Transients in Tubular Reactors: Comparison of One- and Two-Dimensional Models

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The accuracy of one-dimensional models for transients in nonadiabatic tubular reactors relative to the two-dimensional models they approximate is reported. A recently developed one-dimensional model yields sufficient accuracy to promote its use in model-based control and process design.

Accurate and easy-to-solve models for the dynamic simulation of nonadiabatic, fixed-bed chemical reactors are important for real-time control and process design. Tubular reactors are modeled by partial differential equations spanning axial, radial, and temporal dimensions (Karanth and Hughes, 1974). Direct numerical solution of these equations, however, requires a large amount of computation (Pirkle et al., 1987). The amount of required computation is often reduced (Beek and Singer, 1951) by, in essence, approximating the reaction rate to be independent of radial position, thereby allowing analytic solution of the radial dependence of temperature and composition. By averaging the conservation equations over the reactor cross section, the radial dimension is eliminated from the modeling equations. We refer to these resulting equations with one spatial dimension (1-D) as the standard model.

Recently, Hagan et al. (1988; see also Pirkle et al., 1987) found asymptotically correct radial variations of reaction rate—and, accordingly, temperature and composition—in tubular reactors, again eliminating the radial dimension by averaging over the reactor cross section; we refer to this as the asymptotic model (1-D). They compared solutions of the two 1-D models for reactor steady states with solutions of the two-dimensional modeling equations and found that the asymptotic model better approximates the behavior of the 2-D model, especially for reactors susceptible to thermal runaway.

In this paper we assess the accuracy of the asymptotic and standard models for reactor transients. Comparisons are based on 1-D and 2-D model equations described in Table 1. Comparison implies that there is a source of discrepancy between the 1-D models and the 2-D models they imitate which stems from the unsteady change in radial temperature profile. Nevertheless, the asymptotic model still yields improved accuracy over the standard model.

Solution of Model Equations

Finite-difference methods are used to solve both 1-D and 2-D models. Axial derivatives are approximated by three-point upwind (second-order backward) differences. Radial derivatives are approximated by second-order central differences. Temporal derivatives are approximated by first-order backward differences. A one-Newton-step, predictor/corrector algorithm developed for Navier-Stokes applications (Kheshgi, 1983) is used to select time step-size. An evenly spaced array of 101 axial by 21 radial nodes (for the 2-D model) proved accurate enough to enable us to probe approximation error of the 1-D models. Solutions are computed out to an axial position of $z = 1$.

Results

In this section we compare solutions of the two one-dimensional reactor models, the standard and asymptotic models, with those of the two-dimensional equations for two choices of physical parameters. In both cases the heat capacity of the fluid is small relative to that of the reactor bed—$\delta = 0.002$—as is expected in a gas phase reactor; the concentration c is the quasisteady state at the current reactor temperature at all but short times. The Biot number $Bi = 4.8$ implies that thermal resistance within the bed, and between the bed and reactor coolant, are comparable; about half the temperature drop between the reactor axis and coolant occurs in the catalyst bed. A choice of $\gamma = 10$ implies a moderate nonlinear growth of reaction rate with temperature.

A radial Peclet number $Pe_H = 0.05$ is chosen for the first case and results in a mild temperature rise of less than a factor of 0.03 times the temperature of the reactor coolant. Figure 1 shows the start-up temperature rise predicted by the three mod-

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Table 1. Dimensionless Modeling Equations

2-D Modeling Equations

$$\frac{\partial T}{\partial t} + \frac{\partial T}{\partial z} = \frac{1}{Pe_H}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \Delta T_{ad}\, c\, e^{\gamma(1-1/T)}$$

$$\delta\frac{\partial c}{\partial t} + \frac{\partial c}{\partial z} = \frac{1}{Pe_M}\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) - c\, e^{\gamma(1-1/T)}$$

Boundary conditions

$$\frac{\partial c}{\partial r} = \frac{\partial T}{\partial r} = 0 \quad \text{at } r = 0,$$

$$\frac{\partial c}{\partial r} = 0 \quad \text{and} \quad \frac{\partial T}{\partial r} = Bi(1 - T) \quad \text{at } r = 1$$

$$c = 0 \quad \text{and } T = 1 \quad \text{at } t = 0,$$
$$c = 1 \quad \text{and } T = 1 \quad \text{at } z = 0$$

1-D Models

$$\frac{\partial \bar{T}}{\partial t} + \frac{\partial \bar{T}}{\partial z} = \Delta T_{ad}\,\bar{c}\, e^{\gamma(1-1/\bar{T})} - \frac{2U(\bar{T} - 1)}{Pe_H}$$

$$\delta\frac{\partial \bar{c}}{\partial t} + \frac{\partial \bar{c}}{\partial z} = -\bar{c}\, e^{\gamma(1-1/\bar{T})}$$

Standard model overall heat transfer coefficient

$$U = \frac{1}{\frac{1}{Bi} + \frac{1}{4}}$$

Asymptotic model overall heat transfer coefficient

$$\gamma\frac{(\bar{T} - 1)}{\bar{T}^2} = \frac{(\bar{T} - 1)U\gamma}{\bar{T}^2\, Bi} - \ln\left[1 - \frac{(\bar{T} - 1)U\gamma}{4\,\bar{T}^2}\right] - \frac{\bar{T}}{3\gamma}\ln^2\left[1 - \frac{(\bar{T} - 1)U\gamma}{4\,\bar{T}^2}\right]$$

els. The asymptotic model closely reproduces the results of the 2-D model for the steady state temperature profile, as Hagan et al. (1988) found; however, the asymptotic model overpredicts temperature rise during the transient by as much as 7% relative to the current temperature rise in the reactor. Discrepancy between the asymptotic and 2-D models is due to inaccuracy of the approximate radial temperature profile used in the asymptotic model; during the start-up transient, the radial temperature variation predicted by the 2-D model is smaller than that used by the asymptotic model. The time required for the reactor to heat up is of $O(Pe_H)$, making the heat accumulation term, $\partial T/\partial t$ (Table 1), the same order of magnitude as the radial dispersion term; neglecting this term in the derivation of radial temperature profile (Pirkle et al., 1987) leads to the discrepancy. The standard model mimics the asymptotic model initially, but underpredicts temperature rise of the steady state (Hagan et al., 1988).

In the second comparison case $Pe_H = 0.1$, which results in a temperature rise of nearly a factor of 0.1 times the temperature of the reactor coolant. Figure 2 shows the start-up transients predicted by the three models. The accuracy of the standard model is inadequate. The asymptotic model results still overestimate temperature rise during the transient and at steady state. As reported by Hagan et al., the accuracy of the asymptotic model for steady steate solutions deteriorates as Pe_H increases, increasing temperature rise and approaching thermal runaway.

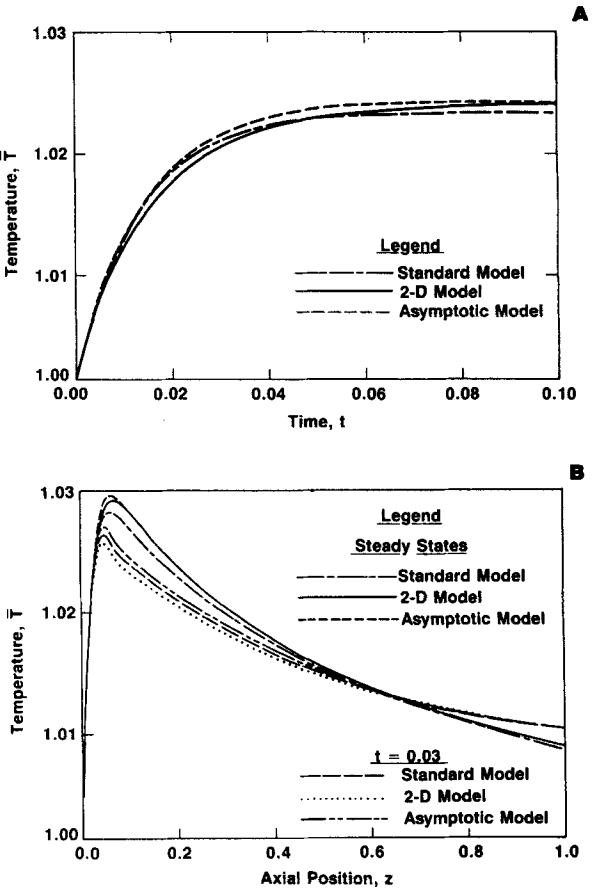

Figure 1. Time evolution of temperature $\bar{T}$ predicted by the three models for a reactor with a small temperature rise.

$Pe_M = 0.0625$; $Pe_H = 0.05$; $\delta = 0.002$; $\Delta T_{ad} = 2$; $Bi = 4.8$
a. $\bar{T}$ vs. t at axial position $z = 0.2$.
b. $\bar{T}$ vs. z at time $t = 0.03$ and steady state.

The accuracy of the asymptotic model transient relative to the current temperature rise is, however, better than when $Pe_H = 0.05$.

Conclusions

Predictions of the standard and asymptotic model (two 1-D models), are compared with those of the two-spatial-dimension model equations describing transients in fixed-bed reactors. The standard model has sufficient accuracy when temperature rise is mild. The asymptotic model has high accuracy for steady state predictions, as reported by Hagan et al. (1988), and lower, but sufficient, accuracy for predictions of reactor transients.

The minimal time for computer-aided solution (Pirkle et al., 1987) along with acceptable accuracy, compared with solutions of the 2-D equations, makes the asymptotic model attractive for model-based control.

Notation

$Bi = hR/\Lambda$, Biot number
c = dimensionless concentration
C_p = specific heat
D = radial mass dispersion coefficient
E = activation energy

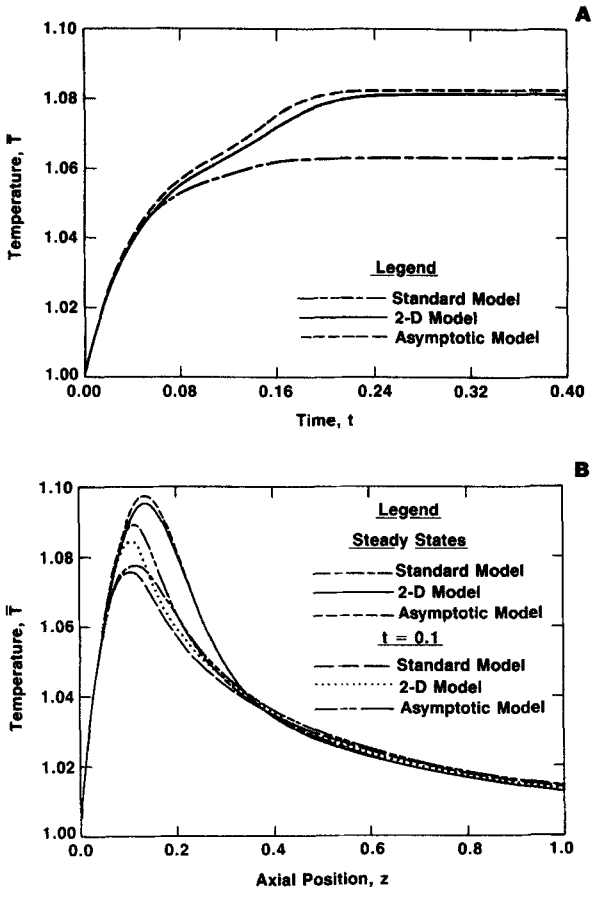

Figure 2. Time evolution of temperature $\bar{T}$ predicted by the three models for a reactor with a large temperature rise.

$Pe_M = 0.125$; $Pe_H = 0.1$; $\delta = 0.002$; $\Delta T_{ad} = 2$; $Bi = 4.8$

a. $\bar{T}$ vs. t at axial position $z = 0.2$.

b. $\bar{T}$ vs. z at time $t = 0.1$ and steady state.

$L = c_o u/S(c_o, T_o)$, unit of axial length measure

$Pe_H = u\rho_f C_{pf} R^2/\Lambda L$, radial Peclet number for heat dispersion

$Pe_M = uR^2/DL$, radial Peclet number for mass dispersion

S = dimensional reaction rate

r = dimensionless radial coordinate

R = unit of radial length measure, reactor radius

R_g = universal gas constant

t = dimensionless time

$t' = L/u\delta$, unit of time measure

T = dimensionless temperature

$\Delta T_{ad} = -\Delta H c_o/\rho_f C_{pf} T_o$, dimensionless adiabatic temperature rise

U = overall heat transfer coefficient

z = dimensionless axial coordinate

Greek letters

$\delta = \epsilon\rho_f C_{pf}/[(1-\epsilon)\rho_s C_{ps} + \epsilon\rho_f C_{pf}]$, heat capacity ratio

ϵ = void fraction

$\gamma = E/R_g T$, dimensionless activation energy

Λ = radial heat dispersion coefficient

Subscripts

f = interstitial fluid

o = inlet, wall and initial values

s = pellet

overbar = reaction-weighted, radially averaged value

Literature Cited

Beek, J., and E. Singer, "A Procedure for Scaling-up a Catalytic Reactor," *Chem. Eng. Prog.*, **47**, 534 (1951).

Hagan, P. S., M. Herskowitz, and J. C. Pirkle, Jr., "A Simple Approach to Highly Sensitive Tubular Reactors," *SIAM J. Appl. Math.* (1988).

Karanth, N. G., and R. Hughes, "Mathematical Modeling of Heterogeneous Catalytic Reactions," *Cat. Rev. Sci. Eng.*, **9**(2), 169 (1974).

Kheshgi, H. S., "The Motion of Viscous Liquid Films," Ph.D. Thesis, Univ. Minnesota, Minneapolis (1983).

Pirkle, J. C., S. C. Reyes, P. S. Hagan, H. S. Kheshgi, and W. E. Schiesser, "Solution of Dynamic Distributed-Parameter Model of Nonadiabatic, Fixed-Bed Reactor," *Comp. Chem. Eng.*, **11**, 737 (1987).

Manuscript received Dec. 10, 1987, and revision received Jan. 26, 1988.