Pattern formation in fixed-bed catalytic reactors—II

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Abstract—Following Trinh and Ramkrishna (1996a, Chem. Engng Sci., in press), spatial patterns due to steady-state multiplicity in catalyst particles in a packed-bed catalytic reactor is investigated further under isothermal conditions. In this work, axial dispersion is included in the fluid phase while the assumption of lumped resistance to transport (within the particles) at the particle surface is retained. A region is identified in the relevant parameter space in which spatial patterns are assured to exist. Conditions are established for asymptotic stability as well as stability in a specially defined ‘topology’ due to Weinberger (1982, Lecture Notes in Numer. Appl. Anal., Vol. 5, p. 354). This topology signifies how much the prevailing profile in the reactor may vary from a specific steady-state pattern. It is used to specify the initial perturbation of the reactor from the pattern in order that the reactor output stays within some stipulated range of product quality thus allowing the reactor to remain within a particular class of patterns. © 1997 Elsevier Science Ltd

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1. INTRODUCTION
In Part I (Trinh and Ramkrishna, 1996a), the authors have shown that, by instituting appropriate initial conditions, an immense variety of steady-state patterns can be created in a catalytic, fixed-bed reactor. The attractiveness of such spatial patterns lies in their potential to substantially improve product quality at the outlet of the reactor as by enhancing selectivity and conversion (see Trinh and Ramkrishna, 1996b).

Although a large variety of spatial patterns can exist, it was pointed out in Part I that the reactor output is relatively insensitive to the steady-state pattern in a suitably defined class of patterns. Thus, a class of patterns of interest might be the set of all patterned steady states which maintain reactor output within a stipulated range. It will be useful to develop methods to maintain (controlling) reactor operation within an appropriate class of patterns in order that product quality is ensured at all times. Of course, the problem of maintaining the reactor within a class of patterns in the constant presence of external perturbations lies in the domain of process control. However, the development presented in this paper should be useful for formulating the associated control problem.

The objective of this paper is to investigate patterned steady states in the axially dispersed packed-bed reactor. We determine the range of model parameters for which patterns exist and pursue the important question of stability of a patterned steady state. Further, we will elucidate the allowable initial perturbations of the reactor from a specific pattern in order for the reactor to either attain that pattern or a neighboring pattern within a given class. This class includes all patterns assuring a reactor output within a stipulated range.

The paper is organized as follows, we first briefly recapitulate the reactor model from Part I. Next, we show the steady state and dynamics analysis of pattern formation. We then present the mathematical analysis which shows how the displacement of the reactor of a specific pattern from this class can be controlled at all times by suitably restricting its initial displacement from that pattern. The mathematical development begins with defining the proper measures of ‘distance’ (norm) between any two states of the reactor. A reactor state is determined by both fluid and the catalyst profiles. Based on this norm, conditions are derived for maintaining the reactor within the proximity of a small suitably defined class of patterns. Finally, the implications of the mathematical development to the practical operation of a reactor within a class of pattern are presented.

2. REACTOR MODEL
Since Part I provides a discussion of the reactor and model, we present forthwith the reactor equations and initial and boundary conditions.
\[
\frac{\partial u}{\partial t} = \frac{1}{Pe} \frac{\partial^2 u}{\partial x^2} - \frac{\partial u}{\partial x} - \alpha (u - v)
\]  
(1)

\[
\frac{\partial v}{\partial t} = \beta (u - v) - R(v) = 0
\]  
(2)

\[
\frac{\partial u}{\partial x} = Pe(u - 1), \quad x = 0; \quad \frac{\partial u}{\partial x} = 0, \quad x = 1
\]  
(3)

An extension of the model to a multiple reaction system for demonstrating the role of patterns in improving selectivity is presented elsewhere (Trinh and Ramkrishna, 1996b). Since the objective here is to develop ways of producing and maintaining steady-state patterns, we focus attention on a single reaction with the following reaction kinetics:

\[
R(v) = \frac{Da v}{(1 + \sigma v)^2}
\]

The values of \( Da \) and \( \sigma \) are chosen such that the particles admit multiple steady states and give rise to patterns. Figure (1) shows the graph of \( R(v) \) for \( Da = 138 \) and \( \sigma = 40 \). Figure (2) shows the graph of the mass balance equation in the catalyst phase for these parameter values. The interval of multiplicity, \((u_{\text{min}}, u_{\text{max}})\), is indicated.

Clearly, the reactant concentration in either phase must be bounded. The same can be shown, mathematically, by using the concept of a positive invariant set. A positive invariant set is a domain which contains the reactant states for all times provided the initial reactor states is in this domain.

To construct a positive invariant set, eqs (1) and (2) are written as follows:

\[
u_t = Au + f
\]  
(4)

where

\[
A = \begin{bmatrix}
\frac{1}{Pe} \frac{d^2}{dx^2} & -\frac{d}{dx} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

and

\[
f = \begin{bmatrix}
-\alpha (u - v) \\
\beta (u - v) - R(v)
\end{bmatrix}
\]

Let \( \partial \mathcal{D}_1, \partial \mathcal{D}_2, \partial \mathcal{D}_3 \) and \( \partial \mathcal{D}_4 \) be the lines defined by \( u = 0, u = 1, v = 0 \) and \( v = 1 \), respectively, and let the region, \( \mathcal{D} \), be the interior of a square formed by the union of these lines. Let \( \vec{P}_i \) be the normal vector on \( \partial \mathcal{D}_i \). From geometry,

\[
\vec{P}_1 = \begin{bmatrix}
-1 \\
0
\end{bmatrix}, \quad \vec{P}_2 = \begin{bmatrix}
1 \\
0
\end{bmatrix}, \quad \vec{P}_3 = \begin{bmatrix}
0 \\
-1
\end{bmatrix}, \quad \vec{P}_4 = \begin{bmatrix}
0 \\
1
\end{bmatrix}
\]

The vector \( f \) on the boundaries of \( \mathcal{D} \) is given by

\[
f_1 = f|_{\vec{P}_1} = \begin{bmatrix}
\alpha u \\
-\beta v - R(v)
\end{bmatrix}
\]

\[
f_2 = f|_{\vec{P}_2} = \begin{bmatrix}
-\alpha (1 - v) \\
\beta (1 - v) - R(v)
\end{bmatrix}
\]

Fig. 1. Reaction kinetic.
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Fig. 2. Mass balance in the catalyst phase.

The governing differential equations for the steady-state packed-bed reactor are

$$\frac{1}{Pe} \frac{d^2 \tilde{u}}{dx^2} - \frac{d\tilde{u}}{dx} = \alpha(\tilde{u} - \bar{v}) = 0$$  \hspace{1cm} (9)

$$\beta(\tilde{u} - \bar{v}) - R(\bar{v}) = 0$$  \hspace{1cm} (10)

$$\frac{d\tilde{u}}{dx} = Pe(\tilde{u} - 1), \quad x = 0, \quad \frac{d\tilde{u}}{dx} = 0, \quad x = 1$$  \hspace{1cm} (11)

Since the system (9)-(11) constitutes a nonlinear boundary value problem, they are conveniently transformed into a nonlinear integral equation by means of the Green’s function. The solution of the steady-state packed-bed reactor is given by the following equivalent integral equation:

$$\tilde{u}(x) = g(x) + \int_0^1 G(x, \xi) [\tilde{u}(\xi)] e^{-Pe\xi} d\xi$$  \hspace{1cm} (12)

where the function $\tilde{u}$ is defined as a solution of Eq. (10), and

$$g(x) = [A \cosh(qx) + B \sinh(qx)] \exp \left( \frac{Pe}{2} x \right)$$  \hspace{1cm} (13)

3. ANALYSIS OF STEADY-STATE PATTERNS

The analysis consists of first constructing a method of solving the steady-state packed-bed equations. Next, we present conditions for the existence of spatial patterns.
with
\[ q = \sqrt{\frac{Pe^2}{4} + \alpha Pe} \]
and the constants
\[ A = \frac{2Pe[2q \cosh(q) + Pe \sinh(q)]}{4Pe q \cosh(q) + Pe^2 \sinh(q) + 4q^2 \sinh(q)} \]
\[ B = \frac{-2Pe [Pe \cosh(q) + 2q \sinh(q)]}{4Pe q \cosh(q) + Pe^2 \sinh(q) + 4q^2 \sinh(q)}. \]
The Green's function, \( G(x, \xi) \), is
\[
G(x, \xi) = \begin{cases} 
4q e^{Pe/2 (x + \xi)} & \text{cosh}(q(\xi - 1)) - \frac{Pe}{2q} \sinh(q(\xi - 1)) \\text{if } x < \xi \\
4q Pe \cosh(q) + 4q^2 \sinh(q) + Pe^2 \sinh(q) & \text{cosh}(q(x - 1)) - \frac{Pe}{2q} \sinh(q(x - 1)) \\text{if } x \geq \xi.
\end{cases}
\]
In Part I (Trinh and Ramkrishna, 1996a) we had denoted \( V^1, V^2 \) and \( V^3 \) the three respective branches of the solution to eq. (10) arising because of catalyst multiplicity. In integrating the right-hand side of eq. (12), one must insert the proper solution branch for \( \bar{v} \). This is particularly important for computing the patterned steady states to be discussed presently.

The actual catalyst profile in the reactor is obtained from the solution to eq. (12) as \( \bar{v}(x) = \bar{v}[\bar{u}(x)] \), fluid in the reactor has concentration in the range \((\bar{u}_{\text{min}}, \bar{u}_{\text{max}})\). Fig. 2, shows this clearly. To achieve this, \( x \) and \( Pe \) must be chosen such that
\[ \bar{u}(0) \geq \bar{u}_{\text{min}}. \]
If, however, \( \bar{u}(0) \geq \bar{u}_{\text{max}} \) and remains so throughout the reactor, patterns are again not possible. Therefore for patterns to exist, we must have
\[ \bar{u}(1) \leq \bar{u}_{\text{max}}. \]

![Fig. 3. Construction of the upper bound for \( v(z) \).](chart.png)
The criterion that the fluid concentration in the reactor must fall in the range of multiplicity for single particles for the existence of patterns presents a special problem. This is due to the fact that the concentrations of the reactant within the reactor at the inlet ($\tilde{u}(0)$) and outlet ($\tilde{u}(1)$) remain unknown in the presence of axial dispersion. Thus, in what follows, we shall attempt to estimate the values of $\tilde{u}(0)$ and $\tilde{u}(1)$.

It is clearly seen from Eq. (12) that $\tilde{u}(x) \geq g(x)$. The condition (15) is satisfied by insisting that

$$g(0) \geq u_{\text{min}}$$

(17)

with $\alpha$ and $Pe$ appropriately chosen.

In order to fulfill the condition (16), we estimate the solution $\tilde{u}(1)$ as follows. Consider a function $z(x)$ as the solution of

$$\frac{1}{Pe} \frac{d^2 z}{dx^2} - \frac{dz}{dx} = -zF(z)$$

(18)

$$\frac{dz}{dx} = Pe(z - 1), \quad x = 0, \quad \frac{dz}{dx} = 0, \quad x = 1$$

where $F(z)$ is to be specified presently. If $F(z)$ is chosen to be greater or equal to $\epsilon[z]$, then from (12) we may conclude that $\tilde{u}(x) \leq z(x)$. Our goal is to construct $F(z)$ to be sufficiently simple so that eq. (18) is solved analytically. The simplest non-constant function is $F(z) = cz$. The constant $c$ is defined such that $F(1) = c = \bar{\epsilon}(1) = 0.910243$. The construction of $F(z)$ is clearly elucidated in Fig. (3). $\bar{\epsilon}(z)$ representing the mass balance in the catalyst phase is shown in the dashed curve, and $F(z)$ in the solid line.

By construction, $z(1) \geq \tilde{u}(1)$. Thus if we choose $z(1) \leq u_{\text{max}}$ then $\tilde{u}(1) \leq u_{\text{max}}$. Since the solution, $z(x)$, of Eq. (17) is readily obtained as a function of the parameters $Pe$ and $\alpha$, the condition (15) is replaced by the a priori condition

$$z(1) \leq u_{\text{max}}.$$ 

(19)

Inequalities (17) and (19) are sufficient conditions for patterns to exist. Contour plots of these conditions are shown in Fig. (4). The parameters $Pe$ and $\alpha$ lie in the region indicated by $\tilde{u}(0) \geq u_{\text{min}}$ and $\tilde{u}(1) \leq u_{\text{max}}$, ensuring the existence of patterns.

Figure (5) shows the upper and lower steady-state solutions, which correspond to the high and low conversions, respectively. In addition to these two steady states, there are patterned steady states where the
concentration in the catalyst phase alternates between the upper and lower steady state.

Figure 6 shows the patterned steady state for $Pe = 1$ and $\alpha = 1.5$ which lie in the parameter region (shown in Fig. 4) where the sufficient condition for the existence of a pattern is satisfied.

The values of $\alpha$ determine the spatial resolution of patterns, i.e., the separation in reactor coordinates between one jump to the next. The larger is the value of $\alpha$, the narrower the separation between the jumps.

Incidentally, the condition for the multiplicity of steady state is also the condition for the existence of patterns. It can be shown that if

$$\frac{\partial \tilde{u}}{\partial \tilde{v}} > 0$$

(20)

then the steady-state solution is unique.

4. STABILITY ANALYSIS

Our interest in this section is to determine the stability of a steady-state pattern. Let $(\tilde{u}, \tilde{v})$ be a steady state. We shall formulate a condition for asymptotic stability of the steady state, i.e., the stability of the steady state when subjected to infinitesimal perturbations. The asymptotic stability of the steady-state solutions is determined by following system of equations which results from linearization of eqs (1) and (2) about $(\tilde{u}, \tilde{v})$

$$\frac{d}{dt} \begin{bmatrix} u \\ v \end{bmatrix} = L \begin{bmatrix} u \\ v \end{bmatrix}$$

(21)

where

$$L = \begin{bmatrix} \frac{1}{Pe} \frac{\partial^2}{\partial x^2} - \frac{\partial}{\partial x} - \frac{\beta}{\alpha} \\ \frac{\partial}{\partial x} - \beta - R'(\tilde{v}(x)) \end{bmatrix}$$

(22)

with the initial and boundary conditions:

$$\frac{\partial u}{\partial x} = Pe u, \quad x = 0, \quad \frac{\partial u}{\partial x} = 0, \quad x = 1$$

and

$$u(x, 0) = u_0, \quad v(x, 0) = v_0.$$

It is readily shown that $L$ is symmetric (for example, see Ramkrishna, and Amundson, 1985), i.e., for any
two vectors $w_1, w_2$

$$\langle Lw_1, w_2 \rangle = \langle w_1, Lw_2 \rangle$$

with respect to the following inner product,

$$\langle w_1, w_2 \rangle = \int_0^1 e^{-Px} u_1 u_2 \, dx + \beta \int_0^1 e^{-Px} v_1 v_2 \, dx$$

(24)

where

$$w_1 = \begin{bmatrix} u_1 \\ v_1 \end{bmatrix}, \quad w_2 = \begin{bmatrix} u_2 \\ v_2 \end{bmatrix}$$

(25)

Consequently, the spectrum of $L$ is real.

The solution of Eq. (21) is represented symbolically (see Ramkrishna and Amundson, 1985),

$$w = \sum_{j=0}^{\infty} e^{\lambda j} \mathbf{P}_j \mathbf{w}_0 + \int_{C(e^{\lambda L})} e^{\lambda j} d\lambda \mathbf{P}_j \mathbf{w}_0$$

(26)

where

$$w = \begin{bmatrix} u \\ v \end{bmatrix}, \quad w_0 = \begin{bmatrix} u_0 \\ v_0 \end{bmatrix}$$

(27)

and $\mathbf{P}_j$ and $\mathbf{P}_k$ are the projection operators which project the vector $w_0$ onto the discrete and continuous eigenspaces of the operator $L$, respectively.

The perturbed solution $w$ vanishes as $t \to \infty$ if the spectrum of $L$ is negative. Thus the stability of the steady-state solution $(\bar{u}(x), \bar{v}(x))$ is determined by the spectrum of the linearized operator $L$ defined by eq. (22).

Determination of the spectrum of $L$ is difficult. In lieu of solving the eigenvalue problem

$$\frac{1}{e^{-Px} x} \frac{d}{dx} \left( e^{-Px} \frac{dx}{dx} \right) - \lambda Pe (u - v) = \lambda u$$

(28)

$$\beta u - \beta v - R'(\bar{v}(x)) = \lambda v$$

(29)

it is easier to solve the following initial value problem to determine whether the spectrum of $L$ is negative (Weinberger, 1982)

$$\frac{du}{dx} = Pe u, \quad x = 0, \quad \frac{dx}{dx} = 0, \quad x = 1$$

(30)

The derivation of eq. (30) is presented in the appendix (Section A.2) and its result is summarized in the following theorem.

**Theorem 1.** Suppose that

$$\beta + R'(\bar{v}) > 0$$

(31)

and that the solution of eq. (30) has the properties

$$r(x) > 0 \text{ on } [0, 1], \text{ and } r'(1) > 0.$$  

(32)

Then the steady-state pattern is asymptotically stable.
The proof of the above theorem is included in Section (A.2) of the appendix. We have established a sufficient condition for asymptotic stability of a patterned steady state. For sufficiently small perturbations and for patterns involving catalyst phase concentration on the upper and lower steady states, the solution of eq. (30) satisfying eqs (31) and (32) implies that the patterned steady state \((\bar{u}(x), \bar{v}(x))\) is asymptotically stable.

Theorem 1 establishes stability of the patterned state depicted in Fig. (6). The solution of eq. (30) is shown in Fig. (7), with the solid curve representing \(r(x)\) and the dashed curve \(r'(x)\). Since \(r(x) > 0\) for \(x \in [0, 1]\) and \(r'(1) > 0\), the patterned state shown is asymptotically stable.

The foregoing result needs further improvement for two reasons. First, the fate of finite perturbations remains to be resolved. Second, a specific pattern out of an infinite class of patterns is embedded in a 'continuum' of neighboring patterns many of which will lead to negligible changes in product quality. For example, it may be entirely acceptable that the reactor may shift (as a result of ever present small perturbations) among a class of patterns as long as the product quality varies within permissible limits. Thus, it is more significant to ask whether the reactor will remain for all times in the proximity of an appropriate class of patterns.

The stability of a given pattern with respect to finite perturbations is a difficult issue. However, some improvement over the result of asymptotic stability for infinitesimal perturbations is possible by following an approach due to Weinberger (1982). In what follows, we dispense with asymptotic stability and instead focus only on the less restrictive notion of stability which implies that the system suitably 'close' to the steady state initially will remain as close to the steady state as is desired for all times. The topology, established by Weinberger (1982), allows finite perturbations as long as they are cumulatively restricted to suitably small intervals. In engineering terms, finite perturbations may be admitted as long as they are restricted to a small reactor length in which initial catalyst phase discontinuities are slightly separated from those at steady state. We will show that this has some significance to the practical aspects of maintaining patterned reactor operation.

The notion of a neighborhood, \(N_r(\delta)\), of a steady-state pattern, \(\bar{v}\) is defined by Weinberger as follows:

\[
N_r(\delta) = \{v \in L_\infty : \text{measure } \{x : |v(x) - \bar{v}(x)| > \delta \} < \delta^4 \}.
\]  

(33)

The neighborhood of a steady-state pattern consists of all bounded functions which differ from the steady-state patterns by less than \(\delta\). Exception is made for those functions which differ in a domain of length [referred to in eq. (33) as measure] \(\delta^4\) or less. In other words, the neighborhood of the steady-state patterns consists of functions that are not too different from the patterns, or if they do, the region in which they differ should be negligible.

With the initial catalyst profile in this neighborhood and with some restriction on the initial fluid

Fig. 7. The solution of eq. (30) to determine stability of the patterned state solution in Fig. 6.
profile to be specified, these profiles will stay close to that of the steady-state pattern. The foregoing discussion is summarized in the following theorem.

**Theorem II.** Let \((\bar{u}, \bar{v})\) be the steady-state pattern, with \(\bar{u}\) piecewise continuous, \(\bar{v}\) continuously differentiable. Suppose that the spectrum of the operator \(L\), defined in eq. (20) is negative. Then there exist positive constants \(\epsilon_0\) and \(A\) with the property that if \((u, v)\) is a solution of eq. (1), such that \(0 \leq u \leq 1, 0 \leq v \leq 1,\)

\[
\|v(x, 0) - \bar{v}(x)\|_{L_2(S_0)}^2 + \|u(x, 0) - \bar{u}(x)\|_{L_2(S_0)}^2 \leq \epsilon^2
\]

(34)

where \(|S'|\) signifies the length of the complimentary intervals \(S\) (the subset of \([0, 1]\) on which \(\|v - \bar{v}\|_{L_2(S)} < \epsilon\) satisfies

\[
|S'| < \epsilon^4
\]

and if \(\epsilon < \epsilon_0\), the inequality

\[
\|v(x, t) - \bar{v}(x)\|_{L_2(S_0)}^2 + \|u(x, t) - \bar{u}(x)\|_{L_2(S_0)}^2 \leq A\epsilon^2
\]

(36)

is valid for all \(t > 0\).

The proof of Theorem II is detailed in the appendix (Section A.3). This theorem ensures us that a steady-state pattern subjected to finite perturbation is stable in the topology described by eq. (33). The reactor state will remain close to that patterned state, provided the initial reactor state is suitably close to the patterned state.

5 CLASSES OF PATTERNS

The engineering interests in patterns are to obtain higher conversion or selectivity. For that purpose, it is not necessary to restrict the packed bed to a single pattern. We can, in fact, operate the reactor in a class of spatial patterns without significantly affecting the reactor output. Let \(u_o\) be the desired output of the reactor. We can define the class of spatial patterns, \(C_\delta\) consisting of those patterns such that the reactor outlet deviates from \(u_o\) by not more than \(\delta\). Mathematically,

\[
C_\delta = \{(u, v): |u(1) - u_o| \leq \delta\}
\]

Section A.4 of the appendix includes the proof of the following theorem.

**Theorem III.** Given the reactor in the neighborhood of the patterned state, \(B_\delta\), the reactor will remain in the class of patterns defined by \(C_\delta\). The neighborhood is given as

\[
B_\delta = \{(u, v): \|u - \bar{u}\|_{L_2(S_0)} + \|v - \bar{v}\|_{L_2(S_0)} \leq \delta^2\}
\]

In order for the reactor to remain in this class, we must select \(\epsilon = \delta/\sqrt{A}\). In other words, we choose the initial state of the reactor such that

\[
\|u(x, 0) - \bar{u}\|_{L_2(S_0)} + \|v(x, 0) - \bar{v}\|_{L_2(S_0)} \leq \frac{\delta^2}{A}
\]

(37)

The significance of the above inequality lies in the following. If we arrange for the reactor state to satisfy the inequality initially (or at any instant) then Theorem III assures us that the reactor product will satisfy the condition imposed in \(C_\delta\). If there were no perturbations the the reactor will eventually reach a pattern that is definitely in the class \(C_\delta\). Because the parameter \(A\) has not been identified explicitly, the practical application of Theorem III to calculate, say, the start-up condition in order for the reactor to reach the desired class of patterns must await further work. What has been proved is that the reactor will operate in a desired class of patterns if the initial perturbation satisfies the inequality (37).

From a practical viewpoint, the important issue here is to control of the reactor to operate within a desired class of patterns in the presence of external perturbations. This issue is not pursued in this paper.

6. DYNAMIC ANALYSIS

It is evident that eqs (1) and (2) cannot be solved analytically. The solution of the equation for the mass balance in the fluid is approximated by the solution of the following system of ordinary differential equations obtained by finite differencing the spatial derivatives, with the steplength \(k\).

\[
dU = \mathbf{L}U + \alpha V + \left(2Pe + \frac{2}{k}\right)\mathbf{e}_i
\]

(38)

where

\[
U = \begin{bmatrix} U_0 \\ U_1 \\ \vdots \\ U_M \end{bmatrix}, \quad V = \begin{bmatrix} V_0 \\ V_1 \\ \vdots \\ V_M \end{bmatrix}, \quad \mathbf{e}_i = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}
\]

(39)

\(U_i \equiv U(ik), V_i = V(ik)\) and

\[
\mathbf{L} = \begin{bmatrix}
\frac{-2}{k^2Pe} & \frac{-2}{k} & -Pe - \alpha \\
\frac{1}{k^2Pe} + \frac{1}{2k} & \frac{-2}{k^2Pe} & 0 & \ldots & 0 \\
\frac{1}{k^2Pe} & \frac{-2}{k^2Pe} & \frac{-1}{k^2Pe} & \ldots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \frac{2}{k^2Pe} & \frac{-2}{k^2Pe} - \alpha
\end{bmatrix}
\]

(40)
which can be shown to be negative definite by the use of Gershgorin theorem (Horn and Johnson, 1993).

Let \( U_n = U(nh) \) and \( V_n = V(nh) \). Integrating eq. (38) from \( t = nh \) to \( t = (n + 1)h \), by using trapezoid rule to approximate the integral, gives,

\[
U_{n+1} = U_n + \frac{h}{2} \mathbf{L} U_{n+1} + \frac{h}{2} \mathbf{L} U_n + \left( 2Pe \frac{h}{2} \right) e_t \\
+ \frac{zh}{2} (V_{n+1} + V_n).
\]

Equation (41) can be written as

\[
U_{n+1} = \left( I - \frac{h}{2} \mathbf{L} \right)^{-1} \left[ U_n + \frac{h}{2} \mathbf{L} U_n + \left( 2Pe \frac{h}{2} \right) e_t \\
+ \frac{zh}{2} (V_{n+1} + V_n) \right].
\]

The equation for mass balance in the catalyst is solved using quadrature.

\[
v(t) = v_0 e^{-\beta t} + \int_0^t \left[ \beta u - R(v) \right] e^{-\beta (t-t')} dt.
\]

Let \( v_{n+1} = v((n + 1)h) \). An equivalent expression is

\[
v_{n+1} = v_n e^{-\beta h} + \int_{nh}^{(n+1)h} \left[ \beta u(t) - R(v(t)) \right] e^{-\beta (t-t')} dt.
\]

For small \( h \), \( v_n \) can be approximated by \( V_n \) which satisfies the following equation:

\[
V_{n+1} = V_n e^{-\beta h} + \frac{h}{2} \left[ \beta U_{n+1} - R(V_{n+1}) \right] \\
+ \frac{h}{2} e^{-\beta h} [\beta U_n - R(V_n)].
\]

As \( (U_n, V_n) \) is known, eq. (41) and eq. (45) constitute a system of nonlinear equation of the form:

\[
y = F(y)
\]

where

\[
y = \begin{bmatrix} U_{n+1} \\ V_{n+1} \end{bmatrix}
\]

\[
F(y) = \begin{bmatrix} 
\left( I - \frac{h}{2} \mathbf{L} \right)^{-1} \left[ \left( I + \frac{h}{2} \mathbf{L} \right) U_n + \frac{h}{2} \beta V_n + \frac{h}{2} \alpha V_{n+1} \right] \\
V_n e^{-\beta h} + \frac{h}{2} e^{-\beta h} [\beta U_n - R(V_n)] + \frac{h}{2} [\beta U_{n+1} - R(V_{n+1})] \end{bmatrix}.
\]

Equation (46) is solved for \( y \) using fixed point iteration.

\[
y^{i+1} = F(y^i), \quad i = 0, 1, \ldots
\]

with \( y^0 \) is an initial guess. The iteration converges to a solution \( \bar{y} \) if the nonlinear operator is a contraction, i.e.,

\[
\| F(x) - F(y) \| < \| x - y \|.
\]

Inequality (48) is satisfied if \( \| DF \| < 1 \), where

\[
DF = \begin{bmatrix} 0 & \frac{h}{2} \beta \left( I - \frac{h}{2} \mathbf{L} \right)^{-1} \\
\frac{h}{2} \beta & -\frac{h}{2} \frac{dR(V_{n+1})}{dV_{n+1}} \end{bmatrix}
\]

and \( DR(V_{n+1}) \) is the differential of \( R \) evaluated at \( V_{n+1} \). Inequality (48) is satisfied by choosing \( h \) sufficiently small.

The foregoing discussion establishes convergence of the iterations. In Section A.5 of the appendix, we show that the numerical solution approaches the actual solution as the steplengths, \( h, k \) approach zero.

Figure 8 shows the dynamics of the packed bed in the fluid phase, starting from a zero concentration in fluid, and the initial profile, \( v(x, 0) \), with spatial oscillation in the catalyst is given by

\[
v(x, 0) = 0.7 \sin 2 (25 x).
\]

The dynamics of the packed bed reactor in the catalyst is shown in Fig. 9, the initial spatial oscillations is translated to temporal oscillations for a brief period of time. These oscillations eventually diminish and the catalyst concentration profile shows spatial discontinuities.

These figures illustrate that patterns can indeed be generated from smooth (i.e., initial without any discontinuities) but oscillatory initial conditions. These initial conditions are difficult to institute in practice. For a given oscillatory initial conditions it is very difficult to predict whether the pattern that is will eventually occur in the reactor is desirable.

7. START-UP STRATEGY

The discussion in the previous section brings out the need for a practical procedure to institute initial patterns in the reactors. The strategy to generate initial patterns in the catalyst phase is first to instigate discontinuities in the fluid phase. By the action of mass transport, these discontinuities are transferred to the catalyst phase. Fluid discontinuities are maintained by implementing multiple side feeds. The locations of the feeds are chosen to coincide with the location of the jumps in the concentration in the catalyst phase.
Pattern formation in fixed-bed catalytic reactors—II

Figure 10 illustrates the reactor configuration to create initial spatial patterns in the catalyst phase.

We demonstrate the method of creating spatial patterns with model simulation. An initial condition is created so that the reactor reaches the patterned steady state depicted in Fig. 6. To create this pattern, there are three additional side feeds into the reactor, as shown in Fig. 10. Without substantial effects on the steady state, each section of the reactor, where the concentration in the catalyst phase is continuous, is considered a packed-bed reactor. There is no dispersion in the fluid preceding the entrance and following the exit of the reactor. For each of these sections, the following equations describe the concentration of reactant in the fluid and catalyst phase.

\[
\frac{\partial u}{\partial t} = \frac{1}{Pe} \frac{\partial^2 u}{\partial x^2} - \frac{\partial u}{\partial x} - \sigma_i(u - v) \tag{50}
\]

\[
\frac{\partial v}{\partial t} = \beta_i(u - v) - \frac{Da_{i,u}}{(1 + \sigma_i v)^2} \tag{51}
\]
the system of equations subjected to the boundary
conditions for the fluid phase,
\[ \frac{\partial u}{\partial x} = P e_i (u - u_i), \quad x = 0, \quad \frac{\partial u}{\partial x} = 0, \quad x = 1 \] (52)
\[ u_i = \frac{\sum_{j=0}^{i-1} f_j c (x_j, t) + f_i c_i}{\sum_{j=0}^{i} f_j c_0} \] (53)
and the initial conditions in the fluid as well as in the catalyst phase,
\[ u(x, 0) = 0, \quad v(x, 0) = 0, \quad \text{for} \quad x \in [x_i, x_{i+1}) \] (54)
\[ i = 0, 1, \ldots, n \]

\[ \sigma_i = u_i \sigma_i, \quad D a_i = \frac{e k V_i}{\sum_{j=0}^{i} f_j}, \quad P e_i = \frac{A \sum_{j=0}^{i} f_j}{D V_i} \] (56)

A is the cross-sectional area, \( V_i \) is the volume of the \( i \)th section of the reactor, and \( F_{0i}, c_0 \) is the flow rate and concentration at the entrance into the reactor, respectively, and \( F_i, c_i \) is the flow rate and concentration at the side feed into the \( i \)th section of the reactor, respectively. \( L_i \) is the length of the \( i \)th section. \( F_i \) and \( c_i \) are selected so that only the appropriate branch of

---

**Fig. 10. Reactor configuration to generate initial patterns.**

**Fig. 11. Steady state of a packed-bed reactor with multiple feeds.**
solution exists at steady state. Equation (53) is written with the convention that \( \sum_{i=0}^{1} f_j = 0 \).

Figure (11) shows the steady state of the multiple-feed reactor. This steady state eventually reaches the pattern previously shown in Fig. 6 after removing the side feeds.

8. CONCLUSIONS
We have shown that with dispersion in the fluid, the packed-bed reactor model under appropriate conditions has infinitely many steady-state solutions. Many of these solutions are, in fact, asymptotically stable. However, for many of these asymptotically stable patterns the concentration at the reactor outlet does not vary significantly. We have evolved the concept of a class of patterns for which the reactor outlet can be within specified limits. Thus, the operation of a reactor at any specific pattern is not of much practical concern.

It will be of considerable interest to investigate in the future issues connected with control of the reactor to operate within a desired class of patterns.

NOTATION

- \( A \): cross sectional area of the reactor
- \( a_p \): area per unit volume of particle
- \( a_e \): area per unit volume of bed
- \( D_{a} \): Damkohler number, \( k V/F \)
- \( c_0 \): feed concentration of reactant at the entrance
- \( c_{0,i} \): feed concentration of reactant at the ith section
- \( c_f \): concentration of reactant in fluid phase
- \( c_p \): concentration of reactant in catalyst phase
- \( F \): volumetric flow rate
- \( F_i \): volumetric flow rate at the ith section
- \( k_m \): mass transfer coefficient
- \( k \): reaction rate constant
- \( L \): the length of the reactor
- \( P_{e} \): Peclet number, \( P_e = FL/(DA) \)
- \( P_{e,i} \): Peclet number in the ith section of the reactor
- \( u_i \): the combined feed into the ith section of the reactor
- \( V \): total volume of reactor
- \( V_i \): volume of the ith section of the reactor

Greek letters

- \( \alpha \): dimensionless mass transfer coefficient, \( k_m a_e V/F \)
- \( \alpha_i \): dimensionless mass transfer coefficient in the ith section of the reactor
- \( \beta_i \): dimensionless mass transfer coefficient in the ith section of the reactor
- \( \sigma^r \): adsorption desorption equilibrium constant
- \( \sigma \): adsorption desorption equilibrium constant, \( \approx \sigma_i c_0 \)
- \( \sigma_i \): adsorption desorption equilibrium constant in the ith section of the reactor, \( \sigma_i = u_i / \sigma \)

REFERENCES


APPENDIX

A.1. Solution of steady-state equations by discretization

A solution of the nonlinear equation (12), where \( u(x) \) is given by the solution of eq. (10), is approximated by a system of nonlinear algebraic equations given below.

To simplify the notation, we introduce the vectors:

\[
\begin{align*}
\mathbf{u} &= \{u(x) : x \in [0, 1]\} \\
\mathbf{v} &= \{v(x) : x \in [0, 1]\} \\
\mathbf{g} &= \{g(x) : x \in [0, 1]\} \\
\mathbf{R} &= \{R(x) : x \in [0, 1]\}
\end{align*}
\]

and

\[
J(v) = \int_0^1 G(x, \xi) \alpha(x, \xi) e^{-P\xi} d\xi.
\] (A1)

Equations (12), (10) becomes

\[
\mathbf{u} = \mathbf{g} + J(v)
\] (A2)

\[
\mathbf{u} = \mathbf{v} + \mathbf{R}(v)
\] (A3)

Let \( (u, v) \) be approximated by \((\mathbf{U}, \mathbf{V})\), where

\[
\mathbf{U} = \begin{bmatrix} U_1 \\ U_2 \\ \vdots \\ U_M \end{bmatrix}, \quad \mathbf{V} = \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_M \end{bmatrix}
\]

with

\[
u(x_i) \approx U_i, \quad v(x_i) \approx V_i
\]

\(J(v)\) is approximated by its discretized version by using Simpson's rule.

\[
J_i(V) = \frac{h}{6} \sum_{j=0}^{M} c_j G(ih, jh) V(U_j) e^{-P\xi}
\]

\[
J_i(V) = \frac{h}{6} \sum_{j=0}^{M} c_j G(ih, jh) V(U_j) e^{-P\xi}
\]
Thus, the solution of the system (12) and (10) is approximated by
\[ U_i = g_i + J_i(V_i) \] (A4)
\[ U_i = V_i + \frac{R(V_i)}{\beta} \] (A5)

More concisely,
\[ U = g + J(V) \] (A6)
\[ U = V + \frac{R(V)}{\beta} \] (A7)

The solution of eqs (A6)-(A7) is obtained by fixed point iteration,
\[ U^{n+1} = g + J(U^n), \quad n = 0, 1, \ldots \] (A8)
\[ U^{(n+1)} = V^{(n+1)} + \frac{R(U^{(n+1)})}{\beta}, \quad n = 0, 1, \ldots \] (A9)

with \( U^0 = g \cdot U^{(1)}, \ V^{(1)} \) obtained by solving (A8) and (A9) respectively. The procedure is then repeated until the iterates converge, i.e. \( \| U^{n+1} - U^n \| < \epsilon \) for a given error tolerance \( \epsilon \).

Using the standard approximation for Simpson's rule, it can also be shown that \( \| U - u \| = O(h^4) \) in the intervals where the solution is smooth. Thus, the approximation converges to an exact solution.

A.2. Proof of Theorem I
The equation
\[ \frac{1}{\lambda} \frac{d}{dx} \left( e^{-\lambda x} \frac{du}{dx} \right) - aPe u = \lambda u \] (A10)
\[ \beta u - [\beta - R'(\beta)] v = \lambda v \] (A11)

with
\[ \frac{du}{dx} = Pe u, \quad x = 0, \quad \frac{dv}{dx} = 0, \quad x = 1 \] (A12)

is represented as
\[ (L - \lambda I) w = \theta \]

which can be inverted to give the solution \( w = \theta \) for \( \lambda \) not in the spectrum of \( L \). For \( \lambda \) in the closure of the range of \(-[\beta + R'(\beta)]\) \( L \) is unbounded. Hence the closure of \(-[\beta + R'(\beta)]\) lies in the continuous spectrum of \( L \). Consequently, a necessary condition for the spectrum of \( L \) to be negative is \( [\beta + R'(\beta)] > 0 \). If \( \lambda \) is outside the closure of the range of \(-[\beta + R'(\beta)]\), then \( \epsilon \) can be eliminated from eq. (A10) using eq. (A11) to obtain
\[ \frac{1}{\lambda} \frac{d}{dx} \left( e^{-\lambda x} \frac{du}{dx} \right) - 2Pe u \left( 1 - \frac{\beta}{\lambda + \beta + R'(\beta)} \right) = \lambda u. \] (A13)

Equation (69) is multiplied by \( e^{-\rho x} u \) and integrated over (0,1) to get
\[ \int_0^1 u \frac{d}{dx} \left( e^{-\rho x} \frac{du}{dx} \right) dx - 2Pe \int_0^1 e^{-\rho x} u^2 \times \left( 1 - \frac{\beta}{\lambda + \beta + R'(\beta)} \right) dx \]
\[ = \lambda \int_0^1 e^{-\rho x} u^2 dx. \] (A14)

The solution of eqs (A6)-(A7) is obtained by fixed point iteration,
\[ U^{(n+1)} = g + J(U^n), \quad n = 0, 1, \ldots \] (A8)
\[ U^{(n+1)} = V^{(n+1)} + \frac{R(U^{(n+1)})}{\beta}, \quad n = 0, 1, \ldots \] (A9)

with \( U^0 = g \cdot U^{(1)}, \ V^{(1)} \) obtained by solving (A8) and (A9) respectively. The procedure is then repeated until the iterates converge, i.e. \( \| U^{n+1} - U^n \| < \epsilon \) for a given error tolerance \( \epsilon \).

Using the standard approximation for Simpson's rule, it can also be shown that \( \| U - u \| = O(h^4) \) in the intervals where the solution is smooth. Thus, the approximation converges to an exact solution.

A.3. Proof of Theorem II
To prepare for the proof of the theorem, we present the following lemmas.

Lemma I. For \( \gamma > 0, \ \gamma' \)
\[ \eta(x,t) \leq \eta_0(x) e^{-\gamma t} + m_1 \int_0^t \eta(x,t) \] (A21)
\[ \left| \eta(x,t) \right|^2 \leq \frac{M}{\gamma} \left( \left| \eta_0(x) \right|^2 e^{-\gamma t} + \int_0^t \left| \eta(x,t) \right|^2 \right) \] (A22)
Proof.
Squaring inequality (A21) and using
\[(a + b)^2 \leq 2(a^2 + b^2)\]
we obtain
\[
[\eta(x,t)]^2 \leq 2 \left[ |\eta_0(x)|^2 e^{-\alpha t} + M_1^2 \right. \\
\left. \times \int_0^t \left[ |\zeta(x,t)| + |\rho(x,t)| \right] e^{-\gamma \tau - \eta t} \, d\tau \right]^2.
\]
(A23)

From Hölder inequality,
\[
\left( \int_0^t |f| \, dx \right)^2 \leq \int_0^t f^2 \, dx \int_0^t g^2 \, dx
\]
we bound the integral of inequality (A23),
\[
\left( \int_0^t \left[ |\zeta(x,t)| + |\rho(x,t)| \right] e^{-\gamma \tau - \eta t} \, d\tau \right)^2
\leq \int_0^t \left[ |\zeta(x,t)| + |\rho(x,t)| \right]^2 e^{-\gamma \tau - \eta t} \, d\tau
\leq \frac{1}{\gamma} \int_0^t \left[ |\zeta(x,t)|^2 + |\rho(x,t)|^2 \right] e^{-\gamma \tau - \eta t} \, d\tau.
\]
Combining with inequality (A23),
\[
[\eta(x,t)]^2 \leq M_1 \left[ |\eta_0(x)|^2 e^{-\alpha t} + \int_0^t \left[ |\zeta(x,t)|^2 + |\rho(x,t)|^2 \right] e^{-\gamma \tau - \eta t} \, d\tau \right] \\
+ |\rho(x,t)|^2 e^{-\gamma \tau - \eta t} \right].
\]
(A24)

where \(M_1 = 2 \max (1, 2m_1^2/\eta)\)

Corollary. Given inequality (A21) the following is true:
\[
\|\eta\|^2_{L^2} \leq M_1 \left[ |\eta_0|^2 e^{-\alpha t} + \int_0^t \|\zeta\|^2 \right. \\
\left. + |\rho|^2 \right] e^{-\gamma \tau - \eta t} \right].
\]
(A25)

where \(m_1 = \min_{0 \leq x \leq 1} \gamma(x)\), and \(M_1 = 2 \max (1, 2m_1^2/\gamma_m)\).

Lemma II. For square integrable function \(\rho\), the following inequality holds:
\[
\int_0^t e^{-\alpha \tau - \eta t} \left( \int_0^t |\rho(\cdot, \tau)|^2 e^{-\gamma \tau - \eta t} \, d\tau \right) \, d\tau
\leq M \int_0^t \left[ |\rho(\cdot, \tau)|^2 e^{-\gamma \tau - \eta t} \right. \\
\left. \times \int_0^t \left[ |\zeta(\cdot, \tau)| + |\rho(\cdot, \tau)| \right] e^{-\gamma \tau - \eta t} \, d\tau \right] \, d\tau.
\]
(A26)

Proof. Interchanging the order of integration in the iterated integral,
\[
\int_0^t e^{-\alpha \tau - \eta t} \left( \int_0^t |\rho(\cdot, \tau)|^2 e^{-\gamma \tau - \eta t} \, d\tau \right) \, d\tau
= \int_0^t e^{-\alpha \tau - \eta t} \left( \int_0^t |\rho(\cdot, \tau)|^2 e^{-\alpha \tau - \eta t} \, d\tau \right) \, d\tau
\leq M \int_0^t \left[ |\rho(\cdot, \tau)|^2 e^{-\gamma \tau - \eta t} \right. \\
\left. \times \int_0^t \left[ |\zeta(\cdot, \tau)| + |\rho(\cdot, \tau)| \right] e^{-\gamma \tau - \eta t} \, d\tau \right] \, d\tau.
\]
(A27)

where \(\gamma = \min(\gamma, \mu)\) and \(M = 1/(\gamma - \mu)\).

Lemma III: For \(\zeta \in H^1([0, 1])\)
\[
\zeta(0) \leq \|\zeta\|^2_{H^1([0, 1])}
\]
(A28)

Proof. Let \(g(x) = f(x) \chi(x)\), where \(f(x) = 1 - x\)
\[
g(0) = \zeta(0) = \int_0^1 \frac{\partial f}{\partial x} \, dx = \int_0^1 \left( \frac{df}{dx} + \frac{f}{x} \right) \, dx
\]
(A29)

and write the system eqs (1) and (2) in the form
\[
\frac{\partial \zeta}{\partial t} = L \zeta, \quad \frac{\partial \eta}{\partial t} = L \eta
\]
(A30)

where
\[
L = \begin{bmatrix}
1 - x & -2x \\
\beta & -\beta - R(\bar{\epsilon}(x))
\end{bmatrix}
\]
(A32)

and
\[
\rho = -R(\eta + \bar{\epsilon}) + R(\bar{\epsilon}) + R(\bar{\epsilon})\eta
\]
(A33)

To estimate \(\|\zeta\|_{L^2}\), multiplying the \(\zeta\)-equation by \(\zeta^2/\beta^2\) and integrating over \((0, 1)\) yields
\[
\int_0^1 \frac{\partial \zeta}{\partial t} \frac{\partial \zeta}{\partial x} \, dx = \int_0^1 \left( \frac{\partial^2 \zeta}{\partial x^2} \right)^2 \, dx - \int_0^1 \frac{\partial \zeta}{\partial x} \frac{\partial \zeta}{\partial x} \, dx
\]
(A34)

Integrating by parts and using the boundary conditions (A31) gives
\[
\frac{\partial \zeta}{\partial x} \zeta(0, t) = \int_0^1 \frac{\partial \zeta}{\partial x} \frac{\partial \zeta}{\partial x} \, dx = \frac{1}{Pe} \int_0^1 \frac{\partial \zeta}{\partial x} \, dx
\]
(A35)

Using
\[
\frac{\partial^2 \zeta}{\partial x^2} \zeta = \left( \frac{\partial}{\partial x} \frac{\partial \zeta}{\partial x} \right)^3
\]
(A36)
and the Young inequality
\[ a \int_0^t \frac{\partial^2 \xi}{\partial t^2} \, dt \leq \frac{\alpha}{2} + \frac{\alpha Pe}{2} \frac{\partial^2 \xi}{\partial t^2} \, dt \]
we obtain
\[ \begin{align*}
1 \frac{d}{dt} \left( Pe \zeta^2(0, t) + \left\| \zeta \right\|_{L^2}^2 \right) & \leq -\frac{\alpha}{2} \left( Pe \zeta^2(0, t) + \left\| \zeta \right\|_{L^2}^2 \right) \\
& + \frac{\alpha^2 Pe}{4} \left\| \eta \right\|_{L^2}^2.
\end{align*} \tag{A36} \]

Multiplying the \( \zeta \)-equation by \( \zeta \) and integrating over \((0,1)\) yield
\[ \int_0^1 \frac{\partial \zeta}{\partial t} + \frac{\partial^2 \zeta}{\partial t^2} \, dx - \int_0^1 \frac{\partial \zeta}{\partial t} \, dx - \int_0^1 \zeta \, dx 
+ \alpha \int_0^1 \left\| \eta \right\|_{L^2} \, dx. \tag{A37} \]

Integrating by parts the right-hand side and using
\[ \frac{\partial \zeta}{\partial t} = \frac{1}{Pe} \left( - Pe \zeta^2(0, t) - \left\| \zeta \right\|_{L^2}^2 \right) \]
we obtain
\[ \begin{align*}
1 \frac{d}{dt} \left\| \zeta \right\|_{L^2}^2 & \leq -\frac{\alpha}{2} \left\| \zeta \right\|_{L^2}^2 + \alpha \int_0^1 \left\| \eta \right\|_{L^2} \, dx.
\end{align*} \tag{A38} \]

By Hölder inequality,
\[ \left\| \eta \right\|_{L^4} \leq \left\| \eta \right\|_{L^2} \left\| \zeta \right\|_{L^2} \leq \frac{1}{4} \left( \left\| \eta \right\|_{L^2}^2 + \left\| \zeta \right\|_{L^2}^2 \right). \tag{A39} \]

Using inequality (A39) in (A38),
\[ \begin{align*}
1 \frac{d}{dt} \left\| \zeta \right\|_{L^2}^2 & \leq -\frac{\alpha}{2} \left\| \zeta \right\|_{L^2}^2 + \frac{\alpha}{2} \left\| \eta \right\|_{L^2}^2.
\end{align*} \tag{A40} \]

Inequality (A36) and (A40) give
\[ \begin{align*}
1 \frac{d}{dt} \left( Pe \zeta^2(0, t) + \left\| \zeta \right\|_{L^2}^2 \right) & \leq -\frac{\alpha}{2} \left( Pe \zeta^2(0, t) + \left\| \zeta \right\|_{L^2}^2 \right) \\
& + \frac{\alpha}{2} \left( 1 + \frac{\alpha Pe}{2} \right) \left\| \eta \right\|_{L^2}^2.
\end{align*} \tag{A41} \]

Integrating eq. (A41) gives
\[ \begin{align*}
\left\| \zeta \right\|_{L^2}^2 & \leq e^{-\alpha \tau} \left( \left\| \zeta \right\|_{L^2}^2 + \left\| \zeta \right\|_{L^2}^2 \right) + \alpha \left( 1 + \frac{\alpha Pe}{2} \right) \int_0^t \left\| \eta \right\|_{L^2} e^{-\alpha \tau} \, d\tau.
\end{align*} \tag{A42} \]

Inequality (A42) requires \( \left\| \eta \right\|_{L^2}^2 \), which is estimated as follows. The catalyst phase equation implies
\[ \begin{align*}
\left\| \zeta \right\|_{L^2}^2 & \leq \left\| \zeta \right\|_{L^2}^2 + \alpha \left( 1 + \frac{\alpha Pe}{2} \right) \int_0^t \left\| \eta \right\|_{L^2} e^{-\alpha \tau} \, d\tau.
\end{align*} \tag{A43} \]

By the corollary
\[ \left\| \eta \right\|_{L^2} \leq m_3 \left\{ \left\| \eta \right\|_{L^2} e^{-\alpha t} + \left( \int \left\| \zeta \right\|_{L^2}^2 + \left\| \rho \right\|_{L^2}^2 e^{-\alpha \tau} \, d\tau \right) \right\}. \tag{A44} \]

Because the fluid-phase equation is parabolic, we can find a bound of the form
\[ \left\| \zeta \right\|_{L^2}^2 \leq c \left\{ \left\| \zeta \right\|_{L^2}^2 e^{-\alpha \tau} + \int_0^t \left\| \eta \right\|_{L^2} \, d\tau \right\}. \tag{A45} \]

Since the spectrum of \( L \) is negative, an estimate (see Henry, 1981) shows that
\[ \begin{align*}
\left\| \zeta \right\|_{L^2}^2 & \leq c \left\{ \left\| \zeta \right\|_{L^2}^2 e^{-\alpha \tau} + \int_0^t \left\| \rho \right\|_{L^2} \, d\tau \right\}.
\end{align*} \tag{A46} \]

it implies that
\[ \begin{align*}
\left\| \zeta \right\|_{L^2}^2 & \leq c \left\{ \left\| \zeta \right\|_{L^2}^2 e^{-\alpha \tau} + \int_0^t \left\| \rho \right\|_{L^2} \, d\tau \right\}.
\end{align*} \tag{A47} \]

Inequalities (A47) and (A45) imply
\[ \left\| \zeta \right\|_{L^2}^2 \leq c \left\{ \left\| \zeta \right\|_{L^2}^2 e^{-\alpha \tau} + \int_0^t \left\| \rho \right\|_{L^2} \, d\tau \right\}. \tag{A48} \]

Substituting inequalities (A48) and (A44) into (A42),
\[ \left\| \zeta \right\|_{L^2}^2 \leq e^{-\alpha \tau} \left[ \left\| \zeta \right\|_{L^2}^2 \right] + \alpha \left( 1 + \frac{\alpha Pe}{2} \right) \int_0^t \left\| \eta \right\|_{L^2} e^{-\alpha \tau} \, d\tau. \tag{A49} \]

The estimate of the catalyst phase perturbation is as follows. Since \( v(x, t) \leq 1 \), it is clear that
\[ \left\| \zeta \right\|_{L^2} \leq \left\| \zeta \right\|_{L^2} + \left\| \rho \right\|_{L^2} \, e^{-\alpha \tau}. \tag{A50} \]

Lemma I implies that
\[ \left\| \zeta \right\|_{L^2} \leq M \left\{ \left\| \zeta \right\|_{L^2} e^{-\alpha \tau} + \int_0^t \left\| \rho \right\|_{L^2} \, d\tau \right\}. \tag{A51} \]

By Lemma II,
\[ \leq M \left\{ |\eta_0| x_{z, a} e^{-\alpha t} + \int_0^t (|\xi(t, r)| x_{z, a}) e^{-\alpha(t-r)} dr \right\}. \]  

(A51)

Hence,
\[ \|\eta\| x_{z, a} \leq M_1 \left( e^{-\alpha t} (|\eta_0| x_{z, a} + \|\zeta_0\| x_{z, a}) e^{-\alpha(t-r)} \right) + \int_0^t e^{-\alpha(t-r)} \|\rho(t, r) x_{z, a}\| dr. \]  

(A52)

We combine inequalities (A49) and (A52) to obtain the inequality,
\[ \|\xi\| x_{z, a} + \|\eta\| x_{z, a} \leq C \left( \left( |\zeta_0| x_{z, a} + \|\zeta_0\| x_{z, a}\right) e^{-\alpha t} \right) + \int_0^t \rho(t, r) x_{z, a} e^{-\alpha(t-r)} + |S'| \right). \]  

(A53)

Equation (A33) implies \(|\rho(x)| x_{z, a} \leq C' \|\xi\| x_{z, a}\), standard argument shows that the perturbation is stable.

A.4. Proof of Theorem III

Proof. Let \(u(x)\) be a steady-state reactor, and \(\hat{u}(x)\) be the patterned state. Both \(u(x)\) and \(\hat{u}(x)\) are solutions of the following equations:

\[ \frac{1}{Pe} \frac{d^2 u}{dx^2} + \frac{d u}{dx} = \beta(u - v) \]  

(A54)

\[ \beta(u - v) = R(v) \]  

\[ \frac{d u}{dx} = Pe(u - 1), \quad x = 0 \]  

\[ \frac{d u}{dx} = 0, \quad x = 1 \]  

(A55)

\[ \frac{1}{Pe} \frac{d^2 \hat{u}}{dx^2} - \frac{d \hat{u}}{dx} = -\beta(\hat{u} - \bar{v}) \]  

(A56)

\[ \beta(\hat{u} - \bar{v}) = R(\bar{v}) \]  

\[ \frac{d \hat{u}}{dx} = Pe(\hat{u} - 1), \quad x = 0 \]  

\[ \frac{d \hat{u}}{dx} = 0, \quad x = 1. \]  

(A57)

Subtracting eqs (A56) and (A57) from eqs (A54) and (A55), we obtain the following equations:

\[ \frac{1}{Pe} \frac{d^2 y}{dx^2} - \frac{d y}{dx} = -\beta(y - z) \]  

(A58)

\[ \beta(y - z) = R(z + \bar{v}) - R(\bar{v}) \]  

\[ \frac{d y}{dx} = Pe y, \quad x = 0 \]

\[ \frac{d y}{dx} = 0, \quad x = 1 \]  

(A59)

where
\[ y = u(x) - \hat{u}(x) \]
\[ z = v(x) - \hat{v}(x) \]

Multiplying eq. (A58) by \(y\) and integrating by parts gives
\[ -\frac{1}{2} \left\{ y^2(0) + y^2(1) \right\} - \frac{1}{Pe} \int_0^1 \left( \frac{d y}{dx} \right)^2 dx \]  

\[ = -z \int_0^1 y \left[ R(z + \bar{v}) - R(\bar{v}) \right] dx. \]  

(A60)

Rearranging and we get
\[ \frac{1}{2} \left\{ y^2(1) + y^2(0) \right\} = -\frac{1}{Pe} \int_0^1 \left( \frac{d y}{dx} \right)^2 dx \]  

\[ + z \int_0^1 y \left[ R(z + \bar{v}) - R(\bar{v}) \right] dx. \]  

(A61)

It follows that
\[ \frac{1}{2} y^2(1) \leq \frac{1}{Pe} \int_0^1 \left( \frac{d y}{dx} \right)^2 dx + z M \int_0^1 y \left[ R(z + \bar{v}) - R(\bar{v}) \right] dx. \]  

(A62)

Estimating the last term as follows:
\[ z M \int_0^1 y \left[ R(z + \bar{v}) - R(\bar{v}) \right] dx \leq 2 M \left| \frac{\sqrt{Pe} \sqrt{\bar{v}}}{\sqrt{2} \sqrt{Pe}} \right| y \]  

\[ \leq \frac{1}{4} z M y^2 \]  

(A63)

It follows that
\[ z M \int_0^1 y \left[ R(z + \bar{v}) - R(\bar{v}) \right] dx \leq \frac{1}{4} z^2 M^2 Pe \int_0^1 \left( z \right)^2 dx + \frac{1}{Pe} \int_0^1 y^2 dx. \]  

(A64)

Using inequality (A63) in (A62) gives
\[ \frac{1}{2} y^2(1) \leq \frac{1}{Pe} \left\{ \frac{y}{z} \right\}_{z=0} + \left\{ \frac{y}{z} \right\}_{z=1} + M' \left( \int_0^1 z^2 dx + \int_0^1 \left( z^2 \right) dx \right) \]  

\[ \leq \frac{1}{Pe} \left\{ \frac{y}{z} \right\}_{z=0} + M' \left\{ \frac{y}{z} \right\}_{z=1} + M' \text{measure}(S) \]  

\[ \leq M' \left\{ \frac{y}{z} \right\}_{z=0} + M' \text{measure}(S) \]  

\[ \text{where} \]
\[ M' = \max_{0 < x < 1} \left\{ \frac{1}{Pe} - \frac{1}{2} Pe \left[ R(\bar{v}(x)) \right]^2 \right\}. \]

The result shows that the reactor output can be controlled by restricting the reactor within a small neighborhood of the pattern.

A.5. Approximation of the dynamic equations of the packed-bed reactor

We have shown that the iterations of the discrete problem converge some function. In what follows, we shall show that the function thus found indeed converges to the continuous solution of eqs (1) and (2) as \(k, h \to 0\).

Let \([u_n, v_n] = [u(ik,jh), v(ik,jh)]\) be a solution of the eqs (1) and (2). Then \([u_n, v_n]\) then satisfies the following difference equations:

\[ u_{n+1} = \left( 1 - \frac{h}{2} e_1 \right)^{-1} u_n + \frac{h}{2} \bar{u} + e_1 \]  

(A59)
and
\[ v_{n+1} = v_n e^{-\beta h} + \frac{h}{2} \beta u_{n+1} - R(v_{n+1}) + \frac{h}{2} e^{-\beta h} [\beta u_n - \beta R(v_n)] + hO(h^2) \mathbf{1} \] (A65)
where \( \mathbf{1} \) is the vector with unit elements. Subtracting eqs (A64), (A65), letting \( E_{n+1} = u_{n+1} - U_{n+1} \), \( F_{n+1} = v_{n+1} - V_{n+1} \), we obtain
\[
\begin{bmatrix}
1 & -\frac{1}{2} (I - \frac{1}{2} \tilde{L})^{-1} & \mathbb{E}_{n+1} \\
-\frac{1}{2} \beta \mathbf{1} & 1 + \frac{1}{2} A_{n+1} & \mathbb{F}_{n+1}
\end{bmatrix}
= \begin{bmatrix}
(I - \frac{1}{2} \tilde{L})^{-1} (I + \frac{1}{2} \tilde{L}) & \frac{1}{2} \beta e^{-\beta h} I \\
\frac{1}{2} \beta e^{-\beta h} I & c^{-\beta h} [I - \frac{1}{2} A_n]
\end{bmatrix}
\mathbb{E}_n + hO(h + k^2) \mathbf{1}
\] (A66)
where
\[
A_n = \int_0^\tau DR \left[ v_n + \epsilon (V_n - v_n) \right] dt
\]
and \( DR \) is the differential of \( R \). Define
\[
e_{n+1} = \begin{bmatrix}
E_{n+1} \\
F_{n+1}
\end{bmatrix}
\]
in terms of \( e_{n+1} \), eq. (A66) becomes
\[
e_{n+1} = P e_n + hO(h + k^2) \mathbf{1}
\] (A67)
where
\[
P = P' Q,
\]
\[
P' = \begin{bmatrix}
1 & -\frac{1}{2} \beta (I - \frac{1}{2} \tilde{L})^{-1} I \\
-\frac{1}{2} \beta \mathbf{1} & 1 + \frac{1}{2} A_{n+1}
\end{bmatrix}^{-1}
\]
\[
= \begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}
- \frac{h}{2} \beta \mathbf{1}
\] (A68)
Letting \( Q = \begin{bmatrix}
(I - \frac{1}{2} \tilde{L})^{-1} (I + \frac{1}{2} \tilde{L}) & \frac{1}{2} \beta e^{-\beta h} I \\
\frac{1}{2} \beta e^{-\beta h} I & c^{-\beta h} (I - \frac{1}{2} A_{n+1})
\end{bmatrix}
\)
we obtain
\[
\begin{align*}
Q &= \begin{bmatrix}
(I - \frac{1}{2} \tilde{L})^{-1} (I + \frac{1}{2} \tilde{L}) & \frac{1}{2} \beta e^{-\beta h} I \\
\frac{1}{2} \beta e^{-\beta h} I & c^{-\beta h} (I - \frac{1}{2} A_{n+1})
\end{bmatrix} \\
&= \begin{bmatrix}
0 & \frac{1}{2} \beta e^{-\beta h} I \\
\frac{1}{2} \beta e^{-\beta h} I & c^{-\beta h} (I - \frac{1}{2} A_{n+1})
\end{bmatrix}
\end{align*}
\] (A69)

For sufficiently small \( h \),
\[
P' = \begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}
+ \frac{h}{2} \beta \mathbf{1} - A_{n+1}
\]
(\( O(h^2) \))
(\( A71 \))
Since \( \tilde{L} \) is negative definite, eq. (A68) gives \( \| Q \| \leq \| P' \| \), for sufficiently small \( h \),
\[
\| P' \| \leq \| Q \| \leq \| P' \| ^2.
\] (A72)
It follows that
\[
\sum_{j=0}^n \| P \| ^j \leq \sum_{j=0}^n \| P' \| ^{2j} \leq \sum_{j=0}^n \left( 1 + \frac{h}{2} \| M \| \right) ^{2j}
\leq 2 \left( 1 + \frac{h}{2} \| M \| \right) ^2 \exp \left( \| M \| t \right)
\] (A73)
where
\[
M = \begin{bmatrix}
0 & \beta \mathbf{1} \\
\beta \mathbf{1} & -A_{n+1}
\end{bmatrix}
\]
Substituting (A73) in (A72), and for \( \| e_0 \| = 0 \), we obtain
\[
\| e_{n+1} \| \leq \| Q \| \| e_0 \| + hO(h + k^2)
\] (A74)
It is therefore shown that the approximation converges to the solution of eqs (1) and (2) as the step sizes \( h, k \to 0 \).