Wrong-Way Behavior of Packed-Bed Reactors: II. Impact of Thermal Dispersion

A sudden reduction in the feed temperature of a packed-bed reactor may lead to a transient temperature rise, referred to as a wrong-way behavior. As expected, the axial dispersion of heat decreases the magnitude of the temperature excursion and prolongs the transient shift to a new steady state. In addition, the thermal dispersion may enable the wrong-way behavior to ignite a low-temperature steady state leading to a disastrous runaway of the reactor. Moreover, it may create a transient high-temperature wave, which moves initially in the upstream direction. The axial dispersion of heat can lead to some behavioral features which are qualitatively different from those of a model which ignores it. The transient temperature excursion does not exceed a value, which can be estimated by a simple analytical expression.

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INTRODUCTION

Packed-bed reactors are used widely in the chemical and petrochemical industry. The reactor sometimes exhibits suprising dynamic features, which may lead to unexpected pitfalls in the operation and control and even to a runaway. The rational design of the control and start-up procedures requires a better understanding of these effects.

A lumped-parameter system may exhibit an inverse response: i.e., following a disturbance, it may move initially in the opposite direction of where it eventually ends up. Similarly, the difference in the propagation speed of temperature and concentration disturbances in a packed-bed reactor may lead to a wrong-way response, such as a transient increase (decrease) in the temperature of the bed following a rapid decrease (increase) in the feed temperature. This wrong-way behavior occurs because a sudden cooling of the feed decreases the conversion in the upstream section of the reactor. The increased reactant concentration in the hot downstream section leads to a transient temperature increase.

The wrong-way behavior was predicted by Boreskov et al. (1965), and Crider and Foss (1966). It was observed: by Hoiberg et al. (1971) in a homogenous liquid-phase reaction in a packed-bed reactor; by Van Doesburg and DeJong (1976a,b) in the catalytic methanation of carbon monoxide, and by Sharma and Hughes (1979) during the oxidation of carbon monoxide. Oh and Cavendish (1982) have recently studied the impact of the wrong-way behavior on the temperature of an automobile convertor.

When a packed bed has a unique steady state, a decrease in the feed temperature shifts the reactor eventually to a lower steady-state temperature. The induced transient temperature rise, however, may damage the catalyst or the reactor. Packed-bed reactors may attain, under certain conditions, different steady states depending on the initial conditions so that a transient temperature increase may shift the reactor from a low-temperature to a high-temperature steady state. Thus, a sudden cooling of the feed may lead to a new steady state whose downstream temperature exceeds that of the initial steady state. Sharma and Hughes (1979) reported such a case, in which a 119°C cooling of the feed increased the outlet steady-state temperature by 81°C. Such a disturbance may be caused, for example, by the failure of a furnace to preheat a recycle or feed stream.

Mehta et al. (1981) studied the wrong-way behavior using a pseudohomogeneous, single-phase, one-dimensional model, in which a single reaction occurs. The analysis resulted in a simple algebraic expression which predicts the maximal transient temperature rise. It was found that intraparticle gradients decreased the transient peak temperature and increased the duration of the transient temperature rise. The analysis gave valuable insight into this dynamic response and the parameters affecting it. The simple model ignores the influence of the axial dispersion of heat as well as heat transfer resistance between the particles and the fluid and predicts erroneously that temperature discontinuities (shocks) may exist in the bed. This causes some of the predicted peak temperature to be unreasonably high. Since this simple model cannot predict steady-state multi-

plicity, it fails to predict a potential shift from one branch of solutions to another, as was observed by Sharma and Hughes (1979). Thus, this limiting model has to be modified so that more accurate and reliable predictions can be made.

In this work we study the conditions, under which the wrong-way behavior occurs and its impact by using a pseudohomogeneous model that accounts for the axial dispersion in the packed bed. It can be shown that some predictions of this model differ qualitatively from those found in the previous study and that rather intricate dynamic behavior may be encountered when the reactor can attain multiple steady states.

Mathematical Model and Method of Solution

A pseudohomogeneous, one-dimensional model that accounts for the axial dispersion of heat and species is used to describe the packed-bed reactor. We assume that a single nth-order irreversible reaction occurs in the reactor and that all the physical properties are independent of the temperature and conversion.

The dimensionless species and energy balances are:

$$\frac{1}{Le}\frac{\partial x}{\partial t} = \frac{1}{Pe_m}\frac{\partial^2 x}{\partial z^2} - \frac{\partial x}{\partial z} - Da \exp\left(-\frac{1}{y}\right) x^n \tag{1}$$

$$\frac{\partial y}{\partial t} = \frac{1}{Pe_h}\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} + \beta Da \exp\left(-\frac{1}{y}\right) x^n + U(y_w - y) \tag{2}$$

where

$$x = C/C_f \qquad y = RT/E$$

$$Pe_m = \frac{Lu}{D_e} \qquad Pe_h = \frac{Lu\rho_f c_f}{k_e}$$

$$z = \frac{z'}{L} \qquad Le = 1 + \frac{(1-\epsilon)\rho_s c_s}{\epsilon\rho_f c_f}$$

$$Da = \frac{L\hat{k}_o C_f^{n-1}}{u} \qquad \beta = \frac{R}{E}\frac{(-\Delta H)C_f}{\rho_f c_f}$$

$$U = \frac{2hL}{ru\rho_f c_f} \qquad t = \left(\frac{ut'}{\epsilon L}\right)\frac{1}{Le} \tag{3}$$

We select E/R as the reference temperature so that the dimensionless parameters are independent of the feed temperature.

The corresponding boundary conditions are:

$$-\frac{\partial x}{\partial z} = Pe_m(1 - x) \qquad z = 0$$

$$-\frac{\partial y}{\partial z} = Pe_h(y_{f2} - y) \qquad z = 0$$

$$\frac{\partial y}{\partial z} = \frac{\partial x}{\partial z} = 0 \qquad z = 1 \tag{4}$$

where y_{f2} is the new feed temperature. The initial condition is the steady state corresponding to y_{f1}.

The steady-state equations are obtained by omitting the time derivatives in Eqs. 1 and 2. Many investigators examined the multiplicity features and stability of these equations. Most investigators considered the case of equal Peclet numbers, a Lewis number of unity, and a first-order reaction. A comprehensive review was presented by Varma and Aris (1977).

The literature indicates that up to three steady states may exist for a first-order reaction in an adiabatic reactor, while up to seven solutions may exist in a narrow range of parameters for a cooled reactor (Heinemann and Poore, 1981). When $2m + 1$ solutions exist, at least m are unstable. An oscillatory solution may appear for a cooled reactor (Heinemann and Poore, 1981). However, Jensen and Ray (1982) showed that this behavior is expected to occur only for a Lewis number smaller than a critical value, which is of order unity. Thus, oscillatory solutions are not expected to exist in a packed-bed reactor as the Lewis number is usually rather large.

The steady-state profiles reported in this work were computed by a shooting technique using an efficient stiff integration routine (STIFF 3) described by Villadsen and Michelsen (1978). The transient simulations were carried out by a modified Crank-Nicolson method developed by Eigenberger and Butt (1976), which positions the space grid points in an optimal nonequidistant grid.

Analysis of Wrong-Way Behavior

The nonlinear equations (Eqs. 1–2) describing the transient behavior were solved numerically. The analysis requires the use of extensive numerical simulations to determine the key dynamic features and to compare these with the predictions of the simpler model. Unlike the simple limiting model used by Mehta et al. (1981), it is not possible to predict analytically the behavioral features of the system.

We analyze first cases, in which a unique steady state exists for all feed temperatures, and later examine the behavior when three steady states exist over a bounded range of feed temperatures.

The model used by Mehta et al. (1981) predicts that the maximal peak temperature is independent of the Lewis number, which is the ratio between the propagation speed of the concentration and the temperature disturbances. Preliminary simulations using Eqs. 1–2 indicated, as expected, that the maximal peak temperature was a monotonically increasing function of the Lewis number, reaching an asymptotic value for a Lewis number higher than about 100. In all the simulations reported here, the value of the Lewis number was taken to be between 500 and 2,000, which is a typical value for an atmospheric gas-solid reactor. It is implied in several places in the literature that the axial dispersion of heat can lead to steady-state multiplicity only in short reactors having small Peclet numbers. This, however, is not correct and, as shown by Puszynski et al. (1981), multiplicity can occur even for very large Peclet numbers. The use of large Peclet numbers leads to very steep temperature gradients, which significantly increases the numerical effort but does not affect the qualitative features and structure of the solutions. In all the simulations presented here except when specified, we assigned the mass and heat Peclet numbers the values of 2,000 and 500, respectively, and the Lewis number was assigned the value of 2,000. In all the simulations, we assumed that the reaction is of first order and that the dimensionless overall heat transfer coefficient U is equal to unity.

Unique steady state for all feed temperatures

We consider first the case, in which a unique steady state exists for any feed temperature: i.e., the bifurcation diagram of

the maximal temperature in the reactor vs. the feed temperature has the shape shown in Figure 1. We examine first the adiabatic case and discuss later the modifications introduced by cooling.

In general, the feed temperature may be divided into four regions corresponding to the different steady-state behavior. "Region a" of Figure 1 consists of states with low feed temperatures, for which the conversion and the temperature rise are very small. "Region b" consists of states for which an intermediate level of conversion and temperature rise occurs, while "region c" consists of those, for which almost complete conversion is attained with a reaction zone inside the reactor. "Region d" consists of states, for which a very high conversion occurs in a narrow zone close to the reactor inlet. A schematic steady-state temperature profile in each region is shown in Figure 1.

The simulations show that a sudden reduction in the feed temperature for a reactor operating in "region a" produces a negligible transient temperature rise which moves out of the reactor with a dimensionless velocity (dz/dt) of unity. This result agrees with the prediction of Mehta et al. (1981) that a transient temperature rise occurs only in reactors with appreciable conversion. For a reactor operating in "region b," a suddent reduction in the feed temperature causes a transient temperature increase in the downstream section of the reactor. A typical example is shown in Figure 2. The transient temperature wave moves out of the reactor again with a unit velocity.

In "region c," very high conversion is attained in the reactor and a sudden temperature decrease reduces the upstream temperature to that of the new steady state (NSS), Figure 3. The temperature increases sharply in a narrow zone, where the reactant is consumed. This temperature peak moves forward and attains a constant shape in a sufficiently long reactor. The fully developed reaction zone moves downstream with a dimensionless speed smaller than unity. The simulations show that as the step change of the feed temperature is increased, the peak temperature approaches asymptotically a characteristic value of y^*, which is the maximal transient peak temperature in "regions b and c." This maximum transient temperature y^* is approached when the new feed temperature is so low that the reaction rate in the final steady state is very low. The characteristic temperature

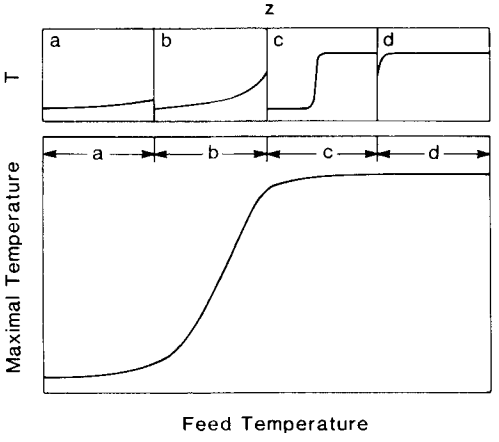

Figure 1. Division of the feed temperature into four regions with different steady-state behavior (shown in small rectangles) for a case that a unique solution exists for all feed temperatures.

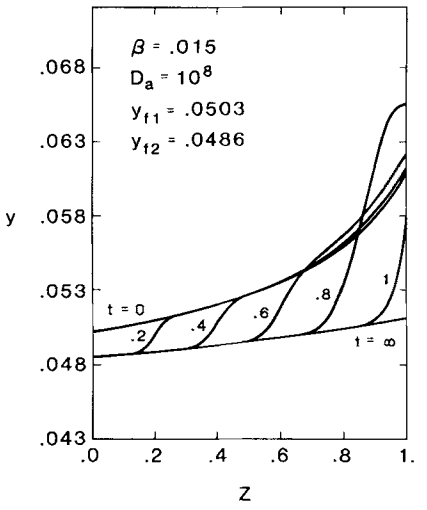

Figure 2. Typical response to a sudden feed temperature decrease ($y_{f1} \rightarrow y_{f2}$) for a reactor operating in "region b."

y^* is also the boundary between "regions c and d" in the steady-state diagram, Figure 1. The predicted temperature rise in Figures 2 and 3 is much smaller and more realistic than that predicted by the model of Mehta et al. (1981).

In "region d," a reduction in the feed temperature leads to a very small transient temperature increase. The dynamic behavior depends strongly on the new feed temperature. When the new feed temperature exceeds y^*, complete conversion is attained at the inlet section and the temperature profile shifts smoothly to the new steady state, Figure 4. This behavior is rather different from the prediction of Mehta et al. (1981) that a transient temperature rise will always develop in a reactor even if the initial conversion is very high.

A more intricate behavior is obtained when the new feed temperature is below y^* so that the new steady state is outside "region d." In such cases, Figure 5, a temperature wave with a maximal temperature of y^* is formed during the transient peri-

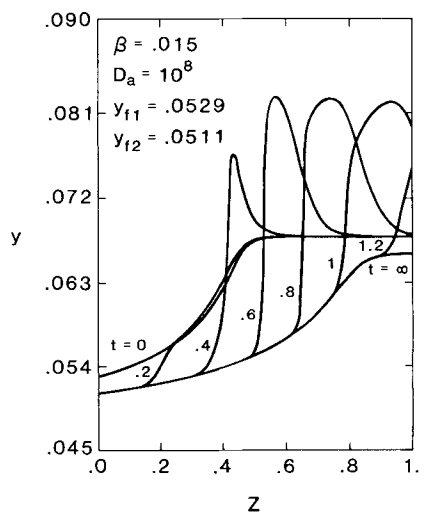

Figure 3. Typical response to a sudden feed temperature decrease for a reactor operating in "region c."

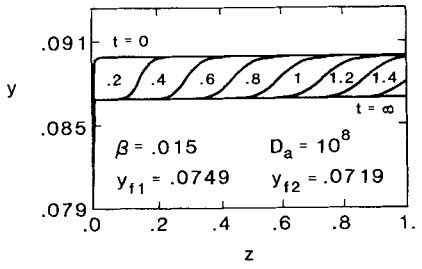

Figure 4. Typical response to a sudden feed temperature decrease for a reactor operating in "region d."

od. This wave moves eventually out of the reactor and the new steady state is attained. This transient approach to a constant temperature y^* is a novel feature, which has not yet been reported in the literature.

Figure 6 describes the dependence of the maximal transient temperature (dash-dot line) on the new and initial feed temperature. The solid line represents the maximal steady-state reactor temperature vs. the initial feed temperature. Each dash-dot line describes the maximal transient temperature vs. new feed temperature for a specific initial feed temperature (intersection of solid and dash-dot lines). The diagram shows that a wrong-way behavior with a substantial transient temperature rise is observed only in "regions b and c." Note that the simple model used by Mehta et al. (1981) predicts unrealistically high transient temperature rise under the same conditions. The maximal transient peak temperature in "regions b and c" cannot exceed the characteristic temperature y^*, which depends only on the parameters defining the reactor. The characteristic temperature y^* can be found by a numerical simulation of the transient response in "region c." It is shown in the Appendix that for an nth-order reaction y^* can be computed by the approximate relation:

$$\frac{\beta Pe_h}{Da} = \int_0^{y^*} \exp(-1/y)\left(1 - \frac{y}{y^*}\right)^{n-1} dy \qquad (5)$$

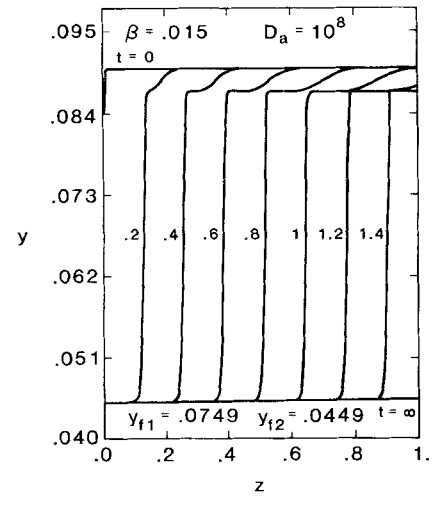

Figure 5. Typical response for a reactor operating in region d to a sudden reduction in the feed temperature below y^*.

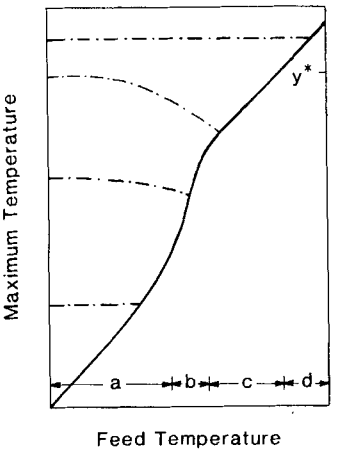

Figure 6. Dependence of the maximal transient temperature (dash-dot line) on the original (solid line) and new feed temperature.

which for a first-order reaction predicts that:

$$\frac{\beta Pe_h}{Da} = y^* \exp\left(-\frac{1}{y^*}\right) - E_1\left(\frac{1}{y^*}\right) \qquad (6)$$

where

$$E_1(x) = \int_x^\infty \frac{\exp(-t)}{t}\, dt \qquad (7)$$

Equation 5 is very useful for estimating the dependence of the maximal transient temperature on the operation conditions. It predicts that y^* is a monotonically increasing function of $\beta Pe_h/Da$. Thus, an increase of the thermal conductivity or equivalently a decrease in Pe_h decreases the value of y^*.

Figure 7 shows that the value of y^* predicted by Eq. 6 agrees very well with that found by numerical simulations. Kiselev and Matros (1980) derived another expression for predicting the maximal transient peak temperature. They predicted that y^* should be a linear function of $\log(\beta Pe_h/Da)$ in an adiabatic

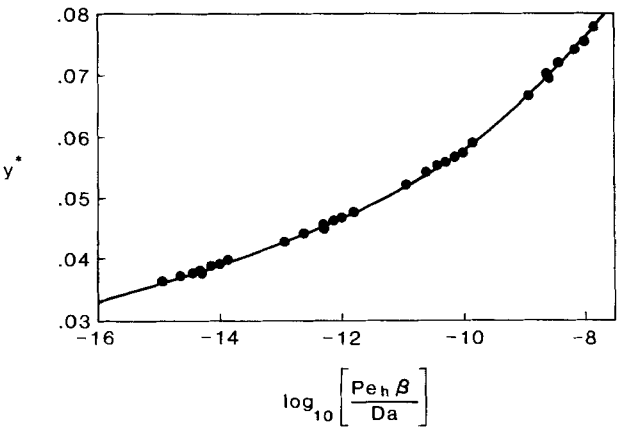

Figure 7. Comparison of y^* computed by Eq. 6 (solid line) with numerical simulations.

case. The simulations shown in Figure 7 indicate that this prediction is incorrect.

Equation 6 and Figure 7 imply that for large Lewis numbers the dispersion of species does not affect the maximum transient temperature response. The maximum transient temperature depends only on Damköhler and Peclet numbers and the adiabatic temperature rise β. When the axial dispersion of heat is very small, the maximal transient peak temperature may be very large due to the high Peclet number for heat transfer. This is consistent with the earlier predictions by Mehta et al. (1981).

The limiting model used by Mehta et al. (1981) predicts that the maximal transient temperature rise increases monotonically with an increase in either the adiabatic temperature rise or the activation energy. The axial dispersion model predicts, on the other hand, that for a fixed *Da* the maximal transient temperature rise occurs for some intermediate value of β, Figure 8, which is proportional to the feed concentration of the reactant, i.e., the heat generated by the complete conversion of the reactant. The reason for this behavior is that, for low values of β, the reactor operates in "region a," in which the transient temperature rise is small. For large β values, the reactor operates in "region d," in which the transient temperature rise is small. The maximal temperature rise occurs at intermediate values of β, for which the reactor operations in "region b." The same features persist even for larger Peclet numbers. Experiments carried out recently in our laboratory agree with this prediction of the axial dispersion model.

The dynamic response of a cooled packed-bed reactor to a sudden reduction in the feed temperature is qualitatively similar to that of an adiabatic one. Again four different regions exist. In the first region (low feed temperatures), the conversion is low and the temperature profile decreases following a reduction in the feed temperature. No wrong-way behavior can occur in this region. In the second region, a sudden reduction in the feed temperature generates a transient temperature rise. A fully developed reaction zone is not formed and the highest peak temperature is found at the exit of the reactor.

"Region c" consists of states with high conversion for which the high reaction zone is not close to the inlet. Here a fully developed transient reaction zone appears in the reactor and then

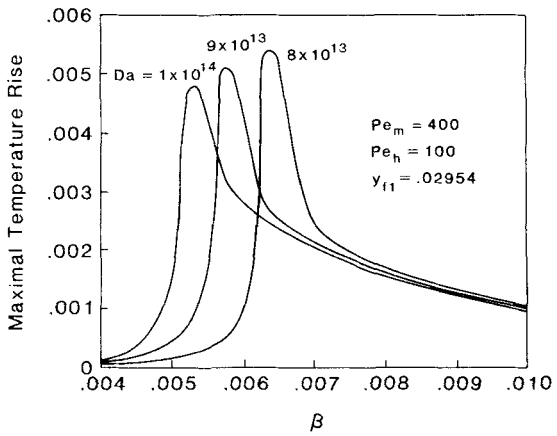

Figure 8. Dependence of the maximal transient temperature rise on β and *Da*. The wrong-way behavior was caused by a sudden 8% decrease in the feed temperature (*Le* = 500).

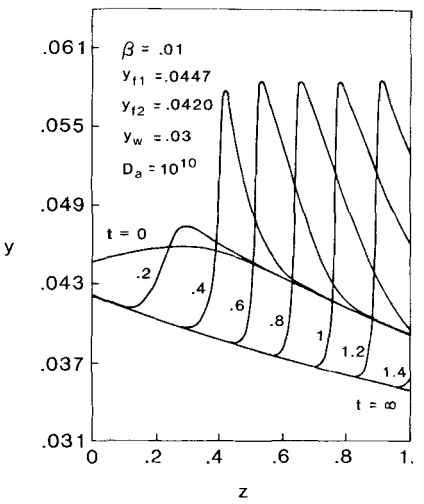

Figure 9. Response of a cooled reactor operating in "region c" to a sudden drop in feed temperature (Pe_m = 800, Pe_h = 200).

moves downstream with a constant speed, Figure 9. The simulations show that the peak temperature for a given reactor attains an asymptotic value as the feed temperature reduction is increased. This value is obviously lower than that found in the adiabatic case.

"Region d" is of states for which a very high conversion is obtained in the upstream section. For these states, a sudden reduction in the feed temperature leads to a very small temperature increase.

Our simulations show that a reactor with large Peclet numbers (Pe_m = 2,000 and Pe_h = 500) gives qualitatively the same transient features as a reactor with smaller Peclet numbers (Pe_m = 200 and Pe_h = 50). Increasing the Peclet numbers for heat and mass increases the slope of the temperature wave and causes the numerical solution to become stiffer.

Multiple steady states for some feed temperatures

The steady-state model predicts that, for certain sets of parameters, a packed-bed reactor may have multiple steady-state solutions for some feed temperatures. Up to seven solutions may be found for a set of parameters of extreme values in a very narrow range of feed temperatures for a cooled reactor (Heinemann and Poore, 1981). For most practical situations at most three steady-state solutions exist for an nth-order exothermic reaction. Thus, we consider only such cases and use them to illustrate the new behavioral features introduced by the multiplicity.

Figure 10 shows the dependence of the maximal steady-state temperatures on the feed temperature for a case in which three solutions exist over a bounded range of feed temperatures. When the conversion is low (states in "regions a and b"), the behavior is very similar to that in "regions a and b" of the adiabatic case. Similarly, for the high conversion states ("region e"), the behavior is very similar to that in "region d" of the adiabatic case. The major new features are found for states with an initial feed temperature close to either the ignition ("region c") or the extinction point ("region d").

The nature of the wrong-way behavior in "region c" (next to ignition) depends on the location of the new feed temperature

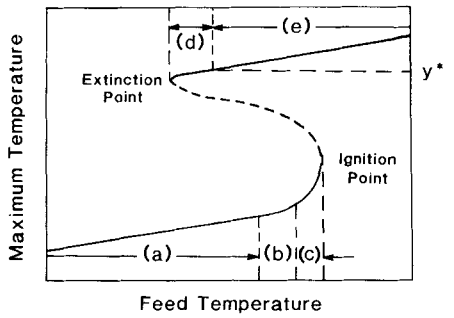

Figure 10. Schematic dependence of maximal temperature on feed temperature and classification for a case that three different steady states exist for some feed temperatures.

relative to the ignition and extinction temperatures. When the new feed temperature is lower than the extinction point, the new steady state is on the low-temperature steady-state branch. During the transient period, a temperature peak develops at the downstream section of the reactor. (This maximum transient temperature is always lower than y^*, which can be predicted by Eq. 5.) The fully developed reaction zone moves downstream at a very low speed ($0 < \omega \ll 1$) as shown in Figure 11 for a typical case. This slowly moving temperature peak may damage the catalyst or the reactor, and may initiate undesired side reactions. The slow movement of this temperature wave is a new feature not predicted by the limiting model of Mehta et al. (1981) and is due to the axial heat conduction.

When the new feed temperature is higher than the extinction point, a suddent reduction in the feed temperature can lead to two different behaviors. In the first case, a transient temperature peak develops and eventually moves out of the reactor. No ignition occurs in this case due to the insufficient transient temperature rise and the response is rather similar to that in "region b." The other possibility is that the transient temperature rise shifts the reactor to the high temperature state following a larger feed temperature decrease, Figure 12. Here, a reaction

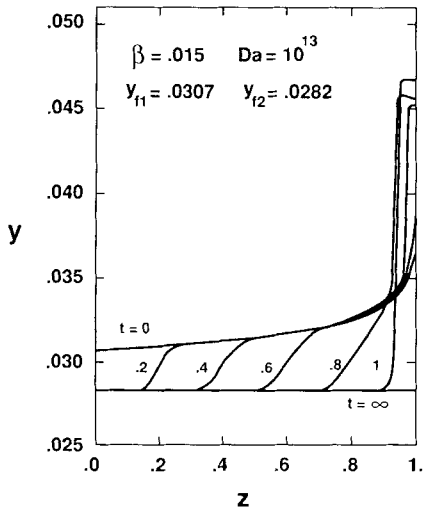

Figure 11. Typical response of a reactor operating in "region c" to a sudden reduction in the feed temperature below the extinction point.

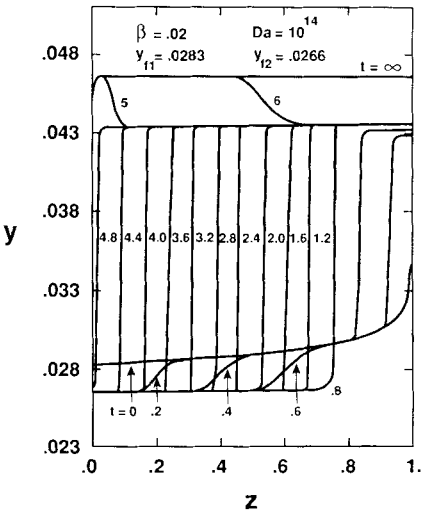

Figure 12. Response of a reactor operating in "region c" to a sudden reduction in the feed temperature to a value above that at which extinction occurs.

zone with a temperature of y^* moves initially slowly in the upstream direction. The reactor is then ignited and the temperature wave moves in the downstream direction shifting the reactor to a high temperature steady state. This ignition, if not prevented by a proper control action, can have a disastrous impact on the operation of the reactor.

The formation of a backwards moving reaction front is caused by the thermal dispersion of heat, indicating that even for very large Peclet numbers, the dispersion affects the qualitative features of the reactor. A similar behavior has been reported by Rajaiah et al. (1988) in a recent study of noncatalytic reactors.

A master diagram showing the dependence of the maximal transient temperature on the original and new feed temperatures is given in Figure 13. Whenever ignition occurs, this maximal transient temperature is equal to that of the high-temperature steady state at the new feed temperature. An ignition does not occur if the maximal transient temperature is below that of the high-temperature state.

The calculations show that the wrong-way behavior can lead to a steady-state ignition only if the initial feed temperature is

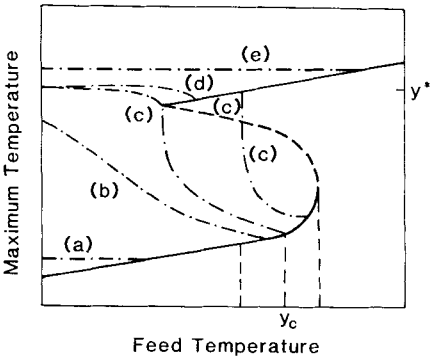

Figure 13. Dependence of the maximal transient temperature (dash-dot line) on the original (solid line) and new feed temperatures.

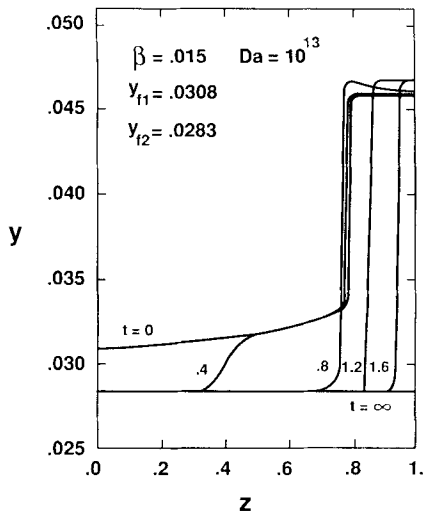

Figure 14. Response of a reactor operating in "region d" to a sudden reduction of feed temperature below that at which extinction occurs.

between the ignition temperature and some critical feed temperature y_c. When the ignition and extinction temperatures are very close to each other (a narrow region of multiplicity), it may not be possible to ignite the reactor by a sudden reduction in the feed temperature: i.e., y_c may not exist. Clearly, knowing y_c is essential for predicting the probability that the wrong-way behavior can shift the reactor to a high-temperature branch.

"Region d" of Figure 10 consists of states with high conversion and a fully developed reaction zone within the reactor. The behavior in this case is similar to that in "region c" when a unique solution exists. The only difference is that a sufficiently large reduction in the feed temperature (below the extinction temperature) shifts the reactor to a low-temperature state, Figure 14. During the transient period, a fully developed reaction zone with a dimensionless temperature y^* moves in the downstream direction and eventually moves out of the reactor.

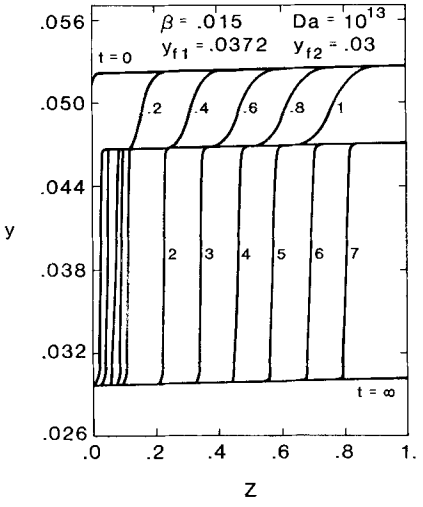

Figure 15. Response of a reactor operating in "region e" to a sudden drop of feed temperature below that of the extinction point.

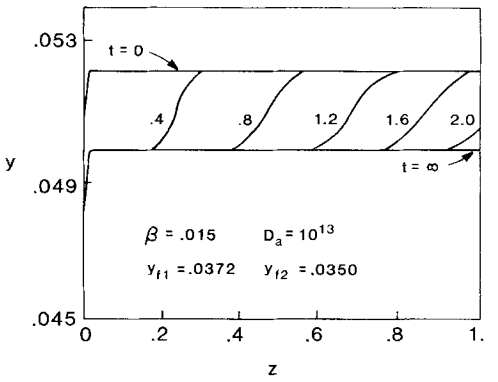

Figure 16. Response of a reactor operating in "region e" to a sudden drop of feed temperature above that of the extinction point.

"Region e" of Figure 10 consists of ignited states with an exit bed temperature exceeding y^*. A sudden reduction of the feed temperature in these cases does not lead to a noticeable temperature increase, and the behavior is similar to that in "region d" for a single steady-state case. When the new feed temperature is below the extinction point, the reactor cools in two steps, Figure 15. In the first step, a reaction zone with temperature y^* is formed. This zone then moves continuously in the downstream direction and eventually moves out of the reactor creating a new extinguished state. Figure 16 shows a case where both the initial and new feed temperatures are in "region e" so that complete conversion occurs very close to the entrance of the reactor. No transient temperature peak was formed in this case and the reactor is cooled smoothly to the new steady state.

When y^* is below the maximal temperature of the steady state at the extinction point, "region d" does not exist, and "region e" consists of all the solutions on the ignited branch.

Figure 17 describes the dependence of the maximal transient temperature rise on the adiabatic temperature rise β for a case

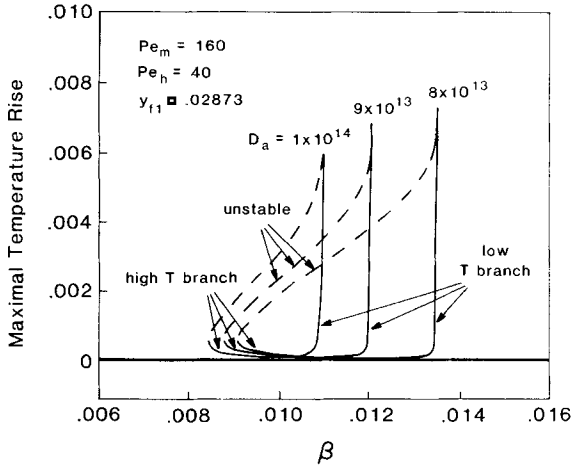

Figure 17. Dependence of the maximal transient temperature rise on β and *Da* for a case that three solutions exist for some β. The wrong-way behavior was caused by a sudden 8% decrease in the feed temperature (*Le* = 500).

in which three steady-state solutions exist for some β. The calculations reveal a very sharp increase in the transient temperature rise as the reactor approaches the ignition point on the low temperature branch. The maximal temperature excursion corresponds to the case in which the reactor was initially at the ignition point. Similar behavior is found in cases where the activation energy is changed keeping the other parameters constant and in a cooled reactor. Experiments carried out in our laboratory agree with the above predictions of the axial dispersion model, which contradict the predictions of Mehta et al. (1981) that the temperature excursion is a monotonically increasing function of the adiabatic temperature rise.

The behavior of a cooled reactor is qualitatively similar to that of an adiabatic reactor except that the constant temperature regions are replaced with cooled regions. Figure 18 describes a case in "region c." Here, a sudden cooling of the feed causes first a formation of a reaction zone with a constant temperature, which then moves slowly in the upstream direction causing an ignition to the high-temperature state. This behavior is similar to that shown in Figure 12 for the adiabatic case.

Figure 19 describes a similar case, in which only a unique steady state exists for the new feed temperature. Here again a reaction zone with a constant temperature appears and moves slowly in the downstream direction until the reactor eventually attains the low temperature steady state. This behavior is similar to that shown in Figure 11 for the adiabatic case.

Concluding Remarks

The analysis predicts, as expected, that thermal dispersion decreases the magnitude of the transient temperature rise caused by the wrong-way behavior and prolongs the transient shift to the new steady state. The axial dispersion model also predicts that the maximal temperature excursion is not a monotonic function of the adiabatic temperature rise. This prediction, which agrees with experimental observations, differs qualitatively from that of the limiting model used by Mehta et al., (1981). The calculations show that the axial dispersion of heat has a major effect even for very large Peclet numbers.

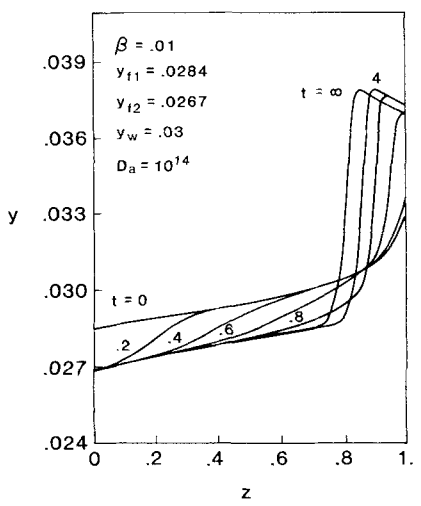

Figure 18. Response of a cooled reactor operating in "region c" to a sudden decrease in the feed temperature (Pe_m = 200, Pe_h = 50, Le = 500).

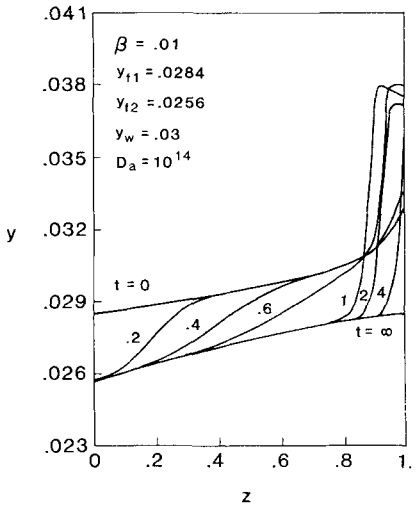

Figure 19. Response of a cooled reactor operating in "region c" to a sudden decrease in the feed temperature below that of extinction (Pe_m = 200, Pe_h = 50, Le = 500).

The thermal dispersion model is also capable of predicting the experimental observation by Sharma and Hughes (1979) in which the wrong-way behavior may lead to an ignition to a new high-temperature steady state. This unexpected event may lead, if not prevented by proper control action, to a disastrous runaway, especially when some undesired exothermic reactions, not occuring at normal operating conditions, take over at a higher temperature. Our simulations show that this surprising ignition occurs mainly when the reactor is initially operating close to the ignition point. The region of operating conditions for which this occurs may be larger for reactions with different kinetics or for systems in which several reactions occur simultaneously. The calculations show that axial dispersion may lead to steady-state multiplicity and ignition of the reactor due to the wrong-way behavior even for very large Peclet numbers. The increase in the Peclet number leads to an increase in the slope of the temperature peak which makes the numerical calculations stiffer.

The master diagram presented in this study is very useful for characterizing the dependence of the wrong-way behavior of a packed bed reactor on the initial steady state and the feed temperature decrease. The simulations revealed several novel unexpected features which have not yet been reported or predicted. Among these are the transient formation of a wave with temperature y^* (see, for example, Figures 5, 12, 14, 15), and the formation of a temperature wave which moves initially in the upstream direction (Figure 12).

The analysis indicates that thermal dispersion of heat has an important impact on the wrong-way behavior in a packed bed reactor. Thus, it must be accounted for in the predictions of the potential impact of the wrong-way behavior and in the design of a control policy to minimize its impact.

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Notation

C = concentration
c = specific heat
Da = Damköhler number, defined by Eq. 3
D_e = effective dispersion coefficient for mass
E = activation energy
$(-\Delta H)$ = heat of reaction
h = overall heat transfer coefficient
k_e = effective thermal conductivity
k_o = frequency factor
L = reactor length
Le = Lewis number, defined by Eq. 3
n = reaction order
Pe_h = Peclet number for heat, defined by Eq. 3
Pe_m = Peclet number for mass, defined by Eq. 3
R = universal gas constant
r = radius of reactor
T = temperature
t = dimensionless time, defined by Eq. 3
t' = time
U = dimensionless heat transfer parameter, defined by Eq. 3
u = superficial velocity
x = dimensionless concentration, C/C_f
y = dimensionless temperature, RT/E
y_c = characteristic feed temperature
y^* = maximal transient peak temperature
z' = axial position coordinate
z = dimensionless axial position, z'/L

Greek letters

β = parameter defined by Eq. 3
ϵ = void fraction of bed
μ = dimensionless axial position, z-ωt
ρ = density
ω = propagation speed of temperature wave

Subscripts

1 = initial steady state
2 = new steady state
f = feed
s = solid
w = wall

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Appendix: Estimation of the Value of y^*

We derive here an estimate for the value of the asymptotic maximal peak temperature, y^*, which also separates "regions c and d" in the single steady-state case, and "regions d and e" for the three steady-state case.

We assume that the reactor is very long so that a constant shape temperature wave, which moves at a constant velocity of ω, develops. Using the transformation:

$$\mu = z - \omega t \tag{A1}$$

Equations 1 and 2 can be transformed to

$$\frac{1}{Pe_m}\frac{d^2x}{d\mu^2} - \left(1 - \frac{\omega}{Le}\right)\frac{dx}{d\mu} - Da \exp\left(-\frac{1}{y}\right)x^n = 0 \tag{A2}$$

$$\frac{1}{Pe_h}\frac{d^2y}{d\mu^2} - (1-\omega)\frac{dy}{d\mu} + \beta\, Da \exp\left(-\frac{1}{y}\right)x^n = 0 \tag{A3}$$

The boundary conditions are

$$\begin{aligned} &x = 1, \quad y = y_f && \mu \to -\infty \\ &x = 0, \; y = y^* && \mu \to \infty \\ &\frac{dx}{d\mu} = \frac{dy}{d\mu} = 0 && \mu \to \pm\infty \end{aligned} \tag{A4}$$

Combining Eqs. A2 and A3 to eliminate the reaction term and integrating from $-\infty$ to ∞, we get a relation between the propagation speed and y^*, namely

$$y^* - y_f = \frac{\beta(1-\omega/Le)}{1-\omega} \tag{A5}$$

Assuming $Le \gg \omega$ and $Pe_m \gg Pe_h$, Eq. A6 can be obtained by using Eq. A5 when we combine Eqs. A2 and A3 and integrate it once.

$$\frac{1}{Pe_h}\frac{dy}{d\mu} = \beta\left(x - \frac{y^*-y}{y^*-y_f}\right) \tag{A6}$$

Since $dy/d\mu > 0$ for an adiabatic reactor

$$x > \frac{y^* - y}{y^* - y_f} \tag{A7}$$

If $Pe_m \gg 1$, Eqs. A2 and A6 give

$$-\frac{Pe_h\beta}{Da}\frac{dx}{dy} = \frac{\exp\left(-\frac{1}{y}\right)x^n}{x - \frac{y^* - y}{y^* - y_f}} > \exp\left(-\frac{1}{y}\right)x^{n-1} > \exp\left(-\frac{1}{y}\right) \cdot \left(\frac{y^* - y}{y^* - y_f}\right)^{n-1} > \exp\left(-\frac{1}{y}\right)\left(\frac{y^* - y}{y^*}\right)^{n-1} \tag{A8}$$

Integrating Eq. A8 from y_f to y^* one obtains

$$\frac{Pe_h\beta}{Da} > \int_{y_f}^{y^*} \exp\left(-\frac{1}{y}\right)\left(\frac{y^* - y}{y^*}\right)^{n-1} dy \tag{A9}$$

which may be approximated by

$$\frac{Pe_h\beta}{Da} > \int_{0}^{y^*} \exp\left(-\frac{1}{y}\right)\left(\frac{y^* - y}{y^*}\right)^{n-1} dy \tag{A10}$$

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