Korean J. of Chem. Eng., 5(1) (1988) 53-59

ANALYSIS OF A CFSTR WITH TWO CONSECUTIVE REACTIONS IN TRANSIENT STATES

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(Received 6 May 1987 • accepted 21 August 1987)

Abstract—The sensitivity of a chemical reactor is defined by the matrix which relates the steady state gain of output variables to unit step changes in input variables. This definition proves applicable to reactors with arbitrary residence time distributions. The sensitivity calculation is illustrated by treating a specific example.

Three ordinary differential equations which govern the transient behavior of a CFSTR with two consecutive reactions are numerically solved to demonstrate the parametric sensitivity and temperature runaway phenomena for some parameters such as the feed temperature, the feed concentration, the heat transfer coefficient and the wall temperature. The estimation of the regions of parametric sensitivity is briefly discussed.

INTRODUCTION

Since the landmark report on autothermic processes by Van Heerden[1], numerous theoretical and experimental investigations have been presented concerning the multiplicity, stability and sensitivity of various chemical reactor systems. During the early stage of theoretical developments in the 1950's and 1960's, Amundson, Aris and their coworkers' contribution was the most noticeable whereas, in the 1970's, Poore's introduction of Hopf bifurcation theorem was a major step in the analysis of dynamical systems. The introduction of the catastrophe theory in the analysis of multiple steady state solutions and Vejtasa and Schmitz'[2] experimental verification of multiple solutions and stability of a continuous flow stirred tank reactor (CFSTR) should also be noted. For extensive reviews on the multiplicity, stability and sensitivity of chemical reactors, the reader may be referred to Schmitz[3], Hlavacek and Rompay[4], Ray[5] and Lapidus and Amundson[6].

To date, in spite of the enormous number of articles published, most of these have been focused on reactors with single reactions. It is only in the late 1970's that Luss and his coworkers[7-9] analyzed extensively the multiple steady states of a CFSTR with parallel or consecutive reactions. Westerterp[10] treated a fluidized bed reactor with consecutive reactions to show that there could be as many as five steady states. It was pointed out that all of those steady states could not be obtained in an actual reactor not only because of the instability but also due to the temperature safety limit. Liu and Amundson[11] also investigated a series of consecutive reactions in a polymerization reactor.

The stability analysis of a CFSTR with consecutive reactions was first given by Sabo and Dranoff[12] whose work also included the estimation of regions of asymptotic stability by the Liapunov direct method. A systematic study of multiplicity and stability was given by Hlavacek et al.[13] and the problem of small bifurcating orbits was investigated by Cohen and Keener [14] by the method of multiscale analysis. Hopf bifurcation theorem for multi-dimensional systems was introduced by Poore[15] and used to analyze a CFSTR with two consecutive reactions by Halbe and Poore [16]. Recently, Westerterp and his coworkers[17,18] considered the design of a plug flow reactor (PFR) with two parallel or consecutive reactions. They obtained a runaway criterion by considering both the selectivity of the desired product species and the maximum allowable temperature due to Van Welsenare and Froment[19].

As one may notice, there are a growing number of articles on multiple reaction systems. Analysis of multiple reaction systems is important not only because it can be directly applied to actual systems but also because it gives the basis for understanding more complex systems. Here we consider the sensitivity and parametric sensitivity of a CFSTR with two consecutive reactions in transient states. We first define the sensitivity of a chemical reactor with an arbitrary residence time distribution. The sensitivity defined in this way is calculated for a CFSTR with consecutive reactions and the result is found useful in choosing a proper steady state for a stable operation of the reactor. Numerical integration of the governing equations is also carried out to show that the dynamics exhibit parametric sensitivity and the reactor temperature rises in an uncontrollable way for some parameter values. This indicates that, even when the steady state is unique and stable, the reactor cannot be operated with those parameter values.

MATHEMATICAL MODEL

Let us consider a continuous flow stirred tank reactor in which two consecutive, irreversible, exothermic, first order reactions A → B → C occur. If constant physical and chemical properties, constant reactor wall temperature, and a feed containing only reactant A are assumed, the material and energy balance equations can be written as

$$\theta \frac{dC_A}{dt} = C_{Af} - C_A - \theta C_A k_{10} \exp(-E_1/RT) \tag{1}$$

$$\theta \frac{dC_B}{dt} = -C_B + \theta C_A k_{10} \exp(-E_1/RT) - \theta C_B k_{20} \exp(-E_2/RT) \tag{2}$$

$$\theta \frac{dT}{dt} = T_f - T + (-\Delta H_1/\rho C_p)\,\theta C_A k_{10} \exp(-E_1/RT) + (-\Delta H_2/\rho C_p)\,\theta C_B k_{20} \exp(-E_2/RT) - \kappa(T - T_w) \tag{3}$$

where the notation is explained in the nomenclature.

In the following, we shall consider the sensitivity and the transient response of the reactor governed by the above equations. For the transient analysis, we choose the reactor temperature T as the representative variable from the view point of the temperature control. It will be evident that the temperature control is very important in designing CFSTR's with highly exothermic reactions.

SENSITIVITY

The sensitivity of chemical reactors has been considered for PFR's, whereas the stability has been the major concern for CFSTR's. For a PFR, due to its unique characteristic of "no-mixing", it would be reasonable to define the sensitivity as Coste, Aris and Amundson[20]; that is, the standard deviation of an output to a standard deviation of an input when the input is subject to a small random perturbation superimposed on its steady state value. This definition has been applied only for the case of a PFR and, for a reactor with mixing (e.g., a CFSTR), this definition cannot be applied.

To treat this mixing problem properly, we introduce the following for a CFSTR with R independent reactions,

$$\sum_{j=1}^{N} \alpha_{ij} A_j = 0, \quad i=1,\cdots,R \tag{4}$$

where N is the total number of components. The reaction rate r_i of the i-th reaction is a function of N concentrations C_j and the temperature T. Then the material and energy balance equations can be written in the form

$$\theta \frac{dC_j}{dt} = C_{jf} - C_j + \theta \sum_{i=1}^{R} \alpha_{ij} r_i, \quad j=1,\cdots,N \tag{5}$$

$$\theta \frac{dT}{dt} = T_f - T + \theta \sum_{i=1}^{R} J_i r_i - Q(T) \tag{6}$$

This system of equations may have more than one steady state solution depending upon the input conditions and the operating parameters.

Consider now the unsteady state solution in the neighborhood of one of the steady state solutions. Let

$$C_j(t) = C_{js} + \delta_j(t), \quad j=1,\cdots,N \tag{7}$$

$$T(t) = T_s + \delta_{N+1}(t) \tag{8}$$

where $\delta_j, j = 1,\cdots,N+1$, is assumed to be sufficiently small, and the subscript s denotes the steady state value. We can then linearize the right hand side of Eqns. (5) and (6) about the local steady state using the Taylor series expansion as follows:

$$\theta \frac{d\delta_j}{dt} = \delta_{jf} + \sum_{i=1}^{N+1} m_{ij}\delta_i, \quad j=1,\cdots,N+1 \tag{9}$$

where the matrix $\mathbf{M} = [m_{ij}]$ is the Jacobian matrix the element of which is a function of the steady state solution. In vector form, these equations read

$$\frac{d\delta}{d\tau} = \mathbf{M}\delta + \delta_f \tag{10}$$

where $\tau = t/\theta$. The solution to this equation is

$$\delta = \delta_0 + \int_0^{\tau} \exp[\mathbf{M}(\tau - \eta)]\,\delta_f(\eta)\,d\eta \tag{11}$$

which clearly reveals that δ is dependent upon the history of δ_f.

The steady state gain of δ is

$$\lim_{\tau\to\infty} \delta = -\mathbf{M}^{-1}\delta_f = \mathbf{S}\delta_f \tag{12}$$

Now we define the sensitivity of the system as the matrix **S**. Then each element of **S** represents the steady state gain of one of the output variables with respect to the unit change in one of the input variables. We note that the sensitivity of a CFSTR defined here gives the fluctuation of the output variable in transient states whereas the sensitivity defined by

Chemburkar et al.[21] gives the change in the steady state reactor temperature when one of the parameters is changed.

For a PFR, we may apply the same method as described above. With the assumptions used in the case of a CFSTR, material and energy balances are

$$\frac{\partial C_j}{\partial t}+u\frac{\partial C_j}{\partial x}=\sum_{i=1}^{R}\alpha_{ij}r_i,\ j=1,\cdots,N \tag{13}$$

$$\frac{\partial T}{\partial t}+u\frac{\partial T}{\partial x}=\sum_{i=1}^{R}J_i r_i+Q(T) \tag{14}$$

There is only one steady state for this set of equations. If we introduce the deviation variables

$$C_j(x,t)=C_{js}(x)+\delta_j(x,t),\quad j=1,\cdots,N \tag{15}$$

$$T(x,t)=T_s(x)+\delta_{N+1}(x,t) \tag{16}$$

and linearize the equations about the steady state, we obtain

$$\frac{\partial \delta_j}{\partial t}+u\frac{\partial \delta_j}{\partial x}=\sum_{i=1}^{N+1}m'_{ij}\delta_i,\quad j=1,\cdots,N+1 \tag{17}$$

where $\mathbf{M}'=[m'_{ij}]$ is the Jacobian matrix. We note that the element of this matrix is a function of the position variable x in contrast to the case of a CFSTR.

Now the sensitivity $\mathbf{S}'=[s'_{ij}]$ of a PFR is defined as the matrix which relates the steady state gain of the output variable to the step change in the input variable at $x=0$: that is,

$$\delta=(\exp[\frac{1}{u}\int_0^L\mathbf{M}'\,dx])\delta_o=\mathbf{S}'\ \delta_o \tag{18}$$

We note that this definition of sensitivity is the same as that of Coste, Aris and Amundson based on the statistical analysis for the special case of a PFR. As shown in the two limiting cases, the sensitivity may be defined in this manner for reactors with arbitrary residence time distributions.

As we have the generalized definition of sensitivity of a chemical reactor, let us consider, as an example, the case of a CFSTR in which two consecutive reactions occur. The governing equations are given by Eqns. (1)-(3) and the elements of the Jacobian matrix for this system are shown in Table 1. Since the sensitivity of a CFSTR can be related to extinction or ignition, let us avoid this complexity by considering the case when there is only one steady state for moderate changes in parameters. For this purpose we shall use the example treated by Coste, Aris and Amundson. The numerical values of the system and operating parameters are given in Table 2, and the corresponding sensitivity matrix $[s_{ij}]$ is shown in Table 3. From this matrix, we can easily calculate the range of fluctuation in output variables due to fluctuation in input variables.

Table 1. Elements of Jacobian matrix, $\mathbf{M}=[m_{ij}]$.

$m_{11}=-1-Da_1$

$m_{12}=0$

$m_{13}=-C_{As}Da_1X_1$

$m_{21}=Da_1$

$m_{22}=-1-Da_2$

$m_{23}=C_{As}Da_1X_1-C_{Bs}Da_2X_2$

$m_{31}=J_1Da_1$

$m_{32}=J_2Da_2$

$m_{33}=-1-\varkappa-J_1C_{As}Da_1X_1-J_2C_{Bs}Da_2X_2$

where $Da_1=\theta\,k_{10}\exp(-E_1/RT_s)$

$Da_2=\theta\,k_{20}\exp(-E_2/RT_s)$

$X_1=E_1/RT_s^2$

$X_2=E_2/RT_s^2$

$J_1=(-\Delta H_1/\rho C_p)$

$J_2=(-\Delta H_2/\rho C_p)$

Table 2. Numerical values of the system and operating parameters.

k_{10}	: 6.566 × 10^{10}/sec	k_{20}	: 6.566 × 10^{10}/sec
E_1/R	: 11323 K	E_2/R	: 11606 K
J_1	: 7300 cm^3K/mol	J_2	: 3650 cm^3K/mol
C_{Af}	: 0.02 mol/cm^3	C_{Bf}	: 0.0 mol/cm^3
T_f	: 340 K	T_w	: 345 K
$\varkappa$	: 10.0	θ	: 1200 sec

Table 3. Sensitivity matrix $[s_{ij}]$ for the system with parameters given in Table 1.

	C_{Af}	C_{Bf}	T_f
C_A	0.319	-0.063	-6.8×10^{-5}
C_B	0.420	0.767	2.7×10^{-5}
T	538.0	140.4	0.149

This matrix can also be used in determining the proper steady state for stable operation of the reactor. To illustrate this, we plot s_{i3}, $i=1, 2, 3$, against T_f as shown in Fig. 1. As T_f increases, the variation in T increases while the variation in C_B decreases. Hence, there is an optimum value of T_f for the proper control of the reactor.

PARAMETRIC SENSITIVITY

Bilous and Amundson[22] demonstrated that, in plug flow reactors, some operating characteristics

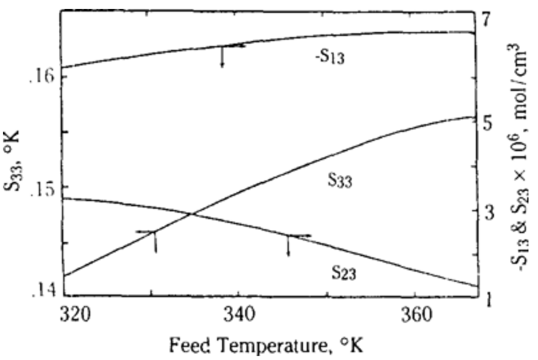

Fig. 1. Sensitivities of C_A, C_B and T with respect to the feed temperature.

showed an extreme change for only a slight change in system or operating parameters. For example, the hot spot temperature is very sensitive to relatively small changes in system parameters such as the heat transfer coefficient and the wall temperature. Therefore, if care is not taken, the temperature may rise in an uncontrollable way, which gives rise to temperature runaway. This phenomenon is known as the parametric sensitivity.

Since Bilous and Amundson, some criteria have been developed to avoid such phenomena in plug flow reactors with single reactions. To the authors' knowledge, however, there has been no report on the parametric sensitivity of CFSTR's in transient states. Here, we are not concerned with the steady state solutions. In a CFSTR at a steady state, large changes in output due to small variations in system parameters are usually related to multiple solutions of the system equations and hence to the stability problems. This problem is not sought in this paper. In the following, we give some examples of parametric sensitivity exhibited during transient states. This information enables us to choose proper start up conditions as well as proper control schemes.

For the analysis of the transient characteristics, the governing equations (1) to (3) are solved numerically with the Runge-Kutta scheme using double precision arithmetic. The required time increment for accuracy and stability of the scheme was found to be 0.01-0.05 sec. In Fig. 2, transient temperature profiles are shown for the reactor initially filled with an unreacted feed. If the heat transfer coefficient takes a value less than 10, its small change gives rise to a severe change in the transient behavior of the reactor. In other words, the system exhibits parametric sensitivity.

In Fig. 3, typical concentration and temperature profiles are shown when there is temperature runaway. Here, the reactor temperature shoots up almost by the adiabatic temperature rise, and then falls off toward its steady value. The shapes of temperature profiles are similar to those of PFR's, so that Van Welsenare and Froment's criteria[19] for runaway regions may be used. In this case, however, Van Welsenare and Froment's criteria should be modified to obtain a proper criterion for consecutive reactions. Westerterp et al. [17] considered this problem for plug flow reactors. They used two-dimensional approximation, which overestimates the heat effect. In the case of a CFSTR, for a given set of initial conditions (for a PFR, feed conditions are the initial conditions), the profiles are dependent upon additional parameters such as C_{Af} and T_f. This is totally absent in the case of plug flow reactors.

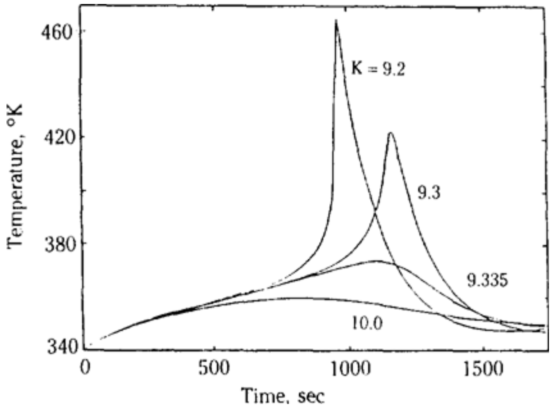

Fig. 2. Effect of the heat transfer coefficient on the temperature profile when the reactor is initially filled with unreacted feed.

Parametric sensitivity has been observed also with respect to other parameters such as the feed concentration and the wall temperature (see Figs. 4 and 5). For a fixed set of parameters, however, parametric sensitivity was not observed with respect to the mean resi-

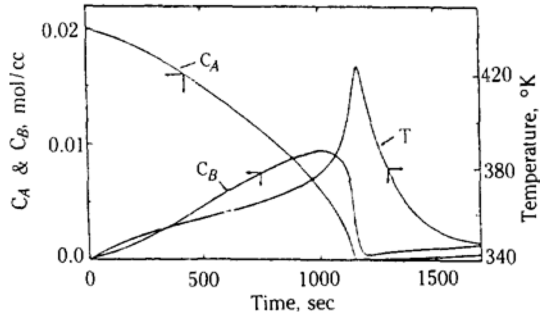

Fig. 3. Concentration and temperature profiles when a parameter set is within the region of parametric sensitivity.

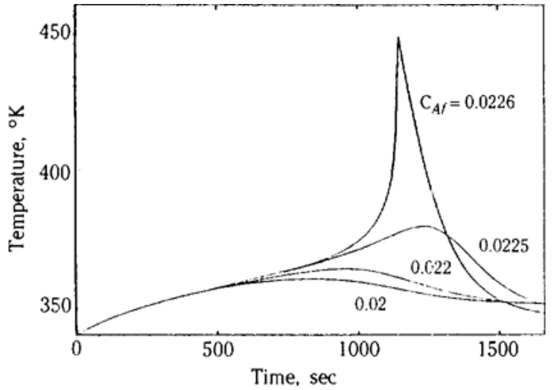

Fig. 4. Effect of the feed concentration on the reactor temperature profile.

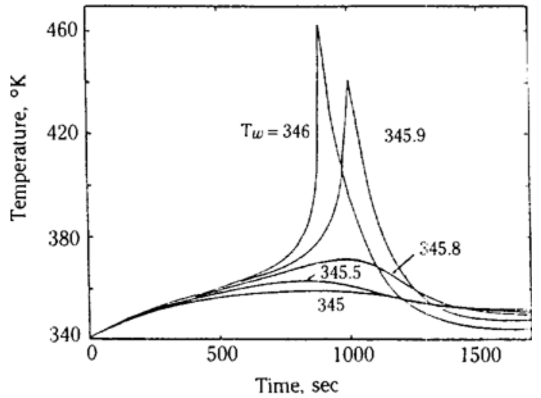

Fig. 5. Effect of the wall temperature on the reactor temperature profile.

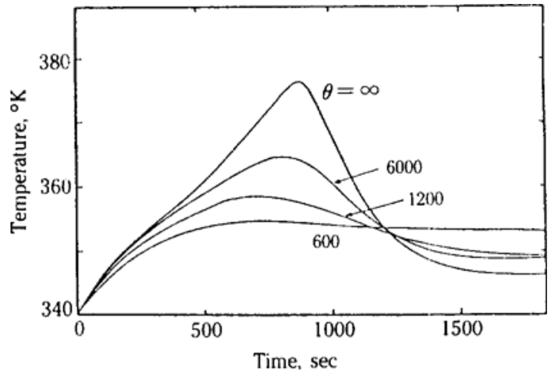

Fig. 6. Effect of the mean residence time on the reactor temperature profile.

dence time (see Fig. 6).

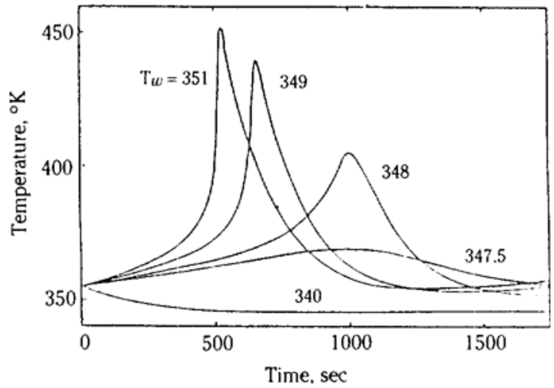

Fig. 7. Effect of the wall temperature on the reactor temperature profile when the reactor is initially at a steady state.

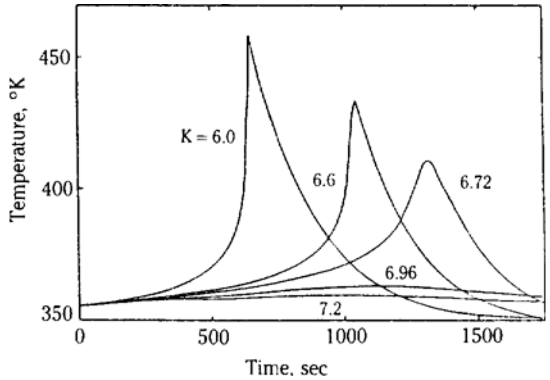

Fig. 8. Effect of the heat transfer coefficient on the reactor temperature profile when the reactor is initially at a steady state.

In Fig. 7, a different case is shown where parametric sensitivity can be observed. In this case, a reactor at a steady state (C_{As} = 0.009490, C_{Bs} = 0.007071, T_s = 355), is disturbed by changing the wall temperature with all other parameters fixed. For ΔT_w<2.5K, the reactor temperature change remains within 15K, while for ΔT_w = 3K, the temperature rises by more than 50K, and for ΔT_w = 4K, by 85K. Since the steady state is unique in all the cases, the reactor temperature will return to a new steady value, which is not far from the original value. However, the reactor temperature rise is considered too large. Therefore one may conclude that the reactor should be operated only under the strict control of the wall temperature. In Fig. 8, the reactor operated at the same steady state is disturbed by changing the heat transfer coefficient. The same phenomenon is observed as in the case of the wall temperature change. Parametric sensitivity was also observed for variation in the feed concentration (see Fig. 9).

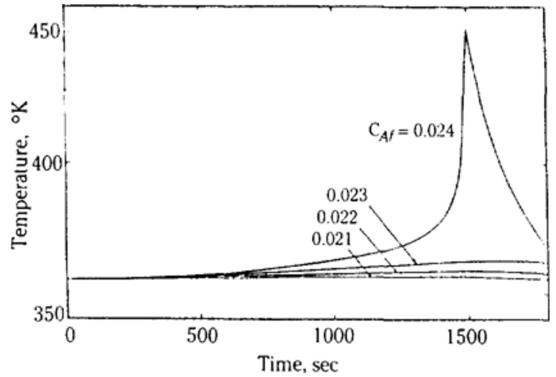

Fig. 9. Effect of the feed concentration on the reactor temperature profile when the reactor is initially at a steady state.

ESTIMATION OF REGIONS OF PARAMETRIC SENSITIVITY

As stated earlier, Van Welsenare and Froment's criterion for the estimation of temperature runaway regions for a PFR is not readily applied to the case of a CFSTR: the assumption of $T_w = T_f$ is hardly justified and, furthermore, the additional parameters of initial conditions are present. For consecutive reaction systems, direct application is not possible even in the case of a PFR since it is necessary to use the three-dimensional space. This fact led Westerterp and Ptasinski [17] to use the two-dimensional approximation for the analysis of a PFR.

In the case of a CFSTR considered here, it was observed that temperature runaway could be avoided if the steady state temperature to be reached was below a certain value when a parameter changed from its reference value. As an example, let us consider the cases shown in Figs. 2, 4 and 5. If the steady state temperature to be reached is below 351.8K, no inflexion point in the temperature profile is observed before the temperature maximum and it is from this value of the parameter that an inflexion point is about to appear. However, this observation is totally empirical and it certainly bears further investigation.

CONCLUDING REMARKS

Here, we have investigated the sensitivity and parametric sensitivity of a CFSTR with two consecutive reactions A → B → C. The sensitivity of a chemical reactor is defined as the matrix which relates the steady state gain of output variables to unit step changes in input variables. This definition can be applied to a reactor with an arbitrary residence time distribution and was found to be the same as Coste, Aris and Amundson's definition given in the case of a PFR.

A requirement in the calculation of sensitivity is that the fluctuation is small enough so that the linearization is valid. In essence, therefore, sensitivity is a local property of a steady state. For the analysis of the dynamic property of a nonlinear system, it is necessary to integrate the governing equations directly. By performing an extensive numerical integration, we have shown that for some parameters the system exhibits parametric sensitivity in transient states. A small change in the feed temperature, the feed concentration, the heat transfer coefficient or the wall temperature can lead to a large variation in the temperature profile. For a CFSTR, this is not related to sensitivity problems while sensitivity analysis would be utilized to predict the region of parametric sensitivity in the case of a PFR. The essential difference between the two reactor systems arises from the mixing property.

NOMENCLATURE

A_j : j-th component
C : concentration, mol/*l*
C_p : specific heat, cal/g°C
E : activation energy, cal/mol
H : enthalpy, cal/mol
J : parameter representing the heat of reaction
k : rate constant, 1/sec
M : Jacobian matrix
N : Number of components
m_{ij} : element of the Jacobian matrix
R : gas constant or number of reactions
S : sensitivity matrix
s_{ij} : element of the sensitivity matrix
T : temperature
t : time
u : velocity
x : coordinate along a PFR axis

Greek Letters

α_{ij} : stoichiometric coefficient
δ : deviation variable
κ : dimensionless heat transfer coefficient
ρ : density
θ : mean residence time
τ : dimensionless time

Subscripts

A, B : reactant A or B
f : feed
i : reaction
j : chemical species
w : wall

1 : reaction A → B
2 : reaction B → C

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