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III. Effect of Recycle

This paper reports on an investigation of the individual effects of radial gradients and axial mixing on the steady state and stability characteristics of the tubular reactor-recycle system, differing in this respect from most previous studies which have concentrated on the case in which the reactor is a plug-flow tubular reactor (PFTR).

Bilous and Amundson (*2*) used Laplace domain techniques to show that unstable steady states are possible in the PFTR-recycle system. A thorough analysis of the PFTR-recycle system by Reilly and Schmitz (*9, 10*) showed that multiple steady states and unique unstable steady states are also possible. The transient behavior of the system was represented by a system of discrete equations, relating the reactant concentration and temperature of an element of fluid on its $(k+1)^{th}$ pass through the reactor exit to the conditions on the k^{th} pass through the exit.

Luss and Amundson (*5*) restricted their analysis to the adiabatic PFTR-recycle system, which allowed a graphical argument to be used to locate the steady states and determine their stability character. Root and Schmitz (*11*) investigated the adiabatic PFTR-recycle system experimentally and verified the presence of multiple steady states.

Schmeal and Amundson (*12*) solved the unsteady state material balance for an isothermal tubular reactor with axial mixing and recycle (TRAM-recycle). The analysis showed that the addition of a recycle line to the TRAM changes the character of the unsteady state response from nonoscillatory to oscillatory; that is, the dominant eigenvalue of the linear system changes from a real to a complex number.

THE TUBULAR REACTOR WITH RADIAL MIXING AND RECYCLE

The steady state material and energy balances and the boundary conditions of the tubular reactor with finite radial mixing were given in Part II (*8*):

$$\frac{\partial y}{\partial z} = \frac{1}{N_{Pe'}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial y}{\partial r} \right] - \mathcal{R}(y, \eta) \qquad (1)$$

$$\frac{\partial \eta}{\partial z} = \frac{1}{N_{Pe}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial \eta}{\partial r} \right] + \mathcal{R}(y, \eta) \qquad (2)$$

$$r = 0: \quad \left.\frac{\partial y}{\partial r}\right|_0 = \left.\frac{\partial \eta}{\partial r}\right|_0 = 0 \qquad (3)$$

$$r = 1: \quad \left.\frac{\partial y}{\partial r}\right|_1 = 0, \quad \left.\frac{1}{N_{Pe}} \frac{\partial \eta}{\partial r}\right|_1 = U_r [\eta_w - \eta(1)] \qquad (4)$$

An additional condition is needed at the reactor entrance in order to account for the recycle line. It is assumed that the recycle line is adiabatic, that no chemical reaction occurs outside the reactor, and that the recycle stream passes instantaneously from the exit to the entrance of the reactor, where it is instantaneously mixed with fresh feed. Inspection of the schematic flow diagram in Figure 1 shows that

$$z = 0: \quad y(0, r) = y_0 = (1 - R_r) + R_r \bar{y}(1) \qquad (5)$$

$$\eta(0, r) = \eta_0 = (1 - R_r)\, \eta_F + R_r \bar{\eta}(1)$$

where $\bar{y}(1)$ and $\bar{\eta}(1)$ are the radial average concentration and temperature at the exit:

$$\bar{y}(1) = 2 \int_0^1 y(1, r)\, r\, dr \qquad (6)$$

$$\bar{\eta}(1) = 2 \int_0^1 \eta(1, r)\, r\, dr \qquad (7)$$

The last assumption—instantaneous recycle—is seldom satisfied in practice. Indeed, the presence of dead time in the recycle line can be a prime cause of instability in such

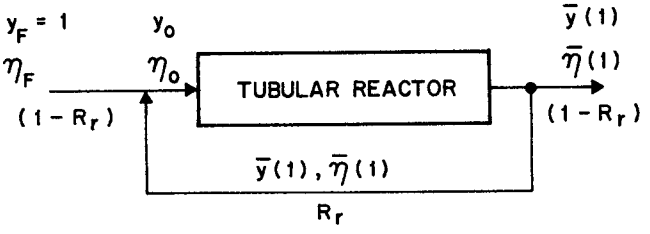

Fig. 1. Schematic diagram of tubular reactor recycle system.

a system. In the discussion of the TRRM-recycle system that follows, however, it will become evident that this system is unaffected by dead time in the recycle line, because the different elements of fluid in the reactor and the recycle line behave independently of one another.

Local Stability and Steady State Analysis

Since no axial dispersion is present in the TRRM-recycle system, each slab of fluid perpendicular to the reactor axis behaves independently of every other slab. Thus the same technique used by Reilly and Schmitz (9) in their analysis of the PTFR-recycle system may be adopted. The transient behavior of the system follows the discrete equations

$$y_0^{(k+1)} = f_y\,[y_0^{(k)},\ \eta_0^{(k)}] \tag{8}$$

$$\eta_0^{(k+1)} = f_\eta\,[y_0^{(k)},\ \eta_0^{(k)}] \tag{9}$$

where the superscripts (k) and $(k+1)$ refer to the k^{th} and the $(k+1)^{\text{th}}$ pass of a given slab of fluid around the reactor-recycle loop, and $y_0^{(k)}$ and $\eta_0^{(k)}$ refer to the reactant concentration and temperature of the slab of fluid as it passes through the reactor entrance on its k^{th} pass. Equations (8) and (9) are linearized about the steady state operating conditions to give

$$\begin{bmatrix} y_0^{(k+1)} \\ \eta_0^{(k+1)} \end{bmatrix} = \begin{bmatrix} \dfrac{\partial y_0^{(k+1)}}{\partial y_0^{(k)}} & \dfrac{\partial y_0^{(k+1)}}{\partial \eta_0^{(k)}} \\ \dfrac{\partial \eta_0^{(k+1)}}{\partial y_0^{(k)}} & \dfrac{\partial \eta_0^{(k+1)}}{\partial \eta_0^{(k)}} \end{bmatrix} \begin{bmatrix} y_0^{(k)} \\ \eta_0^{(k)} \end{bmatrix} = \mathbf{K} \begin{bmatrix} y_0^{(k)} \\ \eta_0^{(k)} \end{bmatrix} \tag{10}$$

Using the chain rule, the matrix $\mathbf{K}$ is expanded to

$$\mathbf{K} = R_r \begin{bmatrix} \overline{U}_y(1) & \overline{U}_\eta(1) \\ \overline{V}_y(1) & \overline{V}_\eta(1) \end{bmatrix} \tag{11}$$

In Equation (11), the variables $\overline{U}_y(1)$, $\overline{U}_\eta(1)$, $\overline{V}_y(1)$, and $\overline{V}_\eta(1)$ are radial averages of the first partial derivatives of the reactant concentration and temperature at the reactor exit with respect to both entrance concentration and temperature. The auxiliary variables—U_y,U_η, V_y, and V_η—are described by the following system of equations and boundary conditions:

$$\frac{\partial U_y}{\partial z} = \frac{1}{N_{Pe'}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial U_y}{\partial r} \right] - \mathcal{R}_y(y,\eta)\, U_y - \mathcal{R}_\eta(y,\eta)\, V_y \tag{12}$$

$$\frac{\partial U_\eta}{\partial z} = \frac{1}{N_{Pe'}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial U_\eta}{\partial r} \right] - \mathcal{R}_y(y,\eta)\, U_\eta - \mathcal{R}_\eta(y,\eta)\, V_\eta \tag{13}$$

$$\frac{\partial V_y}{\partial z} = \frac{1}{N_{Pe}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial V_y}{\partial r} \right] + \mathcal{R}_y(y,\eta)\, U_y + \mathcal{R}_\eta(y,\eta)\, V_y \tag{14}$$

$$\frac{\partial V_\eta}{\partial z} = \frac{1}{N_{Pe}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial V_\eta}{\partial r} \right] + \mathcal{R}_y(y,\eta)\, U_\eta + \mathcal{R}_\eta(y,\eta)\, V_\eta \tag{15}$$

$$z = 0: \quad U_y(0,r) = V_\eta(0,r) = 1, \qquad U_\eta(0,r) = V_y(0,r) = 0 \tag{16}$$

$$r = 0: \quad \left.\frac{\partial U_y}{\partial r}\right|_0 = \left.\frac{\partial U_\eta}{\partial r}\right|_0 = \left.\frac{\partial V_y}{\partial r}\right|_0 = \left.\frac{\partial V_\eta}{\partial r}\right|_0 = 0 \tag{17}$$

$$r = 1: \quad \left.\frac{\partial U_y}{\partial r}\right|_1 = \left.\frac{\partial U_\eta}{\partial r}\right|_1 = 0, \quad \left.\frac{1}{N_{Pe}} \frac{\partial V_y}{\partial r}\right|_1 = -U_r V_y(z,1), \quad \left.\frac{1}{N_{Pe}} \frac{\partial V_\eta}{\partial r}\right|_1 = -U_r V_\eta(z,1) \tag{18}$$

The necessary and sufficient condition for Equation (10) to be asymptotically stable and for the steady state of the TRRM-recycle system to be locally stable is that the magnitudes of the eigenvalues of the matrix $\mathbf{K}$ are less than unity (9).

Equations (12) through (15) are solved simultaneously with the steady state material and energy balances. The auxiliary variables are also used in the Newton-Raphson iterative solution for the entrance and exit concentration and temperature distributions that satisfy the recycle boundary condition at the feed point. The details of the Newton-Raphson computation are discussed in detail in the Reilly and Schmitz paper (9). The elements of the matrix $\mathbf{K}$ are evaluated using the results of the final Newton-Raphson iteration. As a result, no further computations are required to determine the local stability character of the system once the steady state profiles have been obtained.

The Collocation Method

The collocation method, a form of the method of weighted residuals, is used to solve the steady state material and energy balances of the TRRM-recycle system. In Part II of this series (8) it was shown that the collocation solution is in excellent agreement with a solution obtained using an implicit finite-difference technique, even when only five collocation points are used. The collocation method requires substantially less computation than the finite-difference solution to generate numerical solutions of comparable accuracy.

The collocation method reduces Equations (1) and (2) to a system of ordinary differential equations, describing the axial profiles of y and η at a series of collocation points (8). Similar reduced collocation equations are obtained for the Newton-Raphson auxiliary variables.

The radial averages of y, η, U_y, U_η, V_y, and V_η at the reactor exit are computed using the quadrature expression:

$$\int_0^1 f(r)\ r\ dr = \sum_{j=1}^{m+1} W_j\, f(r_j) \tag{19}$$

in which r_j is the j^{th} collocation point, and the quadrature constants W_j are computed using the same procedure used to obtain the collocation constants (12). The resulting expressions for $\overline{y}(1)$ and $\overline{\eta}(1)$ are

$$\overline{y}(1) = 2\left[\sum_{j=1}^{m-1} W_j\, y(1,r_j) + (W_m + W_{m+1})\, y(1,r_m) \right] \tag{20}$$

$$\overline{\eta}(1) = 2\left[\sum_{j=1}^{m-1} W_j\,\eta(1, r_j) + (W_m + aW_{m+1})\,\eta(1, r_m) + bW_{m+1}\right] \quad (21)$$

and similar expressions are obtained for $\overline{U}_y(1)$, $\overline{U}_\eta(1)$, $\overline{V}_y(1)$, and $\overline{V}_\eta(1)$.

The axial profiles of y, η, U_y, U_η, V_y, and V_η at the collocation points are obtained by numerical integration of the reduced collocation equations from $z = 0$ to $z = 1$, using the initial conditions

$$z = 0: \quad y(0, r_i) = y_0, \quad \eta(0, r_i) = \eta_0$$
$$U_y(0, r_i) = V_\eta(0, r_i) = 1$$
$$U_\eta(0, r_i) = V_y(0, r_i) = 0$$

Numerical Results

Steady state operating curves, showing the radial average reactant concentration at the reactor exit as a function of the feed temperature, were generated for various combinations of the radial Peclet numbers and the heat transfer coefficient. As a by-product of the steady state computation, local stability character was determined using the Newton-Raphson auxiliary variables as described earlier.

The chemical reaction was assumed to be first order and irreversible, with Arrhenius temperature dependence

$$\mathcal{R}(y, \eta) = k_0' \exp(-\gamma/\eta)\, y \quad (23)$$

For convenient comparisons, the dimensionless parameters are taken from Reilly and Schmitz' analysis of the PFTR-recycle system (9):

$$\eta_w = 2.50 \qquad \gamma = 75$$
$$R_r = 0.5 \qquad k_0' = 1.0 \times 10^{11}$$

Steady state operating curves are shown in Figure 2 for a range of values of the radial Peclet numbers and for a heat transfer coefficient equal to 0.79. Figure 3 shows similar curves for Peclet numbers equal to five and for several values of the heat transfer coefficient. Five collocation points were used in the solution of the steady state and the Newton-Raphson auxiliary equations. The loca-

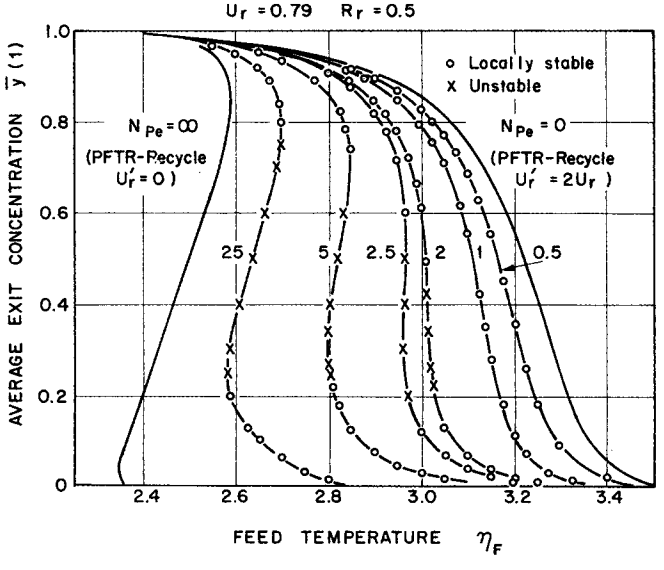

Fig. 2. Steady state operating curves for TRRM-recycle system.

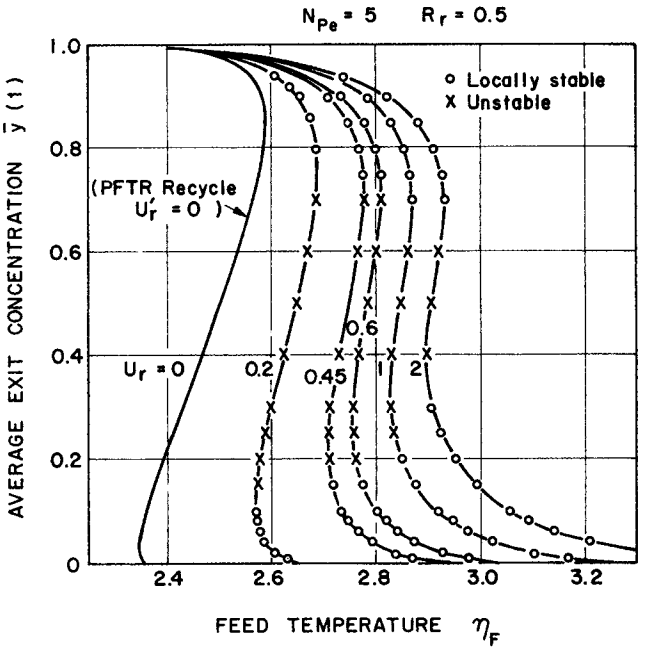

Fig. 3. Steady state operating curves for TRRM-recycle system.

tions of the collocation points and the collocation constants for the Laplacian and quadrature expressions are given in Part II (8). The collocation equations were integrated using the fourth-order Runge-Kutta formula (3), with the integration increment ranging between 0.01 for $N_{Pe} = 25$ and 0.00125 for $N_{Pe} = 0.5$.

Those steady states found to be unstable are marked "x," while locally stable steady states are marked "o" in the figures. All steady states located on the positively sloped portions and some located on the lower negatively sloped portions of the operating curves are unstable and therefore unattainable in the absence of external control.

Discussion

In Part II it was shown analytically that the TRRM system reduces to an adiabatic plug-flow tubular reactor in the limit as radial dispersion approaches zero, and to a nonadiabatic PFTR with heat transfer coefficient equal to twice that of the TRRM system ($U_r' = 2U_r$) in the limit as radial mixing approaches infinity. Thus the steady state operating curves for $N_{Pe} = \infty$ (zero radial dispersion) and $N_{Pe} = 0$ (infinite radial dispersion) in Figure 2 are identical to those of the PFTR-recycle system for $U_r' = 0$ and $U_r' = 2 \times 0.79 = 1.58$, respectively. Figure 2 shows that the steady state and stability characteristics of the TRRM-recycle system exhibit uniform transitions between the characteristics of the two limiting cases. The steady state operating curve for $U_r = 0$ in Figure 3 also corresponds to the operating curve for the adiabatic PFTR-recycle system.

Further examination of the operating curves in Figures 2 and 3 shows that (1) for Peclet numbers less than about 2.5 and $U_r = 0.79$ and for heat transfer coefficients up to at least 2.0 and $N_{Pe} = 5$, three steady states exist for limited ranges of the feed temperature, and unique steady states exist otherwise; (2) unique steady states are locally stable except for Peclet numbers between approximately 1.5 and 2.5 and $U_r = 0.79$. In this range, some unique steady states are unstable, resulting in a limit cycle or continuous oscillation of the reactant concentration and temperature. And (3) in systems having three steady states, the low conversion steady state is always locally

stable, the intermediate steady state is always unstable, and the high conversion steady state is usually but not always locally stable. The high conversion steady state may be unstable for $U_r = 0.79$ and radial Peclet numbers less than about 5 and for $N_{Pe} = 5$ and a heat transfer coefficient greater than about 0.45. In these circumstances, the low conversion steady state is the only attainable one in the absence of an external feedback controller.

Except for very low conversion steady states located on the positively sloped portions of the operating curves, the eigenvalues of the matrix **K** in Equation (10) were complex for each steady state that was found. Thus the discrete transient response of the TRRM-recycle system has an oscillatory character in most cases. Reilly and Schmitz (9) noted that the real parts of the eigenvalues of the matrix **K** were positive for every steady state computed in their analysis of the PFTR-recycle system. This was not uniformly true for the system studied here. For $U_r = 0.79$ and intermediate values of the Peclet numbers and for $N_{Pe} = 5$ and heat transfer coefficients greater than 0.20, for example, some steady states located on the lower portions of the operating curves are associated with complex eigenvalues with negative real parts. As discussed by Reilly and Schmitz (*10*), the significance of having eigenvalues with negative real parts in a linear discrete system, such as Equation (10), is that the signs of the reactor entrance concentration and temperature disturbances tend to alternate on successive passes around the recycle loop. Since the eigenvalues of **K** in the TRRM-recycle system analysis having negative real parts are also complex, however, the entrance concentration and temperature disturbances would be expected to change sign every few cycles around the recycle loop anyway. Thus the fact that the eigenvalues of the discrete representation of the TRRM-recycle system transient behavior have negative real parts in some cases is not of great practical importance.

As an illustration of the discrete transient response of the TRRM-recycle system, a selected limit cycle is plotted in Figure 4 in the coordinates, reactant concentration versus temperature. The initial condition of the fluid element is located near the unique unstable steady state, which is marked by a plus sign. The numbered points show the condition of the plug of fluid as it passes through the reactor entrance during successive passes around the recycle loop. The limit cycle is reached after approximately 40 cycles around the recycle loop, and the period of the limit cycle is approximately 10 cycles. The reactor parameters that yielded the limit cycle include $N_{Pe} = 2$, $U_r = 0.79$, $R_r = 0.5$, and $\eta_F = 3.015$, and the operating point is located on the unstable portion of the steady state operating curve, $N_{Pe} = 2$, in Figure 2. The transient response was generated by recursively integrating the reduced collocation forms of Equations (1) and (2) from $z = 0$ to $z = 1$, computing the radial average concentration and temperature at the reactor exit using Equations (20) and (21), and using the recycle boundary conditions (5) to compute updated entrance conditions.

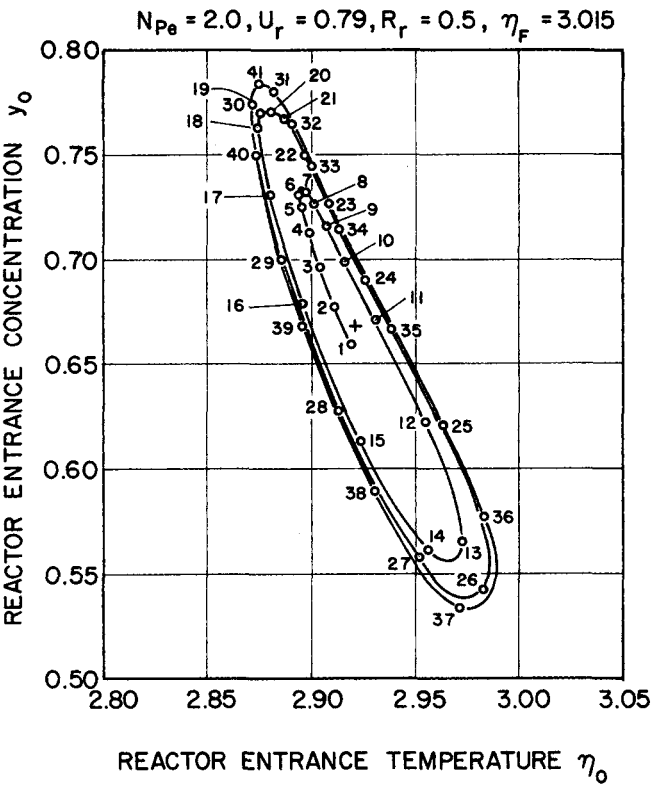

Fig. 4. Discrete transient response and limit cycle for TRRM-recycle system.

THE TUBULAR REACTOR WITH AXIAL MIXING AND RECYCLE

The mathematical model for the tubular reactor with axial mixing (TRAM) was given in Part I of this series (*7*). The time-dependent reactant material and energy balances are

$$\frac{\partial y}{\partial \tau} = \frac{1}{N_{Pe'}} \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - \mathcal{R}(y, \eta) \tag{24}$$

$$\frac{\partial \eta}{\partial \tau} = \frac{1}{N_{Pe}} \frac{\partial^2 \eta}{\partial z^2} - \frac{\partial \eta}{\partial z} + \mathcal{R}(y, \eta) + U_r(\eta_w - \eta) \tag{25}$$

The boundary conditions for the TRAM-recycle system are obtained by substitution of the recycle boundary conditions, Equation (5), for the reactor inlet conditions in the TRAM boundary conditions:

$$z = 0: \quad \frac{1}{N_{Pe'}} \frac{\partial y}{\partial z}\bigg|_0 = y(0) - y_0$$

$$= y(0) - (1 - R_r) - R_r\, y(1) \tag{26}$$

$$\frac{1}{N_{Pe}} \frac{\partial \eta}{\partial z}\bigg|_0 = \eta(0) - \eta_0$$

$$= \eta(0) - (1 - R_r)\eta_F - R_r\, \eta(1)$$

$$z = 1: \quad \frac{\partial y}{\partial z}\bigg|_1 = \frac{\partial \eta}{\partial z}\bigg|_1 = 0 \tag{27}$$

As in the analysis of the TRRM-recycle system, the entrance boundary conditions, Equation (26), assume instantaneous recycle; however, unlike the TRRM-recycle system, the stability and transient response of the TRAM-recycle system are affected by the presence of dead time in the recycle line.

Steady state behavior of the TRAM-recycle system is described by the equations

$$\frac{1}{N_{Pe'}} \frac{d^2 y}{dz^2} - \frac{dy}{dz} - \mathcal{R}(y, \eta) = 0 \tag{28}$$

$$\frac{1}{N_{Pe}} \frac{d^2 \eta}{dz^2} - \frac{d\eta}{dz} + \mathcal{R}(y, \eta) + U_r(\eta_w - \eta) = 0 \tag{29}$$

and the boundary conditions, Equations (26) and (27).

Local Stability and Steady State Analysis

As detailed elsewhere (6), the collocation method may be used to study the stability of the TRAM-recycle system. The method reduces the linearized equations

$$\frac{\partial \hat{y}}{\partial \tau} = \frac{1}{N_{Pe'}} \frac{\partial^2 \hat{y}}{\partial z^2} - \frac{\partial \hat{y}}{\partial z} - \mathcal{R}_y(z)\,\hat{y} - \mathcal{R}_\eta(z)\,\hat{\eta} \quad (30)$$

$$\frac{\partial \hat{\eta}}{\partial \tau} = \frac{1}{N_{Pe}} \frac{\partial^2 \hat{\eta}}{\partial z^2} - \frac{\partial \hat{\eta}}{\partial z} + \mathcal{R}_y(z)\,\hat{y} + [\mathcal{R}_\eta(z) - U_r]\,\hat{\eta} \quad (31)$$

to a set of $2m$ reduced collocation equations, describing the concentration and temperature disturbances at each of m collocation points. The reduced system is linear and homogeneous, has constant coefficients, and is conveniently written in the compact matrix-vector notation:

$$\frac{d\mathbf{x}}{d\tau} = \mathbf{A}\,\mathbf{x} \quad (32)$$

$$\mathbf{x}^T = [\,\hat{y}(z_1)\ \hat{y}(z_2)\ \ldots\ \hat{y}(z_m)\ \ \hat{\eta}(z_1)\ \ldots\ \hat{\eta}(z_m)\,]$$

The necessary and sufficient condition for local stability is that as the number of interior collocation points increases, the dominant eigenvalue of the matrix **A** converges to a constant value whose real part is negative. In a previous paper (6) it was shown that the dominant eigenvalue of the linearized TRAM-recycle equations, estimated using the collocation method, converges to a constant value in an oscillatory manner. This allows the local stability character to be established before convergence actually occurs, since once the amplitude of the oscillations becomes less than the magnitude of the dominant eigenvalue itself, the sign cannot change as m is increased further. It should be noted, however, that convergence of the collocation method has not been proved, and it has even been found to diverge in a few cases (6).

Steady state operating curves were generated for the TRAM-recycle system by using the Newton-Raphson procedure, described in Part I, to obtain solutions of Equations (28) and (29), satisfying the boundary conditions given in Equations (26) and (27).

Ten collocation points were used in the local stability analysis. Marginally stable steady states, located on the boundaries of the region of instability, were obtained by half-interval search along each steady state operating curve. The steady state concentration and temperature at each collocation point were calculated using Newton's divided difference formula (3) to perform third-degree polynomial interpolation of the tabulated steady state profile data. The eigenvalues of the matrix **A** were computed using the QR method (4), an iterative technique involving successive unitary transformations of **A**.

Numerical Results and Discussion

Figures 5 and 6 show steady-state operating curves for $N_{Pe} = 100$ and $N_{Pe} = 0$ and for several values of the heat transfer coefficient. For a range of axial Peclet numbers and for $U_r = 0.2$ and $U_r = 0.79$, similar results are shown in Figures 7 and 8.

The operating curves and the region of instability, shown in Figure 5 for the TRAM-recycle system, are almost identical to those of the PFTR-recycle system, computed by Reilly and Schmitz (9). The transitions between multiple and unique steady state behavior and those between unstable and stable steady states occur for the same values of U_r in both systems. Thus for $N_{Pe} = 100$, the

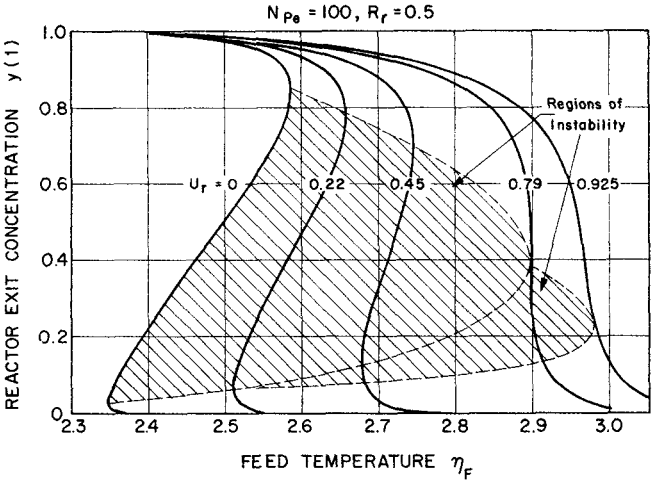

Fig. 5. Steady state operating curves for TRAM-recycle system.

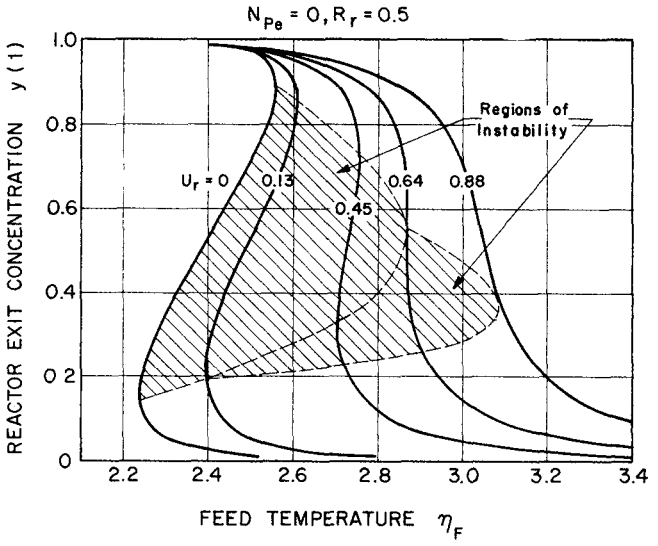

Fig. 6. Steady state operating curves for TRAM-recycle system.

TRAM-recycle system behaves as if it were a PFTR-recycle system. For $0 \leq U_r < 0.22$, three steady states exist over limited ranges of the feed temperature, of which the intermediate conversion steady states are unstable and the low and high conversion steady states are locally stable. For feed temperatures outside these limited ranges, unique, locally stable steady states exist. For $0.22 \leq U_r < 0.79$, three steady states are still possible; however, the high conversion steady state is unstable in some cases, and the low conversion steady state is the only stable one. For $0.79 \leq U_r < 0.925$, only unique steady states exist. Some of these unique steady states are unstable and exhibit limit cycle behavior. Unique unstable steady states and limit cycle behavior are also possible for U_r slightly less than 0.79. Finally, only unique, locally stable steady states are possible for $U_r \geq 0.925$.

For $N_{Pe} = 0$ (infinite axial mixing), the TRAM-recycle system is equivalent to the continuous stirred-tank reactor with recycle (CSTR-recycle). As the heat transfer coefficient increases, the transitions from one type of behavior to another occur at $U_r = 0.13$, 0.64, and 0.88 in the order noted earlier for $N_{Pe} = 100$ (Figure 6).

Figures 7 and 8 show that as the axial Peclet numbers vary, the steady state operating curves exhibit uniform transitions between the operating curves of the equivalent CSTR-recycle and PFTR-recycle systems. For $U_r =$

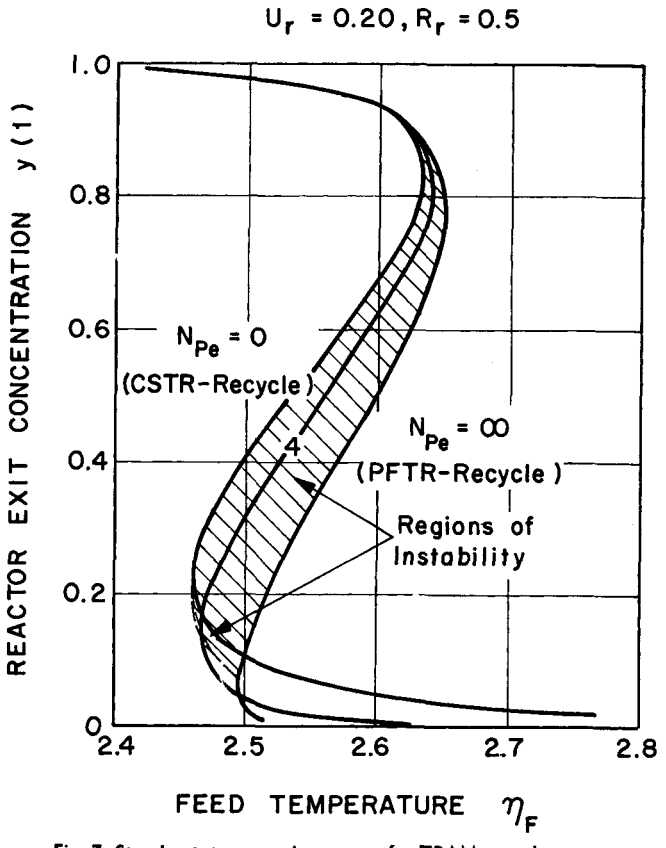

Fig. 7. Steady state operating curves for TRAM-recycle system.

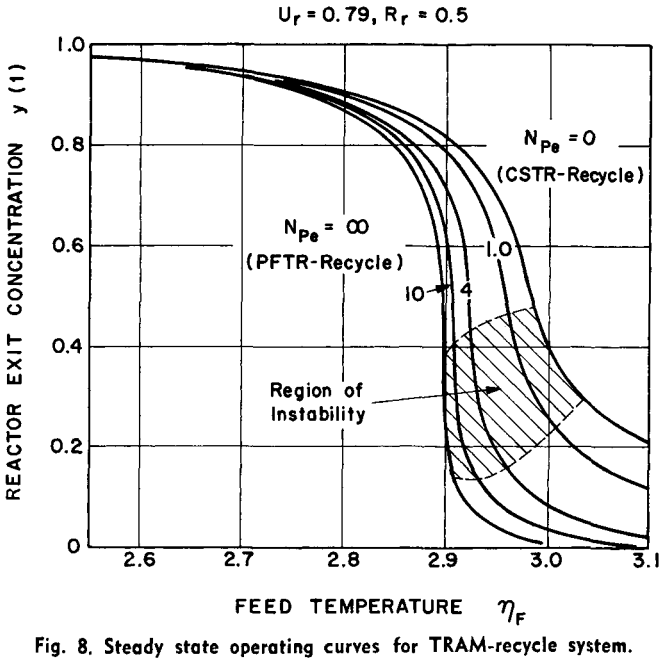

Fig. 8. Steady state operating curves for TRAM-recycle system.

0.20 (Figure 7) three steady states are possible over the full range of Peclet numbers, and unique steady states are locally stable. In most systems having three steady states, only the intermediate conversion steady state is unstable. When the axial Peclet numbers are less than seven, the high conversion steady state of systems having three steady states is unstable in some cases. For $U_r = 0.79$ (Figure 8) only unique steady states exist, and unique unstable steady states are possible over the full range of Peclet numbers, leading to limit cycle behavior.

Transient Response to Uniform and Split Disturbances

A severe limitation of the mathematical model for the PFTR-recycle system is that it cannot predict the correct transient response to disturbances from the steady state profiles that are discontinuous or cross over the steady state profiles of unstable steady states. In the absence of axial mixing, each element of fluid in the system is independent, which allows discontinuities to occur in the temperature and concentration profiles. All real physical reactor systems have some degree of axial mixing, however, and therefore discontinuities in the concentration and temperature profiles cannot be sustained.

The transient responses of two TRAM-recycle systems were obtained for two types of disturbances from unstable steady states. Finite-difference solutions of the unsteady state material and energy balances were generated for both the uniform disturbance

$$\hat{y}(z) = a$$

$$\hat{\eta}(z) = b \tag{33}$$

and the split disturbance

$$\hat{y}(z) = \begin{cases} a\,[0.5(\cos 4\pi z - 1)]; & 0 \leq z \leq 0.25 \\ a \sin[2\pi(z - 0.5)]; & 0.25 \leq z \leq 0.75 \\ a\,[0.5(\cos\,[4\pi(z - 0.75)] + 1)]; & 0.75 \leq z \leq 1 \end{cases} \tag{34}$$

$$\hat{\eta}(z) = \frac{b}{a}\,\hat{y}(z)$$

The split disturbance, given in Equation (34), is a continuous function of z, and is formulated such that it is positive over half of the system and negative over the other half. In addition, the constants a and b in Equations (33) and (34) were always chosen to be of opposite sign in order to obtain concentration and temperature disturbances of opposite sign. Because the transient responses of the concentration profiles are similar to those of the temperature profiles, only graphs of the latter are given here.

System A, whose parameters are $N_{Pe} = 100$, $U_r = 0.45$, and $\eta_F = 2.727$, has three steady states, of which only the intermediate one is unstable. Its responses to a uniform

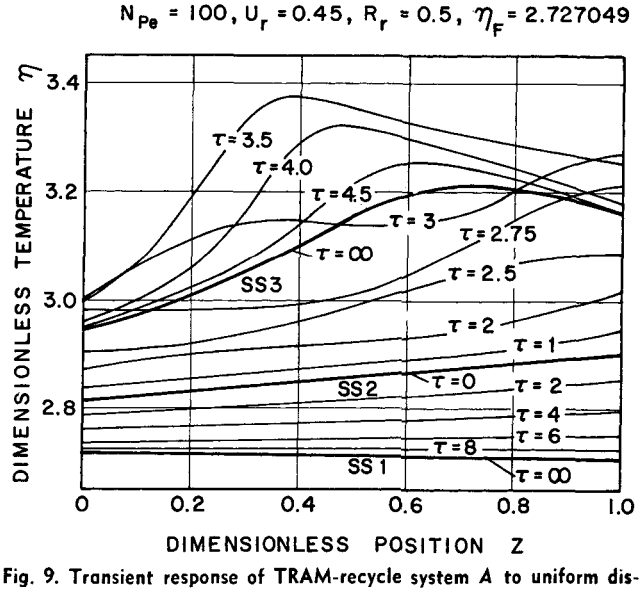

Fig. 9. Transient response of TRAM-recycle system A to uniform disturbances.

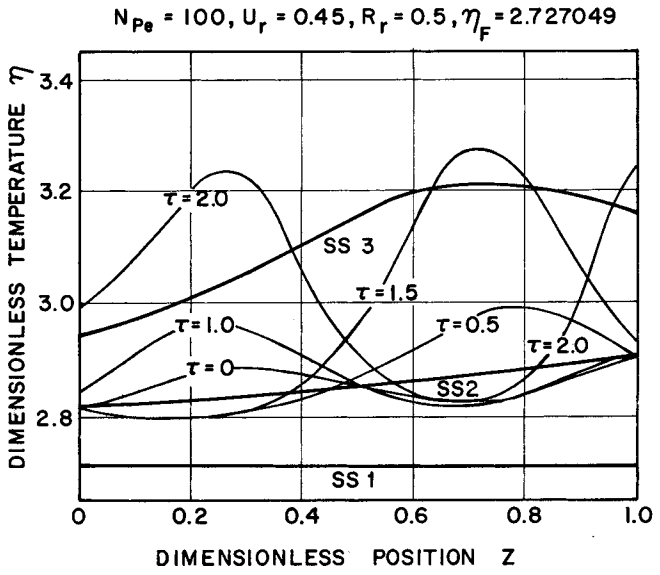

Fig. 10a. Transient response of TRAM-recycle system *A* to a split disturbance (for $\tau \leq 2$).

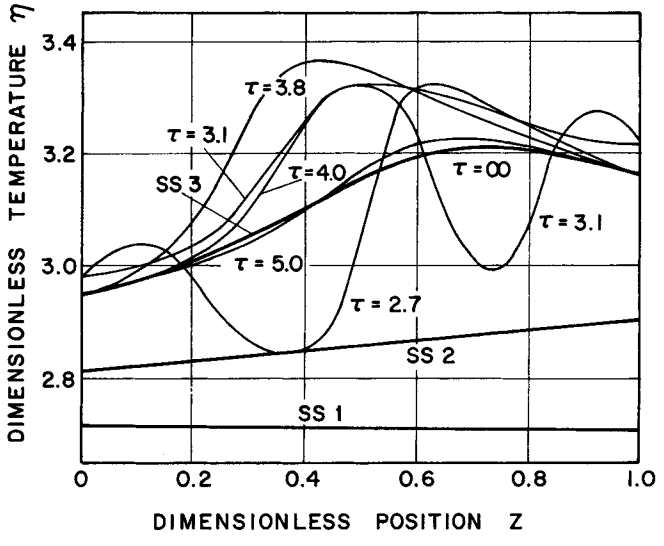

Fig. 10b. Transient response of TRAM-recycle system *A* to a split disturbance (for $\tau \geq 3.1$).

negative concentration and positive temperature disturbance ($a = -0.001$, $b = 0.01$) and to a similar disturbance of opposite sign are shown in Figure 9. The responses are similar to those that would be predicted by the model for the PFTR-recycle system; that is, the positive temperature disturbance decayed to the high temperature steady state after initially overshooting its steady state profiles, while the negative temperature disturbance decayed to the low temperature steady state. The response of system *A* to the split disturbance, Equation (34), with $a = 0.02$ and $b = -0.05$ is shown in Figures 10*a* and 10*b*. After an initial period of oscillation, lasting about three time units, the system moved toward, overshot, and finally came to rest at the high temperature steady state. The response of a similar PFTR-recycle system to the same split disturbance would ultimately leave part of the system at the high temperature steady state and the remainder at the low temperature steady state, resulting in abrupt discontinuities in the concentration and temperature profiles.

System *B*, whose parameters are $N_{Pe} = 100$, $U_r = 0.79$, and $\eta_F = 2.90$, has a unique unstable steady state, which exhibits the limit cycle plotted in Figure 11. The period of the limit cycle is approximately 17 time units. The initial condition used to generate the limit cycle was the uniform disturbance, Equation (33), with $a = -0.001$ and $b = 0.01$. The system took approximately 70 time units to attain the limit cycle from this initial condition. Figure 12 shows the initial transient response of system *B* to the split disturbance, Equation (34), with $a = -0.05$ and $b = 0.10$. After approximately five time units, the split nature of the disturbance has disappeared, and the system eventually approaches the limit cycle plotted in Figure 11. The response of a similar PFTR-recycle system to the same split disturbance would again be unrealistic—abrupt discontinuities would develop in the concentration

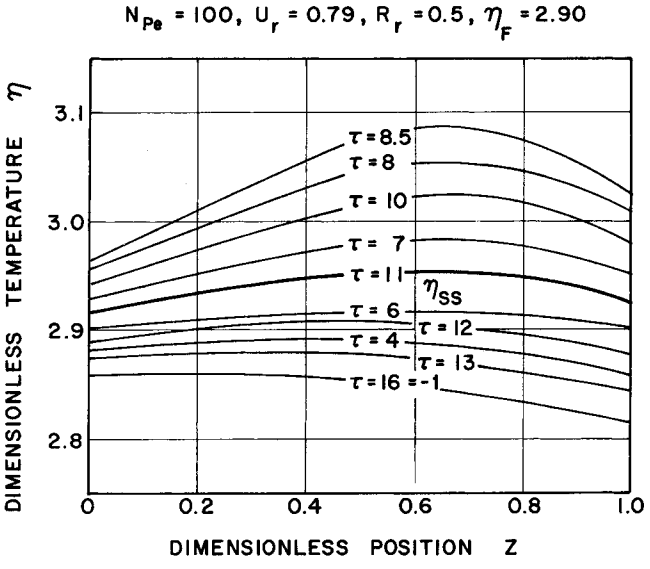

Fig. 11. Limit cycle response of TRAM-recycle; system *B*.

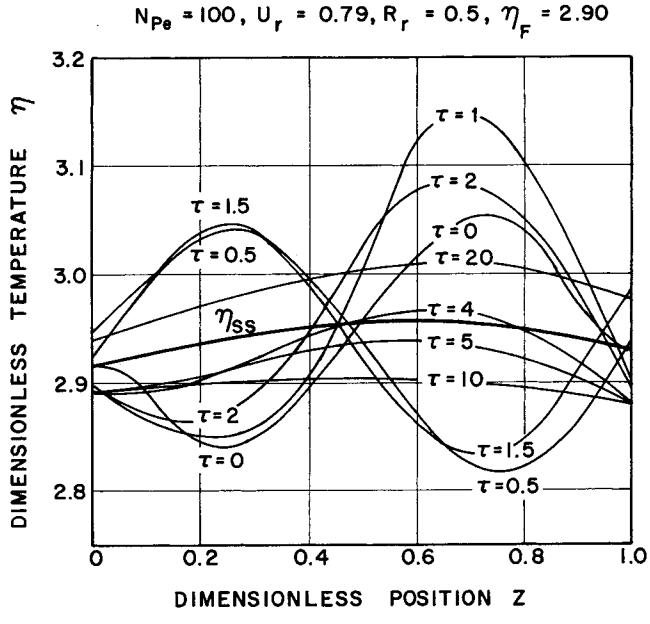

Fig. 12. Initial transient response of TRAM-recycle system *B* to a split disturbance.

and temperature profiles as different segments of the fluid elements in the reactor approach different parts of the limit cycle. Thus in simulations of the transient behavior of tubular reactor-recycle systems, it is important to include axial mixing effects in the mathematical model in order to predict the correct response to all types of disturbances.

Comparison of Radial and Axial Effects

A comparison between the operating curves of the TRRM-recycle system and those of the TRAM-recycle system shows that the tubular reactor-recycle system is much more sensitive to changes in the radial Peclet numbers than to changes in the axial Peclet numbers. In most cases the number of steady states that occur and the local stability character of the steady states remain the same in the TRAM-recycle system as axial mixing varies over a wide range. In the TRRM-recycle system, however, relatively small variations in the radial Peclet numbers can cause a significant change in the character of the system operating condition.

For example, Figure 8 shows that for $\eta_F = 2.90$ and $U_r = 0.79$, the TRAM-recycle system possesses a unique unstable steady state and exhibits limit cycle behavior for axial Peclet numbers between approximately 1.0 and 4.0. Figure 2 shows that the TRRM-recycle system possesses a unique low conversion steady state for radial Peclet numbers equal to 2.5, two locally stable and one unstable steady state for $N_{Pe} = 3.0$, and a unique high conversion steady state for Peclet numbers greater than about 3.5. The sensitivity of the TRRM-recycle system to variations in the radial Peclet numbers increases as the heat transfer coefficient increases, since the steady state operating curves for the two limiting cases—the PFTR-recycle system with $U_r' = 0$ and $U_r' = 2U_r$—move further apart as U_r increases. When recycle flow is large relative to the reactor throughput, the recycle line provides the dominant mode of axial mass and energy feedback. Thus the tubular reactor-recycle system is not expected to be particularly sensitive to axial Peclet number variations, particularly when the axial Peclet numbers are large.

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NOTATION

a = algebraic constant as defined in Part II and text
$\mathbf{A}$ = matrix used in local stability analysis of TRAM-recycle system
b = algebraic constant as defined in Part II and text
C = reactant concentration, g.-mole/cc.
C_p = heat capacity of fluid, cal./(g.-mole)(°K.)
D = effective diffusivity, sq.cm./sec.
E = activation energy, cal./g.-mole
$f(r)$ = hypothetical function of r
f_y, f_η = functions used in discrete representation of TRRM-recycle transient behavior
$(-\Delta H_r)$ = heat of reaction, cal./g.-mole
k_0 = frequency factor, sec.$^{-1}$
k_0' = dimensionless frequency factor (k_0L/v)
$\mathbf{K}$ = matrix used in local stability analysis of TRRM-recycle system
L = reactor length, cm.
m = number of interior collocation points
N_{Pe} = axial or radial heat transfer Peclet number (vL/α or $vR'^2/L\alpha$)
$N_{Pe'}$ = axial or radial mass transfer Peclet number (vL/D or vR'^2/LD)
r = dimensionless radial position (r'/R')
r' = radial position, cm.
r_i = i^{th} radial collocation point
R = gas constant, 1.987 cal./(g.-mole)(°K.)
R' = reactor tube radius, cm.
R_r = fraction reactor effluent that is recycled
$\mathcal{R}(y, \eta)$ = dimensionless reaction rate
$\mathcal{R}_y(y, \eta) = \partial\mathcal{R}/\partial y$
$\mathcal{R}_\eta(y, \eta) = \partial\mathcal{R}/\partial\eta$
$\mathcal{R}_y(z) = \mathcal{R}_y(y_{ss}, \eta_{ss})$
$\mathcal{R}_\eta(z) = \mathcal{R}_\eta(y_{ss}, \eta_{ss})$
t = time, sec.
T = temperature, °K.
U = wall heat transfer coefficient, cal./(sq.cm.)(sec.)(°K.)
U_r = dimensionless wall heat transfer coefficient (TRRM: $UL/\rho C_pR'v$, TRAM: $2UL/\rho C_pR'v$)
$U_y = \partial y/\partial y_0$
$U_\eta = \partial y/\partial\eta_0$
v = flow velocity, cm./sec.
$V_y = \partial\eta/\partial y_0$
$V_\eta = \partial\eta/\partial\eta_0$
W_j = collocation constants used in quadrature expression
x = axial position, cm.
y = dimensionless reactant concentration (C/C_F)
z = dimensionless axial position (x/L)
z_i = i^{th} axial collocation point

Greek Letters

α = thermal diffusivity, sq.cm./sec.
γ = dimensionless activation energy $(\rho C_pE/(-\Delta H_r)C_FR)$
η = dimensionless temperature $(\rho C_pT/(-\Delta H_r)C_F)$
ρ = fluid density, g./cc.
τ = dimensionless time (vt/L)

Superscripts

$\wedge$ = disturbance from steady state condition
$\overline{\ }$ = radial average value
(k) = cycle number

Subscripts

F = evaluated at feed stream conditions
0 = evaluated at reactor entrance conditions
ss = evaluated at steady state conditions
w = evaluated at wall conditions

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