Runaway Limits for Adiabatic Packed-Bed Catalytic Reactors

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Most existing criteria for predicting the critical residence time (or flow rate) at which runaway occurs in an adiabatic catalytic packed-bed reactor do not account for interphase heat-transfer resistance and intraparticle diffusion. When these transport limitations exist, the critical residence time at which runaway occurs is given by

$$\tau = \frac{RT_o}{E}\frac{T_o}{\Delta T_{ad}}\frac{f(\phi_o)}{k(T_o)} - 2.72\left(\frac{\rho_f C_{pf}}{ha_v}\right).$$

This simplified equation gives the runaway locus as a function of the feed temperature (T_o), adiabatic temperature rise (ΔT_{ad}), activation energy (E), reaction rate constant at feed temperature [$k(T_o)$], fluid-solid heat-transfer coefficient (h), the interfacial area per unit bed volume (a_v), and the normalized Thiele modulus (ϕ_o). The function $f(\phi_o)$ accounts for the intraparticle diffusional effects and may be approximated by the two asymptotes, $f(\phi_o) = 1$ when $\phi_0 < 1/2$ and $f(\phi_o) = 2\phi_o$ when $\phi_o > 1/2$. Similar analytical results are presented for other reactor models and also for more complicated reaction networks. A practical example shows the calculation of the runaway boundary for industrial hydrogenation reactions obeying Langmuir-Hinshelwood kinetics.

Introduction

Parametric sensitivity or runaway of a chemical reactor describes a situation in which a small change in an operating variable such as feed temperature, concentration, or flow rate induces a large change in the temperature profile of the reactor. A reactor runaway can promote undesired side reactions, catalyst deactivation, loss of production, and selectivity of the desired product. Whenever possible, one would like to design reactors whose performance is insensitive to small changes in the operating conditions and design variables. Therefore, it is important to be able to predict the boundary of the region of operating conditions beyond which a reactor runaway may occur due to a small design error, or perturbation of an operating variable.

There have been many studies in the literature on the derivation of runaway criteria (Wilson, 1946; Barkelew, 1959, 1984; Thomas, 1961; Adler and Enig, 1964; van Welsenaere and Froment, 1970; Rajadhyaksha et al., 1975; Zeldovich et al., 1985; Morbidelli and Varma, 1986, 1987; Hagan et al., 1987, 1988a,b; Bauman and Varma, 1990; Balakotaiah, 1989; Balakotaiah and Luss, 1991; Balakotaiah et al., 1995). In these prior works, there are two runaway criteria that have been developed. In the first one (which may be referred to as the criterion for unconditionally safe operation), the residence time (or equivalently, the length of the reactor or velocity) does not appear. When this first criterion is satisfied (which can be done by adjusting other operating variables such as inlet concentrations, temperature or pressure), there is no temperature runaway irrespective of what residence time is used. It guarantees that the maximum slope of the exit-tem-

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perature vs. residence-time diagram is small enough so that small changes in the operating variables cause only small changes in the temperature profile of the reactor. However, in order to ensure such a small slope (or insensitivity), the criterion severely limits the inlet concentrations that can be used by limiting the adiabatic temperature rise. Mathematically speaking, this first criterion is derived by requiring that the bifurcation diagram of temperature vs. residence time has no ignition (or inflection) points. The calculation of this runaway boundary can be done once a model is written and the kinetics are known (Moribidelli and Varma, 1986, 1987; Balakotaiah et al., 1995). For the case of a first-order reaction, this criterion requires that the parameter B $(=E/RT_o^*(\Delta T_{ad}/T_o))$ should be smaller than about 4 for the adiabatic reactor. A detailed analysis of this first runaway criterion for many cooled reactors has been presented by Balakotaiah et al. (1995). It should be pointed out that in many practical situations in which either the adiabatic temperature (ΔT_{ad}) rise or the activation energy is large, this criterion cannot be satisfied unless the reaction mixture is diluted (e.g., by lowering the partial pressure of the key reactant). While such dilution may increase the region of safety, it also reduces the productivity of the reactor, and hence, is not always desired in practice.

The second criterion (which we shall refer to as the weak safety criterion) involves the residence time and is applicable when the first one cannot be satisfied. In this case, there is a critical residence time at which temperature rises very rapidly and one has to limit the actual residence time to smaller than this critical value. In the theory of thermal explosions (Zeldovich et al., 1985), this critical residence time is referred to as the induction period. Again, mathematically speaking, this is the ignition point (or inflection point for the case of the plug-flow model) in the bifurcation diagram of temperature vs. residence time. Because of this limitation on the residence time, the conversion in a single adiabatic bed may be limited before the reaction mixture is cooled. In the design and control of multiple adiabatic reactors in series with interstage cooling, the weak safety criterion provides a rational basis for specifying the reactor length or flow rate in the design, and likewise for determining the maximum conversion in each reactor.

For the case of a single reaction in a homogeneous reactor, Zeldovich et al. (1985), Barkelew (1984), and Balakotaiah (1989) have determined analytical expressions for this critical residence time. For the case of a first-order reaction in an adiabatic reactor, this criterion is approximately given as $Da * B = a$, where Da is the Damköhler number (rate constant at feed conditions times residence time) and B is the parameter defined earlier. The constant a is equal to unity for the plug-flow case and 0.368 for the well-mixed reactor. This criterion is extremely useful, as it can be used to determine the critical residence time (or flow rate) at which runaway occurs as a function of the feed temperature and the kinetic and design parameters.

A major goal of this work is to develop a runaway criterion for adiabatic catalytic reactors similar to the second runaway criterion defining the critical residence time or induction period when the interphase resistances and intraparticle gradients are important. A second goal is to extend the runaway criterion for a single reaction to the multiple-reaction case.

In the next section, we review and interpret the runaway criterion for a single reaction in an adiabatic reactor in which interphase gradients are negligible. In the third section, we examine the influence of external heat-transfer resistance and intraparticle diffusion on the critical residence time for runaway. In the fourth section, we present some analytical expressions as well as calculations for determining the critical residence time for the case of two consecutive (and parallel or simultaneous) reactions. Finally, in the fifth section, we present an example illustrating the calculation procedure and the applicability of our results for industrial hydrogenation and partial oxidation reactions.

Runaway Criterion for a Single Reaction (Pseudohomogeneous Models)

In this section, we review the runaway criterion presented by Zeldovich et al. (1985), Barkelew (1984), and Balakotaiah (1989) for a single reaction in a homogeneous system. This criterion may be applied to catalytic reactors when the interphase transport resistances and intraparticle diffusional effects are negligible.

Plug-flow model

We consider the pseudohomogeneous one-dimensional adiabatic plug-flow model of a catalytic reactor in which a first-order irreversible reaction occurs. The exit conversion (x) and the dimensionless temperature (θ) are given by

$$x = \frac{\theta}{B} \tag{1a}$$

$$\frac{d\theta}{dDa} = (B-\theta)\exp\left(\frac{\theta}{1+\theta/\gamma}\right) \tag{1b}$$

$$\theta = 0 \quad \text{at} \quad Da = 0. \tag{1c}$$

The dimensionless variables and parameters in the preceding equations are defined as follows:

$$x = 1 - \frac{C}{C_o} \qquad \theta = \frac{E}{RT_o}\frac{T-T_o}{T_o} \qquad \gamma = \frac{E}{RT_o}$$

$$\Delta T_{\text{ad}} = \frac{(-\Delta H_R)y_o}{\hat{C}_{pf}} \qquad B = \gamma\frac{(\Delta T_{\text{ad}})}{T_o}$$

$$Da = \tau k(T_o) = \tau k_o \exp\left(-\frac{E}{RT_o}\right).$$

The dimensional activation energy, γ, is a measure of the sensitivity of the rate constant to changes in the temperature, (ΔT_{ad}) is the adiabatic temperature rise (which depends on the mole fraction y_o of the key reactant), and τ is the residence time.

The runaway limit for this model is defined as the inflection point in the bifurcation diagram of the exit temperature vs. the residence time (Da). It can be shown (by differentiation of Eq. 1b), that this inflection point exists only if $B > 1$. Thus, for low values of the activation energy and adiabatic temperature rise, runaway is not a concern. For $B > 1$, the critical residence time at the inflection point may be obtained by integrating Eq. 1b from $Da = 0$ to the inflection point:

$$BDa = \int_0^{B-1} \frac{\exp[-\theta/(1+\theta/\gamma)]}{(1-\theta/B)}\, d\theta. \tag{2a}$$

For B and $\gamma \gg 1$, we can neglect the reactant consumption and use the positive exponential approximation to simplify the integral to give the following slightly conservative expression for the runaway boundary:

$$BDa \approx \int_0^{\infty} e^{-\theta} d\theta = 1.0. \tag{2b}$$

In terms of the residence time, we get

$$\tau = \frac{RT_o}{E}\frac{T_o}{(\Delta T_{\text{ad}})}\frac{1}{k(T_o)} = \frac{RT_o}{E}\frac{T_o}{(\Delta T_{\text{ad}})}\frac{\exp(E/RT_o)}{k_o}. \tag{3}$$

The value of residence time evaluated by Eq. 3 represents the critical residence time above which the temperature in the reactor becomes very sensitive to small variations of the input variables and runaway occurs. Equation 3 gives an explicit formula for this critical residence time for a single reaction in a PFR in terms of the inlet conditions such as feed temperature, adiabatic temperature rise, activation energy, and the frequency factor.

CSTR model

For the case of a homogeneous adiabatic well-mixed reactor, the following simple algebraic equations determine the exit conversion and temperature of the reactor:

$$x = \frac{\theta}{B} \tag{4a}$$

$$\frac{\theta}{Da} = (B-\theta)\exp\left(\frac{\theta}{1+\theta/\gamma}\right). \tag{4b}$$

Once again, we consider the limiting case of B, $\gamma \gg 1$ for which Eq. 4b simplifies to

$$BDa = \theta e^{-\theta}. \tag{4c}$$

The runaway limit is the ignition (or limit) point of Eq. 4c and may be determined analytically to be

$$BDa = e^{-1} = 0.368, \tag{5}$$

or in terms of critical residence time:

$$\tau = 0.368\frac{RT_o}{E}\frac{T_o}{(\Delta T_{\text{ad}})}\frac{1}{k(T_o)} = 0.368\frac{RT_o}{E}\frac{T_o}{(\Delta T_{\text{ad}})}\frac{\exp(E/RT_o)}{k_o}. \tag{6}$$

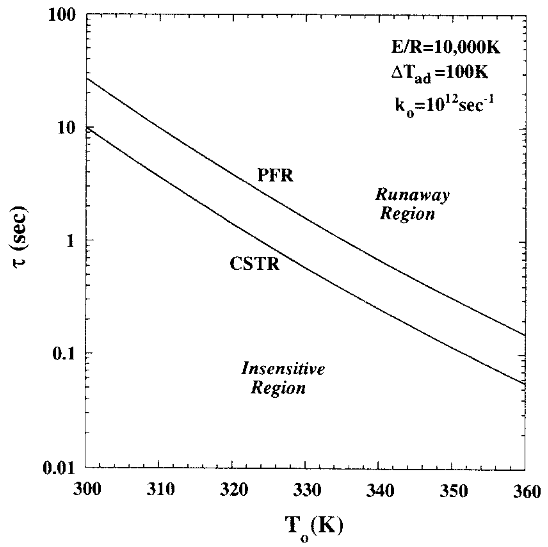

Figure 1. Runaway locus for the two homogeneous models of PFR and CSTR for the case of a single reaction.

The runaway limit can also be calculated for other adiabatic reactor models with intermediate levels of mixing. It was shown by Barkelew (1984) and Balakotaiah (1989) that the numerical constant on the righthand side of Eq. 6 increases from 0.368 for the CSTR to 1.0 for the PFR as the axial heat Peclet number, Pe_h changes from zero (complete mixing) to infinity (no mixing or plug flow).

We show in Figure 1 a plot of the runaway loci given by Eqs. 3 and 6 in the residence time-feed temperature plane for a typical set of parameter values. The most important observation from this plot (and Eqs. 3 and 6) is that the critical residence time decreases exponentially with increase in the feed temperature and is inversely proportional to the inlet reactant mole fraction.

Runaway Criterion for a Single Reaction in an Adiabatic Catalytic Reactor

In this section we extend the runaway criterion of the pseudohomogeneous model to catalytic reactors in which interphase heat-transfer resistance and intraparticle diffusional resistance are significant.

PFR model

We consider the plug-flow model of a catalytic reactor with external heat- and mass-transfer resistances. The solid and fluid temperatures and conversions as a function of residence time are determined by the differential-algebraic system:

$$\frac{d\theta_f}{dDa} = \frac{\theta_s - \theta_f}{Da_{ph}} \tag{7a}$$

$$\frac{\theta_s - \theta_f}{Da_{ph}} = \frac{(B-\theta_f)\exp\left(\dfrac{\theta_s}{1+\theta_s/\gamma}\right)}{1 + Da_{pm}\exp\left(\dfrac{\theta_s}{1+\theta_s/\gamma}\right)} \tag{7b}$$

$$\theta_f = 0 \quad \text{at} \quad Da = 0 \tag{7c}$$

$$x_f = \frac{\theta_f}{B} \qquad x_s = x_f + \frac{(\theta_s - \theta_f)}{B} Le_p. \tag{7d}$$

Here $\theta_s(\theta_f)$ is the dimensionless temperature of the solid (fluid) phase and $x_s(x_f)$ is the conversion of the reactant in the solid (fluid) phase. The new dimensionless parameters that appear in the heterogeneous model are the particle mass and heat Damköhler numbers (Da_{pm} and Da_{ph}) and the particle Lewis number, Le_p, defined as follows:

$$Da_{ph} = \frac{k(T_o)\rho_f C_{pf}}{h a_v} \quad Da_{pm} = \frac{k(T_o)}{k_c a_v} \quad Le_p = \frac{Da_{pm}}{Da_{ph}} = \frac{h}{\rho_f C_{pf} k_c}. \tag{8}$$

The particle mass Damköhler number, Da_{pm}, is defined as the ratio of the characteristic time for interphase mass transfer to that for reaction. Similarly, the particle heat Damköhler, Da_{ph}, is the ratio of the characteristic time for interphase heat transfer to that for reaction. In the limit of $Da_{pm} \to 0$ and $Da_{ph} \to 0$, external mass- and heat-transfer resistances are negligible and the model defined by Eqs. 7a–7d reduces to the pseudohomogeneous plug-flow model. The particle Lewis number, Le_p, is the ratio of the characteristic times for external mass to heat transfer. In the limit of $Le_p \to 0$ interphase mass-transfer resistance is negligible and only the external heat-transfer resistance is important in determining the runaway locus.

It should be pointed out that when the interphase heat-transfer resistance is finite, the solid-phase temperature will always be higher (for exothermic reactions) than the fluid temperature. Hence, using the pseudohomogeneous model, a much lower heat-generation rate is estimated and safe operation may be predicted in the runaway region.

In order to develop a slightly conservative analytical runaway criterion, we make the two usual assumptions of negligible reactant consumption ($B \gg 1$ and $Da_{pm} \ll 1$) and $\gamma \gg 1$ (positive exponential approximation). With these assumptions, Eq. 7b simplifies to

$$\theta_s - \theta_f = BDa_{ph} e^{\theta_s}. \tag{9}$$

The critical residence time at which runaway occurs for the model defined by Eqs. 7a, 7c and 9 may be determined by assuming that at runaway, the particle at the exit of the bed ignites. Thus, in addition to Eqs. 7a, 7c and 9, the following equation (defining particle ignition) must be satisfied:

$$BDa_{ph} e^{\theta_s} = 1. \tag{10}$$

(This equation is obtained by differentiating Eq. 9 with respect to θ_s.) Simplification of the preceding equations gives the runaway locus in the following parametric form:

$$BDa_{ph} = \theta_{so} e^{-\theta_{so}} \tag{11a}$$

$$BDa = e^{-\theta_{so}}(1 - \theta_{so} + \theta_{so} \ln \theta_{so}), \quad 0 \le \theta_{so} \le 1. \tag{11b}$$

Here, θ_{so} is the solid phase temperature at the inlet of the reactor. The corresponding exit solid phase temperature is given by

$$\theta_s = \theta_{so} - \ln(\theta_{so}). \tag{12}$$

When $\theta_{so} \to 0$, the runaway locus approaches that of the pseudohomogeneous model. At the other extreme, when $\theta_{so} \to 1$, $Da = 0$ and $BDa_{ph} = e^{-1}$. The physical interpretation of this limit is that when interphase heat-transfer resistance is significant ($BDa_{ph} > 0.368$), the catalyst particles ignite upon first contact with the fluid (at the inlet of the reactor or equivalently, at zero residence time).

For practical use, it is convenient to write the runaway locus given by Eq. 11 in an explicit form. Rearranging Eqs. 11a and 11b gives

$$BDa + eBDa_{ph} = g(\theta_{so}), \tag{13a}$$

where

$$g(\theta_{so}) = e^{-\theta_{so}}(e\theta_{so} + 1 - \theta_{so} + \theta_{so} \ln \theta_{so}). \tag{13b}$$

Figure 2 shows the dependence of the lefthand side of Eq. 13a on the solid temperature at inlet conditions (θ_{so}) in the range $0 \le \theta_{so} \le 1$. We note that the function $g(\theta_{so})$ decreases from a value of unity (pseudohomogeneous model) to a minimum value of 0.84 as θ_{so} increases from 0 to 0.2. As θ_{so} increases to unity (corresponding to particle ignition), $g(\theta_{so})$ increases and approaches asymptotically the same maximum value of unity. Thus, a good approximation to the runaway locus may be obtained by considering $g(\theta_{so})$ to be unity in the entire range of θ_{so} values. This gives the following explicit analytical expression for the runaway locus:

$$BDa + eBDa_{ph} = 1.0. \tag{14}$$

In terms of the critical residence time, this runaway locus is expressed as

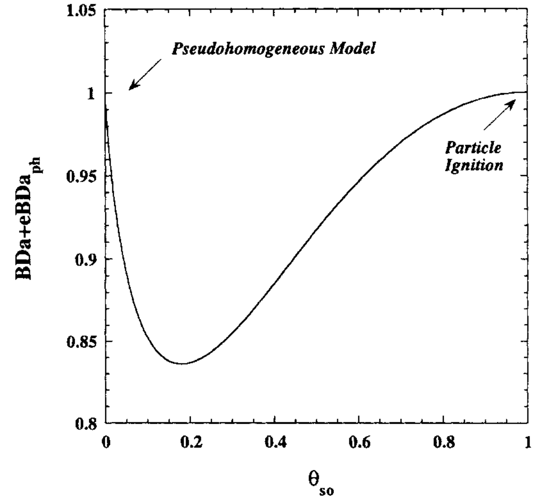

Figure 2. Function $g(\theta_o)$ defining the runaway boundary of a heterogeneous PFR.

$$\tau = \frac{RT_o}{E}\frac{T_o}{\Delta T_{\text{ad}}}\frac{1}{k(T_o)} - e\left(\frac{\rho_f C_{pf}}{ha_v}\right). \tag{15}$$

Equation 15 is a significant new result of our analysis. It indicates that when interphase heat-transfer resistance is significant, the critical residence time is reduced by 2.7 times the characteristic time for interphase heat transfer ($t_h = \rho_f C_{pf}/ha_v$). It should be pointed out that the error involved in the approximations used to derive Eq. 15 is of the same order of magnitude as the uncertainty associated with the determination of the rate constant and the heat-transfer coefficient.

The external surface area per unit bed volume (a_v) depends on the particle size, while the heat transfer coefficient h is a function of the fluid properties and the flow conditions in the vicinity of the particle. One correlation for interphase heat-transfer characteristic time is given by (Froment and Bischoff, 1990; Dwivedi and Upadhay, 1977)

$$\frac{\rho_f C_{pf}}{ha_v} = 0.366 Pr^{2/3}\left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{d_p u_o \rho_f}{\mu_f}\right)^{0.4}\left(\frac{d_p}{u_o}\right). \tag{16}$$

Equations 15 and 16 may be combined to estimate the critical flow rate (or velocity or length of bed) at the runway boundary.

CSTR model

We now extend the preceding result for the case of a two-phase well-mixed adiabatic reactor model. The temperatures of the solid and fluid phases are given by Eq. 7b and

$$\frac{\theta_f}{Da} = \frac{\theta_s - \theta_f}{Da_{ph}}, \tag{17}$$

while the conversions of the reactant in fluid and solid phases are still given by Eqs. 7b and 7d. With the assumptions of B and $\gamma \gg 1$, these equations may be simplified to obtain the following algebraic equation for the solid-phase temperature:

$$BDa + BDa_{ph} = \theta_s e^{-\theta_s}. \tag{18}$$

The ignition point of Eq. 18 occurs at $\theta_s = 1$ and is given by

$$BDa + BDa_{ph} = 0.368. \tag{19}$$

Equivalently, the critical residence time is

$$\tau = 0.368\left[\frac{RT_o}{E}\frac{T_o}{(\Delta T_{\text{ad}})}\frac{1}{k(T_o)} - e\frac{\rho_f C_{pf}}{ha_v}\right]. \tag{20}$$

Again, when there is no interphase heat-transfer resistance, Eq. 19 simplifies to the one that describes the runaway limit for the pseudohomogeneous CSTR model. At the other extreme, when the external heat-transfer resistance is controlling, the catalyst particles ignite at zero residence time.

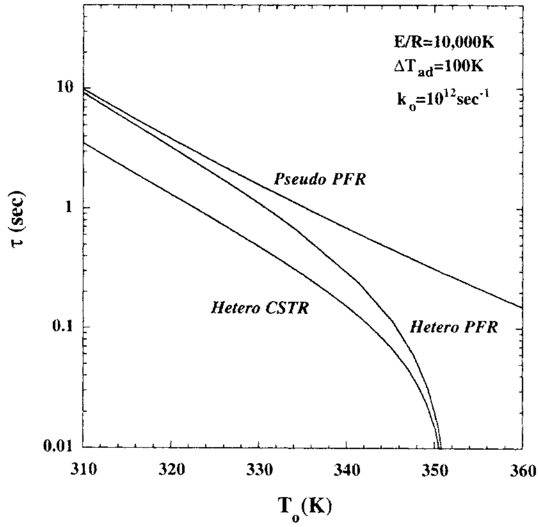

Figure 3. Runaway locus for pseudohomogeneous PFR model vs. heterogeneous PFR and CSTR models for the case of a single reaction.

Figure 3 presents the runaway locus for the pseudohomogeneous and heterogeneous models for a typical set of parameters. For low temperatures of the feed, the pseudohomogeneous and the heterogeneous models predict almost the same critical residence time. As the inlet temperature is further increased, the slopes of the runaway loci, corresponding to the heterogeneous CSTR and PFR models, decrease rapidly and, beyond some critical inlet fluid temperature, intersect the feed temperature axis, indicating that the reactor has come to runaway due to the particle ignition at inlet fluid conditions (zero residence time). In other words, at that point the runaway locus is independent of the type of the reactor (or the flow pattern of the reactor). Therefore, the loci for heterogeneous CSTR and PFR coincide. The physical interpretation of this result is that as the feed temperature increases, the reaction rate (or equivalently the heat-generation rate) in the particles increases more rapidly (exponentially) and the particles ignite due to poor heat removal. In this limiting case, reactor runaway is determined by the transport processes occurring at the particle level.

Influence of intraparticle concentration gradients

We now examine the influence of the intraparticle diffusion on the runaway boundary of a well-mixed heterogeneous model. We neglect the temperature gradients inside the particles, since they are usually very small in most practical situations due to the high conductivity of the particles. The temperature of the solid phase (with the usual assumptions of $B \gg 1$, $Da_{pm} \ll 1$ and $\gamma \gg 1$) is now given by

$$\theta_s = (BDa + BDa_{ph})e^{\theta_s}\eta. \tag{21}$$

The effectiveness factor η is a measure of the pore diffusional resistance and is expressed as a function of the normalized (or generalized) Thiele modulus ϕ as

$$\eta = \frac{3\phi \coth 3\phi - 1}{3\phi^2} \qquad \phi^2 = \frac{k(T)}{D_e}\left(\frac{V_p}{S_p}\right)^2. \tag{22}$$

We define ϕ_o as the normalized Thiele modulus at inlet conditions so that

$$\phi^2 = \phi_o^2 e^{\theta_s} \qquad \phi_o^2 = \frac{k(T_o)}{D_e}\left(\frac{V_p}{S_p}\right)^2. \tag{23}$$

Here ϕ_o^2 is defined as the ratio of the characteristic time for intraparticle diffusion over the characteristic time for reaction at inlet conditions. A small Thiele modulus implies that intraparticle mass transfer dominates over reaction, and therefore intraparticle diffusional resistance is negligible. The runaway locus (or the ignition point of Eq. 21) is presented in the following parametric form:

$$\phi_o = \frac{\psi}{3}\exp\left(\frac{\psi \coth \psi - 1}{\psi^2 \operatorname{cosech}^2 \psi - \psi \coth \psi}\right) \tag{24a}$$

$$\theta_s = 2\ln\left(\frac{\psi}{3\phi_o}\right) \tag{24b}$$

$$BDa + BDa_{ph} = \frac{6\phi_o^2}{\psi(\coth \psi - \psi \operatorname{cosech}^2 \psi)}, \quad 0 < \psi < \infty. \tag{24c}$$

The runaway boundary defined by Eq. 24 is presented in Figure 4. When ϕ_o is small, the effectiveness factor approaches unity and the model just given reduces to the heterogeneous model with only the external heat-transfer resistance examined previously and the runaway criterion is given by Eq. 19. At the other extreme case of strong intraparticle resistance, the runaway locus is directly proportional to ϕ_o and depends on the diffusivity of the reactant inside the catalyst and the particle size. These two asymptotes can be expressed as

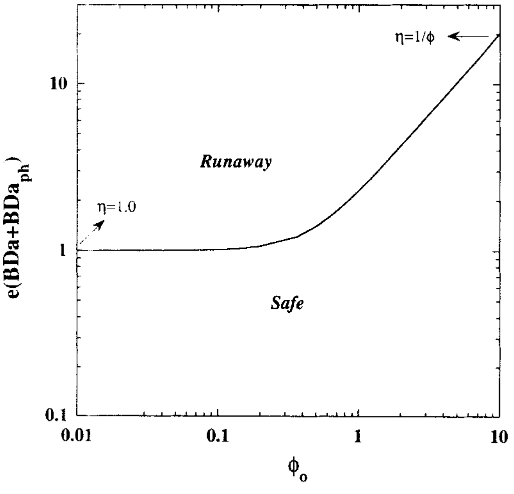

Figure 4. Influence of intraparticle diffusional resistance on the runaway locus of the heterogeneous CSTR.

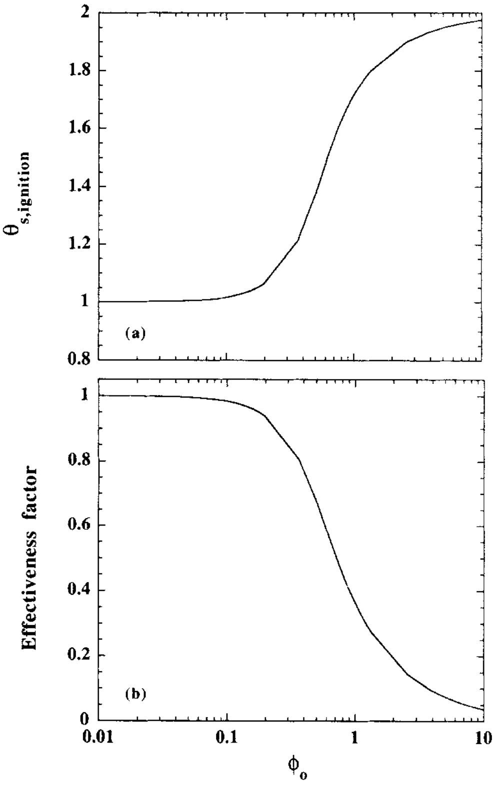

Figure 5. (a) Dependence of the solid-phase ignition temperature on the Thiele modulus (ϕ_o) for heterogeneous CSTR model; (b) dependence of the effectiveness factor at the runaway limit on the Thiele modulus (ϕ_o).

$$BDa + BDa_{ph} = \begin{cases} e^{-1}, & \phi_o \leq 0.5 \\ (2\phi_o)e^{-1}, & \phi_o > 0.5. \end{cases} \tag{25}$$

Similar results can be derived for the case of a plug-flow reactor model. In this case, the preceding analysis can be repeated and it can be shown that a good approximation to the runaway boundary is given by

$$BDa + eBDa_{ph} = \begin{cases} 1, & \phi_o \leq 0.5 \\ 2\phi_o, & \phi_o > 0.5. \end{cases} \tag{26}$$

In both cases, the transition between these two limits occurs when $\phi_o = 0.5$. Figures 5a and 5b show the solid temperature and the effectiveness factor on the runaway boundary. As expected, the rate of heat generation decreases as the intraparticle diffusional resistance increases, and hence, the runaway region decreases. Table 1 summarizes the runaway loci for a single reaction for the various models and limiting cases examined so far.

Runaway Criterion for Multiple Reactions

Thus far, we have determined the runaway locus for the different reactor models assuming single first-order reaction. However, the majority of the industrial processes describe multiple reaction networks in which the side reactions are

Table 1. Summary of Runaway Criteria for a Single Reaction for Various Cases

Model	PFR	CSTR
Pseudohomogeneous	$BDa = 1.0$	$eBDa = 1.0$
Heterogeneous		
(i) $\phi_o < 1/2$	$BDa + eBDa_{ph} = 1.0$	$eBDa + eBDa_{ph} = 1.0$
(ii) $\phi_o > 1/2$	$BDa + eBDa_{ph} = 2\phi_o$	$eBDa + eBDa_{ph} = 2.0\phi_o$

very significant in determining the sensitivity of the system. This occurs because many undesirable side reactions are highly exothermic and have higher activation energies as compared to the main reaction. Therefore, the objective is to suppress the side reactions whose rate becomes significant at elevated temperatures. In this section, we examine how the critical residence time is influenced by the presence of side reactions.

PFR model

We start the analysis by examining the case of two consecutive first-order reactions $A \rightarrow B \rightarrow C$ in a homogeneous adiabatic plug-flow reactor. Neglecting reactant consumption and using positive exponential approximation, the energy balance that describes the temperature variation with residence time is given by

$$\frac{d\theta}{dDa} = B(e^{\theta} + \lambda e^{\mu\theta}), \qquad \theta(0) = 0. \tag{27}$$

The dimensionless variables and parameters in Eq. 27 have the same meaning as in the case of a single reaction and the new groups that account for the multiple-reaction network are

$$\mu = \frac{E_2}{E_1} \qquad \lambda = \frac{(-\Delta H_R)_2}{(-\Delta H_R)_1}\frac{r_2(C_o,T_o)}{r_1(C_o,T_o)} = \Lambda \exp\left(\frac{E_1 - E_2}{RT_o}\right)$$

and

$$\Lambda = \frac{(-\Delta H_R)_2 C_{2o} k_{2o}}{(-\Delta H_R)_1 C_{1o} k_{1o}}. \tag{28}$$

Here, μ is the ratio of the activation energies and λ is the ratio of heat generation rates at inlet conditions. The runaway locus of Eq. 27 may be presented in the integral form

$$BDa = \int_0^{\infty} \frac{\exp(-\theta)d\theta}{[1 + \lambda\exp(\mu - 1)\theta]} = \int_0^1 \frac{dt}{[1 + \lambda t^{1-\mu}]}. \tag{29a}$$

In terms of the critical residence time, the runaway boundary is written as

$$\tau = \frac{RT_o}{E}\frac{T_o}{\Delta T_{ad}}\frac{1}{k_1(T_o)}\int_0^1 \frac{dt}{[1 + \Lambda\exp((E_1 - E_2)/RT_o)t^{1-\mu}]}. \tag{29b}$$

We note that when $\lambda = 0$, the runaway locus simplifies to the single reaction case, while for $\lambda \leq -1$ $BDa \rightarrow \infty$ and there is no runaway. (The case of $\lambda < 0$ corresponds to the second reaction being endothermic.) The integral in Eq. 29a can be evaluated analytically only for rational values of μ. Some of these are listed in Table 2. It is interesting to note that this integral is not analytic at $\lambda = 0$ for all $\mu \geq 2$ (i.e., the slope at $\lambda = 0$ is $-\infty$). Thus, it may be concluded that the side reaction influences the critical residence time significantly only if it has an activation energy of about twice or higher as compared to the main reaction.

Table 2. Analytic Representation of the Runaway Locus for Two Reactions in a Homogeneous PFR

μ	BDa
0	$\frac{1}{\lambda}\ln(1+\lambda)$
1/2	$\frac{2}{\lambda}\left(1 - \frac{\ln(1+\lambda)}{\lambda}\right)$
1	$\frac{1}{1+\lambda}$
3/2	$1 - 2\lambda + 2\lambda^2 \ln\left(\frac{1+\lambda}{\lambda}\right)$
2	$1 - \lambda \ln\left(\frac{1+\lambda}{\lambda}\right)$
3	$1 - \sqrt{\lambda}\tan^{-1}\left(\frac{1}{\sqrt{\lambda}}\right)$

Figure 6 presents a plot of the runaway locus for various μ values. From this graph, it may be concluded that in most practical cases in which $0 < \lambda \leq 0.1$, side reactions have a significant impact on the runaway locus only when $\mu \geq 2$. In Figure 7, the runaway locus of a single reaction is compared to that for two consecutive reactions when the activation energy of the second reaction is twice that of the first reaction. For the low feed temperature region, the runaway boundaries for the two reaction networks are almost identical, but for higher feed temperatures, the side reaction influences the runaway boundary and decreases the critical residence time

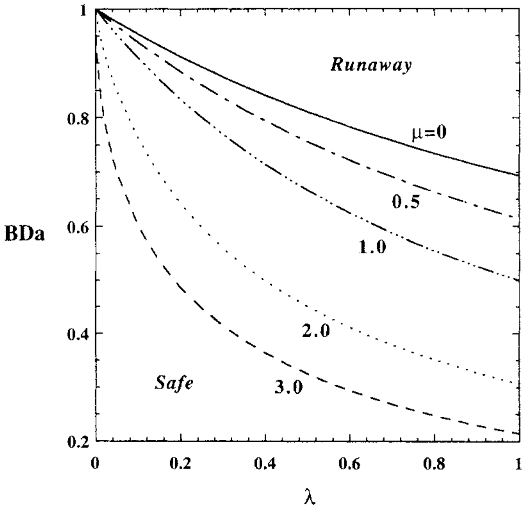

Figure 6. Runaway locus for different ratios of activation energies for two consecutive reactions in a homogeneous PFR.

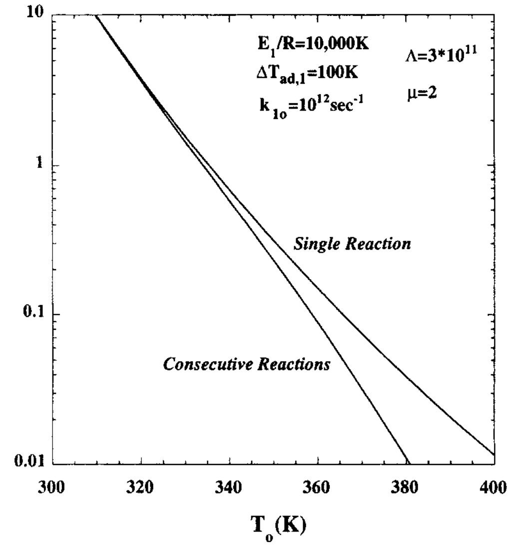

Figure 7. Runaway locus of a single reaction vs. two consecutive reactions in a homogeneous PFR.

due to its high sensitivity to temperature variations (high activation energy).

It should be pointed out that the preceding runaway criterion is also applicable to two parallel reactions ($A \rightarrow P$, $B \rightarrow C$) or two simultaneous reactions ($A \rightarrow B$, $A \rightarrow C$) (when reactant consumption can be neglected). This is due to the fact that the total heat generated in the system is the sum of the heat generated by various reactions whether they are consecutive, simultaneous, or parallel. Thus, when reactant consumption is neglected, Eq. 27 describes the temperature variation in any system with two reactions.

CSTR model

We now examine the case of two first-order consecutive reactions in a homogeneous well-mixed adiabatic reactor (CSTR). The species balances for A and B and the energy balance have the following form:

$$C_A = \frac{C_{Ao}}{1 + k_1\tau} \tag{30a}$$

$$C_B = \frac{C_{Bo}}{1 + k_2\tau} + \frac{C_{Ao}k_1\tau}{(1 + k_1\tau)(1 + k_2\tau)} \tag{30b}$$

$$\frac{T - T_o}{T_o} = \sum_{i=1}^{2} \beta_i \frac{k_i\tau}{1 + k_i\tau} + \beta_1 \frac{(-\Delta H_R)_2}{(-\Delta H_R)_1} \frac{(k_1\tau)(k_2\tau)}{(1 + k_1\tau)(1 + k_2\tau)} \tag{30c}$$

where

$$\beta_1 = \frac{(-\Delta H_R)_1 C_{Ao}}{(\rho C_p)_f T_o}, \quad B = \frac{E_1}{RT_o}\beta_1 \quad Da = k_1(T_o)\tau$$

$$\beta_2 = \frac{(-\Delta H_R)_2 C_{Bo}}{(\rho C_p)_f T_o}, \quad B_2 = \frac{E_1}{RT_o}\beta_2. \tag{30d}$$

We define

$$\mu = \frac{E_2}{E_1} \quad \hat{\lambda} = \frac{k_2(T_o)}{k_1(T_o)} \tag{30e}$$

and simplify the model by using the positive exponential approximation and neglecting the reactant consumption ($k_i\tau \ll 1$). This simplifies Eq. 30c to

$$\theta = BDae^{\theta} + B_2Da\hat{\lambda}e^{\mu\theta}. \tag{31}$$

When both A and B are present in the feed, the runaway locus is described by the following parametric form:

$$BDa = \left(\frac{1 - \mu\theta}{1 - \mu}\right)e^{-\theta} \tag{32a}$$

$$\hat{\lambda} = \left(\frac{\beta_1}{\beta_2}\right)\left(\frac{\theta - 1}{1 - \mu\theta}\right)e^{(1-\mu)\theta}, \quad \frac{1}{\mu} < \theta < 1. \tag{32b}$$

Here θ is the temperature at ignition (runaway) and it decreases from unity ($\mu = 1$) to zero ($\mu \rightarrow \infty$). When both reactions have the same activation energy ($\mu = 1$), the runaway locus simplifies to the following analytic expression:

$$Da[B + \hat{\lambda}B_2] = 0.368. \tag{33}$$

When the first reaction has a much higher rate constant as compared to the second reaction at feed conditions ($\hat{\lambda} \ll 1$), the runaway criterion given by Eq. 33 may be simplified to an explicit form:

$$Da[B + \hat{\lambda}B_2e^{\mu-1}] = 0.368 + O(\hat{\lambda}^2). \tag{34}$$

Multiple Reactions in a Catalytic Reactor

In this section, we consider a more practical case of two consecutive reactions $A \rightarrow B \rightarrow C$ in a catalytic reactor with Langmuir–Hinshelwood-type kinetics. This example is typical of many partial oxidation and hydrogenation reactions encountered in industrial applications. We use a heterogeneous plug-flow reactor with uniform reactant concentration inside the catalyst particles. We assume that all the fluid properties are constant (including the density and viscosity) and neglect the pressure drop in the bed. The relevant mathematical model consists of three differential equations coupled to three algebraic equations, representing the species balances for A and B and the energy balance for each phase. The model equations are written in the following form:

$$\frac{dy_{Af}}{d\tau} = -k_{cA}a_v(y_{Af} - y_{As}) \tag{35a}$$

$$\frac{dy_{Bf}}{d\tau} = -k_{cB}a_v(y_{Bf} - y_{Bs}) \tag{35b}$$

$$\frac{dT_f}{d\tau} = \frac{ha_v}{\rho_f C_{pf}}(T_s - T_f) \tag{35c}$$

$$C_o k_{cA} a_v (y_{Af} - y_{As}) - r_1(y_{As}, y_{Bs}, T_s) = 0 \qquad (35d)$$

$$C_o k_{cB} a_v (y_{Bf} - y_{Bs}) - r_2(y_{As}, y_{Bs}, T_s) + r_1(y_{As}, y_{Bs}, T_s) = 0 \qquad (35e)$$

$$C_o \frac{h a_v}{\rho_f C_{pf}} (T_s - T_f) - \frac{(-\Delta H_{R1})}{\hat{C}_{pf}} r_1 - \frac{(-\Delta H_{R2})}{\hat{C}_{pf}} r_2 = 0 \qquad (35f)$$

$$y_{Af} = y_{Afo}, \quad y_{Bf} = y_{Bfo}, \quad T_f = T_{fo} \quad \text{at} \quad \tau = 0. \qquad (35g)$$

Here, C_o is the total molar concentration of the reaction mixture and y_A, y_B are the mole fractions of A and B, respectively. We assume that the rate expressions are of the form:

$$r_1 = \frac{k_1(T_s) K_A(T_s) y_{As} C_o}{[1 + K_A(T_s) y_{As} + K_B(T_s) y_{B_s}]} \qquad (36a)$$

$$r_2 = \frac{k_2(T_s) K_B(T_s) y_{Bs} C_o}{[1 + K_A(T_s) y_{As} + K_B(T_s) y_{Bs}]} \qquad (36b)$$

with

$$K_A = K_{Ao} \exp\left(\frac{E_A}{RT_s}\right) \qquad K_B = K_{Bo} \exp\left(\frac{E_B}{RT_s}\right) \qquad (37a)$$

and

$$k_i = k_{io} \exp\left(-\frac{E_i}{RT_s}\right) \qquad i = 1,2. \qquad (37b)$$

Here k_1 and k_2 are the reaction rate constants while K_A and K_B are the adsorption equilibrium constants for species A and B, respectively. The values of activation and adsorption energies determine the sensitivity of the system to temperature variations and can influence significantly the runaway boundary. The numerical values of the different parameters used in the calculation of the runaway locus are listed in Table 3. The kinetic expressions given by Eqs. 36 and 37 and the parameter values listed are typical of an industrial hydrogenation reaction at high pressure.

We determine the runaway locus of the preceding model in the feed-temperature–residence-time plane by integrating the differential-algebraic system defined by Eqs. 35. First, we determine the behavior of the individual catalyst particles by computing how the particle temperature changes as the local fluid conditions vary. This is accomplished by solving the three particle balance equations given by Eqs. 35d, 35e, and 35f for y_{As}, y_{Bs}, and T_s as a function of T_f (a similar computation can be done by varying y_{Af} or y_{Bf}). Figure 8 shows the numerically computed bifurcation diagram of T_s vs. T_f for three different values of the particle Lewis number, $Le_p = 0.5$, 1.0, and 2.0 (and for other parameter values listed in Table 3). It is clear from this figure that the particle Lewis number plays an important role in the determination of the ignition point and hence the critical feed temperature (or equivalently, the residence time). When the Le_p exceeds two, the critical feed temperature is governed by the second reaction, while for lower values of Le_p, the first reaction ignites and dictates the critical feed temperature (T_{fo}^*).

Table 3. Numerical Values of the Parameters Used in the Calculation of the Runaway Boundary

$k_{cA} \cdot a_v$	5.0 s^{-1}	k_{1o}	2.7×10^{21} s^{-1}
$k_{cB} \cdot a_v$	5.0 s^{-1}	k_{2o}	1.3×10^{31} s^{-1}
Le_p	2, 1.0, 0.5	E_1/R	17,000 K
y_{Afo}	0.005	E_2/R	26,000 K
y_{Bfo}	0.3	K_{Ao}	9×10^{-8}
C_o	0.0015 mol/cm^3	K_{Bo}	3×10^{-8}
$(-\Delta H_{R1})/\hat{C}_{pf}$	2,800 K	E_A/R	9,600 K
$(-\Delta H_{R2})/\hat{C}_{pf}$	2,200 K	E_B/R	7,200 K

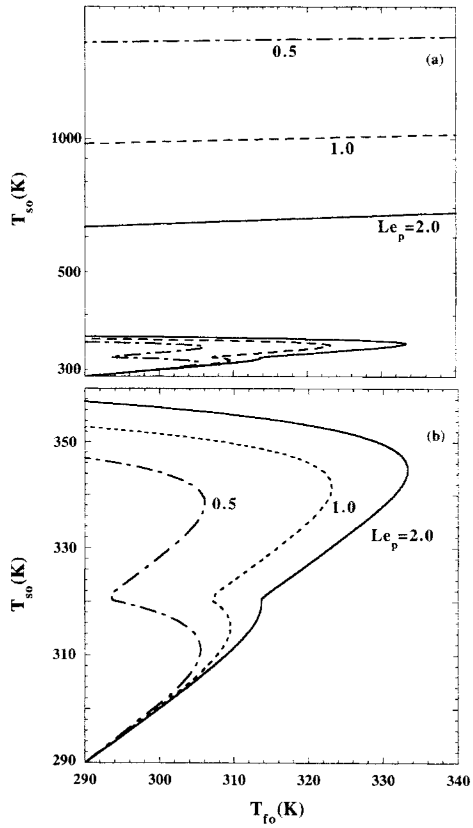

Figure 8. Bifurcation of particle temperature vs. the fluid temperature for two consecutive reactions with the Langmuir Hinshelwood kinetics for different Lewis numbers.

For an inlet temperature smaller than the critical feed temperature ($T_{fo} < T_{fo}^*$), the differential-algebraic system is integrated using an implicit method and the temperatures as well as the concentrations of species A and B in the fluid and solid phase are determined as a function of τ. The critical residence time is computed at the particle ignition (when the Jacobian of the three particle equations (Eqs. 35d, 35e, and 35f) with respect to y_{As}, y_{Bs}, and T_s vanishes).

The numerically computed runaway boundary for the model defined by Eqs. 35 is presented in Figure 9 for three different values of the particle Lewis number. The results in this figure show that the critical residence time decreases monotonically with increasing feed temperature, confirming our earlier analytical results for a first-order reaction. When the feed temperature exceeds the critical value, the catalyst

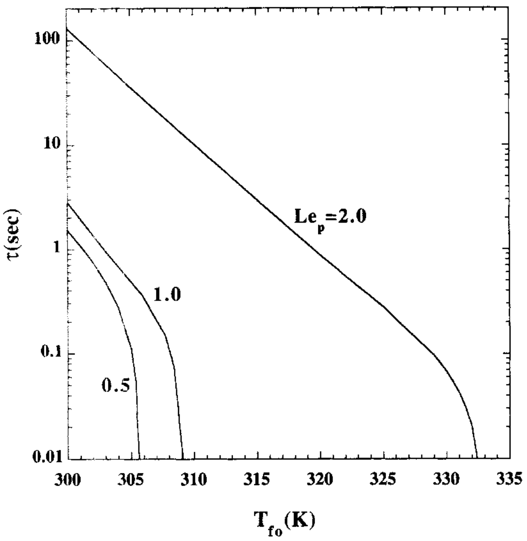

Figure 9. Computed runaway locus for two consecutive reactions in a heterogeneous PFR (other parameter values are listed in Table 3).

particles ignite at zero residence time. This critical value depends strongly on Le_p and equals 306 K, 309 K, and 333 K for $Le_p = 0.5$, 1.0, and 2.0, respectively.

Figure 10 shows the temperature profiles of the solid and fluid phases for conditions on the runaway boundary of Figure 9 for the case of $Le_p = 2.0$. For an inlet temperature of 310 K, the heat-transfer resistance is not significant and the fluid and solid temperatures are almost identical along the reactor (Figure 10a). As the feed temperature is increased to 320 K, the difference between the temperature of the catalyst particles and the fluid phase becomes significant even at the inlet of the reactor (Figure 10b). Finally, when the feed temperature approaches the critical value, the region of safe operation is drastically decreased and at $T_{f_o} = 333$ K the particles ignite upon first contact with the fluid.

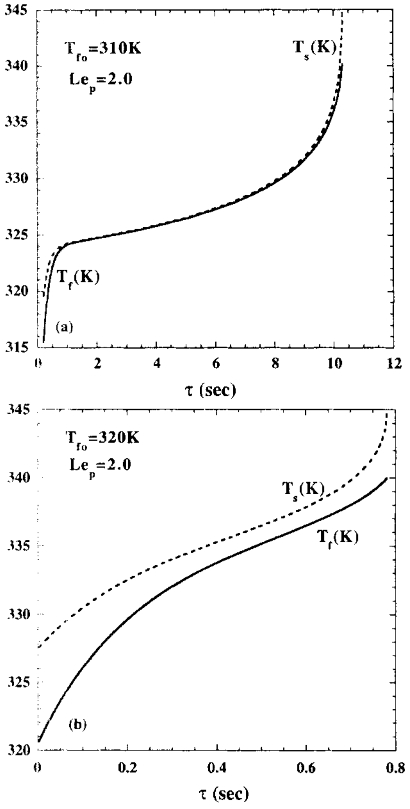

Figure 10. Dependence of the solid- and fluid-phase temperatures on the residence time for (a) $T_{fo} = 310$ K and (b) $T_{fo} = 320$ K.

Conclusions

The main objective of this work is to present a procedure for determining the critical residence time at which runaway occurs in an adiabatic packed-bed reactor. (We have termed this runaway boundary the weak safety criterion.) For the case of a single reaction, we presented an explicit analytical expression for determining this critical residence time. A major result of this work is that the critical residence time is reduced by 2.7 times the interphase heat-transfer time and can be zero (leading to runaway at inlet conditions), when the interphase heat-transfer resistance is significant. For multiple reactions, we have shown how the runaway boundary is influenced by the side reactions and presented a procedure for calculating this boundary for multiple reactions with complex kinetics. The analytical expressions and the calculation procedure presented in this article can be used to determine the safe region of operation for adiabatic catalytic reactors. When an accurate prediction of the runaway boundary is required, the simplified models and results presented here can be used as a first approximation and a good starting point in order to perform detailed numerical computations using more complicated kinetics and reactor models.

As stated in the introduction, this work focused mainly on the weak safety criterion, and hence the results presented here are relevant only in the design of reactors for which the strong safety criterion is not applicable. However, in some industrial operations such as the removal of trace impurities from gaseous streams, the main reactant is only present in a much smaller concentration as compared to other reactants and the objective is to suppress the side reactions. In such cases, the strong safety criterion for the main reaction can easily be satisfied and should be combined with the weak safety criterion for the side reactions to obtain the proper stability boundary This point will be illustrated further in a future publication.

Acknowledgment

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Notation

B = adiabatic temperature rise
$\hat{C}_{pf}$ = specific heat, $J \cdot mol^{-1} \cdot K^{-1}$
C_{pf} = specific heat, $J \cdot Kg^{-1} \cdot K^{-1}$
d_p = particle diameter, m
D_e = effective diffusivity of reactant in the catalyst, $m^2 \cdot s^{-1}$
$(-\Delta H_R)$ = heat of reaction, $J \cdot mol^{-1}$
k_c = fluid–particle mass transfer coefficient, $m \cdot s^{-1}$
k_o = frequency factor, s^{-1}
Pr = Prandtl number

R = universal gas constant, 8.314 $J \cdot mol^{-1} \cdot K^{-1}$
S = surface area, m^2
u_o = superficial velocity, $m \cdot s^{-1}$
V = volume, m^3
ϵ = porosity
$\theta_{f(s)}$ = dimensionless fluid (solid) temperature
μ = fluid viscosity, $kg \cdot s^{-1} \cdot m^{-1}$
ξ = dimensionless axial position
ρ_f = density, $kg \cdot m^{-3}$

Subscripts

f = fluid
R = reaction

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