On the Number of Steady States of the Nonadiabatic Tubular Reactor

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Tubular reactors have been the subject of many theoretical and experimental studies. A summary of these results can be found in review articles by Varma and Aris (1977) and Razon and Schmitz (1987). One main issue was to find criteria for the uniqueness of the steady state and the number of steady state solutions. Using computational and asymptotic methods, it is now established that the maximum number of steady states for an adiabatic tubular reactor in which a single exothermic reaction occurs is three. For the nonadiabatic tubular reactor, Varma and Amundson (1973) found five steady state solutions. Kapila and Poore (1982) extended this maximum number from five to seven using large activation energy asymptotics. In a recent study, Alexander (1990) showed using the method of averaging that the nonadiabatic tubular reactor may have an arbitrarily large number of steady states, provided the activation energy is sufficiently large.

We show here that the last restriction is not necessary. For any activation energy that lies above the boundary for uniqueness of a steady state, an arbitrarily large number of steady states can exist. We analyze the limiting Neumann model (Balakotaiah, 1989) using bifurcation theory and find an infinite number of bifurcation points on the unstable branch. This leads to the conclusion that there are always parameter regions that give rise to arbitrarily many steady states. The results for the limiting model are compared with those of the complete model by numerical calculations.

We consider a cooled tubular reactor in which an irreversible first-order reaction occurs. For simplicity, we assume that the cooling temperature is equal to the inlet temperature. The dimensionless energy and species balances are

$$\frac{1}{Pe_h}\frac{d^2\theta}{dz^2} - \frac{d\theta}{dz} + \Delta \exp\left(\frac{\theta}{1+\theta/\gamma}\right)x - St\theta = 0 \qquad (1)$$

$$\frac{1}{Pe_m}\frac{d^2x}{dz^2} - \frac{dx}{dz} - \frac{\Delta}{B}\exp\left(\frac{\theta}{1+\theta/\gamma}\right)x = 0 \qquad (2)$$

where θ is the dimensionless temperature, x is the dimensionless concentration, and z is the axial coordinate. Pe is the Peclet number (heat and mass), γ is the activation energy, B is the dimensionless heat of reaction, St is the Stanton number, and Δ is a Damkoehler number. The corresponding boundary conditions are

$$\frac{1}{Pe_h}\frac{d\theta}{dz} = \theta \quad \frac{1}{Pe_m}\frac{dx}{dz} = x - 1 \quad \text{at} \quad z = 0$$

$$\frac{d\theta}{dz} = 0 \quad \frac{dx}{dz} = 0 \quad \text{at} \quad z = 1 \qquad (3)$$

If B is much larger than Δ, then the reactant consumption is negligible and we may drop the species balance. The energy balance may then be written as

$$\frac{1}{\Delta Pe_h}\frac{d^2\theta}{dz^2} - \frac{1}{\Delta}\frac{d\theta}{dz} + \exp\left(\frac{\theta}{1+\theta/\gamma}\right) - \frac{St}{\Delta}\theta = 0 \qquad (4)$$

In the limiting case of large values of St and Δ and small values of Pe_h, Eq. 4 simplifies to

$$\frac{1}{\delta}\frac{d^2\theta}{dz^2} + \exp\left(\frac{\theta}{1+\theta/\gamma}\right) - \frac{1}{Se}\theta = 0 \qquad (5)$$

where

$$\delta = \Delta Pe_h \quad Se = \frac{\Delta}{St} \qquad (6)$$

The new parameters are the Frank-Kamenetskii number, δ, and the Semenov number, Se. Equation 5 is known as the Neumann model for strongly cooled tubular reactors (Balakotaiah, 1989).

The boundary conditions for the Neumann model are

$$\frac{d\theta}{dz} = 0 \quad \text{at} \quad z = 0, 1 \tag{7}$$

Equations 5 and 7 have solutions that are constant over the whole reactor length. If we assume that θ is independent of z, then Eq. 5 becomes

$$\exp\left(\frac{\theta_c}{1 + \theta_c/\gamma}\right) = \frac{1}{Se}\theta_c \tag{8}$$

The subscript c stands for constant (spatially homogeneous) solution. It can easily be verified that Eq. 8 has one solution for $\gamma < 4$ and three solutions for $\gamma > 4$, for some range of the Semenov number. To find nonuniform solutions we rewrite Eq. 5 as

$$\frac{d^2\theta}{dz^2} = \delta\left[\frac{1}{Se}\theta - \exp\left(\frac{\theta}{1 + \theta/\gamma}\right)\right] \equiv \delta f(\theta) \tag{9}$$

Nontrivial (spatially inhomogeneous) solutions of Eq. 9 bifurcate from the constant solutions when the linear operator

$$Lu \equiv \frac{d^2u}{dz^2} - \delta f'(\theta_c)u; \quad \frac{du}{dz} = 0 \quad \text{at} \quad z = 0, 1 \tag{10}$$

is not invertible (f' stands for the derivative of f with respect to θ). If we denote $\delta f'(\theta_c)$ to be λ, then the linear operator with the boundary conditions leads to the eigenvalue problem

$$\frac{d^2u}{dz^2} = -\lambda u \quad \frac{du}{dz} = 0 \quad \text{at} \quad z = 0, 1 \tag{11}$$

The solution of Eq. 11 gives the eigenfunctions and corresponding eigenvalues

$$u_m = \cos(m\pi z) \quad \lambda_m = m^2\pi^2 \quad m = 0, 1, 2, \ldots \tag{12}$$

Comparison of Eq. 12 and Eq. 10 gives the values of δ at the bifuraction points:

$$m^2\pi^2 = -\delta f'(\theta_c) \quad m = 1, 2, \ldots \tag{13}$$

It follows from Eq. 13 that bifurcation points exist only on branches where

$$f'(\theta_c) < 0 \tag{14}$$

When $\gamma < 4$, Eq. 14 never holds. For $\gamma > 4$, Eq. 14 holds for the middle solution (whenever it exists). This means that no new solution branches off the upper or lower constant solution. Only the middle uniform solution has bifurcation points at

$$\delta_m = -\frac{m^2\pi^2}{f'(\theta_c)} \quad m = 1, 2, \ldots \tag{15}$$

The local nature of the bifurcation diagram may be determined using the Liapunov-Schmidt reduction (Golubitsky and Schaeffer, 1985). Writing

$$\theta = \theta_c + x\cos(m\pi z) \tag{16}$$

the branching equation is

$$g(x, \mu) \equiv \alpha_1 x^3 + \alpha_2 \mu x + \ldots \tag{17}$$

where x is the amplitude and $\mu = \delta - \delta_m$. The coefficients α_1 and α_2 may be calculated as

$$\alpha_1 = -\frac{\delta_m}{16}f'''(\theta_c) - \frac{5}{24}\frac{\delta_m^2}{m^2\pi^2}[f''(\theta_c)]^2 \tag{18}$$

$$\alpha_2 = -\tfrac{1}{2}f'(\theta_c) \tag{19}$$

It follows from Eq. 14 that α_2 is always positive. Numerical calculations have shown that α_1 is always negative. Thus, the local bifurcation diagram is a supercritical pitchfork.

In Figure 1 we show the bifurcation diagram of exit temperature vs. δ, of Eq. 5 for fixed γ and Se. At the values predicted by Eq. 15, new solutions bifurcate supercritically from the unstable middle branch. All new solutions lie between the stable upper

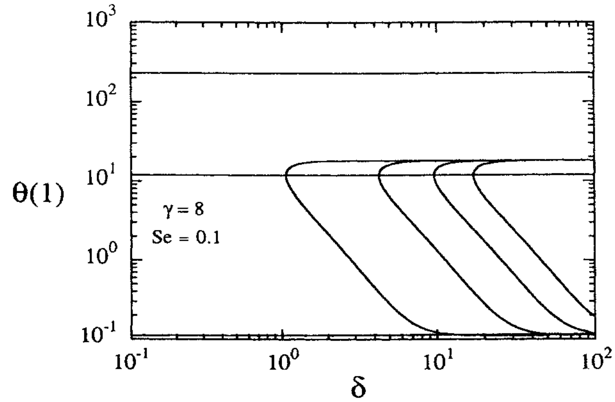

Figure 1. Bifurcation diagram of exit temperature vs. Frank-Kamenetskii number for Neumann model.

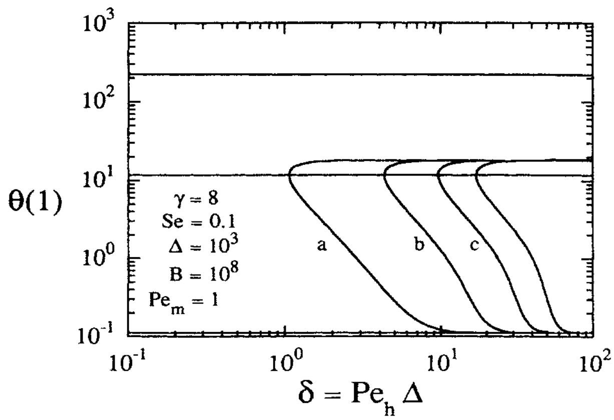

Figure 2. Bifurcation diagram of exit temperature vs. Frank-Kamenetskii number for full model.

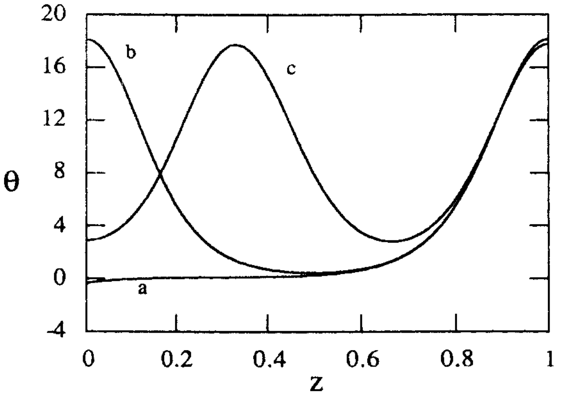

Figure 3. Temperature profiles of nonuniform solutions above the middle branch.
Parameters as in Fig. 2, $\delta = 16$

and lower branches. Because they bifurcate from an unstable solution, all new branches are also unstable close to the bifurcation point. For increasing values of δ more and more solutions exist.

To show that this phenomenon is not restricted to the Neumann model, we solve the full model given by Eqs. 1–3 numerically for parameters that are close to this limiting model. In Figure 2 we see that there is no qualitative difference, because the bifurcation diagram is very similar to the one in Figure 1. There are three nearly constant solutions and from the middle constant solution new spatially oscillatory solutions branch off supercritically. In Figure 3 and 4 the six nonuniform solutions of the full model for $\delta = 16$ are shown. In Figure 3 we see the solution branches that lie above the middle branch and in Figure 4 the ones below. The temperature profiles look roughly like the cosine eigenfunctions of Eq. 11.

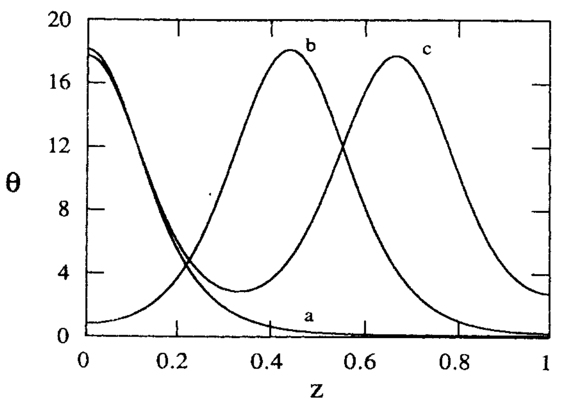

Figure 4. Temperature profiles of nonuniform solutions below the middle branch.
Parameters as in Fig. 2, $\delta = 16$

The parameters we used for the calculations are unrealistic. In more realistic parameter regions this approach is not useful and no conclusions on the number of steady states can be drawn. The goal of this note is not to provide a guide to finding new solutions, but to relate the features of the classic nonadiabatic tubular reactor to those of the simplified Neumann model.

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NOTATION

- B = dimensionless heat of reaction
- Pe_h = Peclet number (heat)
- Pe_m Peclet number (mass)
- Se = Semenov number
- St = Stanton number
- u = eigenfunction
- x = dimensionless concentration
- z = dimensionless axial direction

Greek letters

- γ = dimensionless activation energy
- δ = Frank-Kamenetskii number
- Δ = Damkoehler number
- λ = eigenvalue
- θ = dimensionless temperature

Subscripts

- c = spatially homogeneous solution
- m = mth bifurcation point

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