed in the plant. There is no way to change the plant throughput without changing the reactants feed. Consequently, in plant-wide control structures, reactant feeds must change (directly or indirectly) when production change is required. For stand-alone reactors, it is enough to modify the reaction conditions in order to change the production rate.

2. When a reactant is recycled, the reactor must transform the whole amount fed in the process. Hence, in order to prevent accumulation and infinite recycle, large reactor volume or fast kinetics are required. The minimum-volume constraint depends on the control structure. It can be expressed in terms of plant Damkohler number and separation specifications. For one reactant recycle, $Da^*$ correspond to a transcritical bifurcation of the mole-balance equations. When two reactants are recycled, multiple steady states may exist, and $Da^*$ correspond to a fold bifurcation of the mole-balance equations. Near $Da^*$, the system exhibits high sensitivity to disturbances. Hence, control structures must use the reaction conditions as manipulated variables, in order to reject effectively the disturbances. There are no restrictions on the size of a stand-alone reactor.

3. The feed ratio of reactants must reflect the reaction stoichiometry. Consequently, only one reactant feed may be on flow control. The other reactants must be fed in such a way to control their inventory in the process. For stand-alone reactors, the ratio of reactants in the feed may have any value.

The results of this study reveals the important role played by the chemical reactor in the (plantwide) controllability of recycle plants.

Literature cited


Appendix. Solution of mole-balance equations for first-order reaction in CSTR-separator-recycle system, for two control structures.

We consider that the reaction takes place in a solvent S, which is recovered in the separation section and recycled. Because the solvent does not leave the plant, its flow rate is constant throughout the recycle loop ($F_S$). The molar volumes of A and B species are assumed to be equal. The dimensionless parameters $v_S = V_{s,S} / V_{s,A}$ corresponds to the molar volume of the solvent. The product stream is pure ($\alpha_{Y,S} = 1$), but some amount of B is recycled ($z_{A,Y} < 1$).

Conventional control structure, dual composition control

The parameters of the mole-balance equations are: flow rates of A and B in the feed stream ($F_A$, $F_B = 0$); reactor volume ($V$); separation performance, ($z_{B,P} = 1$ and $z_{A,Y}$); solvent flowrate ($F_S$). The mole-balance equations give:

\[
\begin{align*}
x_A &= \frac{D_a \cdot z_{A,Y} - 1}{z_{A,Y} \cdot (D_a + f_S \cdot v_S) + (1 - z_{A,Y}) \cdot (f_S - 1)} \quad (A7.1) \\
z_{B,S} &= \frac{(D_a - 1) \cdot z_{A,Y} + f_S \cdot (1 - z_{A,Y}) \cdot (D_a - 1 + v_S)}{D_a \cdot z_{A,Y} + f_S \cdot (D_a - 1 + v_S)} \quad (A7.2) \\
s &= \frac{D_a \cdot z_{A,Y} + f_S \cdot (D_a + v_S - 1)}{D_a \cdot z_{A,Y} - 1} \quad (A7.3)
\end{align*}
\]
Luyben control structure, dual composition control

The parameters of the mole-balance equations are: flow rates of A and B in the feed stream ($F_A$, $F_B = 0$); flowrate to separation ($S$); separation performance, ($z_{B,R} = 1$ and $z_{A,Y}$); solvent flowrate ($F_S$). The mole-balance equations give:

\[
x_A = \frac{1}{s \cdot z_{A,Y} + (1 - s)} \quad \text{(A7.4)}
\]

\[
z_{BS} = (1 - z_{A,Y}) + \frac{z_{A,Y}}{s} \quad \text{(A7.5)}
\]

\[
\frac{k \cdot V}{F_A \cdot V_{p,A}} = s + s \cdot (v_s - 1)
\]

\[
(\text{s} - 1) \cdot z_{A,Y} - s \quad \text{(A7.6)}
\]