Design and control of recycle systems by nonlinear analysis
Kiss, A.A.

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Chapter 3: Non-linear Analysis of PFR-Separator-Recycle Systems

Abstract

This article explores the non-linear behaviour of isothermal and non-isothermal PFR – separator – recycle systems, with reference to radical polymerization. The steady state behaviour of six reaction systems of increasing complexity, from one-reactant first-order reaction to chain-growth polymerization, is investigated. In PFR – separator – recycle systems feasible steady states exist only if the reactor volume exceeds a critical value. For one-reaction systems, one stable steady state is born at a transcritical bifurcation. In case of consecutive-reaction systems, including polymerization, a fold bifurcation can lead to two feasible steady states. The transcritical bifurcation is destroyed when two reactants are involved. In addition, the thermal effects also introduce state multiplicity. When multiple steady states exist, the instability of the low-conversion branch sets a lower limit on the conversion achievable at a stable operating point. A low-density polyethylene (LDPE) process is presented as a real plant example.

The results obtained in this study are similar to CSTR-separator-recycle systems. This suggests that the behaviour is dictated by the chemical reaction and flowsheet structure, rather than by the reactor type.
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Introduction

Reaction systems involving material recycles are very usual in chemical industry. The flexibility of such systems must be ensured by the reactor design and its operation policy. The study presented in this article originated from an unexpected bifurcation diagram (Figure 3.11), obtained for a low-density polyethylene plant (Figure 3.10). Figures 3.10 and 3.11 will be discussed in detail in a following section. To understand the origins of this surprising behaviour, we started the investigation with the CSTR reactor model (Kiss et al., 2002) that is computationally less-demanding. The present work concludes the endeavour, considering the non-linear behaviour of PFR – Separator – Recycle systems, with reference to radical polymerization. In the following, we explain how analysing systems involving PFRs, and comparing the results with those obtained for CSTRs, contributes to better understanding of the effect of mass recycle.

The dependence of reaction rate vs. temperature and concentration is a nonlinearity that is present in chemical reactors. Coupled with a feedback mechanism, this dependence can lead to state multiplicity, isolated solution branches, instability, sustained oscillations, strange attractors or chaotic behaviour. Energy feedback is often present due to: mixing (Balakotaiah and Luss, 1984), axial dispersion (Jensen and Ray, 1982), recycle of reactor’s effluent (Reilly and Schmitz, 1966, 1967), autothermal operation (Lovo and Balakotaiah, 1992) and heat integration (Bildea and Dimian, 1998). In practice, the above-mentioned phenomena are undesired. For this reason, energy feedback is often excluded by means of control loops. These manipulate, for example, the coolant flow rate, the by-pass around a feed-effluent heat exchanger, or the duty of a heater/cooler upstream the reactor.

In many chemical plants, feedback is also present due to material recycle (Figure 3.1). In such systems, the reactor effluent is first processed by a separation section, and afterwards recycled. The product (4) and recycle (3) streams have fixed composition. This is achieved by local control of the separation units. Hence, the composition at reactor inlet is not directly dependent on the reactor effluent. Moreover, the temperature at the reactor inlet is either the ambient temperature or has a constant value due to a heat exchanger placed upstream the reactor. Luss and Amundson (1967) recognized this structure as representative for chemical plants. Pareja and Reilly (1969) acknowledged that recycle reactors could become unstable solely as a result of material recycle, but they did not present any result. The interest in reactor
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-- separator -- recycle systems is further motivated by plantwide control studies (Luyben and Luyben, 1997) that reported control difficulties due to the “snowball effect”. Bilda et al. (2000) analysed the relationship between design and control of several systems, showing that the nonlinear behaviour leads to control problems. However, the study was restricted to the steady state behaviour of an isothermal reactor.

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

The nonlinear behaviour of CSTR -- separator -- recycle systems was the subject of few recent articles. Pushpavanam and Kienle (2001) considered a first-order reaction and demonstrated that state multiplicity, isolas, instability and limit cycles can easily arise. Although the flowsheet included inter-units heat-exchangers, energy feedback was still present inside the CSTR due to the mixing. Kiss et al. (2002) studied the case of complex reactions, including polymerization, in isothermal CSTR -- separator -- recycle systems. It was shown that the nonlinearity of a consecutive mechanism is sufficient for multiplicity and instability to occur. The same phenomena are exemplified by Sagale and Pushpavanam
(2002), who considered several different modes of operation for the simple autocatalytic reaction \( A + 2B \rightarrow 3B \), in an isothermal CSTR – flash – recycle system.

Such phenomena, induced by heat effects (for example, Balakotaiah and Luss, 1984) or complex kinetics (Gray and Scott, 1983, 1984), can also occur in a stand-alone CSTR. For this reason, in this article we consider the plug-flow reactor (PFR). Although the generic structure of PFR – separator – recycle is present in many industrial plants, no results concerning its nonlinear behaviour have been reported. In contrast to the stand-alone CSTR, the model of the stand-alone PFR is an initial-value ODE problem that always has a unique solution. Axial dispersion and radial temperature gradients are important for detailed mathematical modelling. However, these phenomena were deliberately neglected because they are sources of state multiplicity and instability in stand-alone reactors (Jensen and Ray, 1982). Therefore, our analysis is expected to reveal nonlinear phenomena that can be attributed exclusively to the recycle of mass. In addition, when heat effects are included, we are certain that state multiplicity and instability are not the result of heat feedback. It should also be remarked that the plug-flow model has been applied with success for kinetic studies, design and simulation of many industrial reactors, including polymerization (for example: Chen et al., 1976; Gupta, Kumar & Krishnamurthy, 1985; Zabisky et al., 1992; Kiparissides et al., 1996).

The nonlinearity introduced by the reaction stoichiometry clearly affects the type of behaviour. In order to assess this effect, we choose six reaction systems, of increasing complexity, denoted by S1 to S6 and shown in Table 3.1.

S1 and S2 are the simplest cases, representing the global stoichiometry of self-initiated and chemically-initiated polymerization. These systems show regions of unfeasible operation, a feasible solution of the balance equations being born at a transcritical bifurcation. A fold bifurcation can occur when heat-effects are introduced, leading to state multiplicity and instability. An additional but important result is that state multiplicity is not restricted to exothermic reactions in cooled reactors, but can also occur in heated reactors carrying on endothermic reactions. S3 and S4 take into account the initiation step. The autocatalytic, consecutive-reaction mechanism is enough to induce state multiplicity and instability, even in the isothermal case. Moreover, the transcritical bifurcation is destroyed when two reactants are involved. Heat effects do not change the qualitative picture, although the unstable
operating points cover a larger conversion range. Finally, detailing the propagation-termination steps (S5 and S6) does not add anything new to the qualitative behaviour.

Table 3.1. Investigated reactions mechanisms.

<table>
<thead>
<tr>
<th>Self-initiation</th>
<th>Chemical initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S1. One reactant</strong></td>
<td><strong>S2. Two reactants</strong></td>
</tr>
<tr>
<td>( M \xrightarrow{k_1} P )</td>
<td>( M + I \xrightarrow{k_1} P )</td>
</tr>
<tr>
<td><strong>S3. Consecutive reactions</strong></td>
<td><strong>S4. Consecutive reactions</strong></td>
</tr>
<tr>
<td>( M \xrightarrow{k_1} R )</td>
<td>( I \xrightarrow{k_1} R )</td>
</tr>
<tr>
<td>( M + R \xrightarrow{k_1} P )</td>
<td>( M + R \xrightarrow{k_1} P )</td>
</tr>
<tr>
<td><strong>S5. Chain-growth polymerisation</strong></td>
<td><strong>S6. Chain-growth polymerisation</strong></td>
</tr>
<tr>
<td>( M \xrightarrow{k_2} I )</td>
<td>( I_2 \xrightarrow{k_3} 2I )</td>
</tr>
<tr>
<td>( M + I \xrightarrow{k_1} R, \bullet )</td>
<td>( M + I \xrightarrow{k_1} R, \bullet )</td>
</tr>
<tr>
<td>( R_n \bullet + M \xrightarrow{k_2} R_{n+1} )</td>
<td>( R_n \bullet + M \xrightarrow{k_p} R_{n+1} )</td>
</tr>
<tr>
<td>( R_n \bullet + R_m \xrightarrow{k_1} P_n + P_m )</td>
<td>( R_n \bullet + R_m \xrightarrow{k_1} 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.

Interestingly, the bifurcation diagrams are qualitatively similar to recycle systems involving a CSTR (Kiss et al., 2002). Moreover, there is also a quantitative agreement with respect to the parameter values at which different bifurcation phenomena occur. This suggests that the type of behaviour is dictated mainly by the reaction stoichiometry and flowsheet structure, rather than by the reactor type.

**One-reactant recycle systems (S1)**

We start our study with one-reactant first-order reaction \( M \rightarrow P \), carried out in a PFR-separator - recycle system. This is the simplest case, but having a stoichiometry equivalent to the global stoichiometry of a self-initiated polymerization. A steady state model, containing the mass and energy balance, can be written in the following dimensionless form:
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M balance:  \[ \frac{dM}{d\xi} = - \frac{Da}{f_2} \cdot M \cdot \exp\left( \frac{a\theta}{1+\theta} \right) \]  (3.1a)

Heat balance:  \[ \frac{d\theta}{d\xi} = \frac{Da}{f_2} \left( B \cdot M \cdot \exp\left( \frac{a\theta}{1+\theta} \right) - H \cdot (\theta - \theta_c) \right) \]  (3.1b)

\[ M(0) = 1; \quad \theta(0) = 0; \]  (3.1c)

Reactor flow rate:  \[ f_2 = 1/(1 - M(1)) \]  (3.1d)

The dimensionless variables and parameters, defined with the feed flow rate \( F_0 \), feed concentration \( c_{M,0} \) and reactor inlet temperature \( T_1 \) as reference values, are: the axial coordinate \( 0 \leq \xi \leq 1 \), concentration \( M(\xi) = c_M(\xi)/c_{M,0} \), temperature \( \theta(\xi) = (T(\xi) - T_1)/T_1 \), reactor flow rate, \( f_2 = F_2/F_0 \); plant Damköhler number \( Da = k(T_1) \cdot V \cdot c_{M,0}/F_0 \), Arrhenius temperature \( \alpha = T_A/T_1 \), adiabatic temperature rise \( B = (\Delta H)c_{M,0}/(\rho c_p T_1) \), heat-transfer capacity \( H = UA/(V \cdot \rho c_p, k(T_1)) \), coolant temperature \( \theta_c = (T_c - T_1)/T_1 \). In this study we consider a sharp separation; therefore the recycle consists of pure reactant \( M \), while no \( M \) is found in the product stream.

The model equations can be solved by a shooting technique: start with an initial guess for \( M(1) \), calculate the reactor outlet flow rate \( f_2 \) using Eq. 3.1d, integrate the PFR equations 3.1a – 3.1c, check and update the guess \( M(1) \). By setting equal reactor-inlet and coolant temperatures (\( \theta_c = \theta_1 = 0 \)) and zero adiabatic temperature rise (\( B = 0 \)), the model of the reactor operated isothermally at \( \theta = 0 \) is obtained. Then, integration of Eq. 3.1a, followed by the substitution of \( f_2 \) from Eq. 3.1d leads to:

\[ \ln M(1) = -Da \cdot (1 - M(1)) \]  (3.2)

It follows from Eq. 3.2 that \( M(1) = 1 \) is a trivial solution, satisfying the balance equation irrespective of the \( Da \) value. Although unfeasible because of the corresponding infinite flow rates, accounting for this solution helps understanding the mechanism by which feasible states occur.

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The non-trivial solution, given by:

\[ Da = -\frac{1}{1-M(1)} \ln(M(1)) \] (3.3)

is feasible (positive flow rates) if, and only if \( Da > Da_T \), where:

\[ Da_T = \lim_{M(1)\to1} Da = 1 \] (3.4)

The relationship expressing the limiting value is identical to the one given for CSTR – separator – recycle system by Bildea et al., 2000. Such a feasibility constraint does not exist in the case of stand-alone reactors. As consequence, this is characteristic to recycle systems. The explanation is that the separation section does not allow the reactant to leave the process. Therefore, for a given reactant feed flow rate \( F_0 \), a large reactor volume \( V \) or fast kinetics \( k(T_1) \) are necessary to consume completely the reactant fed in the process, and consequently to avoid reactant accumulation. The dimensionless plant Damköhler number conveniently includes these three variables (flow-rate, reactor volume and kinetics).

Figure 3.2 shows the dependence of reaction conversion, \( X = 1 - M(1) \), versus \( Da \) number (bifurcation diagram) for different values of the adiabatic temperature rise \( B \geq 0 \). At transcritical value \( Da = Da_T \), the trivial and non-trivial steady-state manifolds cross each other, in the combined space of state variable \( X \) and parameter \( Da \). Simultaneously, one eigenvalue of the linearized dynamic model is zero (this can be easily shown by using a CSTR model) and the two solution branches exchange their stability. Thus, \( (X, Da) = (0, 1) \) is a transcritical bifurcation point (Guckenheimer and Holmes, 1983). This type of bifurcation occurs only in special cases, and is expected that it will disappear under model perturbations, for example more complex kinetics (see Chapter 2 for a more detailed discussion).

The entire bifurcation diagram (including the unfeasible domain) contains one fold point. This enters the feasible region at a boundary limit singularity (Golubitsky and Schaeffer, 1985). For the CSTR – separator – recycle system, Pushpavanam and Kienle (2001) assumed infinite activation energy and equal coolant and reactor inlet temperatures, and derived an analytical expression of this singularity. If these assumptions are removed, it can be shown that the fold point is feasible whenever:
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\[(H \cdot \alpha \cdot \theta_c) > 1 - B \cdot \alpha \quad (3.5)\]

Remarkably, this relationship also applies to PFR – separator – recycle systems. Eq. 3.5 demonstrates that state multiplicity is not restricted to exothermal reactions in cooled reactors, but it can also occur in heated reactors carrying on endothermal reactions.

![Diagram](attachment:image.png)

**Figure 3.2. One-reactant, first-order reaction (S1)**

One solution is unfeasible, corresponding to zero conversion and infinite recycle flow rate. For isothermal operation \((B = 0)\) a feasible solution exists if, and only if \(Da > 1\). For the non-isothermal operation and \(\alpha B > 1\), multiple steady states exist.

In the non-isothermal case, feasible non-trivial solutions are possible for \(Da < Da_T = 1\). The trivial solution \((X = 0)\) is stable when \(Da < Da_T\), but loses stability at \(Da = Da_T\). Simultaneously, for increasing \(Da\) values,

- if the fold point is unfeasible \((B\alpha < 1)\), the non-trivial solution gets physically meaningful values and gains stability
- if the fold point is located in the feasible region \((B\alpha > 1)\), the low-conversion branch of the non-trivial solution gains stability, but becomes unfeasible.
Analysing more complex systems, we will disregard the trivial, unfeasible solution \((X=0, \infty)\).

In the multiplicity region, the instability of the low-conversion state can be proven using the steady state model. For a stand-alone reactor, the amount of reactant consumed \((F_1X)\) depends on the reactor's feed flow rate. This dependence is shown in Figure 3.3, using the dimensionless variables \(\alpha = \frac{F_1}{(k_1(T_1)c_{M,0})V} = 1/Da_1\) and \(\beta = \frac{F_1X}{(k_1(T_1)c_{M,0})V} = X/Da_1\).

![Figure 3.3](image)

Figure 3.3. Instability of the low-conversion steady state.

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

In a reactor – separator – recycle system, the intersections of this curve with the dimensionless amount of reactant fed in the process \(\alpha = \frac{F_0}{(k_1(T_1)c_{M,0})V} = 1/Da_1\), provides the steady state values of the reactor-inlet flow rate. Two steady states exist for \(H = 30, B = 0.25, \alpha = 25, \theta_c = 0\) and \(Da = 0.6\). To analyse the stability of the low-conversion state B, let us consider an increase of the reactor inlet flow rate. At the right of point B, the amount of reactant fed in the process is larger than the amount of reactant consumed. Reactant accumulation occurs, leading to a further increase of the recycle and reactor-inlet flow rates. These arguments do not guarantee the stability of the high-conversion state, because stability
can be lost at Hopf bifurcation points, simultaneously with occurrence of a limit cycle. Identifying such phenomena is beyond the scope of this article, because it requires a full dynamic model, including the composition – controlled separation, the delay introduced by recycle and the temperature – controlled heat – exchanger.

**Two-reactants 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 polymerization. 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 reactor-inlet concentration at a prescribed value \((z_{1,1})\). The dimensionless model is given by:

\[
\begin{align*}
\text{M balance:} & \quad \frac{dM}{dx} = -\frac{Da}{f_2} \cdot M \cdot I \cdot \exp\left(\frac{\alpha \theta}{1 + \theta}\right) \\
\text{I balance:} & \quad \frac{dI}{dx} = -\frac{Da}{f_2} \cdot M \cdot I \cdot \exp\left(\frac{\alpha \theta}{1 + \theta}\right) \\
\text{Heat balance:} & \quad \frac{d\theta}{dx} = \frac{Da}{f_2} \left( B \cdot M \cdot I \cdot \exp\left(\frac{\alpha \theta}{1 + \theta}\right) - H \cdot (\theta - \theta_0) \right) \\
M(0) & = 1 - z_{1,1}/z_{1,0} ; \quad I(0) = z_{1,1} ; \quad \theta(0) = 0 \\
\text{Fixed } z_{1,1}: & \quad z_{1,1} - \frac{f_{1,0} \cdot z_{1,0}}{f_2} = 0 \\
\text{Flow rate:} & \quad f_2 \left( 1 + f_2 \cdot M(1) + f_{1,0} \right) = 0
\end{align*}
\]

where, in addition to the variables already defined:

\[
Da = k_i (T_i) \frac{1}{F_0 \cdot c_{M,0}} ; \quad I = c_i(\xi) / c_{M,0} ; \quad z_{1,0} = c_{1,0} / c_{M,0} ; \quad z_{1,1} = c_{1,1} / c_{M,0}
\]

For isothermal operation \((B=0, \theta = 0)\) a closed-form parametric solution can be obtained:

\[
M(1) = m
\]
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\[ Da = - \frac{z_{i,0}^2 \ln \left( \frac{(z_{i,0} - z_{i,1})(z_{i,0}z_{i,1} + z_{i,1} - z_{i,0} + z_{i,0} \cdot m)}{z_{i,0}^2 \cdot z_{i,1} \cdot m} \right)}{(z_{i,0}z_{i,1} - z_{i,0} + z_{i,1}) \cdot (z_{i,0}m - z_{i,0} + z_{i,1})} \]  

(3.7b)

\[ I(1) = z_{i,1} - (1 - \frac{z_{f,1}}{z_{f,0}} - m) \]  

(3.7c)

\[ f_2 = \frac{1}{1 - m - z_{i,1}/z_{i,0}} \]  

(3.7d)

\[ f_{i,0} = \frac{z_{i,1}}{z_{i,0} - z_{i,0} \cdot m - z_{i,1}} \]  

(3.7e)

where: \( m \in \left[ \max \left( 0,1 - \frac{z_{f,1}}{z_{f,0}} - z_{i,1} \right), 1 - z_{i,1}/z_{i,0} \right] \)

Figure 3.4, diagram A, presents the conversion \( X \) versus the plant Damköhler number, for \( z_{i,0} = 1 \) and different values of \( z_{i,1} \). Similarly to S1, a feasible solution occurs at a transcritical bifurcation. This results by setting \( m = 1 - z_{i,1}/z_{i,0} \) in Eq. 3.7b:

\[ Da_T = \frac{z_{i,0}}{z_{i,1} \left( z_{i,0} - z_{i,1} \right)} \]  

(3.8)

Moreover, the minimum value of \( Da_T \) is given by:

\[ \min Da_T = (Da_T)_{z_{i,1} \rightarrow 0} = 4 \]  

(3.9)

Relationships 3.8 and 3.9 are identical to the ones found for isothermal CSTR - separator - recycle system (Kiss et al., 2002).

Diagram B of Figure 3.4 presents results for the non-isothermal case. Similarly to the one-reactant system S1, multiple steady states occur as the result of thermal effects, while the transcritical bifurcation remains intact. A high value of \( B \) has a severe effect on state multiplicity, shifting the fold point to high conversions. When multiple steady states exist, the low-conversion branch is unstable.
Figure 3.4. Two - reactants, second order reaction (S2).

A. Isothermal: a feasible solution exists only if $Da$ exceeds the transcritical bifurcation.

B. Non-isothermal: heat effects induce state multiplicity.
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 polymerization, these roughly correspond to the initiation and propagation-termination steps, and the radical species, respectively.

The dimensionless parameters are defined following the procedure presented by Kiss et al. (2002), where the reactant rate constant used in the Damköhler number is related to the consumption rate of reactant M under quasi steady-state approximation (QSSA). A second parameter, \( \beta \), is related to the QSSA concentration of the intermediate component. We assume small activation energies, with the exception of the initiation step (dimensionless parameter \( \alpha \)). Moreover, we consider that heat is released only by the propagation step (dimensionless parameter \( B \)).

Self-initiation (S3)

The stoichiometry and kinetic model of self-initiated consecutive reactions are given in Table 3.1. The dimensionless model of the PFR-separator-recycle system can be written in the following form:

\[
\frac{dM}{d\xi} = - \frac{Da}{2f_2} \left( M \cdot \exp \left( \frac{\alpha \theta}{1+\theta} \right) + \beta \cdot M \cdot R \right) \quad (3.10a)
\]

\[
\frac{dR}{d\xi} = \frac{Da}{2f_2} \left( M \cdot \exp \left( \frac{\alpha \theta}{1+\theta} \right) - \beta \cdot M \cdot R \right) \quad (3.10b)
\]

\[
\frac{d\theta}{d\xi} = \frac{Da}{2f_2} \left( B \cdot \beta \cdot M \cdot R - H \cdot (\theta - \theta_c) \right) \quad (3.10c)
\]

\[
M(0) = 1; \ R(0) = 0; \ \theta(0) = 0; \quad (3.10d)
\]

Flow rate:
\[
f_2 = 1/(1-M(1)) \quad (3.10e)
\]

where \( Da = 2k_i(T_1) \frac{V}{F_0/c_{M0}} \); \( \beta = \frac{k_i c_{M0}}{k_i(T_1)} \); \( \alpha = \frac{T_{3i}}{T_1} \); \( B = \frac{(-\Delta H_2) c_{M0}}{\rho c_p} \frac{1}{T_1} \); \( R(\xi) = c_R / c_{M0} \).
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Figure 3.5. Consecutive reactions with self-initiation (S3).

A. Isothermal: 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 \(Da < 1\).

B. Non-isothermal: state multiplicity appears as a result of thermal effects.
Diagram A of Figure 3.5 presents the dependence of reaction conversion vs. plant Damköhler number, for different values of $\beta$ and isothermal conditions. All curves pass through the transcritical bifurcation point $(Da, X) = (2, 0)$. When the second reaction is slow ($\beta < 1$), the system behaves similarly to the first-order isothermal reaction in a PFR – separator – recycle system: a unique, feasible steady state ($X > 0$) exists if, and only if $Da > 2$. When the second reaction is fast ($\beta > 1$) the system exhibits multiple steady states. For very large $\beta$, the conversion on the unstable branch has very small values. As in the case of CSTR – separator – recycle systems (Kiss et al., 2002),

$$\lim_{\beta \to \infty} Da_p = 1$$

(3.11)

In diagram B of Figure 3.5, a bifurcation diagram for the non-isothermal case is presented. State multiplicity appears as result of thermal effects. A higher value of $B$ shifts the fold point to higher conversions. The $Da - X$ space is divided in two regions with different stability.

In order to illustrate the change of stability the dynamic model for system S3 is being used:

M balance:

$$\frac{dM}{d\tau} = - \frac{dM}{d\xi} - \frac{Da}{2f_2} \left( M \cdot \exp\left( \frac{\alpha}{1+\theta} \right) + \beta \cdot M \cdot R \right)$$

(3.12a)

R balance:

$$\frac{dR}{d\tau} = - \frac{dR}{d\xi} + \frac{Da}{2f_2} \cdot \left( M \cdot \exp\left( \frac{\alpha}{1+\theta} \right) - \beta \cdot M \cdot R \right)$$

(3.12b)

Heat balance:

$$\frac{d\theta}{d\tau} = - \frac{d\theta}{d\xi} + \frac{Da}{2f_2} \left( B \cdot \beta \cdot M \cdot R - H \cdot (\theta - \theta_c) \right)$$

(3.12c)

Flow rate:

$$f_2 = 1/(1 - M(1))$$

(3.12d)

Diagram A of Figure 3.6 shows the dynamic simulation results. The system is initially in the unstable low-conversion state. At $\tau = 10$, the Damköhler number $Da$ is changed by $\pm 1\%$ for a limited period of time ($\Delta \tau = 1$). Depending on the disturbance direction, the high- or zero-conversion stable states are reached. In the diagram B of the same figure the dimensionless concentration profile of reactant $M$ is plotted along the reactor length at different times.
Figure 3.6. Instability of the low-conversion steady state (S3).

A. Small disturbances lead to zero conversion (reactant accumulation) or higher conversion state (reactant depletion).

B. Concentration profiles of reactant $M$ along the reactor, during the transition from low-to high-conversion branch.
**Chemical initiation (S4)**

This system extends S2, by including an intermediate component (Table 3.1). The dimensionless model is given by the following equations:

\[
\frac{dM}{d\xi} = -\frac{Da}{f_2} \cdot \beta \cdot M \cdot R \quad (3.13a)
\]

**M balance:**

\[
\frac{dI}{d\xi} = -\frac{Da}{f_2} \cdot I \cdot \exp\left(\frac{\alpha \theta}{1+\theta}\right) \quad (3.13b)
\]

**I\(_2\) balance:**

\[
\frac{dR}{d\xi} = \frac{Da}{f_2} \cdot \left( I \cdot \exp\left(\frac{\alpha \theta}{1+\theta}\right) - \beta \cdot M \cdot R \right) \quad (3.13c)
\]

**R balance:**

\[
\frac{d\theta}{d\xi} = \frac{Da}{f_2} \left( B \cdot \beta \cdot M \cdot R - H \cdot (\theta - \theta_c) \right) \quad (3.13d)
\]

**Heat balance:**

\[
M(0) = 1 - z_{1,1} / z_{1,5} \quad I(0) = z_{1,1} \quad R(0) = 0 \quad \theta(0) = 0 \quad (3.13g)
\]

**Fixed \(z_{1,1}\):**

\[
z_{1,1} - \frac{f_{1,0} \cdot z_{1,0}}{f_2} = 0 \quad (3.13e)
\]

**Flow rate:**

\[
f_2 - (1 + f_2 \cdot M(1) + f_{1,0}) = 0 \quad (3.13f)
\]

where:

\[
Da = k_i(T_i) \cdot \frac{V}{F_0/c_{M,0}} \quad \beta = \frac{k_i c_{M,0}}{k_i(T_i)}
\]

Diagram A of Figure 3.7 presents the dependence of reaction conversion versus plant Damköhler number, for different values of \(\beta\), \(z_{1,0} = 1\), and \(z_{1,1} = 0.5\). All curves exhibit a turning (fold) point, represented by the dotted line. When the QSSA for the intermediate component R is valid (large \(\beta\)), the conversion at the turning point has very small values. Moreover, similar to CSTR – separator – recycle systems,

\[
\lim_{\beta \to \infty} Da_{\infty} = \frac{1}{z_{1,1}} \quad (3.14)
\]

Comparing Figure 3.7 with Figures 3.2, 3.4A and 3.5A, we see a dramatic effect due to the introduction of the second reactant \(I\), in the reaction mechanism. For finite \(\beta (\beta < \infty)\), the transcritical bifurcation has vanished, and state multiplicity turns out to be a generic feature.
Figure 3.7. Consecutive reactions with chemical initiation (S4).

A. Isothermal: all the curves exhibit a fold point, presented by the dotted lines for different values of $\beta$. For large $\beta$, the conversion on the lower branch has small values.

B. Non-isothermal: heat effects shift the fold point to higher conversion.
When thermal effects are considered the unstable branch extends to high conversions, as shown in diagram B of Figure 3.7. The pattern of the curves is similar to the one observed for previous systems.

We conclude that state multiplicity occurs generically in isothermal reactor – separator – recycle system where consecutive reactions involving two reactants take place. Nevertheless, when the QSSA of the intermediate component is valid, the conversion on the unstable branch is very low.

**Polymerization recycle systems**

In this section we consider radical polymerization systems (Table 3.1, S5 and S6). Only the main steps of radical polymerization are included: initiation, propagation and 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 (QSSA). This is usually valid for polymerization systems. Furthermore, the results do not change by removing this assumption. One manifestation of chain reactions is that the total concentration of the active intermediates is very small. A typical value for radical polymerization is \( 10^{-8} \) mol/l. The quasi steady-state approximation considers that initiation and termination rate of the intermediates are virtually equal. The QSSA is remarkable accurate under most conditions. Most kinetic analysis of chain reactions rely on the QSSA for computation of intermediate concentrations. For a detailed explanation about the QSSA validity the reader is referred to the book of Biesenberger (1993).

In the case of polymerization systems, the dimensionless parameter \( \alpha \) represents the activation energy of the dissociation step. \( B \) is heat of reaction for the propagation step. The model parameters \( Du \) 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.
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Chain-growth polymerization, with self-initiation (S5)

In case of self-initiated chain-growth polymerization the monomer is also acting as an initiator. The kinetic model is given in Table 3.1 (S5). The dimensionless equations are given by:

\[ \frac{dM}{d\xi} = -\frac{Da}{f_2} \left( 2 \frac{\gamma}{\beta} M \cdot \exp\left( \frac{\alpha \theta}{1+\theta} \right) + \beta \cdot M \cdot R \right) \]  
(3.15a)

\[ \frac{dR}{d\xi} = \frac{Da}{f_2} \left( \frac{\gamma}{\beta} M \cdot \exp\left( \frac{\alpha \theta}{1+\theta} \right) - \gamma \cdot \beta \cdot R^2 \right) \]  
(3.15b)

Heat balance:

\[ \frac{d\theta}{d\xi} = \frac{Da}{f_2} \left( B \cdot \beta \cdot M \cdot R - H \cdot (\theta - \theta_c) \right) \]  
(3.15c)

\[ M(0) = 1; \quad R(0) = 0; \quad \theta(0) = 0; \]  
(3.15d)

Flow rate:

\[ f_2 - (1 + f_2 \cdot M(1)) = 0 \]  
(3.15e)

where:

\[ Da = k_p \left( \frac{k_d c_{M_0}}{2k_i} \right)^{V/F_0} \]  
\[ \beta = \frac{2k_i c_{M_0}}{k_d} \]  
\[ \gamma = \frac{2k_i}{k_p} \]  
\[ R(\xi) = \frac{\sum c_R(\xi)}{c_{M_0}} \]

Diagram A of Figure 3.8 shows the monomer conversion \((X)\) versus the plant Damköhler number, for \(\beta = 10^6\) and different termination/propagation ratios, \(\gamma\). Feasible steady states do not exist for low values of \(Da\). Two feasible steady states appear at a fold bifurcation point:

- for large values of \(\gamma\) (fast termination, for example \(\gamma > 10^3\)), the corresponding conversion has extremely small values. In this case, the low-conversion unstable branch has no practical implication.

- 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.

The thermal effects have the expected effect of shifting the fold point to higher values of conversion (Figure 3.8, diagram B).
Figure 3.8. Chain-growth polymerization systems with self-initiation (S5).

A. Isothermal: two feasible steady states appear at a fold bifurcation point. For large \( \gamma \) values (fast termination), the fold point corresponds to low conversion.

B. Non-isothermal: heat effect shifts the fold point to higher conversion
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Chain-growth polymerization, with chemical initiation (S6)

For this system the kinetic model is presented in Table 3.1. The dimensionless model (Eqs. 3.16) assumes small initiator concentration at reactor inlet, \( z_{i,1} \). Therefore, the initiator feed flow rate \( f_{i,0} \) can be neglected.

\[
\frac{dl_2}{d\xi} = -\frac{Da \cdot \gamma \cdot l_2 \cdot \exp\left(\frac{\alpha \theta}{1+\theta}\right)}{f_2} \quad (3.16a)
\]

\[
\frac{dM}{d\xi} = -\frac{Da \cdot \left(\beta \cdot M \cdot R + \frac{\gamma}{\beta} \cdot l_2 \cdot \exp\left(\frac{\alpha \theta}{1+\theta}\right)\right)}{f_2} \quad (3.16b)
\]

\[
\frac{dR}{d\xi} = \frac{Da \cdot l_2 \cdot \exp\left(\frac{\alpha \theta}{1+\theta}\right) - \gamma \cdot \beta \cdot R^2}{f_2} \quad (3.16c)
\]

\[
\frac{d\theta}{d\xi} = \frac{Da \cdot \left(B \cdot \beta \cdot M \cdot R - H \cdot (\theta - \theta_c)\right)}{f_2} \quad (3.16d)
\]

\[
M(0) = 1 - z_{i,1}/z_{i,0}; \quad l(0) = z_{i,1}; \quad r(0) = 0; \quad \theta(0) = 0 \quad (3.16e)
\]

Flow rate:

\[
f_2 - (1 + f_2 \cdot M(1)) = 0 \quad (3.16f)
\]

where:

\[
Da = k_r \sqrt{\frac{k_d (T_i) c_{M,0}}{k_i \cdot \frac{V}{F_0/c_{M,0}}}; \quad \beta = \sqrt{\frac{k_i \cdot c_{M,0}}{k_d}; \quad \gamma = \frac{2k_i}{k_p}}
\]

The diagram \( A \) of Figure 3.9 shows the solution of Eqs. 3.16, for different termination/propagation ratios, dimensionless termination/propagation ratios and \( z_{i,1} = 10^{-4} \), \( \beta = 10^3 \). Each bifurcation diagram exhibits one fold (turning) point. Thus, no steady states exist for \( Da < Da_k \) and two steady states exist for \( Da > Da_r \). 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 a very small value. Hence, only the upper state, existing for \( Da > Da_r \), has practical significance. However, when the termination/propagation ratio is further increased, the conversion becomes limited by the amount of initiator fed in the process. As in CSTR – separator – recycle systems,

\[
\lim_{\gamma \to \infty} Da_f = \frac{1}{\sqrt{z_{i,1}}} \quad (3.17)
\]

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Figure 3.9. Chain growth polymerization systems with chemical initiation (S6).

A. Isothermal: two feasible steady states appear at a fold bifurcation point. For slow termination (small $\gamma$), the unstable branch extends to high conversion.

B. Non-isothermal: heat effect shifts the fold point to higher conversion.
Diagram B of Figure 3.9 presents the results for the case when the thermal effects are considered. As predicted by the behaviour of previous non-isothermal systems, higher reaction heat $B$ shifts the fold point to higher conversions.

**Case study – low density polyethylene (LDPE) process**

In this section, we use the high-pressure low-density polyethylene process as a case study, in order to show that state multiplicity and instability can occur in realistic PFR – separator – recycle systems. In addition, we also check the validity of several assumptions that were employed throughout the previous sections.

![LDPE process flowsheet](image.png)

**Figure 3.10. LDPE process flowsheet.**

The process and most important specifications are presented in Figure 3.10. Fresh ethylene is fed at 100°C and 2025 bar to the mixing section, where the recycle is added. The mixed stream is heated in a pre-heater where the temperature increases to 170°C. The heated stream is passed then through the reactor. This has a diameter of 0.05 m and a total length of 2000 m. In view of the large value of the reactor length, resulting in a small value of the Peclet number, the PFR model is realistic. The initiator (benzoyl peroxide) is fed at four
different locations, at a concentration of \( 0.18 \text{ mol/m}^3 \). The reaction mixture leaves the reactor and goes to the high-pressure separation flash operated at 250 bar. Here, about 95% of the monomer is separated and sent to the recycle mixer. The second flash operates at a lower pressure (2 bar) and makes the final separation. The rest of the monomer is sent to the recycle mixer, while the LDPE is recovered at the bottom, at purity higher than 99%. The high- and low-pressure recycles of monomer are mixed and then compressed at the same pressure as the fresh ethylene stream. The compressed recycle stream is mixed with the fresh ethylene and fed again to the reactor.

The (simplified) model is very similar to Eqs. 3.16, adding the reactions of chain transfer to monomer and solvent, initiator feed at four points along the reactor, and temperature dependence for all reaction constants. This is compared with a rigorous Aspen Polymers Plus™ (AspenTech, 2001) simulation that accounts for variable physical properties, imperfect separation, and heat effects for all reaction steps. The kinetic parameters are chosen from Mavridis et al. (1985). The physical properties were calculated using the Sanchez-Lacombe model, with the parameter values available in Aspen Polymer Plus™. Similar results were obtained using the SAFT model with regressed parameter data (Orbey et al., 1998).

Vadapalli and Seader (2001) described the framework for tracing arbitrary bifurcation diagrams using commercial simulators. In our study we used a simpler, although less general approach: the user specifies the reaction conversion, and the simulator calculates the corresponding feed flow rate. This procedure can be easily implemented by means of a design specification block.

The dimensionless parameters indicate large termination / propagation ratio \( (\gamma = 9.35 \times 10^4) \), but also high heat of reaction \( (B = 3.595) \) and near adiabatic operation \( (H = 5.87 \times 10^{-3}) \). Therefore, a fold point is expected, with a significant value of the corresponding conversion. Unexpectedly, the bifurcation diagram (Figure 3.11A) looks as the superposition of four (the number of initiator feeds) bifurcation diagrams similar to the ones presented in Figure 3.9, and shows seven fold points. A rather large range of conversion \((0...0.07, 0.09...0.11, \text{ and } 0.15 - 0.20) \) correspond to an unstable operating point. High sensitivity of the conversion to changes of plant Damköhler number, around \( Da = 80 \), should be also remarked.
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Figure 3.11. LDPE process: $Da - X$ bifurcation diagram.

A. Several fold points exist in the practical range of conversion. The simplified model agrees with the rigorous simulation (Aspen Polymer Plus™).

B. Molecular Weight Distribution for four different operating points.
The agreement between the simplified and the rigorous models is good, except the region of very low conversions. As $X \to 0$, the solution of the simplified model goes to $Da = \infty$, while the solution of the rigorous model turns back towards $Da = 0$. This difference has no practical implication because of the extremely low value of the conversion. It can be explained by the difference in modeling the separation unit. In the simplified model, separation is perfect and no monomer is allowed to leave the plant. In practice, perfect separation is not possible because some monomer is dissolved in the polymer product. This amount is significant for very low conversion, when the separation unit has to recover a small amount of polymer from a huge amount of monomer. The rigorous model correctly predicts this behavior.

Figure 3.11B shows different molecular weight distributions for several feed flow rates of monomer, corresponding to operating points 1 to 4 in diagram A. Transitions 1 $\to$ 2 and 3 $\to$ 4 are expected when the production rate is changed (i.e. $Da$). It can be observed that the quality of the polymer is greatly affected. In the first case (1 $\to$ 2), a small increase of the feed flow rate reduces the conversion from 0.2 to 0.125, and the polydispersity index (PDI) from 5.21 to 4.23. In the second case (3 $\to$ 4), for small decrease of the feed flow rate, the conversion and polydispersity index increase from 0.17 to 0.215, and from 4.94 to 5.27, respectively. In practice, these changes might be unacceptable. Therefore, the design of recycle system should take into account the state multiplicity and instability.

Conclusions

Six reactions with different stoichiometry taking place in PFR – separator - recycle systems were investigated. For a fixed feed flow rate and a given kinetics, feasible steady states are possible only if the reactor volume exceeds a critical value. For simple stoichiometry (S1, S2) and isothermal operation, the critical point represents a transcritical bifurcation. When heat-effects are included or for consecutive, stoichiometry involving one reactant (S3, S5), one fold point may enter the feasible range of positive conversion leading to state multiplicity. If two reactants are involved in consecutive-autocatalytic reactions (S4, S6), state multiplicity is a generic feature.

This behaviour is identical to the one previously found in similar isothermal systems involving a CSTR. The agreement refers not only to qualitative features, but also to the parameter values at which different bifurcation phenomena occur. This suggests that the
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behaviour is determined by reaction stoichiometry, recycle policy and control structure, and not by the reactor type.

The multiplicity of states is important because it is accompanied by the instability of the low-conversion branch that sets a lower limit on the achievable conversion. For isothermal reactor – separator – recycle polymerization systems, this behaviour has practical importance (i.e. the conversion on the unstable branch is significant) when the radicals’ quasi steady state approximation is not valid (slow termination, gel-effect). For non-isothermal systems the large heat effect of polymerization reactions renders multiplicity to be very probable. When designing PFR-separator-recycle systems one must be aware of the non-linear behaviour and its implications on plant operability.

Notation

\( A \) = heat transfer area, \( m^2 \)
\( c \) = concentration, \( mol/m^3 \)
\( c_p \) = specific heat, \( J/(kgK) \)
\( F \) = flow rate, mole/s
\( \Delta H \) = heat of reaction, \( J/(molK) \)
\( k \) = reaction rate constant, \( (mol/m^3)s^{-1}, s^{-1} \)
\( T \) = temperature, K
\( T_A \) = Arrhenius temperature, K
\( U \) = heat transfer coefficient, \( W/(m^2K) \)
\( V \) = reactor volume, \( m^3 \)
\( X \) = conversion, dimensionless

References

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