PATTERN FORMATION IN FIXED BED CATALYTIC REACTORS—I

SINH TRINH and DORAISWAMI RAMKRISHNA*
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, U.S.A.

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Abstract - The possibility of spatial patterns in packed-bed catalytic reactors to improve reactor operation is addressed in this paper with respect to several fundamental issues. The analysis is accomplished with an early model of Liu and Amundson (1962, Ind. Engng Chem. Fundam. 1, 200) which assumes plug flow of the fluid phase and lumped transport resistance in the catalyst particles. Such patterns involve discontinuous concentration profiles in the catalyst phase. It is shown that patterns, which arise due to multiplicity behavior of individual catalyst particles, can be created by providing for an initial pattern in the reactor. Start-up strategies for such initial patterns are established using multiple feeds. Asymptotic stability of patterns in which neighboring particles lie in distinct stable branches is established. Computations demonstrating the achievement of spatial patterns from suitable initial conditions are made. It is shown that reactor operation is concerned with a class of patterns which can provide for an acceptable range of product quality. The significance of patterns lies in improving selective productivities of desired products in multi-reaction systems.

Keywords: Spatial pattern, catalytic fixed bed reactor, heterogeneous model.

1. INTRODUCTION

Heterogeneous models of catalytic reactors have been shown to be essential from dynamic as well as steady-state viewpoints. Ramkrishna and Arce (1989) discredit dynamic analysis with pseudohomogeneous models because they imply two incompatible assumptions in regard to the catalyst phase: (i) negligible capacity, and (ii) negligible transport resistance in it; thus heterogeneous models are a necessity rather than simply a more realistic alternative. From a steady-state viewpoint, Ramkrishna and coworkers, in a series of papers (Arce and Ramkrishna, 1991; Trinh and Ramkrishna, 1994) have pointed out the importance of pattern formation in the catalyst phase which accommodates discontinuous profiles. Such discontinuous patterns offer more flexibility of reactor operation with provision for higher selectivities or selective productivities in multi-reaction systems.

Before we discuss issues relating to how steady-state patterns can be created in the reactor, we shall briefly deliberate on the practical aspects of why patterns are desirable in a reactor. Broadly, patterns can promote selectivity of specific products in multi-reaction systems. Consider, for example, the following reaction system:

\[
\begin{align*}
A_1 & \\
A_0 & \rightarrow A_1 + A_2 \\
A_2 & \rightarrow A_3
\end{align*}
\]

in which we regard, say \(A_3\), to be the desirable product and we wish to increase the selectivity of this product. We further assume that the reaction producing \(A_3\) satisfies a standard Langmuir–Hinshelwood type kinetics with inhibition at high concentrations of the reactant and the reaction producing \(A_2\) satisfies the saturation kinetics. The reaction to form \(A_3\) follows second-order kinetics with respect to \(A_1\) and \(A_2\). We deem the reactor to be operating under isothermal conditions.

For fixed-reactor volume, production of \(A_3\) is maximized if \(A_1\) and \(A_2\) are produced in equal amounts. Under 'normal' operating conditions, the packed-bed reactor can achieve two steady states, one with high and one with low concentration of reactant. For the kinetics considered, at high concentration, production of \(A_2\) dominates; at low concentration, production of \(A_1\) dominates. Neither of these steady states produces much of \(A_3\). By appropriately alternating between high and low concentration states, it is possible to form equal amounts of \(A_1\) and \(A_2\), so that maximum \(A_3\) is obtained. Trinh and Ramkrishna (1996) show that the selectivity of \(A_3\), when operating at a patterned steady state, is more than double that of \(A_3\) when operating at either of the steady states.

Other similar examples can be found to demonstrate that pattern formation can be of great value to reactor operation.

The objective of this paper is to address the different issues connected with the establishment of patterned steady states in a packed bed reactor. The different issues of interest are (i) characterization of patterns, (ii) stability of patterns, and (iii) dynamics towards the identification of start-up conditions.
leading to patterned steady states. These issues will lay the ground work for control of the reactor at a patterned steady state. The last mentioned issue, however, will not be dealt with in this paper.

2. REACTION SYSTEM

The analysis of patterns will be restricted in this paper to the single reaction

$$A \rightarrow \text{Products}$$

although the interest in patterns lies in their use for improving reactor performance for reaction systems of the type referred to in the Introduction. However, the various fundamental issues connected with patterns are more easily addressed for a single reaction of the type mentioned above. Also, for the same reason, we will restrict analysis to isothermal situations. The extensions to non-isothermal conditions and multi-reaction systems, however, are not conceptually difficult. The reaction above, deemed to satisfy Langmuir–Hinshelwood kinetics, has been used by Arce and Ramkrishna (1991), and by Trinh and Ramkrishna (1994) in the analysis of patterns in a continuous-stirred tank reactor. The kinetic expression for the reaction rate is given by

$$\frac{k c_s}{(1 + \sigma c_s)^2} \quad (1)$$

where $c_s$ is the concentration of the reactant in the solid (catalyst) phase, $k$ is a rate constant and $\sigma$ is the adsorption equilibrium constant for the reactant. The above expression allows the reaction rate to go through a maximum before eventually decreasing with increase in reaction concentration characteristic of substrate inhibition. For a catalyst particle exposed to a fluid of concentration $c_f$, mass balance under isothermal conditions leads to the equation

$$k_c a p (c_f - c_s) = V_F \frac{k c_s}{(1 + \sigma c_s)^2} \quad (2)$$

where the lumping of transport resistance at the particle surface is evident.

In anticipation of dimensionless variables applicable to the fixed-bed reactor, we non-dimensionalize eq. (2) above using reactor parameters, by letting

$$u \equiv \frac{c_f}{c_0}, \quad v \equiv \frac{c_s}{c_0}, \quad \sigma \equiv \sigma c_0, \quad D_u \equiv \frac{eVk}{F}, \quad \beta \equiv \frac{k a p e V}{F}$$

where $c_0$ is the concentration of the reactant in the feed to the reactor,

$$\beta(u - v) = D_u \frac{v}{(1 + \sigma v)^2}. \quad (3)$$

For multiplicity steady state of the catalyst particle to exist [see Luss (1971)], it is essential that $D_u > 27\beta$ and that $\sigma$ is suitably constrained. Under this condition the right-hand side of eq. (3) has a local maximum, say $u$, followed by a local minimum, say $y (u < y)$, both $u$ and $y$ depending on the entrance concentration of the fluid and the parameters $D_u$, $\beta$ and $\sigma$. The necessary and sufficient condition for multiplicity is given by $y < u < u$. Thus, wherever the fluid concentration in the packed-bed reactor lies within the foregoing range, multiplicity can exist for the local catalyst particle. Since the dimensionless reactant concentration in the fluid must decrease progressively from its reference value of 1, the possibility of multiple steady states for any of the catalyst particles in the reactor depends upon the potential for the fluid phase concentration to drop to within the required range above. When multiplicity exists, the single reaction case admits at most three solutions, two of which are known to be asymptotically stable. One of these which corresponds to lower conversion will be referred to as the 'upper' steady-state, signifying a higher reactant concentration in the catalyst, while the other is the 'lower' steady state, representing a higher amount of reaction. Between the upper and lower steady states there exists an intermediate steady state which will not interest us because it is an unstable steady state. At larger fluid concentrations only the upper steady state exists, while at sufficiently lower concentrations only the lower steady state exists. Suppose now that the fluid concentration in the reactor can drop to the multiplicity range. Since before doing so, the fluid will allow only the 'upper' steady state corresponding to small conversion, the catalyst phase must necessarily show no pattern from the entrance to the point at which multiplicity becomes a possibility. Beyond this point, multiplicity of particle steady states in the reactor suggests the possibility of the catalyst phase showing discontinuous spatial patterns, caused by adjacent particles being at the upper and lower steady states. We have not raised here the possibility of patterns with the intermediate catalyst particle steady state because we will show that such patterns in the reactor cannot be stable.

3. HETEROGENEOUS REACTOR MODEL

The reactor model will lump diffusional resistance in the catalyst particle at its surface. The advantage of this model lies in its retaining the heterogeneous nature of the packed-bed reactor and allowing a relatively simpler framework for the analysis of patterns. Besides, the model is not without precedence (Liu and Amundson, 1962; Froment, 1987). The fluid will be assumed to be in plug flow for the analysis, although axial dispersion has been included in the equations below. As pointed out earlier, we consider an isothermal reactor in order to elucidate the basic issues concerning pattern formation without excessive complications. The dimensionless mass balance equations in the fluid phase and the catalyst phase are given by

$$\frac{1}{Pe} \frac{\partial^2 u}{\partial x^2} - \frac{\partial u}{\partial x} - \frac{1}{2} (u - \alpha) = \frac{\partial u}{\partial t} \quad (4)$$

$$\beta (u - v) - R(v) = \frac{\partial v}{\partial t} \quad (5)$$
Pattern formation in fixed bed catalytic reactors I.

where

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

is the reaction rate expression appearing in eq. (5) for the reaction system introduced earlier. Equation (4) is subject to the so-called Danckwerts boundary conditions:

\[ \frac{\partial u}{\partial x} + \text{Pe}(u - 1) = 0 \quad \text{at} \quad x = 0; \]
\[ \frac{\partial u}{\partial x} = 0 \quad \text{at} \quad x = 1 \]  

and the initial conditions for the system

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

The above mass balance equations (4), (5), following Arce and Ramkrishna (1991), may be succinctly represented by

\[ \frac{du}{dt} = Lu + R \]  

where

\[ L = \begin{bmatrix} \frac{1}{\text{Pe}} \frac{\partial^2}{\partial x^2} & -\frac{x}{\beta} \\ -\frac{x}{\beta} & -\beta \end{bmatrix} \]  

and

\[ u = \begin{bmatrix} u \\ v \end{bmatrix}, \quad R = \begin{bmatrix} 0 \\ R(v) \end{bmatrix}. \]  

In this paper, we analyse the reactor with \( \text{Pe} = \infty \). So the operator \( L \) now becomes

\[ L = \begin{bmatrix} -\frac{x}{\beta} & -\frac{x}{\beta} \\ -\frac{x}{\beta} & -\beta \end{bmatrix}. \]  

In this case, \( L \) is not self-adjoint. Moreover, it has no eigenvalues which will be an issue of interest to the stability analysis of the reactor. Returning to the reactor equations for the plug flow case, we have

\[ \frac{\partial u}{\partial t} + \frac{\partial u}{\partial x} + x(u - v) = 0 \]  

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

subject to the feed condition for the fluid phase,

\[ u(0, t) = 1 \]  

and the same initial conditions (8). In general, the system of differential eqs (13), (14) allows discontinuous solutions since no smoothness requirements are implied by the equations for the catalyst phase.

4. STEADY-STATE PATTERNS

The steady-state equations for the reactors are obtained by setting the time derivative equal to zero in eqs (13) and (14).

\[ \frac{du}{dx} + x(u - v) = 0 \]  

\[ u = F(v) = v + \frac{R(v)}{\beta}. \]  

A straightforward strategy to solve for the reactor steady state is to solve eq. (17) for the catalyst-phase concentration as a function of the local fluid phase concentration, \( u \). Denoting this solution by \( V(u) \) we represent the reactor steady state by \( [u, V(u)] \).

Whether or not \( V(u) \) can be obtained uniquely from eq. (17) depends on the derivative \( \frac{dF}{dv} \). Equation (17) is uniquely invertible for \( V(u) \) in which case the solution of the system (16), (17) is unique. Multiple steady states exist for the reactor when the particle eq. (17) has multiple solutions. In other words, \( F(v) \) is not uniquely invertible. Alternatively, for multiple steady states in the reactor we must have

\[ \frac{dF}{dv} \neq 0 \quad \text{and} \quad \frac{d^2F}{dv^2} \neq 0 \]  

for some \( v \in (0, 1) \). This condition is satisfied, for example, by choosing \( Du = 138 \), and \( \sigma = 40 \). The graph of eq. (14) for these parameter values is shown in Fig. 1. Let \( \tilde{u} \) and \( \bar{u} \) be solutions of eq. (19) and the corresponding values of \( u \) be \( \tilde{u} \) and \( \bar{u} \). Thus, for each \( u \in (\tilde{u}, \bar{u}) \), eq. (17) admits multiple solutions \( V(u) \). Let \( V^\text{in}(u) \) be the continuous upper branch of solutions of \( u = F(v) \) for \( u \in (\tilde{u}, \bar{u}) \), \( V^\text{lo}(u) \) be the lower branch solutions of \( u = F(v) \) for \( u \in (0, \tilde{u}) \) such that \( V^\text{in}(u) > V^\text{lo}(u) \) for \( u \in (\tilde{u}, \bar{u}) \). It will become subsequently evident from the point of view of stability that the intermediate branch \( V^\text{in}(u) \) (between \( V^\text{lo}(u) \) and \( V^\text{in}(u) \)) is of interest to us. Only for \( u \in (\tilde{u}, \bar{u}) \) the steady-state reactor equations admits possibly discontinuous solutions (patterned solutions). Whether \( u \in (\tilde{u}, \bar{u}) \) depends on the solution of eq. (16) so that \( u \) is a function of \( x \). For \( x \) sufficiently large, it is possible for \( u \) to be in the interval of multiplicity \( (\tilde{u}, \bar{u}) \). Because patterns can only occur for the fluid concentration in the interval of multiplicity if the reactor is long enough to let the fluid to drop below \( \tilde{u} \) every conceivable pattern can be accommodated in the reactor. On the other hand, in order for a pattern to exist, the fluid must enter the upper limit, \( \bar{u} \), of the multiplicity interval. The above argument results in the following existence theorem for a patterned steady state.

**Theorem 1.** A necessary condition for the existence of a steady state to have at least one discontinuity is

\[ \frac{1}{\tilde{u}} \int_{\tilde{u}}^{\bar{u}} \frac{du}{u - V^\text{in}(u)} < 1 \]
and the sufficient condition for the existence of any steady-state pattern is

\[ \frac{1}{a} \int_{0}^{1} \frac{du}{u - V'(u)} < 1. \tag{21} \]

These conditions are inconvenient to use because they involve computation of integrals. By bounding the integrand appropriately the above integrals can be calculated to provide more usable conditions for predicting the existence of patterns in reactors.

The bounds on the integrands are obtained by bounding the catalyst-phase concentration. The bounds on the catalyst-phase concentration, obtained by linear approximation of the nonlinear curve representing catalyst particle mass balance, are presented as Lemmas 1 and 2.

**Lemma 1.** \( V'(u) \) satisfies the following inequality:

\[ V'(u) \leq V'(1) + m_0(u - 1) \tag{22} \]

where

\[ m_0 = \frac{1}{F'(V'(1))} \text{ for } u > 1. \tag{23} \]

A less conservative bound of \( V'(u) \) is the following:

\[ V'(u) \leq V'(u_i) + \bar{m}_i(u_i - u_i) \tag{24} \]

for \( u \in (u_{i-1}, u_i) \) and \( u_i \in (y, \bar{u}) \)

where

\[ \bar{m}_i = \frac{1}{F'(V'(u_i))} \text{ for } i = 0, \ldots, n - 1 \text{ and } u_0 = 1. \tag{25} \]

**Proof.** \( V'(u) \) is a concave down for \( u \in (1, y) \). The bounds are readily obtained by Taylor series expansion of \( V'(u) \) about \( u_i \).

**Lemma 2.** \( V''(u) \) satisfies the following bound:

\[ V''(u) \leq \frac{V''(y)}{y - u} \text{ for } u \in (0, y). \tag{26} \]

A less conservative bound for \( V''(u) \) is given by the following:

\[ V''(u) \leq V''(u_i) + m_i(u - u_i) \tag{27} \]

for \( u \in (0, u_i) \) and \( u_i \in (y, \bar{u}) \)

where

\[ m_i = \frac{V''(u_{i+1}) - V''(u_i)}{u_{i+1} - u_i} \tag{28} \]

**Proof.** Equations (26) and (27) follow from the fact that \( V''(u) \) is a convex function for \( u \in (0, \bar{u}) \).
Corollary 1. A necessary condition for the existence of a steady state to have at least one discontinuity is
\[
\frac{1}{2(1 - m_0)} \ln \left| \frac{1 - V'(1)}{(1 - m_0)u + m_0 - V'(1)} \right| < 1
\]
and the sufficient condition for the existence of any steady-state pattern is
\[
\frac{1}{2(1 - m_0)} \ln \left| \frac{1 - V'(1)}{(1 - m_0)u + m_0 - V'(1)} \right| < 1.
\]

Proof. Using the bound of \( V'(u) \) is the integrals in eqs (20) and (21).

In what follows, we will represent the catalyst-phase concentration by \( V(u) \) with the understanding that it can jump between \( V'(u) \) and \( V''(u) \) along the reactor. We characterize a patterned steady state by stipulating the concentrations of the fluid at which the catalyst phase takes jumps.

\[ \text{Discont}[V] = \{ u_1 > u_2 > \cdots > u_n \} \]

where \( n \) is an arbitrary integer and \( u_i \in (u, \bar{u}) \), the values of \( u \) at which discontinuities in \( V \) occur. The spatial distribution of catalyst phase discontinuities in the reactor can be recovered from setting \( u_i = u(x_i) \). The necessary and sufficient condition for the steady-state reactor to have the specified pattern is readily obtained by recognizing the values of \( u \) at which the \( n \)th point of discontinuity in the catalyst phase must take place inside the reactor. Hence, the following theorem is obtained.

Theorem 2. The necessary and sufficient condition for the existence of the patterns given by eq. (31) is
\[
\frac{1}{2} \sum_{i=1}^{n} \ln \frac{u_i}{u - V(u_i)} < 1 \quad \text{where} \quad u_0 = 1
\]

where
\[ V(u) = \begin{cases} V'(u) & \text{for} \ i \ \text{odd} \\ V''(u) & \text{for} \ i \ \text{even} \end{cases} \]

Using Lemmas 1 and 2 the following corollary is readily obtained.

Corollary 2. A sufficient condition for the existence of the patterned state characterized by eq. (31) is
\[
\frac{1}{2} \sum_{i=0}^{[n-1/2]} \ln \frac{u_{2i+1}(1 - m_0) + m_0 - V'(1)}{u_{2i+1}(1 - m_0) + m_0 - V'(1)} + \frac{\tilde{m}}{u - \tilde{u}} \sum_{i=0}^{[n/2]} \ln \frac{u_{2i+2}}{u_{2i+2}} \leq \alpha.
\]

5. STABILITY ANALYSIS

We have seen in the previous section that the steady state in the plug-flow fixed-bed reactor under suitable conditions can have an arbitrary large number of discontinuities. Clearly, solutions with different discontinuities represent different steady states. Because the number and location of discontinuities can be arbitrary, this leads to an uncountably large number of steady states. In this section, we are concerned with the issues of whether any of these patterns can be maintained under small perturbations due to operational uncertainties. In other words, we are interested in the stability of these patterns.

We shall first address the issue of asymptotic stability, which is concerned with whether or not a reactor perturbed from a patterned steady state will eventually return to that steady state. Asymptotic stability is generally approached by examining the eigenvalues of
Fig. 2. Patterned steady state characterized by eq. (35) for $x = 2.52439$ calculated using ineq. (33).

Fig. 3. Patterned steady state characterized by eq. (35) for $x = 2.41839$ calculated using ineq. (34).
the operator linearized about the steady state. However, since our linearized operator possesses no eigenvalues, an alternative approach is taken for the analysis of asymptotic stability.

To this end, we need the following inequality due to Wendroff (Lakshmikantham et al., 1989), which states that if \( m, h \) and \( k \) satisfy the inequality

\[
m(x, t) \leq h(x, t) + \int_a^b k(s, y) m(s, y) \, ds \, dy
\]

then they must also satisfy

\[
m(x, t) \leq h(x, t) + \int_a^b k(s, y) h(s, y) \, ds \, dy
\]

The inequality (37) essentially bounds for all times the function \( m(x, t) \) satisfying the implicit integral inequality (36) in which the functions \( k \) and \( h \) are specified continuous non-negative functions of their arguments. Our approach to asymptotic stability is as follows.

We first convert the linearized reactor equations to an integral equation in the fluid-phase concentration. We then obtain an inequality in the form of inequality (36) for the absolute value of the perturbed local fluid-phase concentration. The Wendroff inequality (37) is invoked to obtain conditions under which the right-hand side of the inequality will decay to zero so that the perturbation in the fluid will also decay to zero at large times, thus implying asymptotic stability.

The reactor eqs (13)–(14) are linearized about the steady-state pattern \((\bar{u}(x), \bar{v}(x))\) to obtain

\[
\frac{\partial u}{\partial t} + \frac{\partial u}{\partial x} = -2(u - v) \quad \text{and} \quad \frac{\partial v}{\partial t} = \beta(u - v) - R'(\bar{v})v
\]

subject to \( u(0, t) = 0, u(x, 0) = u_0(x) \) and \( v(x, 0) = v_0(x) \). The initial perturbation in the fluid phase, \( u_0(x) \), and that in the catalyst phase, \( v_0(x) \), may be either continuous or discontinuous functions of \( x \). Since any initial discontinuity in the fluid phase will wash out of the reactor in finite time (because of plug flow), no discontinuous perturbation in the fluid need be considered. The initial perturbation in the catalyst phase about the patterned steady state may feature discontinuities different from those of the pattern provided, however, that they are small enough to allow the linearization. Nevertheless, we will restrict ourselves, for the sake of simplicity, to initially continuous perturbations. However, discontinuities are introduced in the catalyst phase at \( t > 0 \) because of the following reason. The right-hand side of eq. (39) features the derivative of the reaction rate which, although a smooth function of concentration, inherits the spatial

![Pattern formation in fixed bed catalytic reactors—1.](image-url)
discontinuities of the catalyst-phase concentration. Thus, a continuous initial perturbation in the catalyst phase will develop discontinuities at the same locations as the steady state pattern during evolution.

In order to use Wendroff’s inequality, we convert eqs (38) and (39) to the following integral equation by eliminating in the fluid perturbation the catalyst variable, and integrating the resulting fluid equation. Our strategy is to express the fluid concentration at any instant in each reactor subinterval, in which the catalyst-phase concentration is continuous, in terms of its values at the beginning of the interval at a suitably earlier time using the method of characteristics. More precisely, we express the fluid concentration in the reactor subinterval \( (x_i, x_{i+1}) \), \( i = 0, 1, \ldots, n \) with \( x_0 = 0 \) and \( x_n = 1 \), at any time \( t \) in terms of its value at \( x_i \) and the correspondingly earlier time \( t - (x - x_i) \) lying in the characteristic passing through \( (x_i, t) \):

\[
 u(x, t)e^{\pi x} = \begin{cases} 
 u(x_i, t + x_i - x) + \int_{x_i}^{x} v_0(x - t + \tau)e^{-[\beta + R'(\rho)](x - \tau)}d\tau & x > x_i \\
 u_0(x - t)e^{\pi x} + \int_{x_i}^{x} u(x_i, t + x_i - x)e^{-[\beta + R'(\rho)](x - \tau)}d\tau & x < x_i
\end{cases}
\]

(40)

Setting \( \rho = x + t - x \), eq. (40) is transformed to:

\[
 u(x, t)e^{\pi x} = \begin{cases} 
 u(x_i, t + x_i - x) + \int_{x_i}^{x} v_0(x - t + \tau)e^{-[\beta + R'(\rho)](x - \tau)}d\tau & x > x_i \\
 u_0(x - t)e^{\pi x} + \int_{x_i}^{x} u(x_i, t + x_i - x)e^{-[\beta + R'(\rho)](x - \tau)}d\tau & x < x_i
\end{cases}
\]

(41)

For \( t > 1 \), we obtain

\[
 |u(x, t)| \leq |u(x_i, t + x_i - x)| + \int_{x_i}^{x} v_0(x - t + \tau)e^{-[\beta + R'(\rho)](x - \tau)}d\tau + \int_{x_i}^{x} u(x_i, t + x_i - x)e^{-[\beta + R'(\rho)](x - \tau)}d\tau
\]

(42)

We shall show that the perturbation, \( |u(x, t)| \), decays to zero for each \( x \) in the reactor as \( t \) becomes arbitrarily large provided that the stability condition (43) is satisfied,

\[
 \beta + R'(\rho(x)) > 0, \quad x \in (0, 1).
\]

(43)

We shall establish condition (43), by applying Wendroff’s inequality to inequality (42),

\[
 |u(x, t)| \leq |u(x_i, t + x_i - x)|
\]

\[
 + \int_{x_i}^{x} v_0(x - t + \tau)e^{-[\beta + R'(\rho)](x - \tau)}d\tau + \int_{x_i}^{x} u(x_i, t + x_i - x)e^{-[\beta + R'(\rho)](x - \tau)}d\tau
\]

(44)
Again, using Wendroff inequality,
\[ u(x, t) \geq \int \int v_0(x) e^{- [\beta + R'(\alpha)(\xi + t - \varphi)] d\rho} \]
\[ + \int \int v_0(x) e^{- [\beta + R'(\alpha)(\xi + t - \varphi)] d\rho} \times \left\{ e^{\beta \int \int v_0(\rho) e^{- [\beta + R'(\alpha)(\xi + t - \varphi)] d\rho}} \right\} \times \exp \left\{ \frac{\beta}{2} \int \int v_0(\rho) e^{- [\beta + R'(\alpha)(\xi + t - \varphi)] d\rho} \times ds d\gamma, t \geq 1 \right\} \] (47)

Inequality (47) shows that \( u(x, t) \to 0 \) as \( t \to \infty \) if eq. (45) is satisfied. We have thus shown that inequality (43) is the necessary and sufficient condition for asymptotic stability of a pattern. Furthermore, since condition (43) is violated for any catalyst particle at the intermediate branch \( V''(u) \), we also conclude that such patterns cannot be maintained in the reactor.

We have thus established that the only patterns that can be asymptotically stable are those that are formed by switching between branches \( V^1 \) and \( V^m \). The question of what starting conditions will assure the attainment of a specific pattern is of course not covered by the foregoing proof of asymptotic stability.

The generally relevant question of the region of stability is of no significance to our context, because there is a class of uncountable contiguous stable patterns which do not make a substantial difference to the reactor product measured in terms of the outlet fluid state as demonstrated in Fig. 9. Thus, we are more interested in the class of patterns that will maintain a product of quality within a suitably specified range so that the asymptotic stability region of any specific steady state is of no particular significance. On the other hand, it will be more relevant to raise the question of what set of initial conditions will keep the reactor state within a specified range for all times thereafter (in the absence of all external perturbations). This question is important to control of the reactor to operate within a class of patterns. In this connection, we wish to allude to a theorem by Weinberger (1982) that may be seen to address a problem with finite values of Peclet number, \( P_c \), and will be the subject of a follow-up paper by us. In this paper, however, we will limit further concern to producing start-up conditions that will lead to a chosen pattern. In doing so, we will determine initial states that have discontinuities at the same points in the reactor as the steady state pattern sought. It will transpire that such discontinuities can be produced by introducing multiple feeds precisely at the locations of discontinuity. This is discussed in the later section.

6. TRANSIENT ANALYSIS

The analysis so far has been concerned with the steady-state equation. The time evolution of the reactor is governed by eqs (13) and (14). These equations cannot be solved analytically. However, we will show that they can be approximated as accurately as possible by the following difference equations:

\[ u_{m,n} = u_{m-1,n-1} - \frac{h}{2} \left( u_{m,n} - u_{m-1,n} + u_{m-1,n-1} - u_{m-2,n-1} \right) \] (48)

\[ v_{m,n} = v_{m,n-1} + \frac{h}{2} \left( v_{m,n} - v_{m-1,n} + v_{m-1,n-1} - v_{m-2,n-1} \right) \] (49)

by choosing \( h \) sufficiently small. In the foregoing equations, \((u_{m,n}, v_{m,n})\) are approximations of \((U(x_m, t_n), V(x_m, t_n))\), and \( x_m = mh \) and \( t_n = nh \). Mathematically, we show that \((u_{m,n}, v_{m,n}) \to (U(x_m, V_m))\) as \( h \to 0 \). (\( U(x_m, V_m) \)) satisfy the following equations:

\[ U_{m,n} = U_{m-1,n-1} - \frac{h}{2} \left( U_{m,n} - V_{m,n} \right) \]
\[ V_{m,n} = V_{m,n-1} + \frac{h}{2} \left( U_{m,n} - V_{m-1,n} + U_{m-1,n} - V_{m-2,n} \right) \]
\[ - \frac{h}{2} \left( R(U_{m,n}) + R(V_{m-1,n}) \right) + O(h^2). \] (50)

Let \( E_{m,n} = U_{m,n} - u_{m,n} \) and \( F_{m,n} = V_{m,n} - v_{m,n} \). Subtracting eqs (48) and (49) from eqs (50) and (51), respectively, to get

\[ E_{m,n} = E_{m-1,n-1} - \frac{h}{2} \left( E_{m,n} - F_{m,n} + E_{m-1,n-1} \right) - F_{m-1,n-1} + O(h^2) \] (52)
\[ F_{m,n} = F_{m,n-1} + \frac{h}{2} \left( E_{m,n} - F_{m,n} + E_{m,n-1} - F_{m-1,n} \right) + \frac{h}{2} \left( R(F_{m,n} + E_{m,n-1}) \right) + R(F_{m-1,n} + E_{m,n-1}) + O(h^2) \] (53)

Let \( E_n = \sup_{x \in \mathbb{R}} |E_{m,n}| \) and \( F_n = \sup_{x \in \mathbb{R}} |F_{m,n}| \). eqs (52)-(53) in terms of \((E_n, F_n)\) become

\[ E_n \leq E_{n-1} + \frac{h}{2} E_{n-1} + \frac{h}{2} E_n + O(h^2) \] (54)
\[ F_n \leq F_{n-1} + \frac{h}{2} F_{n-1} + \frac{h}{2} F_n + O(h^2) \] (55)

In matrix notation,

\[ (I - hA)E_n \leq (I + hA)E_{n-1} + O(h^2) \] (56)
where I is a vector of unit elements and

\[ A = \left[ \begin{array}{c} \frac{\partial}{\partial x} \\
\frac{\partial}{\partial y} + (\beta + R(\psi)) \end{array} \right], \quad e_n = \left[ \begin{array}{c} e_{n,x} \\
E_{n,y} \end{array} \right] \]  

(57)

with convention that \( x \leq y \) to imply \( x_i \leq y_i \), where \( x_i \) and \( y_i \) being the \( i \)th components of \( x \) and \( y \). For \( h \) sufficiently small,

\[ (I - hA)^{-1} = I + hA + O(h^2)I. \]  

(58)

Using eq. (58), eq. (56) becomes

\[ e_n \leq (I + 2hA)e_{n-1} + O(h^2)I. \]  

(59)

Taking the norm

\[ \|e_n\| \leq \|I + 2hA\|\|e_{n-1}\| + O(h^2) \]  

(60)

and iterating this inequality to get

\[ \|e_n\| \leq \|I + 2hA\|^n\|e_0\| + O(h^2) \sum_{i=0}^{n-1} \|I + 2hA\|^i \]  

(61)

\[ \sum_{i=0}^{n-1} \|I + 2hA\|^i \leq \sum_{i=0}^{n-1} (1 + 2h\|A\|)^i \leq \frac{\exp(2\|A\|t)}{2h\|A\|} = \frac{2}{2h\|A\|} \]  

(62)

With \( \|e_0\| = 0 \), we arrive,

\[ \|e_n\| \leq O(h) \rightarrow 0 \text{ as } h \rightarrow 0. \]

The differences between approximations and solutions vanish as \( h \) becomes sufficiently small.

Equations (13) and (14) admit discontinuous solutions even for small time. If \( u_0(0) \neq 1 \) then \( u(x, t) \) shows discontinuity. The discontinuity propagating along the reactor diminishes as time gets large even as it 'washes out' of the reactor. Let \( d(x, t) \) be the jump at the point of discontinuity. Then we obtain

\[ d(x, t) = |u_0(0) - 1|e^{-nt} = |u_0(0) - 1|e^{-nt} \]  

(63)

by integrating eq. (13) along the characteristic.

To show that transient as well as steady-state solutions starting from continuous initial conditions can display discontinuities in the fluid as well as catalyst phase, we present the results of computations in Figs 5-10 where we have used the initial conditions, \( u_0(x) = 0 \) and \( v_0(x) = 0.7 \sin^2 (40x) \). Figure 5 shows an exponentially dwindling discontinuity in the fluid in the process of washing out and several potential discontinuities in the catalyst phase. Figure 6 shows a continuous fluid concentration profile following washout of the discontinuity while discontinuities continue to develop in an emerging patterned steady state. Figure 7 shows a transient pattern in which several of what appeared to be potential discontinuities in the early transients have disappeared by mass transfer and reaction. Figure 8 shows the final steady-state profile with only three surviving discontinuities. Figure 9 shows two steady states, one starting with \( v(x, 0) = 0.7 \sin^2 (40x) \) and another starting with

\[ \text{Fig. 5. Transient concentration profiles of the packed bed reactor at } t = 0.2 \text{ starting with } u(x, 0) = 0 \text{ and } v(x, 0) = 0.7 \sin^2 (40x). \]
Fig. 6. Transient concentration profiles of the packed bed reactor at \( t = 1.0 \) starting with \( u(x, 0) = 0 \) and \( v(x, 0) = 0.7 \sin^2(40x) \).

Fig. 7. Transient concentration profiles of the packed bed reactor at \( t = 5 \) starting with \( u(x, 0) = 0 \) and \( v(x, 0) = 0.7 \sin^2(40x) \).
Fig. 8. Transient concentration profiles of the packed bed reactor at $t = 50$ starting with $u(x, 0) = 0$ and $v(x, 0) = 0.7 \sin^2 (40x)$.

Fig. 9. Concentration profiles of two steady state patterns showing small differences in outlet concentrations.
v(x, 0) = 0.7 \sin^2(90x), which yield very little difference in the outlet concentration in the fluid.

Indeed, the initial conditions in the above demonstration is a highly contrived reactor state which brings us to the issue of how start-up conditions can be organized for a reactor in order to obtain a desired steady state pattern. This is considered in the next section.

7. START-UP STRATEGIES FOR PATTERNS

Since the number of asymptotically stable patterns is uncountably large, it is essential that appropriate initial conditions be provided so that desirable patterns may be achieved. As seen in the previous section, it is in general very difficult to determine a set of initial conditions which will create a given patterned steady state. In what follows, we restrict ourselves to initial conditions having the same discontinuities in the catalyst phase as that of the steady-state patterns. For practical reasons, we will confine ourselves to relatively coarse patterns.

To generate initial discontinuities in the catalyst phase, we must first maintain these discontinuities in the fluid phase. By the indirect interaction these discontinuities will be transferred to the catalyst phase. The discontinuities in the fluid phase can be produced by introducing multiple side feeds. Locations of these feeds are chosen to coincide with the locations of the discontinuities. The concentrations and flow rates of these feeds are adjusted so that the discontinuities in the catalyst phase exist at steady state. The reactor is divided into sections. In each section of the reactor, the catalyst-phase concentration is continuous and the mass balance equations have the same form with different dimensionless mass transfer coefficients to reflect the differences in feed concentrations and flow rates.

Given a pattern with

$$\text{Discont} \{V\} = \{x_1, x_2, \ldots, x_n\}$$

where $x_i$s are the reactor coordinates at which discontinuities occur. The whole reactor is now partitioned into $n + 1$ sections. In each of the sections, the following differential equations describe the time evolution of concentrations:

$$\frac{\partial u}{\partial t} + \frac{\partial u}{\partial x} + z_i(u - v) = 0$$

$$\frac{\partial v}{\partial t} - \beta(u - v) + \frac{Du_i\beta}{(1 + \sigma_i\beta)^2} = 0$$

the system of equation subject to the feed conditions for the fluid phase,

$$u(x_i, t) = u_i(t) = \frac{\sum_{j=0}^{i-1} F_j c(x_j, t) + F_i c_i}{\sum_{j=0}^{i} F_j c_0}$$

and the initial conditions in the fluid as well as in the catalyst phase,

$$u(x, 0) = 0, \quad v(x, 0) = 0,$$

for $x \in (x_i, x_{i+1}) \quad i = 0, 1, \ldots, n$
where $x_0 = 0$, $x_{n+1} = 1$ and

$$
\alpha_i = \frac{k_a a_i V_i}{\sum_{j=0}^{i-1} F_j}, \quad \theta_i = \frac{\varepsilon V_i}{\sum_{j=0}^{i-1} F_j}, \quad \beta_i = \frac{k_m a_i \varepsilon V_i}{\sum_{j=0}^{i-1} F_j} \tag{69}
$$

$$
\sigma_i = u_i(t) \sigma', \quad D_{ai} = \frac{e V_i}{\sum_{j=0}^{i-1} F_j} \tag{70}
$$

$V_i$ is the volume of the $i$th section of the reactor, and $F_{00}$, $c_0$ 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 chamber, respectively. $F_i$ and $c_i$ are selected so that only the appropriate branch of solution exists at steady state. Equation (67) is written with the convention that $\sum_{j=0}^{i-1} F_j = 0$.

We illustrate the start-up procedure to generate an initial condition to obtain the pattern depicted in Fig. 8. The dimensionless parameters have values chosen so that the pattern may be generated are shown in Table 1. The subscript $0$ shown in Table 1 is used to denote the parameter values without side feeds.

Table 1. Parameter values for the multiple feeds reactor to generate a pattern

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\alpha_i$</th>
<th>$\beta_i$</th>
<th>$D_{ai}$</th>
<th>$\sigma_i(t = \infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i = 0$</td>
<td>5</td>
<td>1</td>
<td>138</td>
<td>40</td>
</tr>
<tr>
<td>$i = 1$</td>
<td>1.51333</td>
<td>0.908</td>
<td>125.304</td>
<td>40.0</td>
</tr>
<tr>
<td>$i = 2$</td>
<td>0.1714285</td>
<td>0.1028571</td>
<td>14.19428</td>
<td>33.20867</td>
</tr>
<tr>
<td>$i = 3$</td>
<td>0.0953846</td>
<td>0.0572308</td>
<td>7.89785</td>
<td>38.049</td>
</tr>
<tr>
<td>$i = 4$</td>
<td>0.5812245</td>
<td>0.3487347</td>
<td>48.12538</td>
<td>10.60464</td>
</tr>
</tbody>
</table>

Figure 10 shows an early transient (for multiple feeds) with the inception of discontinuities in the catalyst phase. Figure 11 shows the steady-state eventually reached for the reactor with multiple feeds. The side feeds are removed in favor of the regular feed at the entrance; as planned the steady-state pattern eventually obtained is shown in Fig. 8.

8. CONCLUSIONS

We have established in this paper that spatial steady-state patterns can be obtained in a packed-bed reactor by exploiting multiplicity behavior of single catalyst particles. Each pattern involves discontinuities in the catalyst-phase profile caused by allowing neighboring particles to operate on different steady-state branches. It has emerged that an uncountable family of such patterns may be found, all of which may be stable as long as the jump occurs from one stable branch to another stable branch. Patterns involving any particle in an unstable branch are found to be unstable. The 'discontinuities' in the catalyst phase arise because of the simplicity of the model which allows no direct communication between the catalyst particles. If diffusive smoothing were allowed, the resulting patterns would be continuous but retaining fine variations, as pointed out by Arce and Ramkrishna (1991), depending on the magnitude of the diffusion coefficient.

Start-up conditions for achieving a specific steady-state pattern have been shown to be possible by instituting multiple reactor feeds at exactly the location of

![Fig. 11. Transient concentration profiles of the multiple feeds packed bed reactor at $t = 50$ with initial conditions of zero concentrations in fluid and catalyst phase.](image-url)
the discontinuities. While asymptotic stability of patterns has been established in this paper, we shall demonstrate in a follow-up paper that strong results are possible in this regard which are of particular significance to maintaining patterned reactor behavior. Thus, the problem of practical interest lies more in maintaining the reactor among a class of patterns rather than a single pattern, for the reactor output may not vary substantially for an entire class of patterns. Clearly, therefore, the practical issue is associated with a class of such patterns assuring a restricted range of product quality. This is also of particular significance to the control of a packed bed reactor to operate within a desired class of patterns.

The analysis in this paper has been restricted to isothermal reaction situations specifically for the sake of simplicity. Indeed, non-isothermal operation can give rise to a considerably richer variety of behavior which bears investigation in the future. Also, axial dispersion has been neglected in the model. In a follow-up paper which focuses on issues related to pattern classes, we also include axial dispersion. The discontinuous patterns continue to exist in the presence of axial dispersion although existence and stability criteria and stability behavior are somewhat different. Finally, the most important attribute of patterns presented in this paper is concerned with improving selectivity of reaction systems. An example was provided in the Introduction. Other reaction systems for which patterns can significantly improve the selective productivity of a desired product can also be identified.

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**NOTATION**

- $a_p$: area per unit volume of particle
- $a_B$: area per unit volume of bed
- $D_{tu}$: Damköhler number (= $kaV/F$)
- $c_0$: feed concentration of reactant at the entrance
- $c_{0,i}$: feed concentration of reactant at the $i$th 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 $i$th section
- $k_m$: mass transfer coefficient
- $k$: reaction rate constant
- $V$: total volume of reactor
- $V_i$: total volume of the $i$th section of the reactor

**Greek letters**

- $\chi$: dimensionless mass transfer coefficient
  ($= k_m a V/F$)
- $\beta$: dimensionless mass transfer coefficient
  ($= k_m a_p c V/F$)
- $\epsilon$: void fraction
- $\sigma$: adsorption desorption equilibrium constant
  ($= \sigma c_0$)

**REFERENCES**


