Stability of Tubular Reactors

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The stability of tubular reactors has been investigated by many workers for the case of equal mass and heat transfer Peclet numbers (Amundson, 1965, Amundson and Raymond, 1964; Gupalo and Ryazantsev, 1969; Hlavacek et al., 1970, 1971; Nishimura and Matsubara, 1969; Van Heerden, 1958). The case of unequal mass and heat transfer Peclet numbers has been considered by Nishimura and Matsubara (1969) and Clough and Ramirez (1972) using the Lyapunov direct method. Nishimura and Matsubara (1969) have obtained sufficient conditions for local stability which require the solution of some matrix differential equations, whereas Clough and Ramirez (1972) have obtained a sufficient condition in the form of an inequality which requires steady state information. The result obtained by Ramirez and Clough has been shown to be erroneous (McGreavy and Soliman, 1972) and it is our purpose here to provide some inequalities which serve as sufficient conditions for local stability of tubular reactors.

A BASIC INEQUALITY

Tubular reactors are usually modeled by a set of coupled parabolic partial differential equations in the case when axial diffusion is taken into account. In this sense the means of investigations of stability of tubular reactors parallel those for the catalyst particle. The extension of the Lyapunov direct method to distributed parameter systems (Hahn, 1963) has been successfully applied in studying the stability of a catalyst particle as well as tubular reactors. A useful inequality for such studies is included in the following theorem (Mikhlin, 1964; Yang, 1971).

THEOREM

For any continuously differentiable function $u(x)$, $x \in [0, 1]$ satisfying the boundary conditions $u^1(0) = Au(0)$ and $u^1(1) = -Au(1)$, the following inequality holds:

$$A(u^2(0) + u^2(1)) + \int_0^1 u^{1,2}(x)dx \geq \lambda_1^2 \int_0^1 u^2(x)dx \tag{1}$$

where A is a positive constant and λ_1 is the smallest positive root of

$$\lambda \tan \frac{\lambda}{2} = A \tag{2}$$

SUFFICIENT CONDITIONS FOR STABILITY

A nonadiabatic tubular reactor in which a chemical reaction $A \rightarrow$ product occurs can be modeled by the following dimensionless equations:

$$\frac{\partial y}{\partial t} = \frac{1}{Pe_M} \frac{\partial^2 y}{\partial x^2} - \frac{\partial y}{\partial x} - R \tag{3}$$

$$\frac{\partial z}{\partial t} = \frac{1}{Pe_H} \frac{\partial^2 z}{\partial x^2} - \frac{\partial z}{\partial x} + R + m(z_w - z) \tag{4}$$

at $x = 0$:

$$\frac{\partial y}{\partial x} = Pe_M\,(y - 1)$$

$$\frac{\partial z}{\partial x} = Pe_H\,(z - 1) \tag{5}$$

at $x = 1$:

$$\frac{\partial y}{\partial x} = \frac{\partial z}{\partial x} = 0$$

where

$$y = \frac{C}{C^0}, \quad z = \frac{T}{\Delta T_{ad}}, \quad \Delta T_{ad} = \frac{(-\Delta H)C^0}{C_p\rho}$$

$$Pe_M = \frac{vl}{D}, \quad Pe_H = \frac{C_p\rho vl}{k}, \quad R = \frac{rl}{C^0 v}, \quad m = \frac{2hl}{C_p\rho av}$$

Consider the stability of the reactor around some steady state (y^*, z^*). For this purpose, define the perturbation variables

$$Y = y - y^*$$
$$Z = z - z^*$$

Whereby linearizing Equations (3) to (5) around this steady state we obtain

$$\frac{\partial Y}{\partial t} = \frac{1}{Pe_M} \frac{\partial^2 Y}{\partial x^2} - \frac{\partial Y}{\partial x} - R_y^*\,Y - R^*_z\,Z \tag{6}$$

$$\frac{\partial Z}{\partial t} = \frac{1}{Pe_H} \frac{\partial^2 Z}{\partial x^2} - \frac{\partial Z}{\partial x} + R_y^*\,Y + (R^*_z - m)\,Z \tag{7}$$

at $x = 0$:

$$\frac{\partial Y}{\partial x} = Pe_M\,Y$$

$$\frac{\partial Z}{\partial x} = Pe_H\,Z \tag{8}$$

at $x = 1$:

$$\frac{\partial Y}{\partial x} = \frac{\partial Z}{\partial x} = 0$$

By substituting

$$Y = u_1 \exp\left(\frac{Pe_M}{2} x\right) \qquad Z = u_2 \exp\left(\frac{Pe_H}{2} x\right)$$

the linearized partial differential equations can be written in the form

$$\frac{\partial u_1}{\partial t} = p_{11} \frac{\partial^2 u_1}{\partial x^2} - q_{11}(x) u_1 - q_{12}(x) u_2 \qquad (9)$$

$$\frac{\partial u_2}{\partial t} = p_{22} \frac{\partial^2 u_2}{\partial x^2} - q_{21}(x) u_1 - q_{22}(x) u_2 \qquad (10)$$

with the boundary conditions

$$\text{at} \quad x = 0: \quad p_{11} \frac{\partial u_1}{\partial x} = ½ u_1, \qquad p_{22} \frac{\partial u_2}{\partial x} = ½ u_2 \qquad (11)$$

$$\text{at} \quad x = 1: \quad p_{11} \frac{\partial u_1}{\partial x} = -½ u_1, \quad p_{22} \frac{\partial u_2}{\partial x} = -½ u_2 \qquad (12)$$

where

$$p_{11} = \frac{1}{Pe_M}, \quad p_{22} = \frac{1}{Pe_H} \qquad (13)$$

$$\left.\begin{aligned} q_{11}(x) &= \frac{Pe_M}{4} + R_y^*, \\ q_{12}(x) &= R_z^* \exp\left(\frac{Pe_H - Pe_M}{2} x\right) \\ q_{21}(x) &= -R_y^* \exp\left(\frac{Pe_M - Pe_H}{2} x\right), \\ q_{22}(x) &= \frac{Pe_H}{4} + m - R_z^* \end{aligned}\right\} \qquad (14)$$

Consider a positive definite Lyapunov functional of the following form:

$$V = \frac{1}{2} \int_0^1 [u_1^2 + C^2 u_2^2] \, dx \qquad (15)$$

where C^2 is a constant.

Differentiating V with respect to time, we obtain

$$\begin{aligned} \frac{dV}{dt} &= \int_0^1 \left[u_1 \frac{\partial u_1}{\partial t} + C^2 u_2 \frac{\partial u_2}{\partial t} \right] dx \\ &= \int_0^1 \left[p_{11} u_1 \frac{\partial^2 u_1}{\partial x^2} + C^2 p_{22} u_2 \frac{\partial^2 u_2}{\partial x^2} \right] dx \\ &\quad - \int_0^1 [q_{11} u_1^2 + C^2 q_{22} u_2^2 + u_1 u_2 (q_{12} + q_{21} C^2)] \, dx \end{aligned} \qquad (16)$$

Integrating the first integral by parts and substituting the boundary conditions (11) and (12) we obtain

$$\begin{aligned} \frac{dV}{dt} &= -\left(\frac{u_1^2(0) + u_1^2(1)}{2}\right) - \frac{C^2}{2} (u_2^2(0) + u_2^2(1)) \\ &\quad - \int_0^1 \left[p_{11} \left(\frac{\partial u_1}{\partial x}\right)^2 + C^2 p_{22} \left(\frac{\partial u_2}{\partial x}\right)^2 \right] dx \\ &\quad - \int_0^1 [q_{11} u_1^2 + C^2 q_{22} u_2^2 + u_1 u_2 (q_{12} + C^2 q_{21})] \, dx \end{aligned} \qquad (17)$$

Making use of inequality (1) we obtain

$$½ (u_1^2(1) + u_1^2(0)) + \int_0^1 p_{11} \left(\frac{\partial u_1}{\partial x}\right)^2 dx \geq \lambda_{11}^2 \int_0^1 p_{11} u_1^2 \, dx \qquad (18)$$

where λ_{11} is the smallest positive root of

$$2\lambda p_{11} \tan \frac{\lambda}{2} = 1 \qquad (19)$$

Also

$$½ (u_2^2(1) + u_2^2(0)) + \int_0^1 p_{22} \left(\frac{\partial u_2}{\partial x}\right)^2 dx \geq \lambda_{22}^2 \int_0^1 p_{22} u_2^2 \, dx \qquad (20)$$

where λ_{22} is the smallest positive root of

$$2\lambda p_{22} \tan \frac{\lambda}{2} = 1 \qquad (21)$$

Substituting inequalities (18) and (20) into Equation (17) we obtain

$$\begin{aligned} \frac{dV}{dt} \leq &- \int_0^1 [(\lambda_{11}^2 p_{11} + q_{11}) u_1^2 \\ &+ C^2 (\lambda_{22}^2 p_{22} + q_{22}) u_2^2 + (q_{12} + C^2 q_{21}) u_1 u_2] \, dx \end{aligned} \qquad (22)$$

For dV/dt to be negative definite, it is sufficient that

$$\lambda_{11}^2 p_{11} + q_{11} > 0 \qquad \forall \; x \in [0, 1] \qquad (23)$$

$$C^2 (\lambda_{11}^2 p_{11} + q_{11}) (\lambda_{22}^2 p_{22} + q_{22}) > ¼ (q_{12} + C^2 q_{21})^2 \qquad \forall \; x \in [0, 1] \qquad (24)$$

Inequality (23) is already satisfied for $R_y^* > 0$. If C^2 exists for which inequality (24) is satisfied then the steady state is locally stable.

For the case of equal Peclet numbers, that is, $Pe_H = Pe_M = Pe$ and for an adiabatic reactor, that is, $m = 0$, inequality (24) can be written as

$$C^2 \left(\lambda_{11}^2 + Pe\left(\frac{Pe}{4} + R_y^*\right)\right) \left(\lambda_{11}^2 + Pe\left(\frac{Pe}{4} - R_z^*\right)\right) > \frac{Pe^2}{4} (-R_z^* + C^2 R_y^*)^2 \qquad (25)$$

However, a stronger condition can be obtained as follows. Nishimura and Matsubara (1969) have shown that for this case the stability of the governing equations can be obtained by studying the stability of a single partial differential equation:

$$\frac{\partial u_1}{\partial t} = \frac{1}{Pe} \frac{\partial^2 u_1}{\partial x^2} - \left(\frac{Pe}{4} + R_y^* - R_z^*\right) u_1 \qquad (26)$$

$$\left.\begin{aligned} &\text{at} \quad x = 0, \quad \frac{1}{Pe} \frac{\partial u_1}{\partial x} = ½ u_1; \\ &\text{at} \quad x = 1, \quad \frac{1}{Pe} \frac{\partial u_1}{\partial x} = -½ u_1 \end{aligned}\right. \qquad (27)$$

By choosing a Lyapunov functional

$$V = \frac{1}{2} \int_0^1 u_1^2 \, dx \qquad (28)$$

and going through the above analysis, a sufficient condition for local stability is

$$\lambda_1^2 + Pe\left(\frac{Pe}{4} + R_y^* - R_z^*\right) > 0 \quad \forall\, x \epsilon\, [0, 1] \quad (29)$$

where λ_1 is the smallest positive root of

$$2\lambda \tan \frac{\lambda}{2} = Pe \quad (30)$$

Inequality (29) can be rewritten in the following form

$$\frac{R_z^*}{Pe} < \frac{1}{4} + \frac{R_y^*}{Pe} + \frac{\lambda_1^2}{Pe^2} \quad (31)$$

whereas the erroneous condition obtained by Clough and Ramirez (1972) requires

$$\frac{R_z^*}{Pe} < 1 \quad (32)$$

Therefore, the stability of the solutions of the numerical example studied by Clough and Ramirez (1972) should be studied using inequality (31) rather than (32).

CONCLUDING REMARKS

The stability of tubular reactors with axial diffusion has been studied through the Lyapunov direct method with a Lyapunov functional in a quadratic form with a diagonal weighting matrix having constant elements. Another approach which in some cases may yield stronger conditions is to use a Lyapunov functional of the following form

$$V = \frac{1}{2}\int_0^1 [u_1 u_2] \begin{bmatrix} w_1(x) & w_3(x) \\ w_3(x) & w_2(x) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} dx \quad (33)$$

where

$$w_i = P_i \cos \pi \bar{a}_i \,(x - 1/2) \quad i = 1, 2, 3$$

P_i's are constants and $0 < \bar{a}_i < 1$.

This approach has been used by Murphy and Crandall (1970) to study the stability of a catalyst particle and by McGreavy and Soliman (1972) to study the stability of a fixed bed catalytic reactor. The extension of this approach to stability studies of tubular reactors is straightforward, for example, for the case of equal Peclet numbers for heat and mass transfer, the following condition can be easily obtained

$$\frac{R_z^*}{Pe} < \frac{1}{4} + \frac{R_y^*}{Pe} + \frac{\bar{\lambda}_1^2}{2Pe^2} \quad (34)$$

where $\bar{\lambda}_1$ is the smallest positive solution of

$$\lambda \tan \frac{\lambda}{2} = Pe \quad (35)$$

Inequality (34) is generally weaker than inequality (31).

Finally, it should be mentioned that the idea of applying Lyapunov direct method to distributed parameter systems with the aid of Rayleigh type inequalities [inequality (1)] has been used to study the stability of some other physical systems (for example, Movchan, 1959).

NOTATION

a = reactor radius
A = positive constant
C = concentration of the reactant
C^0 = initial concentration of the reactant
C_p = specific heat
D = diffusion coefficient
h = heat transfer coefficient
$(-\Delta H)$ = heat of reaction
k = thermal conductivity
l = length of reactor
m = dimensionless heat transfer coefficient
q, p = parameters defined in Equations (13) and (14)
Pe_H = Peclet number of heat transfer
Pe_M = Peclet number of mass transfer
R = dimensionless reaction rate
r = reaction rate
T = temperature of the reactant
T^0 = initial temperature of the reactant
ΔT_{ad} = adiabatic temperature rise
u_1, u_2 = perturbation variables
V = Lyapunov functional
v = velocity in the reactor
x = dimensionless length
y = dimensionless concentration
z = dimensionless temperature

Greek Letters

λ = parameter
ρ = density

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