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

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

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

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 4 Stability and Multiplicity Approach to the Design of Heat-Integrated Multibed PFR

Abstract

The non-linear behaviour of the heat-integrated multibed plug flow reactor, consisting of feed-effluent heat exchanger (FEHE), furnace, multibed adiabatic tubular reactor with intermediate cooling, and steam-generator is studied. A first-order, reversible, exothermic reaction is considered. The hysteresis, isola, boundary-limit, double-zero and double-Hopf varieties are calculated. They divide the parameter space into regions with different steady-state and dynamic behaviour. State multiplicity, isolated branches and oscillatory behaviour may occur for realistic values of model parameters. Implications on design are discussed.
Introduction

The multibed, adiabatic, tubular reactor with intermediate cooling is the usual option when the reaction is exothermic, but equilibrium limited. Significant energy saving can be achieved if the reactor effluent is used to preheat the feed. Apparently, there is no need of an additional heat source. However, there are several reasons to add supplementary units:

1. A heater (furnace) is always required for start-up. It may be placed upstream or downstream of the feed-effluent heat exchanger (FEHE). It is favourable to place the FEHE before the furnace, as it will work at lower temperatures. Frequently, a purge stream is available as fuel.

2. The size of the FEHE limits the energy recovery. Consequently, a cooler is required. It is advantageous to place a steam-generator before the FEHE, as it will allow heat recovery at high temperature.

3. In autothermal reactors, multiple steady-states may exist. The classic analysis of van Heerden (1958) shows that the middle steady-state is always unstable. Moreover, stability can be lost due to Hopf bifurcation. In such cases, stable operation is possible only if a control system is in place. If the furnace and steam-generator are included, their duties are available as manipulated variables in temperature control loops.

![Diagram of Heat-integrated Multibed PFR](image)

**Figure 4.1. Heat-integrated multibed PFR**
Chapter 4. Design of Heat-Integrated Multibed PFR

The inclusion of furnace and steam-generator leads to the structure presented in Figure 4.1. This structure, with the reactor playing the role of a heat pump, is called heat-integrated multibed PFR. This site integration solution is more efficient than process-process heat integration, as proposed by Douglas (1988).

Typical initial design data are the condition of the feed stream; reactor type (empty tube or packed bed; and the required conversion. Reaction kinetics and thermodynamics are also known. During conceptual design, the designer is mainly interested in beds’ volume, FEHE area, and furnace and steam-generator duties. An optimisation problem, according to some steady-state related economic criteria, can be formulated. The solution is expected to recommend a small reactor because this is an expensive unit. The difference between the heat provided in the furnace and the heat recovered in the steam-generator should be low, in order to achieve energy saving. Moreover, their absolute values should be related to the plant energy balance.

However, the operating conditions may be different. There is always uncertainty of the kinetic parameters. Feed flow rate or concentration may deviate from the design values. Disturbances in feed temperature, furnace and steam-generator duties are unavoidable. FEHE efficiency may change due to fouling. Therefore, the operating point may become unstable and / or sustained oscillations may occur. In addition, the system may exhibit high sensitivity, which makes control difficult. Consequently, the design must be assessed with regard to steady-state multiplicity, stability and sensitivity issues.

Several articles dedicated to the nonlinear behaviour of the heat-integrated reactors have been published. Lovo and Balakotaiah (1992) computed the uniqueness-multiplicity boundary of the tubular reactor with internal or external heat exchange and CSTR with external heat exchange. For limiting cases, they presented analytical expressions of the ignition, extinction, and cusp points. Subramanian and Balakotaiah (1996) classified the steady-state and dynamic behaviour of several distributed reactor models, including the CSTR with external heat exchange and the tubular reactor with internal heat exchange. Silverstein and Shinnar (1982) evaluated the stability of the heat-integrated PFR using the frequency response of individual equipment components.

Although singularity theory (Balakotaiah and Luss, 1982, 1984, Golubitsky and Schaeffer, 1985) and bifurcation theory (Iooss and Joseph, 1981, Guckenheimer and Holmes, 1983, Scott, 1993) proved their power during the analysis of nonlinear systems, few
applications to design are reported. Russo and Bequette (1995) studied the influence of design parameters on the multiplicity behaviour of the jacketed exothermic CSTR. Heiszwolf and Fortuin (1997) presented an application-oriented design procedure for unique and stable operation of first-order reaction systems in a CSTR. Morud and Skogestad (1998) discussed the dynamics of an industrial multibed ammonia reactor, where positive feedback due to heat integration led to oscillatory behaviour. They showed that instability occurs at a Hopf bifurcation point. Khinast et al. (1998) analysed the continuously stirred decanting reactor.

They computed loci of codimension-2 singular points, which divide the space of the design parameters into regions with different steady-state and dynamic bifurcation diagrams. This way, desirable regions of operation and potential stability or operability issues were identified.

In a recent article (Bildea and Dimian, 1998) the heat-integrated adiabatic PFR where a first-order, irreversible, exothermic reaction takes place, was investigated. Its nonlinear behaviour was studied. A design procedure was proposed to ensure a desired multiplicity pattern and a stable point of operation, and to avoid high sensitivity. The procedure was applied to three reaction systems with different kinetic and thermodynamic characteristics.

This work analyses a more complex system. We consider a first-order, reversible, exothermic reaction, and adiabatic operation of two-bed tubular reactor. We present the model equations and the types of bifurcation of interest. Afterwards, we classify the steady-state and dynamic behaviour by computing the hysteresis, isola, boundary-limit, double-zero and double-Hopf varieties. State multiplicity, isolated branches and oscillatory behaviour are possible for realistic values of model parameters. Subsequently, we discuss how the results may be used to avoid operational problems.

**Model equations**

The dynamic behaviour of the heat-integrated PFR is described by plug-flow, pseudo-homogeneous models. The dimensionless equations are given below:

**FEHE (tube and shell-side):**

\[
M_t \frac{\partial \theta_t}{\partial \tau} = -\frac{\partial \theta_t}{\partial \xi} + NTU \cdot (\theta_s - \theta_t) \\
M_s \frac{\partial \theta_s}{\partial \tau} = \frac{\partial \theta_s}{\partial \xi} - NTU \cdot (\theta_s - \theta_t)
\]  

(4.1a)
Chapter 4. Design of Heat-Integrated Multibed PFR

Furnace:

\[
M_n \frac{\partial \theta_n}{\partial \tau} = -\frac{\partial \theta_n}{\partial \xi} + Q_n \quad (4.1b)
\]

First bed:

\[
\frac{\partial X_1}{\partial \tau} = -\frac{\partial X_1}{\partial \xi} + Da \cdot r(X_1, \theta_1) \quad (4.1c)
\]

\[
Le \frac{\partial \theta_1}{\partial \tau} = -\frac{\partial \theta_1}{\partial \xi} + B \cdot r(X_1, \theta_1)
\]

Intermediate cooler:

\[
M_{cl} \frac{\partial \theta_{cl}}{\partial \tau} = -\frac{\partial \theta_{cl}}{\partial \xi} - Q_{cl} \quad (4.1d)
\]

\[
M_{cl} \frac{\partial X_{cl}}{\partial \tau} = -\frac{\partial X_{cl}}{\partial \xi}
\]

Second bed:

\[
\frac{\partial X_2}{\partial \tau} = -\frac{\partial X_2}{\partial \xi} + \alpha \cdot Da \cdot r(X_2, \theta_2) \quad (4.1e)
\]

\[
Le \frac{\partial \theta_2}{\partial \tau} = -\frac{\partial \theta_2}{\partial \xi} + \alpha \cdot B \cdot r(X_2, \theta_2)
\]

Steam-generator:

\[
M_a \frac{\partial \theta_a}{\partial \tau} = -\frac{\partial \theta_a}{\partial \xi} - Q_{c2} \quad (4.1f)
\]

with appropriate initial and boundary conditions.

For a first-order, reversible reaction, the dimensionless reaction rate is given by:

\[
r(X, \theta) = e^{\varphi \theta / (1 + \theta)} \cdot (1 - X) \cdot \left(1 - \varphi \cdot e^{\theta / (1 + \theta)} \cdot \frac{X}{1 - X}\right) \quad (4.2)
\]

The model variables are dimensionless temperatures in the shell and tube-side of the FEHE (\(\theta_s, \theta_t\)), furnace (\(\theta_b\)), reactor (\(\theta_1, \theta_2\)), intermediate cooler (\(\theta_{cl}\)), and steam-generator (\(\theta_2\)), and conversion (\(X\)). The parameters represent reactor residence time (\(Da\)), FEHE area (\(\delta\)), activation energy (\(\gamma\)), adiabatic temperature rise (\(B\)), furnace, cooler and steam-generator duties (\(Q_b, Q_{cl}, Q_{c2}\)), feed temperature (\(\theta_0\)), residence time ratios (\(\alpha, M_n, M_0, M_0, M_{cl}, M_{c2}\)), pre-exponential factors ratio (\(\varphi\)), heat capacity (\(\delta\)) and heat capacity ratio (\(Le\)).

To study the steady-state and dynamic behaviour with varying feed temperature, only one dimensionless parameter must depend on it; hence, the reference temperature \(\bar{T} = T_0\) is not
a good choice. For this reason, we follow Heiszwolf and Fortuin (1997) and arbitrarily set \( \gamma = 25 \). Then we calculate the corresponding temperature and use it as reference. In this way, changes of furnace, cooler or steam-generator duty, feed temperature and concentration, and FEHE efficiency are reflected by independent changes of the model parameters: \( Q_h, Q_{c1}, Q_{c2}, \theta_0, B, \) and \( \varepsilon \), respectively. Chen and Luss (1989) used a similar procedure setting \( Da = 1 \).

The steady-state model is obtained by dropping the time derivatives in Eq. 4.1. After analytical integration of the FEHE, furnace, cooler and steam-generator equations, the following boundary value problem is obtained:

\[
\begin{align*}
\frac{\partial X_1}{\partial \xi} &= Da \cdot r(X_1, \theta_1) \\
\frac{\partial \theta_1}{\partial \xi} &= B \cdot r(X_1, \theta_1) \\
\frac{\partial X_2}{\partial \xi} &= \alpha \cdot Da \cdot r(X_2, \theta_2) \\
\frac{\partial \theta_2}{\partial \xi} &= \alpha \cdot B \cdot r(X_2, \theta_2) \\
X_1(0) &= 0 \\
X_2(0) &= X_1(1) \\
\theta_2(0) &= \theta_1(1) - Q_{c1} \\
g(\theta_1(0), p^*) &= (1 - \varepsilon)\theta_0 + (Q_h - \varepsilon Q_{c2}) + \varepsilon \cdot \theta_2(1) - \theta_1(0) = 0
\end{align*}
\]

where:

\[
\varepsilon = \frac{NTU}{1 + NTU}
\]

is the FEHE efficiency

and

\[
p^* = (\theta_0, Q_h, Q_{c1}, Q_{c2}, \varepsilon, B, \gamma, \varphi, \delta, Da, \alpha)
\]

is the vector of model parameters.

The methodology we will use to classify the steady-state and dynamic behaviour may be applied to systems that are described by a single intrinsic variable. This implies that, at least theoretically, it is possible to reduce the model equations to one equation with one variable. To demonstrate the validity of this assumption, we outline one possible approach to the solution of model equations: start with an initial guess for \( \theta_1(0) \), integrate Eqs. 4.3a-c to find \( \theta_2(1) \), check the boundary condition (Eq. 4.3d) and update \( \theta_1(0) \).
Bifurcation points

In this section, we will introduce the types of bifurcation occurring in the heat-integrated multibed PFR. The reader is referred to the cited literature on bifurcation and singularity theories for a mathematically rigorous presentation. Details on the bifurcation points computation are given in the Appendix.

The S-shaped curves (bifurcation diagrams) in Figure 4.2 represent the conversion vs. furnace duty (bifurcation variable), for a given set of values of model parameters. Each curve is associated with a fixed value of \( NTU \). The number of possible steady-states may change at \textit{fold bifurcation points}. The upper and lower branches of the fold curve correspond to reaction \textit{extinction} and \textit{ignition}, respectively.

The middle steady-state is always unstable (dashed-line). A steady-state may also become unstable at \textit{Hopf bifurcation point}. Here a branch of oscillating solution arises.

\[ X_2 \]

\( \varepsilon = 0.5 \)

\( \varepsilon = 0.252 \)

\( \varepsilon = 0.375 \)

\( \varepsilon = 0.16 \)

\( \varepsilon = 0.116 \)

\( \varepsilon = 0.091 \)

\( Q_h \)

\( 0.45 \quad 0.5 \quad 0.55 \quad 0.6 \quad 0.65 \quad 0.7 \)

Figure 4.2. Conversion vs. furnace duty for different values of the FEHE efficiency.
\( \gamma = 25, B = 0.293, \delta = 50.50, Da = 0.00361, \alpha = 3.54, \varphi = 10^4, Q_{cl} = 0.214, Q_{cr} = 0.286, \Theta_i = 0.325, Le = 2000 \). Continuous lines represent stable steady-states. Dashed lines represent unstable steady-states. Bold lines are the loci of fold and Hopf bifurcations. Points C, DH, DZ, I and BL correspond to cusp, double-Hopf, double-zero, isola and boundary-limit bifurcations. When multiple steady-states exist, the middle one is always unstable (dashed line).
When the FEHE efficiency is fixed, the feed temperature, furnace and steam-generator duties may be coupled in one parameter, which will be called net energy input:

\[ Q = (1 - \varepsilon) \cdot \theta_h + Q_h - \varepsilon Q_c \]

(4.5)

Note that \( \theta_h \), \( Q_h \) and \( Q_c \) appear coupled as \( Q \) in the steady-state equation (Eq. 4.3) and they do not appear in the equations describing the bifurcation points (Eqs A4.5 and A4.7).

The qualitative shape of the bifurcation diagram changes when the second parameter (\( \varepsilon \)) is varied. At the cusp point (C) two fold points appear or disappear and the number of steady-states changes by two. The locus of cusp points is called hysteresis variety.

The bifurcation diagram may also change when isola variety is crossed (point I in Figure 4.2). Here, two separate solution branches coalesce. The existence of the isola variety depends on the choice of the bifurcation parameter. For the heat-integrated multibed PFR, the isola variety exists when the FEHE efficiency (\( \varepsilon \)) is the bifurcation parameter.

When the \( \varepsilon \) parameter has very large values (\( \varepsilon \rightarrow 1 \)) the bifurcation parameter on the ignition and extinction branches reaches the asymptotic values \( Q_h=0.5 \) and \( Q_h=0.28 \) (not shown in Figure 4.2), respectively. They are called boundary-limit points (BL).

For a first-order reaction, the heat-integrated multibed PFR exhibits at most three steady-states, hence the double-limit variety (where the qualitative nature of the bifurcation diagram may also change) does not exist.

The number of Hopf bifurcation points may also change. At the double-Hopf (DH) bifurcation point two Hopf bifurcation points appear or disappear. At double-zero (DZ) bifurcation point, a Hopf bifurcation point appears or disappears.

**Steady-state behaviour**

First, we consider the net energy input as bifurcation parameter. It captures the influence of feed temperature, furnace and steam-generator duties on the steady-state. In this case the existence of multiple steady-states depends on the (fixed) value of FEHE efficiency, but is independent on how the net energy input is distributed between feed temperature, furnace and steam-generator duties.

For the multibed, adiabatic reactor where an exothermic, reversible reaction takes place, one can choose the thermal policy (beds inlet and outlet temperatures) in order to get a reactor with minimum volume. However, computation of the fold bifurcation points revealed
that, when state multiplicity exists, the required energy input is dangerously close to the extinction value (Figure 4.3).

![Figure 4.3. Extinction, ignition and required energy input for optimum reactor design](image)

Figure 4.3. Extinction, ignition and required energy input for optimum reactor design

Therefore, the FEHE efficiency should be chosen in the unicity region, which is bounded by the hysteresis variety. We remark that extinction may not be a problem when the thermal policy is sub-optimal. In this case the FEHE efficiency should be chosen so that the operating point is far enough from the cusp point, so high sensitivity is not a concern.

The steady-state behaviour is more complex when we consider the FEHE efficiency as bifurcation parameter. In this case, no other parameters are allowed to depend on it. Hence, $\theta_b$, $Q_h$ and $Q_{c2}$ can not be coupled in a single parameter ($Q$), and their effect must be investigated separately.

Figure 4.4 presents a typical phase diagram in the $(Q_{c2}, Q_h)$ space. In addition to the hysteresis variety, one isola and two boundary-limit varieties exist. The isola variety approaches asymptotically the BL$_1$ and BL$_2$ varieties. The isola and hysteresis varieties intersect at a pitchfork bifurcation point.
Figure 4.4. Phase diagram of the heat integrated multibed PFR with FEHE efficiency as bifurcation parameter.

$$\gamma=25, \beta=0.293, \sigma=50.50, D\sigma=0.00361, \alpha=3.54, \varphi=10^4, Q_{c1}=0.214, \theta_0=-0.325.$$ 

The different types of bifurcation diagrams existing in regions I-VIII are presented in Figure 4.4.

These singularities divide the parameter space into eight regions where qualitative different bifurcation diagrams exist (they are presented in Figure 4.5). In region I there is a unique steady-state. Crossing the hysteresis variety to region II, two fold points appear and state multiplicity is possible. When the BL$_1$ variety is crossed to region III, a low-conversion isolated branch appears and the multiplicity pattern becomes 1-3-1-3. The two branches coalesce when the isola is intersected and two fold points disappear. Hence, in region IV, a low conversion branch exists for all values of FEHE efficiency, while high conversion is possible only for high values of the $\varepsilon$ parameter. When moving to regions V or VII, the high conversion branch disappears (at BL$_2$), or multiple states appear on the low-conversion branch (at hysteresis), respectively. From region VII, the high conversion branch disappears at BL$_2$ (region VI) or the two branches coalesce at isola (region VIII).
Chapter 4. Design of Heat-Integrated Multibed PFR

Figure 4.5. Conversion vs. FEHE efficiency bifurcation diagrams
Diagrams I-VIII correspond to regions I-VIII in Figure 5.4.

Dynamic behaviour

Dynamic classification involves dividing the parameter space into regions where a different number of Hopf bifurcation points exists. Due to the large number of parameters, a complete classification is difficult. We consider the energy input as the bifurcation parameter and restrict our analysis to the influence of the FEHE efficiency and dimensionless adiabatic temperature rise. We consider a catalytic reactor because its “wrong-way” behaviour (Mehta et al., 1981) is the cause of oscillations (and hence of Hopf bifurcations). This is reflected in the large value of the $Le$ parameter.
A typical phase diagram is presented in Figure 4.6. The cusp, double-zero and double-Hopf varieties divide the ($\varepsilon$-$B$) space into regions where different types of bifurcation diagrams exist. The bifurcation diagrams of conversion vs. energy input are presented in Figure 4.7. In region I, one stable steady-state exists. After crossing the double-Hopf locus to region II, two Hopf points appear. In-between, no stable steady-state exists and the system exhibits oscillatory behaviour. When the hysteresis variety is crossed, two fold points appear. Therefore, in region III there are multiple steady-states. Oscillatory behaviour is possible on both the ignited and extinguished branches. In region IV, after crossing the double-zero locus, one Hopf point disappears and oscillatory behaviour is possible only on the ignited branch.

![Phase diagram](image)

**Figure 4.6.** Phase diagram of the heat-integrated multibed PFR with energy input as bifurcation parameter.

$\gamma=25$, $B=0.293$, $\delta=50.50$, $Da=0.00361$, $\alpha=3.54$, $\varphi=10^4$, $Q_{cl}=0.214$, $Le=2000$.

The different types of bifurcation diagrams existing in regions I-IV are presented in Figure 4.7.
**Design considerations**

During the conceptual design, we are mainly interested in the reactor thermal policy and the values of FEHE efficiency, furnace and steam-generators duties.

According to economic criteria, optimisation will give close to minimum reactor volume (an expensive unit) and high FEHE efficiency (for energy savings). However, the operating point will be in the multiplicity region, near the extinction point. When the net energy input accidentally decreases, the system will be driven in the unicity region, where only the extinguished state is possible. In this case, a special procedure will be required to restart the reaction. For these reasons, when the reactor had been designed close to its optimum, operation in the multiplicity region is not recommended. Because the hysteresis variety bounds the unicity region, FEHE efficiency should be less than the value corresponding to the cusp bifurcation. We remark that the system exhibits high sensitivity if the operating point is close to the hysteresis. This may be undesirable. Also, note that state unicity does not ensure stability.

---

**Figure 4.7. Conversion vs. energy input bifurcation diagrams**

The diagrams I-IV correspond to regions I-IV in Figure 4.6.
- ○ - fold bifurcation; ■ - Hopf bifurcation

**Diagram (I)**

**Diagram (II)**

**Diagram (III)**

**Diagram (IV)**
Chapter 4. Design of Heat-Integrated Multibed PFR

One can increase the energy saving by reactor overdesign (sub-optimal thermal policy). In this case the system exhibits *input multiplicity*, i.e. the same conversion may be obtained on the middle or on the upper branch. In the first case, the net energy input is lower, but the operating point is always unstable. In the second case, the operating point may be stable or unstable. Dynamic simulation can be used to assess the stability, but no information about the extent of the stability region will be obtained. We recommend the computation of the Hopf bifurcation points (which are on the boundary of the oscillatory region) to find possible instability near the operating point. Note that working at an unstable operating point is possible, as a temperature controller may stabilise the system. More dangerous is the loss of stability due to disturbances or design parameter uncertainty.

When FEHE efficiency is constant, the number of steady-states and their stability depends only on the net energy input \( (Q) \) and does not depend on how this is distributed between feed temperature, furnace and steam-generator duties. Consequently, these variables can be linked to plant energy balance, site integration, combined heat and power production or low equipment cost considerations. To prevent operational problems due to isolated branches when FEHE efficiency may change, operation in region I of Figure 4.4 should be preferred.

**Conclusions**

Nonlinear behaviour of a multibed heat-integrated PFR was studied, for a first-order, reversible reaction. Hysteresis, isola, boundary-limit, double-Hopf and double-zero varieties were used to classify the steady-state and dynamic behaviour of the system. State multiplicity, isolated branches and oscillatory behaviour are possible for realistic values of the model parameters. The phase diagrams are similar with those obtained for different adiabatic reactor models, as reported by Subramanian and Balakotaiah (1996) and Bildea and Dimian (1998).

There is a strong relationship between the design of individual pieces of equipment and the non-linear behaviour of the whole system. The results of significance are:

1. If the reactor is designed for a minimum volume, the selection of FEHE efficiency is constrained by the requirement of state unicity. This design rule ensures against reaction extinction due to thermal disturbances. The rejection of disturbances becomes difficult before state multiplicity appears (near the cusp bifurcation point). Consequently, optimal reactor design is robust only coupled with a proper FEHE efficiency.
2. When energy saving is of interest, a large FEHE must be used to achieve autothermal operation (defined by the existence of an ignited state). However, the reactor thermal policy should be sub-optimal, resulting in reactor overdesign.

3. The same conversion may be obtained for two different values of the net energy input (feed enthalpy, furnace and steam-generator duties). When multiple steady-states exist, the operating point corresponding to low net energy input is always unstable. Even when only one steady-state exists, its stability is not guaranteed. Hence, stabilising control may be necessary. Alternatively, stability can be achieved by changing the design such that the operating point corresponds to high net energy input.

Bifurcation and singularity theories may be applied to similar problems, where the design is constrained by state multiplicity and instability. In this way, desirable regions of operation are identified and potential stability or operability problems are avoided.

Notation

\( A_T \) = FEHE area, m\(^2\)

\( B \) = adiabatic temperature rise, dimensionless

\[ = \frac{\Delta T_{ad}}{I} \]

\( c_p \) = specific heat, J/(kg K)

\( Da \) = Damkohler number, dimensionless

\[ = k(T)\frac{V\rho}{F} \]

\( E_a \) = activation energy, J/mol

\( F \) = mass flow rate, kg/s

\( K_T \) = FEHE heat transfer coefficient, W/(m\(^2\) K)

\( k_i \) = pre-exponential factor (i=1,-1), s\(^{-1}\)

\( L \) = length, m

\( Le \) = Lewis number, dimensionless

\[ = 1 + \frac{1 - \epsilon_\pi}{\epsilon_\pi} \cdot \frac{\rho_d \cdot c_{p,ad}}{\rho_\pi \cdot c_{p,\pi}} \]

\( M_k \) = residence time ratio (k = t, s, c1, c2)

\[ = \frac{t_{0k}}{t_{01}} \]
Chapter 4. Design of Heat-Integrated Multibed PFR

\[ NTU = \text{number of transfer units, dimensionless} \]
\[ = \frac{K^*A_r}{F_{cp}} \]

\[ q_k = \text{duty (k = h, c1, c2), W} \]
\[ Q_k = \text{duty (k = h, c1, c2), dimensionless} \]
\[ = \frac{q_k}{F_{cp}T} \]

\[ Q = \text{energy input, dimensionless} \]
\[ = (1-\varepsilon)\theta_c - \varepsilon Q_c + Q_h \]

\[ R = \text{gas constant, J/(mol K)} \]
\[ T = \text{temperature, K} \]
\[ \bar{T} = \text{reference temperature, K} \]
\[ \Delta T_{ad} = \text{adiabatic temperature rise, K} \]
\[ r = \text{reaction rate, mol/(m}^3\text{s}) \]
\[ t = \text{time, s} \]
\[ t_{0i} = \text{residence time (i=1,2), s} \]
\[ = \frac{V_i\rho}{F} \]

\[ u, v = \text{eigenfunctions} \]
\[ X = \text{conversion, dimensionless} \]
\[ z = \text{axial coordinate, m} \]
\[ V_i = \text{reactor volume (i=1,2), m}^3 \]

**Greek letters**

\[ \alpha = \text{residence time ratio, dimensionless} \]
\[ = \frac{t_{01}}{t_{02}} \]

\[ \gamma = \text{activation energy, dimensionless} \]
\[ = \frac{E_{a1}}{RT} \]

\[ \varepsilon = \text{FEHE efficiency, dimensionless} \]
\[ \phi = \text{pre-exponential factors ratio, dimensionless} \]
\[ \frac{k_i}{k_{-i}} = \lambda \]

\( \lambda \) = eigenvalue

\[ \rho = \text{density, kg/m}^3 \]

\( \tau \) = time, dimensionless

\[ \tau = \frac{t}{t_{01}} \]

\( \theta \) = temperature, dimensionless

\[ \theta = \frac{T - \overline{T}}{\overline{T}} \]

\( \xi \) = axial coordinate, dimensionless

\[ \xi = \frac{z}{L} \]

\( u, \nu \) = eigenfunctions

**Subscripts**

- c1 - intermediate cooler
- c2 - steam-generator
- h - furnace
- s - FEHE shell side
- sf - solid phase
- ff - fluid phase
- t - FEHE tube side
- 0 - feed
- 1 - first reactor bed
- 2 - second reactor bed
- b - feasibility boundary

**Literature cited**


Chapter 4. Design of Heat-Integrated Multibed PFR


Subramanian, S. and V. Balakotaiah, “Classification of Steady-State and Dynamic Behaviour
Chapter 4. Design of Heat-Integrated Multibed PFR


Appendix. Bifurcation points computation

To derive the defining equation of the fold points, we consider the condensed form of the mathematical model:

\[ Ay(\tau,0) + By(\tau,1) - c = 0 \]

\[ y(0,\xi) = y_0(\xi) \]

where \( y \) is the vector of model variables; \( C \) is a diagonal capacity matrix; \( f(y) \) is a non-linear function; \( \mu \) is the bifurcation parameter; and \( p \) is the vector of remaining parameters. \( A \) and \( B \) are constant matrices and \( c \) is a constant vector.

Its steady-state solution is given by the boundary value problem:

\[ \frac{\partial y_s}{\partial \xi} = f(y_s, \mu, p) \]  

\[ Ay_s(0) + By_s(1) - c = 0 \]

When equation (A4.1) is linearized around steady-state and separation of variables is applied, the following eigenvalue problem is obtained:

\[ C(\lambda_1 + \lambda_2 i)(u + iv) = -\frac{d(u + iv)}{d\xi} + f_y(u + iv) \]

where:

\[ \delta = (y(\xi, \tau) - y(\xi)) = (u(\xi) + iv(\xi)) \cdot e^{(\lambda_1 + \lambda_2)\tau} \]

At fold points, one real eigenvalue crosses the imaginary axis. Substitution of \( \lambda_1 = \lambda_2 = 0 \) in Eq. A4.3 and identification of real and imaginary parts gives:

\[ \frac{du}{d\xi} = f_y \cdot u \]  

with the boundary condition:

123
Chapter 4. Design of Heat-Integrated Multibed PFR

\[ Au(0) + Bu(1) = 0 \]  \hspace{1cm} (A4.5b)

The eigenfunctions can be determined up to a multiplicative constant. Hence \( u(0) \) may be given an arbitrary value. We have two equations for two unknowns: the state variable \( y \) and the bifurcation parameter \( \mu \). Shooting technique is available as solution method.

At Hopf bifurcation points, a pair of complex eigenvalues crosses the imaginary axis. Two additional conditions must be satisfied:

\[ \frac{d\lambda}{d\mu} \neq 0 \]  \hspace{1cm} (A4.6a)

- the real parts of the other eigenvalues are negative.  \hspace{1cm} (A4.6b)

Substitution of \( \lambda_1=0 \) in Eq. A4.3 and identification of real and imaginary parts gives:

\[ \frac{\partial u}{\partial \xi} = f_y u + C\lambda_2 v \]  \hspace{1cm} (A4.7a)

\[ \frac{\partial v}{\partial \xi} = f_y v - C\lambda_2 u \]

with the boundary conditions:

\[ Au(0) + Bu(1) = 0 \]  \hspace{1cm} (A4.7b)

\[ Av(0) + Bv(1) = 0 \]

As the eigenfunctions are determined up to a multiplicative constant, initial values \( u(0) \) and \( v(0) \) may be fixed, so the eigenvalue \( \lambda_2 \) and the bifurcation parameter may be found using a shooting method.

The fold and Hopf points have codimension-1 because they fix the value of one parameter.

For the case of one algebraic equation (Eq. 4.3d) with one state variable (\( y = \theta_i(0) \)), the defining condition for the cusp variety is:

\[ g(y, \mu, p) = \frac{\partial g(y, \mu, p)}{\partial y} = \frac{\partial^2 g(y, \mu, p)}{\partial y^2} = 0 \]  \hspace{1cm} (A4.8)

A direct method for computing the cusp variety in distributed parameter systems is presented by Witmer et al. (1986). However, we used a simpler approach based on the following observation: the loci of the ignition and extinction points meet at the cusp point.

The defining condition for the isola variety is:

\[ g(y, \mu, p) = \frac{\partial g(y, \mu, p)}{\partial y} = \frac{\partial g(y, \mu, p)}{\partial \mu} = 0 \]  \hspace{1cm} (A4.9)
Point I in Figure 4.2 belongs to the locus of fold points; hence the first equality in Eq. A4.9 is satisfied. Moreover, it also satisfies the second equality in Eq. A4.9 because it is common to all steady-state solutions corresponding to varying $\varepsilon$; hence, point I represents an isola bifurcation when $\varepsilon$ is considered as bifurcation parameter. We note that it can be identified as an extreme of the fold locus.

If a fold point is located at a feasibility boundary ($\varepsilon=1$), we speak about a boundary-limit point (BL), defined by:

$$g(y,\mu,\nu) = \frac{\partial g(y,\mu,\nu)}{\partial y} = 0$$  \hspace{1cm} (A4.10a)

$$y = y_0 \quad \text{or} \quad \mu = \mu_0$$  \hspace{1cm} (A4.10b)

At double-Hopf bifurcation, the transversality condition defined by Eq. A4.6a is broken. It can be identified as an extreme on the locus of Hopf points.

When double-zero variety is crossed, the condition A4.6b is no longer satisfied. The double-zero point can be identified as the intersection between the loci of Hopf and fold bifurcation points.

Cusp, isola, boundary-limit, double-Hopf and double-zero points fix the value of two parameters; hence, they are codimension-2 varieties.

When codimension-2 bifurcation points were calculated by continuation of codimension-1 varieties, tracing the locus of Hopf points required the main computing effort. The local parametrization technique (Seydel and Hlavacek, 1987) with secant predictor worked well (only the temperatures $\theta_1(0)$, $\theta_b(0)$, $\theta_1(0)$, $\theta_1(0)$ and $\theta_2(0)$ were admitted as local parameters). A significant reduction of computing time was achieved by using the Broyden method (instead of Newton) as corrector. The step length control strategy recommended by Seydel (1984) was used.