Dynamics of a Tubular Reactor with Recycle:
Part I. Stability of the Steady State

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An analysis of the stability of a plug-flow tubular reactor with recycle is presented for a model in which axial dispersion of heat and mass is neglected. A method is developed which permits determination of stability or instability for small disturbances immediately upon attainment of the steady state solution. The method, which is applicable to a large class of recycle processes, is based on a Newton-Raphson iteration technique for steady state solution and on the stability theory of nonlinear difference equations. The feasibility of the method is demonstrated by means of numerical examples which illustrate the occurrence of steady state multiplicity and unstable situations.

The transient behavior of continuous flow chemical reactors has been the subject of a number of studies through the past decade. A rather complete summary of these works is available in three recent books (*1*, *2*, *3*) and two review articles (*4*, *5*). The vast majority of previous works has been concerned with perfectly mixed reactors, where the lumped-parameter model permits application of well-established theorems concerning stability and transient response. Tubular reactors, on the other hand, have been previously considered only to a limited degree.

The present work is a theoretical study of the dynamics of a plug-flow tubular reactor with recycle. The objectives of the study, which will be presented in two parts, are to establish stability criteria and to investigate the compelte transient nature of the system. This paper is addressed to the first of these objectives. The scope is limited to situations in which axial dispersion of heat and mass is negligible and the reaction is homogeneous. The mathematical description would apply roughly to solid-catalyzed reactions if the solid had negligible capacity and if surface kinetics were rate-determining.

The only previously reported study of the dynamics of a tubular reactor with recycle was a cursory examination by Bilous and Amundson (*6*) in a study directed toward steady state sensitivity in plug-flow reactors. They employed Laplace transform methods to analyze the linearized transient response and showed theoretically that the possibility of instability exists when the reactor is partially fed with a recycle stream.

Stability arguments in the present paper are based on the theory of nonlinear difference equations. A systematic procedure is developed whereby stability of a steady state to small disturbances may be rigorously determined immediately upon attainment of a steady state solution.

MATHEMATICAL MODEL

In the system under consideration a fraction of the effluent stream from a tubular reactor is returned through a recycle line to join the fresh feed at the inlet. Major assumptions employed throughout the analysis are that plug flow exists in the reactor, there is no axial dispersion of heat or material, radial gradients in temperature and concentration do not exist, and fluid properties are constant. A reaction of the form

$$\sum_{i=1}^{m-1} a_i A_i - A = 0 \tag{1}$$

occurs in the reactor. Although the methods employed in this paper are described in terms of a single reaction, the approach can readily be extended to more complex reaction systems. In Equation (1), a_i, the stoichiometric coefficient for the species A_i, is negative for reactants and positive for products. One of the reactants, component A, is chosen as a reference component. The rate of formation r_i of component A_i is related to the rate of formation of the reference component by the expression

$$-r_i/a_i = r \tag{2}$$

where r may be a function of the temperature and all concentrations.

Transient material balances, in dimensionless form, for the individual components are

$$\partial\gamma/\partial\tau + \partial\gamma/\partial\xi = \mathcal{R}\ (\gamma, \gamma_i, \theta) \tag{3}$$

$$\partial\gamma_i/\partial\tau + \partial\gamma_i/\partial\xi = \mathcal{R} \tag{4}$$

$$i = 1,2, \ldots, m-1$$

An energy balance on a plug of material in the reactor may be written in the following dimensionless form:

$$\partial\theta/\partial\tau + \partial\theta/\partial\xi = U_r\ (\theta_w - \theta) - \mathcal{R} \tag{5}$$

The wall temperature T_w is assumed to be independent of time, but may be a function of position. The heat transfer coefficient U is assumed constant.

Solution of the above system of equations requires a knowledge of reactor inlet conditions. For a simple recycle process in which a fraction of the exit material is returned with negligible heat loss and no concentration change, the inlet state is given by

$$\gamma_o(\tau) = (1 - R_r)\ \gamma_F + R_r\gamma_e\ (\tau - \delta) \tag{6}$$

$$\gamma_{io}(\tau) = (1 - R_r)\ \gamma_{iF} + R_r\gamma_{ie}\ (\tau - \delta) \tag{7}$$

$$\theta_o(\tau) = (1 - R_r)\ \theta_F + R_r\theta_e\ (\tau - \delta) \tag{8}$$

In general a reactor-recycle system may involve any number of processes in the recycle line such as further chemi-

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cal conversion, heat exchange, or component removal or addition. In the present study the analysis is first carried out in detail for the simple recycle process described by Equations (6), (7), and (8). Extension of the methods to more complicated cases is brought out in a later paragraph.

Although the primary goals of the present work involve a study of time-dependent behavior, in particular the stability of a steady state, it is of necessity as well as of interest to investigate first some methods of obtaining steady state solutions. It will be shown later that the method described in the following section allows an immediate determination of stability or instability of a steady state to small disturbances.

THE STEADY STATE

The dimensionless equations which govern the steady state regime of the reactor are the ordinary differential equations which result from Equations (3), (4), and (5) by setting the time derivatives equal to zero. These are

$$d\gamma/d\xi = \mathcal{R}(\gamma, \gamma_i, \theta) \tag{9}$$

$$d\gamma_i/d\xi = \mathcal{R} \tag{10}$$

$$i = 1, 2, \ldots, m-1$$

$$d\theta/d\xi = U_r(\theta_w - \theta) - \mathcal{R} \tag{11}$$

In addition, a steady state solution must satisfy the time-independent recycle conditions

$$\gamma_o = (1 - R_r)\,\gamma_F + R_r\gamma_e \tag{12}$$

$$\gamma_{io} = (1 - R_r)\,\gamma_{iF} + R_r\gamma_{ie} \tag{13}$$

$$\theta_o = (1 - R_r)\,\theta_F + R_r\theta_e \tag{14}$$

It is noted that the steady state solution is independent of any time delay in the recycle line.

Due to the usual complexity of the reaction rate function $\mathcal{R}$, solution of Equations (9) through (14) must generally be carried out by numerical integration. Furthermore, since the inlet conditions, γ_o, γ_{io}, and θ_o, needed to start the integration cannot be calculated from the recycle equations unless the steady state outlet conditions, γ_e, γ_{ie}, and θ_e are known, it is necessary to employ some trial and error or iterative procedure. The system of equations to be integrated numerically may be reduced to just Equations (9) and (11). The following relationship between γ_i and γ results from combining Equations (9) and (10):

$$\gamma_i(\xi) - \gamma_{io} = \gamma(\xi) - \gamma_o \tag{15}$$

$$i = 1, 2, \ldots, m-1$$

Furthermore, Equations (12) and (13), together with Equation (15) evaluated at $\xi = 1$, yield the following relationship between exit concentrations of component A_i and the reference component:

$$\gamma_{ie} - \gamma_{iF} = \gamma_e - \gamma_F \tag{16}$$

Numerical Procedure

With assumed values of γ_e and θ_e Equations (9) and (11) may be integrated numerically to $\xi = 1$. The γ_i's may be obtained at the inlet by means of Equations (13) and (16) and at any position in the reactor by means of Equation (15). The newly computed values of γ_e and θ_e depend on the assumed values, designated now as γ_e' and θ_e'. Thus

$$\gamma_e = \gamma_e\,(\gamma_e', \theta_e') \tag{17}$$

$$\theta_e = \theta_e\,(\gamma_e', \theta_e') \tag{18}$$

For a steady state solution γ_e and θ_e are identically equal to γ_e' and θ_e', respectively.

In a search for a solution, successive estimates of the outlet concentration and temperature may be systematically generated by any one of several methods. One of these, known as the method of successive substitutions, employs the computed outlet state of the n^{th} iteration as the estimated outlet state for the $n + 1^{st}$ iteration. It will become clear in the discussion of the transient state that such a procedure would never converge to an unstable state. On the other hand, iterative schemes based on the Newton-Raphson root-finding method are usually convergent. The following technique was found to converge rapidly in all cases studied. Here $\gamma_e'^{(n+1)}$ and $\theta_e'^{(n+1)}$, the estimates for the $n + 1^{st}$ iteration, are obtained from the matrix equation

$$(J^{(n)} - \mathrm{I}) \begin{pmatrix} \gamma_e'^{(n+1)} - \gamma_e'^{(n)} \\ \theta_c'^{(n+1)} - \theta_e'^{(n)} \end{pmatrix} = \begin{pmatrix} \gamma_e'^{(n)} - \gamma_e(\gamma_e'^{(n)}, \theta_e'^{(n)}) \\ \theta_e'^{(n)} - \theta_e(\gamma_e'^{(n)}, \theta_e'^{(n)}) \end{pmatrix} \tag{19}$$

where J, the Jacobian matrix, is defined by

$$J = \begin{pmatrix} \partial\gamma_e/\partial\gamma_e' & \partial\gamma_e/\partial\theta_e' \\ \partial\theta_e/\partial\gamma_e' & \partial\theta_e/\partial\theta_e' \end{pmatrix} \tag{20}$$

$J^{(n)}$ is obtained by evaluating the partial derivatives in Equation (20) for the n^{th} iteration. Employment of this method requires that $\gamma_e'^{(1)}$ and $\theta_e'^{(1)}$ be assumed with succeeding estimates of the outlet state obtained from the recurrence relations of Equation (19). In addition it requires that the Jacobian matrix be obtainable for each iteration. It will be shown later that the Jacobian defined in Equation (20) has particular significance regarding stability of the steady state. The technique presented below for its evaluation follows the procedure described elsewhere for the numerical solution of boundary-value problems (7, 8).

From the chain rule of differentiation of γ_e and θ_c, it follows that the Jacobian can be written as

$$J = \begin{pmatrix} \partial\gamma_e/\partial\gamma_o & \partial\gamma_e/\partial\theta_o \\ \partial\theta_e/\partial\gamma_o & \partial\theta_e/\partial\theta_o \end{pmatrix} \begin{pmatrix} \partial\gamma_o/\partial\gamma_e' & \partial\gamma_o/\partial\theta_e' \\ \partial\theta_o/\partial\gamma_e' & \partial\theta_o/\partial\theta_e' \end{pmatrix} + \sum_{i=1}^{m-1} \begin{pmatrix} \partial\gamma_e/\partial\gamma_{io} \\ \partial\theta_c/\partial\gamma_{io} \end{pmatrix} (\partial\gamma_{io}/\partial\gamma_e' \quad \partial\gamma_{io}/\partial\theta_e') \tag{21}$$

This equation may be further simplified by means of Equations (12) through (15) to yield

$$J = R_r \begin{bmatrix} \partial\gamma_e/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\gamma_e/\partial\gamma_{io} & \partial\gamma_e/\partial\theta_o \\ \partial\theta_e/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\theta_e/\partial\gamma_{io} & \partial\theta_e/\partial\theta_o \end{bmatrix} \tag{22}$$

An auxiliary set of differential equations for the elements of the matrix of Equation (22) is derived by differentiating Equations (9), (10), and (11) with respect to the inlet conditions γ_o, γ_{io}, and θ_o. Thus if M is defined as

$$M = \begin{bmatrix} \partial\gamma/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\gamma/\partial\gamma_{io} & \partial\gamma/\partial\theta_o \\ \partial\theta/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\theta/\partial\gamma_{io} & \partial\theta/\partial\theta_o \end{bmatrix} \tag{23}$$

The following system of ordinary differential equations results from the differentiation and with the aid of Equation (15):

$$dM/d\xi = \begin{bmatrix} \partial\mathcal{R}/\partial\gamma + \sum_{i=1}^{m-1} \partial\mathcal{R}/\partial\gamma_i & \partial\mathcal{R}/\partial\theta \\ -\partial\mathcal{R}/\partial\gamma - \sum_{i=1}^{m-1} \partial\mathcal{R}/\partial\gamma_i & -\partial\mathcal{R}/\partial\theta - U_r \end{bmatrix} M \qquad (24)$$

The matrix M evaluated at $\xi = 1$ and multiplied by R_r gives the required Jacobian matrix. Thus

$$J = R_r M(1) \qquad (25)$$

The matrix of coefficients in Equation (24) depends upon the values of γ and θ at a point ξ; hence this auxiliary system of four first-order ordinary differential equations must be numerically integrated simultaneously with Equations (9) and (11) for each iteration. The initial condition for this auxiliary system is clearly

$$M(0) = I \qquad (26)$$

Numerical Examples

To illustrate the feasibility of methods described above and for the sake of definiteness in succeeding discussions some results of numerical solutions are presented here.

Under consideration is a first-order irreversible reaction of the form $A \rightarrow$ Products. The reaction rate is assumed to be described by an Arrhenius type expression, so that the reduced reaction rate expression may be written

$$\mathcal{R} = -P_r\,\gamma \exp\,(-E_r/\theta) \qquad (27)$$

Since $\mathcal{R}$ depends only on the concentration of the reference component and the temperature, Equation (24) is

$$dM/d\xi = \begin{pmatrix} \partial\mathcal{R}/\partial\gamma & \partial\mathcal{R}/\partial\theta \\ -\partial\mathcal{R}/\partial\gamma & -\partial\mathcal{R}/\theta - U_r \end{pmatrix} M \qquad (28)$$

The numerical integration of Equations (9) and (11) and of the auxiliary Equation (28) was performed on an IBM 7094 digital computer using the variable step size routine described by Nordsieck (9). The maximum allowable error in γ and θ at each step of the integration was set at 10^{-6}, and the step size was adjusted to meet this requirement.

The numerical values of the dimensionless parameters were taken to be

$E_r = 75.0 \qquad P_r = 10^{11}$
$U_r = 0.79 \qquad R_r = 0.5$

Such values would result for example if the system had the following properties:

$p = 2.5 \times 10^{10}$ sec.$^{-1}$
$-\Delta H = 24{,}000$ cal./mole
$C_p = 0.60$ cal./(g.) (°C.)
$D = 1.25$ cm.
$u = 0.75$ meters/sec.
$E_a = 16{,}394$ cal./(mole) (°C.)
$\rho = 0.80$ g./cc.
$U = 0.0296$ cal./(sq. cm.) (°C.) (sec.)
$L = 3.0$ meters
$C_F = 2.2$ moles/liter

Other combinations are possible, however, since the set of four dimensionless quantities does not uniquely define a set of dimensional constants. A steady state solution is sought first for a reduced feed temperature θ_F of 2.90. The wall temperature θ_w is assumed to be constant at 2.50. With the dimensional quantities listed above, these temperatures correspond to 319° and 274°K., respectively. The outlet concentration and temperature were initially assumed to be 1.0 and 2.90, respectively. Table 1 shows the convergence of the iterative procedure.

TABLE 1. CONVERGENCE OF THE ITERATIVE PROCEDURE

Iteration No., n	Predicted values $\gamma'^{(n)}_e$	$\theta'^{(n)}_e$	Computed values $\gamma_e(\gamma'^{(n)}_e,\theta'^{(n)}_e)$	$\theta_e(\gamma'^{(n)}_e,\theta'^{(n)}_e)$
1	1.0	2.90	0	3.27266
2	0.0	3.02320	0.14703	2.93256
3	0.19307	2.95895	0.21243	2.94700
4	0.23238	2.94534	0.23367	2.94438
5	0.23855	2.94280	0.23859	2.94277
6	0.23879	2.94270	0.23879	2.94270

The steady state reduced concentration and temperature profiles for this example are shown in Figure 1. It should be noted that the maximum temperature in the reactor occurs at a distance from the inlet of approximately 65% of the total reactor length. Near the inlet the temperature rises because the rate of heat generation by the reaction is greater than the rate of heat transfer to the wall. When the reaction rate decreases because of the depletion of the reactant, the rate of heat generation no longer exceeds the rate of heat removal and the temperature begins to drop. Although in this example the temperature at its maximum is only a few degrees greater than it is at the reactor outlet, other cases have been found in which the maximum is significantly greater than either the inlet or the outlet temperature.

This example is of particular interest as it will be shown later to be an unstable situation. The steady state solution obtained in this case is unique. Regardless of the set of initially assumed outlet values, the iterative procedure would always converge to the same steady state. This is not always the case, however, as is shown in the following example.

Here all data and parameters remain the same, except that the reduced heat transfer coefficient is taken to be 0.45 and the feed temperature is 2.737. In this case three steady states are possible, although this fact is not known initially. It is necessary, therefore, to start with a number of different sets of initially assumed outlet values $\gamma_e'^{(1)}$ and $\theta_e'^{(1)}$ and to perform the iterative procedure for each set until all three solutions have been obtained.

The three steady state concentration profiles are shown in Figure 2 and the three temperature profiles in Figure

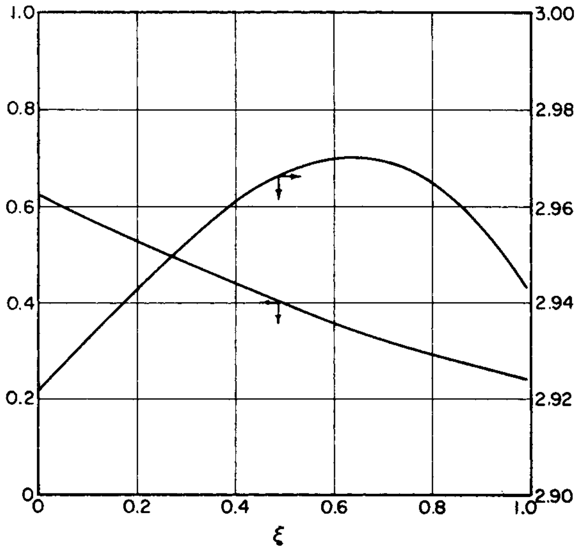

Fig. 1. Concentration and temperature profiles for a unique steady state. $\theta_F = 2.90$, $U_r = 0.79$.

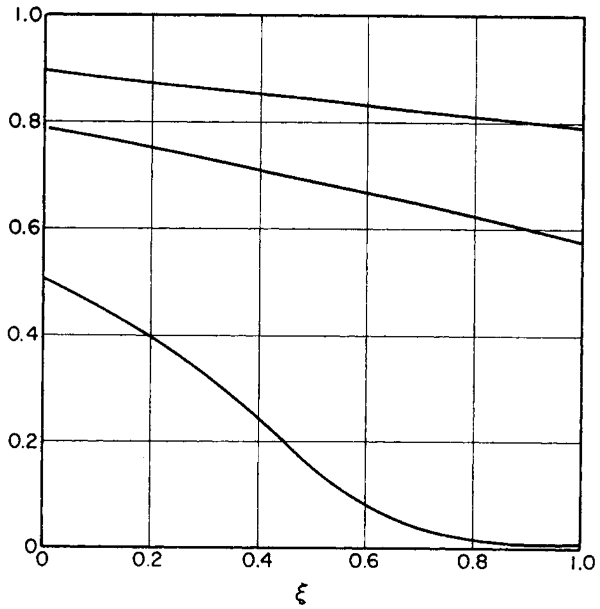

Fig. 2. Concentration profiles for multiple steady states. θ_F = 2.737, U_r = 0.45.

3. The low conversion state was obtained by taking $\gamma_e'^{(1)}$ to be 1.0 and $\theta_e'^{(1)}$ to be 2.7. With the same choice for $\gamma_e'^{(1)}$, the intermediate conversion and the high conversion states were found by taking $\theta_e'^{(1)}$ to be 2.8 and 2.9, respectively. In all cases, the maximum deviation in the outlet values was less than 10^{-5} after six iterations had been performed.

It is interesting to observe from Figure 3 that the temperature profile for the low conversion state is almost constant. This indicates that the rate of heat generation is approximately equal to the rate of heat loss to the wall throughout the reactor. On the other hand, the high conversion temperature profile shows an interior maximum as in the preceding example. The low and intermediate conversion profiles in Figure 2 are almost linear, which indicates that the rise in temperature compensates for the depletion of reactant so that the reaction rate remains approximately constant throughout the reactor. The reactant is consumed too rapidly near the inlet for this to occur in the high conversion state.

An Alternate Method of Steady State Calculations

The method described above for obtaining steady state solutions has the associated premium of transient information. This feature will be brought out subsequently. However, it has certain obvious disadvantages if the primary concern is to explore steady state characteristics. First, in order to obtain more than one solution when multiplicity exists, it is often necessary to try a large number of starting values for the outlet state. Furthermore, if only one steady state is found, one can never be absolutely certain that this is indeed a unique one.

A second disadvantage is that the feed temperature must be initially specified. It is often desirable to choose the feed temperature and other operating conditions so as to yield a desired conversion. With the above method this can be done only by finding steady states for different feed temperatures and then interpolating or iterating until one is found which yields the desired conversion.

These disadvantages can be eliminated by modifying the iterative procedure so that the outlet concentration γ_e is fixed, and consequently the inlet concentration γ_o is determinable from Equation (12). The feed temperature θ_F is left unspecified and the outlet temperature θ_e is unknown initially. The problem now is one of a univariable search to find the value of θ_o which yields the desired outlet concentration. The inlet reactant temperature is assumed to be some value, say $\theta_o^{(1)}$, and Equations (9) and (11) are integrated to yield values of θ_e and γ_e. The value of γ_e is compared with the desired value and if they do not agree satisfactorily, a Newton-Raphson technique can be used to predict an improved value of θ_o for the next iteration. If $\theta_o^{(n)}$ is the value of the inlet temperature assumed for the n^{th} integration and $\gamma_e(\theta_o^{(n)})$ is the resulting outlet concentration value, then the value of $\theta_o^{(n+1)}$, predicted for the $n + 1^{st}$ iteration is given by

$$\theta_o^{(n+1)} = \theta_o^{(n)} + \frac{\gamma_e - \gamma_e(\theta_o^{(n)})}{\partial\gamma_e/\partial\theta_o} \qquad (29)$$

where γ_e is the desired outlet concentration. To obtain the value of $\partial\gamma_e/\partial\theta_o$, it is necessary to integrate only the two auxiliary equations of Equation (38) which involve partial derivatives with respect to θ_o. When this procedure has converged, the exit temperature θ_e has also been found, and the required feed temperature θ_F is obtainable from Equation (14).

This alternate iterative procedure is superior to the original procedure so long as there is only one feed temperature θ_F which yields the desired outlet concentration γ_e. This is always the case for the reaction system considered in the preceding examples. On the other hand, one would not expect this to be necessarily true if the reaction were reversible.

Figure 4 presents a number of curves of the steady state outlet concentration γ_e as a function of the feed temperature θ_F for the reaction system of the preceding examples. Each curve corresponds to a different value of the reduced heat transfer coefficient U_r, with all other parameters being the same as before. These curves were readily constructed from the steady state solutions obtained by using the alternate procedure. All states enclosed by the dashed curves of Figure 4 are unstable; this feature will be discussed in the following section.

It can be seen from Figure 4 that when the reduced heat transfer coefficient is less than 0.79, there exists a

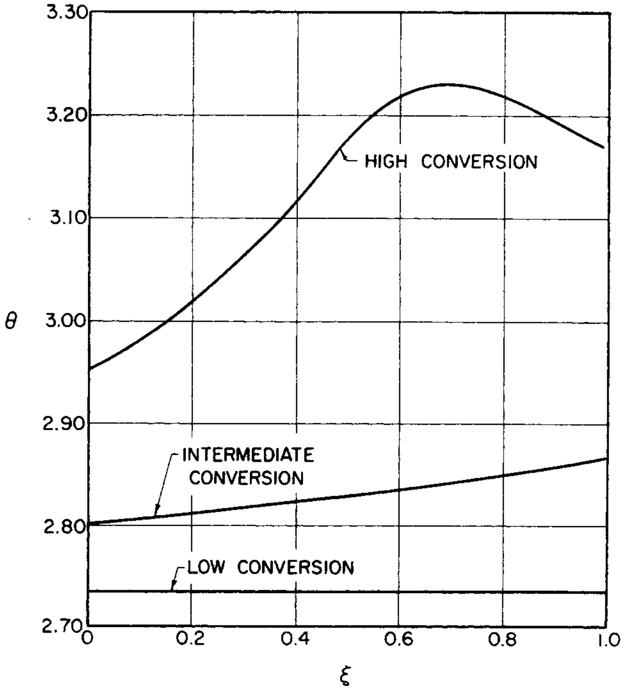

Fig. 3. Temperature profiles for multiple steady states. θ_F = 2.737, U_r = 0.45.

range of feed temperatures for which there are three steady outlet states. The range of feed temperatures for which this multiplicity exists increases as the reduced heat transfer coefficient decreases until the limiting case of no heat transfer to the wall is reached. Thus one would conclude that if multiple steady states do not exist for the adiabatic reactor, they would not exist for any value of the heat transfer coefficient.

STABILITY CRITERION

Some insight into the stability requirements and the transient nature of the reactor-recycle process may be acquired by considering the history of a single infinitesimal plug of reactant fluid. At some time, this plug is found at the reactor outlet with a temperature and a concentration which are supposedly not the steady state outlet values. A portion of the plug is recycled to the reactor inlet and mixed with fresh feed to form a new plug. The inlet conditions of this new plug depend upon the outlet conditions of the former plug and the feed conditions, according to the transient recycle relationships. Since the feed conditions are constant, the new plug may be identified solely with the old one.

As the new plug flows through the reactor, its temperature and concentration change as a result of the chemical reaction and the heat transfer to the wall. These changes, however, are independent of the condition of any other plug in the reactor, since plug flow and negligible axial dispersion of heat and mass have been assumed. Furthermore, since the wall temperature is independent of time, the condition of this plug depends only upon its location in the reactor and its inlet condition. In particular, the state of this plug at the reactor outlet is a function only of its state at the reactor inlet. It has been seen, however, that the inlet state depends only on the outlet state of the preceding plug.

Once the second plug reaches the reactor outlet, a portion of it is recycled to the inlet and the process is repeated. Thus, if $\gamma_e^{(n)}$, $\gamma_{ie}^{(n)}$ and $\theta_e^{(n)}$ represent the outlet condition of the plug after the n^{th} pass through the reactor, then the conditions after the $n + 1^{\text{st}}$ pass are represented by the functional equations:

$$\gamma_e^{(n+1)} = \gamma_e(\gamma_e^{(n)}, \gamma_{ie}^{(n)}, \theta_e^{(n)}) \tag{30}$$

$$\gamma_{ie}^{(n+1)} = \gamma_{ie}(\gamma_e^{(n)}, \gamma_{ie}^{(n)}, \theta_e^{(n)}) \tag{31}$$

$$\theta_e^{(n+1)} = \theta_e(\gamma_e^{(n)}, \gamma_{ie}^{(n)}, \theta_e^{(n)}) \tag{32}$$

It is clear that if the reactor is at a steady state, the outlet values do not change from one pass to the next. On the other hand, if $\gamma_e^{(n)}$, $\gamma_{ie}^{(n)}$, and $\theta_e^{(n)}$ differ from the steady state values by some arbitrary amount, then the outlet values on the next pass would also be expected to differ. Thus in the transient regime a single plug generates a sequence of outlet states. In the stability problem one is interested in knowing if this sequence approaches the steady outlet state as the number of passes through the reactor increases. In the present study a steady state is considered to be stable if the sequence converges to that state with increasing n when the outlet state is only infinitesimally perturbed from its steady value. Since at the steady state all plugs are in identical states at a given position, it is sufficient to examine the history of a single plug. (Certain anomalous situations in which different plugs may have different states at a given position at steady conditions are pointed out later.) Thus the problem of determining steady state stability or instability reduces to the problem of determining the convergence or divergence of the sequence defined by Equations (30), (31), and (32).

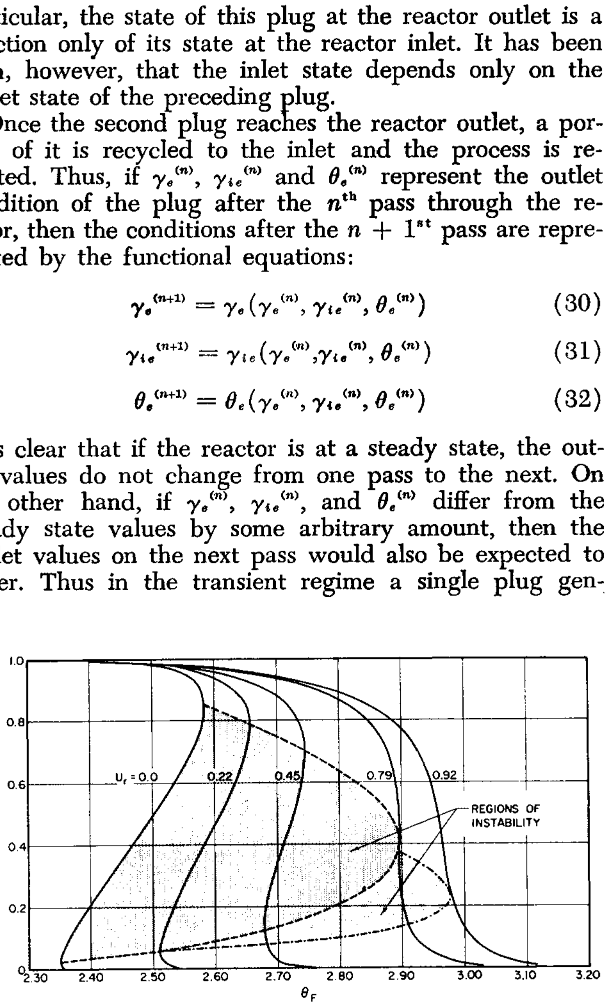

Fig. 4. Steady state solutions and regions of instability.

In order to investigate the convergence of this sequence, it is necessary to be able to evaluate the functional relationships expressed by Equations (30), (31), and (32). From the theory of partial differential equations it is known that any first-order linear partial differential operator may be expressed as a directional differential operator along a family of lines known as the characteristics (*10, 11*). Therefore, Equations (3), (4), and (5) may be written as

$$d\gamma/d\sigma = \mathcal{R} \tag{33}$$

$$d\gamma_i/d\sigma = \mathcal{R} \tag{34}$$

$$d\theta/d\sigma = U_r(\theta_w - \theta) - \mathcal{R} \tag{35}$$

along any characteristic line with parameter σ. The entire family of characteristics may be expressed in terms of a second parameter η:

$$\tau = \sigma + \eta \tag{36}$$

$$\xi = \sigma \tag{37}$$

It should be noted that the transformed Equations (33), (34), and (35) are identical in form to the steady state Equations (9), (10), and (11), since the variables ξ and σ are only dummy variables of integration. The full significance of this fact will become apparent shortly when the stability criterion is presented. Furthermore, since Equations (33), (34), and (35) are ordinary differential equations, they may be integrated numerically along the characteristics by any of the usual methods. Numerical integration of Equation (34) is unnecessary since Equation (15) applies equally well here with the substitution of σ for ξ. That is

$$\gamma_i(\sigma) - \gamma_{i_0} = \gamma(\sigma) - \gamma_0 \tag{38}$$

The characteristics may be given a physical interpretation by noting that they relate the position of any plug in the reactor with the time required to reach that point. Thus a single characteristic corresponds to the flow of a single plug through the reactor. Equations (30), (31), and (32) are therefore solved by first substituting the outlet conditions from the n^{th} pass into the transient recycle relationships to obtain the inlet conditions for the $n + 1^{\text{st}}$ pass, and then integrating Equations (33), (34), and (35) along the characteristic until the outlet is reached.

Equations (30), (31), and (32) are recognized as being nonlinear difference equations. Bellman (*12*) has discussed the linearization of difference equations and the stability of their solutions and has shown that linearization about a steady state and subsequent analysis of the linear system in the neighborhood of the steady state is valid. The stability theory of solutions of linear difference equations is presented in many texts such as the one by Goldberg (*13*). Linearization of Equations (30), (31), and (32) about the steady state outlet values γ_{es}, γ_{ies}, and θ_{es} results in the following system of linear difference equations:

$$\begin{bmatrix} \hat{\gamma}_e^{(n+1)} \\ \vdots \\ \hat{\gamma}_{ie}^{(n+1)} \\ \vdots \\ \hat{\theta}_e^{(n+1)} \end{bmatrix} = K \begin{bmatrix} \hat{\gamma}_e^{(n)} \\ \vdots \\ \hat{\gamma}_{ie}^{(n)} \\ \vdots \\ \hat{\theta}_e^{(n)} \end{bmatrix} \tag{39}$$

where $\hat{\gamma}_e^{(n)}$, $\hat{\gamma}_{ie}^{(n)}$, and $\hat{\theta}_e^{(n)}$ represent deviations from the steady outlet state after the n^{th} pass through the reactor. Thus

$$\hat{\gamma}_e^{(n)} = \gamma_e^{(n)} - \gamma_{es}$$

$$\hat{\gamma}_{ie}^{(n)} = \gamma_{ie}^{(n)} - \gamma_{ies}$$

$$\hat{\theta}_e^{(n)} = \theta_e^{(n)} - \theta_{es}$$

If, in general, the transient recycle relationships which give the inlet state of the plug on the $n + 1^{\text{st}}$ pass in terms of its outlet state on the n^{th} pass are represented by G_γ, G_i, and G_θ for γ_o, γ_{io}, and θ_o, respectively, then upon applying the chain rule of differentiation, the matrix of linearized coefficients is given by

$$K = \begin{bmatrix} \partial\gamma_e/\partial\gamma_o \cdots \partial\gamma_e/\partial\gamma_{jo} \cdots \partial\gamma_e/\partial\theta_o \\ \vdots \qquad \vdots \qquad \vdots \\ \partial\gamma_{ie}/\partial\gamma_o \cdots \partial\gamma_{ie}/\partial\gamma_{jo} \cdots \partial\gamma_{ie}/\partial\theta_o \\ \vdots \qquad \vdots \qquad \vdots \\ \partial\theta_e/\partial\gamma_o \cdots \partial\theta_e/\partial\gamma_{jo} \cdots \partial\theta_e/\partial\theta_o \end{bmatrix} \times$$

$$\begin{bmatrix} \partial G_\gamma/\partial\gamma_e \cdots \partial G_\gamma/\partial\gamma_{je} \cdots \partial G_\gamma/\partial\theta_e \\ \vdots \qquad \vdots \qquad \vdots \\ \partial G_i/\partial\gamma_e \cdots \partial G_i/\partial\gamma_{je} \cdots \partial G_i/\partial\theta_e \\ \vdots \qquad \vdots \qquad \vdots \\ \partial G_\theta/\partial\gamma_e \cdots \partial G_\theta/\partial\gamma_{je} \cdots \partial G_\theta/\partial\theta_e \end{bmatrix} \tag{40}$$

evaluated at the steady state.

It is known that solutions to the system of linear difference equations for $\hat{\gamma}_e^{(n)}$, $\hat{\gamma}_{ie}^{(n)}$, and $\hat{\theta}_e^{(n)}$ exist in the form λ^n, where λ is an eigenvalue of the matrix K. In order that $\hat{\gamma}_e^{(n)}$, $\hat{\gamma}_{ie}^{(n)}$, and $\hat{\theta}_e^{(n)}$ approach zero as n increases, that is, that the steady state in question be stable, it is necessary and sufficient that the absolute values, that is, the *norms*, of the eigenvalues of K be less than unity. For the coincidental case of the norms being exactly equal to unity Bellman (*12*) has shown that no conclusion regarding stability can be drawn from the linearized system.

The study of the eigenvalues of K may be simplified considerably when the recycle process is described by Equations (6), (7), and (8). In this case Equation (40) may be written as

$$K = R_r \begin{bmatrix} \partial\gamma_e/\partial\gamma_o \cdots \partial\gamma_e/\partial\gamma_{jo} \cdots \partial\gamma_e/\partial\theta_o \\ \vdots \qquad \vdots \qquad \vdots \\ \partial\gamma_{ie}/\partial\gamma_o \cdots \partial\gamma_{ie}/\partial\gamma_{jo} \cdots \partial\gamma_{ie}/\partial\theta_o \\ \vdots \qquad \vdots \qquad \vdots \\ \partial\theta_e/\partial\gamma_o \cdots \partial\theta_e/\partial\gamma_{jo} \cdots \partial\theta_e/\partial\theta_o \end{bmatrix}_s \tag{41}$$

By means of Equation (38) evaluated for $\sigma = 1$, the partial derivatives of γ_{ie} in Equation (41) can be related to those of γ_e. Substitution into Equation (41) and simplification of the result lead to the following characteristic equation for the eigenvalues of K:

$$\begin{aligned} (R_r - \lambda)^{m-1} \Bigg\{ \lambda^2 - R_r \left[\frac{\partial\gamma_e}{\partial\gamma_o} + \sum_{j=1}^{m-1} \frac{\partial\gamma_e}{\partial\gamma_{jo}} + \frac{\partial\theta_e}{\partial\theta_o} \right] \lambda \\ + R_r^2 \left[\frac{\partial\gamma_e}{\partial\gamma_o} + \sum_{j=1}^{m-1} \frac{\partial\gamma_e}{\partial\gamma_{jo}} \right] \frac{\partial\theta_e}{\partial\theta_o} \\ - R_r^2 \left[\frac{\partial\theta_e}{\partial\gamma_o} + \sum_{j=1}^{m-1} \frac{\partial\theta_e}{\partial\gamma_{jo}} \right] \frac{\partial\gamma_e}{\partial\theta_o} \Bigg\}_s = 0 \end{aligned} \tag{42}$$

It is clear from Equation (42) that $m - 1$ eigenvalues are equal to the recycle ratio. Since R_r is always positive and less than unity, these eigenvalues can never lead to instabilities. Thus only the two eigenvalues defined by the expression enclosed in braces need to be investigated. Since the steady state Equations (9), (10), and (11) are the same as the transient Equations (33), (34), and (35) along the characteristic, this expression is identical to the characteristic equation of the matrix J, given by Equation (22), with the elements evaluated at the steady state. It will be recalled that J is calculated and used in the Newton-Raphson procedure which involved iterations on outlet values γ_e and θ_e to obtain the steady state solution. Thus once a steady state has been found by that method, its stability can be immediately determined simply by computing the eigenvalues of the final J. In the event that the alternate method is employed to locate the steady state, this matrix is not available and an additional iteration, in which the complete system of auxiliary Equation (23) is integrated, is required to obtain J.

It was mentioned earlier that the steady state solution was independent of any time delay in the recycle line. It is interesting to note also that the stability of a steady state is likewise independent of the time delay, since δ does not enter into Equation (42). This fact results from neglecting axial dispersion in the reactor and from the assumption that the recycle process is one of pure time delay. [It has been shown (*14*), for example, that time delay in a reactor system with complete backmixing does affect stability criteria.] Thus the only effect of the time delay is upon the rate of convergence to or divergence from the steady state.

It can also be seen why, in searching for a steady state solution, the values of γ_e and θ_e calculated from one iteration should not be used as the assumed values for the next iteration. In such a procedure, the mathematical attempts to obtain a steady state solution and the physical process by which the reactor is attempting to achieve a steady state are identical in fashion. Naturally, this procedure could not converge to an unstable steady state.

The steady state Jacobian J, computed for the reaction system discussed in the first example above (the steady state of which was presented in Figure 1), has the value

$$\begin{pmatrix} -0.58215 & -3.37250 \\ 0.78209 & 2.55028 \end{pmatrix}$$

The eigenvalues of this matrix are complex conjugates which have a norm of 1.07375. Therefore, this steady state is unstable. This case is of particular interest since the system possesses only the single steady state. Because it is physically impossible for the reactor to operate in an unstable state, time-independent behavior can never be observed for this example. One expects therefore that the state of the reactor would oscillate continuously. This type of transient behavior will be explored in detail in Part II of this study.

The eigenvalues of J computed for each of the three steady states of the second example (steady state solutions for which were presented earlier in Figures 2 and 3) show that both the high and low conversion states are stable and that intermediate state is unstable. In fact it can be shown (see Appendix) that the intermediate state is always unstable for a reaction of the type considered in the numerical examples.

Results of the application of the above stability criterion to the steady state results presented earlier are summarized in Figure 4. The dashed curves enclose regions of unstable steady states. In particular, the uniformly dashed curve encloses only the intermediate conversion states. Of particular note in Figure 4 are the certain critical values of U_r. As shown in the figure, when U_r exceeds 0.92, only unique and stable steady states are possible for any value of θ_F. For values of U_r between 0.79 and 0.92, unique unstable steady states are found on a range of θ_F values. When U_r lies between 0.22 and 0.79, three steady state solutions exist, and it is possible for the high conversion state to be unstable as well as the intermediate state. Finally for U_r less than 0.22, three steady states exist, and only the intermediate one is unstable. The critical values of U_r of course depend on the values of the other parameters involved, but in general such divisions are possible.

The fact that more than one stable steady state may exist for a given set of conditions leads to some possible anomalous behavior of the reactor-recycle process. Since the model permits no communication by means of heat or mass transfer between infinitesimal plugs as they flow through the reactor and the recycle line, two adjacent plugs could theoretically approach different stable states. Hence the outlet steady state of the reactor could be discontinuous with random jumps between stable states. However, since axial dispersion is never identically zero, such discontinuities are physically impossible and point out an inadequacy in the simplified model.

EXTENSION TO COMPLICATED RECYCLE LINES

It is not always possible to describe the recycle line by equations as simple as Equations (6), (7), and (8). A more complicated mathematical description is necessary if the recycle tube is heated or cooled, if chemical reaction occurs in the tube, or if a component is removed from the stream before it is fed back. These complexities could enter into the system either accidentally or intentionally, as perhaps a possible means of reactor control. Nevertheless, the above methods of analysis remain applicable so long as the recycle process has negligible capacity and can be described by equations of the form

$$\gamma_o(\tau) = G_\gamma\,[\gamma_e(\tau-\delta), \ldots, \gamma_{je}(\tau-\delta), \ldots, \theta_e(\tau-\delta)] \tag{43}$$

$$\gamma_{io}(\tau) = G_i\,[\gamma_e(\tau-\delta), \ldots, \gamma_{je}(\tau-\delta), \ldots, \theta_e(\tau-\delta)] \tag{44}$$

$$\theta_o(\tau) = G_\theta\,[\gamma_e(\tau-\delta), \ldots, \gamma_{je}(\tau-\delta), \ldots, \theta_e(\tau-\delta)] \tag{45}$$

The feed conditions are involved as parameters in these expressions.

Steady state solutions can apparently be found in the same way as was demonstrated earlier for a simple recycle line. Outlet values can be assumed for γ_e and θ_e, and the outlet values of the other $m - 1$ components can be taken to satisfy Equation (15) for $\xi = 1$. However, since Equation (16) is no longer applicable, this approach might require an iterative procedure to determine the proper values of γ_{ie} from Equations (43), (44), and (15) for the assumed values of γ_e and θ_e. Therefore, it may not always be convenient to assume only γ_e and θ_e, and perhaps it is more efficient to assume outlet values for each of the $m + 1$ variables, γ_e, γ_{ie}, and θ_e.

If $\gamma_e'^{(n)}$, $\gamma_{ie}'^{(n)}$, and $\theta_e'^{(n)}$ represent the assumed outlet values for the n^{th} iteration, then, according to the Newton-Raphson method, the estimated outlet values for the $n + 1^{\text{st}}$ iteration are obtained from

$$(J^{(n)} - I)\begin{bmatrix} \gamma_e'^{(n+1)} - \gamma_e'^{(n)} \\ \vdots \\ \gamma_{ie}'^{(n+1)} - \gamma_{ie}'^{(n)} \\ \vdots \\ \theta_e'^{(n+1)} - \theta_e'^{(n)} \end{bmatrix} = \begin{bmatrix} \gamma_e'^{(n)} - \gamma_e^{(n)} \\ \vdots \\ \gamma_{ie}'^{(n)} - \gamma_{ie}^{(n)} \\ \vdots \\ \theta_e'^{(n)} - \theta_e^{(n)} \end{bmatrix} \tag{46}$$

where $\gamma_e^{(n)}$, $\gamma_{ie}^{(n)}$, and $\theta_e^{(n)}$ are the calculated outlet values from the n^{th} iteration, and J is the Jacobian matrix given by

$$J = \begin{bmatrix} \partial\gamma_e/\partial\gamma_e' \ldots \partial\gamma_e/\partial\gamma_{je}' \ldots \partial\gamma_e/\partial\theta_e' \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial\gamma_{ie}/\partial\gamma_e' \ldots \partial\gamma_{ie}/\partial\gamma_{je}' \ldots \partial\gamma_{ie}/\partial\theta_e' \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial\theta_e/\partial\gamma_e' \ldots \partial\theta_e/\partial\gamma_{je}' \ldots \partial\theta_e/\partial\theta_e' \end{bmatrix} \tag{47}$$

The Jacobian matrix can be expressed as

$$J = J_1 J_2 \tag{48}$$

where

$$J_1 = \begin{bmatrix} \partial\gamma_e/\partial\gamma_o \ldots \partial\gamma_e/\partial\gamma_{jo} \ldots \partial\gamma_e/\partial\theta_o \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial\gamma_{ie}/\partial\gamma_o \ldots \partial\gamma_{ie}/\partial\gamma_{jo} \ldots \partial\gamma_{ie}/\partial\theta_o \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial\theta_e/\partial\gamma_o \ldots \partial\theta_e/\partial\gamma_{jo} \ldots \partial\theta_e/\partial\theta_o \end{bmatrix} \tag{49}$$

and

$$J_2 = \begin{bmatrix} \partial G_\gamma/\partial\gamma_e \ldots \partial G_\gamma/\partial\gamma_{je} \ldots \partial G_\gamma/\partial\theta_e \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial G_i/\partial\gamma_e \ldots \partial G_i/\partial\gamma_{je} \ldots \partial G_i/\partial\theta_e \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \partial G_\theta/\partial\gamma_e \ldots \partial G_\theta/\partial\gamma_{je} \ldots \partial G_\theta/\partial\theta_e \end{bmatrix} \tag{50}$$

The matrix J_2 can be obtained by differentiating Equations (43), (44), and (45), and the matrix J_1 can be obtained as before from an auxiliary system of ordinary differential equations which are obtained by differentiating Equations (9), (10), and (11) with respect to the inlet conditions γ_o, γ_{io}, and θ_o.

Stability arguments for a complicated recycle system can be developed in a fashion identical to those presented earlier for a simple recycle process. As before, the norms of the eigenvalues of the matrix J of Equation (47), at the steady state, must be less than unity for that state to be stable. In general, however, one cannot show that the norms of $m - 1$ of these eigenvalues are less than unity, and hence the eigenvalues of an $m + 1^{\text{st}}$ order matrix must be examined. Nevertheless, here again the Newton-Raphson procedure for obtaining steady state solutions provides, at the same time, a means of examining its stability.

SUMMARY

A convenient method for investigating the stability to small disturbances of a plug-flow tubular reactor with recycle has been developed. The method requires an investigation of the eigenvalues of a Jacobian matrix which arises naturally in the search for a steady state solution by a technique based on a Newton-Raphson iteration scheme. By means of this method a steady state solution is obtained and its stability or instability ascertained simultaneously. The method is shown to be applicable to a large class of reactor-recycle processes, but is limited to cases in which axial dispersion of heat and mass is negligible.

Results of numerical computations for a first-order, exothermic reaction have been presented to illustrate the feasibility of the method as well as the existence of multiple steady states and the occurrence of instabilities. The results show that in some situations the reactor would possess no stable steady state and would be expected to oscillate continuously. The complete transient nature will be explored in Part II of this study.

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NOTATION

A = reference component
A_i = i^{th} component
a_i = stoichiometric coefficient for component A_i
C = concentration of reference component
C_i = concentration of component A_i
C_p = heat capacity
d = determinant of Jacobian matrix J
D = reactor diameter
E_a = activation energy
E_r = dimensionless activation energy, $E_a \rho C_p / R(-\Delta H) C_F$
G_γ = recycle function defined in Equation (43)
G_i = recycle function defined in Equation (44)
G_θ = recycle function defined in Equation (45)
ΔH = heat of reaction
I = identity matrix
J = Jacobian matrix defined by Equation (20) or Equation (48)
J_1 = matrix defined by Equation (49)
J_2 = matrix defined by Equation (50)
K = matrix defined by Equation (40)
L = reactor length
M = matrix defined by Equation (23)
m = number of components in reaction
p = pre-exponential factor
P_r = dimensionless pre-exponential factor, pL/u
R = gas constant
R_r = recycle ratio, fraction of product stream returned to reactor inlet
r = rate of formation of reference component
r_i = rate of formation of component A_i
$\mathfrak{R}$ = dimensionless reaction rate, rL/uC_F
t = time
T = temperature
T_w = wall temperature
tr = trace of Jacobian matrix J
u = velocity
U = heat transfer coefficient
U_r = dimensionless heat transfer coefficient, $4UL/D\rho u C_p$
x = distance variable

Greek Letters

γ = dimensionless concentration of reference component, C/C_F
γ_i = dimensionless concentration of component A_i, $-C_i/a_i C_F$
δ = dimensionless time delay in recycle line
η = parameter along characteristic curve
θ = dimensionless temperature, $T\rho C_p/(-\Delta H) C_F$
θ_w = dimensionless wall temperature, $T_w \rho C_p/(-\Delta H) C_F$
λ = eigenvalue
ξ = dimensionless distance variable, x/L
ρ = density
σ = parameter along characteristic curve
τ = dimensionless time, tu/L

Subscripts

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

Superscripts

n = n^{th} iteration or n^{th} pass through reactor
$'$ = assumed reactor outlet condition
$\wedge$ = deviation from steady state

LITERATURE CITED

1. Kramers, H., and K. R. Westerterp, "Elements of Chemical Reactor Design and Operation," Academic Press, New York (1963).
2. Aris, Rutherford, "An Introduction to the Analysis of Chemical Reactors," Prentice-Hall, Englewood Cliffs, N. J. (1965).
3. Denbigh, K. G., "Chemical Reactor Theory," Cambridge Univ. Press, England (1965).
4. Mukherjee, S. P., and L. K. Doraiswamy, *Brit. Chem. Eng.*, **10**, 93 (1965).
5. Doraiswamy, L. K., *ibid.*, **6**, 315 (1961).
6. Bilous, O., and N. R. Amundson, *A.I.Ch.E. J.*, **2**, 117 (1956).
7. Fox, L., "Numerical Solution of Ordinary and Partial Differential Equations," Addison-Wesley, Reading, Mass. (1962).
8. McGinnis, P. H., Jr., *Chem. Eng. Progr. Symposium Series No. 55*, **61** (1965).
9. Nordsieck, A. T., *Mathematics of Computation*, **16**, 22 (1962).
10. Courant, R., and D. Hilbert, "Methods of Mathematical Physics," Vol. 2, Interscience, New York (1962).
11. Acrivos, A., *Ind. Eng. Chem.*, **48**, 703 (1956).
12. Bellman, R., "A Survey of the Theory of the Boundedness, Stability and Asymptotic Behavior of Solutions of Linear and Non-linear Differential and Difference Equations," pp. 141-156, Office of Naval Research, Washington, D. C. (1949).
13. Goldberg, S., "Introduction to Difference Equations," Wiley, New York (1958).
14. Nemanic, D. J., J. W. Tierney, Rutherford Aris, and N. R. Amundson, *Chem. Eng. Sci.*, **11**, 199 (1959).

APPENDIX

Stability of the Intermediate States

By means of Equations (15) and (16), the derivatives of the steady state outlet concentration and temperature with respect to the feed temperature can be expressed in the form

$$\begin{bmatrix} d\gamma_e/d\theta_F \\ d\theta_e/d\theta_F \end{bmatrix} = \begin{bmatrix} \partial\gamma_e/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\gamma_e/\partial\gamma_{io} & \partial\gamma_e/\partial\theta_o \\ \partial\theta_e/\partial\gamma_o + \sum_{i=1}^{m-1} \partial\theta_e/\partial\gamma_{io} & \partial\theta_e/\partial\theta_o \end{bmatrix} \begin{bmatrix} d\gamma_o/d\theta_F \\ d\theta_o/d\theta_F \end{bmatrix} \tag{A1}$$

Differentiation of the recycle conditions, given by Equations (12) and (14), with respect to θ_F and substitution of the result into Equation (A1) yield the following system:

$$\begin{bmatrix} d\gamma_e/d\theta_F \\ d\theta_e/d\theta_F \end{bmatrix} = J \begin{bmatrix} d\gamma_e/d\theta_F \\ d\theta_e/d\theta_F + 1/R_r - 1 \end{bmatrix} \tag{A2}$$

Here, J is the Jacobian matrix, presented by Equation (22) and evaluated at the steady state. It is clear from Equation ($A2$) that the derivatives of the outlet conditions are given by

$$\begin{bmatrix} d\gamma_e/d\theta_F \\ \\ d\theta_e/d\theta_F \end{bmatrix} = (J - I)^{-1} J \begin{bmatrix} 0 \\ \\ 1 - 1/R_r \end{bmatrix} \tag{A3}$$

The inverse of the matrix $(J - I)$, which exists whenever its determinant does not vanish, may be expressed as

$$(J - I)^{-1} = \frac{1}{d - tr + 1} \begin{bmatrix} R_r\, \partial\theta_e/\partial\theta_o - 1 & -R_r\, \partial\gamma_e/\partial\theta_o \\ \\ -R_r \left[\partial\theta_e/\partial\gamma_o + \sum\limits_{i=1}^{m-1} \partial\theta_e/\partial\gamma_{io} \right] & R_r \left[\partial\gamma_e/\partial\gamma_o + \sum\limits_{i=1}^{m-1} \partial\gamma_e/\partial\gamma_{io} \right] - 1 \end{bmatrix} \tag{A4}$$

The following expression for $d\gamma_e/d\theta_F$ can be readily obtained from Equations ($A3$) and ($A4$).

$$d\gamma_e/d\theta_F = \frac{1 - R_r}{d - tr + 1}\, \partial\gamma_e/\partial\theta_o \tag{A5}$$

Since the characteristic equation, as given in Equation (42), of the Jacobian matrix J can be written in the form

$$\lambda^2 - tr\,\lambda + d = 0 \tag{A6}$$

it can readily be shown that whenever the quantity $(d - tr + 1)$ in Equation ($A5$) is negative, one of the solutions of Equation ($A6$) exceeds unity. Consequently, the corresponding steady state is unstable. It follows that a necessary, but not sufficient, condition for steady state stability is that the sign of $d\gamma_e/d\theta_F$ be the same as the sign of $\partial\gamma_e/\partial\theta_o$.

This condition can now be applied to show that the intermediate conversion state is always unstable for irreversible reactions such as those considered in the preceding examples. An examination of the curves in Figure 4 shows that $d\gamma_e/d\theta_F$ never vanishes; thus it follows from Equation ($A5$) that the sign of $\partial\gamma_e/\partial\theta_o$ can never change. Furthermore, the sign of $\partial\gamma_e/\partial\theta_o$ must be negative, since one can argue that, at least at sufficiently low inlet temperatures, the outlet reactant concentration would be expected to decrease with an increase in inlet temperature for an irreversible reaction. An intermediate conversion steady state violates the above condition for stability, therefore, since $d\gamma_e/d\theta_F$, being positive, does not agree in sign with $\partial\gamma_e/\partial\theta_o$.

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The Finite-Difference Computation of Natural Convection in a Rectangular Enclosure

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A study is made of the natural convection of a fluid contained in a long horizontal enclosure of rectangular cross section with one vertical wall heated and the other cooled. Two-dimensional motion is assumed. The governing vorticity and energy transport equations are solved by an implicit alternating direction finite-difference method. Transient and steady state isothermals and streamlines are obtained for Grashof numbers up to 100,000 and for height-to-width ratios of 1, 2, and 3.

This work is part of a research program whose object is to develop numerical methods for solving the partial differential equations governing the conservation of mass, momentum, and energy in problems of natural and free convection. In the initial investigation (7), Martini and Churchill measured the temperature and velocity fields for air contained in a long hollow horizontal cylinder with one vertical half heated and the other cooled. They did not complete a numerical solution, mainly because of the limitations of the then available computer (an IBM 650). Aided by an IBM 704 computer, Hellums and Churchill (4) developed an explicit finite-difference method for generating the transient solution to the above problem and also for free convection at a vertical plate. In both cases they were able to employ boundary-layer types of equations in which only one momentum balance actually proved to be necessary. The computed transient velocity and temperature fields ultimately converged to steady state values. For the plate, these values agreed excellently with the theoretical solutions of Ostrach (9) and Schmidt