G = dimensionless gravity, $gb^2\rho/12\mu U$
g = acceleration due to gravity, cm./sec.^{2}
h = channel height, cm.
k = permeability, sq.cm.
n = integer (dimensionless)
p = pressure, g./sq.cm.
R = dimensionless velocity, $b^2U\rho/\mu h$
T = dimensionless surface tension, $\sigma b/6\mu Uh$
U = secondary fluid velocity, cm./sec.
u = average velocity in x direction, cm./sec.
V = primary fluid velocity, cm./sec.
v = average velocity in y direction, cm./sec.
$\mathbf{v}$ = velocity vector
x = coordinate, cm.
y = coordinate, cm.

Greek Letters

λ = finger width, $y/h \equiv V/U$
ϕ = flow potential, sq.cm./sec.
ψ = stream function, sq.cm./sec.
ρ = density, g./cc.
σ = surface tension, g./sec.^{2}
μ = viscosity, centipoise

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Stability of Loop Reactors

DAN LUSS and NEAL R. AMUNDSON

University of Minnesota, Minneapolis, Minnesota

A method of determining all the possible steady states of a tubular recycle reactor with plug flow is presented. The information needed to determine the steady states can be used to ascertain the asymptotic and global stability of the reactor without performing transient computations. The effects of changes in the recycle ratio and start-up conditions are examined. Several numerical examples are included to demonstrate the use of the method for various types of recycle reactors.

Many industrial reactors use recycling as a convenient means of temperature and concentration control, or to improve the yield if conversion per pass is small. An extensive survey of chemical processes that use recycle can be found in the monograph by Nagiev (*1*).

Few papers have investigated the stability problems associated with the operation of such reactors. It has been shown (*2*) that under certain conditions the use of a recycle stream in a tubular reactor might give rise to instabilities. That treatment was, however, limited to a case in which only one steady state could exist and the criteria which were derived were based upon the tedious numerical computations of a matrizant. Gall and Aris (*3*) considered the problem of steady state operation of a tubular reactor followed by a stirred tank with mass and thermal feedback. It was demonstrated that the presence of feedback affects considerably the heat generation curve of the stirred tank. Reilly and Schmitz (*6*) have recently developed a method of analyzing the stability of a loop reactor from numerical solutions of the steady state equations. This paper presents a new and different approach to that problem.

In many processes the recycle system consists of a reactor connected to a separation unit such as a distillation column. The behavior of the combined system is largely dependent on the operation and characteristics of the specific separation unit, which often masks the inherent pathological characteristics of the reactor. The aim of this work is to investigate the special trends which are caused by a recycle stream. The discussion is therefore limited to loop reactors; that is, a reactor in which there is no separation unit and no lag in time between the exit and the reentrance of the recycle stream to the reactor. The following cases will be considered: recycle in a tubular loop adiabatic reactor; recycle in a semi-isothermal loop reactor with constant feed concentration; and recycle in a semi-isothermal loop reactor.

ADIABATIC LOOP TUBULAR REACTOR

Consider an adiabatic loop tubular reactor through which the reactants flow with a uniform plug velocity. The external feed and draw-off is v and the total amount of internal flow is V. $1 - \lambda$ is defined as the recycle parameter where

$$\lambda = v/V \tag{1}$$

If $\lambda = 1$ the system reduces to a conventional tubular reactor. It is assumed that the mixing between the recycled stream and the fresh feed is instantaneous and perfect. The number of independent chemical reactions occurring in the reactor is m, and there are n species present. Let f_{ij} be the reaction rate in moles per unit volume of component i, formed in the j^{th} reaction per unit time, where

$$\sum_{i=1}^{i=n} a_{ij} A_i = 0 \qquad j = 1,2,\ldots m$$

The a_{ij} are stoichiometric coefficients which are taken as positive for a product and negative for a reactant. The variables of the system are the temperature and m independent concentrations.

The governing differential equations are

$$u\frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial t} = \sum_{j=1}^{m} f_{ij} \qquad i = 1,2,\ldots,m \tag{2}$$

$$u\frac{\partial T}{\partial x} + \frac{\partial T}{\partial t} = \frac{1}{\rho c_p}\sum_{j=1}^{m} f_j\,(-\Delta H_j) \tag{3}$$

The initial and boundary conditions are

$$T(x,0) = T(x) \tag{4}$$

$$c_i(x,0) = c_i(x) \tag{5}$$

$$T(0,t) = (1-\lambda)\,T(l,t) + \lambda T_o \tag{6}$$

$$c_i(0,t) = (1-\lambda)\,c_i(l,t) + \lambda c_{i,o} \tag{7}$$

$c_{i,o}$ and T_o are the fresh feed concentration and temperature.

One must first investigate the number of possible steady states to discuss the stability of the reactor. They will be obtained by finding all possible solutions of the set of equations

$$u\frac{dc_i}{dx} = \sum_{j=1}^{m} a_{ij} f_j \qquad i = 1,2,\ldots,n \tag{8}$$

$$u\frac{dT}{dx} = \frac{1}{\rho c_p}\sum_{j=1}^{m} f_j\,(-\Delta H_j) \tag{9}$$

with the boundary conditions

$$T(0) = (1-\lambda)\,T(l) + \lambda T_o \tag{10}$$

$$c_i(0) = (1-\lambda)\,c_i(l) + \lambda\,c_{i,o} \tag{11}$$

This is a system of $n + 1$ ordinary differential equations. However, one has to consider only m independent variables, and all the other $n + 1 - m$ concentrations can be expressed as a linear function of the temperature and $m - 1$ concentrations. Physically this corresponds to the use of mass and enthalpy balance to reduce the number of the variables.

The difficulty in obtaining the steady states increases with the number of independent reactions. The case in which there is only one reaction is the easiest to describe, since the system has only one dependent variable, either the temperature or the concentration of one of the species. Such a system will be discussed first and the more complicated cases will be illustrated later.

RECYCLE WITH ONE INDEPENDENT REACTION

In the case of only one independent reaction all concentrations in the reaction mixture can be expressed as a linear function of the temperature by use of an enthalpy balance. Hence, the reaction rate can be expressed as a function of the temperature alone, say $f = f(T)$.

The steady state is obtained as the solution of the differential equation

$$\frac{dT}{dx} = \frac{1}{u}\,\frac{(-\Delta H)}{\rho c_p}\,f(T) \tag{12}$$

with boundary condition (10).

Douglas and Eagleton (*4*) have shown that Equation (12) can be integrated analytically for many types of reactions. Thus, for a given set of parameters one can find $T(l)$ as a function of $T(0)$. [A simple numerical procedure to obtain the curve is to find the temperature profile for a very long adiabatic reactor with inlet temperature $T = T_o$. The curve of $T(l)$ vs. $T(0)$ is then constructed by use of the temperature values of points which are separated by the length of the given reactor.] The curve of $T(l)$ vs. $T(0)$ obtained in this way will be defined as the *reaction curve*. Note that all points of the reaction curve satisfy the differential equation. Boundary condition (10) can be rewritten for the steady state as

$$T(l) = \frac{T(0)}{1-\lambda} - \frac{\lambda}{1-\lambda}\,T_o \tag{13}$$

In the $[T(l),T(0)]$ plane Equation (13) will be represented by a straight line of slope $1/1 - \lambda$ which passes through the point where $T(l) = T(0) = T_o$. This line will be defined as the boundary conditions line. The possible steady states are the intersections of the reaction curve with the boundary conditions line.

Example 1.

Consider the first-order, irreversible reaction $A \rightarrow B$; Equation (12) will be of the form

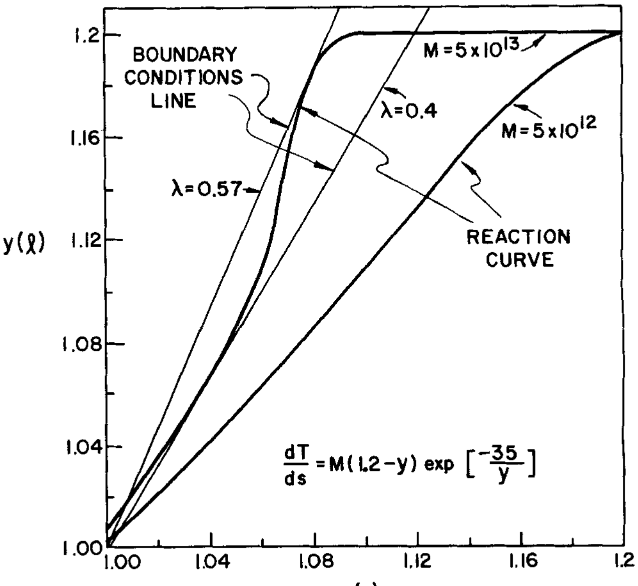

Fig. 1. Reaction curves for a first-order, irreversible reaction in an adiabatic reactor.

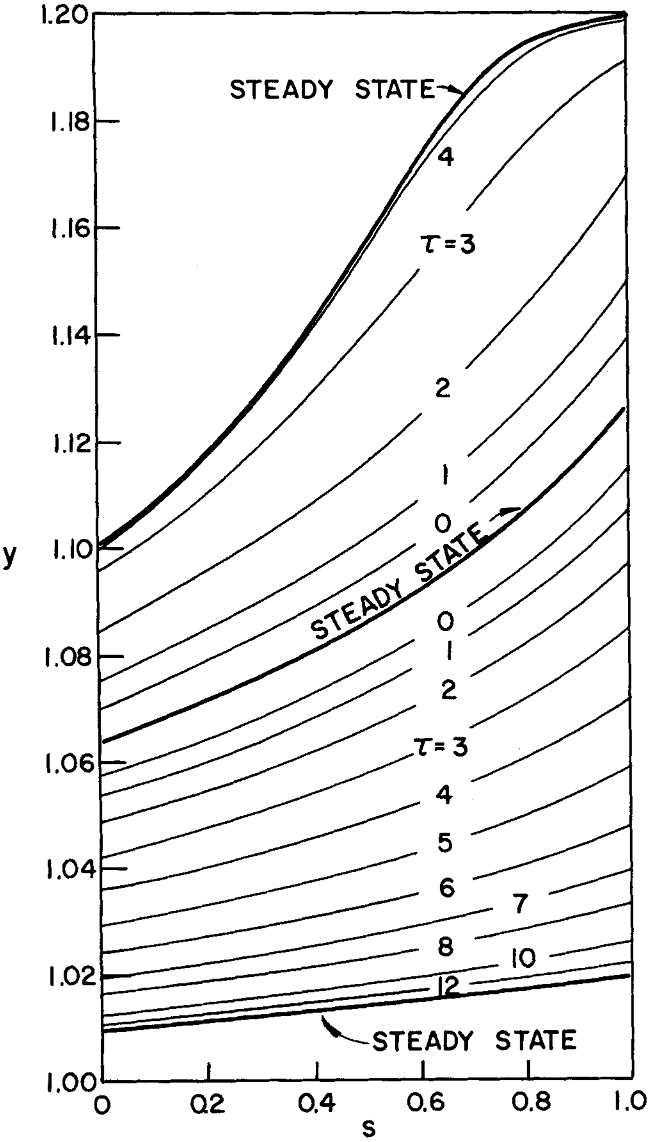

Fig. 2. Transient behavior of a reactor (same reaction as in Figure 1). $M = 5 \cdot 10^{13}$, $\lambda = 0.5$.

$$\frac{dy}{ds} = M(y_{\text{ad}} - y) \exp\left(-\frac{q}{y}\right)$$

Figure 1 shows the reaction curve for two different values of M. By construction of the boundary conditions lines for various values of the recycle parameter λ it can be seen that only one intersection can exist between the reaction curve for $M = 5 \times 10^{12}$ and most boundary conditions lines. For this value of M there are three possible steady states for $0.05 < \lambda < 0.11$ and only one possible steady state for the system for any other prescribed value of λ. However, for $M = 5 \times 10^{13}$ there are three possible steady states for $0.57 > \lambda > 0.4$ and one steady state for all other values of λ. It is seen that the possibility of multiple steady states depends on the length of the reactor, the rate expression and properties of the reactants, and the magnitude of the recycle parameter. Temperature profiles of three possible steady states can be seen in Figure 2.

STABILITY OF A REACTOR WITH ONE REACTION

A chemical reactor is considered to be stable if a perturbation in the input will decay with time. A reactor is unstable if any disturbance, no matter how small, increases with time.

It is easily shown that the reaction curve for one reaction must have a positive slope for any $T(0)$ for the range of interest $T_o < T(0) < T_{\text{ad}}$. It will be shown that the necessary and sufficient condition for a reactor to be unstable is

$$\left[\frac{dT(l)}{dT(0)}\right]_{\text{ss}} > \frac{1}{1-\lambda} \tag{14}$$

The necessary condition for a steady state to be stable is

$$\left[\frac{dT(l)}{dT(0)}\right]_{\text{ss}} < \frac{1}{1-\lambda} \tag{15}$$

The proof of these statements is as follows. The transient equations [(2) and (3)] can be solved by the use of the method of characteristics. All characteristic directions have the same constant direction. Hence the temperature is propagated along the characteristics in exactly the same way as it is along the x axis in the steady state. Therefore the reaction curve represents also the change of temperature with time as the reactants move from the inlet of the reactor. In this way the propagation with time of any perturbation can be easily predicted from the reaction curve. It will be assumed that a disturbance inside the reactor arises from a disturbance at the inlet at some previous time. The only limitation is that such a disturbance at the inlet must not violate the enthalpy balance.

The propagation of a disturbance at the inlet occurs in the following way. Consider steady state II in the schematic Figure 3*a*. If at time $t = 0$ the temperature of the influent stream is perturbed to A, the outlet temperature at $t = \theta$, where θ is the residence time of the reactor, will be B. The temperature at $x = 0$ at $t = \theta$ will have to satisfy the boundary condition (6), which is the same as boundary condition (10). The boundary conditions line satisfies Equation 6. Hence if $T(l,\theta) = B$, $T(0,\theta)$ will be on the boundary conditions lines and its value will be C. In the same way it can be shown that $T(0,2\theta) = D$. If one continues to follow the behavior of the reactor with time, it can be seen that the temperature will shift toward the upper steady state. In a similar way a negative temperature disturbance will shift the reactor toward the lower steady state. It is evident that since the slope of the reaction curve is larger than that of the boundary conditions line, every disturbance will shift the reactor to another steady state. This means that the reactor is unstable if condition (14) is satisfied. In the same way it can be shown that both the upper and the lower steady states that satisfy condition (15) are stable. Because the slope of the reaction curve is positive no oscillations around the steady state are possible. This, however, is true only for the case of one adiabatic reaction. Other cases will be discussed later.

A word should be inserted here on the nature of the small disturbance and how it is propagated. If a small perturbation enters the reactor at time zero, then it grows or decreases in magnitude depending upon whether the reactor is unstable or stable. Its spread in the direction of the axis remains fixed, since under the conditions of the model there is no communication in the axial direction. At the outlet a portion of the effluent is recycled and mixed with fresh unperturbed influent. After a succession of passes through the reactor the perturbation has passed to a new steady state if the reactor was unstable or has disappeared if the reactor was stable. If the duration of the perturbation to an unstable reactor is less than one residence time, then the steady state of the reactor effluent ultimately cycles between at least two steady states,

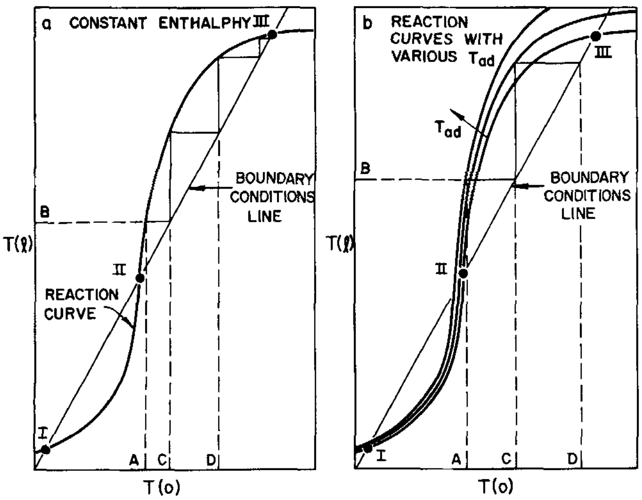

Fig. 3. Schematic description of the use of reaction curve and boundary conditions line to determine transient behavior.

one a higher or lower steady state and the other an unstable state, depending upon whether the perturbation was positive or negative. If the perturbation was of sufficient duration that during its time of entry it contained both positive and negative values at different times, then the reactor effluent would ultimately show a sequence of three steady states, these steady states occurring in the same order as the corresponding components of the perturbation entered the reactor. If in an unstable reactor the perturbation has a duration of one residence time and is positive, then the reactor effluent will arrive at the upper steady state ultimately. If the reactor was initially stable the perturbations eventually damp to zero and the original steady state is achieved. These arguments are consistent with the mathematical model which does not take into consideration axial mixing. In the latter case the perturbation would tend to spread out and result in a reactor whose influent was in either the high or the low steady state for all time.

The stability criterion was derived for a condition under which T_{ad} is unchanged by the disturbance. It will now be shown that the criterion is valid for the case in which the disturbance is small and nonisenthalpic, and how to treat the case in which the disturbance is large.

Consider the case in which for a short time interval a small arbitrary disturbance occurs in the inlet stream such that

$$T_{ad,o} = T_o + \frac{(-\Delta H)\, c_o}{\rho\, c_p} = T^* + \epsilon$$

where T^* is the value of T_{ad} when no disturbances occur. The only way the enthalpy of the stream can be changed in the recycle reactor is by mixing at the inlet with the recycled stream. One can easily show that at time t, $n\theta \leqq t < (n+1)\,\theta$ (where θ is the residence time in the tubular reactor).

$$T_{ad} = T^* + \epsilon(1-\lambda)^{n+1} \qquad (16)$$

This means that the nonisenthalpic part of the disturbance decays with time. To determine how an arbitrary disturbance propagates with time one must compute the reaction curves for several values of T_{ad} and use for each θ a different curve, whose value of T_{ad} is found from Equation (16). The procedure is best understood by observing the schematic Figure 3*b* in which the distances between the various reactions curves are exaggerated.

If the disturbance is arbitrary but small the change in T_{ad} is also very small, and the reaction curves for T^* and $T^* + \epsilon(1-\lambda)$ would be close together. Therefore the stability criterion (15) should still hold.

The transient behavior of the reactor is obtained by integrating equation (3) by the method of characteristics. Figure 2 shows the transient behavior of a reactor whose reaction curve is shown in Figure 1.

The determination of the slope $\frac{dT(l)}{dT(0)}$, which is needed for checking the stability criterion, can be found either from a reaction curve or analytically, as will now be shown. Consider first a stoichiometric mixture that reacts irreversibly. The differential equation governing the temperature will be of the form

$$\frac{dT}{ds} = M(T_{ad}-T)^n \exp\left(-\frac{E}{RT}\right) \qquad (17)$$

which becomes after integration

$$M\int_0^1 ds = \int_{T(0)}^{T(l)} \frac{\exp\left(\frac{E}{RT}\right)}{(T_{ad}-T)^n}\, dT$$

From this one obtains

$$\frac{dT(l)}{dT(0)} = \left[\frac{T_{ad}-T(l)}{T_{ad}-T(0)}\right]^n \exp\left[\frac{E}{R}\left(\frac{1}{T(0)}-\frac{1}{T(l)}\right)\right] \qquad (18)$$

Use of boundary condition (10) yields

$$\frac{dT(l)}{dT(0)} = \left[\frac{T_{ad}-T(l)}{T_{ad}-(1-\lambda)\,T(l)-\lambda T_o}\right]^n \exp\left[\frac{\lambda\, E(T(l)-T_o)}{RT(l)\,[(1-\lambda)\,T(l)+\lambda T_o]}\right] \qquad (19)$$

Equation (19) indicates that if $T(l) \rightarrow T_{ad}$, *then* $\frac{dT(l)}{dT(0)} \rightarrow 0$. Thus a steady state very close to complete conversion will always satisfy the stability criterion (15) for any λ. If $T(l) \rightarrow T_o$, which means very low conversion, then $\frac{dT(l)}{dT(0)} \rightarrow 1$ and again the stability criterion will be satisfied for any λ.

In a similar way one can treat the reaction $nA + mB \rightarrow \gamma R$ in which the reactants are not present in stoichiometric proportions. If the reaction rate is $kC_A{}^n\, C_B{}^m$ and A is the less abundant species, it can be shown in exactly the same way:

$$\frac{dT(l)}{dT(0)} = \left[\frac{T_{ad}-T(l)}{T_{ad}-(1-\lambda)\,T(l)-\lambda T_o}\right]^n \left\{\frac{T_{ad}-T(l)+\gamma'\left[C_{Bo}-C_{Ao}\frac{m}{n}\right]}{T_{ad}-(1-\lambda)\,T(l)-\lambda T_o+\gamma'\left[C_{Bo}-C_{Ao}\frac{m}{n}\right]}\right\}^m \times \exp\left\{\frac{\lambda E}{RT(l)}\,\frac{(T(l)-T_o)}{[(1-\lambda)\,T(l)-\lambda T_o]}\right\} \qquad (20)$$

where

$$\gamma' = \frac{-\Delta H}{\rho c_p}$$

Also in this case the stability criterion (15) will be satisfied for very high or very low conversions. Equation (20) also indicates that the effect of using an excess of one reaction is to increase $dT(l)/dT(0)$. In a similar fashion the slope $dT(l)/dT(0)$ can be determined for various types of reaction kinetics, including those for which no analytical integration of the differential equation of (dT/ds) can be obtained.

RECYCLE WITH MORE THAN ONE INDEPENDENT REACTION

When more than one independent reaction occurs, the system can no longer be characterized by the temperature alone. If there are m independent species in the mixture, the variables of the system will be $m - 1$ concentrations and the temperature. The m^{th} concentration can be obtained from an enthalpy balance. The determination of the possible steady state is more tedious in this case than it was before. In the case of *m independent reactants* one has to satisfy m differential equations subject to m boundary conditions. A boundary conditions line drawn in a plane of $c_i(0)$ vs. $c_i(l)$ or $T(0)$ vs. $T(l)$ satisfies only one of the m necessary boundary conditions, (10) or (11). Therefore in order to be able to satisfy all the m boundary conditions, m graphs of reaction curves are needed: $m - 1$ of $c_i(l)$ vs. $c_i(0)$ and that of $T(l)$ vs. $T(0)$. Each graph consists of a family of reaction curves, each of which corresponds to certain prescribed values of the other variables at $x = 0$. Each point of the reaction curves has to be obtained by numerical integration of the differential equations (8), (9) for the given values of $T(0)$ and $c_i(0)$. The simple numerical scheme to generate the whole reaction curve by one integration for a very long reactor which was used in the case of one reactant cannot be applied.

Every steady state has to satisfy both the differential equations (8), (9) and the boundary conditions (10), (11). Hence the possible steady states are all combinations of points $T(0)$ and $c_i(0)$ which lie on the intersection of the boundary conditions line and the reaction curve in *each* of the m graphs. The determination of a steady state corresponds to finding a certain point in an m dimensional space. The construction of such graphs would require a large amount of computation. Instead it is more convenient to use less detailed graphs and find the exact values of the variables by a simple search procedure. The reaction curves should be used to find the number of possible steady states on the one hand and to get a good estimate of the values of the variables at the inlet on the other hand.

The construction of the graphs can be simplified to a large extent by the fact that the values of the variables must obey certain restrictions imposed by enthalpy and mass balances. These restrictions reduce to a large extent the region in which one must search for a possible steady state. With some experience one is able by examining the shape of one or two graphs to decide that for certain combinations of the initial values of $c_i(0)$ and $T(0)$ no steady state can exist for the prescribed value of the recycle parameter. In this way one is able to restrict the region in which the search must be done and thus reduce the amount of computation.

In this case all the variables in the system are coupled through the differential equations and a perturbation in one of the variables will give rise to disturbances in the other variables. The coupled effects of all perturbations will determine whether the reactor will return to its initial steady state or shift to a new steady state.

The system of equations describing the steady state behavior (which is similar to that describing the transient behavior along the characteristic directions) is

$$\frac{d\overline{y}}{ds} = \overline{F(\overline{y})} \tag{21}$$

where

$$\overline{y} = \begin{bmatrix} c_1 \\ \vdots \\ c_{m-1} \\ \vdots \\ T \end{bmatrix} \qquad \overline{F(\overline{y})} = \begin{bmatrix} f_1(\overline{y}) \\ \vdots \\ \vdots \\ f_m(\overline{y}) \end{bmatrix}$$

Consider the case in which some disturbances occur for a short time at the inlet to the reactor such that

$$\overline{\eta}(0, t) = \overline{y}(0,t) - \overline{y}(0)_{\text{ss}} \tag{22}$$

The disturbances $\overline{\eta}(0,t)$ will propagate along the reactor. If the disturbances are very small, $\eta(0,t) << \overline{y}(0,t)$, the resulting disturbance at the outlet will be

$$\overline{\eta}(l,t + \theta) = \overline{\overline{A}}\,\overline{\eta}(0,t) \tag{23}$$

where

$$\overline{\overline{A}} = \begin{bmatrix} \dfrac{\partial y_1(l)}{\partial y_1(0)} & \cdots\cdots & \dfrac{\partial y_1(l)}{\partial y_n(0)} \\ \vdots & & \vdots \\ \vdots & & \vdots \\ \dfrac{\partial y_n(l)}{\partial y_1(0)} & \cdots\cdots & \dfrac{\partial y_n(l)}{\partial y_n(0)} \end{bmatrix}_{\text{ss}}$$

Since the disturbance at the outlet is fed back to the inlet of the reactor, one can write

$$\overline{\eta}(0,t + \theta) = (1 - \lambda)\,\overline{\overline{A}}\,\overline{\eta}(0,t)$$

or

$$\overline{\eta}(0,t + n\theta) = [(1 - \lambda)\overline{\overline{A}}]^n\,\overline{\eta}(0,t) \tag{24}$$

The steady state is stable if and only if $\overline{\eta}(0,t + n\theta) \to 0$ as n increases. It can be shown that the necessary and sufficient conditions for the stability of the reactor are that all the eigenvalues β of the matrix equation

$$[(1 - \lambda)\,\overline{\overline{A}} - \overline{\overline{I}}\beta]\,\overline{X} = 0 \tag{25}$$

are smaller than one in absolute value. Equation (25) can be written as a polynomial of order m in β. The stability conditions require that all the zeroes of the polynomial be smaller than one in absolute value. For example, consider the case $m = 1$. In this case

$$\overline{\overline{A}} = \frac{\partial T(l)}{\partial T(0)}$$

and stability is guaranteed if and only if

$$\left|(1 - \lambda)\,\frac{dT(l)}{dT(0)}\right|_{\text{ss}} < 1$$

which is identical to condition (15), since $\dfrac{dT(l)}{dT(0)} > 0$.

If $m = 2$

$$\overline{\overline{A}} = \begin{vmatrix} \dfrac{\partial c_1(l)}{\partial c_1(0)} & \dfrac{\partial c_1(l)}{\partial T(0)} \\ \dfrac{\partial T(l)}{\partial c_1(0)} & \dfrac{\partial T(l)}{\partial T(0)} \end{vmatrix}_{\text{ss}}$$

The necessary and sufficient conditions for stability in this case are (5):

$$(1 - \lambda)\,\left|\frac{\partial c_1(l)}{\partial c_1(0)} + \frac{\partial T(l)}{\partial T(0)}\right|$$

$$\underset{\text{ss}}{\leqq} (1 - \lambda)^2 \left[\frac{\partial c_1(l)}{\partial c_1(0)}\,\frac{\partial T(l)}{\partial T(0)} - \frac{\partial c_1(l)}{\partial T(0)}\,\frac{\partial T(l)}{\partial c_1(0)}\right]_{\text{ss}} + 1 < 2$$

A sufficient but by no means necessary condition for stability is

$$\sum_{j=1}^{m} \left| A_{ij} \right| < 1 \qquad i = 1,2,\ldots,m \tag{26}$$

In practice one is interested not only in stability to small disturbances, but in the domain of stability. The various reaction curves still enable one to predict how a disturbance in the inlet will propagate in time and to check in this manner the stability of the steady state to any given disturbance. Suppose that due to a certain perturbation the values of the variables at the inlet $x = 0$ are $c_i(0)$, $(i = 1, \ldots, m-1)$, $T(0)$. From the reactions curve in the $[T(l), T(0)]$ plane one can find for a given $T(0)$ at time $t = 0$ the value of $T(l)$ at $t = \theta$. For a given recycle parameter one can draw the boundary condition line and determine with it what will be $T(0)$ at $t = \theta$. In a similar way one can determine the values of $c_i(0)$ at $t = \theta$ for all the species. Knowing the values of $c_i(0)$ and $T(0)$ at $t = \theta$ one can proceed to find their values at $t = 2\,\theta$ and so on until a steady state is reached. It was found in most cases that the steady state was practically reached for times less than $5\,\theta$ even though the small final deviations from the exact steady state values (differences in the order of 10^{-3} of the steady state values) decayed much slower. In contrast to the case of one independent concentration, it was found that some oscillations and overshoot occurred during the approach to the steady state.

Knowledge of the reactor's response to disturbances in the inlet is sufficient to determine stability, since every disturbance at any point in the reactor can be considered as due to a certain disturbance at the inlet. To clarify the concepts used it is best to consider an example.

Example 2.

In a loop tubular adiabatic reactor two consecutive reactions occur:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

$$B \xrightarrow{k_3} C$$

B is the desired product. The fresh feed is at temperature T_o and contains only A at a concentration of c_A. Determine all the possible steady states and their stability for different values of λ.

The governing steady state differential equations will be

$$\frac{dy}{ds} = (K_1A - K_2B)\,Q_1 + K_3B\,Q_2 \tag{27}$$

$$\frac{dA}{ds} = -K_1A + K_2B \tag{28}$$

$$\frac{dB}{ds} = K_1A - (K_2 + K_3)\,B \tag{29}$$

with the boundary conditions

$$y(0) = (1-\lambda)\,y(l) + \lambda \tag{30}$$

$$A(0) = (1-\lambda)\,A(l) + \lambda \tag{31}$$

$$B(0) = (1-\lambda)\,B(l)$$

where

$$A = \frac{c_A}{c_{A_o}} \qquad B = \frac{c_B}{c_{A_o}}$$

$$Q_1 = \frac{(-\Delta H_1)\,c_{A_o}}{\rho\,c_p\,T_o} \qquad Q_2 = \frac{(-\Delta H_2)\,c_{A_o}}{\rho\,c_p\,T_o} \tag{32}$$

$$K_i = P_i\frac{l}{u}\exp\left[-\frac{E_i}{R\,T_o\,y}\right] \qquad i = 1,2,3$$

The three differential equations, (27) to (29), can be combined to give

$$B = \frac{1}{Q_2}\left[1 + (Q_1 + Q_2)\,(1 - A) - y\right] \tag{33}$$

One must therefore solve only two differential equations, (27) and (28), with the boundary conditions, (30) and (31).

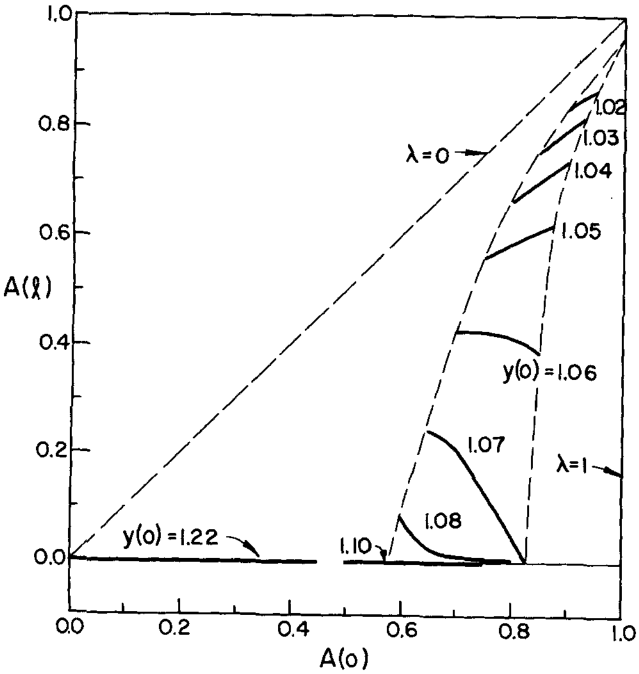

Fig. 4. Reaction curves in $[c(l), c(0)]$ plane (example 2).

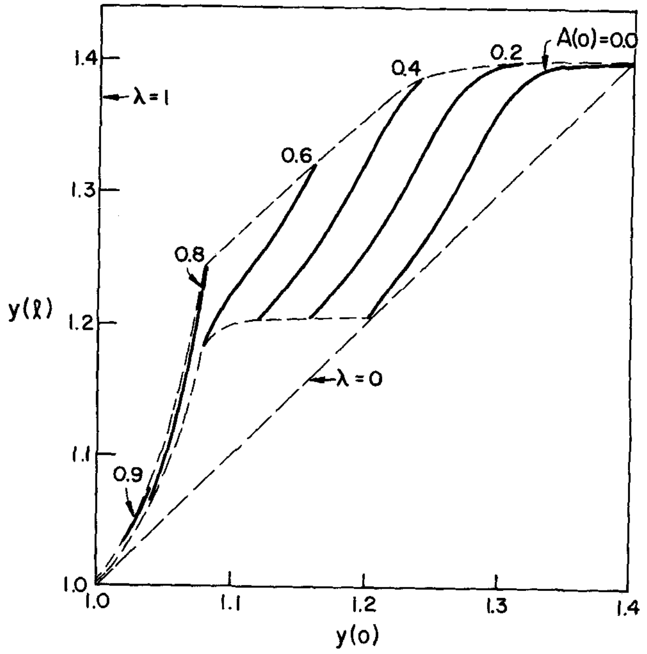

Fig. 5. Reaction curves in $[y(l), y(0)]$ plane (example 2).

Before starting any computations to obtain the reaction curve, one should use mass balances to restrict the region in which the curves should be computed. The mass balance restrictions which can be used in this case are:

$$B \geq 0 \tag{34}$$

$$A + B \leq 1 \tag{35}$$

If one uses these restrictions together with the enthalpy balance (33), the following relations are obtained:

$$A\left(1 + \frac{Q_1}{Q_2}\right) \leq \frac{1}{Q_2}[1 + Q_1 + Q_2 - y] \tag{36}$$

$$A\frac{Q_1}{Q_2} \geq [1 + Q_1 + Q_2 - y]\frac{1}{Q_2} - 1$$

The values of the parameters used in the given example are

$$Q_1 = Q_2 = 0.2$$
$$K_1 = 5 \times 10^{13} \quad \exp(-35/y)$$
$$K_2 = 5 \times 10^{13} \quad \exp(-42/y)$$
$$K_3 = 5 \times 10^{19} \quad \exp(-60/y)$$

Figures 4 and 5 show the shape of the reaction curves obtained while using restrictions (34) and (35) for the upper and lower limit of the range in which the curves had to be computed. It is seen immediately that the bounds on the variables decrease to a large extent the amount of needed computations. Figure 4 indicates that if the temperature is above 1.1 the concentration of A at the outlet will be practically zero and for those temperatures $A(0) = \lambda$. If the value of λ is very small, steady states can exist only at high inlet temperatures and they can be obtained from Figure 5 by finding the intersection of the boundary conditions line with the reaction curve $A(0) = \lambda$. If one draws a few boundary conditions lines it becomes clear that for a low value of the recycle parameter only one steady state can exist. In the same way it can be seen that for a value of λ close to 1, both $T(0)$ and $A(0)$ must have a value very close to 1.0, which means very little conversion. Again it can be easily shown that only one steady state is possible. It was found that for intermediate values of the recycle parameter three steady states are possible. It was found that values of the inlet concentrations and temperature are sometimes very sensitive to rather small changes in the recycle rates. In Table 1 the values of the variables for two different recycle rates are shown. It can be seen that for $\lambda = 0.375$ all steady states are at higher temperatures than for $\lambda = 0.4$. From Table 1 it is clear that operation with $\lambda = 0.4$ is superior to that with $\lambda = 0.375$, since at the greater λ a better conversion and higher purity of product B is obtained and also the output of the reactor is larger.

As explained earlier one can use Figures 4 and 5 to determine how a disturbance in the inlet propagates with time; that is, the determination of the changes in the concentration and temperature beginning at $s = 0$ and with time increments of θ. Table 2 shows the results obtained by using a very large reaction curves graph. The convergence to the steady state value of the concentration was very rapid, while the temperature disturbance first exceeded the steady state value and only then converged smoothly to it. For practical purposes the steady state was reached after four steps even though the exact steady state value was achieved only after a longer time (in this case at $t = 20\ \theta$). The use of the reaction curves enables one to determine very easily which steady state will be reached for each value of inlet concentration and temperature and a prescribed recycle parameter. In this way it is possible to obtain regions of stability for each steady state.

TABLE 1. STEADY STATE VALUES FOR TWO ADIABATIC REACTIONS (EXAMPLE 2)

λ	$y(0)$	$y(l)$	$A(0)$	$A(l)$	$B(0)$	$B(l)$	Remarks
0.4	1.021	1.035	0.8956	0.826	0.1043	0.1729	Stable
0.4	1.040	1.067	0.8000	0.667	0.1997	0.3330	Unstable
0.4	1.128	1.213	0.4007	0.00106	0.5590	0.9317	Stable
0.375	1.135	1.216	0.3756	0.00108	0.5750	0.9194	Stable
0.375	1.219	1.351	0.3764	0.00222	0.1517	0.2428	Unstable
0.375	1.236	1.377	0.3759	0.00148	0.7025	0.1133	Stable

TABLE 2. CHANGES IN TIME OF VALUES OF CONCENTRATION AND TEMPERATURE AT $x = 0$ AS OBTAINED FROM FIGURES 5 AND 7 FOR $\lambda = 0.4$

τ	y	A	B
0.0	1.080	0.8000	0.0000
1.000	1.147	0.4009	0.4651
2.000	1.142	0.4008	0.4879
3.000	1.139	0.4008	0.5057
4.000	1.136	0.4007	0.5195
5.000	1.133	0.4007	0.5299
6.000	1.132	0.4007	0.5376
7.000	1.131	0.4007	0.5434
8.000	1.130	0.4007	0.5476
9.000	1.130	0.4006	0.5507
10.000	1.128	0.4006	0.5530
20.000	1.128	0.4006	0.5588

Figure 6 shows the shape of the stability regions for two values of λ. It is seen that a small change in λ greatly influences the regions of stability as well as the steady state values. The plot is especially useful in attempting to avoid troubles in start-up. For example, in the case of $\lambda = 0.375$ it is evident that overheating during start-up might cause the reactor to operate at the high temperature steady state, at which according to Table 1, the yield of the desired product is very small. On the other hand, for $\lambda = 0.4$ overheating will cause no trouble and the reactor will shift to the desired third steady state.

The only disadvantage of this scheme is that one is limited in this treatment to isenthalpic systems. Non-isenthalpic disturbances cannot be examined on the reaction curve and one must investigate the transient equations numerically.

The effect of an arbitrary disturbance for which the enthalpy is different from that of the steady state value may be determined by generating the m surfaces of reaction curves for various values of the enthalpy in a way similar to that used in the case of one reaction. In principle, the transient behavior can be determined from these curves by the same method as was used in Figure 3*b*. However, if m is larger than three the additional computational effort needed to generate these curves may be larger than that required for a direct solution of the transient equations.

LOOP SEMI-ISOTHERMAL TUBULAR REACTORS

In practice, loop reactors are often cooled to prevent an undesirable rise of temperature due to the heat of reaction. In the treatment here it will be assumed that the temperature of the wall is kept at a constant value by use of some coolant. The determination of the possible steady states and their stability is usually more complex than that of an adiabatic reactor due to the addition of one more dependent variable to the system.

The treatment of these reactors can be simplified if one assumes that the inlet concentrations are kept at a constant

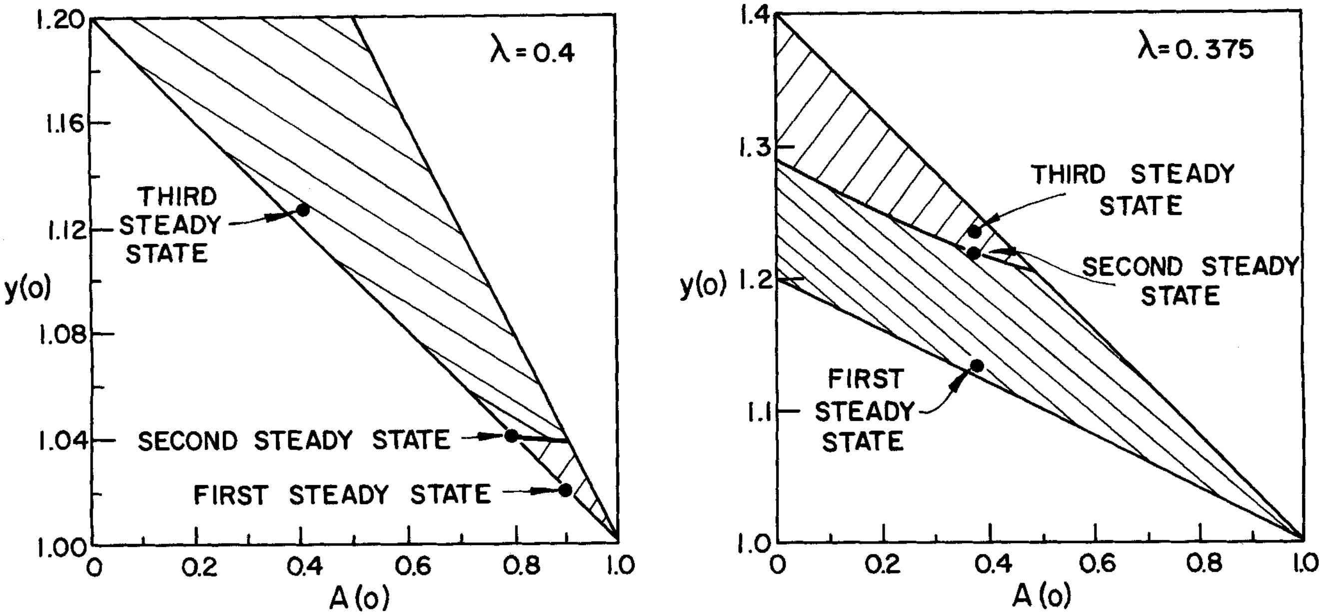

Fig. 6. Region of stability for example 2.

value independent of the value of the concentration at $x = l$. This means that one neglects any concentration feedback effect and considers only the thermal feedback. Use of such a model is adequate if one wants to check the behavior of the system for a single prescribed value of the recycle parameter and if the concentration of the recycle stream can be assumed to be constant. This will be the case when the conversion is either very low or very high. This model may also be useful for the description of the steady state operation of a reactor, which is followed by a separation unit from which a recycle stream of constant composition is obtained. This simple model will be discussed first and the more general case, in which this assumption is waived, will be discussed later.

CONSTANT INLET CONCENTRATION

The differential equations governing the steady state behavior are Equations (2) and (3), the boundary conditions will be

$$T(0,t) = (1-\lambda)\ T(l,t) + \lambda T_o \qquad (37)$$

$$c_i(0,t) = c_i(0) \qquad (38)$$

With this model one can obtain the steady state from one reaction curve in the $[T(l), T(0)]$ plane in the same way as was done for an adiabatic reactor with one reaction. Since the concentrations at the inlet are known, the only variable is the inlet temperature of the steady state. The reaction curve is obtained by integrating numerically the steady state equation with boundary condition (33) for different values of $T(0)$. The steady states are intersections of the temperature boundary condition line with the reaction curve.

There is one essential difference between the reaction curve obtained in this case and the one obtained for an adiabatic reactor with one reaction. In this case the slope of the reaction curve $dT(l)/dT(0)$ need not always be

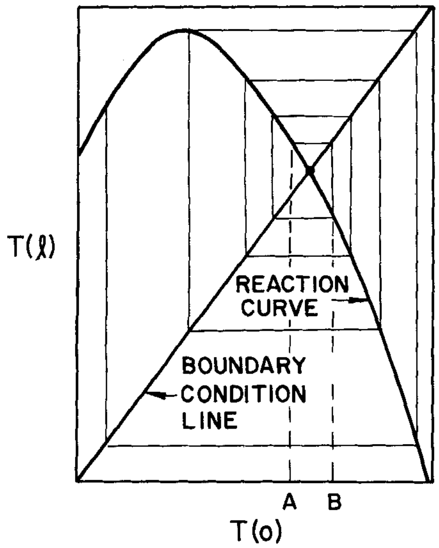

Fig. 7. Schematic diagram of reaction curve with increasing oscillations.

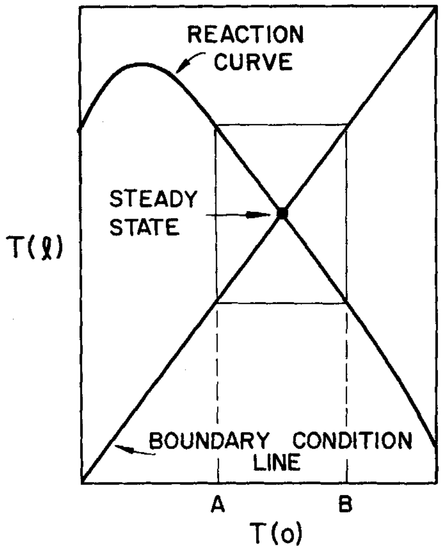

Fig. 8. Schematic diagram of reaction curve with sustained oscillations.

positive. It was shown for the adiabatic reactor with one reaction how the change of the temperature in the inlet with time could be determined by use of the reaction curve and the boundary condition line. The same method can be applied here. In Figures 7, 8, and 9 three different schematic reactions curves are shown. The initial temperature was in all three cases perturbed to A, and it is seen that at time $t = \theta$ the inlet temperature will be B. In the same manner one can follow the change of temperature with time on the plot.

An important conclusion that can be immediately drawn from Figures 7, 8, and 9 is that for a steady state for which $dT(l)/dT(0) < 0$, the approach or the departure from steady state will be accompanied with oscillations around the steady state values.

Figures 7 to 9 show that the nature of the oscillations will depend on the relative slope of the reaction curve and the boundary condition line. The following criteria about the nature of the oscillations hold [for cases in which $dT(l)/dT(0) < 0$]:

$$-\frac{dT(l)}{dT(0)} > \frac{1}{1-\lambda} \quad \text{increasing oscillations} \tag{39}$$

$$-\frac{dT(l)}{dT(0)} = \frac{1}{1-\lambda} \quad \text{sustained oscillations} \tag{40}$$

$$-\frac{dT(l)}{dT(0)} < \frac{1}{1-\lambda} \quad \text{damped oscillations} \tag{41}$$

The stability conditions are again that the eigenvalues of the matrix Equation (25) are smaller in absolute value than one. For the case of one reaction one obtains

$$\left|\frac{dT(l)}{dT(0)}\right| > \frac{1}{1-\lambda} \quad \text{unstable steady state} \tag{42}$$

$$\left|\frac{dT(l)}{dT(0)}\right| < \frac{1}{1-\lambda} \quad \text{stable steady state} \tag{43}$$

The following example will clarify the treatment.

Example 3.

The first-order, irreversible reaction $A \rightarrow B$ occurs in semi-isothermal loop reactor with constant concentration of A at the inlet, with a recycle parameter $\lambda = 2/3$. Determine the number of possible steady states and their stability.

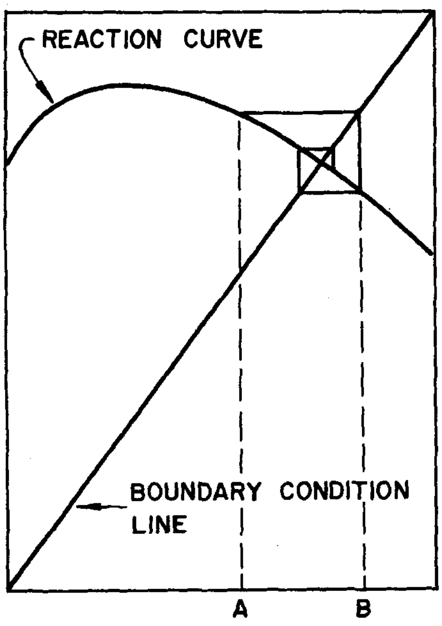

Fig. 9. Schematic diagram of reaction curve with dampened oscillations.

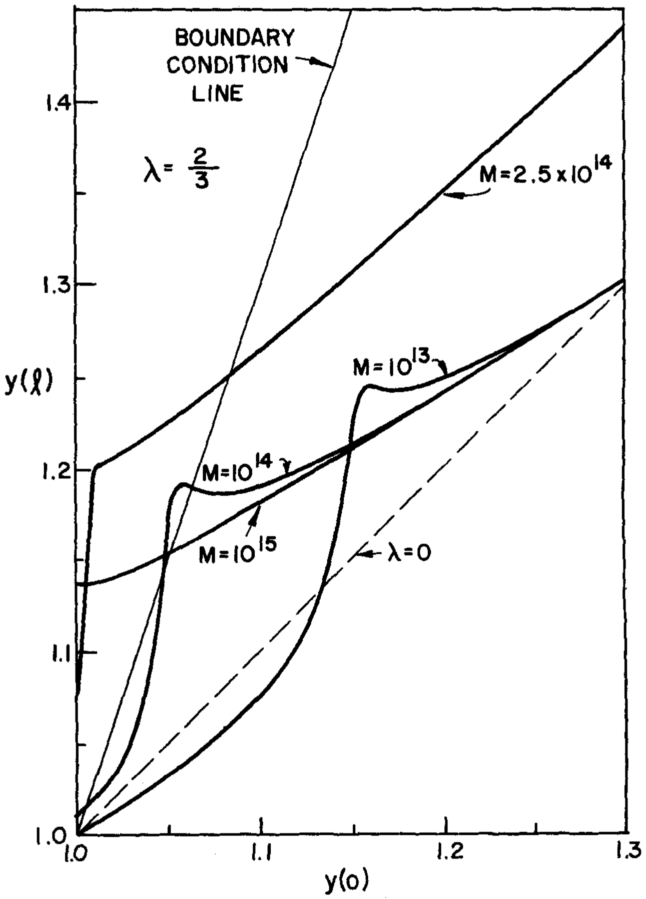

Fig. 10. Reaction curve for semi-isothermal loop reactor with constant inlet concentration (example 3).

The governing steady state differential equations are

$$\frac{dA}{ds} = M\ A \exp\left(-\frac{q}{y}\right) \tag{44}$$

$$\frac{dy}{ds} = Q\ M\ A \exp\left(-\frac{q}{y}\right) + H(y_\omega - y) \tag{45}$$

with the boundary conditions

$$y(0) = (1-\lambda)\, y(l) + \lambda \tag{46}$$

$$A(0) = 1 \tag{47}$$

The values of the parameters used in the numerical example are

$$q = 35.0 \qquad H = 0.5 \qquad Q = 0.2 \qquad y_\omega = 1.0$$

Figure 10 represents the reaction curves for various values of M. For $M = 10^{13}$ only one steady state is possible, for $M = 10^{14}$ three steady states are possible. The first and the third steady states are stable, while the second is unstable. The approach to the third steady state should be accompanied by damped oscillations, since $dT(l)/dT(0)$ is negative. It can be seen that the oscillations should have a rather small amplitude. For $M = 2.5 \times 10^{14}$ only one steady state is possible and the same is true for $M = 10^{15}$.

It is interesting to note the unusual shape of the reaction curve for $M = 2.5 \times 10^{14}$. It is seen that a very small change at $y(0)$ will cause a large change in $y(l)$

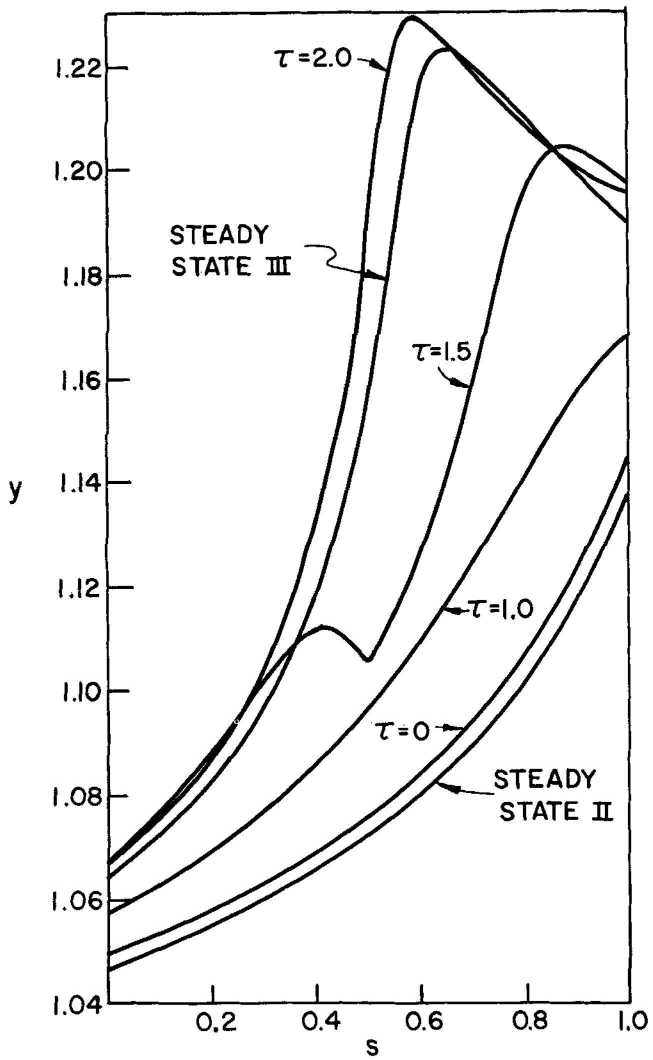

Fig. 11. Transient temperature profile for example 3 ($M = 10^{14}$).

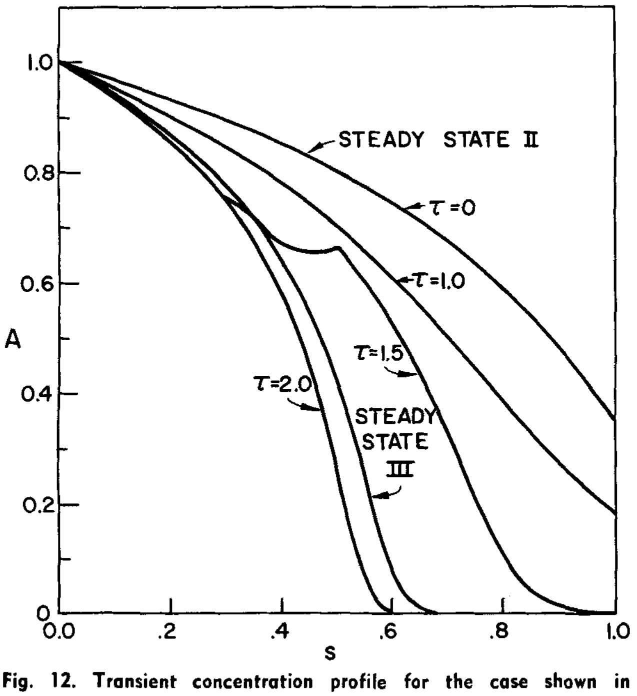

Fig. 12. Transient concentration profile for the case shown in Figure 11.

for values of $y(0)$ close to 1.0. The reason is that for this value of M the tubular reactor is very sensitive, while for smaller or larger values of M the reactor is less sensitive.

The transient computation for this system can be made easily by the use of the method of characteristics. It is interesting to obtain the approach to the third steady state. Figures 11 and 12 show how a small perturbation in the temperature of the second unstable steady state causes the reactor to shift to the third steady state. It can be seen that both the temperature and the concentration profile overshoot the steady state values at $t = 2\ \theta$. For higher values of t there are more oscillations; however, their amplitude was too small to be shown on the graphs. The profiles for $t = 1.50$ are due to the special way in which the temperature at $x = \theta$ changes in the time increment $\theta < t < 1.5\ \theta$, while $A(0,t)$ was assumed to remain constant.

SEMI-ISOTHERMAL LOOP REACTOR WITH HEAT AND MASS FEEDBACK

Consider a semi-isothermal loop reactor in which the recycle stream causes heat and mass feedback effects. The governing differential equations for the transient state are

$$\frac{Dc_i}{Dt} = \sum_{j=1}^{m} f_{ij}(c,T) \qquad i = 1,2,\ldots m \tag{48}$$

$$\frac{DT}{Dt} = \frac{1}{\rho\, c_p} \left[\sum_{j=1}^{m} f_j(c,T)\,(-\Delta H_j) + \frac{4h}{D}\,(T_w - T) \right] \tag{49}$$

The boundary conditions are the same as for the adiabatic case [Equations (4) to (7)].

In the adiabatic case it was possible to express one of the concentrations as a linear function of the other concentrations and temperature and to reduce in this way the number of variables in the system. In this case this is not possible since the enthalpy balance does not hold and therefore one must deal with $m + 1$ variables in the semi-isothermal case. For the adiabatic case with only one reaction a simple determination of the steady states and their stability is possible. In cases of more than one independent reaction the determination of the steady state and the stability criterion are more complex. The determination of the steady state and their stability for the semi-isothermal case is done in exactly the same way as was done for an adiabatic reactor with more than one reaction. One must draw $m + 1$ reaction curves and this may be used to predict the propagation with time of any disturbance at the inlet and to find stability regions for each steady state. The details will be repeated here.

The necessary and sufficient conditions for asymptotic stability are again that all the eigenvalues of the matrix Equation (25) be smaller than one in absolute value. The only difference is that in this case the matrix $\bar{\bar{A}}$ is of order $m + 1$, since the system has $m + 1$ independent variables (the temperature and m concentrations) as compared with m in the adiabatic case.

It was shown for the adiabatic case that the use of enthalpy and mass balances can produce very helpful restrictions on the regions in which to seek possible steady states.

To obtain a restriction on the enthalpy at the inlet, one must know the amount of heat lost or gained by the recycle stream by means of heat exchange with the walls. This quantity is not known a priori; however one can very often find a lower and upper bound for its value. In this way one can obtain at least a conservative restriction on the enthalpy at the inlet and use this relation to decrease the domain in which one needs to search for possible steady states.

In the adiabatic case oscillations around the steady state values were possible only when more than one independent reaction took place. In the semi-isothermal case oscillations are possible even if only one reaction occurs due to the interaction of the temperature and concentration effects. A simple example is given to demonstrate the treatment in the case of a semi-isothermal reactor.

Example 4.

A simple irreversible reaction $A \rightarrow B$ occurs in a semi-isothermal loop reactor.

The steady state equations are

$$\frac{dy}{ds} = Q\ M\ A\ \exp\left(-\frac{q}{y}\right) + H(y_\omega - y) \qquad (50)$$

$$\frac{dA}{ds} = M\ A\ \exp\left(-\frac{q}{y}\right) \qquad (51)$$

The boundary conditions are

$$y(0) = (1-\lambda)\,y(l) + \lambda \qquad (52)$$

$$A(0) = (1-\lambda)\,A(l) + \lambda \qquad (53)$$

The numerical values of the parameters used in the example are

$M = 2 \times 10^{12}$

$y_\omega = 1.0$ $\qquad Q = 0.3$

$H = 0.5$ $\qquad q = 50$

Figures 13 and 14 illustrate the shape of the reaction curves in the two planes $[A(l), A(0)]$ and $[y(l), y(0)]$. To obtain an enthalpy restriction one must estimate the minimum amount of heat lost by the recycle stream to the coolant. Here it was assumed that this minimum equals zero and the following restriction was obtained:

$$y(0) + Q\,A(0) < 1 + Q \qquad (54)$$

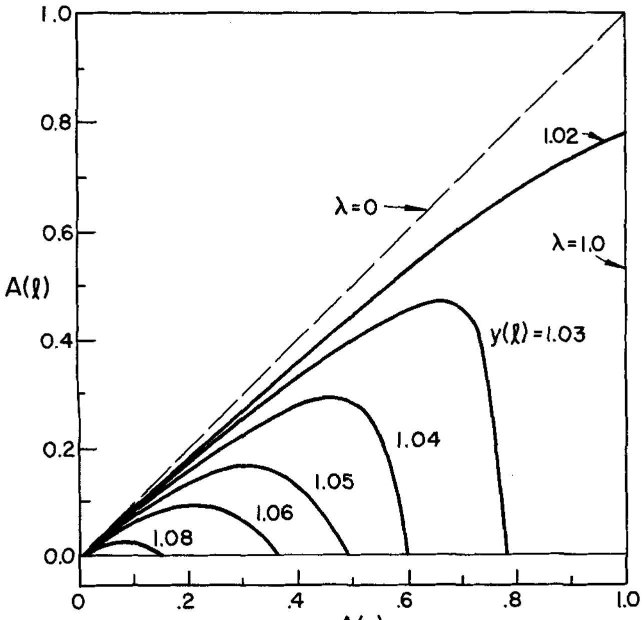

Fig. 13. Reaction curve for semi-isothermal loop reactor (example 4).

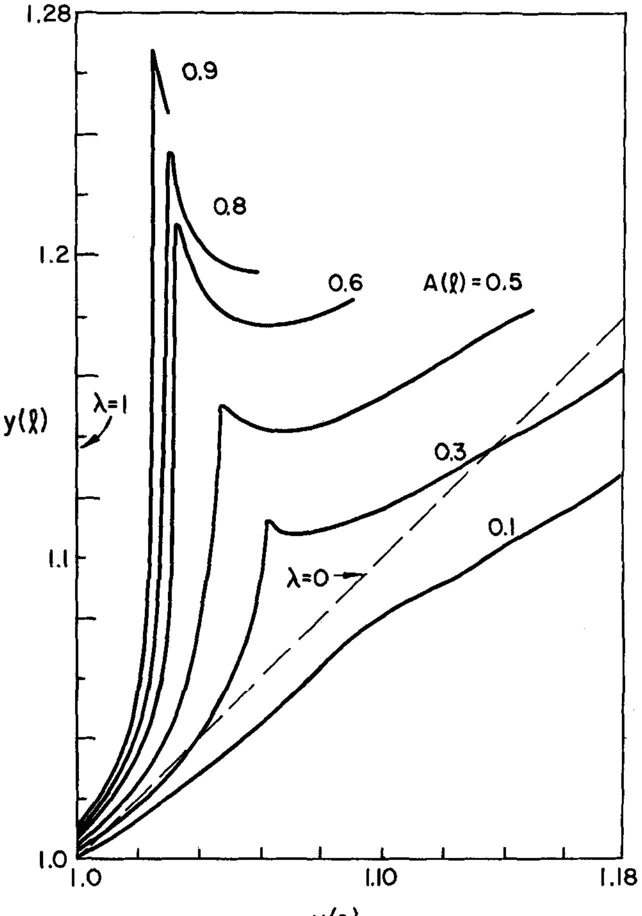

Fig. 14. Reaction curves for semi-isothermal loop reactor (example 4).

It can be seen from Figure 14 that this simple restriction decreases the domain in which one needs to compute the reaction curves. Figure 13 illustrates that for values of λ close to 1 the possible steady states will have a rather low value of $y(0)$. It also shows that for temperatures above $y(0) = 1.08$ the value of $A(l)$ will be practically zero. For those inlet temperatures one obtains the condition $A(0) = \lambda$. Hence to obtain a possible steady state for which $y(0) > 1.08$ one must draw the boundary condition line in Figure 14 and find the intersection with the reaction curve $A(0) = \lambda$ for $y(0) > 1.08$. By drawing a few boundary condition lines in Figure 14 one can convince himself that no such intersection can exist for any value of the recycle parameter. From this, the important conclusion is obtained that for this reactor no steady state can exist for $y(0) > 1.08$. Table 3 shows the inlet values for three different possible steady states. Figure 15 shows the regions of stability for the three steady states. The graph was obtained in the same way as in the case of an adiabatic reactor with more than one reaction. The dashed line in Figure 15 represents the enthalpy restriction (54). Thus during steady state op-

TABLE 3. THREE POSSIBLE STEADY STATES FOR SEMI-ISOTHERMAL LOOP REACTOR

Example 4 with $\lambda = 0.8$

	$C(0)$	$C(l)$	$T(0)$	$T(l)$	Remarks
1	0.984920	0.924601	1.003320	1.016601	Stable
2	0.900105	0.500508	1.024259	1.121339	Unstable
3	0.800	0.0	1.041181	1.205906	Stable

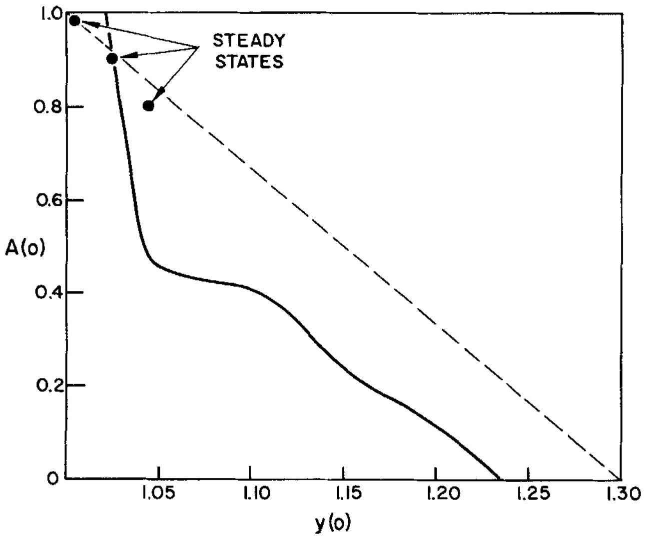

Fig. 15. Stability region for three possible steady states for a semi-isothermal loop reactor (example 4). $\lambda = 0.8$.

eration all possible disturbances will be represented by some point below the dashed line. During start-up one may initially heat the system or use higher feed concentration to decrease the start-up period. In such a case restriction (54) does not hold any more and one may obtain points above the dashed line. It is seen from Figure 15 that the first low temperature steady state has a very large region of stability. In order to start up the reactor and reach the high temperature steady state one should heat the system through the wall and reach some point in the region above the dashed line. Then one can start to use the cooling stream and the reactor will shift to the third steady state. The time of approach to a steady state depends on the initial disturbance and is of the order of 5 θ. In some cases the approach to the steady state is accompanied with oscillations.

Also in this case the reactor is stable to small disturbances if the eigenvalues of the matrix Equation (25) are smaller than one in absolute value. One should note that in this case the matrix A is of rank $m + 1$. The values of all the partial derivatives can be obtained from the reaction curves.

SUMMARY

It was shown that tubular recycle reactors with plug flow may possess several possible steady states. A method was developed by which one can obtain all the possible steady states. The computations needed for this method yield all the necessary information for determination of the stability of the various steady states and their global regions of stability without performing any transient computation. The amount of required computational effort depends on the number of independent reactions. The method can be applied for several types of recycle reactors, but is limited to cases in which there is no axial diffusion of heat or mass.

Several examples were treated to demonstrate the use of the method and how to start up such reactors to obtain the desired steady state. It was shown that a slight change of the recycle ratio might have an important effect on the conversion of the reactants, on the number of possible steady states and on their region of stability.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation.

NOTATION

a_{ij} = stoichiometric coefficient
$\bar{\bar{A}}$ = Jacobi matrix as defined by Equation (23)
A = dimensionless concentration as defined by Equation (32)
A_i = atomic species
c_i = concentration of A_i
c_p = heat capacity
D = diameter of reactor
E = activation energy
f_j = intrinsic rate of reaction j
f_{ij} = reaction rate of component i in reaction j
h = heat transfer coefficient
H = dimensionless heat transfer coefficient, $\dfrac{4hl}{Du\rho c_p}$
$-\Delta H_j$ = heat of j^{th} reaction
k = reaction rate constant
K = dimensionless reaction rate constant as defined by Equation (32)
l = length of reactor
M = dimensionless groups, lP/u
P = frequency factor
Q = dimensionless adiabatic temperature rise, $\dfrac{(-\Delta H)c_o}{\rho\, c_p\, T_o}$
q = dimensionless activation energy, E/RT_o
R = universal gas constant
s = dimensionless length, x/l
t = time
T = temperature
T_{ad} = adiabatic temperature, $T_o(1 + Q)$
T_ω = wall temperature
u = velocity
v = external feed draw off
V = total internal flow
$\underline{y}$ = dimensionless temperature, T/T_o
y = vector of disturbances as defined by Equation (21)

Greek Letters

β = eigenvalues of matrix Equation (25)
γ' = quantity as defined by Equation (20)
η = disturbance as defined by Equation (22)
θ = residence time
λ = recycle parameter as defined by Equation (1)
τ = dimensionless residence time, t/θ

Subscripts

o = at fresh feed conditions
i = i^{th} species
j = j^{th} reaction
ss = at steady state conditions

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