x = axial coordinate
y = distance from pipe wall

Greek Letters

δ = distance between correlation points
λ_f = longitudinal microscale (in axial direction)
ρ = density
ν = kinematic viscosity
τ = delay time
τ_w = shear stress at the wall

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Dynamics of a Tubular Reactor with Recycle: Part II. Nature of the Transient State

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A theoretical study of the transient state of a plug-flow tubular reactor with recycle is presented for a model in which axial dispersion of heat and mass is negligible. A qualitative description of the temporal behavior near the steady state is obtained from an analysis of the linearized transient equations, and some large-scale transient characteristics are studied by means of numerical solution of the nonlinear transient equations. A cursory study of the application of the Liapunov's direct method to predict regions of asymptotic stability is also presented. Numerical examples illustrate sustained oscillatory behavior as well as the transient nature of systems with multiple steady states.

In a previous paper (*1*) the stability of the steady state of a plug-flow tubular reactor with recycle was analyzed. It was shown that stability or instability to small disturbances could be rigorously determined immediately upon attainment of a steady state solution by a Newton-Raphson iterative procedure. Numerical examples were presented which illustrated the possible existence of unstable steady states.

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The purpose of this paper is to investigate the complete transient nature of the reactor-recycle system. The methods utilize the notion of a phase plane representation of the transient outlet state. The study of the behavior in the phase plane is based first on linearized transient equations and second on numerical solution of the nonlinear transient equations for some numerical examples. Finally, results obtained by applying the Liapunov's direct method to predict regions of asymptotic stability are presented and compared with those obtained by numerical solution of the transient equations.

DESCRIPTION OF THE TRANSIENT STATE

Basic Equations

The mathematical description of a plug-flow tubular reactor in which m components are involved in a single chemical reaction is given by Equations (1) through (8) of Part I of this study (*1*). It was assumed in that description, as it will be throughout the present paper, that the recycle line is adiabatic and that no further change in composition occurs after the material leaves the tube exit. Other assumptions and considerations are discussed elsewhere (*1, 2*).

The governing transient equations may be written as ordinary differential equations along a characteristic line with parameter σ as follows:

$$\frac{d\gamma}{d\sigma} = \mathcal{R}\,(\gamma, \gamma_1, \gamma_2, \ldots, \gamma_{m-1}, \theta) \qquad (1)$$

$$\frac{d\gamma_i}{d\sigma} = \mathcal{R} \qquad i = 1, 2, \ldots, m-1 \qquad (2)$$

$$\frac{d\theta}{d\sigma} = U_r(\theta_w - \theta) - \mathcal{R} \qquad (3)$$

The entire family of characteristic lines is given by

$$\xi = \sigma \qquad (4)$$

$$\tau = \sigma - \xi_{\text{in}} + n(1+\delta) \qquad (5)$$

$$0 < \xi_{\text{in}} \leqq 1 + \delta$$

$$n = 0, 1, 2, \ldots$$

A particular subset of this family for $\xi_{\text{in}} = \xi'_{\text{in}}$, shown in Figure 1, characterizes the history of a single infinitesimal plug of fluid which is initially at location ξ'_{in}. This "parent" plug follows the line for $n = 0$ in Figure 1 to $\xi = 1$, and after a time delay δ, its first heir—a plug formed by mixing a portion of the parent plug with fresh feed—enters the reactor at $\xi = 0$ and follows the line for $n = 1$. The succession of heirs continues indefinitely—the n^{th} heir reaches position ξ'_{in} at $\tau = n\,(1+\delta)$.

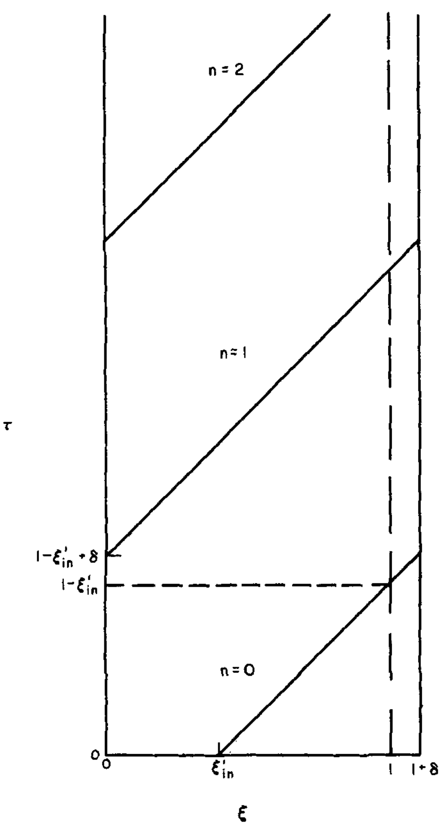

Fig. 1. Characteristic curves.

The number of transient equations which must be integrated along the characteristic lines may be reduced to just two by the following arguments.

Consider the sequence of plugs which is generated by a parent plug whose initial position was ξ'_{in}. The n^{th} heir reaches position $\xi' > \xi'_{\text{in}}$ at some later time τ' given by

$$\tau' = \xi' - \xi'_{\text{in}} + n(1+\delta) \qquad (6)$$

In Equation (6) n may have the value zero or any positive integer. By combining Equations (1) and (2) and integrating along the n^{th} characteristic line, there is obtained

$$\gamma_i(\xi', \tau') - \gamma(\xi', \tau') = K_{i,n} \qquad (7)$$

where

$$\left.\begin{aligned} K_{i,o} &= \gamma_i(\xi'_{\text{in}}, 0) - \gamma(\xi'_{\text{in}}, 0) \\ K_{i,n} &= \gamma_{io}\,[n(1+\delta) - \xi'_{\text{in}}] - \gamma_o[n(1+\delta) - \xi'_{\text{in}}] \\ n &= 1, 2, \ldots \end{aligned}\right\} \qquad (8)$$

From conditions on γ and γ_i at the inlet [Equations (6) and (7) of reference *1*], $K_{i,n}$ may be expressed as follows:

$$\begin{aligned} K_{i,n} = {} & (1 - R_r)(\gamma_{iF} - \gamma_F) \\ & + R_r(\gamma_{ie}\,[n(1+\delta) - \xi'_{\text{in}} - \delta] \\ & - \gamma_e\,[n(1+\delta) - \xi'_{\text{in}} - \delta]) \end{aligned} \qquad (9)$$

But since the difference between γ_i and γ is constant for a given n, it follows that

$$\begin{aligned} & \gamma_{ie}\,[n(1+\delta) - \xi'_{\text{in}} - \delta] - \gamma_e\,[n(1+\delta) - \xi'_{\text{in}} - \delta] \\ & \quad - \gamma_{io}\,[(n-1)(1+\delta) - \xi'_{\text{in}})] \\ & \quad - \gamma_o\,[(n-1)(1+\delta] - \xi'_{\text{in}}] \\ & \quad = K_{i,n-1} \end{aligned} \qquad (10)$$

Thus from Equation (9) and (10) the following recurrence relationship results:

$$\begin{aligned} K_{i,n} &= (1 - R_r)(\gamma_{iF} - \gamma_F) + R_r K_{i,n-1} \\ n &= 1, 2, \ldots \end{aligned} \qquad (11)$$

Solution of the above difference equation yields

$$\begin{aligned} K_{i,n} &= (\gamma_{iF} - \gamma_F) + R_r^n\,[K_{i,o} - (\gamma_{iF} - \gamma_F)] \\ n &= 0, 1, 2, \ldots \end{aligned} \qquad (12)$$

Finally from Equations (7), (8), and (12) there is obtained

$$\omega_n = \frac{\gamma_i(\xi', \tau') - \gamma(\xi'\ \tau') - (\gamma_{iF} - \gamma_F)}{\gamma_i(\xi'_{\text{in}}, 0) - \gamma(\xi'_{\text{in}}, 0) - (\gamma_{iF} - \gamma_F)} = R_r^n \qquad (13)$$

The above arguments may be repeated for $\xi' < \xi'_{\text{in}}$ to obtain a result identical to Equation (13), with the exception that the case $n = 0$ must be omitted.

By means of Equation (13), concentrations γ_1, γ_2, $\ldots$, γ_{m-1} in Equations (1) and (2) may all be expressed in terms of the reference concentration γ and R_r^n together with other known constants. The entire transient history of the reactor from a given initial state then may be obtained by integrating only Equations (1) and (3) along a set of characteristic lines, such as those shown in Figure 1, and repeating the integration for various ξ'_{in} between zero and $1 + \delta$. The concentration γ_i at any point along the characteristic lines may be obtained from the computed value of the reference concentration γ at that point by means of Equation (13).

Other facts regarding ω_n as defined in Equation (13) might be made at this point. Since R_r is always less than unity in a continuous flow reactor, ω_n is a null sequence. Thus as n becomes large, a simple relationship between any γ_i and γ is approached completely independently of any other transients in the system. Furthermore, if the feed and initial concentrations are in stoichiometric proportions, then $K_{i,o} = \gamma_{iF} - \gamma_F$, and it follows that $\omega_n = 0$ and $\gamma_i = \gamma$ at all times and positions.

Since it is clear that the null sequence ω_n has no qualitative effect on the transient state, considerable convenience and clarity are gained by considering it to be zero throughout. Further analysis in this paper will be confined to those equations describing the transient state of the reference concentration γ and of the temperature θ.

MATHEMATICAL DESCRIPTION IN TERMS OF DIFFERENCE EQUATIONS

Integration of Equations (1) and (3) along a characteristic line of Figure 1 yields an outlet state, γ_e and θ_e at $\xi = 1$, which depends only on the state at $\xi = 0$ for that line. Furthermore, the state at $\xi = 0$ depends only on the outlet state on the preceding line. Thus

$$\gamma_e^{(n+1)} = \Gamma\,[\gamma_e^{(n)}, \theta_e^{(n)}] \tag{14}$$

$$\theta_e^{(n+1)} = \Theta\,[\gamma_e^{(n)}, \theta_e^{(n)}] \tag{15}$$

Equations (14) and (15) are nonlinear difference equations and define a sequence of outlet states. The sequence is initiated by computation of $\gamma_e^{(0)}$ and $\theta_e^{(0)}$, and since these quantities depend on the initial state and ξ_{in}, Equations (14) and (15) represent a sequence of functions with ξ_{in} as a parameter. Other features of the sequence will be brought out in subsequent sections.

Phase Plane Representation

A convenient and illustrative picture of the transient state of the reactor-recycle system may be obtained by plotting the sequence given by Equations (14) and (15) on a graph of γ_e vs. θ_e. This technique, which is similar to the phase plane representations for lumped-parameter systems, is demonstrated in Figure 2. The curve for $n = 0$ is the locus of initial outlet states—$\gamma_e^{(0)}$ and $\theta_e^{(0)}$—resulting from the initial reactor profiles for $0 < \xi_{in} \leqq 1 + \delta$. Accordingly the curve for $n = 1$ is the locus of exit states of first heirs of those states on the curve for $n = 0$. In the vicinity of a steady state, the locus of exit states must shrink to a point, the steady state point.

It is interesting to note that the outlet state of the reactor, as predicted by the mathematical description employed here, is generally discontinuous in time. Only in the event that the initial inlet state $\gamma_o(0)$, $\theta_o(0)$ as obtained from the reactor inlet conditions, given by Equations (6) and (8) of reference *1*, is equal to the limit of $\gamma(\xi_{in}, 0)$, $\theta(\xi_{in}, 0)$ as $\xi_{in} \to 0$ will the sequence of curves of Figure 2 be joined to form a continuous curve leading to the steady state. The fact that the curve for a given n in Figure 2 is continuous implies that the initial concentration and temperature profiles within the reactor are continuous. It is the assumption of plug flow with no axial dispersion that leads to discontinuities in the time-dependent state. In an actual situation these would not of course be true discontinuities, since some axial dispersion of heat and mass would always occur.

A still more convenient representation of the transient state on the phase plane is that of a point sequence. Such a sequence would result from Equations (14) and (15) for a *single* value of ξ_{in}. The heavy dots on the curves of Figure 2 illustrate such a point sequence for $\xi_{in} = 1$. Physically the dot on the curve for $n = 0$ gives the outlet state of a parent plug which is initially located at the reactor exit. The dots on succeeding curves give the outlet states of the heirs of the parent plug. A smooth curve connecting the dots, as shown in Figure 2, is analogous to a trajectory in the phase plane of a stirred-tank reactor (3). It should be emphasized, however, that the connecting curve has significance only at the dotted points, and simply serves to connect the dots in sequence.

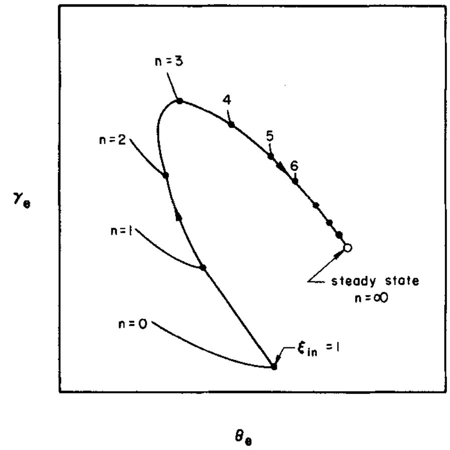

Fig. 2. Phase plane representation.

BEHAVIOR NEAR THE STEADY STATE

In a previous study (*1*) a criterion for stability of a steady state was obtained from the linearized form of the difference Equations (14) and (15). It is reasonable to expect that a qualitative description of the transient behavior of the reactor in the neighborhood of the steady state could also be obtained through the technique of linearization.

Equations (14) and (15), linearized about the steady state, may be written in matrix form as

$$\begin{bmatrix} \hat{\gamma}_e^{(n+1)} \\ \hat{\theta}_e^{(n+1)} \end{bmatrix} = J_s \begin{bmatrix} \hat{\gamma}_e^{(n)} \\ \hat{\theta}_e^{(n)} \end{bmatrix} \tag{16}$$

where

$$J_s = \begin{bmatrix} \dfrac{\partial\Gamma}{\partial\gamma_e} & \dfrac{\partial\Gamma}{\partial\theta_e} \\ \dfrac{\partial\Theta}{\partial\gamma_e} & \dfrac{\partial\Theta}{\partial\theta_e} \end{bmatrix}_s \tag{17}$$

It is recalled from reference *1* at this point that the steady state Jacobian matrix J_s is generated naturally when a steady state solution is obtained by a Newton-Raphson iterative procedure. It was also shown in reference *1* that a necessary and sufficient condition for stability of the steady state to small disturbances is that the eigenvalues of J_s, given by the roots of the following quadratic equation, have norms less than unity:

$$\lambda^2 - (tr)\lambda + d = 0 \tag{18}$$

It will now be shown that further information regarding transient behavior may be obtained through a knowledge of these eigenvalues.

It is noted at this point, and proved elsewhere (*2*), that the determinant d is always positive and, as a result, the eigenvalues, if real, are always of the same sign. If complex, they are complex conjugates since tr and d are real.

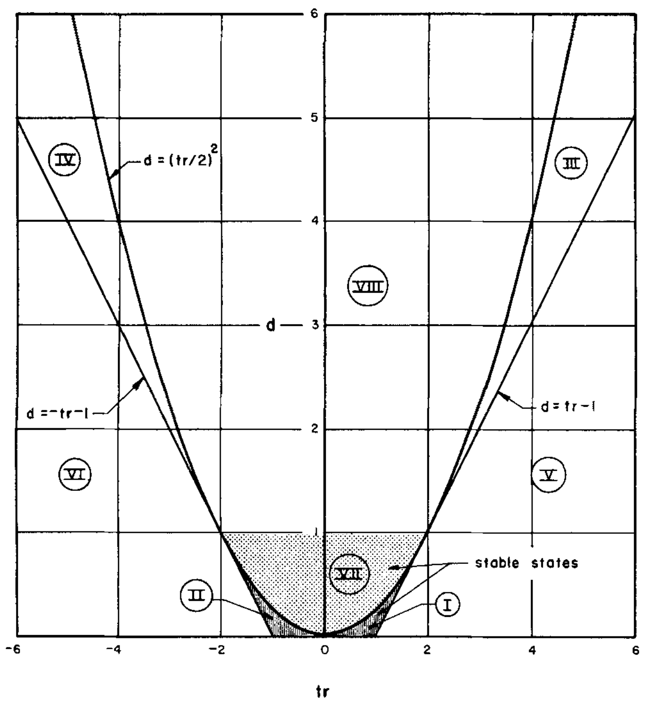

Fig. 3. Trace determinant plane.

Equations (21) and (22) provide two asymptotes in the phase plane. That given by Equation (22) is a negative asymptote in the sense that a sequence will diverge from it unless $\hat{\gamma}_e^{(0)}/\hat{\theta}_e^{(0)}$ is identically equal to q_{12}/q_{22}. Thus except for that coincidental case, the sequence of outlet states approaches a straight line, given by Equation (21), in the phase plane, and this line is independent of $\hat{\gamma}_e^{(0)}$ and $\hat{\theta}_e^{(0)}$, thus independent of ξ_{in}.

Consider a case in which the norms of both eigenvalues are less than unity, a stable steady state. In Figure 3 such a state would lie in region I if both eigenvalues are positive and in region II if both are negative. In the former case, the transient behavior shown in Figure 4*a* results. As shown, the point sequence of outlet states converges to the steady state asymptotically to the line given by Equation (21). The sequence remains entirely within one of the four regions formed by the intersection of the asymptotes. This type of transient behavior is analogous to that near a nodal point in the phase plane of a continuous stirred-tank reactor (3).

On the other hand, when both eigenvalues are negative, the state is in region II of Figure 3 and the unusual behavior shown in Figure 4*b* results. Here the point sequence converges to the steady state in an alternating

The following equation results from the recursion relationship of Equation (16):

$$\begin{bmatrix} \hat{\gamma}_e^{(n)} \\ \hat{\theta}_e^{(n)} \end{bmatrix} = J_s^{(n)} \begin{bmatrix} \hat{\gamma}_e^{(o)} \\ \hat{\theta}_e^{(o)} \end{bmatrix} \qquad (19)$$

If it is assumed that the eigenvalues λ_1 and λ_2 of J_s are distinct, then the solution of Equation (19) leads to the following expression for the phase plane representation of the sequence of outlet states in the vicinity of the steady state:

$$\frac{\hat{\gamma}_e^{(n)}}{\hat{\theta}_e^{(n)}} = \frac{\lambda_1^n q_{11} [q_{22} \hat{\gamma}_e^{(0)} - q_{12} \hat{\theta}_e^{(0)}] + \lambda_2^n q_{12} [q_{11} \hat{\theta}_e^{(0)} - q_{21} \hat{\gamma}_e^{(0)}]}{\lambda_1^n q_{21} [q_{22} \hat{\gamma}_e^{(0)} - q_{12} \hat{\theta}_e^{(0)}] + \lambda_2^n q_{22} [q_{11} \hat{\theta}_e^{(0)} - q_{21} \hat{\gamma}_e^{(0)}]} \qquad (20)$$

The various types of possible phase plane behavior resulting from Equation (20) depend on the nature of the eigenvalues or equivalently on the determinant d and trace tr of the steady state Jacobian matrix J_s as seen from Equation (18). These types are conveniently summarized in the (tr, d) plane as shown in Figure 3.

Consider first the transient behavior in the event that λ_1 and λ_2 are both real. This occurs for states lying below the parabola $d = (tr/2)^2$ in Figure 3. If λ_1 is taken to be that eigenvalue with the largest norm, then according to Equation (20)

$$\hat{\gamma}_e^{(n)} \xrightarrow[n \to \infty]{} \left(\frac{q_{11}}{q_{21}}\right) \hat{\theta}_e^{(n)} \quad \text{for} \quad \frac{\hat{\gamma}_e^{(0)}}{\hat{\theta}_e^{(0)}} \neq \frac{q_{12}}{q_{22}} \qquad (21)$$

and

$$\hat{\gamma}_e^{(n)} = \left(\frac{q_{12}}{q_{22}}\right) \hat{\theta}_e^{(n)} \quad \text{for} \quad \frac{\hat{\gamma}_e^{(0)}}{\hat{\theta}_e^{(0)}} = \frac{q_{12}}{q_{22}} \qquad (22)$$

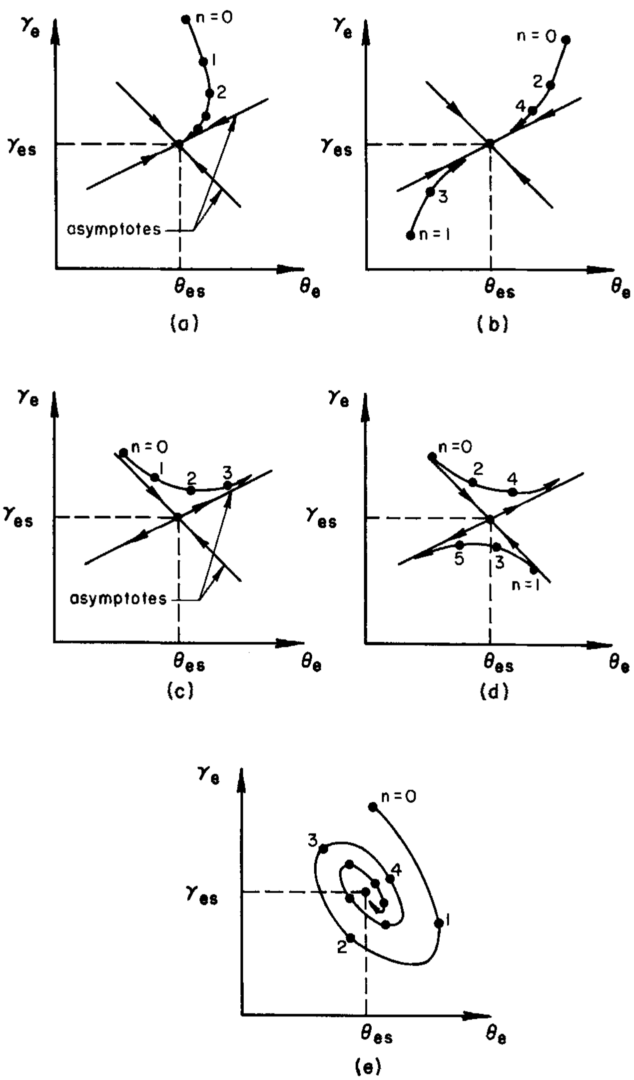

Fig. 4. Types of local transient behavior.

fashion along both branches of the asymptote given by Equation (21). This alternating type of behavior is distinguished from an oscillatory behavior, which will be discussed shortly, and which results when λ_1 and λ_2 are complex, by the existence of definite asymptotes and by the fact that two of the regions formed by these asymptotes contain no points in a given sequence. No analog to this type of behavior exists for the stirred-tank reactor.

The unstable behavior that results when the steady states lie in regions III and IV of Figure 3 is similar to that shown in Figures 4*a* and 4*b*, respectively, except that the sequences *diverge* from the steady states. In region III both eigenvalues are positive and exceed unity, and in region IV *both* are negative with absolute values greater than unity.

Another possible case for real eigenvalues is that of an unstable state in which only one of the eigenvalues, say λ_1, has a norm greater than unity. These states lie in regions V and VI of Figure 3. Two different types of phase plane behavior are possible, depending on whether the eigenvalues are positive (region V) or negative (region VI). If both are positive, a point sequence which originates close to the negative asymptote first approaches the steady state as shown in Figure 4*c* and then begins to move away along the positive asymptote. As shown, the point sequence lies entirely within one of the four regions formed by the asymptotes. This type of behavior is analogous to that near a saddle point in the phase plane of a stirred-tank reactor (3). When both eigenvalues are negative, the point sequence again alternates between opposite regions as shown in Figure 4*d*.

Although the transient behavior described above for negative eigenvalues is quite unusual and interesting, such situations appear to be very unlikely to occur if indeed they are possible at all for physically realistic reaction data. No apparent proof can be constructed to rule out negative eigenvalues, but of the several thousand steady states computed during the course of this study, not one single case of a negative eigenvalue was encountered.

If the steady state lies above the parabola in Figure 3, the eigenvalues of J_s are complex, and since they are complex conjugates, their norms are equal. Consequently, it is necessary to study only two cases, the stable case when both norms are less than unity (region VII of Figure 3) and the unstable case when they both exceed unity (region VIII of Figure 3).

In either case the ratio $\hat{\gamma}_e^{(n)}/\hat{\theta}_e^{(n)}$ given by Equation (20) fails to approach a definite limit as n increases. Instead the ratio may be written in terms of trigonometric functions, and the sequence of outlet states lies on a curve which spirals into or away from the steady state depending on whether the state is stable or unstable. The stable case is demonstrated in Figure 4*e* and is analogous to the behavior for a focal point of a stirred-tank reactor (3). The unstable case is similar except that the sequence diverges from the steady state.

It is worthwhile to point out that only states in regions I and V of Figure 3 are possible in the case of an adiabatic reactor; that is, for $U_r = 0$. In this case it may be shown by means of Equations (1), (3), (14), and (15), together with the steady state recycle relationships [Equations (6) and (8) of reference *1*], that the determinant of J_s is given by

$$d = R_r(tr - R_r) \tag{23}$$

According to Equation (23), all steady states for $U_r = 0$ must lie on a straight line in Figure 3 with a slope of R_r and an intercept on the tr axis of R_r. Furthermore this

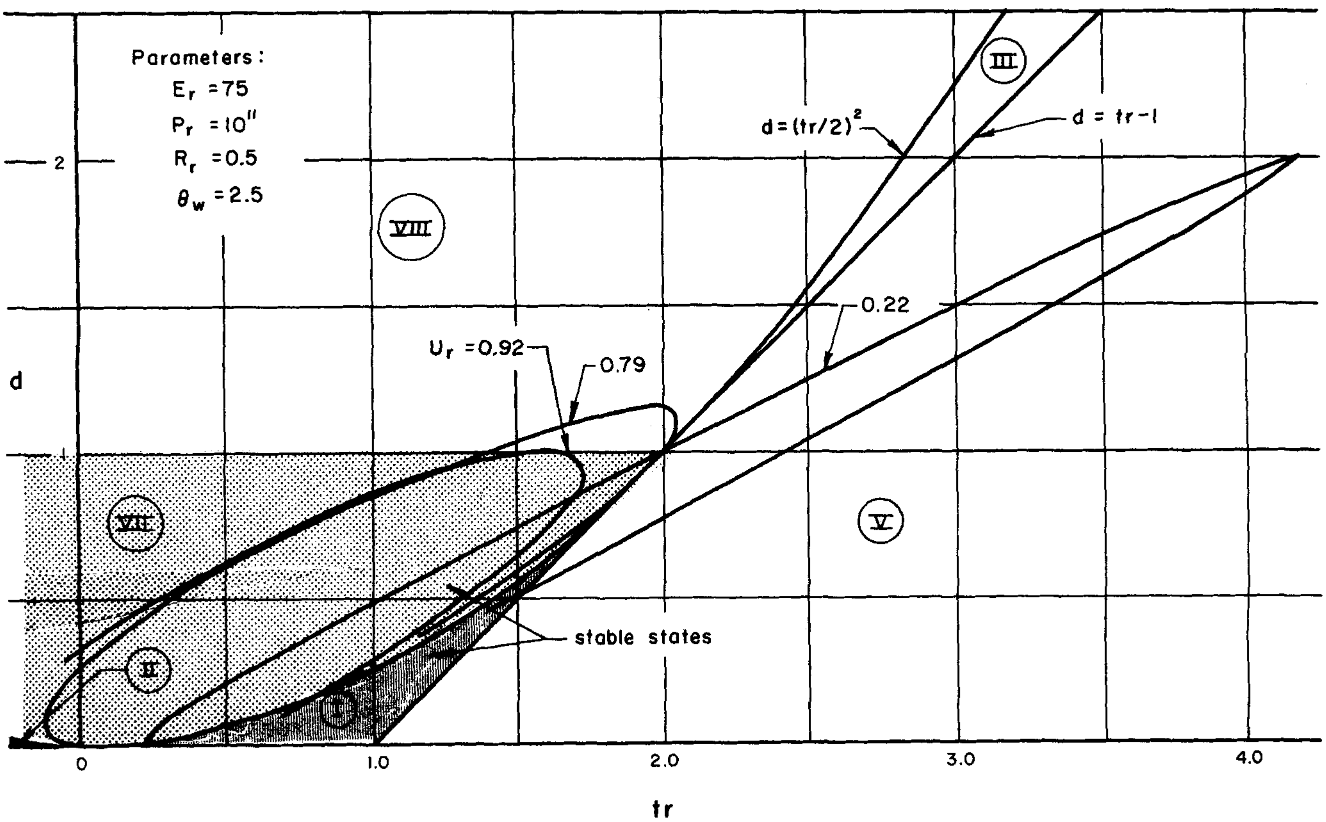

Fig. 5. Steady state solutions in the trace-determinant plane.

straight line lies below the parabola $d = (tr/2)^2$ except at the point $tr = R_r/2$, a point of tangency.

It was shown in an earlier paper (*1*) that the quantity $(d - tr + 1)$ is negative for an intermediate state in those situations where three steady states exist. It follows that the intermediate state always lies in region V of Figure 3 and that this is the only state that can be unstable in an adiabatic reactor.

It follows from the foregoing discussion that the complete transient behavior for small disturbances can be obtained from Figure 3. Once a steady state has been obtained by the Newton-Raphson procedure described elsewhere (*1*), its location on Figure 3 may be readily determined since d and tr are available from J_s.

Figure 5 presents results of numerical solution of the steady state equations for three different values of U_r. The curves, superimposed in this figure on a portion of the tr,d plane of Figure 3, result from steady state equations for a simple reaction $A \rightarrow B$ with the parameters shown in Figure 5 and a reaction rate expression given by $\mathfrak{R} = -P_r\gamma \exp(-E_r/\theta)$. These same parameters were employed and discussed in a previous paper (*1*). On the curve for a given value of U_r in Figure 5, any point is a possible steady state depending on the value of the feed temperature θ_F; that is, to any point on the curve there corresponds a value of θ_F. For any value of θ_F which yields a point to the right of the line $d = tr - 1$, on the curve for $U_r = 0.22$, there exist also two other states to the left of that line. The various types of possible transient responses to small disturbances are evident from Figure 5. Although no curves are shown to pass through region III, steady states do exist there when $0.22 < U_r < 0.79$.

NUMERICAL SOLUTION OF TRANSIENT EQUATIONS

The preceding discussion, as well as the stability analysis presented earlier (*1*) is based entirely on linearized equations. As a result information is given concerning the local transient behavior only. In many cases this information alone may be sufficient. Noteworthy exceptions, however, are those cases in which a single unstable steady state exists or those in which there are more than one steady state. In the latter situation it is of importance to determine not only the stability of a steady state but its *region of asymptotic stability*, the region surrounding a particular steady state in the phase plane throughout which all transients lead to that steady state. In this section the complete transient behavior will be investigated for a few interesting cases by presenting the numerical solutions of Equations (1) and (3) for the parameters employed in Figure 5.

A Unique Unstable Steady State

The steady state situation considered here results when $U_r = 0.79$ and $\theta_F = 2.9$. As shown in Figure 4 of reference *1*, there results a single *unstable* steady state. The steady state reactor concentration and temperature profiles for this case were also shown in reference *1*. The phase plane representation of the transient state for $\delta = 0$, $\gamma(\xi, 0) = 0$, and $\theta(\xi, 0) = 2.9$ is shown in Figure 6. It can be seen that the outlet states approach a closed curve which is analogous to a limit cycle for a lumped-parameter system. The sequence of points lying within the closed curve represents the outlet states of a single plug and its heirs after this plug has been only slightly disturbed from the steady state. As shown, this sequence also approaches the closed curve with increasing time.

Even though any initial state in the phase plane would eventually lead to the closed curve, the eventual behavior of the reactor, as predicted by the plug-flow model, is not independent of its initial state. This is due to the fact

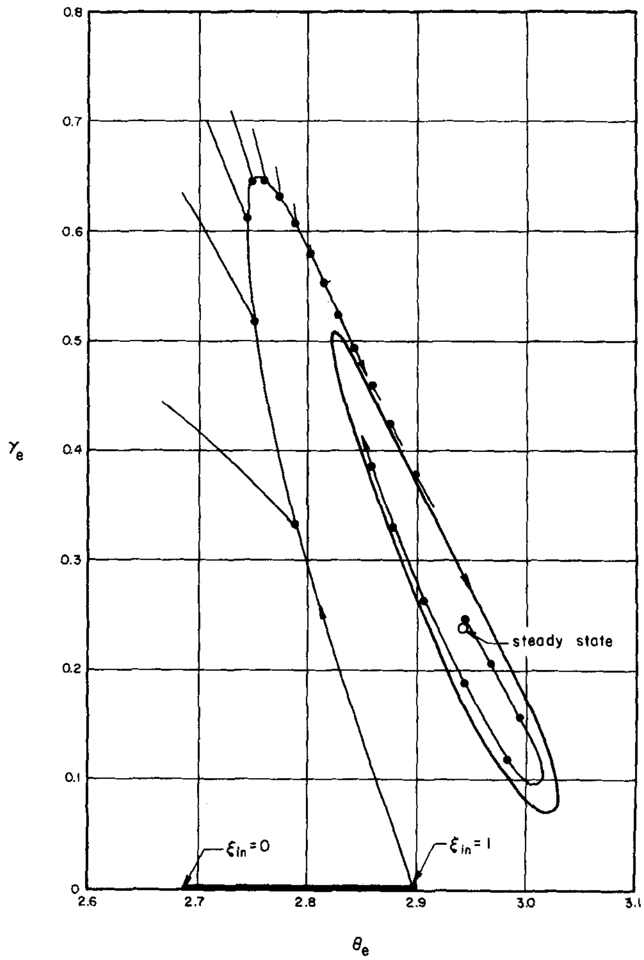

Fig. 6. Transient behavior for a unique unstable state. $\theta_F = 2.9$; $U_r = 0.79$.

that discontinuities in outlet concentration and temperature which are initially present persist for all subsequent times. Such behavior is illustrated in Figure 7, which shows the exit concentration and temperature vs. time on the closed curve of Figure 6. Since discontinuities cannot be present in a real reactor, it may be conjectured that the eventual time dependent behavior of a real reactor would be continuous and independent of the initial reactor state. It is interesting to note from Figure 7 that one cycle of the oscillatory state comprises about nineteen passes through the reactor.

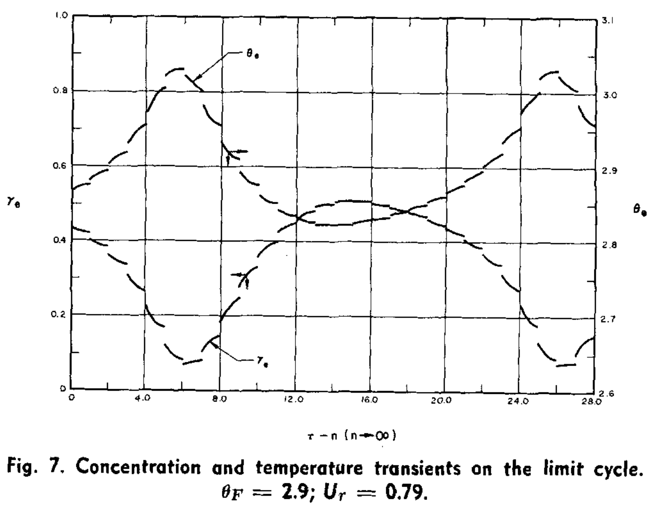

Fig. 7. Concentration and temperature transients on the limit cycle. $\theta_F = 2.9$; $U_r = 0.79$.

Multiple Steady States

When multiple steady states occur, it is of particular interest to be able to identify which of the steady states is attained from a given set of initial or perturbed states. For $U_r = 0.45$ and $\theta_F = 2.737$, three steady states exist, two of which are stable. The steady state temperature and concentration profiles for this example were shown in reference *1*. The phase plane of Figure 8 shows the sequence of outlet states for various initial states with $\delta = 0$. As shown, the sequence of outlet states in some cases approaches a low temperature, low conversion state at point (a) and in others, a high temperature, high conversion state at point (c). State (a) is of the type shown in Figure 4*a*, while state (c) is an oscillatory state as shown in Figure 4*e*, although in Figure 8 the amplitudes of these oscillation are too small to be apparent.

As shown in Figure 8 point sequences diverge from the intermediate state at point (b), which is of the type shown in Figure 4*c*. The divergence is along the positive asymptote. Any initial state which lies exactly on the negative asymptote of Figure 8 will lead to the unstable state. A numerical solution, of course, could never follow the negative asymptote, since small round-off errors would grow, and the resulting sequence would converge to one of the stable states. However, a backward integration procedure was found to be stable. This procedure involved choosing an initial state, state n, very close to state (b) along the negative asymptote as given by the linearized analysis. Equations (1) and (3) were then integrated with *negative* σ increments from $\xi = 1$ to $\xi = 0$. From the inlet state thus determined, the previous exit state $n - 1$ was computed. The procedure was repeated until the sequence intersected the $\gamma_e = 0$ or $\gamma_e = 1$ boundaries.

The negative asymptote is the most important feature of the phase plane of Figure 8, since it defines the exact *regions of asymptotic stability* for the two stable states. The entire region to the left of the negative asymptote is the region of asymptotic stability for state (a), since any plug whose initial exit state or whose state following a disturbance is in that region will approach state (a) as time increases. Similarly the region to the right of the negative asymptote is the region of asymptotic stability for state (c)

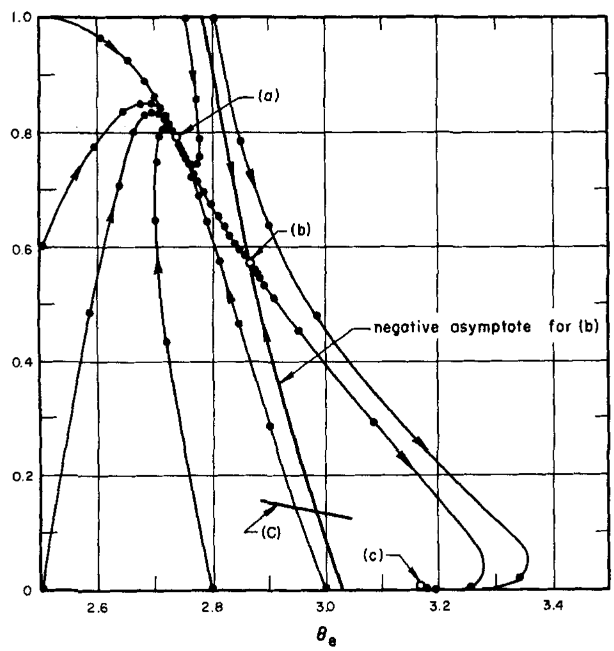

Fig. 8. Transient behavior with two stable states. $\theta_F = 2.737$; $U_r = 0.45$.

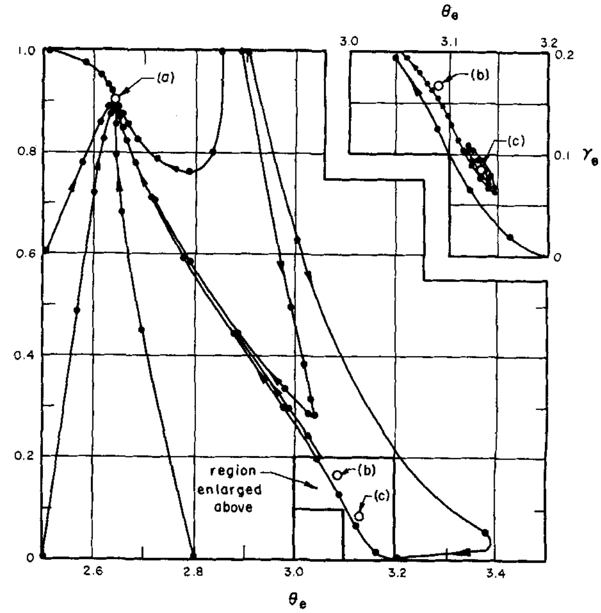

Fig. 9. Transient behavior with two unstable states. $\theta_F = 2.68$; $U_r = 0.45$.

The existence of the negative asymptote provides a possibility for an anomalous situation which could result when the initial state of the reactor is such that the initial locus of outlet states intersects the asymptote as shown by curve C of Figure 8. In this case the ultimate state of the reactor would be one in which some of the outlet plugs were at state (a) and others at state (c). Since discontinuities are not physically possible, one must conclude that the plug-flow model is qualitatively incorrect in its description of the *steady state* in such situations. Nevertheless, if axial dispersion were very slight in a real reactor, and if multiple stable steady states did exist, one might expect that a very long time could be required to reach a steady state and that the reactor may appear during much of this time to be converging to more than one steady state.

Figure 9 shows the interesting case in which only the low conversion state is stable. The parameters here are the same as in Figure 8 with $\theta_F = 2.68$. The unstable state (c) is of the type shown in Figure 4*e*. Figure 9 shows that the stable state (a) is stable for all disturbances. [The unrealistic case of a perturbed state being exactly coincident with either point (b) or (c) is an exception.] However, it is obvious that a long excursion around the unstable state (c) may occur for some disturbances.

REGIONS OF ASYMPTOTIC STABILITY BY LIAPUNOV'S DIRECT METHOD

The methods described in preceding sections for examining the transient behavior of the reactor-recycle system have certain disadvantages. As mentioned earlier, the results of the linearized analysis, which were summarized in Figure 3, apply only in some neighborhood of the steady state, the magnitude of this neighborhood being undeterminable from that analysis. On the other hand, the transient study of the previous section yielded complete transient information but required numerical solution of the nonlinear transient equations. In an effort to obtain a more complete transient description than is possible through a linearized analysis and yet avoid numerical solution of transient equations, a number of recent studies (*4* to *10*) have employed Liapunov's direct method to estimate

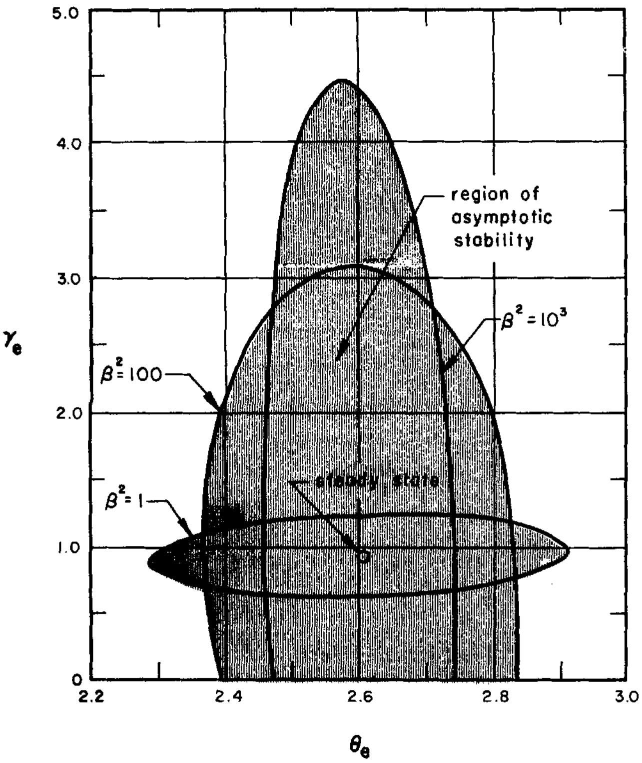

Fig. 10. Predicted regions of asymptotic stability for a unique stable state. $\theta_F = 2.73$; $U_r = 0.79$.

regions of asymptotic stability for continuous stirred-tank reactors. An application of this method to difference equations for some linear processes without chemical reaction may be found in a paper by Koepcke and Lapidus (*11*). This section presents the results of a cursory study of the application of the method to the reactor-recycle system for the sake of seeking a comparison between the regions of asymptotic stability thus obtained and the exact regions as shown in Figure 8. Procedural details regarding the development and application of equations are only briefly sketched here; more complete information is presented elsewhere (*2*).

Liapunov's direct method for a system of difference equations is basically similar to that for a system of ordinary differential equations (*12*). Thus for difference Equations (14) and (15), a steady state is asymptotically stable in a region of the phase plane defined by $V(\hat{\gamma}_e, \hat{\theta}_e) < C$, where C is some constant, yet to be determined, and $V(\hat{\gamma}_e, \hat{\theta}_e)$ is a scalar function, referred to as a Liapunov function. This function must be chosen to satisfy the following criteria in the region defined above:

i. $V(0, 0) = 0$

ii. $V(\hat{\gamma}_e, \hat{\theta}_e) > 0$ for $\hat{\gamma}_e$ or $\hat{\theta}_e \neq 0$

iii. $$\Delta V(\hat{\gamma}_e, \hat{\theta}_e) = V[\Gamma(\hat{\gamma}_e, \hat{\theta}_e), \Theta(\hat{\gamma}_e, \hat{\theta}_e)] - V(\hat{\gamma}_e, \hat{\theta}_e) < 0 \quad \text{for } \hat{\gamma}_e \text{ or } \hat{\theta}_e \neq 0$$

The Liapunov function chosen in this study is given by the quadratic form

$$V(\hat{\gamma}_e, \hat{\theta}_e) = (\hat{\gamma}_e \; \hat{\theta}_e) \; P \begin{pmatrix} \hat{\gamma}_e \\ \hat{\theta}_e \end{pmatrix} \tag{24}$$

where P is a symmetric, positive-definite matrix. This function clearly satisfies conditions *i* and *ii*.

Hohn (*12*) has shown that if condition *iii* is satisfied for the linearized case, the resulting Liapunov function may also be used to determine asymptotic stability in a bounded region for the nonlinear problem.

In order that condition *iii* be met for the linearized case, it is necessary that P result from the solution of the matrix equation

$$J_s^T P J_s - P = -\Omega \tag{25}$$

where Ω is any symmetric positive-definite matrix, represented here by

$$\Omega = \begin{pmatrix} 1 & \alpha \\ \alpha & \beta^2 \end{pmatrix}; \; (\beta^2 - \alpha^2) > 0 \tag{26}$$

The determination of the largest region of asymptotic stability that can be predicted from a Liapunov function given by Equation (24) and a given choice of Ω involves determining the maximum C for which condition *iii* is satisfied in the *nonlinear* case. This determination must be carried out by a numerical procedure, because $\Delta V(\hat{\gamma}_e, \hat{\theta}_e)$ cannot be explicitly expressed in terms of the phase plane coordinates $\hat{\gamma}_e$ and $\hat{\theta}_e$. The particulars of the numerical method employed in this study are given in reference *2*.

Figure 10 presents the results of calculations for the parameters employed earlier with $U_r = 0.79$ and $\theta_F = 2.73$. For this case a single stable steady state exists. Numerical solution of the nonlinear transient equations revealed that the steady state is stable for all disturbances; that is, the actual region of asymptotic stability consists of all positive outlet temperatures and concentrations. Figure 10 gives no indication of this fact but nevertheless shows a region sufficiently large to be worthwhile in a design study. It follows that since the region within each ellipse of Figure 10 satisfies the criteria for asymptotic stability, the entire shaded portion of the phase plane is a region of asymptotic stability. Further increase or decrease in β^2 had an insignificant effect on the region. The extension of the ellipses into negative values of γ is not shown since these values can never be attained physically.

Figure 11 shows the resulting region of asymptotic stability for state (*c*) of Figure 8, a multiple steady state situation. Shown also in Figure 11 is the negative asymptote for state (*b*) of Figure 8, the true boundary of the region of asymptotic stability for state (*c*). It is obvious that the method of estimating the region by the Liapunov method as employed here results in a very conservative

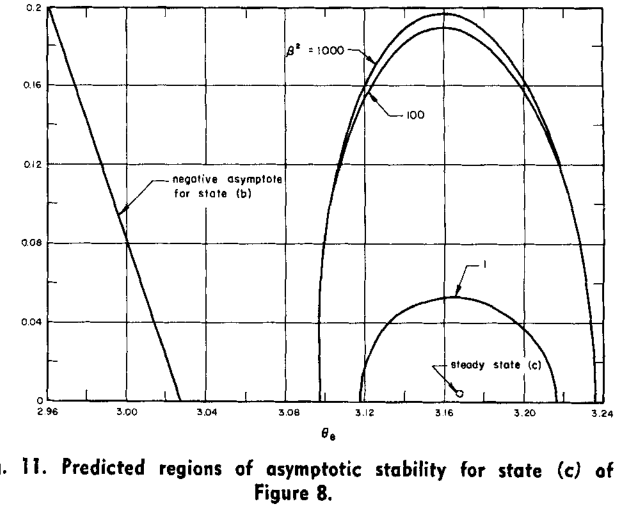

Fig. 11. Predicted regions of asymptotic stability for state (*c*) of Figure 8.

estimate. The method, when applied to state (*a*) of Figure 8, resulted in a region too small to be discernible in the phase plane.

It must be concluded that the Liapunov's direct method applied as described above, which seems to be the simplest of currently available methods, is of interest more for the sake of curiosity than as a practical design tool. For example, computational time and effort required to construct Figure 11 were roughly the same as those required for Figure 8; the extent of information obtained in the two cases is hardly comparable.

SUMMARY

The complete transient nature of a plug-flow tubular reactor with recycle has been investigated by analytical and numerical methods. It has been shown that a qualitative description of the time-dependent behavior near the steady state can be obtained from a knowledge of a steady state Jacobian matrix. It was previously shown (*1*) that this matrix arises naturally in the search for a steady state solution by a Newton-Raphson iteration scheme. A phase plane representation of the sequence of transient exit states has been employed as a convenient means of illustrating transient characteristics.

Large-scale unsteady behavior has been studied by numerical solution of the nonlinear transient equations for some illustrative examples. These include examples of sustained oscillations about a unique unstable steady state and transient nature when multiple steady states exist.

Liapunov's direct method has been employed to predict regions of asymptotic stability. This approach was shown to yield quite conservative estimates of the regions of asymptotic stability for the examples studied. Furthermore, it was concluded that currently available methods of obtaining Liapunov functions for the reactor-recycle system render this technique inferior to solving numerically the complete transient equations.

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NOTATON

a_i = ratio of stoichiometric coefficient for component i to stoichiometric coefficient for reference component
C = concentration of reference component; also constant as defined in Equation (27)
C_i = concentration of i^{th} component
C_p = heat capacity
d = determinant of Jacobian matrix J_s
D = reactor diameter
E_a = activation energy
E_r = dimensionless activation energy, $E_a p C_p / R(-\Delta H) C_F$
ΔH = heat of reaction
J_s = steady state Jacobian matrix as defined in Equation (17)
$K_{i,n}$ = function as defined in Equation (8)
L = reactor length
n = parameter along characteristic curve; also n^{th} element in a sequence
p = pre-exponential factor
p_{ij} = element in i^{th} row and j^{th} column of P
P = matrix as defined in Equation (25)
P_r = dimensionless pre-exponential factor, pL/u
q_{1j} = j^{th} element of eigenvector belonging to λ_1
q_{2j} = j^{th} element of eigenvector beyonging tó λ_2
r = rate of formation of reference component
R = gas constant
R_r = recycle ratio, fraction of exit stream returned to reactor inlet
$\mathfrak{R}$ = dimensionless reaction rate, rL/uC_F
t = time
t_d = time delay in recycle line
tr = trace of Jacobian matrix J_s
T = temperature
T_w = wall temperature
u = velocity
U = heat transfer coefficient
U_r = dimensionless heat transfer coefficient, $4UL/D\rho UC_p$
V = Liapunov function
x = distance variable

Greek Letters

α = element in Ω as defined in Equation (26)
β = element in Ω as defined in Equation (26)
γ = dimensionless concentration of reference component, C/C_F
γ_i = dimensionless concentration of i^{th} component, $-C_i/a_iC_F$
Γ = function as defined in Equation (14)
δ = dimensionless time delay in recycle line, $t_d u/L$
Δ = difference operator
θ = dimensionless temperature, $T\rho C_p/(-\Delta H)C_F$
θ_w = dimensionless wall temperature, $T_w \rho C_p/(-\Delta H)C_F$
Θ = function as defined in Equation (15)
λ_1, λ_2 = eigenvalues of Jacobian matrix, J_s
ξ = dimensionless distance variable, x/L
ξ_{in} = initial position of a single fluid plug
ρ = density
σ = parameter along characteristic curve
τ = dimensionless time, tu/L
ω_n = function as defined in Equation (13)
Ω = matrix as defined in Equation (26)

Subscripts

e = reactor outlet or exit
F = reactor feed
o = reactor inlet
s = steady state

Superscripts

(n) = term number in a sequence
T = transpose of matrix
$\wedge$ = deviation from steady state

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