Simple Runaway Criteria for Cooled Reactors

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Runaway may occur in a chemical reactor when a small change in one of the operating variables such as feed or coolant temperature, flow rate, concentration, etc., causes a large increase in the reactor hot spot or exit temperature. This phenomenon is also referred to as parametric sensitivity and is closely related to the concept of spontaneous ignition in the theory of thermal explosions. When a mathematical model of a chemical reactor includes heat conduction in the system, ignition is well characterized by the existence of a limit point in the bifurcation diagram of temperature vs. an operating variable. When a mathematical model does not account for heat conduction in the system, the bifurcation diagram may be single valued with no limit point, i.e., the mathematical model may exhibit *structural sensitivity*. However, very often there is a narrow range of values of the operating variable in which the temperature increases very rapidly (high sensitivity) and physically, this phenomenon is similar to ignition.

Criteria for runaway in a chemical reactor have been derived by Barkelew (1959, 1984), Adler and Enig (1964), Van Welsenaere and Froment (1970), Morbidelli and Varma (1982, 1987) and many others. Most of these previously developed criteria, with the exception of Barkelew (1984), are conservative, as they are independent of the reactor size (length). Barkelew's (1984) criteria are simple and explicit but are applicable only for the adiabatic case. The purpose of this note is to extend these criteria for cooled reactors.

To develop the criteria, we consider a cooled tubular reactor in which an exothermic reaction occurs. We assume a zeroth order reaction (unlimited supply of reactant). This is a key assumption which leads to slightly conservative criteria but simplifies the mathematical model considerably. Using the pseudo-homogeneous axial dispersion model, the steady-state energy balance is given by

$$\lambda \frac{d^2T}{dx^2} - u_o \rho c_p \frac{dT}{dx} + Q_o e^{-E/RT} - \frac{UA}{V_R}(T - T_c) = 0 \quad (1)$$

subject to the boundary conditions

$$\lambda \frac{dT}{dx} = u_o \rho c_p (T - T_o), \; x = 0 \quad (2)$$

$$\frac{dT}{dx} = 0, \quad x = L \quad (3)$$

Defining the characteristic times

$$t_\lambda = \frac{\rho c_p L^2}{\lambda} \quad t_r = \frac{V_R \rho c_p}{AU}$$

$$t_c = \frac{L}{u_o} \quad t_g = \frac{RT_o}{E} \frac{\rho c_p T_o}{Q_o \exp(-E/RT_o)} \quad (4)$$

and the dimensionless parameters

$$\gamma = \frac{E}{RT_o} \quad \theta_c = \gamma \frac{(T_c - T_o)}{T_o}$$

$$Pe_h = \frac{t_\lambda}{t_c} \quad \Delta = \frac{t_c}{t_g} \quad St = \frac{t_c}{t_r} \quad Se = \frac{t_r}{t_g} \quad (5)$$

Eqs. 1–3 may be written as

$$\frac{1}{Pe_h} \frac{d^2\theta}{d\xi^2} - \frac{d\theta}{d\xi} + \Delta \exp(\theta) - St(\theta - \theta_c) = 0 \quad (6)$$

$$\frac{1}{Pe_h} \frac{d\theta}{d\xi} = \theta, \quad \xi = 0 \quad (7)$$

$$\frac{d\theta}{d\xi} = 0, \quad \xi = 1 \quad (8)$$

In arriving at Eq. 6, we have used the positive exponential approximation to simplify the heat generation term. It is well known that this approximation moves the extinction point to infinity but is accurate for predicting the ignition point for most cases of practical interest. The critical value of the Damkohler number, Δ, for runaway, now depends on three parameters, i.e., the Stanton number, St, the dimensionless coolant temperature, θ_c, and the Peclet number, Pe_h. The runaway criterion may be expressed as

$$\Delta > \Delta_c \equiv f(St, \theta_c, Pe_h) \tag{9}$$

In order to determine the nature of this function, we consider first some limiting cases of the model defined by Eqs. 6–8. These limiting cases become transparent when Eq. 6 is rewritten as

$$\frac{1}{t_\lambda}\frac{d^2\theta}{d\xi^2} - \frac{1}{t_c}\frac{d\theta}{d\xi} + \frac{1}{t_g}e^\theta - \frac{1}{t_r}(\theta - \theta_c) = 0 \tag{10}$$

CSTR (Semenov) Model

When the characteristic time for heat conduction is much smaller than that for convection, generation, or heat removal, the temperature in the system is independent of position, and Eqs. 6–8 may be integrated to give the following steady-state equation:

$$F(\theta) \equiv -\theta + \Delta e^\theta - St(\theta - \theta_c) = 0 \tag{11}$$

This equation represents the heat balance for a CSTR with the first term representing heat removal by flow, the second term, heat generation by reaction, and the third term, heat removal by external cooling. The ignition point of this model is obtained by setting the derivative of F, with respect to θ, to zero and eliminating θ. After some simplifications, the runaway (ignition) criterion may be expressed in the form of Eq. 9 with

$$\Delta_c = (1 + St)\exp\left(-1 - \frac{St\theta_c}{1 + St}\right) \tag{12}$$

The temperature at ignition is given by

$$\theta_i = 1 + \frac{St\theta_c}{1 + St} \tag{13}$$

When $t_r \gg t_c$ (negligible heat removal or adiabatic case) the ignition temperature, θ_i, approaches unity and the runaway criterion simplifies to

$$\Delta > e^{-1} \tag{14a}$$

or equivalently,

$$\frac{V_R Q(T_o)\gamma}{q\rho c_p T_o} > 0.368 \tag{14b}$$

When $t_r \ll t_c$ (strongly cooled case) the ignition temperature, θ_i, approaches $(1 + \theta_c)$ and the runaway criterion simplifies to

$$Se \equiv \frac{\Delta}{St} > e^{-(1+\theta_c)} \tag{15a}$$

or equivalently,

$$\frac{V_R Q(T_o)\gamma}{AUT_o} > e^{-(1+\theta_c)} \tag{15b}$$

Figure 1 shows a plot of the runaway locus given by Eq. 12. The two asymptotes discussed above can be clearly seen in this figure. Note that Δ_c is a monotonically increasing function of St, only if $\theta_c \leq 1$. When $\theta_c > 1$, the smallest value of Δ_c is $\theta_c \exp(-\theta_c)$, and occurs at $St = \theta_c - 1$. Thus, for $\theta_c > 1$ intermediate values of St are more likely to cause runaway. While this result is counter-intuitive and interesting, it is not of importance, as in most practical cases, $\theta_c \leq 0$.

Plug Flow (Dirichlet) Model

When the characteristic time for conduction is much larger than the other three time scales, the first term in Eq. 10 may be dropped and the model defined by Eqs. 6–8, simplified to

$$\frac{d\theta}{d\xi} = \Delta e^\theta - St(\theta - \theta_c), \quad \theta(0) = 0 \tag{16}$$

The critical points of this scalar initial-value problem may be obtained by equating the righthand side of Eq. 16 to zero and solving the following resulting equation for θ:

$$Se = (\theta - \theta_c)\exp(-\theta) \tag{17}$$

This equation has no solution if

$$Se > Se_0 \equiv \exp(-1 - \theta_c) \tag{18}$$

When $Se > Se_0$, the temperature continues to increase along the

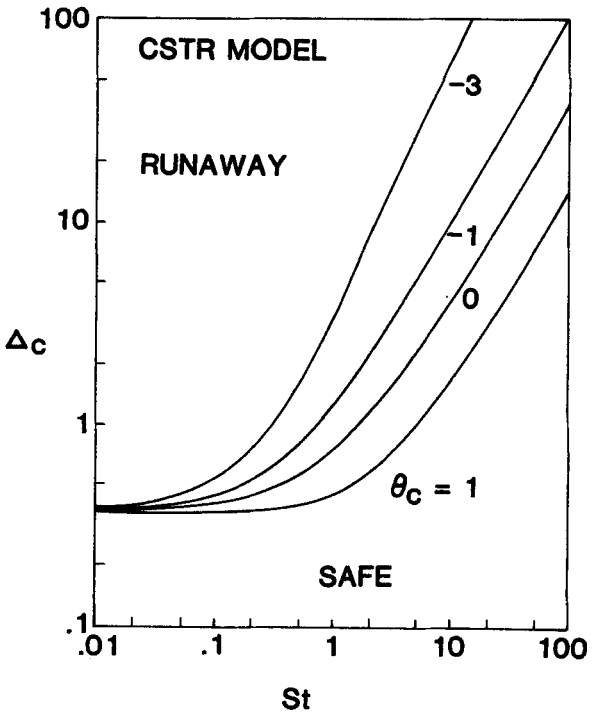

Figure 1. Runaway curves of CSTR model for different coolant temperatures.

tube. Runaway now corresponds to a hot spot at the exit of the reactor. Since we have assumed a zeroth-order reaction, the hot spot temperature will be unbounded, i.e., $\theta(1) = \infty$. After some simplifications, the runaway locus may be expressed in a parametric form as

$$\Delta_c = \int_0^1 \frac{du}{[1 + \eta u(\ln u + \theta_c)]} \tag{19a}$$

$$St = \eta\Delta_c \quad (\eta \geq 0) \tag{19b}$$

The integral in Eq. 19a may be evaluated either numerically or using the series

$$\Delta_c = 1 + \sum_{m=1}^{\infty} \eta^m \left\{ \frac{m!}{(m+1)^{m+1}} \sum_{i=0}^{m} \frac{[-(m+1)\theta_c]^i}{i!} \right\} \tag{20}$$

For the special case of $\theta_c = 0$, Eq. 20 reduces to

$$\Delta_c = 1 + \sum_{m=1}^{\infty} \frac{\eta^m m!}{(m+1)^{1+m}} \tag{21}$$

When $Se < Se_0$, Eq. 17 has two solutions, θ_1 and θ_2, that satisfy the inequalities, $\theta_c < \theta_1 < (1 + \theta_c)$, and $\theta_2 > (1 + \theta_c)$, respectively. In this case, the following three possibilities exist for the initial-value problem defined by Eq. 16:

- When $\theta_c > 0$, $\theta(\xi)$ is monotonically increasing and approaches θ_1 for $\Delta \rightarrow \infty$
- When $-1 < \theta_c < 0$, $\theta(\xi)$ is monotonically decreasing if $0 < Se < (-\theta_c)$, and monotonically increasing if $(-\theta_c) < Se < Se_0$. In both cases, $\theta(\xi)$ approaches θ_1 for $\Delta \rightarrow \infty$ (or equivalently, $St \rightarrow \infty$)
- When $1 + \theta_c < 0$, $\theta(\xi)$ decreases monotonically and approaches θ_1 if $0 < Se < (-\theta_c)$, and increases monotonically without bound if $Se > (-\theta_c)$. Thus, the integral in Eq. 19a converges if $\eta\, Se^* < 1$, where Se^* is equal to $\exp(-1 - \theta_c)$ if $\theta_c > -1$, and to $(-\theta_c)$ if $\theta_c < -1$.

For the adiabatic case, the runaway criterion simplifies to

$$\Delta > 1.0 \tag{22}$$

or equivalently,

$$\frac{V_R Q(T_o)\gamma}{q\rho c_p T_o} > 1.0 \tag{23}$$

For a strongly cooled case, the runaway criterion simplifies to

$$\frac{V_R Q(T_o)\gamma}{AUT_o} > e^{-(1+\theta_c)}; \quad (1 + \theta_c) > 0 \tag{24a}$$

$$\frac{V_R Q(T_o)\gamma}{AUT_o} > (-\theta_c); \quad (1 + \theta_c) < 0 \tag{24b}$$

We show in Figure 2, plots of the runaway criterion defined by Eqs. 19a. The two asymptotes discussed above can be seen clearly in this figure. Eq. 20 may be used to show that the runaway locus has a local minimum if $\theta_c > 0.5$. For example, when

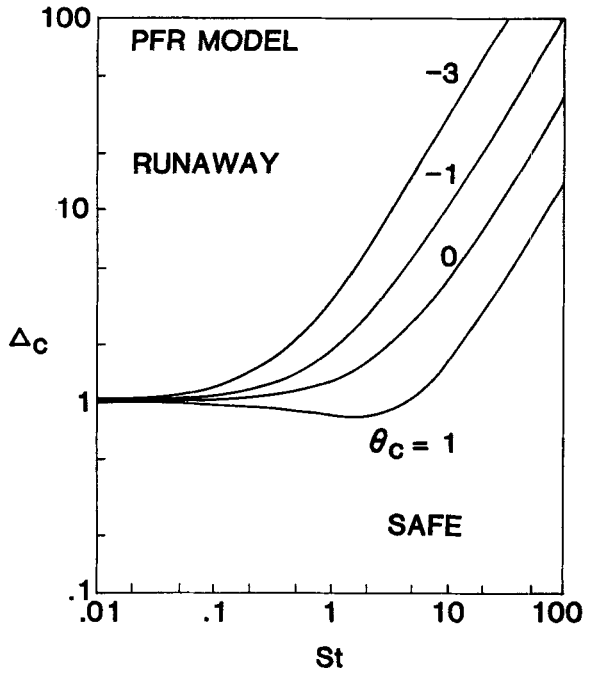

Figure 2. Runaway curves of PFR model for different coolant temperatures.

$\theta_c = 1.0$ (2.0), the minimum value of Δ_c is 0.82 (0.38). Thus, for $\theta_c > 0.5$, intermediate values of St are more likely to cause runaway.

It is interesting to compare the limiting forms of the runaway locus predicted by the above two models for the strongly cooled case. When $1 + \theta_c > 0$, the two models predict identical values of Δ_c, implying that this locus is independent of Pe_h. A surprising result is that when $1 + \theta_c < 0$, the plug flow reactor is more likely to runaway than the well stirred reactor.

Adiabatic (Barkelew) Model

When t_r is much larger than the other three time scales, the heat removal term in Eq. 6 may be dropped to obtain the adiabatic model. It is not possible to determine an exact analytical expression for the ignition point of this model. Barkelew (1984) has examined this limiting case numerically and made a very important observation. He has shown that "the tendency of an adiabatic reactor to runaway depends only on the degree of mixing and not on the specific model used to represent the mixing effects." The three one-parameter models (axial dispersion, tanks in series, and recycle) as well as two-parameter models he has examined, predicted nearly identical values for Δ_c when compared at the same value of the dimensionless variance, σ_θ^2, of the residence time distribution (RTD) function. Using the recycle reactor model, analytical expressions for the ignition temperature, θ_i, and the critical Damkohler number, Δ_c, may be given as

$$\theta_i = \frac{-\ln(\sigma_\theta^2)}{(1 - \sigma_\theta^2)} \tag{25a}$$

$$\Delta_c = (\sigma_\theta^2)^{\sigma_\theta^2/1-\sigma_\theta^2} \tag{25b}$$

For the axial dispersion model,

$$\sigma_\theta^2 = \frac{2}{Pe_h} - \frac{2}{Pe_h^2}(1 - e^{-Pe_h}) \tag{26}$$

Exact solution of the axial dispersion model gives $\Delta_c = 0.37$, 0.43, 0.72, and 0.94 for $Pe_h = 0.1$, 1.0, 10.0, and 100, respectively. The corresponding values predicted by Eq. 25b are 0.37, 0.43, 0.69, and 0.92.

Strongly Cooled (Neumann) Model

When t_r is much smaller than the other three time scales, the reactor is overcooled and $\theta = \theta_c$ is the only physically realizable solution to Eqs. 6–8. In order to have ignition, it is clear from Eq. 10 that at least the last two terms should be of the same order of magnitude. When t_c, $t_\lambda \gg t_g$ and t_r, the conduction and convection terms may be dropped to obtain Eq. 17. The ignition point of this equation is given by Eq. 18. When $t_c \gg t_\lambda$, t_g and t_r, the convective term may be dropped to obtain the Neumann model

$$\frac{1}{\delta}\frac{d^2\theta}{d\xi^2} + \left[e^\theta - \frac{1}{Se}(\theta - \theta_c)\right] = 0 \tag{27a}$$

$$\frac{d\theta}{d\xi} = 0; \quad \xi = 0, 1 \tag{27b}$$

where $\delta = t_\lambda/t_g$ is the Frank-Kamenetskii number. Eqs. 27a and b may have homogeneous as well as (unstable) inhomogeneous solutions. The two homogeneous solutions satisfy Eq. 17. They coalesce and disappear for $Se > Se_0$. Thus, the ignition point of this model is the same as that predicted by Eq. 18.

When $t_\lambda \gg t_c > t_g$, we have a singularly perturbed initial-value problem, the ignition point of which is given by Eq. 24.

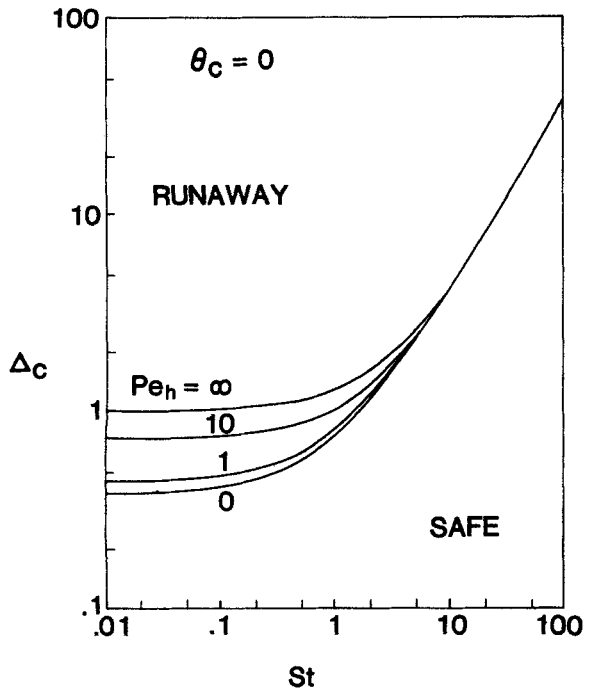

Figure 3. Runaway curves of finite dispersion model for $\theta_c = 0$.

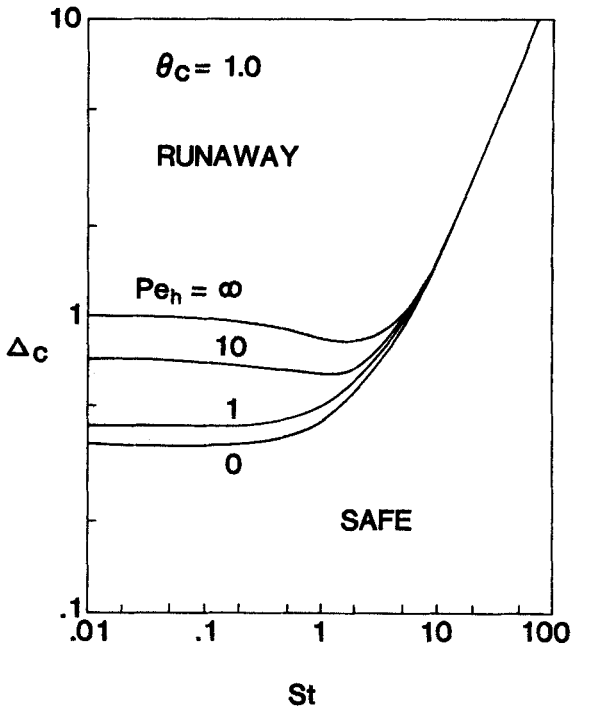

Figure 4. Runaway curves of finite dispersion model for $\theta_c = 1$.

Finite Dispersion Model

Having discussed the various limiting cases, we now consider the finite dispersion model defined by Eqs. 6–8. The ignition point of this model may be determined numerically using either finite differences or the shooting technique. Figures 3–6 summarize the results of the numerical calculations. These results may be understood by considering three different ranges for the coolant temperature.

- $-1 \le \theta_c \le 0.5$. In this case, Δ_c is a monotonic increasing

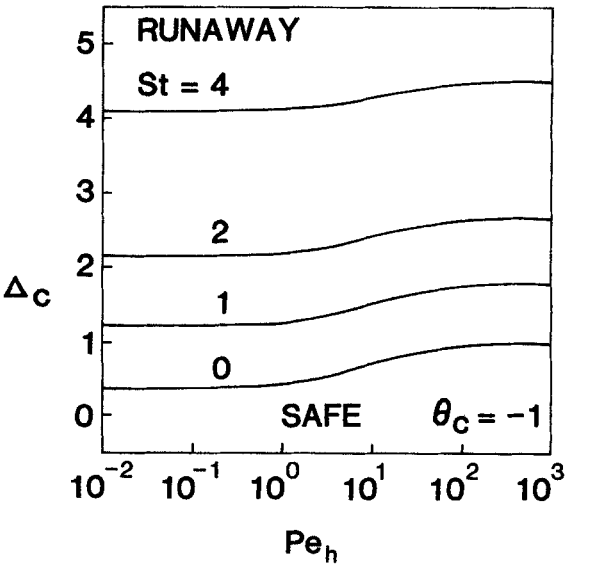

Figure 5. Runaway curves of finite dispersion model for $\theta_c = -1$.

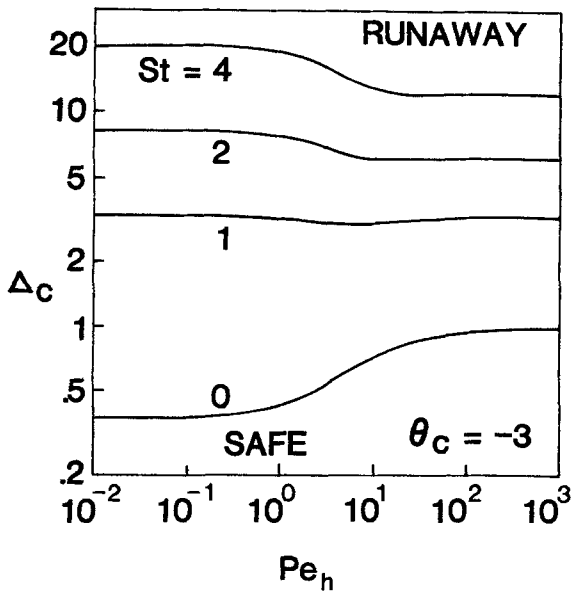

Figure 6. Runaway curves of finite dispersion model for $\theta_c = -3$.

function of both St and Pe_h. As expected, for $Pe_h \ll 1$, the ignition locus approaches that of the CSTR model, while for $Pe_h \gg 1$, it approaches that of the PFR model. Similarly, for $St \ll 1$, the ignition locus approaches that of the adiabatic model, while for $St \gg 1$, it approaches that of the strongly cooled model. In fact, the asymptotes defined by the last two limiting models provide an adequate (but slightly conservative) approximation of the entire ignition locus.

• **$\theta_c > 0.5$.** In this case, Δ_c may be a nonmonotonic function of St and Pe_h, i.e., for a fixed Pe_h, Δ_c vs. St curve may have a local minimum. Similarly, for a fixed St, Δ_c vs. Pe_h curve may have a local minimum. The smallest Δ_c occurs at intermediate values of St and Pe_h and has to be determined numerically. In this case, Eq. 24a provides a conservative approximation to the ignition locus. The approximation approaches the exact result as St increases.

• **$\theta_c < -1$.** In this case, Δ_c is a monotonic function of St but may be nonmonotonic with Pe_h. By analyzing the linearized form of Eqs. 6–8, it can be shown that if $0 < St < St^{**}$, where

$$St^{**} = \frac{-1}{(1 + \theta_c)} \tag{28}$$

Δ_c vs. Pe_h curve is monotonically increasing. In this case, a conservative approximation to the runaway locus is given by Eq. 12. When $St > St^{**}$, the smallest value of Δ_c is $St(-\theta_c)$ and occurs at $Pe_h = Pe_h^*$, where Pe_h^* is the solution of

$$\cot \Lambda = \frac{\Lambda}{Pe_h} - \frac{Pe_h}{4\Lambda}; \quad \Lambda^2 = -St(1 + \theta_c)Pe_h - \frac{Pe_h^2}{4}$$

$$(0 < \Lambda < \pi) \tag{29}$$

The minimum in the runaway curve is too shallow to be noticed in Figure 6. In this case, Eq. 24b provides a conservative approximation to the runaway locus. Calculations have shown that this approximation is extremely close to the exact value for all $Pe_h > Pe_h^*$.

Finally, it should be pointed out that the criteria derived here are also applicable to heterogeneous catalytic reactors if $Q(T_o)$ is interpreted as the rate of heat generation per unit volume of the reactor at inlet conditions. This quantity may be measured or calculated using the kinetics, catalyst properties, etc.

Acknowledgment

This work is supported by an ACS-PRF grant. The computations shown in Figures 5 and 6 were carried out by Mr. Sean Geraghty.

Notation

A = area of heat transfer
c_p = specific heat
E = activation energy
L = length
Pe_h = Peclet number
q = volumetric flow rate
$Q(T_o)$ = rate of heat generation per unit volume, $Q_0 \exp(-E/RT_o)$
R = universal gas constant
Se = Semenov number
St = Stanton number
T, T_o, T_c = temperature, inlet temperature, and coolant temperature
t_c = characteristic time for convection
t_g = characteristic time for heat generation
t_r = characteristic time for heat removal
t_λ = characteristic time for heat conduction
u_0 = velocity
x = position

Greek letters

γ = activation energy
δ = Frank-Kamenetskii number
Δ = Damkohler number
λ = thermal conductivity
θ, θ_c = temperature, coolant temperature
ρ = density
σ_θ^2 = variance of RTD function

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Manuscript received Jan. 23, 1989, and Mar. 17, 1989.