Parametric Sensitivity in Fixed-Bed Catalytic Reactors: The Role of Interparticle Transfer Resistances

The parametric sensitivity behavior of a plug-flow catalytic fixed-bed reactor with negligible intraparticle mass and heat transfer resistances is examined for any positive-order irreversible reaction. By combining information about multiplicity and runaway, a complete picture of the steady state reactor behavior is obtained. Calculations of the parametrically sensitive region for various values of the involved dimensionless parameters are reported.

MASSIMO MORBIDELLI and ARVIND VARMA

Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556

SCOPE

In most of the literature dealing with parametric sensitivity and runaway in tubular catalytic reactors, inter- and intraparticle mass and heat transfer resistances have been ignored and pseudohomogeneous models have been used. However, from a design point of view the temperature of the catalyst particle is really the quantity to be controlled, since it affects both the reaction rate and the catalyst activity.

Runaway of the catalyst particle temperature can occur because of two different phenomena: Either the fluid temperature is running away and the particle temperature simply follows it or, even though the fluid temperature changes smoothly, the particle temperature runs away as a consequence of the competition between inter- and intraparticle mass and heat transport as well as the chemical reaction processes. The former is the same phenomenon also encountered in homogeneous reactors; the latter is strictly related to the heterogeneous nature of the system and typically precedes the occurrence of steady state multiplicity for the catalyst particle. These constitute two types of sensitivity, which are usually called global and local, respectively.

The aim of this paper is to develop a novel sensitivity criterion that includes both types of sensitivity. This requires as background a detailed understanding of the multiplicity pattern and ignition phenomena in the reactor. We address this study to the case where only external heat and mass transfer resistances are significant, such as in the relevant case of externally coated catalyst particles. The effect of intraparticle resistances will be the subject of a subsequent publication.

CONCLUSIONS AND SIGNIFICANCE

The steady state behavior of a plug-flow catalytic reactor with negligible intraparticle heat and mass transfer limitations is examined. It is shown that, based on rigorous application of the implicit function theorem, the reactor model exhibits at most the 1-3-1 multiplicity pattern. Moreover, the multiplicity behavior of the reactor is identical to that of the catalyst particle located at the reactor inlet.

The critical conditions for runaway are determined by applying the Adler and Enig (1964) criterion to the catalyst particle temperature, and solving the relevant equations with the method of isoclines. The criterion developed here includes both local and global sensitivity. Moreover, it refers to the catalyst (and not the fluid) temperature; i.e., the value that directly affects quantities of interest from the design point of view, such as selectivity and catalyst deactivation.

The combination of multiplicity and runaway results produces a complete definition of the parametrically sensitive regions. This provides an exhaustive a priori characterization of the steady state behavior of the reactor. Plots of the sensitive regions for various values of the involved parameters are also presented, which can be applied profitably in the preliminary design of fixed-bed catalytic reactors in order to determine the exact locations of the regions of stable, runaway, and ignited operations.

Finally, the runaway region predicted by the developed criterion is compared with that obtained through the criterion applied to the fluid temperature. The latter can obviously predict only global sensitivity, and thus it may characterize as "safe" situations in which the temperature of the catalyst particle actually is dangerously running away. This occurs when some of the catalyst particles in the reactor are operating in the local sensitivity region.

Correspondence concerning this paper should be addressed to A. Varma.

INTRODUCTION

The temperature profile along a tubular reactor where an exothermic reaction occurs is often characterized by the occurrence of a maximum, usually called a hot spot. It is well known that, for certain values of the operating conditions the entire temperature profile, and in particular the magnitude of the hot spot, become quite sensitive to small variations of the inlet conditions as well as of any of the physicochemical characteristics of the system. In this case, according to the pioneering work of Bilous and Amundson (1956), the reactor is said to operate in the region of parametric sensitivity. Often, this situation is referred to as a runaway or unstable operating condition, but the latter should not be confused with the stability concept according to Liapunov. Specifically, this problem refers only to the reactor steady state, with no direct implication about its transient behavior.

In practice, chemical reactors usually are designed to avoid the region of parametric sensitivity. In fact, excessive excursions of the temperature value can lead to unacceptable changes in the catalyst activity (e.g., sintering) or in the outlet reactor selectivity. Therefore most of the research in this area is directed toward the a priori definition of the region of parametric sensitivity, so that it can be avoided immediately in the first design stage of the reactor. This requires the formulation of an intrinsic criterion for defining reactor runaway, one that is independent of any considerations contingent to the particular problem being examined (e.g., a maximum allowable temperature).

In spite of the intrinsic heterogeneous character of catalytic reactors, most of the published work has dealt with the plug-flow pseudohomogeneous model. The criterion of reactor runaway most widely accepted was first proposed by Adler and Enig (1964) in the context of thermal explosion theory. It states, once transferred to the chemical reactor problem, that the reactor operates in the runaway or parametric sensitive region when the temperature vs. conversion profile exhibits a region of positive second-order derivative before the hot spot.

Dente and Collina (1964) applied this criterion, but instead used the temperature vs. reactor length profile. Later, these criteria were applied under more or less stringent approximation by Hlaváček et al. (1969) and van Welsenaere and Froment (1970) to produce approximate simple relationships among the involved parameters that identify the region of parametric sensitivity.

Recently, Morbidelli and Varma (1982) used the isocline method, first applied by Chambré (1956) and lately revisited by Oroskar and Stern (1979), to calculate the exact values of the critical parameters bounding the region of parametric sensitivity. The final results were reported in a graphical form for irreversible reactions of any positive order, with no limitations on the value of either the activation energy or the inlet temperature.

It is somewhat surprising that the heterogeneous nature of the reactor has been taken into account in only a very few studies. McGreavy and Adderley (1973) introduced the concept of local sensitivity. By considering the heat and mass balances of the catalyst particle alone, they noted that in the region of incipient multiplicity the particle temperature may change dramatically for small changes of the external fluid phase temperature (i.e., the particle temperature vs. fluid temperature curve approaches the horizontal inflection point, which anticipates the occurrence of multiplicity). Thus local sensitivity means that even though the fluid temperature is in a stable region, the particle temperature may be "running away."

Rajadhyaksha et al. (1975) examined the fluid temperature sensitivity problem in a heterogeneous catalytic reactor. This is the same phenomenon that is encountered in homogeneous reactors, and is therefore not exclusively due to the heterogeneous nature of the reacting system. As opposed to local sensitivity, this is termed global sensitivity. Using the approach of van Welsenaere and Froment, Rajadhyaksha et al. extended the expressions for the runaway region of homogeneous reactors in order to account for the effect of mass and heat transfer limitations. However, since they applied the runaway criterion to the fluid temperature, the possible occurrence of local sensitivity phenomena was not accounted for, and it would require a separate analysis. Moreover, they reported results only for four limiting regimes of interest.

The objective of the present work is to identify the region of parametric sensitivity for the reactor from both the global and local points of view. This can be done by applying the above-mentioned Adler-Enig runaway criterion directly to the particle temperature (rather than the fluid temperature), which clearly requires a simultaneous study of reactor multiplicity. It should be mentioned that the particle temperature is really the quantity of most interest in practice, since it is the one that directly affects the rate of reaction (and reactor outlet selectivity in the case of complex reaction networks) and also the rate of sintering or any other possible change of catalyst activity.

In the following, we consider the heterogeneous model of a plug-flow reactor with an irreversible reaction of any positive order, with no limitations on the inlet temperature or the activation energy. At this stage only external heat and mass transfer resistances are considered, while assuming negligible all intraparticle resistances. In particular, this model correctly represents the industrially common case of externally coated catalyst particles.

THE BASIC EQUATIONS

The heterogeneous model of a fixed-bed catalytic reactor with an irreversible nth order reaction consists of mass and energy balances of the fluid and the solid phases. Assuming plug flow in the axial direction and perfect mixing in the radial direction, mass and energy balances for the fluid phase can be written in dimensionless form as follows:

$$\frac{dx}{ds} = A\frac{(1-x_p)^n}{g(\theta_p)};\ s\epsilon[0,1] \tag{1}$$

$$\frac{d\theta}{ds} = B\frac{(1-x_p)^n}{g(\theta_p)} - C\theta;\ s\epsilon[0,1] \tag{2}$$

with initial conditions (IC): $\theta = \theta^i$ and $x = 0$ at $s = 0$. The subscript p indicates quantities referring to the catalyst particle; θ and x represent the dimensionless temperature and conversion, respectively; $g(\theta_p)$ is the Arrhenius term defined as

$$g(\theta_p) = \exp\left[-\theta_p/(1+\theta_p/\gamma)\right], \tag{3}$$

and all the other symbols are explained in the Notation.

The dimensionless mass and energy balances of the solid phase, in the case where only interparticle resistances are significant, are given by

$$x_p = x + A_p\frac{(1-x_p)^n}{g(\theta_p)} \tag{4}$$

$$\theta_p = \theta + B_p\frac{(1-x_p)^n}{g(\theta_p)} \tag{5}$$

As mentioned above, in order to apply the criterion of Adler and Enig (1964), we need to study the solution of the algebraic-differential system of Eqs. 1 to 5, in the θ_p(or θ) $- x$ phase plane. Therefore, the space variable s can be eliminated between Eqs. 1 and 2, and introducing the change of variable

$$z = \alpha(1-x), \tag{6}$$

the original model can be rewritten in a more condensed form as follows:

$$\frac{d\theta}{dz} = \delta\theta \frac{g(\theta_p)}{z_p^n} - 1; \; z\epsilon[\alpha,0] \tag{7}$$

$$\theta_p = \theta + \phi \frac{z_p^n}{g(\theta_p)} \tag{8}$$

$$z_p = z - Le\,(\theta_p - \theta) \tag{9}$$

with IC

$$\theta = \theta^t \quad \text{at} \quad z = \alpha \tag{10}$$

where

$$\delta = \beta\alpha^{n-1}, \quad \phi = \frac{A_p\alpha^{1-n}}{Le}, \quad Le = \frac{A_p\alpha}{B_p}. \tag{11}$$

By comparing these equations with the corresponding pseudo-homogeneous model reported by Morbidelli and Varma (1982), it becomes clear that in addition to the previous parameters representing the heat of reaction α, the cooling rate β, and the activation energy γ, two other parameters have been introduced to represent the interparticle mass and heat transfer processes. In particular, for these we shall use the external Lewis number Le, which represents the ratio between heat and mass transfer diffusivities, and A_p, which represents the ratio between chemical reaction and external mass transfer rates.

It is apparent that as $A_p \to 0$, from Eqs. 8 and 9 $\theta_p \to \theta$ and $z_p \to z$, so that Eq. 7 reduces to the pseudohomogeneous model in the limit of negligible external transport resistance.

In order to study the parametric sensitivity behavior of the model, it is first necessary to fully understand another phenomenon that has much more drastic effects on reactor behavior; namely, the occurrence of multiple steady states.

REACTOR MULTIPLICITY

Multiplicity of Particle at Reactor Inlet

We shall first analyze multiplicity behavior of the first layer of particles of the catalytic bed; i.e., the particles located at the reactor inlet. Substituting Eq. 9 into Eq. 8, and taking into account the IC, Eq. 10, the following equation describing the inlet particle temperature can be derived:

$$A_p = \frac{Le}{\alpha^{1-n}} \frac{(\theta_p - \theta)g(\theta_p)}{[z - Le(\theta_p - \theta)]^n} \equiv F(\theta_p) \tag{12}$$

where $\theta = \theta^t$ and $z = \alpha$.

On physical grounds (since $0 \leqq z_p \leqq z$) the particle temperature is readily seen (from Eq. 9) to be bounded as follows:

$$\theta \leqq \theta_p \leqq \theta + z/Le. \tag{13}$$

Since at the lower and upper bounds, $F = 0$ and $+\infty$ respectively, it can be concluded (Luss, 1971) that the necessary and sufficient condition for uniqueness is $F'(\theta_p) > 0$ in the entire θ_p interval. If this condition is violated, then the particle exhibits multiplicity in the region

$$A_{p_*} \leqq A_p \leqq A_p^* \tag{14}$$

where the lower and upper bifurcation points of A_p correspond to the relative minimum and maximum values of $F(\theta_p)$ in the interval indicated by Eq. 13. In Figure 1, a schematic representation of $F(\theta_p)$ and $F'(\theta_p)$, all the relevant features are indicated.

The problem under examination constitutes a lumped-parameter system with an nth order reaction whose multiplicity behavior has been extensively studied in the literature (van den Bosch and Luss, 1977; Tsotsis and Schmitz, 1979; Leib and Luss, 1981). Therefore we shall only briefly summarize here the numerical procedure adopted for evaluating the bifurcation values of A_p, and the results of relevance from the parametric sensitivity point of view.

From the plot of $F'(\theta_p)$ shown in Figure 1b (the indicated points on the curves represent locations where the value of F' can definitely be proven to be positive) it is apparent that the necessary and sufficient condition for uniqueness is satisfied if

$$F'(\bar{\theta}_p) > 0 \tag{15}$$

where $\bar{\theta}_p$ is given by θ_{p+} for $n > 1$ and θ_{p-} for $n < 1$, with

$$\theta_{p\pm} = \frac{-b_1 \pm [b_1^2 - 12Le(n-1)b_2/\gamma^2]^{1/2}}{6Le(n-1)/\gamma^2}, \tag{15a}$$

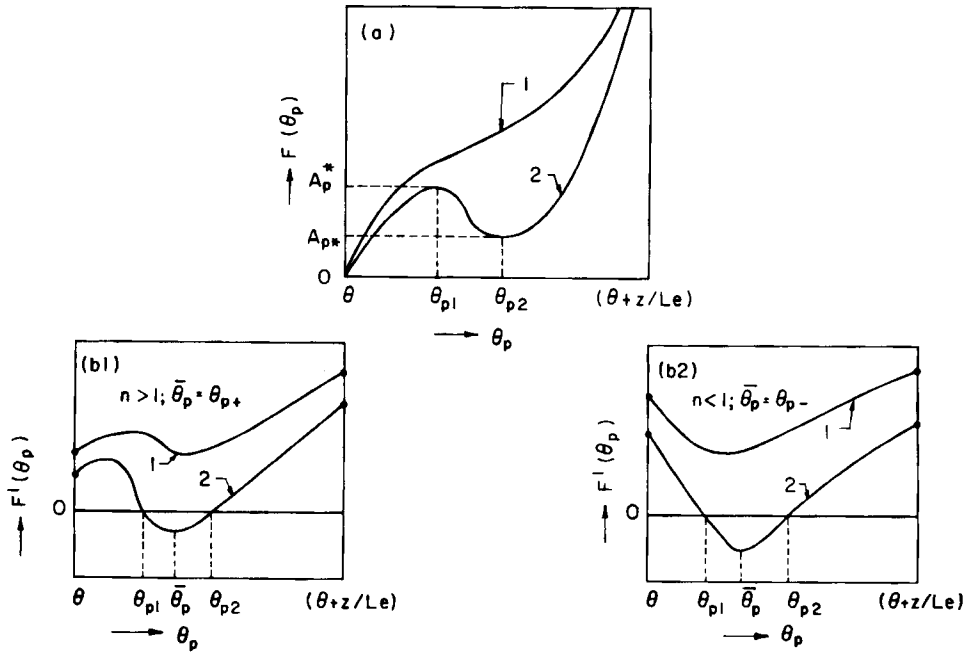

Figure 1. (a) Schematic representation of function $F(\theta_p)$ defined by Eq. 12. (b) Qualitative behavior of the derivative of $F(\theta_p)$ for $n > 1$(b1) and $n < 1$(b2).

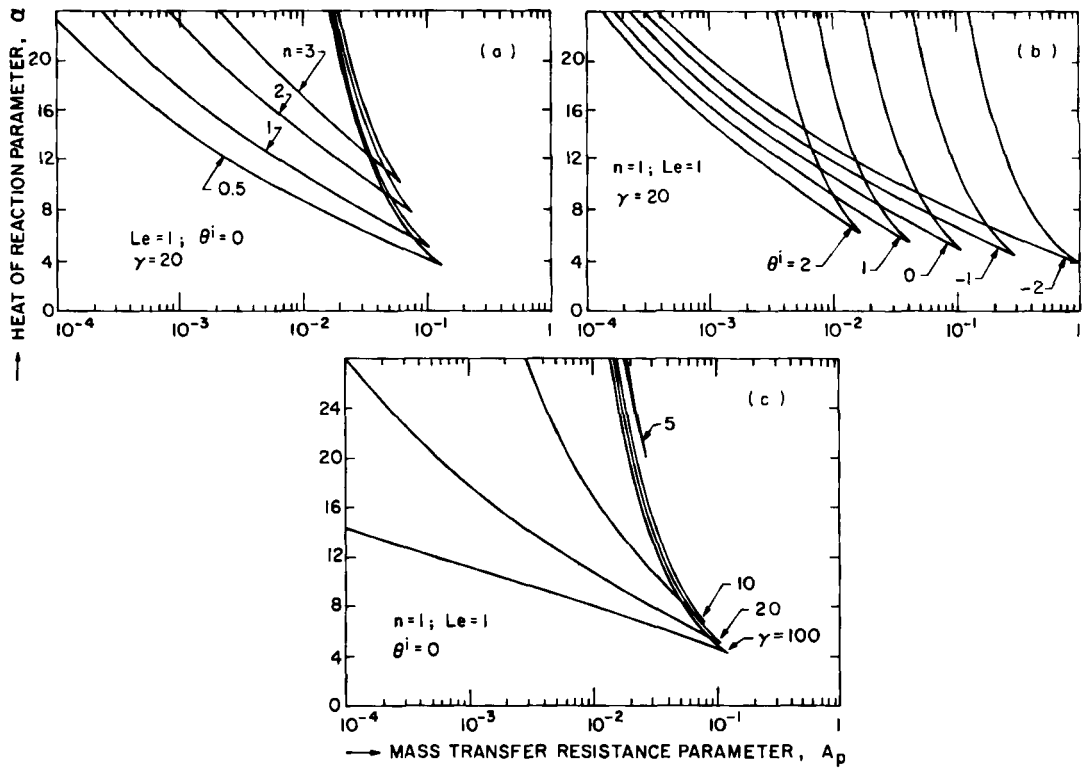

Figure 2. Regions of multiple steady states. (a) Effect of reaction order, n. (b) Effect of inlet fluid temperature, θ^i. (c) Effect of activation energy, γ.

and b_1 and b_2 are defined in the Notation. If the condition in Eq. 15 is violated, then $F(\theta_p)$ exhibits a maximum and a minimum at θ_{p1} and θ_{p2}, respectively. These quantities can readily be calculated as roots of the cubic equation:

$$Le(n-1)(\theta_p-\theta^i)(1+\theta_p/\gamma)^2+Le(\theta_p-\theta^i)^2 + \alpha(1+\theta_p/\gamma)^2-\alpha(\theta_p-\theta^i)=0 \quad (16)$$

in the corresponding intervals: $\theta_{p1}\epsilon[\theta^i,\bar{\theta}_p]$ and $\theta_{p2}\epsilon[\bar{\theta}_p,\theta^i+\alpha/Le]$. Note that for the special cases $n=0$ and 1, Eq. 16 can easily be solved analytically (Leib and Luss, 1981).

In Figures 2a–c the effects of the relevant parameters on the region of multiple steady states, represented in the heat of reaction (α) vs. external mass transfer resistance (A_p) plane, are shown. It is seen that the particle admits at most the 1–3–1 multiplicity pattern; three steady states are found in the region enveloped by the curves representing the lower and upper bifurcation points of A_p.

As previously noted by van den Bosch and Luss (1977), multiplicity is less likely at higher reaction orders (Figure 2a). On the other hand, by increasing the inlet fluid temperature, the region of multiplicity tends to shrink, shifting toward lower mass transfer resistance values (Figure 2b), while by increasing the activation energy it enlarges (Figure 2c).

Reactor Multiplicity

Let us now consider multiplicity behavior of the entire reactor. The model involves solution of an initial-value problem (Eq. 7), along with a constraint given by the nonlinear algebraic Eq. 8, which, using Eq. 9, can be rewritten in the form:

$$\theta - f(\theta,\theta_p,z)=0 \quad (17)$$

This represents an implicit equation that needs to be solved at each integration step to give θ_p. We have already discussed the multiplicity behavior of the inlet particle, which can lead to multiple initial conditions for the differential equation. However, once one of these has been selected, the problem admits only one solution, since Eq. 7 is an initial-value problem.

To clarify this point further, let us consider the pictorial representation of Eq. 17 shown in Figure 3. Once the inlet fluid temperature θ^i and the corresponding value θ_p^i have been chosen, the solution of the model implies solving Eq. 17 over and over again for increasing or decreasing θ values, as given by Eq. 7. From the implicit function theorem (Iooss and Joseph, 1980) it can be seen that the obtained solution of Eq. 17 is unique and continuous as long as the following condition is satisfied:

$$\frac{df}{d\theta_p}\neq 0 \quad (18)$$

Only when the condition in Eq. 18 is violated is a discontinuity in the θ_p solution of Eq. 17 admissible. On physical grounds, this means that once the reactor IC has been established, the reactor admits a single solution. In fact, the solution of Eq. 17 has to lie on the same branch of the θ vs. θ_p curve as the inlet particle. Only if the Eq. 18 condition is violated is a jump from one branch to another allowed. This occurs either at the maximum of the curve shown in Figure 3, when θ is increasing along the reactor, leading to an ignition point at $\theta_p=\theta_{p1}$, or at the minimum of the same curve, when θ is decreasing, leading to an extinction point at $\theta_p=\theta_{p2}$.

While moving along the reactor the conversion (and thus z) changes, thus leading to different θ vs. θ_p curves of the type shown in Figure 3. This does not alter the previous argument, for although the relationship changes with z, the jump from one branch to the other can occur only at a point where $d\theta/d\theta_p=0$; i.e., θ_{p1} or θ_{p2}.

Thus, it can be concluded that the multiplicity behavior of the reactor is fully determined by the inlet particle, so that the multiplicity regions shown in Figure 2 are actually valid also for the entire reactor.

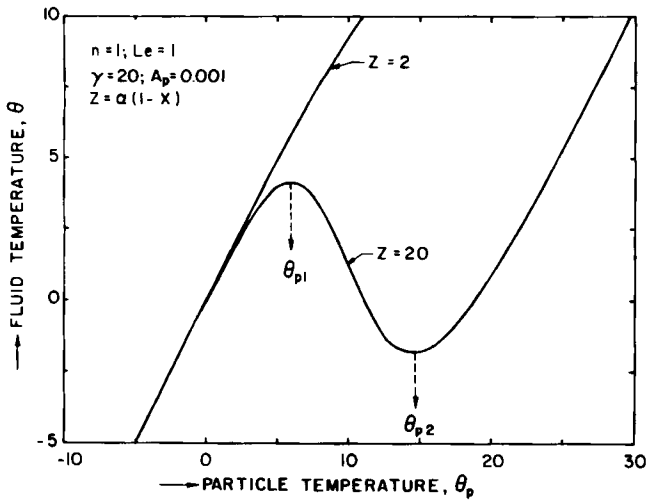

Figure 3. Schematic representation of the catalyst particle steady state, as given by Eqs. 8 and 9 (or alternatively, Eq. 17). For the inlet particle, $x = 0$, $z = \alpha$.

For the adiabatic version of the same model under examination here, Liu and Amundson (1962) and Hlaváček et al. (1974) concluded that an infinite number of steady states is admissible. This was based on the expectation that at any location along the bed, any one of the three particle steady states could be chosen. This feature was shown to remain unchanged while also taking into account axial dispersion in the fluid phase by Sinkule et al. (1976). This physically unsound characteristic of the two-phase model was supposedly resolved by Eigenberger (1972), who showed that the presence of axial heat conduction in the solid phase drastically reduces the number of possible steady states. We have shown here that, based on a rigorous application of the implicit function theorem, this heterogeneous model, even in its simplest form, never admits more than three steady state solutions.

CRITICAL RUNAWAY CONDITIONS FOR THE REACTOR

We shall now calculate the critical values of the involved parameters which bound the region of parametric sensitivity. Following the runaway criterion concept proposed by Adler and Enig (1964), we can state that critical conditions occur when at the inflection point the third derivative of the particle temperature with respect to conversion also vanishes. In fact, this is the situation which immediately precedes the occurrence of a positive second-order derivative region somewhere along the reactor. As a key parameter the heat of reaction parameter α is used, since it is physically evident (at least locally) that once the critical value of α has been found, then runaway occurs for any larger α, while the reactor is stable for smaller α.

In order to evaluate the critical parameter values, the isocline method can be used because of its great computational efficiency. The use of this method has been explained in detail by Morbidelli and Varma (1982) for the case of a pseudohomogeneous reactor. Therefore, we shall here only briefly summarize application of the isocline method to a heterogeneous reactor, while avoiding all mathematical details and rigorous proofs for the benefit of simplicity and readability. For this same reason, the analysis is here limited to the case of the particle temperature runaway for a first-order reaction. The equations for the case of any positive-order reaction rate are summarized in the Appendix, together with equations for applying the runaway criteria to the fluid phase temperature.

Let us first define the isocline, in the θ_p vs. z plane, as the locus of points where the tangent to the operating curve (i.e., the actual θ_p vs. z profile along the reactor) is equal to a fixed constant value θ_{pz}. For the case under examination the isocline equation can be derived by direct differentiation of Eq. 8, using Eq. 7, as follows:

$$\theta_{pz}\left\{z\left[1-\frac{\theta_p-\theta}{(1+\theta_p/\gamma)^2}\right]+Le\,\frac{(\theta_p-\theta)^2}{(1+\theta_p/\gamma)^2}\right\} - z\frac{d\theta}{dz}-(\theta_p-\theta)=0 \quad (19)$$

Next, we introduce the locus curve of points, where the operating curve exhibits an inflection point. Such a curve can alternatively be defined as the locus of points where the tangent to each isocline is equal to the corresponding characteristic parameter θ_{pz}. Using the latter definition, from Eq. 19, it readily follows that

$$\theta_{pz}\left\{\frac{z_p}{(1+\theta_p/\gamma)^2}\left[\frac{d\theta}{dz}-\frac{\gamma+2\theta-\theta_p}{(\gamma+\theta_p)}\frac{d\theta_p}{dz}\right] -\frac{(\theta_p-\theta)}{(1+\theta_p/\gamma)^2}\left[Le\left(\frac{d\theta}{dz}-\frac{d\theta_p}{dz}\right)+1\right]+1\right\} -\frac{d\theta_p}{dz}-z\frac{d^2\theta}{dz^2}=0 \quad (20)$$

Thus, using Eqs. 8, 9, 19, and 20 for a given set of values of the involved parameters (i.e., β, γ, A_p, and Le) it is possible to fully characterize the inflection point of the corresponding locus curve (i.e., θ, θ_p, z_p, and θ_{pz}), for any given value of z. The critical z value is then obtained by requiring the operating curve to have two such inflection points infinitesimally close; i.e., $d^3\theta_p/dz^3 = 0$. This is obtained by forcing the locus curve to be tangent to the isocline, which is expressed by the following critical condition:

$$\theta_{pz}\left\{\frac{2}{(1+\theta_p/\gamma)^3}\left[\frac{d\theta}{dz}-\frac{\gamma+2\theta-\theta_p}{\gamma(1+\theta_p/\gamma)}\frac{d\theta_p}{dz}\right] \left[(1+\theta_p/\gamma)\left(1-Le\frac{d\theta_p}{dz}+Le\frac{d\theta}{dz}\right)-\frac{1}{\gamma}[z-Le(\theta_p-\theta)]\frac{d\theta_p}{dz}\right] +\frac{z-Le\,(\theta_p-\theta)}{(1+\theta_p/\gamma)^2}\left[\frac{d^2\theta}{dz^2}-\frac{d\theta_p}{dz}\frac{d\theta}{dz}\frac{2/\gamma}{(1+\theta_p/\gamma)} +\frac{2}{\gamma}\frac{(1+\theta/\gamma)}{(1+\theta_p/\gamma)^2}\left(\frac{d\theta_p}{dz}\right)^2\right] -Le\frac{\theta_p-\theta}{(1+\theta_p/\gamma)^2}\frac{d^2\theta}{dz^2}\right\}-\frac{d^2\theta}{dz^2}-z\frac{d^3\theta}{dz^3}=0. \quad (21)$$

Thus, the entire procedure for evaluating the critical α can be summarized as follows:

- Given: a set of values of the parameters β, γ, A_p, and Le (which through Eq. 11, allow evaluation of all the parameters in the model given by Eqs. 7 to 9).
- Solve Eqs. 8, 9, 19, 20, and 21 to evaluate the coordinates of the critical point in the phase plane; i.e., θ, θ_p, z, z_p, and θ_{pz}.
- Integrate Eq. 7 backwards from the critical point up to the value $\theta = \theta^*$; according to Eq. 10 the corresponding z value yields the critical value of α.

Note that the procedure outlined above is similar to that adopted for the pseudohomogeneous reactor (Morbidelli and Varma, 1982), and in particular it retains the characteristic of producing a critical α value for each integration of Eq. 7, thus avoiding any tedious trial and error calculations. For example, some of the critical α values thus calculated are shown in Figures 4a and 4b by curve b for two particular sets of parameter values.

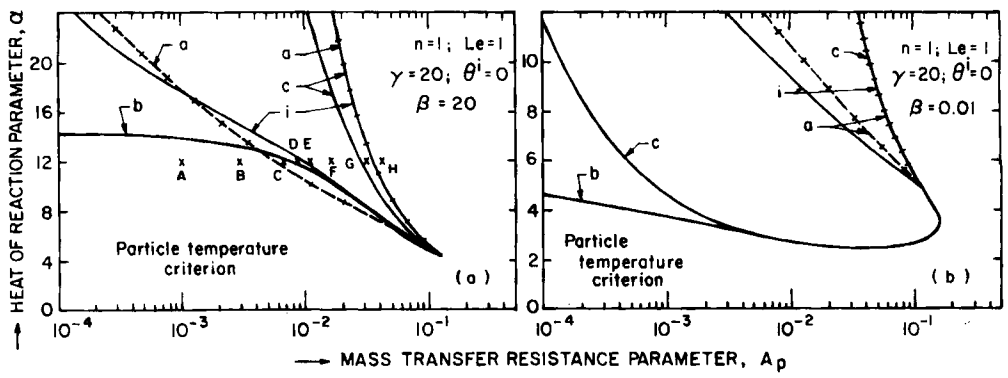

Figure 4. Construction of the parametric sensitivity region using the particle temperature runaway criterion. (a) $\beta = 20$; (b) $\beta = 0.01$. Curves: *a*, reactor multiplicity region; *b*, occurrence of positive second-order derivative of $\theta_p - x$ curve in some region along the reactor; c, region of positive second-order derivative of $\theta_p - x$ curve at the reactor inlet; *i*, occurrence of ignition phenomena along the reactor.

It is worth stressing that in this analysis the possibility of runaway for the reactor is considered only in the case where the reactor operates in the low conversion branch. In other words, the critical point in the phase plane is assumed to lie on the low conversion branch of the particle steady state; i.e., with reference to Figure 1 we have assumed $\theta_p \leqq \theta_{p1}$ at criticality. This assumption is correct because the criticality of parametric sensitivity always must precede ignition—a fact that is discussed next.

It is evident that the ignition phenomenon is much more dramatic than runaway, in the sense that the former implies a discontinuous jump in the particle temperature, while the latter implies "only" a self-accelerating, but continuous, increase of θ_p. So, it seems quite unlikely that in any practical situation ignition but not runaway (in the sense of Adler and Enig, 1964) could occur.

To elaborate this further, note that when the particle temperature approaches θ_{p1} (Figure 3) before jumping to the higher branch (i.e., ignition), it has first to go through a region where small variation of the fluid temperature leads to large variation of the particle temperature (i.e., local sensitivity). This argument shows that at criticality, since the second derivative of the particle temperature vs. conversion is at most zero but never positive, ignition phenomena cannot occur. Since the critical value of θ_p is taken on the low conversion branch, it follows that at criticality all the particles along the reactor also operate on this same branch.

In summary, it can then be concluded that for all other parameters fixed, parametric sensitivity occurs at α values smaller than those leading to ignition phenomena. In Figures 4a and b the locus of α values (curve *i*) at which an ignition point first occurs somewhere along the reactor is shown. It is evident by comparing curves *b* and *i* that ignition phenomena do not occur in the nonsensitive region, although the exact boundaries (i.e., location of curve *i*) are defined in the next section.

It should also be pointed out that due to the very high reaction rate exhibited by particles operating in the higher conversion branch, runaway is rather unlikely to occur while operating on this branch. In this case, the reactant is so rapidly depleted that the reaction cannot provide the amount of heat necessary to sustain a self-accelerating increase of temperature.

REACTOR SENSITIVITY

In order to obtain a complete picture of sensitivity behavior of the reactor, and then formulate a priori criteria, it is necessary to combine information derived separately from both the multiplicity and the criticality analyses. However, before this is done, it is necessary to explore the last possibility of reactor behavior, which involves occurrence of a positive second-order derivative immediately at the reactor inlet, with the hot spot somewhere inside the reactor. Since this situation is not always accounted for by the criticality analysis reported above, this possibility has been examined separately. This is readily done by deriving the expression of $d^2\theta_p/dz^2$ at the reactor inlet by twice differentiating Eq. 8, and then searching for the values of α where $d^2\theta_p/dz^2$ changes sign. In this search the situations in which the reactor does not exhibit a hot spot are obviously not considered.

The results thus obtained are shown, together with those derived from the multiplicity and the criticality analyses, in Figure 4 for two values of the cooling parameter β. Curve *a* represents the multiplicity region as shown earlier in Figure 2. Curve *b* represents the boundary between the runaway and nonrunaway regions as produced by the isocline method. Finally, curve *c* encloses the region where the second-order derivative of θ_p at the reactor inlet is positive; i.e., again a runaway region.

It may be noted that curve *b* ends when it merges with curve *c*. This is because for increasing values of A_p the region of positive second-order derivative of the θ_p vs. *x* curve travels toward the reactor inlet (see discussion of Figure 5 later). At the merging point of curves *b* and *c* this region is located right at the reactor inlet, i.e., $x = 0$. Moreover, note in Figure 4 that the righthand side branches of curves *a* and *c* are coincident. Namely, this curve represents the upper bifurcation point A_p^* for the inlet particle, so that in the region to the right of this curve the particle operates on the high conversion branch (see Figure 1a). As already mentioned, this is a nonrunaway region since the second-order derivative of the particle temperature remains negative for all conversion values; i.e., ignition tends to depress subsequent temperature self-acceleration. It can therefore be concluded that the region of runaway is the area enveloped by curves *b* and *c*.

A more detailed illustration of reactor sensitivity behavior is given in Figure 5, where the particle temperature vs. conversion profiles are shown for increasing values of the mass transfer resistance parameter A_p, along the path indicated in Figure 4a. The first three profiles (*A*, *B*, and *C*) are in the nonrunaway region. (Note that an intersection with the lower bifurcation value of A_p—i.e., the left side of curve *a*—does not affect reactor behavior, since we are considering catalyst particles operating on the low conversion branch.) By increasing A_p to *D*, a runaway profile is obtained since it exhibits a region with

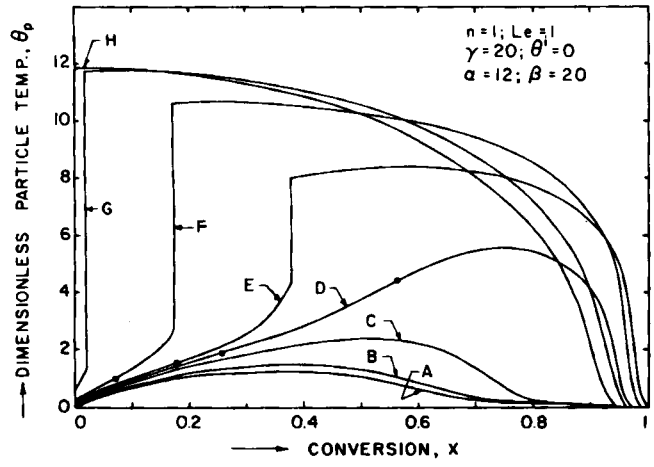

Figure 5. Dimensionless particle temperature vs. conversion profiles for various values of the mass transfer resistance parameter, A_p; • = inflection point. Data as in Figure 4a; A_p = 0.001(*A*), 0.003(*B*), 0.0065(*C*), 0.0085(*D*), 0.01(*E*), 0.015(*F*), 0.03(*G*), 0.04(*H*).

positive second-order derivative. For case *E*, runaway is followed, further down the bed, by the ignition phenomenon. For further increasing A_p values, the critical zone moves toward the reactor inlet, so that for case *G* runaway is already occurring at the reactor inlet. Finally, when A_p reaches *H* the reactor is fully ignited, thus the absolute temperature values are much larger than in the previous cases; however, strictly speaking, the reactor is operating under nonrunaway conditions.

Finally, in Figure 4 the region enveloped by curve *i* corresponds to situations in which ignition phenomenon occurs somewhere along the reactor. Note that the righthand side branch of curve *i* is coincident with the corresponding branches of curves *a* and *c*. To the righthand side of this curve the inlet particle operates on the high conversion branch, thus no further ignition is possible along the bed. It is noticeable that curve *i* lies entirely inside the region enveloped by curves *b* and *c*. Thus, as discussed above, ignition phenomen can occur only in the parametrically sensitive region, i.e., in the region enveloped by curve *i*, as for example for conditions *E*, *F*, and *G* in Figures 4a and 5. However, parametric sensitivity can indeed occur in the absence of ignition phenomena, as for example for condition *D* or in general for homogeneous reactors.

COMPARISON BETWEEN THE FLUID AND PARTICLE TEMPERATURE RUNAWAY CRITERIA

Some further insight into reactor behavior is given by comparing the parametric sensitivity regions obtained by applying the runaway criterion of Adler and Enig (1964) separately to the fluid and the particle temperatures, respectively. In Figure 6 the parametric sensitivity regions for the fluid temperature criteria are shown, corresponding to the cases previously examined in Figure 4. Curve *a* obviously remains unchanged because it refers to the multiplicity region of pellets at the reactor inlet, while curve *b* has been obtained again using the isocline method but now applied to the fluid temperature, θ. Thus, the boundary between nonrunaway and runaway operation is defined as the set of parameter values at which the second and third derivatives of fluid temperature vs. conversion vanish simultaneously. The relevant equations are summarized in the Appendix. Curve *c* is not reported since for the specific parameters in this case the inlet second-order derivative of the fluid temperature is always negative.

In Figure 7 the second-order derivatives of θ and θ_p at the reactor inlet are shown as functions of A_p. As expected from the particle multiplicity characteristics (Figure 1), at the upper bifurcation point A_p^*, both these quantities exhibit a discontinuity. However, the second-order derivative of θ_p attains positive values while that of θ remains negative. Thus in this case, runaway is predicted only with the particle temperature criterion. This feature occurs because of the local sensitivity phenomenon described by McGreavy and Adderley (1973), which is correctly accounted for by the particle temperature runaway criterion, while it is not by the criterion applied to the fluid temperature. This clearly shows that the parametric sensitivity regions described in Figure 4 account for global as well as for local sensitivity, and therefore represent completely the sensitivity behavior of the reactor.

Nevertheless, it can be seen that the sensitivity regions predicted by the two criteria shown in Figures 4a and 6a are quite similar. In fact, the criterion based on the fluid temperature usually predicts runaway for higher conversion values than that based on the particle temperature. However, this feature does not appear in the a priori definition of runaway conditions, which simply requires the existence of a runaway region for some conversion value between 0 and 1. Thus the predicted parametric sensitivity regions can indeed be quite similar. This is certainly not always true. For example, in the nearly adiabatic case shown in Figures 4b and 6b, the two regions are rather different and, as expected, that based on the fluid temperature criterion is smaller.

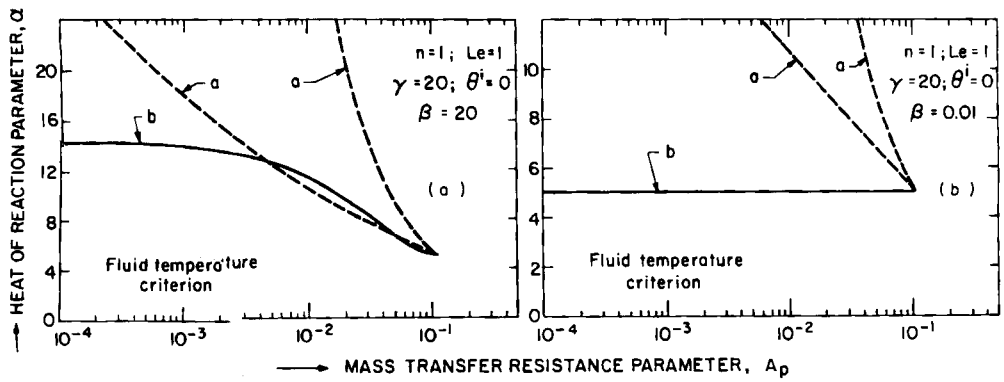

Figure 6. Construction of the parametric sensitivity region using the fluid temperature runaway criterion. (a) $\beta = 20$; (b) $\beta = 0.01$. Curves: a, reactor multiplicity region; b, occurrence of positive second-order derivative of θ vs. x in some region along the reactor.

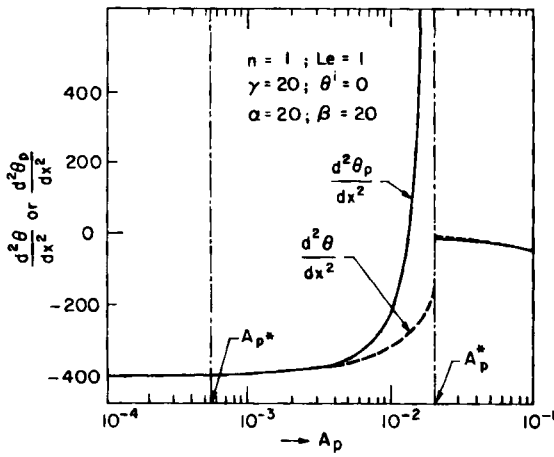

Figure 7. Second-order derivatives of the particle and fluid temperature at the reactor inlet, as a function of the mass transfer resistance parameter, A_p.

The horizontal nature of curve *b* in Figure 6b is readily explained by noting from Eq. 7 that as $\beta \rightarrow 0$ (i.e., $\delta \rightarrow 0$) the θ vs. z profile becomes independent of the particle equations, and thus also of the extent of mass transfer resistance (i.e., A_p).

ANALYSIS OF THE REGIONS OF PARAMETRIC SENSITIVITY FOR THE REACTOR

In the previous sections the procedure for estimating the region of parametric sensitivity of the particle temperature in the reactor has been developed. Some of the results obtained by using this procedure are now reported in order to illustrate the effect of each individual parameter in more detail.

The effect of the reaction order on the sensitivity region is shown in Figure 8a. It appears that runaway is less likely for increasing reaction orders. Note that for vanishing external mass transfer resistance (i.e., $A_p \rightarrow 0$), the critical value of α for the pseudohomogeneous reactor as reported by Morbidelli and Varma (1982) is approached. On the other hand, runaway does not occur at all for large values of A_p, where the reactor becomes mass transfer controlled. These features are common to all the results shown in the rest of the figures as well.

In Figures 8b and 8c the effects of the cooling parameter, β, and the activation energy, γ, are shown. As expected on physical grounds, the region of parametric sensitivity enlarges for decreasing values of β and for increasing values of γ. However, in the latter case, note that a further increase of γ beyond 100 does not appreciably alter the parametrically sensitive region.

Finally, the effect of the inlet temperature, θ^i is displayed in Figure 8d. It is clear that for larger θ^i values, runaway occurs for smaller values of both the heat of reaction parameter, α, and the mass transfer resistance parameter, A_p.

It is worth mentioning that the effect of each parameter on the region of parametric sensitivity is similar to that on the multiplicity region described above (Figure 2). This again stresses the similarity of the intrinsic nature of these two phenomena.

ACKNOWLEDGMENT

M. Morbidelli was recipient of a NATO-CNR Fellowship (Bando n. 215.15/3) during the course of this study.

NOTATION

$A = L\,k(T_w)\,p^{i n-1}\,MP\rho_b/u\rho_f$
$A_p = k(T_w)\,p^{i n-1}/k_g\,a_p$
a_p = particle external surface area, m²/kg
$B = p^{i n}\,k(T_w)L(-\Delta H)\rho_b\gamma/\rho_f C_p u T_w$
$B_p = (-\Delta H)p^{i n}k(T_w)\gamma/ha_p T_w$

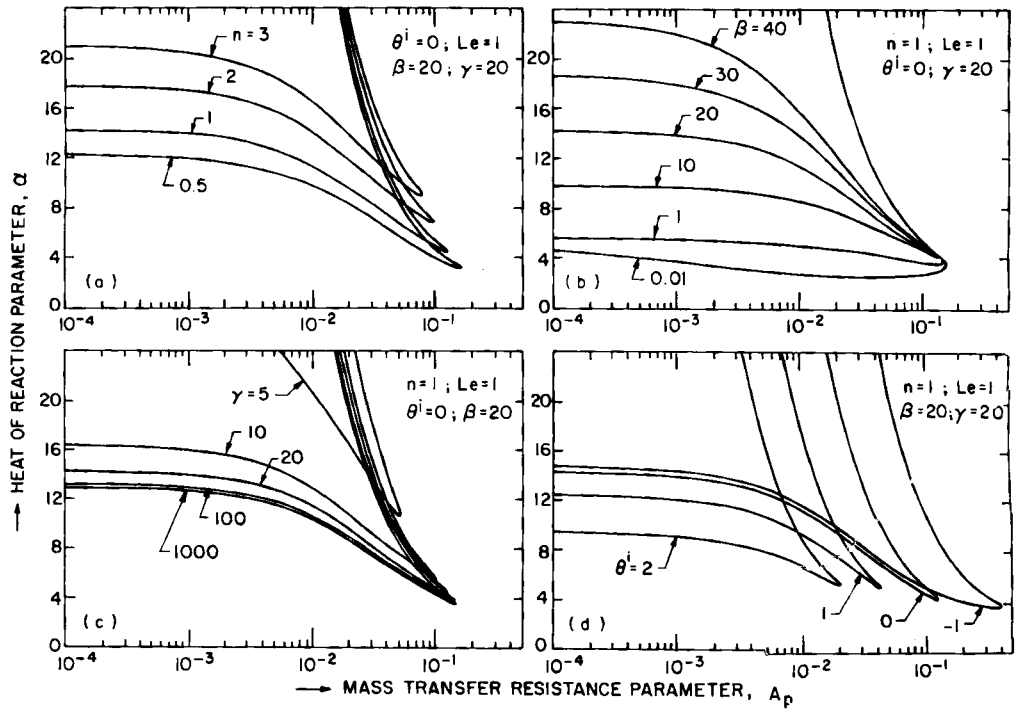

Figure 8. Influence of various physiochemical parameters on the region of parametric sensitivity. (a) reaction order, *n*; (b) heat transfer parameter, β; (c) activation energy, γ; (d) inlet fluid temperature, θ^i.

$b_1 = 2[\alpha + 2Le(n-1)\gamma - Le\theta^i(n-1) + Le\gamma^2]/\gamma^2$
$b_2 = [2\alpha + Le(n-1)\gamma - 2Le\theta^i(n-1) - \alpha\gamma - 2Le\theta^i\gamma]/\gamma$
$C = 4LU/up_fC_pd_t$
C_p = specific heat, J/K · kg
d_t = diameter of the reactor tube, m
E = activation energy, J/mol
h = heat transfer coefficient, J/m² · s · K
L = reactor length, m
Le = external transport Lewis number, $A_p\alpha/B_p = h/k_gMPC_p$
k = reaction rate constant, mol/s · kg · (Pa)^n
k_g = mass transfer coefficient, mol/m² · s · Pa
M = average fluid molecular weight
n = reaction order
P = total pressure, Pa
p = reactant partial pressure, Pa
R = ideal gas constant, J/K · mol
s = reactor axial coordinate, m
T = temperature, K
U = overall heat transfer coefficient, J/m² · K · s
u = superficial velocity, m/s
x = conversion, $(p^i - p)/p^i$
$z = \alpha(1-x)$

Greek Letters

$\alpha = B/A = (-\Delta H)p^i\gamma/T_wMPC_p$
$\beta = C/A = 4U/C_pd_tk(T_w)p^{i(n-1)}MP\rho_b$
$\gamma = E/RT_w$
$\delta = \beta\alpha^{n-1}$
θ = dimensionless temperature, $(T - T_w)E/RT_w^2$
θ_z, θ_{pz} = characteristic parameters of the isocline, defined by Eqs. A1 (or Eq. 19) and A4, respectively
θ_{p1}, θ_{p2} = particle temperature corresponding to upper and lower bifurcation, defined in Figure 1
ρ_b = catalyst bulk density, kg/m³
ρ_f = fluid density, kg/m³
$\phi = A_p\alpha^{1-n}/Le$

Superscripts

i = inlet value
* = upper bifurcation point

Subscripts

p = catalyst particle
w = wall
* = lower bifurcation point

APPENDIX

The basic equations of the isocline method, applied to the Adler and Enig (1964) runaway criterion, in the case of an nth-order irreversible reaction are presented. Two cases, where the criterion is applied to the particle and to the fluid temperature, respectively, are examined separately.

Particle Temperature Runaway Criterion

Isocline equation:

$$\theta_{pz}\left\{\left[1 - \frac{\theta_p - \theta}{(1+\theta_p/\gamma)^2}\right]z_p + nLe(\theta_p - \theta)\right\} - z\frac{d\theta}{dz} - \delta\phi Le(n-1)\theta - (\theta_p - \theta)[n + Le(1-n)] = 0 \quad \text{(A1)}$$

Locus curve equation:

$$\theta_{pz}\left\{\frac{z_p}{(1+\theta_p/\gamma)^2}\left[\frac{d\theta}{dz} - \theta_{pz}\frac{\gamma + 2\theta - \theta_p}{(\gamma+\theta_p)}\right] + \left[1 - \frac{\theta_p - \theta}{(1+\theta_p/\gamma)^2}\right]\left(1 - Le\,\theta_{pz} + Le\frac{d\theta}{dz}\right) + nLe\left(\theta_{pz} - \frac{d\theta}{dz}\right)\right\} - (n-1)[\delta\phi Le - 1 + Le]\frac{d\theta}{dz} - [n + Le(1-n)]\,\theta_{pz} - z\frac{d^2\theta}{dz^2} = 0 \quad \text{(A2)}$$

Criticality condition:

$$\theta_{pz}\left\{\frac{2}{(1+\theta_p/\gamma)^3}\left[\frac{d\theta}{dz} - \frac{\gamma + 2\theta - \theta_p}{\gamma+\theta_p}\theta_{pz}\right]\left[(1+\theta_p/\gamma)\left(1 - Le\theta_{pz} + Le\frac{d\theta}{dz}\right) - \frac{\theta_{pz}}{\gamma}z_p\right] + \frac{z_p}{(1+\theta_p/\gamma)^2}\left[\frac{d^2\theta}{dz^2} - \theta_{pz}\frac{d\theta}{dz}\frac{2}{\gamma+\theta_p} + \frac{2(\gamma+\theta)}{(\gamma+\theta_p)^2}\theta_{pz}^2\right] + Le\frac{d^2\theta}{dz^2}\left[1 - n - \frac{\theta_p - \theta}{(1+\theta_p/\gamma)^2}\right]\right\} - [2 + \phi Le(n-1) - n - Le(1-n)]\frac{d^2\theta}{dz^2} - z\frac{d^3\theta}{dz^3} = 0. \quad \text{(A3)}$$

The second and third derivatives of θ with respect to z can be derived directly from Eq. 7.

It can be easily seen that for $n = 1$, Eqs. A1, A2, and A3 reduce to Eqs. 19, 20, and 21, respectively. The procedure for evaluating the critical parameters remains unchanged. For $n \neq 1$, the critical point, which represents the IC for the backwards integration of Eq. 7, is obtained by solving the system of Eqs. 8, 9, A1, A2, and A3 for the unknowns: z, z_p, θ, θ_p, and θ_{pz}. This represents a system of nonlinear algebraic equations that is easily solved with a standard Newton-Raphson method.

Fluid Temperature Runaway Criterion

Isocline equation:

$$z_p - \left[\frac{\delta\theta g(\theta_p)}{1+\theta_z}\right]^{1/n} = 0 \quad \text{(A4)}$$

Locus curve equation:

$$1 - \frac{z_p}{n}\left[\frac{\theta_z}{\theta} - \frac{d\theta_p}{dz}\frac{1}{(1+\theta_p/\gamma)^2}\right] - Le\left(\frac{d\theta_p}{dz} - \theta_z\right) = 0 \quad \text{(A5)}$$

Criticality condition:

$$\left[1 + Le\left(\theta_z - \frac{d\theta_p}{dz}\right)\right]\left[\frac{d\theta_p}{dz}\frac{1}{(1+\theta_p/\gamma)^2} - \frac{\theta_z}{\theta}\right] + z_p\left[\frac{\theta_z^2}{\theta^2} + \frac{d^2\theta_p}{dz^2}\frac{1}{(1+\theta_p/\gamma)^2} - \frac{2\gamma}{(\gamma+\theta_p)^2}\left(\frac{d\theta_p}{dz}\right)^2\right] - nLe\frac{d^2\theta_p}{dz^2} = 0 \quad \text{(A6)}$$

The first and second derivatives of θ_p with respect to z are directly derived from Eq. 8. The procedure for calculating the critical parameters remains unchanged, except for the critical point, which is now given by the solution of the system of Eqs. 8, 9, A4, A5, and A6.

Finally, note that for negligible interparticle resistance (i.e., $A_p \to 0$ with Le finite), the equations obtained through the two criteria become identical. Also in this limit, both approach the corresponding relationships derived by Morbidelli and Varma (1982) for the pseudohomogeneous model.

LITERATURE CITED

Adler, J., and J. W. Enig, "The Critical Conditions in Thermal Explosion Theory with Reactant Consumption," *Comb. and Flame*, **8**, 97 (1964).

Bilous, O., and N. R. Amundson, "Chemical Reactor Stability and Sensitivity. II," *AIChE J.*, **2**, 117 (1956).

Chambré, P. L., "On the Characteristics of a Nonisothermal Chemical Reactor," *Chem. Eng. Sci.*, **5**, 209 (1956).

Dente, M., and A. Collina, "Sensitivity Behavior of Tubular Chemical Reactors", *Chim. e Industria*, **46**, 752 (1964).

Eigenberger, G., "On the Dynamic Behavior of the Catalytic Fixed-Bed Reactor in the Region of Multiple Steady States. I," *Chem. Eng. Sci.*, **27**, 1,909 (1972).

Hlaváček, V., M. Marek, and T. M. John, "Modeling of Chemical Reactors. XII," *Coll. Czech. Chem. Comm.*, **34**, 3,868 (1969).

Hlaváček, V., J. Votruba, and M. Kubicek, "Modeling of Chemical Reactors. XXVIII," *Chem. Eng. Sci.*, **29**, 2,333 (1974).

Iooss, G., and D. D. Joseph, *Elementary Stability and Bifurcation Theory*, Spring-Verlag, New York, 13, (1980).

Leib, T. M., and D. Luss, "Exact Uniqueness and Multiplicity Criteria for an *n*th-Order Reaction in a CSTR," *Chem. Eng. Sci.*, **36**, 210 (1981).

Liu, S. L., and N. R. Amundson, "Stability of Adiabatic Packed Bed Reactors. An Elementary Treatment," *Ind. Eng. Chem. Fund.*, **1**, 200 (1962).

Luss, D., "Uniqueness Criteria for Lumped and Distributed Parameter Chemically Reacting Systems," *Chem. Eng. Sci.*, **26**, 1,713 (1971).

McGreavy, C., and C. I. Adderley, "Generalized Criteria for Parametric Sensitivity and Temperature Runaway in Catalytic Reactors," *Chem. Eng. Sci.*, **28**, 577 (1973).

Morbidelli, M., and A. Varma, "Parametric Sensitivity and Runaway in Tubular Reactors," *AIChE J.*, **28**, 705 (1982).

Oroskar, A., and S. A. Stern, "Stability of Chemical Reactors," *AIChE J.*, **25**, 903 (1979).

Rajadhyaksha, R. A., K. Vasudeva, and L. K. Doraiswamy, "Parametric Sensitivity in Fixed-Bed Reactors," *Chem. Eng. Sci.*, **30**, 1,399 (1975).

Sinkule, J., et al. "Modeling of Chemical Reactors. XXX," *Chem. Eng. Sci.*, **31**, 23 (1976).

Tsotsis, T. T., and R. A. Schmitz, "Exact Uniqueness and Multiplicity Criteria for a Positive-Order Arrhenius Reaction in a Lumped System," *Chem. Eng. Sci.*, **34**, 135 (1979).

van den Bosch, B., and D. Luss, "Uniqueness and Multiplicity Criteria for an *n*th-Order Chemical Reaction," *Chem. Eng. Sci.*, **32**, 203 (1977).

van Welsenaere, R. J., and G. F. Froment, "Parametric Sensitivity and Runaway in Fixed Bed Catalytic Reactors," *Chem. Eng. Sci.*, **25**, 1,503 (1970).

Manuscript received Sept. 11, 1984, and revision received Apr. 26, 1985.