Design and control of recycle systems by nonlinear analysis

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Chapter 2: Non-linear Analysis of CSTR-Separator-Recycle Systems

Abstract

This article investigates the design and control of isothermal Reactor – Separator – Recycle systems. The multiplicity behaviour of six reaction systems of increasing complexity, from one-reactant, first-order reaction to chain-growth polymerisation, is investigated. Below a critical value of the plant Damkohler number, $Da < Da^{ct}$, the only steady state involves infinite flow rates. Feasible steady states become possible only if the critical value is exceeded, $Da > Da^{ct}$. For one-reaction systems, one stable steady state is born at a transcritical bifurcation. For consecutive-reaction systems, including polymerisation, a fold bifurcation can lead to two feasible steady states. Moreover, the transcritical bifurcation is destroyed when two reactants are involved. If the gel-effect is included, a maximum of four steady states is possible. When multiple steady states exist, the achievable conversion is constrained by the instability of the low-conversion branch. This has practical importance for polymerisation systems when the radicals’ quasi-steady state assumption is not valid or the gel-effect is significant.
Introduction

The nonlinear behaviour of chemical reactors includes state multiplicity, isolated solution branches, instability, sustained oscillations, and exotic phenomena like strange attractors and chaotic behaviour. The first-order exothermic reaction $A \rightarrow B$, taking place in a cooled CSTR, received considerable attention in the chemical reaction engineering literature. For this reaction system, at most three steady states and seven different bifurcation diagrams are possible (Balakotaiah and Luss, 1984). Seven steady states and twenty-three bifurcation diagrams are possible in the case of two consecutive first-order reactions, $A \rightarrow B \rightarrow C$ (Farr and Aris, 1986). For two simultaneous reactions, $A \rightarrow B; A \rightarrow C$, five steady states and forty-eight bifurcation diagrams exist (Balakotaiah and Luss, 1983). The complexity further increases when the dynamic behaviour is considered. For example, the first-order reacting system in a cooled CSTR shows thirty-seven phase-plane diagrams (Uppal, Ray and Poore, 1974, 1976).

Besides non-isothermal operation, autocatalytic kinetics is an additional source of nonlinearity. Examples are: the autocatalytic reaction $A + nB \rightarrow (n+1)B$ in an isothermal CSTR, which exhibits state multiplicity, isolated solutions, and sustained oscillations (Gray and Scott 1983, 1984); models of the Belousov-Zhabotinskii reaction, (for example, the Brusselator and the Oregonator); and interacting biochemical species in a chemostat (Razón and Schmitz, 1987).

In polymerisation reactors, both heat effects and autocatalytic kinetics are present. Hence, nonlinear phenomena are not a surprise. Freitas Filho, Biscaia and Pinto (1994) considered a generic model of the free radical homopolymerisation, which can have up to five steady states. They concluded that state multiplicity should be expected for most polymerisation systems, as reported by many researchers (for example, Hamer, Akramov and Ray, 1981, Schmidt, Clinch and Ray, 1984).

Nonlinear phenomena can be also induced by material recycles. Reilly and Schmitz (1966, 1967) and Luss and Amundson (1967) considered the plug-flow reactor with recycle of a fraction of reactor's effluent. This system exhibits state multiplicity and sustained oscillations around a unique steady state. This behaviour was caused by energy feedback, because the recycle had the same temperature as the reactor outlet. Pareja and Reilly (1969) acknowledged that recycle reactors could become unstable solely as a result of material
feedback. They did not show, however, any example. Further investigations of the recycle tubular reactor reported more complex behaviour, including chaos (Berezowski and Burghardt, 1989, Jacobsen and Berezowski, 1998, Recke and Jørgensen, 1999).

Other reaction systems involving material recycles are common to industrial practice (Figure 2.1). The reactor effluent is handled by a separation section, which provides the product (4) and recycle (3) streams with controlled composition. In polymerisation processes, a sharp reactant (monomer, M) - product (polymer, P) separation is possible, because of the large difference in physical properties. When two reactants are involved, the feed flow rate of the second reactant (initiator, I) can be used as the manipulated variable in a control loop keeping constant concentration at the reactor inlet (dashed drawing in Figure 2.1).

![Figure 2.1. General structure of Reactor-Separator-Recycle systems.](image)

The reactor effluent is processed by the Separation section, and afterwards recycled. Product and recycle streams have fixed composition. Dashed drawing refers to systems with two reactants.

Such systems, which will be called Reactor-Separator-Recycle systems, were recognized as being representative for chemical plants (Luss and Amundson, 1967). The interest in Reactor – Separator – Recycle systems is also motivated by several plantwide control studies
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(Luyben and Luyben, 1997, Wu and Yu, 1996), which reported difficult control of some Reactor - Separator – Recycle systems.

Recently, Pushpavanam and Kienle (2001) considered an exothermic first-order reaction in a CSTR – Separator (instantaneous flash) – Recycle system. Twenty-four different bifurcation diagrams are presented, which include a maximum of two steady states, isolated solution branches and limit cycles. Although the units were decoupled energetically via heat exchangers, energy feedback was still present inside the stirred tank reactor.

In this article, we focus on multiple reactions (including polymerisation) taking place in a CSTR – Separator – Recycle system. We consider that the reaction temperature is controlled, for example, by the coolant flow rate. This agrees with the industrial practice, and completely excludes energy feedback effects. Thus, we expect nonlinear effects that are only due to the recycle and the kinetics.

In a previous communication (Bildea, Dimian and Iedema, 2000) regarding the interaction between design and control of Reactor – Separator – Recycle systems, the plant Damkohler number was introduced and examples of transcritical and fold bifurcations were given. The study had an exploratory character, was restricted to simple kinetics, emphasis being given to the control structure necessary to reject disturbances. In the present article, the effect of reaction kinetics is systematically investigated with emphasis on polymerisation. In order to identify the sources of different nonlinear phenomena, we study systems of increasing complexity (Table 2.1). First two sections consider simple chemical systems (S1, S2), which have a stoichiometry similar to the global stoichiometry of self-initiated and chemically-initiated polymerisation, respectively. A particular feature of chemical reactors in recycle systems will be shown: feasible operation is possible only if the reactor size exceeds a critical value. For systems S1 and S2, this corresponds to a transcritical bifurcation of the balance equations. The following sections will add more complexity by considering consecutive reactions (systems S3 and S4, respectively). In this case, a fold bifurcation can occur, leading to state multiplicity and instability. These are relevant when the quasi-steady state assumption (QSSA) for the intermediate species (R) is not valid. Moreover, the transcritical bifurcation is destroyed if two reactants are involved. Polymerisation systems S5 and S6, which include initiation, propagation and termination reactions, also show state multiplicity. This has a practical significance when the radicals’ QSSA is not valid or the gel effect is present. Our approach, which does not address a particular polymerisation process, is
similar to the work of Freitas Filho, Biscaia and Pinto (1994) and Melo et al. (2001).

Table 2.1. Investigated reactions mechanisms.

<table>
<thead>
<tr>
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<th>Chemical initiation</th>
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<tbody>
<tr>
<td><strong>S1. One reactant</strong></td>
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<td>$M + I \xrightarrow{k} P$</td>
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<td><strong>S3. Consecutive reactions</strong></td>
<td><strong>S4. Consecutive reactions</strong></td>
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<td>$M \xrightarrow{k} R$</td>
<td>$I \xrightarrow{k} R$</td>
</tr>
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<td>$M + R \xrightarrow{k} P$</td>
<td>$M + R \xrightarrow{k} P$</td>
</tr>
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<td><strong>S5. Chain-growth polymerisation</strong></td>
<td><strong>S6. Chain-growth polymerisation</strong></td>
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<tr>
<td>$M \xrightarrow{k} I \cdot$</td>
<td>$I_2 \xrightarrow{k} 2I \cdot$</td>
</tr>
<tr>
<td>$M + I \cdot \xrightarrow{k} R_i \cdot$</td>
<td>$M + I \cdot \xrightarrow{k} R_i \cdot$</td>
</tr>
<tr>
<td>$R_n \cdot + M \xrightarrow{k} R_{n+1} \cdot$</td>
<td>$R_n \cdot + M \xrightarrow{k} R_{n+1} \cdot$</td>
</tr>
<tr>
<td>$R_n \cdot + R_m \cdot \xrightarrow{k} P_n + P_m$</td>
<td>$R_n \cdot + R_m \cdot \xrightarrow{k} P_n + P_m$</td>
</tr>
</tbody>
</table>

1 From the reactor effluent only the reactant M is recycled.
2 From the reactor effluent only the reactant M is recycled. Concentration of I at reactor inlet is fixed.

The results obtained in this way are generic for Reactor – Separator – Recycle systems with a polymerisation reaction. In this article we concentrate on the macroscopic behaviour, which can be described using only the zero-th and first moments of the molecular weight distribution (MWD). Higher moments are important only when the polymer properties are considered.

Throughout this work, $F_k$ and $F_{k,vol}$ are molar and volumetric flow rates, respectively, where the index k follows streams numbering of Figure 2.1. The dimensionless volumetric flow rates are denoted by $f_k = F_{k,vol} \cdot c_{M,0} / F_0$. Concentration and dimensionless concentration of the $i^{th}$ species in the $k^{th}$ stream are denoted by $c_{ik}$ and $z_{ik} = c_{ik} / c_{M,0}$, respectively. The dimensionless reactor concentrations will be written simply as, for example, $M = z_{M,2}$, $R = z_{R,2}$, etc. In this study we will consider a sharp separation, hence $c_{M,4} = z_{M,4} = 0$ and $c_{M,3} = c_{M,0}$, $z_{M,3} = 1$. All reaction rate constants are evaluated at the fixed reactor temperature.
One-reactant recycle systems (S1)

We start our study with the first order reaction $M \rightarrow P$, taking place in a CSTR-Separator-Recycle system. This is the simplest case of chemical reaction, having a stoichiometry that is equivalent to the global stoichiometry of a self-initiated polymerisation. The system can be described by the following dimensionless model, which considers constant density and neglects time delays due to recycle and the capacity of the mixing vessel:

Reactor:

$$\frac{dM}{d\tau} = \frac{1}{Da} \left[ 1 + f_3 - (1 + f_3) \cdot M \right] - M \quad (2.1a)$$

Separation:

$$\tau_s \frac{df_3}{d\tau} = (1 + f_3) \cdot M - f_3 \quad (2.1b)$$

The model variables are the dimensionless time ($\tau = k_i t$), reactant concentration ($M = \frac{c_{M,2}}{c_{M,0}}$) and volumetric flow rate of the recycle stream ($f_3 = \frac{F_{3,vol}}{F_0} \cdot \frac{c_0}{F_0}$). The model is parameterised by the plant Damkohler number ($Da$) and the dimensionless separation time constant ($\tau_s = k_i T_s$).

The definition of the plant Damkohler number,

$$Da = k_i \frac{V}{\frac{F_0}{c_{M,0}}} \quad (2.2)$$

uses the flow rate at plant input as the reference value. For recycle systems this definition is more appropriate than the usual chemical reaction engineering definition, which uses the flow rate at reactor inlet as reference.

The dynamic modelling of the separation unit deserves a special discussion. Using a rigorous model, which might easily contain one hundred differential equations, renders analysis difficult and generalization of the results impossible. To our knowledge, simplified dynamic models are available only for open-loop units, but not for the practical case of closed-loop operation. For this reason we use the simple model (Eq. 2.1b), which assumes that the composition of the outlet streams is constant due to local control. The model considers that changing the flow rate or composition of the inlet stream is reflected by a
gradual change of the flow rate of outlet streams, which follows a first-order dynamics. Clearly, constant compositions of the separation-outlet streams can be achieved at steady state, by manipulating internal flow rates or heat duties. However, the assumption of constant composition during transient operation (as, for example, when sustained oscillations occur due to a limit cycle) is questionable. Consequently, we restrict the use of the dynamic model to illustrate the instability of low-conversion states in the multiplicity region. Note that although a valid dynamic model is necessary to guarantee the state stability, it is possible to prove the instability using only steady state arguments (van Heerden, 1958).

The steady-state model, obtained by dropping the time derivatives in Eq. 2.1, has two solutions:

\[
(M, f_1) = (1, \infty) \quad \text{(2.3a)}
\]

\[
(M, f_3) = \left( \frac{1}{Da}, \frac{1}{Da - 1} \right) \quad \text{(2.3b)}
\]

Figure 2.2 presents the conversion \(X = 1 - M\) vs. the plant Damkohler number. One solution is unfeasible, corresponding to zero conversion and infinite recycle flow rate. The other solution is feasible (\(0 < X < 1\), finite recycle) if, and only if, the following condition is fulfilled:

\[
Da > 1 \quad \text{(2.4)}
\]

Such a feasibility constraint, characteristic to recycle systems, does not appear in the case of stand-alone reactors. It can be explained by the fact that the separation section does not allow the reactant to leave the process. Consequently, for a given reactant feed flow rate \(F_0\), large reactor volume \(V\) or fast kinetics \(k_1\) are necessary to consume the whole amount of reactant fed in the process, and thus to avoid reactant accumulation. These three variables are conveniently grouped in the dimensionless plant Damkohler number.

At the critical value \(Da = 1\), two different manifolds of steady states cross each other, in the combined space of state variables and parameters (point T in Figure 2.2). According to the bifurcation theory, this is a transcritical bifurcation point (Guckenheimer and Holmes, 1983),
where an exchange of stability takes place: for \( Da < 1 \), the trivial solution \((X = 0, f_3 = \infty)\) is stable; this state loses stability at \( Da = 1 \), at which point the feasible solution \((X, f_3) = \left(1 - \frac{1}{Da}, \frac{1}{Da - 1}\right)\) gets physically meaningful values and gains stability.

**Figure 2.2. One reactant, first order reaction (S1): \( X \) vs. \( Da \) bifurcation diagram.**

One solution is unfeasible, corresponding to zero conversion and infinite recycle flow rate. The other solution is feasible \((0 < X < 1, \text{finite recycle})\) if, and only if \( Da > 1 \).

For a general system, the transcritical bifurcation is not generic. This is explained by Figure 2.3, where parameter \((\mu)\) - dependent solutions \((x)\) are presented, for the simplest equation showing this type of bifurcation (normal form) and two of its perturbations (Golubitsky and Schaeffer, 1985). It can be seen that an arbitrary small change of the model \((\varepsilon \neq 0)\) leads to qualitatively different diagrams.

The transcritical bifurcation occurring in Reactor – Separator – Recycle systems does not disappear for changes of the additional model parameters, for example \( z_{M,3} \neq 1 \) or \( z_{M,4} \neq 0 \), but moves to \((Da, X) = \left(1 - z_{M,4} \right) / \left(z_{M,3} \right), 0\). Thus, it is a persistent phenomenon.
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Figure 2.3. The transcritical bifurcation.

Arbitrary small perturbation $\varepsilon \neq 0$ leads to qualitatively different bifurcation diagrams. Solid and dotted lines refer to stable and unstable states, respectively.
To give a visual explanation, consider two straight lines, intersecting in a 3-D space: in general, the intersection point vanishes for arbitrary small perturbations; however, if some mechanism forces the lines to stay in the same plane (fixed composition of product and recycle streams), only the location of the intersection point changes. We note that the isothermal CSTR with quadratic autocatalytic reaction shows a similar behaviour (Gray and Scott, 1983). Two steady states exist: a zero-conversion state, stable for $Da < 1/4$; and a second state, physically meaningful ($X > 0$) and stable for $Da > 1/4$.

However, other perturbations can destroy the transcritical bifurcation. For example, recycling a fraction of the reactant present in reactor effluent leads to a $Da - X$ bifurcation diagrams that has two distinct branches, among which only one has a physical meaning (as diagram B of Figure 2.3, Bildea, Dimian and Iedema, 2000).

For the isothermal (stand-alone) CSTR, changing the autocatalytic kinetics from quadratic to cubic leads to a change of the $Da - X$ dependence from type A to type C (Gray and Scott, 1983). In the following sections, we will show that more complex reactions in CSTR – Separator – Recycle systems can lead to a behaviour that is similar to the one represented in diagram C of Figure 2.3.

Analysing more complex systems, we will disregard the trivial solution ($X = 0$, infinite flow rates).

**Two-reactant recycle systems (S2)**

The second-order reaction $M + I \rightarrow P$ has a stoichiometry that is identical to the global stoichiometry of a chemically - initiated polymerisation. From the reactor effluent, only one reactant ($M$) is recycled. The feed flow rate of the second reactant ($I$) is adjusted in order to keep its concentration at reactor inlet at a prescribed value ($z_{1,1}$). The reactor outlet concentrations $M = c_{M2}/c_{M0}$ and $I = c_{I2}/c_{M0}$, and the volumetric flow rates $f_2$ and $f_{I,0}$ are the variables of the dimensionless model (Eqs. 2.5):

**M balance:** \[ 1 - Da \cdot I \cdot M = 0 \] (2.5a)

**I2 balance:** \[ f_2 \cdot (z_{1,1} - I) - Da \cdot I \cdot M = 0 \] (2.5b)
Fixed \( z_{1,1} \):
\[
\frac{z_{1,1} - f_{1.0} \cdot z_{1,0}}{f_2} = 0
\]  
(2.5c)

Flow rate:
\[
f_2 - (1 + f_2 \cdot M + f_{1.0}) = 0
\]  
(2.5d)

where: \( Da = k_1 \cdot \frac{V}{F_0/c_{M,0}} \); \( z_{1.0} = c_{1.0} / c_{M,0} \); \( z_{1,1} = c_{1,1} / c_{M,0} \)

and \( f_{1.0} = \frac{F_{1.0}}{F_0/c_{M,0}} \); \( f_2 = \frac{F_{2,\text{vol}}}{F_0/c_{M,0}} \)

A closed-form parametric solution is possible (Eqs. 2.6):

\[
Da = \frac{z_{1.0}^2}{(1 - X)(z_{1.0} - z_{1,1})(z_{1.0} - z_{1,0} - X(z_{1.0} - z_{1,1}))}
\]  
(2.6a)

\[
M = (1 - X) \left( 1 - \frac{z_{1,1}}{z_{1.0}} \right)
\]  
(2.6b)

\[
I = z_{1,1} \cdot \frac{(z_{1.0} - z_{1,1}) \cdot X}{z_{1.0}}
\]  
(2.6c)

\[
f_2 = \frac{z_{1.0}}{X \cdot (z_{1.0} - z_{1,1})}
\]  
(2.6d)

\[
f_{1.0} = \frac{z_{1,1}}{X \cdot (z_{1.0} - z_{1,1})}
\]  
(2.6e)

where \( X \in [0,1] \) is the conversion of the reactant M.
Figure 2.4 presents the conversion $X$ versus the plant Damkohler number, for $z_{i,0} = 1$ and different values of $z_{i,1}$. A feasible solution exists only if $Da$ exceeds a critical value, $Da > Da^c$. The critical value results by setting $X = 0$ in Eq. 2.6a:

$$Da^c = \frac{z_{i,0}}{z_{i,1}(z_{i,0} - z_{i,1})}$$

(2.7)

Moreover, the minimum value of $Da^c$ is given by:

$$\min Da^c = (Da^c)_{z_{i,1} = z_{i,0}/2} = \frac{4}{z_{i,0}}$$

(2.8)

Figure 2.4. Two-reactants, second order reaction (S2).

A feasible solution exists only if $Da$ exceeds a critical value, $Da > Da^c$. 
Consecutive-reactions recycle systems

In this section, more complexity is introduced by considering two consecutive reactions and an intermediate component (R). In a chain-growth polymerisation, these roughly correspond to the initiation and propagation-termination steps, and the radical species, respectively.

In general, the parameters of a dimensionless model can be defined in different ways. It is desirable, however, that the dimensionless parameters have physical significance. In the following, we will use a QSSA to obtain a reaction rate constant related to the consumption rate of the recycled reactant (M). This will be used to define the Damköhler number. A second dimensionless parameter will be related to the QSSA concentration of the intermediate component. The procedure is presented in detail for the reaction system S3.

Self-initiation (S3)

Under the quasi steady state assumption, the concentration of the intermediate component R is given by:

\[ c_{R,2} = \frac{k_1}{k_2} \cdot c_{M,2} \quad (2.9) \]

This gives one dimensionless parameter

\[ \beta = \frac{k_2 \cdot c_{M,0}}{k_1} \quad (2.10) \]

which is proportional to the reciprocal value of R’s concentration, when the QSSA is valid.

The balance equations for the recycled reactant (M) can be written as:

\[ F_{z,vol} \cdot (c_{M,1} - c_{M,2}) = k_1 \cdot c_{M,2} + k_2 \cdot c_{M,2} \cdot c_{R,2} = 2k_1 \cdot c_{M,2} \quad (2.11) \]

Thus, the consumption of the recycled reactant follows a first-order kinetics, with a reaction rate constant equal to \(2k_1\). This will be used to define the Damköhler number:
Employing the parameters $Da$ and $\beta$ defined above and discarding the QSSA, the dimensionless model can be written as:

**M balance:**

\[ 1 - \frac{1}{2} Da \cdot [M + \beta \cdot M \cdot R] = 0 \]  
(2.13a)

**R balance:**

\[ -\frac{R}{1-M} + \frac{1}{2} Da \cdot [M - \beta \cdot M \cdot R] = 0 \]  
(2.13b)

or, in a condensed form:

\[ g(M, R, Da, \beta) = 0 \]  
(2.13c)

where $R = \frac{c_{k,2}}{c_{M,0}}$.

The feasible solution can be obtained in a parametric form:

\[ Da = \frac{\beta X - 1 + \sqrt{1 + 6 \beta X + \beta^2 X^2}}{2 \beta X (1 - X)} \]  
(2.14a)

\[ M = 1 - X \]  
(2.14b)

\[ l = \frac{3 \beta X + 1 - \sqrt{1 + 6 \beta X + \beta^2 X^2}}{\beta \left( \beta X - 1 + \sqrt{1 + 6 \beta X + \beta^2 X^2} \right)} \]  
(2.14c)

$X \in [0,1]$

Figure 2.5 presents the dependence of reaction conversion vs. plant Damkohler number, for different values of $\beta$. All the curves pass through the point $(Da, X) = (2, 0)$, which is a
transcritical bifurcation point. When the second reaction is slow ($\beta < 1$), the system behaves in a similar way as the first-order reaction in a CSTR–Separator–Recycle system: a unique, feasible steady state ($X > 0$) exists if, and only if, $Da > 2$.

![Figure 2.5. Consecutive reactions with self-initiation (S3).](image)

All the curves pass through the transcritical bifurcation point $(Da,X) = (2,0)$.

For $\beta > 1$, state multiplicity is possible. No steady state exists for $Da < 1$.

The $X$ vs. $Da$ bifurcation diagram (including the unfeasible domain of negative conversion) exhibits two turning points, corresponding to fold bifurcations. The defining condition:

$$g(X,R,Da,\beta) = 0 \quad (2.15a)$$

$$\det \frac{\partial g(X,R,Da,\beta)}{\partial (X,R)} = 0 \quad (2.15b)$$

has the following closed-form parametric solution:
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\[ Da_r = \frac{1}{2} \frac{3 - 7X \pm \sqrt{17X^2 - 10X + 1}}{(1 - 2X)(1 - X)} \]  

(2.16)

(the expressions of \( R_F \) and \( \beta_F \) are too complex to be presented here)

When the second reaction is slow (\( \beta < 1 \)), both fold points correspond to negative values of the conversion. At \( \beta = 1 \), one fold point enters the feasible region (\( X > 0 \)). This represents a boundary limit point. For \( \beta > 1 \), state multiplicity becomes possible. The steady state behaviour can be summarized as:

- \( Da < Da_r \): no feasible steady state
- \( Da_r < Da < 2 \): two feasible steady states
- \( Da > 2 \): one feasible steady state

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, \( F_i X \), depends on the reactor’s feed flow rate, \( F_i \). This dependence, which can be obtained by solving the balance equations of the stand-alone CSTR, is presented in the first diagram of Figure 2.6 using the dimensionless variables \( F_i/(2k_i c_{M,0} V) = 1/Da \) and \( F_i X/(2k_i c_{M,0} V) = X/Da \).

In a reactor – separator – recycle system, the steady state values of the reactor-inlet flow rate are given by the intersections of this curve with the dimensionless amount of reactant fed in the process, \( F_i/(2k_i c_{M,0} V) = 1/Da \). For \( \beta = 10 \) and \( Da = 1.75 \), two steady states exist. To analyse the stability of the low-conversion state B, let us consider a small, positive / negative deviation of the reactor inlet flow rate. 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 these arguments, independent of the dynamic separation model, 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.

\[ \beta = 10 \]

**Figure 2.6. Instability of the low-conversion steady state.**

a. Steady state analysis gives a necessary, but not sufficient stability condition.

b. Small disturbances lead to reactant accumulation or depletion.
The second diagram of Figure 2.6 shows dynamic simulation results, when the separation unit is modelled by Eq. 2.1b. The system is initially in the low-conversion state B. At the time $\tau = 1000$, the Damkohler number $Da$ is changed by 1% for a limited period of time. Depending on the disturbance direction, the high- or zero-conversion states are reached.

Because a design at an unstable operating point should be avoided in practice, it is of interest to recognize such conditions. Simple algebraic calculations show that the maximum value of conversion at the fold point is $X_{f,\text{max}} = \frac{5-2\sqrt{2}}{17} \approx 0.128$, which occurs for $Da = \frac{3\sqrt{2} - 1}{2} \approx 1.621$ and $\beta = 5 + 2\sqrt{2} \approx 7.828$. Hence, when a conversion $X < 0.128$ is obtained in a Reactor – Separator – Recycle system with $Da < 2$, the operating point might be unstable.

In addition, it should be mentioned that

$$\lim_{\mu \to -1} \left( \frac{Da}{X_f} \right) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

(2.17)

which shows that, irrespective of the value of $\beta$, no feasible state exists for $Da < 1$.

**Chemical initiation (S4)**

This system extends the system S2, by including an intermediate component. The dimensionless model (Eqs. 2.18) was obtained starting with the QSSA and following the procedure outlined in the previous section:

M balance: \[ 1 - \beta \cdot Da \cdot M \cdot R = 0 \quad (2.18a) \]

I$_2$ balance: \[ f_2 \cdot (z_{i_1} - I) - Da \cdot I = 0 \quad (2.18b) \]

R balance: \[ -f_2 \cdot R + (Da \cdot I - \beta \cdot Da \cdot M \cdot R) = 0 \quad (2.18c) \]
Fixed $z_{1,1}$: 

$$z_{1,1} - \frac{f_{1,0} \cdot z_{1,0}}{f_2} = 0$$  \hspace{1cm} (2.18d)

Flow rate: 

$$f_2 - (1 + f_2 \cdot M + f_{1,0}) = 0$$  \hspace{1cm} (2.18e)

where $$Da = k_1 \cdot \frac{V}{F_0/c_{M,0}}$$, $$\beta = \frac{k_2 c_{M,0}}{k_1}$$

A closed-form parametric solution is possible, but too complex to be presented here.

The solid lines of Figure 2.7 present the dependence of reaction conversion versus plant Damkohler number, for different values of $\beta$, $z_{i,0} = 1$, and $z_{1,1} = 0.5$. There is a significant change of the qualitative behaviour, compared to Figures 2.2, 2.4 and 2.5: the transcritical bifurcation point had disappeared. In addition, all the curves exhibit a turning (fold) point, which is presented by the dotted lines, for different values of $z_{1,1}$.

Figure 2.7. Consecutive reactions with chemical initiation (S4).

All the curves exhibit a fold (turning) point, presented by the dotted lines for different values of $z_{1,1}$. For large $\beta$, the conversion on the lower branch has small values.
When the QSSA is valid \((\beta \to \infty)\), the conversion at the turning point has very small values, and:

\[
\lim_{\beta \to \infty} Da_r = \frac{1}{z_{1,1}}
\]  \hspace{1cm} (2.19)

We conclude that state multiplicity occurs in Reactor – Separator – Recycle system where consecutive reactions involving two reactants take place. However, when the QSSA of the intermediate component is valid, the conversion on the unstable branch is very low.

**Polymerisation recycle systems**

In this section we consider simple radical polymerisation systems (Table 2.1, S5 and S6). Only the main steps of radical polymerisation are included: initiation, propagation and the termination. \(P_n\) (length \(n\)) and \(R_n\) denote dead and living polymer, respectively. The concentration of initiator radicals \((I)\) is subject to the quasi steady state approximation, which is usually valid for polymerisation. Removing this assumption does not change the results.

**Chain-growth polymerisation, with self-initiation (S5)**

In the case of self-initiated chain-growth polymerisation, the monomer is also acting as an initiator. The kinetic model is presented in Table 2.1 (S5). The dimensionless equations are given by:

**M balance:**

\[
1 - Da \cdot \left(2 \frac{\gamma}{\beta} M + \beta M \cdot R\right) = 0
\]  \hspace{1cm} (2.20a)

**R balance:**

\[
-\frac{R}{1-M} + Da \cdot \left(\frac{\gamma}{\beta} M - \gamma \cdot \beta \cdot R^2\right) = 0
\]  \hspace{1cm} (2.20b)

where:

\[
Da = k_p \sqrt{\frac{k_d c_{M,0}}{2k_i}} \frac{V}{F_0/c_{M,0}} \; ; \; \beta = \sqrt{\frac{2k_i c_{M,0}}{k_d}} \; ; \; \frac{\gamma}{k_p} = \frac{\sum c_{R,2}}{c_{M,0}}
\]
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The model parameters $Da$ and $\beta$ are related to the QSSA monomer consumption rate and radical concentration, respectively. The parameter $\gamma$ is the ratio between termination and propagation rate constants.

A closed-form parametric solution can be obtained, but it has a very complex form. Figure 2.8 shows the monomer conversion ($X$) versus the plant Damkohler number, for $\beta = 10^6$ and different values of $\gamma$. Feasible steady states do not exist for small $Da$. Two feasible steady states appear at a fold bifurcation point, although the corresponding conversion has extremely small values for $\gamma > 10^4$. All branches terminate at a transcritical bifurcation point, which is difficult to be seen in Figure 2.8.

![Figure 2.8. Chain-growth polymerisation systems with self-initiation (S5).](image)

For small $\gamma$, the system shows state multiplicity.

In the following we will present the steady classification using $Da \cdot \gamma / \beta$ as bifurcation parameter, which gives a clearer picture of the steady state behaviour. It can be shown that, irrespective of the value $\gamma$, the point $\left( Da \frac{\gamma}{\beta}, M \right) = \left( \frac{1}{2}, 1 \right)$ fulfils the balance equations. Moreover, at $\frac{\beta^2}{\gamma} \left( \frac{k_e}{k_a} \right) = 4$, one turning point enters the feasible range of positive
conversion of the \( Da \frac{\gamma}{\beta} \left( \equiv k_d \frac{V}{F_0/c_{M,0}} \right) \) – \( X \) diagram (boundary limit singularity). The steady state behaviour, presented in the first diagram of Figure 2.9, can be summarised as:

- \( \frac{\beta^2}{\gamma} < 4 \): 
  \[
  Da \frac{\gamma}{\beta} < \frac{1}{2}
  \]
  : no feasible steady state

\[
Da \frac{\gamma}{\beta} > \frac{1}{2}
\]
  : one feasible steady state

- \( \frac{\beta^2}{\gamma} > 4 \): 
  \[
  \left( Da \frac{\gamma}{\beta} \right)_f < Da \frac{\gamma}{\beta} < \frac{1}{2}
  \]
  : two feasible steady states; the low-conversion state is unstable

\[
Da \frac{\gamma}{\beta} > \frac{1}{2}
\]
  : one feasible steady state

The second diagram of Figure 2.9 shows the dependence \( Da \gamma/\beta - X \), for \( \beta^2/\gamma = 10^3 \) and different values of \( \gamma \). A fold (turning) point always exists, because \( \beta^2/\gamma > 4 \).

For low values of \( \gamma \) (slow termination), the fold point corresponds to a large value of the conversion. This means that there is a practical range of conversion values that results in an unstable reactor design. For large values of \( \gamma \) (fast termination), the conversion at the fold point is very low. In this case, the instability of the low-conversion branch has no practical implication.
Figure 2.9. Chain-growth polymerisation systems with self-initiation (S5):

\[ X \text{ vs. } Da \cdot \frac{\gamma}{\beta} \] bifurcation diagrams.

All curves pass through \((Da \cdot \gamma/\beta, X) = (1/2, 0)\). State multiplicity is possible for \(\frac{\beta^2}{\gamma} > 4\).
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Chain-growth polymerisation, with chemical initiation (S6)

For this system the kinetic model and dimensionless equations are presented in Table 2.1 (S6) and Eqs. 2.21, respectively. When \( C \neq 0 \), the model takes a gel effect into consideration.

I balance:
\[
\frac{I_1 - I_2}{1 - M} - Da \frac{\gamma}{2\beta} I_1 = 0
\]

M balance:
\[
1 - Da\left(\beta \cdot M \cdot R + \frac{\gamma}{\beta} I_2\right) = 0
\]

R balance:
\[
- \frac{R}{1 - M} + Da \cdot \left(\frac{\gamma}{\beta} I_2 - \gamma \cdot \beta \cdot R^2 \cdot e^{-C(1-M)}\right) = 0
\]

where:
\[
Da = k_p \sqrt{\frac{k_d c_{M,0}}{k_i c_{M,0}}} \frac{V}{F_0/c_{M,0}}; \quad \beta = \sqrt{\frac{k_i c_{M,0}}{k_d}}; \quad \gamma = \frac{2k_i}{k_p}; \quad z_{1,1} = c_{1,1}/c_{M,0}; \quad I_2 = c_{1,2}/c_{M,0}
\]

The first diagram of Figure 2.10 shows the solution of Eqs. 2.21, for different values of \( \gamma \) and \( z_{1,1} = 10^{-4}, \beta = 10^3, C = 0 \). Each bifurcation diagram exhibits one fold (turning) point. Thus, no steady states exist for \( Da < Da_f \), and two steady states exist for \( Da > Da_f \). For small values of \( \gamma \) (slow termination), the conversion at the fold point is high and the multiplicity of states is important. For large values of \( \gamma \) (for example \( \gamma > 10^2 \)), the conversion of the lower branch has very small values. Hence, only the upper state, existing for \( Da > Da_f \), has practical significance.

In the limiting case of QSSA for radicals, only one feasible steady state exists for:

\[
Da > \frac{1}{\sqrt{z_{1,1}}}
\]

The second diagram of Figure 2.10 presents the \( X \) vs. \( Da \) dependence, for different values of \( \beta \) and \( \gamma = 10^3 \). A fold (turning) point always exists. When \( \beta \) decreases, the fold point slightly shifts to larger value of Damkohler number.
Figure 2.10. Chain growth polymerisation systems with chemical initiation (S6).

The conversion on the lower, unstable branch has significant values for slow termination.
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Figure 2.11. Impact of the gel-effect (S6).
Two additional turning points occur, leading to a maximum of four steady states.
To investigate the impact of a gel effect, we consider a conversion-dependent termination rate only. Biesenberger and Sebastian (1993) use the simple exponential model Eq. 2.21c, with the dimensionless constant $C$ in the range $5...15$.

The first diagram of Figure 2.11 presents the conversion vs. plant Damkohler number, for $C = 8, \beta = 10^3, z_{l,1} = 10^{-4}$ and three different values of $\gamma$. For $\gamma = 10^2$ one turning point exists. The conversion on the lower, unstable branch has large values. For larger $\gamma$, two additional turning points exist; hence, there is a range of $Da$ values for which four steady states are possible. Note that the diagrams for $\gamma = 3 \cdot 10^2$ and $\gamma = 10^3$ differ by the relative location of the turning points.

The second diagram of Figure 2.11 illustrates the influence of the gel-effect. For $\beta = 10^3, \gamma = 10^3, z_{l,1} = 10^{-4}$, four steady states can exist for $C > 6$. For increasing $C$, the lower turning points come closer and the range of $Da$ values for which four steady states exist becomes very small.

**Effect of the chain-transfer reactions**

In this section we investigate the effect of the chain-transfer to monomer and solvent reactions. Including additional steps, like termination by combination, transfer to polymer or random-scission, will not affect the conversion. The stoichiometric model and kinetic parameters correspond to the low-density polyethylene process (Table 2.2).

<table>
<thead>
<tr>
<th>Reaction mechanism</th>
<th>( I_2 \xrightarrow{k_1} 2I \cdot )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Initiation:</td>
<td>( M + I \cdot \xrightarrow{k_{l,1}} R_1 \cdot )</td>
</tr>
<tr>
<td>2. Propagation:</td>
<td>( R_n \cdot + M \xrightarrow{k_1} R_{n+1} \cdot )</td>
</tr>
<tr>
<td>3. Termination by disproportionation:</td>
<td>( R_n \cdot + R_m \cdot \xrightarrow{k_{l,1}} P_n + P_m )</td>
</tr>
<tr>
<td>4. Chain Transfer to Monomer:</td>
<td>( R_n \cdot + M \xrightarrow{k_{l,1}} P_n + R_1 \cdot )</td>
</tr>
<tr>
<td>5. Chain Transfer to Solvent:</td>
<td>( R_n \cdot + S \xrightarrow{k_{l,1}} P_n + S \cdot )</td>
</tr>
</tbody>
</table>

Table 2.2. LDPE polymerisation
Chapter 2. Non-linear Analysis of CSTR-Separator-Recycle Systems

Kinetic constants

(Pladis and Kiparissides, 1998; Iedema, Wulkow and Hoefsloot, 2000)

\[ k_d [1/s] = 8.843 \cdot 10^{12} \cdot \exp(-15715/T) \]
\[ \eta [-] = 1 \]
\[ k_p [m^3/(mol\cdot s)] = 1 \cdot 10^3 \cdot \exp(-2709/T) \]
\[ k_i [m^3/(mol\cdot s)] = 3 \cdot 10^4 \cdot \exp(-2041/T) \]
\[ k_m [m^3/(mol\cdot s)] = 1.25 \cdot 10^5 \cdot \exp(-4068/T) \]
\[ k_s [m^3/(mol\cdot s)] = 5 \cdot 10^5 \cdot \exp(-4802/T) \]

\[ T = 448 \text{ K} \]

The dimensionless model equations are:

1. **I_2 balance:**
   \[ \frac{z_{I_2} - I_2}{1 - M} - Da \frac{\gamma}{2\beta} I_2 = 0 \]  \hspace{1cm} (2.23a)

2. **M balance:**
   \[ 1 - Da \left( \beta \cdot M \cdot R + \frac{\gamma}{\beta} I_2 \right) = 0 \]  \hspace{1cm} (2.23b)

3. **R balance:**
   \[ -\frac{R}{1 - M} + Da \left( \frac{\gamma}{\beta} I_2 - \gamma \cdot \beta \cdot R^2 \right) = 0 \]  \hspace{1cm} (2.23c)

4. **S balance:**
   \[ \frac{z_{S_1} - S}{1 - M} - Da \cdot \delta \cdot \beta \cdot R \cdot S = 0 \]  \hspace{1cm} (2.23d)

where:

\[ Da = (k_p + k_m) \sqrt{\frac{k_d c_{M,0}}{k_i}} \]
\[ V = \frac{k_i c_{M,0}}{k_d} \]
\[ \beta = \sqrt{\frac{k_i c_{M,0}}{k_d}} \]
\[ \gamma = \frac{2k_i}{k_p + k_m} \]
\[ \delta = \frac{k_i}{k_p + k_m} \]
\[ S = z_{S,2} = c_{S,2} / c_{M,0} \]
\[ z_{S,1} = c_{S,1} / c_{M,0} \]

Figure 2.12 presents the monomer conversion versus the plant Damkohler number. The chain-transfer steps did not bring up anything new to the qualitative behaviour, which is very similar to the one found for the simpler model S6. Multiple steady states exist. The turning point and the lower branch correspond to small values of the conversion. This agrees with the
high termination / propagation ratio, \( \gamma \). Moreover, two feasible steady states exist for \( Da > 320 \approx \frac{1}{\sqrt{z_{1,1}}} \), which is extremely close to the critical value predicted by Eq. 2.22.

![Graph showing the effect of transfer to monomer, polymer, and solvent in a LDPE CSTR-Separator-Recycle polymerisation system.](image)

**Figure 2.12.** Effect of transfer to monomer, polymer and solvent in a LDPE CSTR-Separator-Recycle polymerisation system.

Chain transfer reactions do not affect the qualitative behaviour.

**Discussion**

In contrast to stand-alone reactors, in Reactor – Separator – Recycle systems a zero-conversion, infinite-recycle steady state always exists. This state is stable if the reactor volume is below a critical value, for a given feed flow rate and reaction kinetics. Feasible steady states are possible only if the reactor volume exceeds the critical value. This constraint can be expressed conveniently using the plant Damkohler number. Feasible states can occur by two mechanisms:

a) A transcritical bifurcation, where the infinite-recycle state loses stability and a non-trivial state gets meaningful values and gains stability. The simple reaction systems S1 and S2 belong to this category.
b) A fold bifurcation (turning point), at which two steady states are born. This behaviour is generic for consecutive-reactions systems involving two reactants (S4, S6). For one-reactant, consecutive-reactions systems (S3, S5), a large propagation/initiation ratio is needed. For large termination/propagation ratio (QSSA for the intermediate component is valid), the turning point is located at low conversion values, and the behaviour is practically similar to that of the simple systems S1 and S2.

In practice, designs near the bifurcation points are dangerous, since changing operating conditions or uncertain design parameters can lead to a behaviour that is different from the expected one. A reactor design close to the transcritical bifurcation is unlikely, because the conversion would have a very small value. When a high-conversion fold point exists (slow termination, gel effect), an optimisation procedure might suggest a reactor with minimum volume. Such a design, close to the fold point, can suffer from serious operability problems. If the reaction rate is over-estimated, or the feed flow rate deviates from the nominal design value, the operating point falls at the left of the turning point in the $Da - X$ map, in the region where no steady state exists. In this case, infinite reactant accumulation occurs, and the plant has to be shut down.

In Figures 2.4 – 2.12 showing state multiplicity, the low-conversion states are unstable. This is important in practice when the turning point is situated at high conversion (slow termination, gel effect). In this case, one cannot obtain low conversion (which might be desirable for product quality reasons) in a CSTR – Separator – Recycle system operating at a stable operating point.
Conclusions

Chemical reactors interacting with separation through material recycle behave differently compared to the stand-alone reactors:

- A minimum reactor volume is necessary for a feasible operating point to exist.
- Multiple steady states are possible, even in the case of a simple reaction scheme and isothermal operation.
- The instability of the low-conversion branch sets a lower limit on the achievable conversion. For polymerisation systems, this has practical significance when the radicals' QSSA is not valid (slow termination, gel-effect).

Further research will consider other reactor types (e.g. PFR), heat-effects, imperfect separation and other complex multi-reactions where selectivity issues are also important.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>concentration</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$F$</td>
<td>flow rate</td>
<td>mol/s</td>
</tr>
<tr>
<td>$F_{\text{vol}}$</td>
<td>volumetric flow rate</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant</td>
<td>(mol/m$^3$)$^{1-n}$s$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$T_S$</td>
<td>time constant</td>
<td>s</td>
</tr>
<tr>
<td>$V$</td>
<td>reactor volume</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$X$</td>
<td>conversion</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
References


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