h, h_o = variable and constant film thickness
h_m, h_{st} = minimum pressure point and stagnation point film thickness
k = rheological constant, consistency index, Equation (14)
$L_m, L_{st} = h_m/h_o, h_{st}/h_o$
n = rheological constant, power law exponent, Equation (14)
p = pressure
Q_h, Q_o = flow rate in the variable and parallel flow region
r = rheological constant, Equation (3)
u, u_s, u_w = vertical, surface and withdrawal velocity
x, y = coordinates
y_1 = location of the yield surface

Greek Letters

μ = viscosity (Newtonian)
μ_o = viscosity (Bingham)
ρ = liquid density
σ = surface tension of the liquid-air interface
τ_o = yield stress
τ_{xy} = xy component of the stress tensor

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Stability of Chemical Reactors

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This note presents an extension of the studies of Chambré (1956) and Barkelew (1959) on the runaway criteria and parametric sensitivity of tubular nonisothermal chemical reactors. Chambré and Barkelew have developed an interesting method of obtaining graphical solutions of the nonlinear differential equation which describes the relation between temperature and degree of conversion in such reactors. The present note reports a simple procedure for determining the exact conditions leading to either stable or runaway reactor operation.

We consider, as an example, the case of an irreversible, first-order, exothermic reaction in the gas phase. Under steady state conditions, the relation between the temperature T and the degree of conversion X at any point in the tubular reactor is

$$\frac{dT}{dX} = \frac{(-\Delta H)y_{Ao}}{C_p} - \frac{4U(T - T_w)}{C_pDZP(1 - X)\exp(-E/RT)} \quad (1)$$

where the effect of radial temperature profiles is neglected.

Equation (1) can be written in the following dimensionless form

$$\frac{d\theta}{dX} = \alpha - \beta\frac{\theta \exp(-\theta)}{1 - X} \quad (2)$$

where

$$\theta = \frac{T - T_w}{T_w}\,\frac{E}{RT_w} \quad (3)$$

$$\alpha = \frac{(-\Delta H)y_{Ao}}{C_pT_w}\,\frac{E}{RT_w} \quad (4)$$

and

$$\beta = \frac{4U}{C_pDPk_w} \quad (5)$$

Chambré and Barkelew have shown that a graphical solution to Equation (2), which will be called the operating curve, can be obtained as follows. Let specific values be assigned to the parameters α and β as well as to the quotient $(d\theta/dX) = \theta_X$ in Equation (2), which can be written as

$$X = 1 - \frac{\beta\theta \exp(-\theta)}{\alpha - \theta_X} \quad (6)$$

Plots of θ vs. X in accordance with Equation (6) are shown in Figure 1 for a set of α and β values and various θ_X values. These plots have been called isoclines. The operating curve can now be drawn with the help of these isoclines and its initial and final slopes (Chambré, 1956):

1. The operating line originates at $\theta = 0$ and $X = 0$, and its initial slope is $\theta_X = \alpha$
2. At every intersection with an isocline, the operating curve must have a slope equal to the value of θ_X for that isocline.
3. The terminal slope of the operating curve at $X \to 1$ is $-\alpha/(\beta - 1)$.

Chambré and Barkelew have indicated the general areas of stable and unstable reactor operation on $\theta - X$ plots but have not determined the critical values of α

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and β which characterize the onset of runaway conditions. These values can be found as is shown below.

It is seen from Figure 1 that the isoclines have the following properties:

1. For all isoclines, $(d\theta/dX) = \infty$ at $\theta = 1$; this condition may occur at negative values of X, which have no physical significance.
2. All isoclines have an inflection point at $\theta = 2$.
3. Isoclines located inside a region enveloped by a particular isocline have θ_X values which are smaller than the θ_X of that isocline and decrease in the direction of increasing X.

A number of arrows have been drawn on the isoclines of Figure 1. The arrows on any given isocline have slopes equal to the value of θ_X for that isocline, and hence indicate the direction which the operating curve must follow at the point of intersection with the isocline. Point A on the isocline $\theta_X = 7$ represents a point where the direction of the arrow coincides with the tangent to that isocline; that is, the slope of the tangent has a value equal to θ_X. Consequently, if the operating curve contacts the isocline $\theta_X = 7$ at point A, it will not intersect the isocline but remain tangent to it. Furthermore, since all isoclines to the left of the isocline $\theta_X = 7$ have increasingly larger θ_X values, the operating curve will rise sharply (θ will increase rapidly with X). This represents an unstable or runaway operating condition. The operating curve may cross, however, the isocline $\theta_X = 7$ at some high value of θ. The same situation will occur wherever the operating curve contacts any isocline at a point similar to point A.

The above qualitative considerations indicate that point A in Figure 1 is a critical point with respect to reactor runaway conditions. By differentiating Equation (6) with respect to θ (with θ_X = constant) and equating

$$\frac{dX}{d\theta} = \frac{1}{\theta_X} \tag{7}$$

one obtains

$$\theta_X = \frac{\alpha}{1 + \beta(\theta - 1)\exp(-\theta)} \tag{8}$$

This relation defines the point, or points, on any isocline of value θ_X where the tangent to the isocline has a slope equal to that θ_X. Substituting Equation (8) into Equation (6), we get

$$X = 1 - \frac{1}{\alpha}\frac{\theta}{\theta - 1}[1 + \beta(\theta - 1)\exp(-\theta)] \tag{9}$$

which is the locus of the points on isoclines where tangents have slopes equal to the θ_X values of the corresponding isoclines. Alternatively, Equation (9) represents the locus of the points on isoclines in the parametric region of interest where the operating curve is tangent to the isoclines. The curve representing this locus has asymptotes at $\theta = 1$, $X \to -\infty$ and at $X = (\alpha - 1)/\alpha$, $\theta \to \infty$.

The significance of the locus curve is straightforward. Any operating curve that intersects the locus curve will turn up, sometimes sharply, which is indicative of runaway operating conditions. This situation is illustrated in Figure 2. The operating curve is seen to intersect the locus curve at point A, where the former has an inflexion point, and to rise sharply. The operating curve intersects the locus curve again at point B, where the former has another inflexion point, then passes through a maximum (the hot point) at some high value of θ, and finally decreases steeply to $\theta = 0$ and $X = 1$. Points A and B can be close to one another or far apart, depending on the values of α and β. In general, for a given value of α, if β is sufficiently small, the operating curve will intersect the locus curve, thus yielding the runaway condition of Figure 2. On the other hand, if β is sufficiently large, the operating curve will not intersect the locus curve but reach a maximum at a relatively low value of θ. This situation is characteristic of stable reactor operation and is illustrated in Figure 3. For the selected α, there will exist a critical value of β, which may be designated β^0, such that the operating curve will just touch the locus

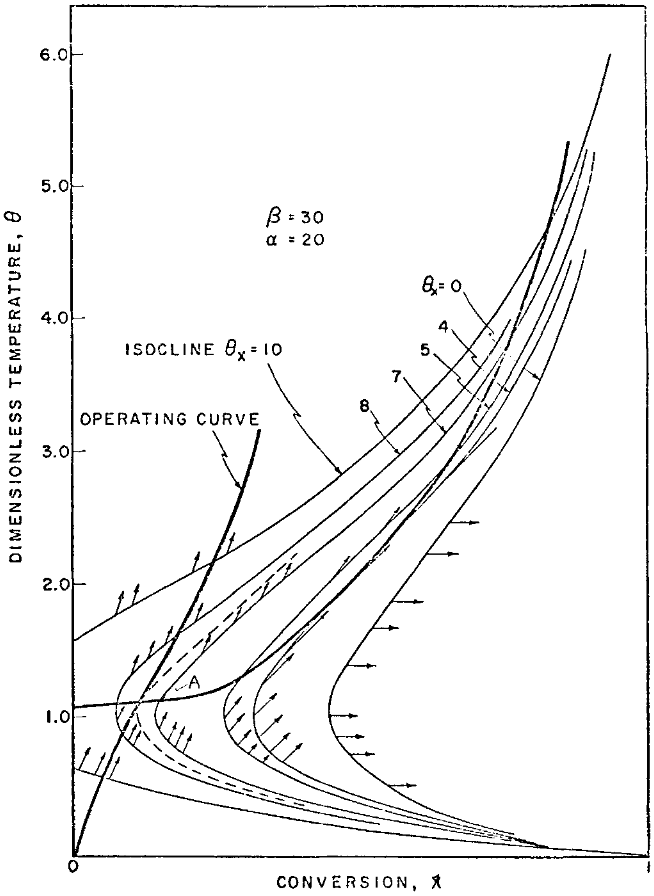

Fig. 1. Isoclines and the operating curve.

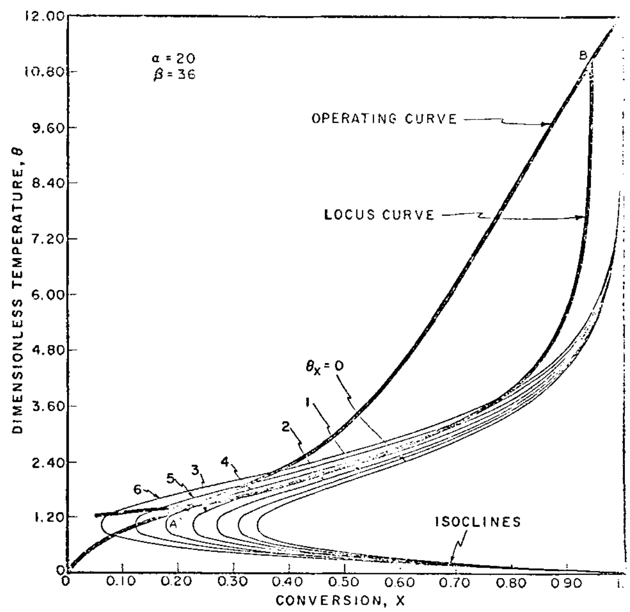

Fig. 2. Example of a runaway operating condition.

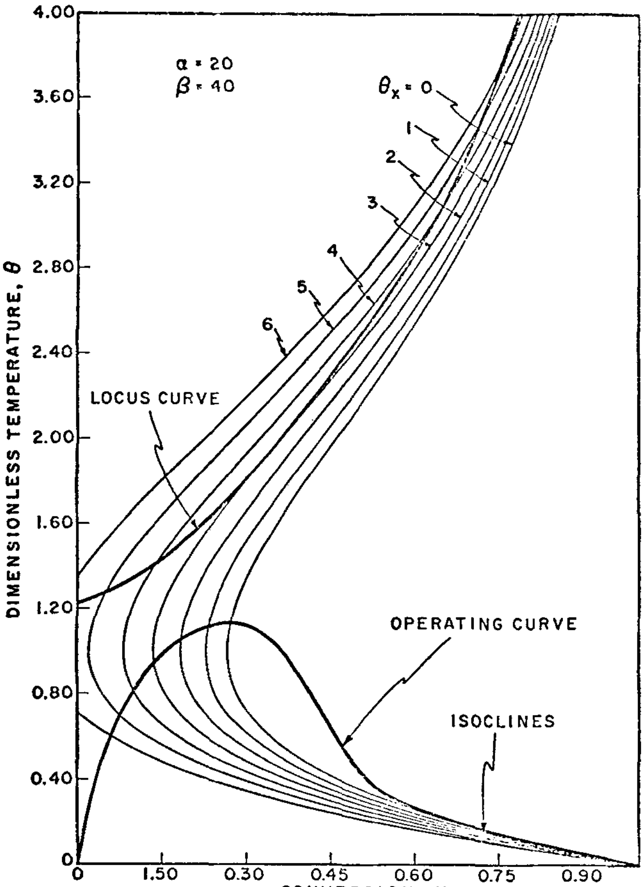

Fig. 3. Example of a stable operating condition.

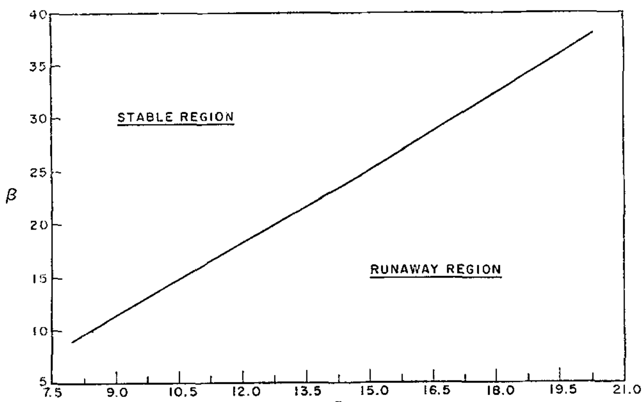

Fig. 4. Plot of critical values of the parameters α and β.

curve. The reactor operation will be stable when $\beta > \beta^0$ and unstable when $\beta < \beta^0$.

To find β^0, it is necessary to determine the point on the $\theta - X$ diagram where the operating and locus curves will just contact one another. The point of contact will lie on some isocline $\theta_X{}^0$, and both the operating and locus curves must be tangent to the isocline $\theta_X{}^0$ at that point. Consequently, the point of contact can be found by substituting Equations (8) and (9) into Equation (7) and solving for θ. One obtains $\theta = 2$ and $\theta = 0$, but only the first value is of interest here. Equation (8) then yields the value of $\theta_X{}^0$; namely

$$\theta_X{}^0 = \frac{\alpha}{1 + \beta \exp(-2)} \tag{10}$$

The operating and locus curves will thus be tangent to this isocline and to one another at $\theta = 2$, that is, at the inflexion point of the $\theta_X{}^0$ isocline. The value of X at the point of contact of the two curves is obtained from Equation (9); for $\theta = 2$, this equation yields

$$X = 1 - \frac{2[1 + \beta \exp(-2)]}{\alpha} \tag{11}$$

To find β^0 for a given value of α it is necessary to perform a numerical integration of Equation (2). β^0 is selected by trial and error until the result of the integration yields the value of X of Equation (11) at $\theta = 2$. One can also find by the same method a critical value of α, which may be designated α^0, for a specified β. Figure 4 shows a plot of the critical values of α and β, with the regions of stable and unstable (runaway) reactor operation.

A related analysis of stability criteria has been reported by Van Welsenaere and Froment (1970) for the case of fixed-bed catalytic reactors. This study differs from the present one in two principal respects. First, Van Welsenaere and Froment have not identified explicitly the points of tangency between the operating and locus curves, which specify the onset of runaway conditions [$\theta = 2$ and Equation (11)]. In order to find such points and avoid laborious trial and error, these investigators employed an approximate rather than an exact locus curve. Second, the results of the present work have been reduced to the simple and useful form of Figure 4 by the use of the dimensionless parameters α and β. The plot of Figure 4 is general and can account for changes in system parameters. Conceptual differences also exist between the study of Van Welsenaere and Froment and the present one in the analysis of the problem, the latter being based on the method of isoclines.

ACKNOWLEDGMENT

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NOTATION

C_p	=	mean specific heat of the reactants
D	=	diameter of the tubular reactor
E	=	activation energy of the reaction
ΔH	=	heat of reaction
k_w	=	reaction rate constant at wall temperature
P	=	total pressure
T	=	absolute temperature of the reacting mixture
T_w	=	absolute wall temperature
U	=	overall heat transfer coefficient
X	=	degree of conversion
y_{Ao}	=	initial mole fraction of the reactant
Z	=	preexponential factor in Arrhenius rate equation
α	=	constant defined by Equation (4)
β	=	constant defined by Equation (5)
θ	=	dimensionless temperature function defined by Equation (3)

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