Design of tubular reactors in recycle systems

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Abstract

The article presents an approach to design tubular reactors in recycle systems, based on non-linear analysis. A pseudo-homogeneous plug-flow reactor model is used. It is assumed that the separation unit delivers product and recycle streams with fixed composition. The stand-alone reactor has a unique stable steady state. The coupled reactor–separation–recycle system shows four types of conversion versus plant Damköhler number bifurcation diagrams. A feasible steady state exists only if the reactor volume exceeds a critical value. For isothermal reactor, the steady state is unique and stable. For non-isothermal reactor, one or two steady states are possible. In the second situation the low-conversion state is unstable. In some parameter regions, the unique state is unstable. The design should ensure state unicity and stability, which are favoured by large heat-transfer capacity, low coolant temperature and high reactor-inlet temperature. A case study demonstrates that these phenomena can be easily found in real plants.

Keywords: Reaction engineering; Recycle systems; Design; Non-linear dynamics

1. Introduction

Reaction systems involving material recycle are common to industrial practice. In a typical flowsheet (Fig. 1), the reactor effluent is first processed by a separation section, and afterwards recycled. The temperature at the reactor inlet is constant, due to a heat exchanger placed upstream the reactor. The separation unit operates in closed-loop, that is, local concentration controllers ensure that the product (4) and recycle (3) streams have fixed composition. This flowsheet differs from the system “tubular reactor with recycle” analysed by some researchers (Reilly & Schmitz, 1966, 1967), which does not consider a separation unit. In this study, we make use of the conventional plantwide control structure, which sets the fresh reactant on flow control. This structure has the advantage of directly setting the production rate. However, the system might exhibit high sensitivity to production rate changes (snowball effect, Luyben, 1994), particularly at low conversions (Bildea, Dimian & Iedema, 2000). In this article, we demonstrate that the operating point can also be unstable. This dangerous situation should be avoided by design.

A typical design starts with the specification of reactor and separation performances, as conversion, selectivity, concentration of product and recycle streams. Then, the mass balance is performed. Finally, the detailed unit design is completed. In a more advanced approach, an optimisation procedure based on economic criteria can be applied, to account for the complex tradeoffs between the cost of reactor, separation units and recycling (Luyben, 2001a). However, economic optimality does not guarantee operability. Reyes and Luyben (2001a,b) give examples of optimum steady-state designs that cannot be controlled, or have poor dynamic responses.

In a series of plantwide control studies, Luyben and Luyben (1997), reported difficult control of reactor–separation–recycle systems due to the “snowball effect”. By analysing the relation between design and control of several systems involving isothermal reactors, Bildea et al. (2000) showed that the source of control difficulties is the non-linear behaviour. Investigation of CSTR–separation–recycle systems (Pushpavanam & Kienle, 2001; Kiss, Bildea, Dimian & Iedema, 2002; Sagale & Pushpavanam, 2002) confirmed this analysis. Besides high sensitivity, other non-linearities detrimental for
control could easily occur, for example multiplicity, isolas, instability, or limit cycles.

In the present article, we propose an approach to design tubular reactors in recycle systems based on non-linear analysis. In this first attempt we consider a pseudo-homogeneous plug-flow reactor model. In contrast with the stand-alone reactor, which has a unique stable steady state, the coupled reactor–separation–recycle system exhibits non-linear phenomena, including unfeasibility, multiplicity and instability. These phenomena should be avoided by design, since they are detrimental for operation. In addition, our analysis can explain theoretically the findings of previous case studies based mainly on simulation (Reyes & Luyben, 2001a,b; Luyben, 2001b).

At this point it is worthy to examine the level of detail in modelling the chemical reactor. Among various phenomena, axial dispersion of heat, as well as diffusion and conduction inside the catalyst particle are sources of internal positive feedback. Coupled with the non-linearity of the reaction rate, the positive feedback can lead to state multiplicity even in stand-alone reactors (Jensen & Ray, 1982; Weisz & Hicks, 1962). In addition, axial dispersion can lead to very complex dynamic behaviour. For example, a fixed-bed reactor with axial dispersion and reactant recycle (Recke & Jørgensen, 1999) showed multiple and high-order periodic solutions.

In order to focus on non-linear phenomena that can be attributed exclusively to the recycle of mass, we use in this study the simple pseudo-homogeneous plug-flow model. This approach has been successfully applied for kinetic studies, design and simulation of many industrial reactors.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$A$</td>
<td>heat-transfer area (m$^2$)</td>
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<td>$B$</td>
<td>adiabatic temperature rise, dimensionless, $(-\Delta H)c_0$ $/ \rho c_p T_{ref}$</td>
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<tr>
<td>$c$</td>
<td>concentration at $T_{ref}$ and $P_{ref}$ (mol/m$^3$)</td>
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<tr>
<td>$c_p$</td>
<td>specific heat J/(kg K)</td>
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<tr>
<td>$Da$</td>
<td>Damköhler number, dimensionless, $k(T_{ref}) V c_0^{n-1}$</td>
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<tr>
<td>$E_A$</td>
<td>activation energy (J/mol)</td>
</tr>
<tr>
<td>$f_k$</td>
<td>flow rate, dimensionless, $F_k/F_0$</td>
</tr>
<tr>
<td>$F$</td>
<td>flow rate at $T_{ref}$ and $P_{ref}$ (m$^3$/s)</td>
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<tr>
<td>$\Delta H$</td>
<td>reaction heat (J/mol)</td>
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<tr>
<td>$k$</td>
<td>pre-exponential factor (mol/m$^3$)$^{1-n}$/s</td>
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<tr>
<td>$n$</td>
<td>reaction order, dimensionless</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure (N/m$^2$)</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant (J/(mol K))</td>
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<tr>
<td>$T$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$U$</td>
<td>heat transfer coefficient (W/(m$^2$ K))</td>
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<tr>
<td>$V$</td>
<td>reactor volume (m$^3$)</td>
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<tr>
<td>$X$</td>
<td>reactor outlet conversion, dimensionless, $1 - z_2/z_1$</td>
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<tr>
<td>$z$</td>
<td>concentration, dimensionless, $c/c_0$</td>
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<table>
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<tr>
<th>Greek symbols</th>
<th>Definition</th>
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<tr>
<td>$\beta$</td>
<td>heat-transfer capacity, dimensionless, $UA$ $/ \rho c_p k(T_{ref}) c_0^{n-1}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>activation energy, dimensionless, $E_A/(RT_{ref})$</td>
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<tr>
<td>$\rho$</td>
<td>density at $T_{ref}$ and $P_{ref}$ (kg/m$^3$)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>temperature, dimensionless, $TT_{ref}$ $/ T_{ref}$</td>
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<tr>
<td>$\xi$</td>
<td>axial coordinate, dimensionless</td>
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<table>
<thead>
<tr>
<th>Subscripts</th>
<th>Definition</th>
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<tr>
<td>$0$</td>
<td>system inlet</td>
</tr>
<tr>
<td>$1$</td>
<td>reactor inlet</td>
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<tr>
<td>$2$</td>
<td>reactor outlet, separation inlet</td>
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<tr>
<td>$3$</td>
<td>recycle</td>
</tr>
<tr>
<td>$4$</td>
<td>product</td>
</tr>
<tr>
<td>$\text{ref}$</td>
<td>reference</td>
</tr>
<tr>
<td>$c$</td>
<td>coolant</td>
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A detailed dynamic model should take into account the dynamics of the reactor and separation unit, the tuning of level, temperature and composition controllers, the bounds on the manipulated variables, the delay introduced by the recycle piping, the digital implementation of control loops and, so on. Such detailed modelling introduces a large number of parameters, which makes generalisation of the results a difficult task. Therefore, our study focuses mainly on the steady state behaviour.

The article is organised as follows. First, the dimensionless model is presented and discussed. Then, the isothermal PFR—separation—recycle system is examined. It is shown that operation of an isothermal reactor in a reactor—separation—recycle system is possible only if the reactor volume exceeds a critical value. The next section considers non-isothermal reactor operation, with fixed inlet temperature. In this case, steady multiplicity and instability are possible. Moreover, in some parameter regions, the unique state is unstable. Steady state classification, achieved by computing relevant singularities, shows four different types of possible behaviour. Design implications are discussed. Finally, the toluene hydro-dealkylation (HDA) case study demonstrates that these phenomena can be easily found in real plants.

### 2. Model equations

The dimensionless model assumes plug flow, constant physical properties and one-reactant, $n$th order reaction. It contains the PFR model Eqs. (1)–(3), the input—output mass balance Eq. (4) and the mass balance at the mixing point Eq. (5):

$$ \frac{dx}{d\xi} = \frac{Da}{1 + f_3} \cdot z_1^{n-1} \cdot (1 - x)^n \cdot \exp \left( \frac{\gamma \theta}{1 + \theta} \right) $$  \hspace{1cm} (1)

The dimensionless variables and parameters are: axial coordinate $0 \leq \xi \leq 1$, conversion $x(\xi)$, temperature $\theta(\xi)$, recycle flow rate $f_3$ and reactor-inlet concentration $z_1$; plant Damköhler number $Da$, activation energy $\gamma$, adiabatic temperature rise $B$, heat-transfer capacity $\beta$, coolant temperature $\theta_c$, concentration of recycle and product streams $z_3$, $z_4$. For convenience, $X \equiv x(1)$ will stand for conversion at reactor outlet.

The dimensionless variables and parameters are defined in Notation. Here we make the following remarks concerning the dimensionless model:

- The reactor-inlet temperature is used as a reference value, $T_{ref} = T_1$. In many practical situations, $T_1$ is kept constant by a heat exchanger placed upstream the reactor, as in Fig. 1.
- The flow rate and composition of the reactor-inlet stream depend on the flow rate and composition of the recycle stream. For this reason, the dimensionless quantities are defined with reference to plant inlet values. The plant Damköhler number defined this way (Eq. (6)) is different from the classical one, which uses values at reactor inlet.

$$ Da = k(T_{ref}) \frac{V}{F_0} z_1^{n-1} $$ \hspace{1cm} (6)

- In this study, the bifurcation parameter is the plant Damköhler number. The overall mass balance requires the equality of the feed and product flow rates, $F_0 = F_a$. Consequently, Damköhler number accounts for production rate changes ($F_0$), reactor design ($V$) and design parameter uncertainty ($k(T_{ref})$).
- Each of the following variables appears in only one dimensionless variable: feed flow rate, heat transfer capacity, coolant temperature, recycle concentration, reaction activation energy, and heat of reaction. Thus, the effect of their change can be easily investigated.

The model equations can be solved by a shooting technique: start with an initial guess $X$ for the conversion $x(1)$, calculate the recycle flow rate $f_3$ from Eq. (4) and reactor-inlet concentration $z_1$ from Eq. (5), integrate the PFR Eqs. (1)–(3), check and update the guess $X$. This implies that it is theoretically possible to reduce the
model to one equation with one variable:
\[ g(X, Da, \gamma, B, \beta, \theta_v, z_3, z_4) = X - x(1) \] (7)

Therefore, the results of singularity theory with a single intrinsic variable (Golubitsky & Schaeffer, 1985) can be applied.

3. Isothermal PFR

An isothermal reactor model can be used when the heat of reaction is negligible or a control loop keeps constant reactor temperature manipulating, for example, the coolant flow rate.

The model of the reactor operated isothermally at \( \theta = 0 \) is obtained by setting equal reactor-inlet and coolant temperatures \( (\theta_c = \theta_1 = 0) \) and zero adiabatic temperature rise \( (B = 0) \). Then, integration of Eq. (1), followed by the substitution of \( f_3 \) from Eq. (4) leads to:
\[
\frac{Da \cdot X \cdot z_3}{(1 - z_4) - X \cdot (1 - z_3)} = \ln \frac{1}{1 - X} \quad \text{for } n = 1
\] (8a)
\[
\frac{Da \cdot X \cdot z_3^n(1 - z_4)^{n-1}}{(1 - z_4) - X \cdot (1 - z_3)^n} = \frac{1}{n - 1} \cdot \left( \frac{1}{1 - X} \right)^{n-1} \quad \text{for } n \neq 1
\] (8b)

Fig. 2 presents the \( X \) versus \( Da \) dependence obtained from Eqs. (8a) and (8b), for \( n = 1 \) and 2. It follows from Eqs. (8a) and (8b) that \( X = 0 \) is a trivial solution, satisfying the balance equation irrespective of the \( Da \) value. However, it is unfeasible, corresponding to infinite flow rates. The non-trivial solution is feasible (positive flow rates) if, and only if:
\[
0 < X < 1 - z_4
\] (9)

or, equivalently
\[
Da_T < Da < Da_{max}
\] (10)

where:
\[
Da_T = \lim_{x \to 0} Da = \frac{1 - z_4}{z_4^n}
\] (11)
\[
Da_{max} = \ln \frac{1}{z_4} \quad \text{for } n = 1
\] (12a)
\[
Da_{max} = \frac{z_4^{1-n} - 1}{n - 1} \quad \text{for } n \neq 1
\] (12b)

The first inequality in Eq. (10) is a feasibility constraint characteristic to recycle systems. The explanation is that the separation section recovers and recycles the reactant, which is not allowed to leave the process. Therefore, for a given reactant feed flow rate \( (F_0) \), a sufficiently large reactor volume \( (V) \) or fast kinetics \( (k(T)) \) are necessary to consume completely the reactant fed in the process, and consequently to avoid reactant accumulation. The Damköhler number includes conveniently these three variables (flow-rate, reactor volume and kinetics).

A separation unit is meaningful only if the desired concentration of reactant in the product stream, \( z_4 \), is smaller than the concentration at the reactor outlet. This leads to the second inequality in Eqs. (9) and (10).

At the critical value \( Da_T \), two different manifolds of steady states cross each other, in the combined space of state variables and parameters. According to the bifurcation theory, this is a transcritical bifurcation point. Here, an exchange of stability takes place: for \( Da < Da_T \), the trivial solution \( X = 0 \) is stable; this state loses stability at \( Da = Da_T \); simultaneously, the non-trivial solution gets physically meaningful values and gains stability.

We note that the value \( Da_T \) at which the transcritical bifurcation occurs is identical with the one found for recycle systems involving a CSTR (Bildea et al., 2000). To explain this, we observe that \( \lim_{x \to 0} f_3 = \infty \). Thus, when the conversion is very close to zero, the flow rate through the reactor is infinitely large. Along the PFR, only a finite amount of reactant is consumed. For non-isothermal operation, a finite amount of heat is transferred to the coolant. Therefore, the concentration and temperature are constant, and the reactor behaves as a lumped system. For this reason, identical phenomena
occur at \( X = 0 \) for recycle systems involving either a PFR or a CSTR.

4. Non-isothermal PFR

In this section, we consider a non-isothermal reactor and restrict the analysis to first-order reactions. We aim to divide the space of the parameters concerning reactor design, \((\beta, 0_b)\), into regions with different qualitative properties. We fix the activation energy \( \gamma \), adiabatic temperature rise \( B \), and recycle and product purities \( z_3, z_4 \).

Fig. 3 presents the \( X \) versus \( Da \) dependence, obtained for different values of the heat transfer capacity \( \beta \), and fixed values of the remaining model parameters. The entire diagram (including the unfeasible domain) contains one turning point representing a fold bifurcation. For large \( \beta \), the turning point is located in the unfeasible region \( X < 0 \) (not shown in Fig. 3). As \( \beta \) decreases, the turning point moves to larger conversion and finally enters the feasible region, leading to state multiplicity.

When two steady states exist, the low-conversion one is unstable. This can be demonstrated showing that a slope condition is not fulfilled. The amount of reactant consumed by the reactor is given by \( F_1 c_1 X \), where \( F_1 \) and \( c_1 \) are dimensionless variables. Its dependence on the reactor-inlet flow rate \( F_1 \) is presented in Fig. 4 using the dimensionless variables \( F_1 (kV) = 1/Da_1 \) and \( F_1 c_1 X / (\gamma c_0 kV) = z_1 X / Da_1 \), where \( Da_1 \) is defined using the reactor-inlet flow rate as reference. In a reactor–separation–recycle system, the steady state values of the reactor-inlet flow rate \( F_1 \) are the intersections of this curve with the horizontal line representing the net amount of reactant fed in the process. This is given, in a dimensionless form, by \( F_0 c_0 (1 - z_2) / (\gamma c_0 kV) = (1 - z_4) / Da_1 \). Let us consider a small, positive deviation of the reactor-inlet flow rate, from the steady state \( B \). 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; hence the steady state \( B \) is unstable. This is independent of the units’ dynamics, because the proof is based only on steady state considerations.

Fig. 4. Instability of the low-conversion steady state. A necessary, but not sufficient stability condition can be derived based on steady state arguments.

Reactant accumulation occurs, leading to a further increase of the recycle and reactor-inlet flow rates; hence the steady state \( B \) is unstable. This is independent of the units’ dynamics, because the proof is based only on steady state considerations.

Tubular reactors can exhibit “wrong-way” behaviour, for example, an initial decrease of outlet temperature for an increase of feed concentration. This phenomenon, occurring due to concentration and temperature waves travelling along the reactor at different speeds, is predicted by the plug-flow pseudo-homogeneous model (Mehta, Sams & Luss, 1981). Because of the feedback from the reactor-outlet to the reactor-inlet through recycle, sustained oscillations might occur. Therefore, the steady-state arguments cannot guarantee the stability of the high-conversion branch. The high-conversion branch is stable if an additional dynamic stability condition is fulfilled, which is equivalent to non-existence of Hopf bifurcations. While dynamic reactor modelling is straightforward, it was beyond the scope of this work to develop a reasonably simple, but accurate dynamic model for the separation section. For an instantaneous separation model and a large range of parameters, our computations indicated that the upper steady state is stable:

- Time-dependent solutions converged to the upper steady state.
- Numerical computation revealed negative eigenvalues of the linearised model.
- Direct methods for computation of Hopf bifurcation points failed to find a solution.

However, for other dynamic models, we cannot exclude the possibility of oscillatory behaviour on the high-conversion branch. For an axial-dispersion fixed-bed reactor with reactant recycle, Recke and Jørgensen (1999) showed that periodic solutions are possible.

Stability is a requirement that must be fulfilled by any design. For a given conversion \( X \), often imposed by
selectivity or safety considerations, we aim to find the range of coolant temperatures \( \theta_c \) and heat transfer capacities \( \beta \) resulting in a stable operating point. These points are located on the stable branch of the \( X \) versus \( Da \) bifurcation diagram (Fig. 3), above the turning (fold) point. Therefore, we fix \( X \) and, at different values \( \theta_c \), solve the defining conditions of the fold singularity for the two unknowns \( (Da, \beta) \):

\[
g(X, Da, \theta_c, \beta) = X - x(1) = 0 \tag{13}
\]

\[
dg(X, Da, \theta_c, \beta) \frac{dX}{dX} = 0 \tag{14}
\]

This way, we map the locus of fold points (singular set) into the \( \theta_c - \beta \) space, at a desired operating point (for example, \( X = 0.5 \) in Fig. 5).

To compute the fold bifurcation point, we define the sensitivity functions

\[
\frac{\partial x(\tilde{\xi})}{\partial f_3} = S_x(\tilde{\xi}), \quad \frac{\partial \theta(\tilde{\xi})}{\partial f_3} = S_\theta(\tilde{\xi}) \tag{15}
\]

Applying the chain rule of differentiation in Eq. (14) leads to:

\[
\frac{dg}{dX} = 1 - \frac{dx(1)}{dX} = 1 - \frac{\partial x(1)}{\partial f_3} \frac{dX}{dX} = 1 + S_x(1) \frac{1 - z_4}{z_3} \frac{1}{X^2} \tag{16}
\]

\( S_x(1) \) results from integration of:

\[
\frac{dS_x}{d\tilde{\xi}} = \frac{\partial h_1}{\partial \theta} S_x + \frac{\partial h_1}{\partial \theta} S_\theta + \frac{\partial h_1}{\partial f_3} \tag{17}
\]

\[
\frac{dS_\theta}{d\tilde{\xi}} = \frac{\partial h_2}{\partial \theta} S_x + \frac{\partial h_2}{\partial \theta} S_\theta + \frac{\partial h_2}{\partial f_3} \tag{18}
\]

\[ S_x(0) = 0; \quad S_\theta(0) = 0 \tag{19} \]

where \( h_1 \) and \( h_2 \) are the right-hand sides of Eqs. (1) and (2), respectively.

Therefore, the fold point is the solution of Eqs. (13) and (16), where \( x(1) \) and \( S_x(1) \) result from simultaneous integration of Eqs. (1)–(5) and Eqs. (17)–(19).

In addition to the singular set, other varieties divide the \( (\beta, \theta_c) \) space:

- The boundary-limit set: a limit point exists at a feasibility boundary. There are two such sets \( (BL_1, BL_2) \), corresponding to limit points at the feasibility limits \( X = 0 \) and \( X = 1 - z_4 \), respectively. The \( BL_1 \) variety bounds the region of design space where a unique, stable state exists. This region is optimal from a flexibility and robustness viewpoint. A closed-form expression for the \( BL_1 \) variety can be derived, based on the observation that the behaviours of reactor–separation–recycle systems involving CSTR or PFR are identical near \( X = 0 \). Therefore, we can replace Eqs. (1)–(3) by their CSTR equivalents to show that the fold point is feasible whenever:

\[
(\beta \cdot \theta_c) > \frac{1}{\gamma} \left( \frac{z_3 - z_4}{1 - z_4 - B \cdot \gamma \cdot z_3} \right) \tag{20}
\]

Pushpavanam and Kienle (2001) derived a similar relationship for equal reactor-inlet and coolant temperatures, \( \theta_c = 0 \). In this case, state multiplicity was restricted to exothermic reactions. The more general Eq. (20) shows that multiplicity can also occur in heated reactors carrying on endothermic reactions.

- The double-cross set \( (DC) \): the relative position of two solutions located at the feasibility boundary changes. There is one double-cross set, corresponding to solutions \( X = 0 \) and \( X = 1 - z_4 \) occurring for the same value of the bifurcation parameter \( Da \).

Fig. 5 presents the classification of the steady state behaviour, for fixed values of \( \gamma, B, z_3 \) and \( z_4 \). The bifurcation diagrams existing in different regions of Fig. 5 are presented in Fig. 6. In region I, one feasible steady state exists, if \( Da \) exceeds the critical value \( Da_T \) given by Eq. (11). Crossing the boundary-limit set \( BL_1 \) to region II, one fold point enters the feasibility region through the boundary \( X = 0 \), leading to state multiplicity. Let us label the upper and lower solution branches as U and L, respectively. Then, the multiplicity pattern in region II is \( 0 \rightarrow 2 \rightarrow 1(U) \rightarrow 0 \). Crossing the double-cross set DC to region III, the relative position of the two solutions located at the feasibility boundaries changes. The multiplicity pattern becomes \( 0 \rightarrow 2 \rightarrow 1(L) \rightarrow 0 \). Finally, when the boundary-limit set \( BL_2 \) is crossed to region IV, the fold point exits the feasible region through the boundary \( X = 1 - z_4 \). Hence, in region IV a unique, unstable state exists. If some conversion is required (for example, \( X = \)}
0.5 in Fig. 5), the singular set $S$ bounds the range of $(\theta_c, \beta)$ values resulting in a stable $(Da, X)$ operating point.

Several conclusions can be drawn from Figs. 3, 5 and 6. An operating point located on the unstable branch is more likely when low conversion is required. Instability can be removed by lower coolant temperature $\theta_c$, and larger heat-transfer capacity $\beta$. Region I of Fig. 5 should be preferred, because of state unicity and stability. This region might be unachievable, for example, due to restricted heat-transfer area or heat-transfer coefficient. In this case, increasing the reactor-inlet temperature $T_1$ is an option. This decreases the dimensionless parameters $g$ and $B$, shifting the bifurcation varieties of Fig. 5 in a favourable direction. These results explain the conclusions of previous case studies. For example, Reyes and Luyben (2001a,b) showed that high reactor-inlet temperature was beneficial from a dynamic point of view. Luyben (2001b) concluded that controllability worsens as specific reaction rates, activation energies, and tube diameters increased. Designs with large reactor heat-transfer areas were easily controlled. Tube diameter had a great impact on controllability, while reactant dilution appeared to be less effective.

An optimisation procedure might suggest a small reactor, corresponding to an operating point close to the fold bifurcation. Such system will suffer from serious operability problems. If the reaction kinetics is overestimated, or the feed flow rate deviates from the nominal design value, the operating point falls at the left of the turning point of the $Da - X$ map, in the region where no feasible steady state exists. In this case, reactant accumulation occurs, and the plant has to be shut down.

5. Case study

The HDA plant (Douglas, 1988) case study will demonstrate that state multiplicity and instability can easily occur in recycle systems involving tubular reactors. Benzene is produced by toluene hydrodealkylation, a mildly exothermic reaction with moderate activation energy:

$$\text{C}_6\text{H}_5\text{-CH}_3 + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{CH}_4$$

$$\Delta H_{950K} = -50,450 \text{ J/mol}; \quad E_a = 217,600 \text{ J/mol}$$

The reaction takes place in an adiabatic tubular reactor. After cooling, the flash separation of the reactor effluent leads to two recycles. A purge is necessary to avoid methane accumulation. The flowsheet and the conventional control structure are presented in Fig. 7. By neglecting the secondary reactions and assuming perfect separation, the following equations can be derived:

$$\mathcal{F}_b = \mathcal{F}_1$$ \hspace{1cm} (21)

$$\mathcal{F}_p = \mathcal{F}_2$$ \hspace{1cm} (22)

$$\frac{y_{\text{H}_2}}{y_{\text{H}_3}} = \frac{\mathcal{F}_1}{\mathcal{F}_2}$$ \hspace{1cm} (23)

$$\frac{y_{\text{H}_3}}{y_{\text{T}_3}} = \frac{X}{\mathcal{F}_1} \cdot (\mathcal{F}_R \cdot y_{\text{H}_2} + \mathcal{F}_2 \cdot y_{\text{H}_2})$$ \hspace{1cm} (24)

$$\mathcal{F}_T = \mathcal{F}_1 \cdot \frac{1 - X}{X}$$ \hspace{1cm} (25)

$\mathcal{F}_j$ and $y_{k,j}$ denote the mole flow rate of stream $j$ and the molar fraction of the $k$ component (H, hydrogen; T, toluene) in stream $j$, respectively; $X$ is the reaction conversion.
In addition, the conversion $X$ depends upon the reactor volume:

$$X = X(V)$$  \hspace{1cm} (26)

Equations 21 to 26 involve 11 variables. We assume constant purity of the fresh hydrogen, $y_{H_2} = 0.95$. The control structure fixes the fresh toluene flow rate $F_1 = 120 \text{ kmol/h}$ and hydrogen/toluene ratio at reactor inlet, $y_{H_2}/y_{T,3} = 5$. Specifying two additional variables, for example reactor volume $V$ and gas recycle flow rate $F_R$, the mass balance equations can be solved for six unknowns: $F_2$, $F_B$, $F_T$, $F_P$, $X$ and $y_{H,P}$. Fig. 8 presents the conversion $X$ versus reactor volume $V$, for different values of the gas recycle flow rate $F_R$. Two operating points were considered for further investigation: Design A, on the stable branch, far from the fold bifurcation; and Design B, on the unstable branch, close to the fold bifurcation. Then, the remaining units were designed and rigorous simulation was performed using AspenPlus. Finally, the simulation was exported to AspenDynamics, where control loops were provided and tuned.

For Design A, no operating problems were encountered. The plant was robust in face of various disturbances (e.g. $\pm 25\%$ production change) or uncertain design parameters.

In contrast, Design B suffers from serious operability problems. Starting from steady state, reaction ignition occurs (Fig. 9a). Reaction extinction takes place when the reactor-inlet temperature deviates by only $-2 \degree C$ from the design value (Fig. 9b). The plant moves towards the trivial ($X=0$) steady state. All flow rates increase and one of the levels becomes uncontrollable.

An alternative control strategy fixes the reactor-inlet toluene flow rate (Luyben, Tyreus & Luyben, 1999). Fresh toluene is fed in the condenser drum of the last distillation column, on level control. Production rate changes can be achieved by changing the setpoint of toluene reactor-inlet flow, or the setpoint of the reactor-inlet temperature controller. When this control structure is used, the whole range of conversion becomes stable.
6. Conclusions

1. The integration of the chemical reactor in a recycle system can lead to non-linear phenomena that are detrimental for operation. This work focuses on the behaviour of tubular reactors, modelled as PFRs. The stand-alone reactor has a unique stable state. However, the interaction between reaction and separation through material recycle can lead to unfeasibility, state multiplicity and instability.

2. In contrast to stand-alone reactors, a minimum volume is necessary for feasible operation in a recycle system. For isothermal reactors, this condition is expressed by Eqs. (10) and (11), where the plant Damköhler number groups variables referring to production rate, kinetics and reactor volume.

3. For non-isothermal operation, multiple steady states are possible. This means that the reactor conversion can have different values, for the same dimensionless design variables as plant Damköhler number $Da$, heat transfer capacity $\beta$, coolant temperature $\theta_c$, separation performance $z_3$ and $z_4$. The low-conversion state is always unstable, which is demonstrated by steady state considerations. The high-conversion state appears to be stable, for the plug flow reactor model and instantaneous separation that we considered in this work.

4. Four different types of conversion versus plant Damköhler bifurcation diagrams are possible: I, single, stable steady state; II, two steady states plus a single stable state; III, two steady states plus a single unstable state; IV, single, unstable steady state. From a design point of view, type I is recommended. Types II and III are acceptable, as long as the operating point is on the stable branch and far away from the fold bifurcation. Type IV should be avoided.

5. A systematic approach to design tubular reactors in recycle systems consists in dividing the design space into regions with different types of behaviour. The recommended design region I is bounded by the boundary limit variety BL1, for which an analytical expression is given by Eq. (20). The optional design regions IIa and IIIa are bounded by the singular set S, for which a numerical algorithm is presented (Eqs. (13)–(19)).

6. HDA case study demonstrates that state multiplicity and instability can be easily found in real plants. When the design is on the stable branch, far from the turning point, the plant is stable and robust in face of large disturbances. On the contrary, the design on the unstable branch close to the fold bifurcation leads to an un-operable plant.

References


