Model Prediction of Hot Spots Formation in Shallow Adiabatic Packed-Bed Reactors

Ganesh A. Viswanathan and Dan Luss
Dept. of Chemical Engineering, University of Houston, 4800 Calhoun Road, Houston, TX 77204

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Transversal hot zones have been observed in many industrial and laboratory reactors. Yet, previous models which utilized rate expressions that depended only on the temperature and concentration of the limiting reactant failed to predict formation of stable hot zones. We previously proved that pseudohomogeneous models of a uniformly active shallow adiabatic packed-bed reactor cannot predict a bifurcation to stable hot zones when the transversal heat dispersion is larger than that of the species, and the reaction rate depends only on the temperature and concentration of the limiting reactant. We prove here that the same is true also for a two-phase model of a uniformly active shallow, adiabatic packed-bed reactor. It is shown that a shallow reactor model, which uses more detailed kinetic expression, may attain stable, transversal hot zones. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 1533-1538, 2006

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Introduction

Transversal (perpendicular to the flow direction) hot zones have been reported to form in packed-bed reactors. Boreskov et al.[1] observed hot zones in a large diameter packed-bed reactor during the partial oxidation of isobutyl alcohol. Barkelew and Gambhir[2] reported that small aggregates of molten catalyst pellets (clinkers) were generated during the hydrodesulfurization of crude oil. Moving hot spots formed on Pt-Rh gauzes during the synthesis of hydrogen cyanide and ammonia oxidation to NO. Wicke and Onken[3,4] observed a transversal hot region in a laboratory packed-bed reactor. Various types of transversal hot regions were observed in a shallow packed-bed reactor by Marwaha et al.[5,6] and on a catalytic glass fiber cloth by Digilov et al.[7] Transversal hot regions have a deleterious impact on the reactor performance and may pose severe safety hazards when present next to the reactor wall.

Several investigators attempted to explain and predict the formation of transversal hot regions in commercial packed-bed reactors. For example, Jaffe[8] showed that internal obstruction may cause hot spot formation in trickle-bed reactors. Boreskov et al.[1] showed that nonuniform packing of the bed can generate local hot zones. Subramanian and Balakotaiah[9] (and references, therein) showed that, at rather low-feed rates, the temperature dependence of the fluid properties may generate spatiotemporal flow and temperature patterns in packed-bed reactors. Sundarram et al.[9] have shown that global coupling can lead to formation of hot zones on the top of a packed-bed reactor. We do not address here transversal temperature nonuniformities generated either by nonuniform packing or by variation in fluid properties with temperature or concentration, or by global coupling. We consider here transversal hot zone formation in a uniformly active adiabatic packed-bed reactor. Balakotaiah et al.[10] reported that stationary transversal hot zones may form in adiabatic packed-bed reactors when the axial dispersion of the limiting reactant exceeded that of heat. This condition is analogous to the evolution of a Turing pattern[11] in reaction-diffusion systems, that is, that the diffusion

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Correspndence concerning this article should be addressed to D. Luss at dluss@uh.edu.

coefficient of an inhibitor exceeds that of the autocatalytic variable.[12] However, as pointed out by Yakhnin and Menzinger[13] this condition is not satisfied in packed-bed reactors.

The goal of our study was to determine whether the failure of previous modeling attempts to predict the formation of stable transversal hot zones in a uniformly-active adiabatic packed-bed reactor was caused by the choice of unsuitable kinetic parameters or unsuitable model. Simulations of Viswanathan et al.[15], using a pseudohomogeneous model of a uniformly active shallow, adiabatic packed-bed reactor, showed that stationary stable nonuniform states exist on a branch of nonuniform states that emanates from a stable uniform state. They proved that, for a two dynamic-variables pseudohomogeneous model, under the practical condition that the transversal heat dispersion is larger than that of the species, such a bifurcation cannot occur using a kinetic model which depends only on the temperature and reactant concentration (such as an n^th^ order reaction). That analysis explained the failure of previous simulations to predict stable, transversal hot zones using realistic parameters.[13] Moreover, numerical calculations by Viswanathan et al.[15] showed that a two-phase model of a shallow adiabatic packed-bed reactor also cannot predict stable transversal hot zones in those cases. We present here a proof of those observations and explain the changes that need to be made in the model so that it can predict observed spatiotemporal transversal temperature patterns.

Two-Phase Model of a Shallow Adiabatic Packed Reactor

We consider the two-phase model of an adiabatic packed-bed reactor

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

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

$$\frac{\partial \theta_s}{\partial \tau} = \frac{1}{(Le - \varepsilon)}\left[\frac{1}{Pe^h_{s,\perp}}\nabla^2_\perp \theta_s + \frac{1}{Pe^h_{s,a}}\frac{\partial^2 \theta_s}{\partial \eta^2} - St_h(\theta_s - \theta_f) + \beta\mathbb{R}(\theta_s, x_f)\right] \quad (3)$$

where

$$\begin{aligned}
&\theta = (T - T_{in})/T_{in}, && x_f = (C_{in} - C_f)/C_{in}\\
&\eta = z/L, && \xi = r/R\\
&\gamma = E/(\bar{R}T_{in}), && \beta = (-\Delta H)C_{in}/((\rho C_p)_f T_{in}),\\
&St_m = ka_v L/v, && St_h = ha_v L/((\rho C_p)_f v),\\
&Pe^h_{f,a} = \frac{vL}{\varepsilon\lambda_{f,a}/(\rho C_p)_f}, && Pe^m_{f,a} = vL/(\varepsilon D_{f,a}),\\
&Pe^h_{s,a} = \frac{vL}{(1-\varepsilon)\lambda_{s,a}/(\rho C_p)_f}, && Pe^h_{f,\perp} = \frac{vR^2}{L\varepsilon\lambda_{f,\perp}/(\rho C_p)_f},\\
&Pe^m_{f,\perp} = vR^2/(\varepsilon L D_{f,\perp}), && Pe^h_{s,\perp} = \frac{vR^2}{L(1-\varepsilon)\lambda_{s,\perp}/(\rho C_p)_f},\\
&Le = \varepsilon + (1-\varepsilon)\frac{(\rho C_p)_s}{(\rho C_p)_f} && \nabla^2_\perp = \left[\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial}{\partial \xi}\right) + \frac{1}{\xi^2}\frac{\partial^2}{\partial \phi^2}\right]
\end{aligned} \quad (4)$$

and $\mathbb{R}(\theta_s, x_f)$ is the reaction rate. The subscripts *f* and *s* refer to the fluid and solid phases, respectively. For example, for a first-order reaction

$$\mathbb{R}(\theta_s, x_f) = Da\left[\frac{\exp\left(\frac{\gamma\theta_s}{\theta_s + 1}\right)}{1 + \frac{Da}{St_m}\exp\left(\frac{\gamma\theta_s}{\theta_s + 1}\right)}\right](1 - x_f),$$

$$Da = \frac{Lk_\infty e^{-\gamma}}{v} \quad (5)$$

The corresponding boundary conditions are

$$\frac{1}{Pe^h_{f,a}}\frac{\partial \theta_f}{\partial \eta} = \theta_f, \quad \frac{1}{Pe^m_{f,a}}\frac{\partial x_f}{\partial \eta} = x_f, \quad \frac{\partial \theta_s}{\partial \eta} = 0 \quad \eta = 0 \quad (6)$$

$$\frac{\partial \theta_f}{\partial \eta} = 0, \quad \frac{\partial x_f}{\partial \eta} = 0, \quad \frac{\partial \theta_s}{\partial \eta} = 0 \quad \eta = 1 \quad (7)$$

$$\frac{\partial \theta_f}{\partial \xi} = 0, \quad \frac{\partial x_f}{\partial \xi} = 0, \quad \frac{\partial \theta_s}{\partial \xi} = 0 \quad \xi = 1 \quad (8)$$

The simulations and stability analysis of the three-dimensional (3-D) model of the packed-bed reactor are very cumbersome and lengthy. Thus, we consider here a model of a shallow reactor (that is, one that is uniform in the axial direction), which is obtained by a Liapunov-Schmidt reduction[16] of the full model. Balakotaiah et al.[17] used a similar approach in their study of pattern formation in a shallow monolith reactor. The shallow reactor model is

$$\frac{d\theta_f}{d\tau} - \frac{1}{\varepsilon}\left[\frac{1}{Pe^h_{f,\perp}}\nabla^2_\perp \theta_f - \theta_f + St_h(\theta_s - \theta_f)\right] = 0 \quad (9)$$

$$\frac{dx_f}{d\tau} - \frac{1}{\varepsilon}\left[\frac{1}{Pe^m_{f,\perp}}\nabla^2_\perp x_f - x_f + \mathbb{R}(\theta_s, x_f)\right] = 0 \quad (10)$$

$$\frac{d\theta_s}{d\tau} - \frac{1}{(Le - \varepsilon)}\left[\frac{1}{Pe^h_{s,\perp}}\nabla^2_\perp \theta_s - St_h(\theta_s - \theta_f) + \beta\mathbb{R}(\theta_s, x_f)\right] = 0 \quad (11)$$

Details of the reduction procedure are reported by Viswanathan[18]. The corresponding boundary conditions are

$$\frac{\partial \theta_f}{\partial \xi} = 0, \quad \frac{\partial x_f}{\partial \xi} = 0, \quad \frac{\partial \theta_s}{\partial \xi} = 0 \quad \xi = 1 \quad (12)$$

A homogeneous (one with no transversal variation) steady-state solution $(\theta_f, x_f, \theta_s)_{ss}$ of the shallow reactor model (Eq. 9–12) is stable with respect to homogeneous perturbations only if all the eigenvalues of the Jacobian

$$
\mathbb{L}_2 = \begin{bmatrix} \frac{1}{\varepsilon}(-1 - St_h) & 0 & \frac{St_h}{\varepsilon} \\ 0 & \frac{1}{\varepsilon}\left(-1 + \left.\frac{\partial \mathbb{R}}{\partial x_f}\right|_{(\theta_f, x_f, \theta_s)_{ss}}\right) & \frac{1}{\varepsilon}\left.\frac{\partial \mathbb{R}}{\partial \theta_s}\right|_{(\theta_f, x_f, \theta_s)_{ss}} \\ \frac{St_h}{(Le - \varepsilon)} & \frac{\beta}{(Le - \varepsilon)}\left.\frac{\partial \mathbb{R}}{\partial x_f}\right|_{(\theta_f, x_f, \theta_s)_{ss}} & \frac{1}{(Le - \varepsilon)}\left(-St_h + \beta \left.\frac{\partial \mathbb{R}}{\partial \theta_s}\right|_{(\theta_f, x_f, \theta_s)_{ss}}\right) \end{bmatrix} \qquad (13)
$$

have a negative real part. We denote in Eq. 13 and, hereafter, by $\mathbb{R}_{x_f}$ and $\mathbb{R}_{\theta_s}$, the partial derivatives $(\partial\mathbb{R}/\partial x_f)|_{(\theta_f, x_f, \theta_s)_{ss}}$ and $(\partial\mathbb{R}/\partial\theta_s)|_{(\theta_f, x_f, \theta_s)_{ss}}$. We prove in Appendix I that for this model, a Hopf bifurcation cannot exist if

$$
\det(\mathbb{L}_2) = \frac{St_h(-1 + \mathbb{R}_{x_f}) + \beta\mathbb{R}_{\theta_s}(1 + St_h)}{\varepsilon^2(Le - \varepsilon)} < 0 \qquad (14)
$$

is satisfied. When $\det(\mathbb{L}_2) < 0$, all the coefficients of the characteristic polynomial (Eq. A1) are negative. Thus (due to the Descartes' Rule of Signs) all three (real) eigenvalues of $\mathbb{L}_2$ must be *negative*. Hence, condition (Eq. 14) is the necessary and sufficient condition for stability of the uniform solutions with respect to uniform perturbations.

To find when nonuniform states may evolve in a shallow reactor, we subject the uniform steady-state solution to small nonuniform spatial perturbations

$$
\underline{\omega}_{mn}(\xi, \phi) = \begin{bmatrix} \omega_1 J_m(\mu_{mn}\xi)e^{im\phi} \\ \omega_2 J_m(\mu_{mn}\xi)e^{im\phi} \\ \omega_3 J_m(\mu_{mn}\xi)e^{im\phi} \end{bmatrix} \qquad (15)
$$

where m and n are the azimuthal and radial mode numbers, $e^{im\phi}$ and $J_m(\mu_{mn}\xi)$ are the corresponding eigenfunctions. Due to the no-flux boundary condition μ_{mn} satisfies the relation

$$
\left.\frac{dJ_m(\mu_{mn}\xi)}{d\xi}\right|_{\xi=1} = mJ_m(\mu_{mn}) - \mu_{mn}J_{m+1}(\mu_{mn}) = 0 \qquad (16)
$$

A stable uniform steady-state solution (of the shallow reactor model) becomes unstable to nonuniform perturbations (Eq. 15) when

$$
\det(\mathbb{L}_{\mathbb{TP}}) = \det(\mathbb{L}_2 - \mu_{mn}^2\mathbb{P}_2) = 0 \qquad (17)
$$

where the subscript $\mathbb{TP}$ denotes two-phase and

$$
\mathbb{P}_2 = \begin{bmatrix} \frac{1}{\varepsilon}\frac{1}{Pe^h_{f,\perp}} & 0 & 0 \\ 0 & \frac{1}{\varepsilon}\frac{1}{Pe^m_{f,\perp}} & 0 \\ 0 & 0 & \frac{1}{(Le - \varepsilon)}\frac{1}{Pe^h_{s,\perp}} \end{bmatrix}. \qquad (18)
$$

Using Eq. 14, we can rewrite Eq. 17 as

$$
\varepsilon^2(Le - \varepsilon)\left[1 + \frac{\mu_{mn}^2}{Pe^h_{f,\perp}}\frac{1}{(1 + St_h)}\right]\det(\mathbb{L}_2) + \frac{\mu_{mn}^2}{Pe^m_{f,\perp}}\left[\left(\frac{\mu_{mn}^2}{Pe^h_{f,\perp}} + 1 + St_h\right)\left(-St_h + \beta\mathbb{R}_{\theta_s} - \frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\right) + St_h^2\right] + (-1 + \mathbb{R}_{x_f}) \times \left[\frac{\mu_{mn}^2}{Pe^h_{f,\perp}}\frac{St_h^2}{(1 + St_h)} + \frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\left(\frac{\mu_{mn}^2}{Pe^h_{f,\perp}} + 1 + St_h\right)\right] = 0 \qquad (19)
$$

Following substitution of $(-1 + \mathbb{R}_{x_f})$ from Eq. 14 in Eq. 19, we define a modified determinant

$$
\mathbb{D} = \det(\mathbb{L}_2)\varepsilon^2(Le - \varepsilon)\left[1 + \frac{\mu_{mn}^2}{Pe^h_{f,\perp}(1 + St_h)} + \frac{1}{St_h}\left\{\frac{\mu_{mn}^2}{Pe^h_{f,\perp}}\frac{St_h^2}{(1 + St_h)} + \frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\mathbb{K}\right\}\right] \qquad (20)
$$

where

$$
\mathbb{K} = \left(\frac{\mu_{mn}^2}{Pe^h_{f,\perp}} + 1 + St_h\right) \qquad (21)
$$

Condition (Eq. 17) for loss of stability due to nonuniform perturbations can be rewritten as

$$
\mathcal{M}^s_{\mathbb{TP}} = \frac{-\frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\left[\mathbb{K}\left(-St_h + \beta\mathbb{R}_{\theta_f} - \frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\right) + St_h^2\right]}{\mathbb{D} - \frac{\beta\mathbb{R}_{\theta_f}(1 + St_h)}{St_h}\left[\frac{\mu_{mn}^2}{Pe^h_{f,\perp}}\frac{St_h^2}{(1 + St_h)} + \frac{\mu_{mn}^2}{Pe^h_{s,\perp}}\mathbb{K}\right]} \qquad (22)
$$

where we define

$$
\mathcal{M}^s_{\mathbb{TP}} = \frac{Pe^m_{f,\perp}}{Pe^h_{s,\perp}} = \mathcal{M}^f_{\mathbb{TP}}\left(\frac{(1 - \varepsilon)\lambda_{s,\perp}}{\varepsilon\lambda_{f,\perp}}\right) \qquad (23)
$$

and

$$
\mathcal{M}^f_{\mathbb{TP}} = \frac{Pe^m_{f,\perp}}{Pe^h_{f,\perp}} = \frac{(\lambda_{f,\perp}/(\rho C_p)_f)}{D_{f,\perp}} \qquad (24)
$$

Condition (Eq. 22) may be rewritten as

$$\left[\mathbb{D} - \beta\mathbb{R}_{\theta_s} St_h \frac{\mu_{mn}^2}{Pe_{f,\perp}^h} - \frac{\mu_{mn}^2}{Pe_{s,\perp}^h}\left\{\left(\frac{\beta\mathbb{R}_{\theta_s}}{St_h} + \frac{\mu_{mn}^2}{Pe_{s,\perp}^h}\right)\mathbb{K} + \left(\frac{\mu_{mn}^2}{Pe_{f,\perp}^h} + 1\right)St_h\right\}\right] = (1 - \mathcal{M}_{\mathbb{T}\mathbb{P}}^s) \times \left[\mathbb{D} - \frac{\beta\mathbb{R}_{\theta_s}(1 + St_h)}{St_h}\left\{\frac{\mu_{mn}^2}{Pe_{f,\perp}^h}\frac{St_h^2}{(1 + St_h)} + \frac{\mu_{mn}^2}{Pe_{s,\perp}^h}\mathbb{K}\right\}\right] \quad (25)$$

(A detailed derivation of Eq. 25 is presented in Viswanathan and Luss.[19]) $\mathcal{M}_{\mathbb{T}\mathbb{P}}^f$, the ratio between the transversal fluid phase heat to mass dispersion, is of order 1. The heat conductivity of solid phase is much larger than that of the fluid phase that is, $\mathcal{M}_{\mathbb{T}\mathbb{P}}^h = (1 - \varepsilon)\lambda_{s,\perp}/(\varepsilon\lambda_{f,\perp}) \gg 1$. Hence, in packed-bed reactors $\mathcal{M}_{\mathbb{T}\mathbb{P}}^s \gg 1$. For a stable uniform steady state, both $\det(\mathbb{L}_2)$ (Eq. 14) and the modified determinant $\mathbb{D}$ (Eq. 20) are negative. The rate of most chemical reactions increases monotonically with solid phase temperature, that is, $\mathbb{R}_{\theta_s} > 0$. In all these cases, the lefthand side of Eq. 25 is negative definite, and that condition can be satisfied only if $\mathcal{M}_{\mathbb{T}\mathbb{P}}^s < 1$. However, as $\mathcal{M}_{\mathbb{T}\mathbb{P}}^s \gg 1$, we conclude that *a bifurcation from a stable uniform state to a stationary, nonuniform state cannot be predicted by a two-phase model of a shallow, adiabatic reactor in which the reaction rate depends only on the surface temperature and concentration of the limiting reactant.* Such a bifurcation can occur only if we make the unrealistic assumption that $\mathcal{M}_{\mathbb{T}\mathbb{P}}^s < 1$.

Conclusions and Remarks

The proof about the shallow two-phase model complements that by Viswanathan et al.[15] for the pseudohomogeneous model. Together, they lead to the important conclusion that adiabatic packed-bed reactor models (both the pseudohomogeneous and two-phase models) do not predict, for realistic dispersion values, a bifurcation from a stable uniform state to one with a stationary nonuniform transversal temperature using a rate expression which depends only on the surface temperature and limiting reactant concentration, such as an n$^{\text{th}}$ order rate expression. Viswanathan et al.[15] observed that stable states with nonuniform transversal temperature formed only on branches of solutions that bifurcated from a stable uniform state. This suggests that neither one of the two models can predict evolution of a stable nonuniform temperature pattern. This raises the question of how to reconcile the many reported findings of local hot zones in adiabatic packed-bed reactors with these findings. We believe that this quandary is caused by the use of oversimplified kinetic expressions, and that use of more detailed rate expression is needed to enable prediction of hot zone evolution. For example, Viswanathan and Luss[20] recently reported that spatiotemporal transversal patterns may be predicted by a model of a shallow, adiabatic packed-bed reactor using a rate expression that can lead to isothermal oscillations. These rate expressions usually depend in addition to the surface concentration of a limiting reactant and temperature on other variables such as sub-surface reactant concentration, temporal activity of the surface, and so on. An example of such a rate expression is that for CO oxidation.[21,22] We conclude that common packed-bed reactor models fail to predict the formation of local hot spots in an adiabatic packed-bed reactor when using the common two variables rate expressions. However, using more detailed rate expressions may enable them to predict formation of spatiotemporal temperature patterns.

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Notations

a_v = specific surface area, m^2/m^3
C = concentration, mol/m^3
C_p = specific heat capacity, $J/(kg.K)$
det = determinant
D = species diffusion coefficient, m^2/s
$\mathbb{D}$ = modified determinant, defined by Eq. 20
Da = Damköhler number
E = activation energy, J/mol
h = interfacial heat-transfer coefficient, $W/(K.m^2)$
$\mathbb{I}$ = identity matrix
J = Bessel function of first kind
k = interfacial mass-transfer coefficient, m/s
k_∞ = intrinsic reaction rate constant, $1/s$
$\mathbb{K}$ = constant, defined by Eq. 21
L = reactor length, m
$\mathbb{L}$ = first Fréchet derivative
Le = Lewis number, defined by Eq. 4
$\mathcal{M}^f$ = ratio of transversal fluid phase heat to mass dispersions
$\mathcal{M}^h$ = ratio of transversal solid phase heat to fluid phase heat conductivities
$\mathcal{M}^s$ = ratio of transversal solid phase heat to fluid phase mass dispersions
$\mathbb{P}_2$ = transversal perturbation matrix
Pe = Peclet number, defined by Eq. 4
prod = product, defined by Eq. A2
r = radial coordinate, m
R = reactor radius, m
$\mathbb{R}$ = dimensionless reaction rate
$\bar{R}$ = universal gas constant, $J/(mol.K)$
St_h = Stanton number for heat, defined by Eq. 4
St_m = Stanton number for mass, defined by Eq. 4
T = temperature, K
$\mathbb{T}$ = coefficients, defined by Eqs. A8 – A10
tr = trace
v = linear velocity, m/s
x = conversion, defined by Eq. 4
z = axial coordinate, m

Greek

β = adiabatic temperature rise, defined by Eq. 4
γ = dimensionless activation energy, defined by Eq. 4
δ = density, kg/m^3
ε = bed voidage
η = dimensionless axial coordinate
θ = dimensionless temperature, defined by Eq. 4
λ = thermal conductivity,
μ = transversal eigenmode number
ξ = dimensionless radial coordinate
σ = eigenvalue
τ = dimensionless time, defined by Eq. 4
ϕ = azimuthal coordinate
ω = imaginary coefficient of eigenvalue defined in Eq. A3
ω_i = i$^{\text{th}}$ component of nonuniform perturbation
$-\Delta H$ = heat of the reaction, J/mol

Subscripts

a = axial
f = fluid phase
in = inlet
m = azimuthal mode number

n = radial mode number
s = solid phase
ss = transversally uniform steady state
$\mathbb{TP}$ = two-phase
$\perp$ = transversal

Superscripts

h = heat
m = mass
$\mathbb{SR}$ = shallow reactor

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Appendix I

Condition for the existence of a Hopf Bifurcation

The eigenvalues of $\mathbb{L}_2$ are the solutions of the characteristic polynomial

$$\det(\mathbb{L}_2 - \sigma\mathbb{I}) = -\sigma^3 + \mathrm{tr}(\mathbb{L}_2)\sigma^2 - \mathrm{prod}(\mathbb{L}_2)\sigma + \det(\mathbb{L}_2) = 0 \tag{A1}$$

where $\mathbb{I}$ is the identity matrix, $\mathrm{tr}(\mathbb{L}_2)$ the trace of $\mathbb{L}_2$, $\det(\mathbb{L}_2)$ defined by Eq. 14, and

$$\begin{aligned}\mathrm{prod}(\mathbb{L}_2) = {} & \frac{1}{\varepsilon^2}(-1 - St_h)(-1 + \mathbb{R}_{x_f}) + \frac{1}{\varepsilon(Le - \varepsilon)}(-1 - St_h) \\ & \times (-St_h + \beta\mathbb{R}_{\theta_s}) + \frac{1}{\varepsilon(Le - \varepsilon)}(-1 + \mathbb{R}_{x_f})(-St_h + \beta\mathbb{R}_{\theta_s}) \\ & - \frac{\beta\mathbb{R}_{x_f}\mathbb{R}_{\theta_s}}{\varepsilon(Le - \varepsilon)} - \frac{St_h^2}{\varepsilon(Le - \varepsilon)}\end{aligned} \tag{A2}$$

A Hopf bifurcation from a uniform steady state of the shallow reactor model (Eq. 9–12) occurs when a pair of complex eigenvalues of $\mathbb{L}_2$ (Eq. 13) crosses the imaginary axis. At the Hopf bifurcation point, a pair of complex eigenvalues

$$\sigma = \pm i\omega \tag{A3}$$

is the (nontrivial) solution of

$$\pm i\omega^3 - \mathrm{tr}(\mathbb{L}_2)\omega^2 \mp \mathrm{prod}(\mathbb{L}_2)i\omega + \det(\mathbb{L}_2) = 0 \tag{A4}$$

Separating the real and imaginary parts, for the unique nontrivial solution for ω, condition (Eq. A4) reduces to

$$\det(\mathbb{L}_2) - \mathrm{tr}(\mathbb{L}_2)\mathrm{prod}(\mathbb{L}_2) = 0. \tag{A5}$$

After eliminating $(-1 + \mathbb{R}_{x_f})$ using the expression for $\det(\mathbb{L}_2)$ in Eq. 14, a sequence of algebraic manipulations leads to

$$\begin{aligned}\mathrm{tr}(\mathbb{L}_2) = {} & -\frac{1}{\varepsilon} - St_h\left(\frac{Le}{\varepsilon(Le - \varepsilon)}\right) + \frac{\varepsilon(Le - \varepsilon)}{St_h}\det(\mathbb{L}_2) \\ & - \beta\mathbb{R}_{\theta_s}\left(\frac{(1 + St_h)}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right)\end{aligned} \tag{A6}$$

$$\begin{aligned}\mathrm{prod}(\mathbb{L}_2) = {} & -\det(\mathbb{L}_2)\left[(Le - \varepsilon)\frac{(1 + St_h)}{St_h} + \varepsilon\right] \\ & + \frac{\beta\mathbb{R}_{\theta_s}}{\varepsilon}\left[\frac{(1 + St_h)^2}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right] + \frac{St_h}{\varepsilon(Le - \varepsilon)}\end{aligned} \tag{A7}$$

Using A6-A7, Eq. A5 may be rewritten in terms of $\det(\mathbb{L}_2)$ as

$$\mathbb{T}_1\det(\mathbb{L}_2)^2 + \mathbb{T}_2\det(\mathbb{L}_2) + \mathbb{T}_3 = 0 \tag{A8}$$

where

$$\mathbb{T}_1 = \frac{\varepsilon(Le - \varepsilon)}{St_h}\left[\varepsilon + \frac{(Le - \varepsilon)(1 + St_h)}{St_h}\right], \tag{A9}$$

$$\mathbb{T}_2 = -\frac{1}{\varepsilon}\left[1 + \frac{Le\,St_h}{Le - \varepsilon} + \beta R_\theta\left(\frac{1 + St_h}{St_h} - \frac{\varepsilon}{Le - \varepsilon}\right)\right]\left[\varepsilon + \frac{(Le - \varepsilon)(1 + St_h)}{St_h}\right] - \beta R_\theta\left[\frac{Le - \varepsilon}{St_h}\left(\frac{(1 + St_h)^2}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right)\right], \tag{A10}$$

and

$$\mathbb{T}_3 = \frac{St_h}{\varepsilon^2(Le - \varepsilon)}\left(1 + \frac{Le\,St_h}{Le - \varepsilon}\right) + \frac{\beta\mathbb{R}_{\theta_s}}{\varepsilon}\left[\frac{St_h}{Le - \varepsilon} + \beta\mathbb{R}_{\theta_s}\left(\frac{(1 + St_h)^2}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right)\right]\left(\frac{1 + St_h}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right) + \frac{\beta\mathbb{R}_{\theta_s}}{\varepsilon^2}\left(1 + \frac{Le\,St_h}{Le - \varepsilon}\right)\left(\frac{(1 + St_h)^2}{\varepsilon St_h} - \frac{1}{Le - \varepsilon}\right) \tag{A11}$$

(A detailed derivation of Eq. A8 is presented in Viswanathan and Luss[19]). Equation A8 is the condition for a Hopf bifurcation to occur in a shallow, adiabatic packed bed reactor described by a two-phase model (Eqs 9–12) with any kinetic model $\mathbb{R}(\theta_s, x_f)$.

$\det(\mathbb{L}_2) < 0$ on both the ignited and extinguished branches. For most kinetic models the reaction rate increases monotonically with the solid phase temperature, that is, $\mathbb{R}_{\theta_s} > 0$. For $\mathbb{R}_{\theta_s} > 0$ and any practical set of parameters $\mathbb{T}_1 > 0$, $\mathbb{T}_2 < 0$ and $\mathbb{T}_3 > 0$ (Eqs. A8 – A10). Therefore, when $\det(\mathbb{L}_2) < 0$ the lefthand side of Eq. A8 is positive definite while the righthand side is zero. Thus, a Hopf bifurcation cannot occur on either the ignited or extinguished branch of the two-phase model of a shallow, adiabatic packed-bed reactor described by Eqs 9–12. However, a Hopf bifurcation may occur from a uniform unstable steady-state at which $\det(\mathbb{L}_2) > 0$.

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