Parametric Sensitivity in Fixed-Bed Reactors: Inter- and Intraparticle Resistance

The role of inter- and intraparticle transport resistances in the sensitivity behavior of a fixed-bed catalytic reactor is fully elucidated. The parametric sensitivity regions obtained using a heterogeneous one-dimensional plug flow model are reported for various values of the involved dimensionless parameters. Comparisons with previous sensitivity criteria and with experimental data are also presented.

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Introduction

In a recent study, we investigated parametric sensitivity of fixed-bed catalytic reactors with interparticle mass and heat transfer limitations (Morbidelli and Varma, 1986a); in the present work, we extend the analysis to cases involving intraparticle mass transfer resistance as well. This provides a complete picture of the role of mass and heat transfer limitations on the sensitivity behavior of such reactors. The analysis is then completed by detailed comparisons with experimental observations previously reported in the literature, and also with other sensitivity criteria for heterogeneous reactors.

As a result of previous analysis (Morbidelli and Varma, 1985, 1986a), the criterion selected to define parametric sensitivity is the one originally proposed by Adler and Enig (1964) in the context of thermal explosions. It states, once transposed to chemical reactors, that a reactor operates in parametric sensitivity when it exhibits a region with positive second-order derivative of particle temperature vs. conversion somewhere before the hot spot. Note that the use of particle temperature rather than fluid temperature is of crucial importance, since it allows simultaneously accounting for both local and global sensitivity (Morbidelli and Varma, 1986a).

It is worth stressing that this criterion is actually based only on physical intuition about geometrical properties of the steady state temperature profile—a characteristic feature of all criteria proposed to date in the literature. However, its reliability has recently been confirmed through the generalized sensitivity criterion, founded firmly on the rigorous concept of sensitivity (Morbidelli and Varma, 1986b, c). The latter is a rather general approach that can be applied to a variety of reacting systems, for example, cases involving multiple reactions, and cases that do not even have a temperature profile, such as a continuous stirred-tank reactor (Chemburkar et al., 1986). In the case of tubular reactors, the two criteria provide the same answer for all situations of practical interest. Since such a comparison is discussed in detail elsewhere (Morbidelli and Varma, 1986b, c), we do not pursue this topic here. In the sequel, the Adler and Enig criterion applied to the particle temperature is adopted due to its greater simplicity in application to tubular reactors.

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The Heterogeneous One-dimensional Plug Flow Model

Consider a fixed-bed catalytic reactor, operating under steady state conditions, where an irreversible nth-order reaction occurs. This can be simulated by a heterogeneous one-dimensional plug flow model under the following assumptions:

1. Intraparticle thermal gradients are negligible; that is, the catalyst particles are internally isothermal
2. No mixing of heat or mass occurs in the axial direction, while the fluid is perfectly mixed radially; that is, plug flow is assumed inside the reactor

It is worth noting that while the first assumption is quite acceptable in practice (Carberry, 1975; Pereira et al., 1979), unless the special case of nonuniformly active catalyst particles is involved (Lee et al., 1978), the second is probably less realistic. This is particularly true for radial heat transfer in nondiabatic fixed-bed reactors. Some significant, although not conclusive, improvement is obtained by estimating the wall heat transfer coefficient through the relationship proposed by Finlayson (1971). This makes the one-dimensional model equivalent to a two-dimensional model where the radial temperature gradient is estimated using a one-point collocation procedure.

Puszynski et al. (1981) have shown that axial dispersion may also play a role in the behavior of fixed-bed reactors operating in the vicinity of the parametric sensitivity region. In particular, they showed that runaway predicted by a plug-flow model corresponds to the occurrence of ignition, due to multiplicity, in a model that accounts for axial dispersion.

However, besides its accuracy, the heterogeneous one-dimensional model contains a complete description of all inter- and intraparticle mass and heat transfer phenomena, whose effect on reactor sensitivity is the main object of this work.

Using the dimensionless parameters defined in the Notation, the following equations for the fluid phase mass and heat balances are obtained.

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

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

with initial conditions (IC): $\theta = \theta^i$ and $x = 0$ at $s = 0$. Note that x and θ represent conversion and dimensionless temperature, $g(\theta_p)$ is the Arrhenius term

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

and subscript p refers to quantities evaluated at the external surface of the catalyst particle.

The dimensionless mass and heat balances for the solid phase are represented by the following nonlinear algebraic equations

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

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

where the effectiveness factor, η, accounts for intraparticle mass transfer resistances. It is defined as the ratio of the actual overall reaction rate in the particle to that in the absence of all internal transport limitations (i.e., evaluated at the reactant concentration and temperature values at the particle external surface). Thus, η is given by the solution of a Dirichlet problem, where the Thiele modulus is also defined based on the reactant concentration and temperature values at the particle external surface.

Using a suitably normalized Thiele modulus, Φ (Aris, 1965; Bischoff, 1965; Petersen, 1965), η can be represented with reasonable accuracy by a unique function of Φ for any particle geometry and reaction rate expression. In particular, for an irreversible nth order reaction (with $n > -1$)

$$\eta = \frac{3\Phi\coth(3\Phi) - 1}{3\Phi^2} \tag{6}$$

where

$$\Phi^2 = \left(\frac{V_p}{S_p}\right)^2\frac{n+1}{2}\frac{\rho_s k(T_p)C_p^{n-1}}{D_e} \tag{7}$$

The normalized Thiele modulus Φ changes along the reactor axis according to changes of concentration and temperature at the particle surface. It is convenient to make this dependence explicit by introducing a constant normalized Thiele modulus Φ_w as follows

$$\Phi^2 = \Phi_w^2(1-x_p)^{n-1}/g(\theta_p) \tag{8}$$

where Φ_w is the Φ value calculated at the inlet fluid phase reactant concentration and at the reactor wall temperature.

It is worth stressing that as $\Phi_w \to 0$, $\eta \to 1$, and the above model reduces to the interparticle resistances model examined previously (Morbidelli and Varma, 1986a). Moreover, if also $A_p \to 0$, then it further reduces to the pseudohomogeneous model, whose sensitivity behavior has also been analyzed previously in detail (Morbidelli and Varma, 1982).

Critical Conditions for Reactor Runaway

A heterogeneous reactor is said to operate in the parametrically sensitive region, or simply to run away, if it exhibits a region of positive second-order derivative anywhere before the hot spot in the particle temperature vs. conversion plane. Considering the particle temperature rather than the fluid temperature is of major importance when analyzing heterogeneous reactors. In fact, the reaction occurs within the catalyst particle, whose temperature is required to be controlled in order to prevent not only catalyst damage but also deleterious effects on selectivity and productivity in the case of exothermic reactions.

McGreavy and Adderly (1973) first introduced the concept of local sensitivity, indicating with this the situation where the particle temperature is running away even though the external fluid temperature still lies within the safe regime. This occurs when the derivative of the particle temperature vs. the fluid temperature (which can readily be obtained from Eq. 5) approaches infinity—as it does at the bifurcation point to steady state multiplicity for the catalyst particle. As we have discussed in detail previously (Morbidelli and Varma, 1986a), local sensitivity is fully accounted for when the particle temperature rather than the fluid temperature is considered in the above-mentioned runaway criterion. Furthermore, such a criterion leads to sensitivity conditions that also include the case of global sensitivity, which corresponds to the situation where the runaway phenomenon is not due to the intrinsic heterogeneous nature of the reactor. This is the same phenomenon encountered in homogeneous reactors; here the fluid and the particle temperatures run away simultaneously. Thus, in order to obtain a complete description of the sensitivity behavior of the reactor, including both local and global sensitivity, the sensitivity of the reactor profiles in the particle temperature vs. conversion plane needs to be examined.

Taking the conversion, x, as the independent variable, Eqs. 1 and 2 reduce to

$$\frac{d\theta}{dx} = \alpha - \beta\frac{\theta g(\theta_p)}{\eta(1-x_p)^n} \tag{9}$$

which, coupled with Eqs. 3–8, allows one to compute θ, θ_p, and x_p as functions of x.

According to the definition of runaway, noted above, criticality is the situation where a region with positive second-order derivative in the θ_p vs. x plane is just at the verge of appearing. Considering the dimensionless heat of reaction parameter, α in Eq. 9, and indicating as α_c the value of α at criticality, it readily follows that for $\alpha > \alpha_c$ a finite region of positive second-order derivative of θ_p vs. x develops and then the reactor runs away. On the other hand, for $\alpha < \alpha_c$ such a region does not exist and so the reactor is nonsensitive. Since this statement is self-explanatory on physical grounds, we will omit its rigorous proof; the

interested reader can find it, for the case of homogeneous reactors, elsewhere (Morbidelli and Varma, 1982).

This observation allows one to readily identify the region of parametric sensitivity, once the critical condition (i.e., the value of α_c) is found. This can be calculated through two different procedures, depending on which of the two possible routes the system takes to approach criticality:

1. The region with positive second-order derivative of θ_p vs. x develops at some $x\epsilon(0, 1)$, corresponding to some position inside the reactor. Such a region is bounded by two inflection points, which at criticality, where the runaway region is infinitesimally small, coincide. Thus, the critical value α_c is that which makes the second and third derivatives of θ_p vs. x vanish simultaneously at the same positive conversion value:

$$\frac{d^2\theta_p}{dx^2} = \frac{d^3\theta_p}{dx^3} = 0 \tag{10}$$

2. The second-order derivative of θ_p vs. x at the reactor inlet (i.e., $x = 0$) turns from negative to positive. In this case α_c is the α value that makes

$$\frac{d^2\theta_p}{dx^2} = 0 \quad \text{at} \quad x = 0. \tag{11}$$

Note that from a topological point of view the two routes are identical, since also in the second case a region with positive second-order derivative, originating from a point where the condition of Eq. 10 is satisfied, is formed; but this occurs at a negative conversion value where the model is obviously meaningless. Criticality is then attained only when the runaway region where $(d^2\theta_p)/dx^2 > 0$ has grown enough (by increasing α) to reach the value $x = 0$, that is, the reactor inlet.

The numerical procedure adopted for computing α_c from Eq. 10 or 11 is based on the isocline method, as also utilized in previous studies (Morbidelli and Varma, 1982, 1986a). A detailed description of this procedure for the present case is given elsewhere (Morbidelli, 1987).

It is convenient here to mention only briefly the issue of reactor multiplicity, since it has also been discussed in detail elsewhere (Morbidelli and Varma, 1986a) and the presence of intraparticle concentration gradients does not change the picture from this point of view. In particular, it was shown that the multiplicity behavior of plug flow heterogeneous reactors is identical to that of the inlet catalyst particle. When addressing the parametric sensitivity issue, we limit ourselves to the case where the inlet particle, if it exhibits multiplicity, operates in the lower conversion branch. This is because when the particle operates in the higher conversion branch, or in the ignited regime, the reaction rate is so high that the reactant is very rapidly depleted, and so a self-accelerating increase of temperature cannot be sustained. Thus, when the inlet particle operates in the ignited regime, runaway of the reactor is rather unlikely, and in any event it would be of very little practical interest.

A reactor whose inlet particle operates in the low-conversion branch may be characterized by an ignition, that is, a jump from the lower to the higher conversion branch of the catalyst particle somewhere along the reactor length. This is a situation much more drastic than runaway itself, since the particle temperature is not only accelerating with conversion, that is, $(d^2\theta_p)/dx^2 > 0$, but undergoes a discontinuity with a finite increase. Thus, runaway occurs at an α value smaller than those leading to ignition phenomena, or for a fixed α value, ignition along the reactor always follows runaway. This can readily be seen by recalling that ignition can occur only at a bifurcation point; however, as discussed above, when the bifurcation point is approached the reactor exhibits a locally sensitive behavior, which leads to runaway.

In conclusion, when seeking the critical α value leading to runaway, it can safely be assumed that the reactor exhibits a unique steady state that does not involve ignition phenomena. The latter can occur only for operating conditions within the parametrically sensitive region.

Regions of Parametric Sensitivity

It may be seen from Eqs. 1–8 that the steady state behavior of the heterogeneous one-dimensional plug flow reactor is fully characterized by eight dimensionless parameters: reaction order n, inlet temperature θ^i, Lewis number Le, activation energy γ, heat of reaction α, heat transfer coefficient β, Thiele modulus Φ_w, and mass transfer resistance A_p. The last could be replaced by the more common Biot number for mass transfer, $Bi_m = \Phi_w^2/A_p$. However, maintaining A_p has the advantage of a direct connection with our previous results, in the case where intraparticle mass transfer resistance is negligible (Morbidelli and Varma, 1986a).

In Figures 1a–1f the regions of parametric sensitivity, in the heat of reaction, α vs. Thiele modulus Φ_w, plane are shown for various values of each of the other six dimensionless parameters. In all cases, in order to obtain a clear graphical representation only the lower bound of the sensitivity region is shown; the upper bound, corresponding to inlet particle ignition, is omitted. The latter is actually of little practical interest since it separates two regions, one sensitive and the other nonsensitive but where the reactor operates in the ignited regime, of which neither is in fact desirable in industrial applications.

As expected on physical grounds, runaway always occurs for larger α values as the Thiele modulus increases. For sufficiently large Φ_w the reactor becomes controlled by the interparticle transport, and runaway does not occur.

The sensitivity region enlarges for lower reaction order n, Figure 1a, as well as for lower Lewis number Le, Figure 1e. This latter behavior may be explained physically by noting that lower Le values, with fixed A_p and Φ_w, lead to lower interparticle heat transfer coefficients h. Therefore, the temperature gradients between the catalyst particle and the external fluid increase, thus enhancing the sensitivity of the particle temperature itself. A similar behavior is exhibited when, for fixed Le and Φ_w, the value of the external mass transfer resistance parameter A_p is increased. From Figure 1f it appears that for decreasing values of the intraparticle mass transfer coefficient k_g (i.e., increasing A_p), runaway becomes more likely. However, it should be noted that for sufficiently large A_p values the reactor becomes controlled by interparticle mass and heat transfer, and thus runaway cannot occur any further. This is shown more clearly in Figure 2, where the parametric sensitivity regions in the α vs. A_p plane are shown for various values of the Thiele modulus Φ_w. Note in passing that this is the parameter plane previously adopted when studying the case of negligible internal diffusion resistances (Morbidelli and Varma, 1986a); in this case the upper boundary of the sensitivity region, given by the inlet particle ignition point, is shown for consistency with the correspond-

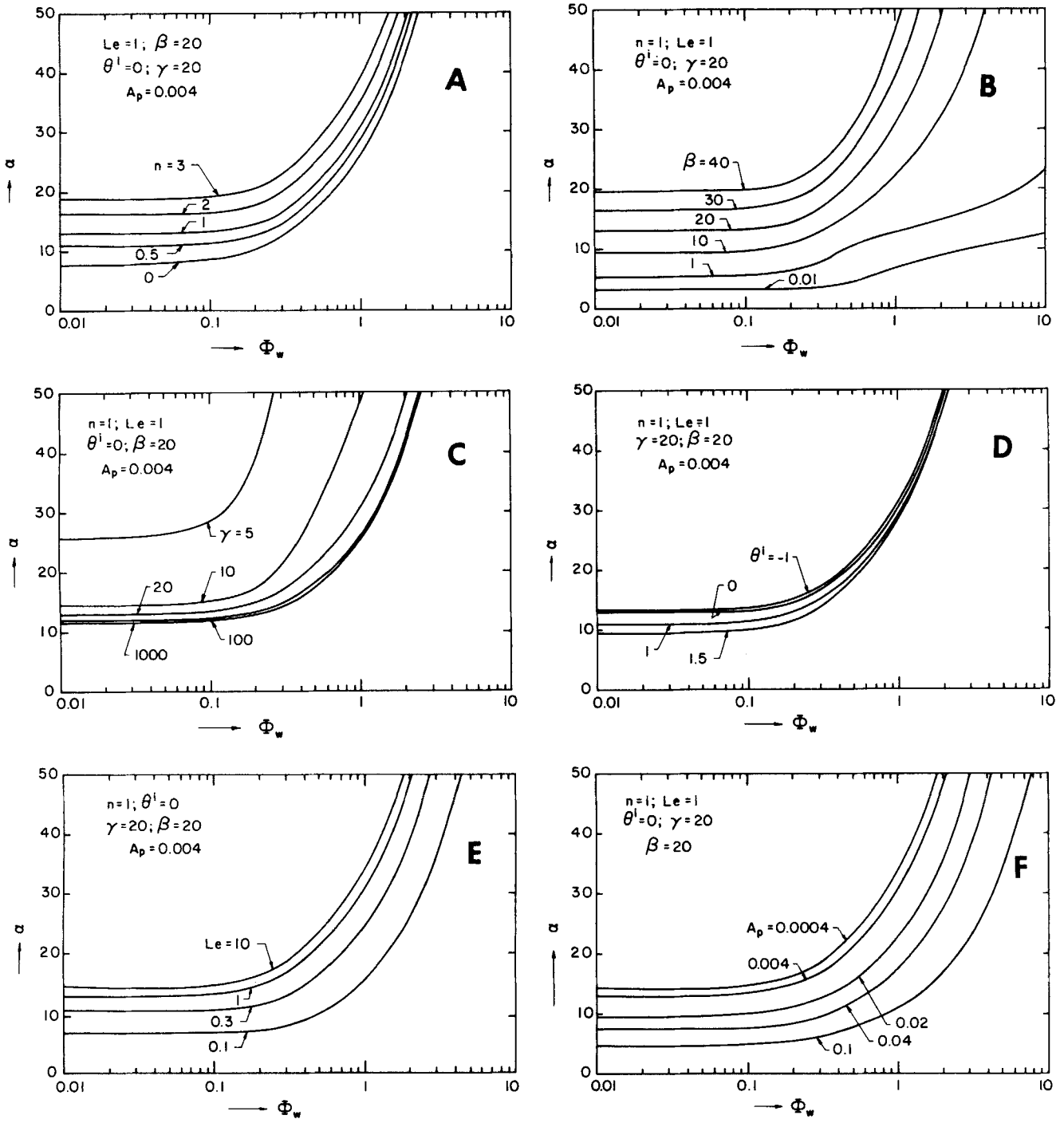

Figure 1. Influence of various parameters on region of parametric sensitivity.

(a) Reaction order n (d) Inlet temperature θ^i
(b) Heat transfer β (e) Lewis number Le
(c) Activation energy γ (f) Interparticle mass transfer resistance A_p

ing Figures 8a–8d reported in the previous paper. It is clear that for increasing values of Φ_w, the parametric sensitivity region progressively shrinks, and eventually disappears for sufficiently large Φ_w values.

Similarly, as has already been established using simpler reactor models, it is found that runaway is more likely for smaller heat transfer parameter β, Figure 1b, larger activation energy γ, Figure 1c, and larger inlet temperature θ^i, Figure 1d.

On the whole, by examining the parametric sensitivity regions shown in Figures 1 and 2, it can be concluded that both inter- and intraparticle transport limitations have a significant impact on reactor sensitivity, which cannot be ignored as is done when using pseudohomogeneous models. It also appears that inter- and intraparticle resistances have a qualitatively different effect on extension of the parametric sensitivity region. As interparticle mass and heat transfer resistances increase, Figure 2, the

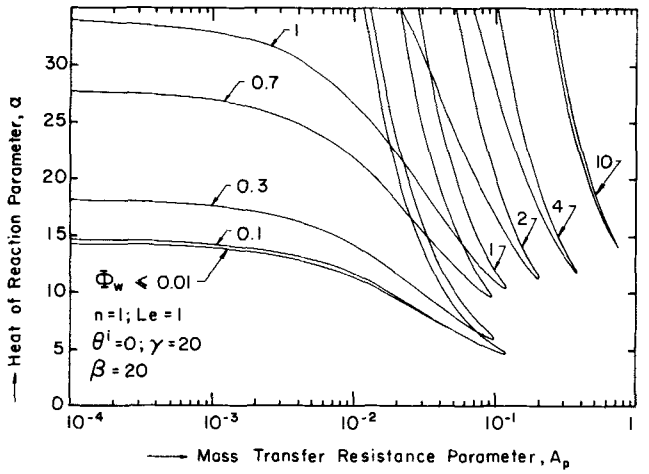

Figure 2. Influence of Thiele modulus Φ_w on region of parametric sensitivity in α-A_p plane.

critical α value for runaway decreases continuously to a point where the reactor is largely controlled by external mass and heat transfer; then runaway is no longer possible. On the other hand, as intraparticle mass transfer resistance increases, Figure 1, runaway becomes less and less likely (i.e., the critical α value increases). Thus, for any given α value there exists a Φ_w value beyond which the reactor is controlled by transport processes, and runaway does not occur.

It is also important to explore, from the catalytic reactor sensitivity point of view, the reliability of local criteria widely used in the literature to establish the importance of inter- and intraparticle concentration and temperature gradients (Doraiswamy and Sharma, 1984). When dealing with tubular reactors in an *a priori* fashion, these local criteria can only be used to check the import of transport limitations at the reactor inlet—the only location where operating conditions are known *a priori*. Considering in particular the local criteria developed by Mears (1971), and for the case of $T^i = T_w$, these can be restated as follows:

1. Interparticle temperature gradients can be neglected when

$$\frac{\alpha A_p}{Le} < 0.05 \tag{12a}$$

2. Intraparticle concentration gradients can be neglected when

$$\Phi_w^2 < 1 \tag{12b}$$

where, for simplicity, reference is made to a first-order reaction. By comparing these criteria with the results shown in Figures 1 and 2, it appears that when the reactor approaches the sensitivity region, they are not reliable for all operating conditions. An example showing that inter- and intraparticle diffusion resistances, although satisfying both conditions, Eqs. 12a and 12b, can still significantly affect the boundary of the sensitivity region, is given in a later section of this work, where a comparison with experimental data is also reported.

Limiting Behavior of the Reactor Model

Some interesting insights into the sensitivity behavior of fixed-bed catalytic reactors can be gained by analyzing the model under consideration for limiting values of the Thiele modulus, Φ_w.

Case of small Thiele modulus, $\Phi_w \ll 1$

From Eqs. 6–8 it readily follows that as $\Phi_w \to 0$, $\eta \to 1$, and thus the heterogeneous model used in this work (HEI), accounting for external as well as internal diffusion resistances, approaches the model (HE) analyzed previously by Morbidelli and Varma (1986a), which accounts only for external transport resistances. It can be seen that the critical values of α, shown in Figures 1a to 1d for $\Phi_w \to 0$, coincide with those shown in Figures 8a to 8d of the earlier paper.

Moreover, when also $A_p \to 0$, and Le is fixed (i.e., when both external mass and heat transfer resistances vanish), both the HEI and HE models approach the pseudohomogeneous (PH) model previously investigated (Morbidelli and Varma, 1982). Also in this case, the critical α values calculated by the HEI model as $A_p \to 0$ and $\Phi_w \to 0$, Figures 1f and 2, become identical with those calculated from the PH model.

Case of large Thiele modulus, $\Phi_w \gg 1$

From inspection of Eqs. 6–8 it is seen that as $\Phi_w \to \infty$, $\Phi \to \infty$, and thus

$$\eta \to 1/\Phi \tag{13}$$

Introducing the new dimensionless temperatures

$$t = T/T_w \text{ and } t_p = T_p/T_w \tag{14}$$

and using Eq. 13, the HEI model (i.e., Eqs. 9, 4, 5) reduces to

$$\frac{dt}{dx} = \frac{\alpha}{\gamma} - \beta\Phi_w \frac{(t-1)\exp\left[-(t_p-1)\gamma/2t_p\right]}{(1-x_p)^{(n+1)/2}} \tag{15}$$

$$t_p = t + \frac{\alpha}{\gamma}\frac{A_p}{Le\Phi_w}\frac{(1-x_p)^{(n+1)/2}}{\exp\left[-(t_p-1)\gamma/2t_p\right]} \tag{16}$$

$$x_p = x + Le\frac{\alpha}{\gamma}(t_p - t) \tag{17}$$

Introducing now the same dimensionless temperatures, Eq. 14, in the HE model, as reported by Morbidelli and Varma (1986a) in their Eqs. 1, 2, 4, and 5, it follows that

$$\frac{dt}{dx} = \frac{\alpha}{\gamma} - \beta\frac{(t-1)\exp\left[-(t_p-1)\gamma/t_p\right]}{(1-x_p)^n} \tag{18}$$

$$t_p = t + \frac{\alpha}{\gamma}\frac{A_p}{Le}\frac{(1-x_p)^n}{\exp\left[-(t_p-1)\gamma/t_p\right]} \tag{19}$$

$$x_p = x + Le\frac{\gamma}{\alpha}(t_p - t) \tag{20}$$

By comparing the two models, it can be concluded that in the limit of large Thiele modulus Φ_w, the HEI model becomes identical to the HE model (where intraparticle gradients are neglected), whose parameters are related to the original ones

through the following relationships:

$$n_s = (n+1)/2 \qquad Le_s = Le$$
$$\gamma_s = \gamma/2 \qquad \alpha_s = \alpha/2 \qquad (21)$$
$$A_{ps} = A_p/\Phi_w \qquad \beta_s = \beta\Phi_w$$

where subscript s refers to parameters of the HE model equivalent to the original HEI model in the limit of large Φ_w.

This result is quite reasonable, since it is well known that under internal diffusion control the reaction rate exhibits an apparent activation energy that is one-half the true value, and an apparent reaction order equal to one-half the true value plus one (Carberry, 1976; Froment and Bischoff, 1979). Moreover, the original parameter, A_p, representing the ratio between reaction rate and interparticle mass transfer rate, is transformed into $A_{ps} = A_p/\Phi_w$, which represents the ratio between reaction rate modified by internal diffusion, and the interparticle mass transfer rate. A similar consideration holds for the heat transfer parameter β as well.

This finding allows one to define the critical value α_c (given by Eq. 10) for the HEI model in the limit of large Φ_w, by analyzing the corresponding HE model, whose parameters are defined by Eq. 21, as $\Phi_w \to \infty$. It may be shown (Morbidelli, 1987) that this limiting value of α_c is given by

$$\alpha_c = 2\beta \frac{\theta_m g(\theta_m)}{(1-\omega)} \Phi_w \qquad (22a)$$

where $\theta_m = \gamma_s[\gamma_s - 2 - \sqrt{\gamma_s(\gamma_s - 4)}]/2$, and $\omega = A_p\beta/Le$. This confirms that for any given α value there exists a Φ_w value beyond which the reactor behavior is controlled by transport phenomena, and thus runaway does not occur.

It may also be shown (Morbidelli, 1987) that the limiting value of α, at which ignition occurs at the reactor inlet (given by Eq. 11), as $\Phi_w \to \infty$ is given by

$$\bar{\alpha} = \frac{2Le}{A_p}(\theta_{p^*} - \theta^i) g(\theta_{p^*}) \Phi_w \qquad (22b)$$

where $\theta_{p^*} = \gamma_s[\gamma_s - 2 - \sqrt{\gamma_s^2 - 4(\gamma_s + \theta^i)}]/2$. Comparing $\bar{\alpha}$ and α_c, it becomes clear that $\bar{\alpha} > \alpha_c$ always, so that as α (i.e., the dimensionless heat of reaction) increases, as expected, parametric sensitivity is encountered prior to ignition.

Comparison of parametric sensitivity regions

Let us now compare the parametric sensitivity regions predicted by the three models: HEI, HE, and PH. In Figure 3 the solid curves represent the lower boundaries of such regions as predicted by the HEI model, as a function of Φ_w, for three different sets of parameter values. For each of these, two broken-line curves obtained from the HE model are also shown: the first, valid for small Φ_w, is obtained using the same parameter values as in the HEI model (but keeping $\eta = 1$ in Eqs. 3, 4, and 9), while the second, valid for larger Φ_w, is obtained using the modified parameters given by Eq. 21 as a function of Φ_w. As expected, the two broken-line curves merge into the solid curve as $\Phi_w \to 0$ and ∞, respectively.

However, it may be noticed that the broken-line curve valid for large Φ_w remains in fact rather close to the solid curve even at

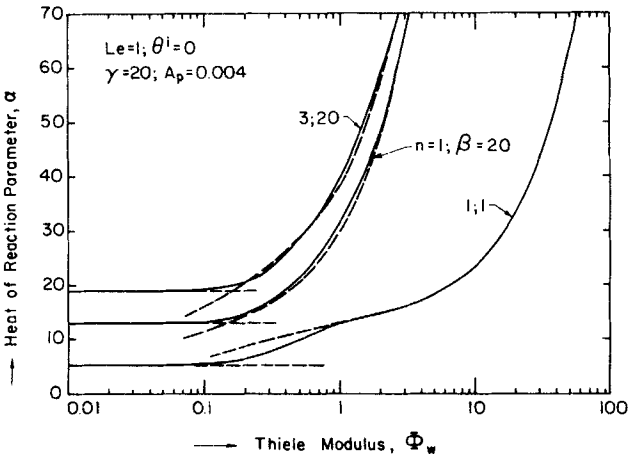

Figure 3. Comparison of regions of parametric sensitivity predictions.
— HEI model; --- HE model

relatively small Φ_w values, almost reaching the region where the other asymptotic curve, for $\Phi_w \to 0$, is still quite accurate. In other words, the HE model, with the parameters modified according to Eq. 21, predicts almost the same parametric sensitivity region as the full HEI model, for Φ_w values ranging from ∞ to as low as about 0.2. This is quite surprising, since it is known that approximation of Eq. 13, on which Eq. 21 is based, provides accurate results only for Φ_w values larger than about 5 (Froment and Bischoff, 1979).

In order to investigate this point further, let us consider the particle temperature vs. conversion profiles shown in Figures 4a and 4b for two different sets of parameter values, both near criticality. The solid and broken-line curves correspond to models HEI and HE, respectively; for the latter, the parameters are modified according to Eq. 21. In Figure 4a, $\Phi_w = 20$ and thus, as expected, the two models predict very similar profiles of θ_p vs. x, and thus also very similar critical α values. On the other hand, in Figure 4b $\Phi_w = 0.15$ and thus the temperature profiles predicted by the two models are vastly different; however, they still predict very similar critical α values. This indicates that although the two models predict quantitatively different reactor behavior, their intrinsic sensitivity character is preserved. Thus, they enter the parametric sensitivity region almost simultaneously, although they lead to completely different temperature and conversion values. This feature could be ascribed at least in part to the intrinsic nature of the runaway criterion that has been adopted in this work.

For practical purposes, this feature may be exploited to obtain a close estimate of the effect of intraparticle mass transfer resistance on the parametric sensitivity region, based on the results of a model that accounts only for interparticle heat and mass transfer resistances.

The solid curves in Figure 5 show the asymptotic behavior of α_c for large Φ_w values, for all three models: HEI, HE, and PH (in the last two the parameters are modified according to Eq. 21, where for the PH model obviously $A_{ps} = 0$). It appears that for each model the critical α approaches the corresponding straight-line asymptote (dash-dot) representing the asymptotic analytical solution. This is given by Eq. 22a, where $\omega = 0$ for the PH model, while $\omega > 0$ for the HEI and HE models (in the case shown in Figure 5, $\omega = 1.6$). In Figure 5 the two curves where

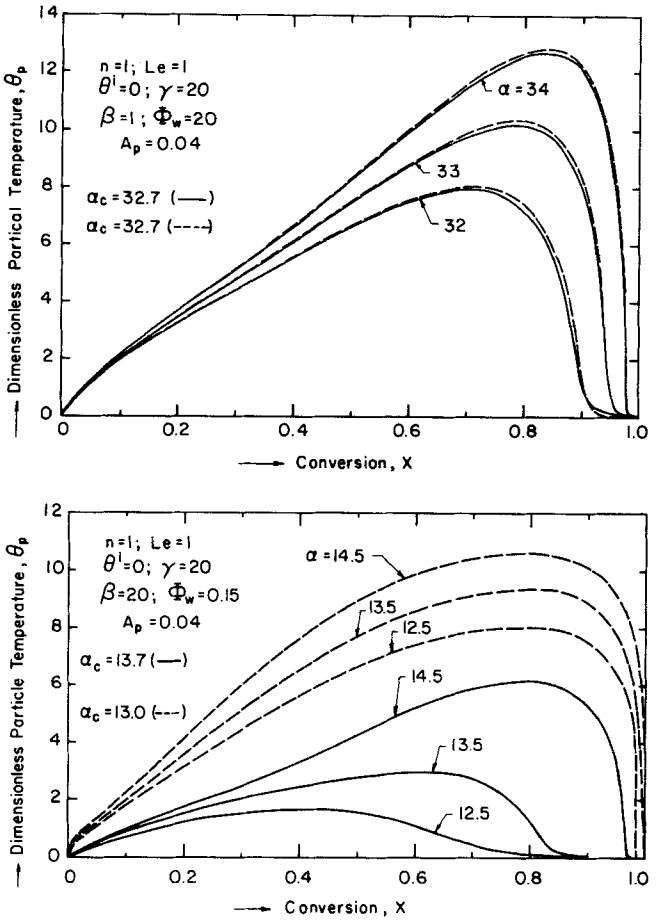

Figure 4. Dimensionless particle temperature vs. conversion profiles for various values of heat transfer parameter α around criticality.

— HEI model; --- HE model, parameters modified according to Eq. 21
(a) $\Phi_w = 20$; (b) $\Phi_w = 0.15$

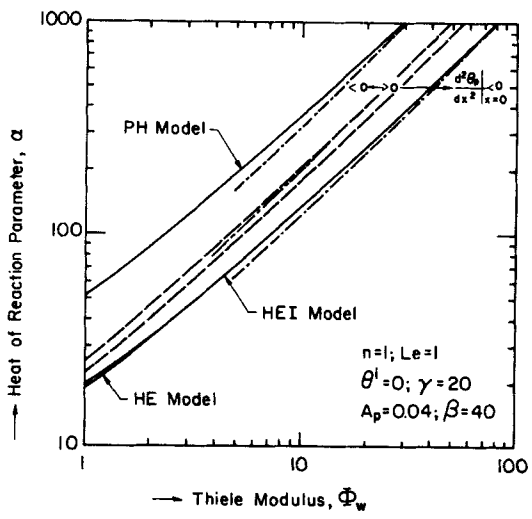

Figure 5. Asymptotic behavior for large Thiele modulus Φ_w.

— Critical α_c (Eq. 10) for HEI, HE, and PH models
--- Occurrence of a sign change in second-order derivative of inlet particle temperature
----- Asymptotic solutions: Eq. 22a for — curves, Eq. 22b for --- curves.

the second-order derivative of the inlet particle temperature changes sign are also shown (dashed curves). The upper one of these, which also indicates the occurrence of ignition at the reactor inlet, for large Φ_w approaches the dash-dot straight line given by the asymptotic analytical solution (i.e., Eq. 22b).

Comparison with Previous Runaway Criteria

In this work, as well as in the related previous paper (Morbidelli and Varma, 1986a), the role of inter- and intraparticle transport resistances on fixed-bed reactor parametric sensitivity has been fully elucidated. This aspect has been overlooked in the prior literature; only two relevant contributions have appeared so far.

The first, by McGreavy and Adderly (1973), deals only with local sensitivity and does not consider global reactor behavior, so that the reported parametric sensitivity criterion requires knowledge of the fluid temperature profile along the reactor, which is not available *a priori*. We have previously shown (Morbidelli and Varma, 1986a) that the criterion based on the particle temperature, which is utilized in this work, fully accounts also for the local sensitivity aspect of the problem.

In the second contribution, by Rajadhyaksha et al. (1975), the runaway criterion proposed by van Welsenaere and Froment (1970) in the context of homogeneous reactors was applied. This criterion is based on the fluid temperature, rather than the particle temperature, so local sensitivity is not accounted for and has to be introduced *a posteriori*. Rajadhyksha et al. considered four separate limiting regimes, and developed separate procedures for calculating the parametric sensitivity region boundary for each of them.

In the particular case where intraparticle mass and heat transfer resistances are negligible, they derived an analytic expression for the critical α value. Using the notation of this work, it is given by the following set of equations:

$$\bar{\alpha} = \beta\bar{\theta}_p g(\bar{\theta}_p)/(1 + \beta A_p/Le) \tag{23}$$

$$\bar{\theta}_p = \gamma[\gamma - 2 + \sqrt{\gamma(\gamma - 4)}]/2 \tag{24}$$

$$\bar{\theta} = \theta_p - A_p\bar{\alpha}/Le\,g(\bar{\theta}_p) \tag{25}$$

$$\alpha_c = \frac{1}{2}\left\{\bar{\alpha} + \bar{\theta} + \bar{\theta}\left[1 + \left(\frac{\beta g(\bar{\theta}_p)}{(1 + \beta A_p/Le)}\right)^{1/2}\right]^2\right\} \tag{26}$$

which according to the original work applies for $A_p < 0.05$ and $\Phi_w = 0$.

A comparison of the boundaries of the parametric sensitivity region calculated by Eqs. 23 to 26 (broken-line curve) and those predicted by this work (solid curve) is shown in Figure 6. It appears that while the qualitative behavior is similar, the discrepancy between the predicted critical values of the heat transfer parameter α, for a given A_p, is significant. This is due to their overlooking local sensitivity, but primarily to their choice of a different basic sensitivity criterion. Specifically, the predicted sensitivity boundaries are different even in the limit $A_p \to 0$, where external resistances are also negligible, and thus the pseudohomogeneous (PH) model behavior is approached (Morbidelli and Varma, 1985).

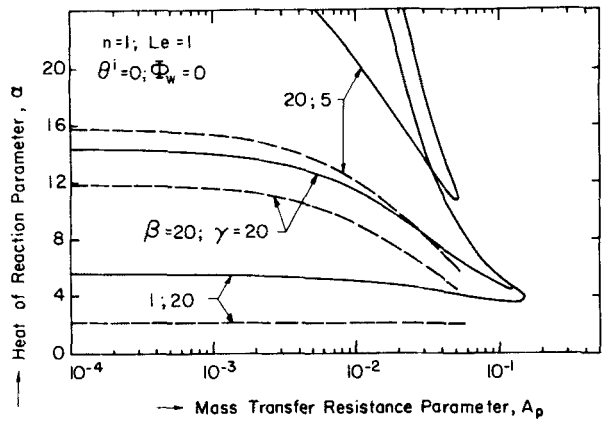

Figure 6. Comparison of regions of parametric sensitivity.

— This work; --- Rajadhyaksha et al. (1975)

Comparison with Experimental Data

Despite the importance of the problem, only one complete experimental analysis devoted to determination of the parametric sensitivity region of a catalytic fixed-bed reactor has been presented to date in the literature (Emig et al., 1980). That work studied vinyl acetate synthesis catalyzed by zinc acetate supported on activated carbon. A previous detailed kinetic study (El-Sawi et al., 1977) showed that this reaction follows first-order kinetics, with dimensionless activation energy $\gamma \simeq 20$ at the wall temperatures examined in the sensitivity experiments.

The reactor was well-instrumented, in order to have close control of inlet flow rate and composition and to measure the fluid temperature at various positions along the reactor axis. In all experiments the inlet temperature was set equal to the wall temperature (i.e., $\theta^i = 0$). As experimental criteria for runaway, a rise in maximum temperature ≥ 3 K/s or a rise above 510 K (upper limit for stability of their catalyst) were considered.

The experimental results are shown in Figures 7a and 7b, where the open circles indicate safe operating conditions, while filled circles indicate runaway situations. Figure 7a also shows the regions of parametric sensitivity predicted by the criteria presented in this work, accounting only for interparticle ($\Phi_w = 0$; solid curves) or for both inter- and intraparticle ($\Phi_w \neq 0$; broken-line curves) mass and heat transfer resistances. It appears that the introduction of transport resistances changes the shape of the critical curve qualitatively, with respect to that predicted by a pseudohomogeneous model (PH model, corresponding to curve $A_p = 0$ in the figure), and yields sensitivity boundaries much closer to those observed experimentally.

It is worth stressing that a quantitative comparison is not attempted here; for example, the various experimental runs involve different Reynolds numbers, but they are compared in the same graph with curves calculated with fixed external transport coefficients. However, the qualitative behavior seems to be sufficient for drawing useful conclusions.

Consider now Figure 7b, where the runaway boundaries for first- and zero-order reactions using the pseudohomogeneous model, taken either from this work (solid curve) or from Barkelew (1959) (broken-line curve), are shown. It is clearly visible that all of these curves have the same shape, a shape different from that indicated by the experimental data. Thus, a change in the reaction order, which Emig et al. (1980) proposed as a possible explanation of their experimental observations, does not seem to provide the shape of the experimental boundary of the runaway region. The dot-dash curve in Figure 7b represents the predictions of a two-dimensional pseudohomogeneous model (as reported in Figure 1 of Emig et al., 1980) whose parameters were determined by directly fitting the experimental data. Again, the shape of this curve does not match the experimental evidence, since it is of the same type as all the others obtained from simpler, but homogeneous, models. Thus, although radial temperature gradients are certainly significant, they do not seem to be responsible for the change of shape of the sensitivity region boundary.

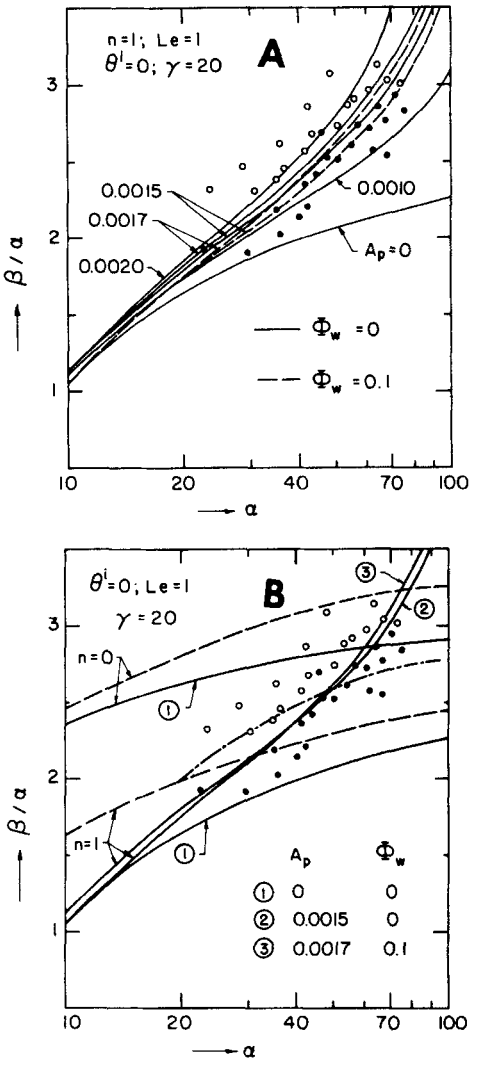

Figure 7. Comparison of predicted region of parametric sensitivity with experimental data.

● Runaway condition, O nonrunaway condition; data of Emig et al. (1980)
(a) — This work, $\Phi_w = 0$; --- this work, $\Phi_w = 0.1$
(b) — This work; --- Barkelew (1959); ·-·-· Emig et al. (1980)

It can therefore be concluded that mass and heat transfer resistances seem to be the only phenomena which can change the typical shape of the pseudohomogeneous boundary into that indicated by the experimental data.

It should be stressed that such a radical qualitative change occurs even for relatively small values of interphase resistances,

$A_p \simeq 10^{-3}$, near that range of values which according to the Mears (1971) local criteria (applied at reactor inlet conditions) should guarantee the absence of interparticle concentration and temperature gradients. In fact, in all the simulations we have performed such temperature gradients are equal to about 1–2 K at the reactor inlet, and rise to no more than 6 K at the hot spot. Thus, interparticle temperature gradients never exceed 1.5%, but they have a strong effect on the boundary of the sensitivity region. This is of course quite reasonable because of the high sensitivity of the model to parameter values in this region. This is also apparent in the results shown in Figure 7a, where small changes in the value of the external mass tranfser parameter A_p (and thus also of the heat transfer parameter, since Le is kept fixed and equal to unity) produce significant changes in the region of parametric sensitivity.

A crosscheck of the reliability of the model can be obtained by comparing the simulated temperature and concentration profiles along the reactor with experimental data. A comparison of the measured maximum temperature values with those predicted by the heterogeneous one-dimensional plug flow model has been described in detail elsewhere (Morbidelli, 1987). It shows that the predicted temperature values closest to the experimental values are obtained for A_p equal to about 0.0017, which is the same value that produces boundaries of the parametric sensitivity region closest to those observed experimentally, Figure 7. This consistency in the model performance supports the conclusion drawn in this work.

Another indication of the reliability of the results described above can be obtained by comparing the A_p values used in Figure 7 with those predicted *a priori* from semiempirical relationships reported in the literature. In particular, using the correlations recommended by Doraiswamy and Sharma (1984) it is found that in the experimental conditions of Emig et al. (1980), A_p lies in the range 0.001–0.004. Moreover, the variation of the Reynolds number in the experiments leads to A_p changes by a factor of about 1.7. Considering the moderate accuracy of these semiempirical correlations, particularly in the presence of chemical reaction, the agreement with the A_p values used in Figure 7 is quite satisfactory.

Finally, it is worth repeating that a detailed quantitative comparison has not been attempted at this stage, because there are phenomena not included in the model that certainly affect reactor performance, for example, the existence of radial temperature gradients. However, the analysis reported above, on the qualitative shape of the parametric sensitivity region boundary, indicates that only interparticle transport resistances can explain the experimental findings. The amount of resistance actually required to significantly affect the runaway region is quite small, such that interphase concentration and temperature gradients could safely be ignored when the reactor operates outside the sensitivity region. This stands as a warning to the pitfall that exists for directly extending knowledge based upon mild operating conditions to situations where the region of parametric sensitivity is approached.

Notation

$A = L\rho_b k(T_w)C^{i^{n-1}}/\bar{v}$
$A_p = \rho_b k(T_w)C^{i^{n-1}}/k_g a_v$
a_v = particle surface per unit reactor volume, m^{-1}
$B = \rho_b k(T_w)(-\Delta H)C^{i^n}L\gamma/\rho_f c_p T_w \bar{v}$
$B_p = \rho_b k(T_w)(-\Delta H)C^{i^n}\gamma/ha_v T_w$
Bi_m = mass Biot number, Φ_w^2/A_p
C = reactant concentration, mol/m^3
$C = 4LU/\bar{v}\rho_f c_p d_t$
c_p = specific heat, J/K · kg
D_e = effective diffusion coefficient, m^2/s
d_t = diameter of reactor tube, m
E = activation energy, J/mol
$g(\theta)$ = Arrhenius factor, $\exp[-\theta/(1+\theta/\gamma)]$
h = heat transfer coefficient, $J/m^2 \cdot s \cdot K$
L = reactor length, m
Le = external transport Lewis number, $A_p\alpha/B_p = h/k_g\rho_f c_p$
k = reaction rate constant, $mol \cdot (m^3/mol)^n/s \cdot kg$
k_g = mass transfer coefficient, m/s
m = integer characteristic of pellet shape; =0 for infinite slab, =1 for infinite cylinder, =2 for sphere
n = reaction order
R = ideal gas constant, J/K · mol
R_p = characteristic pellet dimension; half-thickness ($m = 0$), radius ($m = 1, 2$), m
S_p = particle surface, m^2
s = dimensionless reactor length, s'/L
s' = reactor axial coordinate, m
t = dimensionless temperature, T/T_w
T = temperature, K
U = overall heat transfer coefficient, $J/m^2 \cdot K \cdot s$
V_p = particle volume, m^3
$\bar{v}$ = superficial velocity, m/s
x = conversion, $(C^i - C)/C^i$

Greek letters

$\alpha = B/A = (-\Delta H)C^i\gamma/T_w\rho_f c_p$
$\beta = C/A = 4U/\rho_b k(T_w)\rho_f c_p d_t C^{i^{n-1}}$
$\gamma = E/RT_w$
ΔH = heat of reaction, J/mol
η = effectiveness factor
θ = dimensionless temperature, $(T - T_w)E/RT_w^2$
Φ^2 = normalized Thiele modulus, $(V_p/S_p)^2 (n+1)/2 [\rho_s k(T_p)C_p^{n-1}]/D_e$
Φ_w^2 = normalized Thiele modulus, $(V_p/S_p)^2 (n+1)/2 [\rho_s k(T_w)C^{i^{n-1}}]/D_e$
ρ_b = catalyst bulk density, kg/m^3
ρ_f = fluid density, kg/m^3
ρ_s = catalyst particle density, kg/m^3

Superscript

i = inlet value

Subscripts

c = critical value
p = catalyst particle
s = parameters of equivalent HE model, Eq. 21
w = wall

Models

HE = heterogeneous model accounting for interparticle mass and heat transfer
HEI = heterogeneous model accounting for interparticle mass and heat transfer, and for intraparticle mass transfer
PH = pseudohomogeneous model

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