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REVIEW

Transversal Hot Zones Formation in Catalytic Packed-Bed Reactors

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Spatiotemporal patterns reported to form in the cross sections of packed-bed reactors (PBRs) may pose severe safety hazard when present next to the reactor wall. Understanding what causes their formation and dynamic features is essential for the rational development of design and control strategies that circumvent their generation. We review the current knowledge and understanding about the formation of these transversal temperature patterns. Simulations and model analysis revealed that the formation of the hot spots and their dynamics are sensitive to the assumed kinetic and reactor models. Under practical conditions, stable symmetry-breaking bifurcation to nonuniform states, from stable, stationary, transversally uniform states cannot be predicted by common PBR models with a rate expression that depends only on the surface temperature and concentration of the limiting reactant. However, analysis and simulations reveal that transient nonuniform transversal temperatures may emerge in an upstream moving traveling front under practical conditions. Microkinetic oscillatory reactions predict the formation of a plethora of intricate spatiotemporal temperature patterns and temperature front motions that are sensitive to the reactor operating conditions and properties such as diameter and initial conditions. The predicted temperature patterns may be rather intricate as a result of conjugation of several modes. The nonlinear coupling between the states at different axial positions, that is, the interaction among the local temperature and concentrations at different cross-sections of the bed, may explain the intricate conjugation of several modes and modulation of the observed spatiotemporal patterns. While some simulations predicted spatiotemporal pattern evolution in PBRs, there is a need to understand which reaction mechanisms may lead to their formation. Most previous simulations and analysis utilized two-dimensional reactor models. However, hot zones are three-dimensional structures, often very small, and difficult to detect in large reactors. A 3-D simulation, although tedious, is necessary to provide full information about the size, shape and dynamic features of small hot zones. Moreover, common PBR models may have to be modified to account for the impact of local states such as flow distribution and nonuniform packing. Verification of the various model predictions requires in situ measurements of 3-D hot zones.

1. Introduction

Heterogeneous catalysts are extensively used in chemical and petrochemical reactors and for reduction of environmental pollution generated by automobiles, electrical power stations, and other stationary engines. The most widely used heterogeneous catalysts are pellets of different shapes. Other types include honeycomb impregnated catalysts, catalytic nets, and fiber-cloth. It is usually assumed that the temperature and concentrations of the reactants at any transversal cross section of an adiabatic packed-bed reactor are uniform and azimuthally symmetric in a cooled PBR. However, various industrial and laboratory experimental observations revealed formation of nonuniform temperature and concentration in the reactor cross section.

Symmetry breaking leading to either spatial and/or spatiotemporal pattern formation is a ubiquitous phenomenon. Pattern formation has been observed in micro-, meso-, and macro-scales in a plethora of systems such as biological, physiological, chemical, electro-chemical, optical, and flow systems.[1−12] Various experimental and modeling approaches have been developed to detect and analyze the mechanisms leading to pattern formation. They are generated by the interaction among multiple time and spatial scales of the system states. Identification of these interactions enables a reduction of the number of degrees of freedom needed to capture the system behavior.

Most studies of pattern formation in chemically reacting systems are of homogeneous systems. There has been recently substantial research activity concerning pattern formation in heterogeneous catalytic and electrochemical systems, like wires, pellets, and packed bed reactors. Recent reviews of the dynamics of single catalytic wires and pellets have been presented by Luss[13] and Luss and Sheintuch[14] and of electrochemical systems by Kiss and Hudson[15] and Krischer.[16,17]

Various configurations of catalytic packed-bed reactors exist such as a tubular, reverse-flow, radial-flow, spherical-flow, and wall (muffler) reactors. A special variation is the diesel particulate filter (DPF) in which the catalyst is deposited on the walls of the filtering channels.[18] In the reactors, two phases, solid and fluid, interact with each other, and their interplay governs the performance of the reactor.

It is well established that either stationary or moving hot zones and temperature fronts may form in the axial (flow) direction of an adiabatic or cooled PBR. We briefly review some of these studies. Wicke's group, while studying moving temperature

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fronts during the catalytic oxidation of CO,[19] observed that depending on the operating conditions the front wave moved either in the upstream or downstream direction. Puszynski and Hlavacek[20,21] observed both periodic and aperiodic traveling hot spots in a catalytic packed-bed reactor during CO oxidation on a Pt/alumina catalyst. These waves were apparently caused by the dynamic behavior of the individual catalytic particles that were either oscillatory or excitable. Wicke and Onken[22,23] observed periodic oscillations of a transversal hot zone in a PBR during the oxidation of either CO or ethylene. They attributed this motion to the oscillatory reaction rate in the upstream section of the reactor. Rovinski and Menzinger[24] observed a periodic sequence of traveling concentration pulses when they conducted a Belousov−Zhabotinsky reaction in a catalytic PBR under excitable conditions.

Theoretical studies of creeping temperature fronts were conducted by Frank-Kamenetski,[25] Wicke and Vortmeyer,[26] and Kiselev and Matros.[27] Morbidelli et al.[28] presented an extensive review of the axial hot spot formation and dynamics. The formation of a moving high-temperature peak following a sudden cooling of the reactor, that is, the wrong-way behavior, was studied among others by Crider and Foss,[29] Pinjala et al.,[30] Chen and Luss,[31] and Bos et al.[32] Qualitative classification of axial patterns predicted by homogeneous or heterogeneous models of an adiabatic PBR catalyzing a first-order exothermic reaction subject to reversible activity changes was attempted by Barto and Sheintuch[33] and Sheintuch and Nekhamkina[34,35] (see also Luss and Sheintuch[14]): The main simulated patterns are of stationary or oscillatory front solutions and oscillatory states in which the front quickly sweeps the whole reactor. The behavior can be predicted by the sequence of phase planes spanned by the reactor. Keren and Sheintuch[36] considered the behavior of a catalytic converter during CO oxidation on a Pt catalyst using an oscillatory microkinetics model. They found that due to the almost synchronous nature of the oscillations, a good estimate of the oscillatory behavior domain of the distributed system could be obtained using a lumped model of the catalyst, ignoring convection, and using the feed temperature and reactant concentration.

The present review is concerned mainly with the formation of transversal temperature patterns in a PBR. A hot region present next to the reactor wall can weaken its mechanical strength and lead to cracks. The subsequent release of the hot, high pressure reactants may lead to an explosion. Thus, in addition to intrinsic academic interest, hot zones evolution is of practical importance as it can pose a safety hazard. Understanding which operating conditions and reactions may lead to spatiotemporal pattern formation is essential for the development of control strategies that circumvent them.

2. Experimental Observations of Hot Zones in Packed Bed Reactors

Local hot spots have been observed in the cross section of various catalytic packed-bed reactors. Barkelew and Gambhir[37] observed fused catalyst particles (clinkers) while replacing the catalyst from a hydro-desulfurization trickle-bed reactor. Wicke and Onken[22,23] reported a difference in the temperature at two locations at the same radial position of a cross-section of a PBR; that is, azimuthal symmetry did not exist. Boreskov et al.[38] and Matros[39] observed hot zones at the bottom of a down flow packed bed reactor during the partial oxidation of isobutyl alcohol on copper oxide catalysts (Figure 1). The change in the patterns upon repacking of the PBR indicated that the hot zones were caused by nonuniform packing and not due to inherent

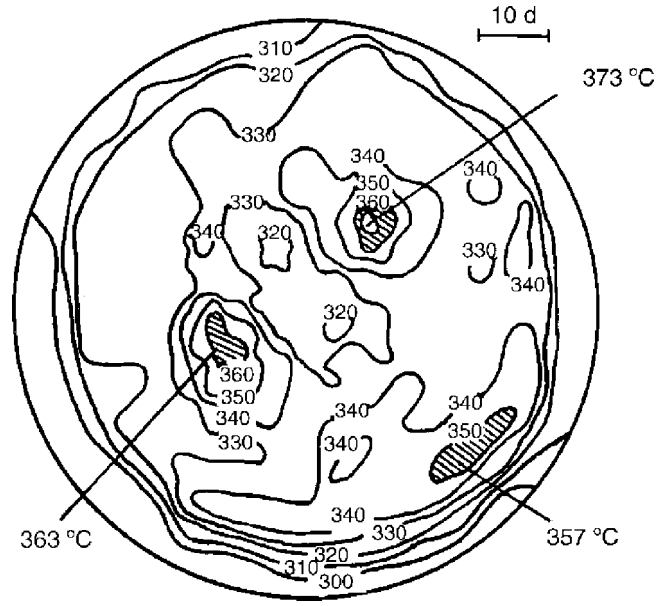

Figure 1. Hot zone formation at the bottom of a down flow packed bed reactor during the partial oxidation of isobutyl alcohol on copper oxide catalysts. Adapted with permission from ref 39. Copyright 1985 Elsevier.

properties of either the reaction or the reactor. Most laboratory in situ measurements of transversal hot regions were conducted using infrared (IR) imaging. Unfortunately, this technique, first used by Pawlicki and Schmitz,[40] provides only two-dimensional information. No experimental data exists about the 3-D geometry of the hot zones.

The formation and motion of hot zones during CO oxidation were studied, in a radial-flow reactor,[41] a shallow packed bed reactor,[42−44] and catalytic glass-fiber cloth reactor.[45,46] Transversal hot regions formed following very slow cooling of a fully ignited uniform state. The reactor temperature affected the size, shape, and the location of the hot spots. Typical transversal motions[43,44] in a shallow reactor were (a) breathing motion, a periodic contraction and expansion of hot zones; (b) antiphase motion, a periodic switching of a hot zone between two diametrically opposite locations; (c) band motion, a periodic cross-movement of a high temperature band across the bed; and (d) a rotating hot zone motion.

Digilov et al.[46] observed, during CO oxidation on a catalytic glass-fiber disk-shaped cloth, a rapid breathing motion (Figure 2,II) with a period of ∼1 min. This period is much shorter than the ∼10−60 min period observed in a shallow packed bed (Figure 2,I). Theoretical studies[46] suggest that the breathing motion is induced by the fixed-temperature boundary conditions at the disk perimeter.

Studies by Sundarram et al.[47] and modeling and simulations by Middya et al.[48] indicated that the hot zone motions were strongly influenced by global-coupling, that is, by the interaction between the unconverted reactants and the catalytic pellets on top of the bed. This global coupling may induce and stabilize motions which would not be stable in its absence.

Marwaha et al.[50] conducted CO oxidation in a radial flow reactor. They found that the rate of effluent removal from the exterior space surrounding the reactor affected the qualitative features of the temperature patterns on the catalytic surface. This is a clear indication of interaction between the catalytic surface and the unconverted reactants in the effluent stream. Thermal patterns during CO oxidation over Pd supported on a glass fiber catalytic cloth, rolled into a tube of 20 mm diameter and 80

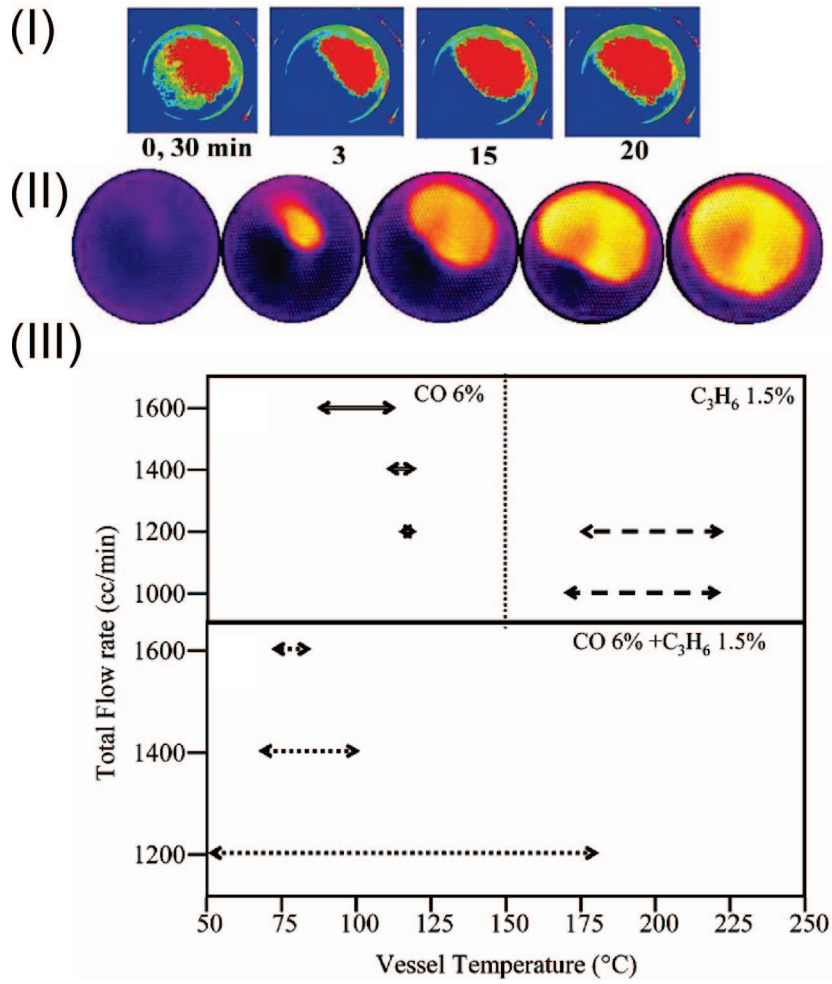

Figure 2. Breathing motion snapshots over one period (I) on top of shallow packed-bed reactor with a period of about 20 min and (II) on glass-cloth reactor with a period of about 40 s. Adapted with permission from refs 44 and 46, respectively. Copyright 2004 Elsevier and American Institute of Chemical Engineers. (III) Range of vessel temperature over which nonuniform states existed at different flow rates for single reactant feed (CO or C_3H_6) and for mixture (CO + C_3H_6). Adapted with permission from ref 52. Copyright 2007 American Chemical Society.

mm long, were studied by Digilov et al.[51] by IR thermography. With flow in the main axial direction and through the tube surface they observed a periodic motion of a pulse, which was generated downstream and propagated upstream. A stationary hot-spot was observed with flow in the main axial direction, parallel to the surface. Heat losses through the sapphire window destroyed the axisymmetric conditions.

Both transport and reaction kinetics affect the pattern formation in a reactor. It is experimentally difficult to isolate the impact of individual rate processes. Sundarram and Luss[52] observed striking differences in the pattern dynamics during the oxidation of a single reactant (either CO or propylene) and of a mixture (CO and propylene) in the same reactor. For example, using the reactants mixture the frequency of the oscillations was 20 times higher than when using only CO and twice higher than when the feed contained only propylene. Moreover, the hot zones existed over a wider range of reactor temperatures when using the mixture than when the feed contained only one reactant (Figure 2,III). These experiments conducted in the same bed suggest that the reaction kinetics has a dominant effect on the dynamics of the hot zones. Pinkerton and Luss[53] observed hot zone oscillatory motion in the shallow reactor during the hydrogenation of ethylene and acetylene mixtures under conditions that the reaction could lead to rate oscillations. The experiments confirmed the predictions by Viswanathan and Luss[54] that oscillatory kinetics may lead to hot zone formation.

3. Modeling of Transversal Hot Zones in Packed Bed Reactors

Describing three-dimensional hot zones in a packed bed reactor requires use of a three-dimensional, two-phase reactor model, which accounts for the variations in the temperature and reactant concentrations in both solid and fluid phases.[55] The analysis of such a model is very intricate. Recent kinetic studies, backed by surface-science understanding, suggest that local patterns require in many reactions the use of a microkinetic model that accounts in addition to the gas and solid phases also for the adsorbed phase. Previous studies have been conducted using limiting forms of the general model, using one or more of the following simplifications:

1. Use of a single-phase *pseudohomogeneous* model[55] instead of a two-phase model. Vortmeyer and Schaeffer[56] showed that this model is adequate using a proper expression for the effective thermal conductivity. Balakotaiah and Dommeti[57] showed that this relationship is not always valid.

2. Use of a *shallow reactor* model, the length of which is very small compared to that of the transversal direction. Balakotaiah et al.[58] presented a systematic approach for

developing such a model and applied it to a study of a catalytic monolith reactor. Another model is a two-dimensional network of connected cells.[59,60]

3. A three-dimensional model may be reduced to a two-dimensional one by ignoring the azimuthal dependence. This, of course, eliminates patterns that do not have an azimuthal symmetry, like rotating patterns.

4. Several studies describe patterns that emerge on the surface of a thin annular cylindrical reactor. These models that neglect radial gradients may predict the behavior of a packed bed when rotating spin waves form on the surface. They cannot predict patterns that form in the cross section of a PBR.

In a somewhat similar problem, Ivleva and Merzhanov[61] (and references therein) compared the transversal temperature profile in a 3-D solid reactants cylinder during self-propagating synthesis with that on the surface of the cylinder. They noted a similarity in the case of spin-waves but pointed out that thin cylindrical models may fail to predict the steady-state multiplicity of the 3-D models and cannot predict the details of the transversal behavior.

We review below the prediction of the hot zone evolution and dynamics by various limiting models. The patterns that evolve depend on the geometry and on the underlying kinetics. A large variety of kinetic models have been suggested, and a general classification of these is not possible. We discriminate, however, between macro-kinetic models, that account only for continuous gas-phase (and solid-phase) concentrations and temperatures, and microkinetics models that account in addition for the impact of localized (nondiffusing) surface species. Previous studies showed that a propagating temperature front may emerge on a long catalytic wire, ring, or a fixed bed using macro-kinetic rate expressions. A bistable microkinetic model may predict, under strictly isothermal fixed fluid-composition conditions, infinitely many solutions in a one-dimensional (1-D) nondiffusive system, as a discontinuity in the surface state may occur at any spatial position.[62] Obviously, surface diffusion destroys many of these solutions. Since supported catalysts consist of very small (nm size) disjoint crystallites, the intercrystallite communication is negligible under isothermal fixed (gas) composition conditions. These stationary fronts will be sustained when the thermal effects, which are always present at atmospheric-pressure oxidation, are weak.[62] However, strong thermal effects will destroy them. The implications of this behavior on pattern formation are described below.

The mathematical tools for predicting the emergence of transversal patterns in reaction−diffusion−convection are at infancy. The convection strongly affects the structure and features of the solutions. This is especially true for macro-kinetic models, where patterns disappear at sufficiently high flow rates. In contrast, certain microkinetic models predict that patterns may form even under high flow rates.

The few existing qualitative analyses of pattern formation are of relatively simple activator−inhibitor diffusion−reaction systems. Most patterns were predicted for complex microkinetic systems described by three or more state variables. Since analytical predictions of evolving patterns are not attainable, linear analysis may be used to predict the spatio-temporal behavior emerging in the vicinity of the numerically computed neutral stability curves. Numerical continuation may then be used to find patterns further away. When the velocity of a planar front on a thin catalytic cylinder is approximately known, nonlinear analysis can be used to predict when the front looses its symmetry and becomes nonplanar.

4. Hot Zone Formation and Dynamics in a Uniformly Active Shallow Reactor

A shallow reactor is the simplest asymptotic model of an adiabatic packed-bed reactor that may exhibit stationary and spatio-temporal pattern formation. This model describes a thin packed bed reactor the height of which is very small compared to its radius. The model is obtained by axial averaging of the state variables in the flow direction using a Liapunov-Schmidt reduction.[63] Details of the procedure are presented by Viswanathan.[64] The shallow reactor may also be viewed as a two-dimensional circular array of communicating catalyst particles (radial, ξ; azimuthal, ϕ).

4.1. Kinetics with Monotonic Dependence on the Temperature. Schmitz and Tsotsis[60] studied the possible evolution of hot zones in a circular array of interacting catalysts (cell model). They found that a stationary pattern may form only when the rate of species exchange between the cells exceeded that of heat exchange. Balakotaiah et al.[65] predicted temperature pattern formation in a PBR under the same assumption. These predictions are not applicable to industrial reactors in which the transversal heat dispersion always exceeds that of the species.[66]

Viswanathan et al.[67] used linear stability analysis to investigate the formation of stationary hot zones by a pseudohomogeneous model of a shallow reactor, that is,

$$\frac{\partial\theta}{\partial\tau}=\frac{1}{Le_{\mathrm{PH}}}\left[\frac{1}{Pe_{\perp}^{h}}\nabla_{\perp}{}^{2}\theta-\theta+\beta(\theta,\chi)\right] \tag{1}$$

$$\frac{\partial\chi}{\partial\tau}=\left[\frac{1}{Pe_{\perp}^{m}}\nabla_{\perp}{}^{2}\chi-\chi+(\theta,\chi)\right] \tag{2}$$

where θ and χ denote the axially averaged temperature and conversion and $\mathbb{R}(\theta,\chi)$ the reaction term that depends only on the temperature and limiting reactant conversion. By exposing the transversally uniform steady states to inhomogeneous perturbations $\underline{\omega}_{mn}(\xi,\phi)=\underline{\omega}J_m(\mu_{mn}\xi)e^{im\phi}$, they showed that the following condition has to be satisfied at a transition from a stable uniform to stationary nonuniform state:

$$\left(1+\frac{\mu_{mn}{}^{2}}{Pe_{\mathrm{PH},\perp}^{h}}\right)Le_{\mathrm{PH}}\{\det(\mathbb{L}_1)\}+\left(\frac{\mu_{mn}{}^{2}}{Pe_{\mathrm{PH},\perp}^{h}}\right)^{2}=(1-\mathscr{M}_{\mathrm{PH}})\left[\left(1+\frac{\mu_{mn}{}^{2}}{Pe_{\mathrm{PH},\perp}^{h}}\right)Le_{\mathrm{PH}}\{\det(\mathbb{L}_1)\}+\frac{\mu_{mn}{}^{2}}{Pe_{\mathrm{PH},\perp}^{h}}\beta\frac{\partial\mathbb{R}}{\partial\theta}\Big|_{(\theta,\chi)_{ss}}\right] \tag{3}$$

m and n in the spatially inhomogeneous perturbations are the azimuthal and radial mode numbers, and $e^{im\phi}$ and $J_m(\mu_{mn}\xi)$ are the corresponding eigenfunctions. As a result of the no-flux boundary condition, the transverse eigenmode μ_{mn} satisfies the relation[65]

$$\frac{\mathrm{d}J_m(\mu_{mn}\xi)}{\mathrm{d}\xi}\Big|_{\xi=1}=mJ_m(\mu_{mn})-\mu_{mn}J_{m+1}(\mu_{mn})=0 \tag{4}$$

Table 1. First Nine Eigenmodes Satisfying Equation 4

no.	m	n	μ_{mn}
1	1	1	1.8412
2	2	1	3.0542
3	0	1	3.8317
4	3	1	4.2012
5	4	1	5.3176
6	1	2	5.3314
7	5	1	6.4156
8	2	2	6.7061
9	0	2	7.0155

Equation 4 has an infinite number of real solutions[68] (eigenfunctions), each corresponding to a particular Bessel-Fourier eigenmode. The first nine transversal eigenmodes are listed in Table 1, and snapshots of the first six eigenmodes are shown in Figure 3,I.

The lhs of eq 3 is positive for a stable uniform steady state as the Jacobian $\det(\mathbb{L}_1) > 0$ for all stable uniform states. On the other hand, the rhs of eq 3 is negative when the reaction rate is a monotonic increasing function of the temperature, that is, $\partial \mathbf{R}/\partial\theta > 0$, and the ratio of the heat dispersion to mass

$$\mathscr{M}_{\mathrm{PH}} = \frac{Pe^{m}_{\mathrm{PH},\perp}}{Pe^{h}_{\mathrm{PH},\perp}} = \frac{\lambda_{\mathrm{PH},\perp}}{D_{\mathrm{PH},\perp}(\rho C_p)} \tag{5}$$

exceeds unity. Thus, *symmetry breaking bifurcation cannot lead to the emergence of a stable nonuniform state from a stable uniform steady state*.

Viswanathan and Luss[69] investigated the prediction of hot zone evolution by a two-phase model of a shallow packed bed reactor in which the transversal fluid mass dispersion is much smaller than the transversal solid heat dispersion, that is,

$$\mathscr{M}^{*}_{\mathrm{TP}} = \frac{Pe^{m}_{f,\perp}}{Pe^{h}_{s,\perp}} = \frac{Pe^{m}_{f,\perp}}{Pe^{h}_{f,\perp}}\left(\frac{(1-\varepsilon)\lambda_{s,\perp}}{\varepsilon\lambda_{f,\perp}}\right) = \frac{(\lambda_{f,\perp}/(\rho C_p)_f)}{D_{f,\perp}}\left(\frac{(1-\varepsilon)\lambda_{s,\perp}}{\varepsilon\lambda_{f,\perp}}\right) >> 1 \tag{6}$$

They proved that a bifurcation to a stationary nonuniform state from a stable stationary transversally uniform state cannot occur when the kinetic model depends only on the surface temperature and concentration of the limiting reactant. However, as nonuniform states were reported to exist, the above conclusion implies that the mathematical model has to be modified and account for additional and/or different rate processes. One such option described below (section 4.2) is the use of a microkinetic rate expression.

4.2. Microkinetic Oscillatory Kinetics. In homogeneous reacting media, spatiotemporal structures with rich dynamics may emerge due to the interaction of oscillatory kinetics with species and/or thermal dispersion. Several mechanisms explaining these dynamic features have been proposed[70,71] including the classical Turing's activator−inhibitor mechanism. Experimental observations suggest that spatiotemporal temperature

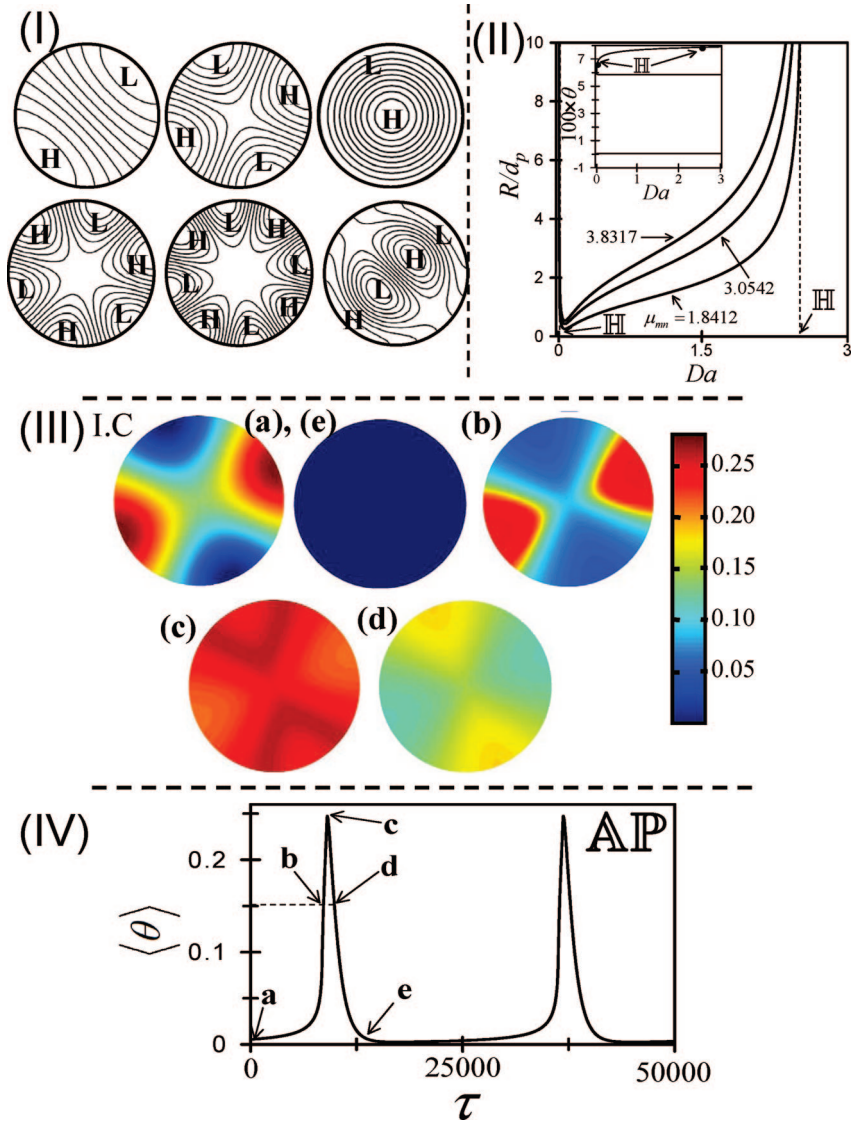

Figure 3. (I) First six eigenmodes corresponding to eq 4. (II) Oscillatory neutral stability curves for the first three transversal eigenmodes while using surface coverage kinetic model (eqs 7 and 8). (III) Snapshots of temperature patterns during one period of an antiphase motion (AP) in a shallow reactor. (IV) Time series of antiphase motion (AP). Adapted with permission from ref 54. Copyright 2006 American Institute of Chemical Engineers.

patterns may evolve in shallow PBRs while conducting reactions that may exhibit oscillatory behavior.[44,52] Rate oscillations can be predicted by kinetic models that account, in addition to the temperature and concentrations, for surface variables such as the temporal state of the surface,[72,73] subsurface reactant concentration,[74] or fractional surface coverage.[75,76] Such microkinetic models have been used to explain the observed oscillatory behavior of various reactions, such as CO oxidation,[76] ethylene hydrogenation,[77] and CO/NO reaction.[78] While atmospheric-pressure CO oxidation is governed by the formation and removal of the subsurface oxygen, ethylene hydrogenation on palladium catalysts proceeds via adsorption of several species such as ethylidene and ethylidyne which block active sites from participating in the reaction. Thus, the oscillatory CO oxidation is attributed to a mechanism different from that during the ethylene hydrogenation.

Microkinetic Models I and III below describe oscillations in CO oxidation, by incorporating dissociative oxygen adsorption at a rate that exponentially declines with oxygen surface (Model I) or subsurface (Model II) coverage. The latter model accounts separately for the two species. Both models can admit oscillatory solutions under isothermal conditions. In Model II and IV the surface activity undergoes deactivation at high temperatures and reactivation at low temperatures and the temperature and surface activity play the roles of activator and inhibitor, respectively; such isothermal systems cannot exhibit multiple or oscillatory solutions.

We describe below several studies that employed microkinetic models:

4.2.1. Microkinetic Model I. Viswanathan and Luss[54] recently showed that spatiotemporal patterns can be predicted by a pseudohomogeneous model, under a practical range of parameters when the reaction rate is described by an oscillatory microkinetic mechanism. They illustrated this for the bimolecular reaction $aA(g) + bB(g) \rightarrow cA_{a/c}B_{b/c}(g)$ which occurs by the following surface coverage mechanism

$$\mathrm{A}(g) + (\mathrm{S}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{A{-}S})$$

$$\mathrm{B}_2(g) + 2(\mathrm{S}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2(\mathrm{B{-}S})$$

$$(\mathrm{A{-}S}) + (\mathrm{B{-}S}) \overset{k_3}{\rightarrow} (\mathrm{AB})(g) + 2(\mathrm{S}) \quad (7)$$

Denoting by x, y, and θ the surface concentrations of species A, B, and the temperature, respectively, the corresponding microkinetic model is[76]

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = \mathbb{G}_1(x, y, c, \theta) - \mathbb{R}(x, y, \theta) \quad (8)$$

$$\frac{\mathrm{d}y}{\mathrm{d}\tau} = \mathbb{G}_2(x, y, \theta) - \mathbb{R}(x, y, \theta) \quad (9)$$

$$\mathbb{G}_1(x, y, c, \theta) = Da_1 \exp\left(\frac{\gamma_1\theta}{1+\theta}\right)c(1-x-y) - Da_{-1} \times \exp\left(\frac{\gamma_{-1}\theta}{1+\theta}\right)x \quad (10)$$

$$\mathbb{R}(x, y, \theta) = Da \exp\left(\frac{\gamma_3\theta}{1+\theta}\right)xy \exp(-\mu y) \quad (11)$$

$$\mathbb{G}_2(x, y, \theta) = Da_2 \exp\left(\frac{\gamma_2\theta}{1+\theta}\right)(1-x-y)^2 - Da_{-2} \exp\left(\frac{\gamma_{-2}\theta}{1+\theta}\right)y^2 \quad (12)$$

where c is a dimensionless concentration $1 - \chi$, where χ is the conversion in eq 2. This surface coverage model (eqs 8 and 9) predicts isothermal rate oscillations for some kinetic parameters. Figure 3,II shows the neutral stability curves, bounded between two Hopf bifurcations, for the first three transversal modes obtained using linear stability analysis of eqs 1, 2, and 8–12.[54] The cup-shaped neutral stability curves that bound the parameters for which a symmetry-breaking bifurcation may lead to formation of spatiotemporal patterns are bounded between two Hopf bifurcations. The neutral stability curve of any mode is nested within that of the lower mode suggesting the possibility that a large number of different types of patterns and mixed mode solutions exist for a sufficiently large reactor diameter. Spatiotemporal patterns such as band ($\mathbb{B}$), antiphase ($\mathbb{AP}$), and target ($\mathbb{T}$) motions, obtained using as initial conditions the first three modes, exist as well as transversally uniform oscillating states in the region of steady-state multiplicity of the transversally uniform states. Snapshots of the periodic $\mathbb{AP}$ motion are shown in Figure 3,III, while the time series of the $\mathbb{AP}$ motion are shown in Figure 3,IV. A principal component analysis (PCA)[79] revealed that the motions preserved the qualitative features of the initial conditions, that is, the number of hot/cold zones of the initial conditions.

4.2.2. Microkinetic Model II. Transversal patterns may be generated by microkinetic models based on rather different mechanisms. For example, Sundarram et al.[80] using a pseudohomogeneous packed-bed reactor model reported formation of spatiotemporal patterns using a kinetic model of Bos et al.[77] that accounted for a blocking-reactivation of the active sites

$$\frac{\partial\Theta_{BL}}{\partial\tau} = Da_{BL}\mathbb{G}_1(\theta, \Theta_{BL}) - Da_{RE}\mathbb{G}_2(\theta, \Theta_{BL}) \quad (13)$$

where

$$\mathbb{G}_1(\theta, \Theta_{BL}) = \exp\left[\frac{\gamma_{BL}\theta}{1+\theta}\right](1-\Theta_{BL}), \quad \mathbb{G}_2(\theta, \Theta_{BL}) = \exp\left[\frac{\gamma_{RE}\theta}{1+\theta}\right]\Theta_{BL} \quad (14)$$

Sundarram et al.[80] proved that a bifurcation from a uniform stable state to a stationary transversal hot zone cannot be predicted by the pseudohomogeneous model using this blocking−reactivation oscillatory kinetic model. Sundarram et al.[80] found that using the surface blocking model an $\mathbb{O}(2)$ symmetry-breaking Hopf bifurcation can lead to a transition from a uniform steady state to a spatiotemporal pattern. The oscillatory neutral stability curve, that is, the locus of the oscillatory neutral stability points, bounds the parameter region in which transversal nonuniform states may exist. The cup shaped neutral stability curve for any transversal mode is nested within that of the lower transversal mode. The neutral stability curves (Figure 4,I) and pattern simulations reveal that the stable simple spatiotemporal motions (involving one dominant mode) and complex motions (involving multiple dominant modes) may form even when only a unique transversally uniform steady state exists. Snapshots of the complex motions are shown by Sundarram et al.[80] Complex motions have qualitatively similar time periods due to mode interactions (Figure 4,II).

In packed-bed reactors, the ratio of transversal thermal dispersion time to the reaction time, that is,

$$\frac{t_d}{t_R} = DaPe_p^h\left(\frac{R}{d_p}\right)^2 \quad (15)$$

plays a crucial role in synchronizing the spatiotemporal patterns. The simulations revealed that the larger the reactor diameter, the more intricate the spatiotemporal patterns can be. For $R/d_p = 100$ both simple and complex band motions (Figure 5,I) were obtained in addition to a uniform oscillating state. Similarly,

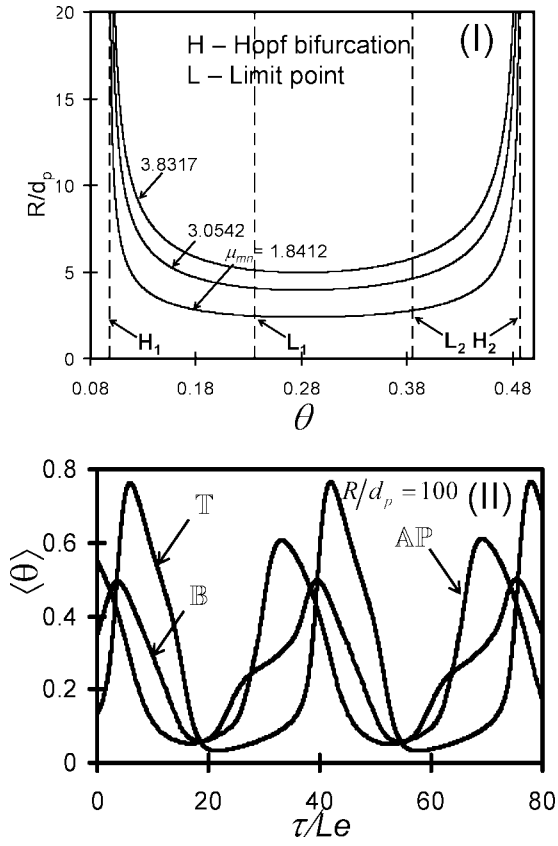

Figure 4. (I) Oscillatory neutral stability curves for the first three transversal modes using the blocking−reactivation[77] kinetic mechanism. (II) Time series of complex motions having qualitatively similar time periods. Adapted with permission from ref 80. Copyright 2007 American Institute of Chemical Engineers.

complex target motions (not shown) in this case involved rings of the hot/cold zones moving both inward and outward. In contrast, during simple target motion the rings moved either outward or inward. The complex motion observed at large values of R/d_p was caused by conjugation of the features of several modes. It is rather difficult to determine the qualitative features of the complex motions by inspection. The task may be simplified by decomposing the motion into orthogonal time-independent spatial modes and time-dependent amplitudes using PCA.[79] The PCA at large reactor diameters (Figure 5,II) showed this possibility of interaction among modes not dominant at low reactor diameters.

4.2.3. Microkinetic Model III. Nekhamkina and Sheintuch[81] studied pattern formation in a shallow bed or a cloth catalyst, subject to no flux conditions at the perimeter, using the oscillatory microkinetic model of CO oxidation. They considered various cases of the reactant mass balance on top of the bed to simulate the experimental conditions of the disk-shaped cloth reactor used by Digilov et al.[46] and to check the sensitivity of the predictions. The kinetic model and associated parameters were those proposed by Slinko and Jaeger[71] based on experimental data. It accounts for CO adsorption and desorption, for oxygen dissociative (and irreversible) adsorption, and for reaction between the two surface species (that is, the mechanism in eq 7, where x and y denote the fractional surface coverage by CO (A−S) and oxygen (B−S)), coupled with a slow, reversible subsurface oxidation

$$\frac{dx}{dt} = k_1 P_{CO}(1 - x - y) - k_{-1}x - k_3 xy - [k_5 xz] \quad (16a)$$

$$\frac{dy}{dt} = k_2 P_{O_2} e^{-\alpha z}(1 - x - y)^2 - k_3 xy - [k_4 y(1 - z)] \quad (16b)$$

$$\frac{dz}{dt} = k_4 y(1 - z) - k_5 xz \quad (16c)$$

where the k_iʼs are temperature dependent and z is the concentration of oxygen in a subsurface layer. The temperature T satisfies an enthalpy balance of the form of eq 1 with $\mathbb{R} \sim k_3 xy$. Assuming a fixed P_{CO} on top of the cloth, linear stability analysis of the four variables (x, y, z, T) model revealed that, close to the upper P_{CO} Hopf bifurcation, the model can predict moving waves with an intrinsic length scale shorter than 1 mm. The bifurcation point from a homogeneous solution on a ring was determined by linear stability analysis assuming a perturbation of the form $\exp(\sigma t + iks)$, where s is the spatial coordinate and k is the wavenumber. The neutral stability curve, when plotted versus k, revealed, within certain domains, a clear minimum, which corresponds to moving waves (that is, complex σ) with a most unstable wavenumber. The transversally homogeneous solution looses stability at this boundary, and the resulting pattern is quite insensitive to initial conditions. Simulations on a disk verified that such patterns may be realized in experimental-size reactors. Simulations of a five-variable model that assumes a well-mixed gas phase on top of the disk-shaped catalyst and using parameters known to induce moving waves showed that under high feed rate (or weak long-range coupling) the system maintains the same intrinsic length scale and produces imperfect spiral waves (Figure 6b,c). The initial conditions were inhomogeneous, but because the homogeneous

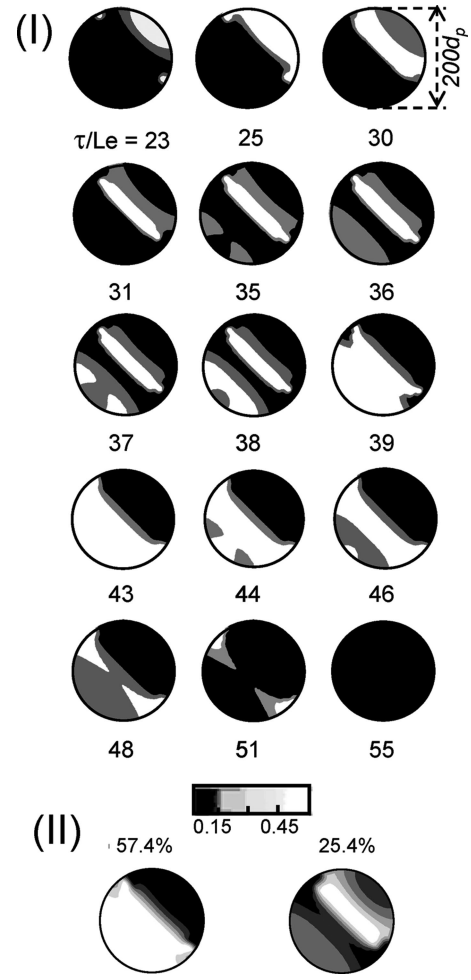

Figure 5. Snapshots of the temperature patterns at different times during one period of complex band motions (I). The corresponding principle component modes (II). Adapted with permission from ref 80. Copyright 2007 American Institute of Chemical Engineers.

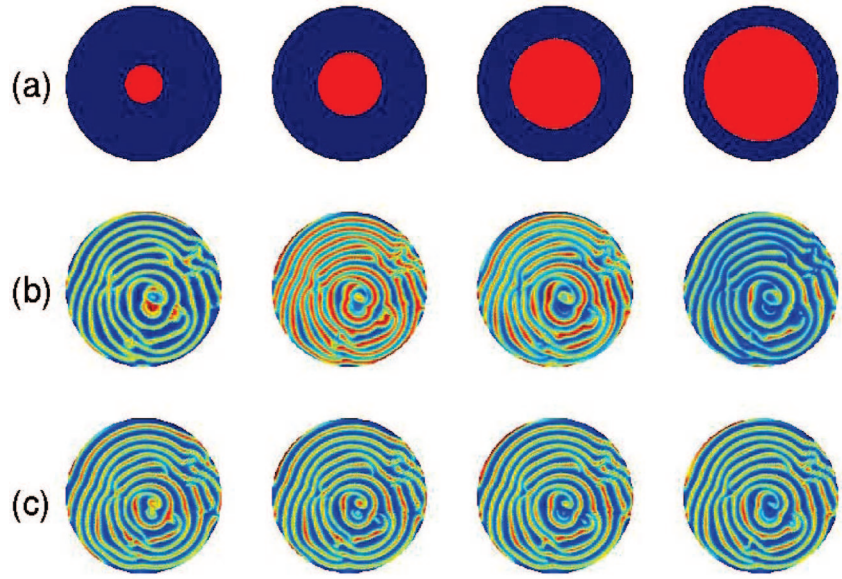

Figure 6. Typical simulated patterns of surface temperature in a shallow disk-shaped bed (or catalyst) using oscillatory microkinetics corresponding to CO oxidation (eq 16a) coupled with energy and mass balances. Each row represents equally intervaled snapshots of the temperature during one quasi-period. Simulations in row (a) were conducted with fixed-temperature boundary conditions and $P_{CO,in} = 300$ Pa, $T_g = 493$ K. The multiwave patterns simulations in rows b and c were conducted with no-flux boundary conditions, $P_{CO,in} = 100$ Pa, $T_g = 480$ K with either moderate (b) or high (c) convection velocity. Adapted with permission from ref 81. Copyright 2005 American Institute of Physics.

state is unstable under these conditions, the system was not highly sensitive to the initial conditions producing the same qualitative patterns for all initial conditions tested. Under low feed rates (that is, high conversions) the intrinsic scale disappears and the disk exhibited homogeneous oscillations (not shown). Imposing fixed temperature at the disk perimeter, which imitate the experimental conditions of Digilov et al.,[46] produced a breathing target pattern (Figure 6a) similar to that observed in the experiments (Figure 2,II).

5. Hot Zone Formation in Uniformly Active Long Reactors

It is of practical importance and academic interest to determine if and what types of transversal hot zones may form in the cross section of a long PBR. This requires determining the hot zone dependence on three directions, namely, axial (η), radial (ξ), and azimuthal (ϕ). The singularity theory suggests that the presence of symmetry in a model simplifies predicting the qualitative features of a given problem and helps identify (via the eigenfunctions of the underlying linear operator) the possible solutions near a symmetry-breaking bifurcation.[82] In classical reaction−diffusion systems, symmetry exists in all dimensions. In packed-bed reactors, no symmetry exists in the axial (flow) direction. The base state solution (in the axial direction) is *nonuniform and nonsymmetric* due to the unidirectional flow. In contrast, the base state solution is uniform in every cross-section of the reactor, and an $\mathbb{O}(2)$ symmetry, reflection and rotation, is preserved. Thus, $\mathbb{O}(2)$ symmetry-breaking bifurcation(s) may lead to transversal stationary spatial and spatiotemporal temperature patterns. We review below attempts to predict the transversal temperature pattern in long packed bed reactors for different classes of rate expressions.

5.1. Steady Transversal Front Patterns. We review below the conditions that enable transversal pattern formation using either a simple thermo-kinetic model or a microkinetic model.

5.1.1. Reaction Rates which Increase Monotonically with Temperature. Several studies attempted to predict formation of the transversal hot zones using rate expressions with monotonic dependence on the temperature. Balakotaiah et al.[65] conducted linear stability analysis of a pseudohomogeneous model of an adiabatic reactor in which a bimolecular reaction proceeds via the Langmuir−Hinshelwood mechanism. The analysis predicted that a transversally uniform stable state may lead to evolution of a nonuniform state and that a larger number of stationary nonuniform states may form as the diameter of the reactor is increased (Figure 7). Yakhnin and Menzinger[66] pointed out that the analysis by Balakotaiah et al.[65] was based on an unrealistic assumption that in a packed bed reactor the transversal effective heat dispersion was smaller than that of the species. That ratio between the dispersion of the autocatalytic and inhibitor state variables is the same as that enabling stationary pattern formation in two variable homogeneous reaction−diffusion systems.[1,83]

Viswanathan et al.,[67] using linear stability analysis, constructed the bifurcation diagrams of 2-D and 3-D stationary nonuniform states that may form in a long adiabatic packed-bed reactor described by a two-phase model

$$\frac{\partial \theta_f}{\partial \tau} = \frac{1}{\varepsilon}\left[\frac{1}{Pe^h_{f,\perp}}\nabla_\perp{}^2\theta_f + \frac{1}{Pe^h_{f,a}}\frac{\partial^2\theta_f}{\partial\eta^2} - \frac{\partial\theta_f}{\partial\eta} + St_h(\theta_s - \theta_f)\right] \quad (17)$$

$$\frac{\partial \chi_f}{\partial \tau} = \frac{1}{\varepsilon}\left[\frac{1}{Pe^m_{f,\perp}}\nabla_\perp{}^2\chi_f + \frac{1}{Pe^m_{f,a}}\frac{\partial^2\chi_f}{\partial\eta^2} - \frac{\partial\chi_f}{\partial\eta} + \mathbb{R}(\theta_s,\chi_f)\right] \quad (18)$$

$$\frac{\partial \theta_s}{\partial \tau} = \frac{1}{(Le-\varepsilon)}\left[\frac{1}{Pe^h_{s,\perp}}\nabla_\perp{}^2\theta_s + \frac{1}{Pe^h_{s,a}}\frac{\partial^2\theta_s}{\partial\eta^2} - St_h(\theta_s - \theta_f) + \beta\mathbb{R}(\theta_s,\chi_f)\right] \quad (19)$$

where, for a first-order reaction,

$$\mathbb{R}(\theta_s, x_f) = Da\left[\frac{\exp\left(\frac{\gamma\theta_s}{\theta_s+1}\right)}{1+\frac{Da}{St_m}\exp\left(\frac{\gamma\theta_s}{\theta_s+1}\right)}\right](1-\chi_f), \quad Da = \frac{Lk_\infty e^{-\gamma}}{v} \quad (20)$$

and θ_f, θ_s, and χ_f are the fluid-phase temperature, solid-phase temperature, and fluid-conversion. (These dimensionless parameters are defined in Viswanathan et al.[67])

As a result of $\mathbb{O}(2)$ symmetry breaking, nonuniform states bifurcate in pairs from the uniform states branch. The nature of the emerging branches of nonuniform states depends upon the stability of the underlying transversally uniform solution. The bifurcation from a stable uniform state can be either super- or subcritical resulting in either a stable or an unstable nonuniform state branch near the bifurcation point. Branches of nonuniform states that emerge from the unstable steady-state branch in the region of uniform steady-state multiplicity are generically unstable. They may attain stability only following a secondary bifurcation.

Figure 8 shows the neutral stability curves of the third transversal mode in the planes of θ_f and R/d_p for various values of the ratio of the fluid transversal heat dispersion to that of mass, $\mathcal{M}^f_{\mathrm{TP}} = \lambda_{f,\perp}/(D_{f,\perp}(\rho C_p)_f)$, and practical values of the other parameters. These neutral stability curves were obtained by perturbing the transversally uniform state solutions with three-dimensional nonuniform spatial perturbations of the form, $\underline{\omega}_{mn}(\eta, \xi, \phi) = \underline{\omega}(\eta)J_m(\mu_{mn}\xi)e^{im\phi}$. Unlike the shallow reactor, the eigenvector $\underline{\omega}(\eta) = (\underline{\omega}_1(\eta), \underline{\omega}_2(\eta), \underline{\omega}_3(\eta))$ is a function of the axial position, η. Figure 8 shows that for practical values of $\mathcal{M}^f_{\mathrm{TP}} \geq 1$, the neutral stability always leads to a bifurcation from the unstable uniform solution. Therefore, a two-phase model cannot predict a bifurcation from a uniform stable state to a stable, transversally nonuniform states branch under the practical condition that $\mathcal{M}^f_{\mathrm{TP}} \geq 1$. For the case of azimuthally symmetric 2D nonuniform states, no global bifurcation (Figure 9,I) leading to stable nonuniform states was found for the realistic case of $\mathcal{M}^f_{\mathrm{TP}} = 1.5$. For certain unrealistic values of $\mathcal{M}^f_{\mathrm{TP}} < 1$, the neutral stability curve is no more bounded by the temperatures corresponding to the unstable uniform state. Thus, a branch of nonuniform state may emerge and end at a stable uniform state. Some of the nonuniform states on this branch may be stable, as shown by Figure 9,I for the unrealistic value of $\mathcal{M}^f_{\mathrm{TP}} = 0.075$. Figure 9,II describes the (azimuthally symmetric) temperature profiles of such a stable nonuniform state for $\mathcal{M}^f_{\mathrm{TP}} = 0.075$. No symmetry-breaking Hopf bifurcation, which may lead to spatiotemporal patterns, has been reported for this class of models. A single-exothermic reaction conducted in a PBR is commonly described using a kinetic model that depends only on the limiting reactant concentration and temperature. The above results (and those for the shallow reactor) suggest that an $\mathbb{O}(2)$ symmetry-breaking bifurcation from a stationary, transversally uniform steady state to either spatial or spatiotemporal stable patterns cannot be predicted using these kinetics by either a pseudohomogeneous or a two-phase model of uniformly active, adiabatic PBR. The above does not preclude formation of transient hot regions, as verified in section 7.

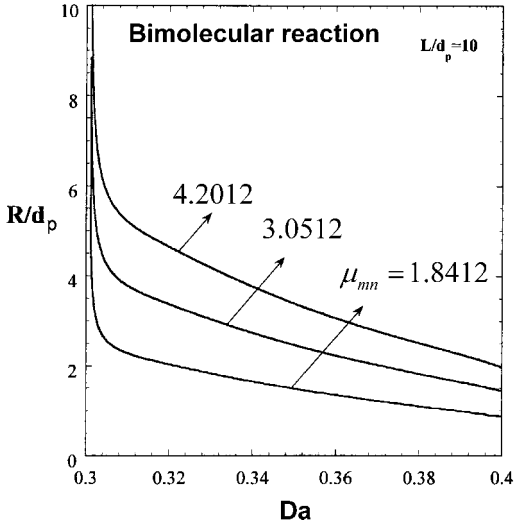

Figure 7. Neutral stability curves for the first three transversal eigenmodes obtained using a pseudohomogeneous model in which a bimolecular reaction proceeds by a Langmuir−Hinshelwood mechanism. Adapted with permission from ref 65. Copyright 1999 Elsevier.

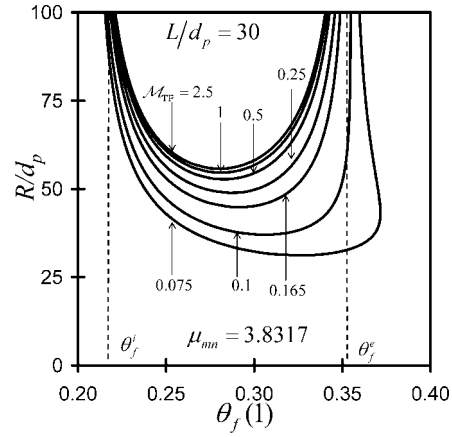

Figure 8. Neutral stability curves of the third transversal mode in the plane of exit θ_f and R/d_pobtained using long reactor two-phase model with first-order reaction kinetics for various values of $\mathcal{M}^f_{\mathrm{TP}} = \lambda_{f,\perp}/(D_{f,\perp}(\rho C_p)_f)$ and practical values of the other parameters. Adapted with permission from ref 67. Copyright 2005 American Institute of Chemical Engineers.

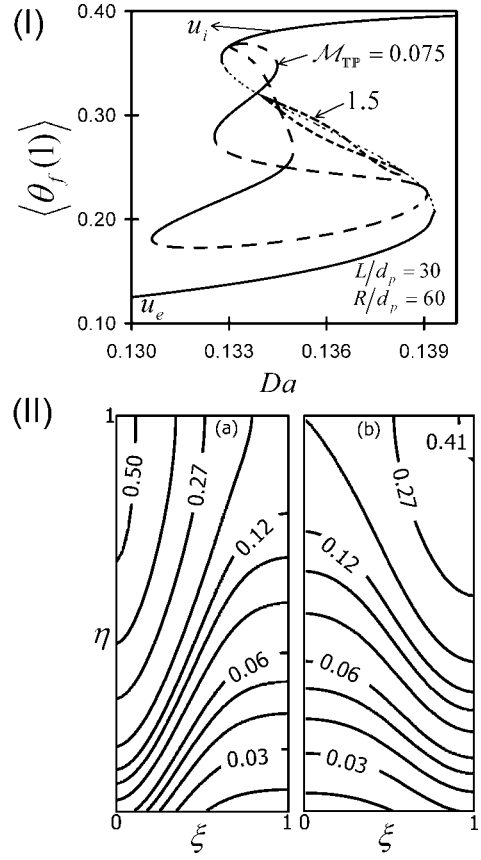

Figure 9. Global bifurcation diagram (I) for the 2-D azimuthally symmetric stationary nonuniform states for $\mathcal{M}^f_{\mathrm{TP}} = 1.5$ and 0.075. (II) Temperature contours of stable nonuniform states for $\mathcal{M}^f_{\mathrm{TP}} = 0.075$ and $Da = 0.134$ at (II-a) $\langle\theta_{f,\mathrm{exit}}\rangle = 0.237$ and (II-b) $\langle\theta_{f,\mathrm{exit}}\rangle = 0.325$. Adapted with permission from ref 67. Copyright 2005 American Institute of Chemical Engineers.

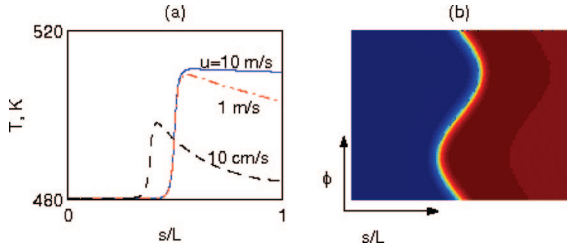

Figure 10. Stationary patterns on a thin cylindrical bed (with flow from the left) with a bistable microkinetic model corresponding to CO oxidation (eq 16, $k_4 = k_5 = 0$). Diagram (a) shows stationary temperature profiles and the effect of convective velocity while (b) shows steady temperature field. Adapted with permission from ref 84 and unpublished results. Copyright 2007 Elsevier.

5.1.2. Microkinetic Model that Exhibits Bistability. Nekhamkina and Sheintuch[84] analyzed the possible axial- and azimuthal spatio-temporal temperature patterns that may emerge on the surface of a thin annular cylindrical fixed bed, using the microkinetic model for CO oxidation (eqs 16a). They coupled the surface balances with a two-dimensional axial- and azimuthal-dispersion reactant mass balance and a solid-phase enthalpy balance while assuming that the fluid temperature was constant, even though the solid temperature was not. They found a domain of stationary front states in the case of a bistable kinetics ($k_4 = k_5 = 0$, eq 16c). Several axial 1-D stationary pulses are presented in Figure 10a for various flow rates. An axial stationary pattern may emerge using as initial conditions a step change in a surface species (x and/or y). It can be placed, by proper choice of initial conditions, at will within a domain of positions. Figure 10b presents the thermal patterns in the unfolded cylinder, starting with step-change axial distribution and a sine-like initial boundary in the azimuthal direction. At high flow rates (Figure 10a) the initial distribution was maintained at steady state, while at low flow rates (not shown) the amplitude of the transversal patterns diminished significantly but did not disappear. Thus, a stationary front may form for a reaction with a microkinetic bistable rate expression when the thermal effects are weak and in the absence of intercrystallite or intraparticle communication by surface diffusion. Recall that surface communication is achieved in this model only by heat conduction and gas-phase diffusion but not by surface diffusion (eq 16) and since isothermal bistability is possible and stationary patterns may form, they persist when thermal effects are weak.

5.2. Oscillatory Kinetics. Localized hot zones are three-dimensional objects. The difficulty of 3-D numerical simulations requires the use of simplified 2-D versions as discussed in section 3. Simulations of 2-D hot zones provide insights into mechanisms that may lead to evolution of intricate 3-D hot zones. In general, patterns in PBR models are more complex than those in the shallow bed due to the interaction of various modes. The spatiotemporal transversal pattern at any axial position strongly affects the concentration and temperature of particles further downstream of that position, and coupling upstream occurs at low flow rates by conduction and dispersion.

5.2.1. Microkinetic Model I. Viswanathan and Luss[85] showed that a pseudohomogeneous model of a long uniformly active, adiabatic reactor can predict the formation of 2-D azimuthally symmetric hot zones when the reaction rate is oscillatory. Using a bimolecular Langmuir−Hinshelwood mechanism (eqs 8−12), various spatiotemporal patterns exhibiting rich dynamics and mode interactions were found. The oscillatory neutral stability curve of mode n was nested within that for mode $n - 1$ (Figure 11).

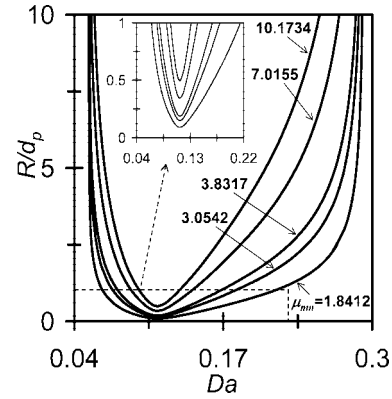

Figure 11. Oscillatory neutral stability curves for the 1st, 3rd, 9th, and 15th transversal eigenmodes. (These are the first three purely radial eigenmodes, which have no azimuthal dependence.) Inset: Zoomed version of a segment of the oscillatory neutral stability curves. Adapted with permission from ref 85. Copyright 2006 American Chemical Society.

Numerical simulations starting from a neutral stability curve and using a combination of base state eigenvectors and transversal eigenmodes led to complex periodic motions (period -2, -4, -8) as well as chaos (Figure 12). Snapshots of chaotic spatial temperature (Figure 12,II) suggest that this state is generated by the nonlinear modulation and juxtaposition among motions corresponding to different modes. These simulations of the chaotic state (Figure 12,II) reveal the existence of very small hot zones within a long bed. These small hot zones are similar to the small "clinkers" of fused catalysts observed by Barkelew and Gambhir.[37]

The simulations of the long PBR revealed a period-2p bifurcation, that is, transitions among states having period-2p features ($p = 1, 2, 3,...$). Even more complex coupling and modulation are expected to be observed in the simulations of 3-D hot zones as these can have length scales much smaller than those observed in 2-D hot zones.

The predictions of the homogeneous and heterogeneous models may lead to qualitatively different predictions when one ignores the heat dispersion in the solid phase and when the transport between the pellet and the surrounding fluid can induce local steady-state multiplicity. A detailed analysis of when the predictions of the two models may differ was presented by Agrawal et al.[86] They showed that this is likely to occur when the fluid Schmidt number is smaller than the Prandtl number. This occurs for reaction mixtures containing a large excess of hydrogen. The likelihood of different pattern predictions by the single and two-phase models increases as the ratio of the heat generation in a single pellet to the heat removal increases.

5.2.2. Microkinetic Model IV. Sheintuch and Nekhamkina[87] studied an oscillatory version of a homogeneous thermo-kinetic model (with mass and energy balance expressed in eqs 17−19 with $\theta_s = \theta_f$) coupled to a slow reversible activity changes in a thin annular cylindrical fixed bed. The activity (Θ) followed the simple kinetics

$$\frac{d\Theta}{d\tau} = K(a - b\Theta - \theta) \tag{21}$$

leading to deactivation (reactivation) at high (low) temperatures (θ). They showed that for sufficiently large perimeter, symmetry breaking may transform an axial front (that is, azimuthally homogeneous) into a rotating pattern. The instability stems from the (anticlinal) nature of the spatial temperature and activity profiles which are opposite in their inclination. In a 1-D problem such kinetics leads to an oscillatory front solution. They derived

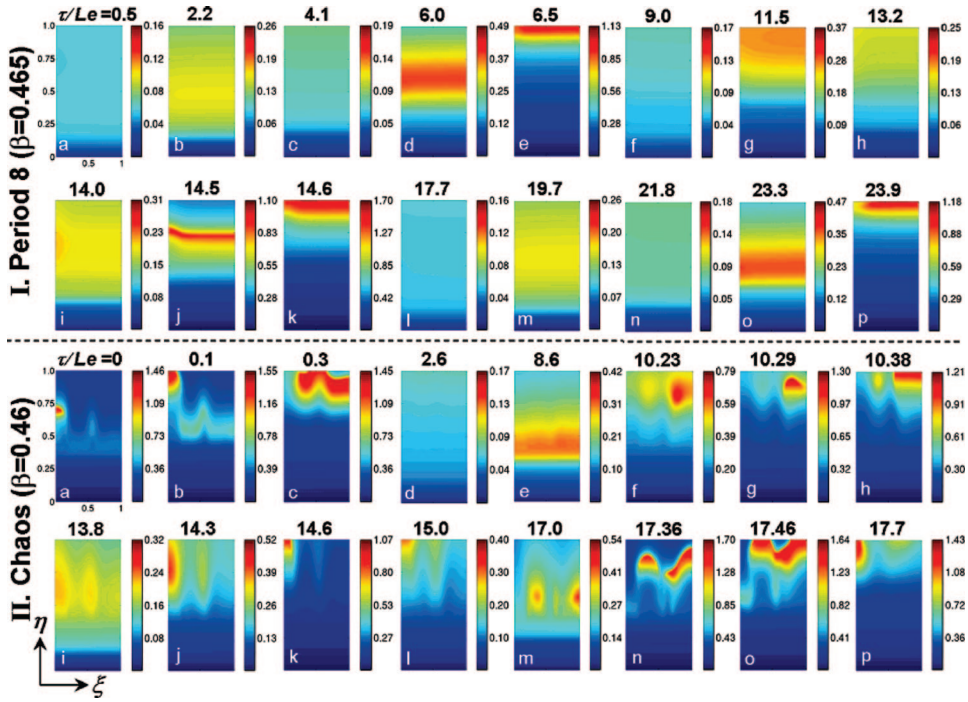

Figure 12. (I) 2-D Temperature contours of the reactor at various τ/Le during period-8 motion. (II) 2-D temperature contours of various spatiotemporal states in the reactor at various τ/Le during chaos. Adapted with permission from ref 85. Copyright 2006 American Chemical Society.

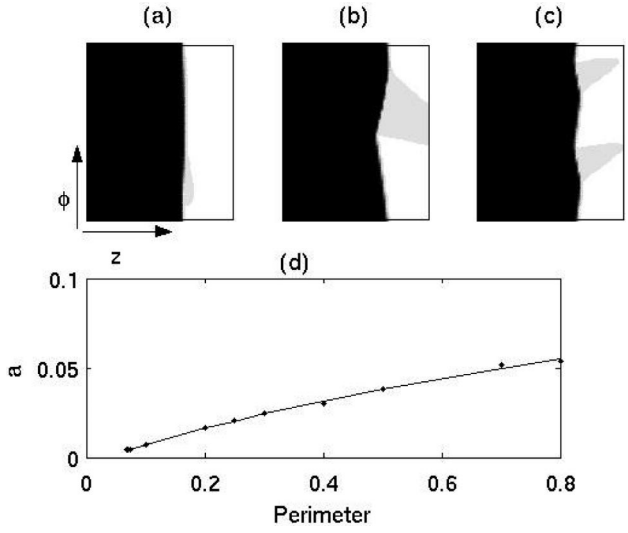

Figure 13. Typical snapshots of "frozen" rotating patterns of one-wave (perimeter/length = 0.1 (a) or 0.5 (b)) and two-wave (c, 0.5) structures simulated on a thin annular cylindrical (two-dimensional) bed using an oscillatory micro-kinetic model IV, and a bifurcation diagram (d) showing the spatial amplitude (a) of the front as a function of perimeter. Adapted with permission from ref 87 and unpublished results. Copyright 2003 Elsevier.

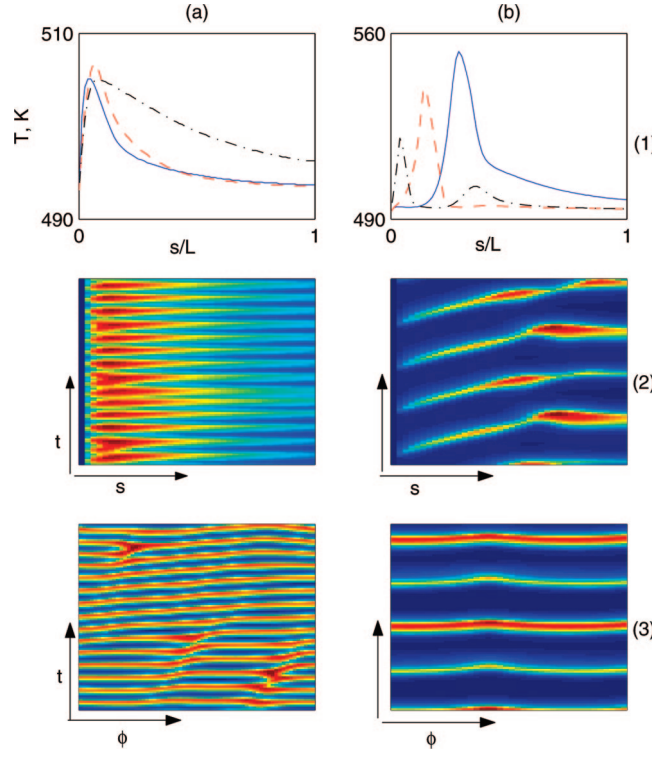

Figure 14. Patterns on a thin cylindrical bed (with flow from the left) with oscillatory microkinetic model III corresponding to CO oxidation (eq 16) coupled with energy and mass balances. Columns refer to patterns of oscillating pulse (a) and traveling pulse (b). Row 1 shows equally timed spatial temperature profiles. Rows 2 and 3 show temperature patterns in the axial (s) or transversal (ϕ) directions. Adapted with permission from ref 84 and unpublished results. Copyright 2007 Elsevier.

a criterion for the emergence of transversal patterns for sufficiently slow activity change.

Typical one- or multiwave patterns rotating at a constant speed and shape are shown in Figure 13 for the realistic case of $Pe_C/Pe_T > 1$. Bifurcation diagrams showing the spatial amplitude dependence on a parameter (e.g., perimeter, Figure 13d) and the coexistence of these solutions were presented. Control procedures suppressing the formation of such transversal patterns were analyzed.[88]

5.2.3. Microkinetic Model III. A microkinetic oscillatory model of CO oxidation (eq 16a) was used by Sheintuch and Nekhamkina[81,84] to study pattern formation in a thin cylindrical bed using a model in which the surface balances were coupled with a two-dimensional axial- and azimuthal-dispersion reactant mass balance and solid-phase enthalpy-balance (assuming the fluid temperature to be constant). As in the case of a disk or shallow bed (section 4.2.3), moving waves with a characteristic

length were found near the Hopf bifurcation at low P_{CO}. The thin cylindrical patterns are 2-D in nature. Figure 14 presents the 2-D patterns on the unfolded surface of the thin cylinder. The axial profiles under two sets of conditions that can be characterized either as an oscillating pulse (Figure 14a) or as a traveling pulse (Figure 14b) are presented in row 1. The corresponding spatio-temporal axial- and azimuthal- patterns are presented in rows 2 and 3 (s and ϕ are the axial and the azimuthal coordinate). The transversal amplitude decays and vanishes close to the high-pressure bifurcation point. The main parameter that characterizes this feature is the wavelength of the emerging pattern.

6. Impact of Flow Mal-Distribution and of Physical Properties

Previous analyses were of pattern formation in a uniformly PBRS and ignored the potential impact of changes in the physical properties and transport phenomena in the reactor. There are other mechanisms that may lead to formation of transversal hot zones in the reactor, and these shall be briefly described. Matros[39] has shown that nonuniform packing of a reactor can lead to formation of several hot regions in the cross section of the reactor. Similarly, Jaffe[59] reported that a hot spot may form due to local obstruction of the flow in the reactor. Our unreported study showed that local hot regions may form if the bed is packed with catalyst having nonuniform activity. Thus, to minimize the probability of local hot zones formation, it is essential to pack the bed as uniformly as possible with pellets having essentially the same activity.

The variation of physical properties in the reactor may also lead to formation of hot spots when conducting a highly exothermic reaction, the rate of which is a monotonic increasing function of the temperature. Viljoen et al.[89] pointed out that various temperature patterns may be generated by the natural convection when an exothermic reaction is conducted in a porous media. Stroh and Balakotaiah,[90,91] Nguyen and Balakotaiah,[92,93] Subramanian and Balakotaiah,[94] and Christforatou and Balakotaiah[95] presented extended analyses of when natural convection will generate spatiotemporal temperature patterns in a PBR. This is expected to happen mainly for flow rates lower than those used in most commercial PBRs.

Agrawal et al.[86] extended previous analyses by accounting for the impact of the velocity variations due to the change in the physical properties on the interphase transport coefficients. They found that the variation in the transport coefficient increased the potential for generating hot zones. Agrawal et al.[96] analyzed the impact of flow mal-distribution and interphase transport resistances on the formation of stationary patterns in a down-flow packed-bed reactor described by a cell model (array of CSTRs each containing a catalytic pellet) in the presence and absence of direct heat and mass interaction between the particles via solid diffusion. In addition, the heat dispersion in the fluid phase is assumed either equal to or lower than the mass dispersion. Thus, the temperature of the solid in the patterned states may exceed both the adiabatic temperature and also the solid temperature in the uniform state. Their analysis suggests that temperature pattern formation requires a reaction rate that exponentially increases with temperature and that these patterns are transport limited under certain interphase transport conditions. Hence, in the absence of solid phase heat interaction, the removal of the heat generated in the solid phase via the interphase transport and the fluid phase dispersion enables the formation of steady-state multiplicity, which may lead to local hot zones. These transport limited patterns exist only in the region of steady-state multiplicity. They emerge as unstable branches from the unstable uniform state and become later stable by a global bifurcation. Pseudohomogeneous models, due to the absence of an interphase transport mechanism, cannot predict interphase transport limited pattern formation. They also found that introducing heat communication between catalysts particles (heat communication among the catalysts in the CSTRs) led to the disappearance of the stable patterns even for a small number of cells. The cell models, that is, models of catalytic pellets in a series of CSTRs, provide useful insights into the mechanisms underlying pattern formation and dynamics. Cell models are always affected by global coupling that may lead to pattern formation for conditions under which they would not form in its absence. The analyses of various models point out that the evolution and stability of the patterned states is sensitive to the assumptions underlying the model of the PBR.

7. Transient Transversal Moving Front Patterns in PBRs

Previous analysis was of periodic or aperiodic hot zone dynamics under steady operation of the reactor. However, hot zones may form during transient operation. A well studied transient behavior is that of a moving front. It is known to form following a transient change of the feed conditions, which may also lead to a wrong-way behavior.[30,31] Approximate predictions of the front velocity (V_f) have been derived for 1-D models with negligible mass dispersion.[27] This section outlines a criterion predicting transversal pattern emergence in moving fronts using 2-D and 3-D models of a homogeneous PBR in which a simple first-order exothermic reaction occurs. These predictions are verified by 2-D and 3-D simulations. The front moves in general either in the upstream (toward the reactor inlet) or downstream direction. A stationary front is a special case.

Nekhamkina and Sheintuch[97] using a linear stability analysis of a moving planar front in a thin cylindrical packed bed showed that a planar front may bifurcate into transversal patterns when

$$Pe_{C\perp}/Pe_{T\perp} < \Delta T_{ad}/\Delta T_m = B/y_m \qquad (22)$$

where ΔT_{ad} and ΔT_m are the adiabatic and maximal temperature rise, y_m the dimensionless maximal temperature, and $B = \gamma \Delta T_{ad}/T_{in}$. Condition 22 predicts that transversal patterns may emerge in stationary fronts when $Pe_{C\perp}/Pe_{T\perp} < 1$ as $y_m = B$, in agreements with the studies in Section 5, extending the bifurcation condition to moving fronts. This condition can be satisfied, within the feasible domain of operating conditions ($Pe_{C\perp}/Pe_{T\perp} > 1$) only for an upstream propagating front for which $\Delta T_m/\Delta T_{ad} < 1$ but cannot be satisfied in a downstream propagating front, for which $\Delta T_m/\Delta T_{ad} > 1$. Numerical simulations of a 2-D thin annular cylindrical reactor model showed that various types of moving transversal patterns formed within a feasible domain. With time the initially perturbed 1-D front solution either converges to a "frozen" transversal pattern or exhibits complex spatio-temporal behavior or grows to a certain amplitude and then decays slowly. Typical transient showing the evolution of transversal pattern is illustrated Figure 15a in a moving coordinate, starting from a small sinusoidal perturbation (dashed line). Beyond profile 5 the pattern amplitude declines slowly for this low-parameter amplitude; for higher perimeters the pattern converges into a constant pattern.

Condition 22 can be satisfied when the axial and the transversal Pe numbers are either related, that is, $Pe_C/Pe_{C\perp} = Pe_T/Pe_{T\perp}$, or when they are not. A similar condition was obtained using a simplified model describing two 1-D reactor channels with heat and mass exchanges between them. A bifurcation diagram showing domains of transversal patterns was constructed for this case.

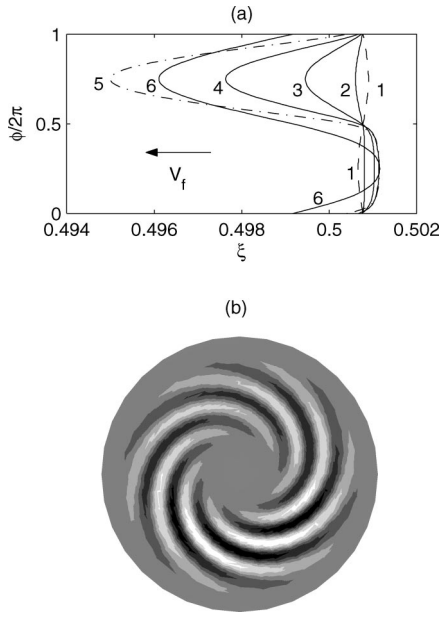

Figure 15. Transversal patterns of an upstream-moving front: (a) Pattern evolution on an unfolded 2-D thin cylinder showing front position at increasing time starting from a small perturbation (line 1). (b) Spiral pattern in a cross-section normal to the direction of a front propagating in a 3-D PBR. (Unpublished data using models of Nekhamkina and Sheintuch.[97,98])

In a second approach,[98] the criteria for pattern emergence was based on the relation between the front velocity (V_f) and the local curvature (K) using the critical condition $dV_f/dK|_{K=0} = 0$.

This impact of the curvature on the front stability is analogous to that occurring in reaction-diffusion systems. The stability analysis revealed that symmetry breaking depends on the value of

$$\alpha = (BPe_T/y_m Pe_C) \tag{23}$$

and may occur only if $1 < \alpha < \alpha^*$, where α^* is a predictable upper bound.

A typical three-dimensional spiral pattern of a front that is moving upstream is shown in Figure 15b[98] showing a cross-section of the bed at one position. The pattern varies as it propagates but does not decay to the planar front solution, as long as the front does not exit the reactor.

8. Perspectives

The ability to predict formation of either stationary or spatiotemporal temperature patterns in catalytic packed-bed reactors are of both practical importance and intrinsic academic interest. Understanding of the mechanisms and reactor models that enable prediction of hot zone formation is essential for a rational development of safe design and operation and control strategies. While various theoretical and experimental advances have been made in understanding hot zone formation and dynamics in 2-D systems, the real problem is 3-D in nature. Given the difficulty of experimental detection of 3-D hot regions and the need for design criteria, the prediction of hot domains will need to rely on simulations and analysis of 3-D models. Such simulations are very demanding at present.

Current predictions of the formation and complex spatiotemporal motions of hot zones in PBRs are very sensitive to the underlying model. Common models use kinetics that depend only on the surface temperature and concentration of the limiting reactant. A catalytic pellet exposed to such conditions exhibits a single steady reaction rate. Such kinetics, when incorporated into a PBR model, cannot predict stable bifurcation to nonuniform states from stable, stationary, transversally uniform states under the realistic case that the thermal dispersion exceeds that of the species. The conclusions may not be valid when a single pellet may exhibit multiple steady states or the reaction rate is time-dependent. Use of oscillatory kinetics enables prediction of stable hot zone formation. Several microkinetic models that predict these behaviors were presented. There are as yet no criteria for classifying such models and predicting the qualitatively expected behavior. It is still unclear which, if any, other rate expressions may predict this behavior.

The simulations of the hot zones, even using simplified models, required a priori knowledge of the range of parameters for which a particular class of hot zones may exist and of the initial conditions that may lead to these. Current predictions of the complex spatiotemporal motions in PBRs are of simplified 2-D cases such as a shallow reactor, azimuthally symmetric long reactor, and a thin cylindrical reactor. Unfortunately, at present there exists no theoretical guidance about the relation between pattern formation in the 3-D and 2-D models.

An infinite number of combinations of the axial eigenfunctions and the transverse eigenmodes exist in the case of a 3-D reactor. It will be very useful to develop, using linear stability analysis, a formula for generating specific initial conditions leading to transversal hot zones evolution in the case of a 3-D reactor. Difficult numerical simulations of the 3-D model will have to be conducted to test the predictions of that analysis. These simulations, although computationally intensive and tedious, are unfortunately necessary to predict the dimensions and shape of the highly localized patterns. Another approach may be to use the underlying symmetries in the 3-D reactor to identify classes of patterns that may form to estimate an appropriate class of initial conditions. Use of a coupled-cell network[99,100] may provide useful insights on the classes of structures that may exist and on how to predict them. Nekhamkina and Sheintuch[97] used this approach to study when two front solutions, of two 1-D reactor channels with heat and mass exchange between them, will propagate together or separate.

Most previous simulations of transversal hot zone patterns in PBRs led to predictions of moving hot zones. Stationary fronts are known to form using simple thermo-kinetic models only for unrealistic transport parameters (sections 5.1, 7) and for certain microkinetic models due to absence of surface diffusion (section 5.2). Industrial reports suggest that stationary hot zones may form. An obvious question is what is the underlying mechanism. Local nonuniformities in the bed packing and/or catalytic activity may lead to the formation of local stationary hot zones in 1-D and 2-D PBR models. In industrial reactors these nonuniformities always exist, but it is essentially infeasible to characterize and model their location and magnitude. Simulations can provide useful guidance about their potential magnitude and impact. A clear demonstration of the impact of these effects is the report by Matros[39] that repacking of a PBR caused a drastic change in the size and location of the hot zones. The granular-discrete nature of catalytic systems may be another reason for such patterns. Stationary fronts are known to emerge in cell-like reaction−diffusion systems and are referred to as "propagation failure". Another possible explanation for the generation of hot zones is that they form during a transient behavior, such as that described in section 7.

The presence of small local hot zones is very difficult to detect in large industrial reactors. Viswanathan and Luss[85] presented

several scenarios where the measurements of the effluent composition and temperature may fail to detect the presence of hot zones in the reactor, especially small ones. The largest safety hazard occurs when a hot zone is located next to the reactor walls. One may attempt to detect these by infrared monitoring of the reactor walls or by painting the exterior reactor wall with a temperature sensitive paint. There exist at present no efficient tools for measurement of small hot zones inside a large-scale reactor. Gladden's group[101−103] attempted to measure local fluid properties at various positions in small PBRs by magnetic resonance imaging (MRI). This method may enable the detection of hot zones within laboratory reactors.

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