Mediating Operation of Catalytic CSTR to Stabilize Intermediate Steady State

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A novel approach for stabilizing the intermediate steady state of a continuous stirred-tank reactor (CSTR) is proposed by using a special type of periodic forced operation, the so-called mediating operation. The mediating operation enables new additional steady states for which one of the new intermediate steady states is stable to be produced. Thus the proposed approach employs a periodic forcing for stabilization of a selected steady state by control of a steady-state multiplicity. The feed flow rate is considered to be a manipulated variable. Changing CSTR multiplicity is investigated for two-step control inputs. It is shown, analytically, that under two-step control CSTR can exhibit at most five steady states with a stable intermediate steady state. A constructive procedure is proposed for finding control parameters corresponding to maximal multiplicity, that is, for stabilizing an intermediate steady state by two-step control.

Introduction

A novel approach for achieving a stable intermediate steady state of a catalytic continuous stirred-tank reactor (CSTR) is considered by using a special type of periodic forcing, the so-called *mediating operation.* The mediating operation as a new periodic operation approach for catalytic CSTR with *widely separated time scales* has been proposed by Gol'dshtein et al. (1996). Mediating operation is introduced as a periodic *intermediate-mode operation with respect to different reactor time scales*. The main goal of the operating method is to control two system responses by manipulating a single control input. The study demonstrates that mediating operation inputs can produce additional steady states of CSTR, for which one new intermediate steady state is stable. Thus the reactor behavior for the *intermediate temperature area* can be stabilized. The proposed novel approach can be formulated as *an application of mediating operation to control a steady-state multiplicity for the achievement of a stable steady state in the selected area*.

The stabilization of chemical reactor operation can be viewed as a potential benefit of the forced periodic operation approach. The unforced classic CSTR with a single reaction may have a single stable steady state as a minimum or three steady states as a maximum. For maximal three multiplicity the lower and upper steady states are stable and the intermediate one is unstable (see, for example, Uppal et al., 1974, 1976). Traditionally, stabilizing reactor operation in the intermediate domain is considered as moving the stable steady state (lower or upper or single) of periodically forced CSTR in an unstable operation domain of the unforced reactor. In this sense, vibrational control by feed-flow-rate manipulation can change multistability to a single stable steady state (Bellman et al., 1983) or can move an upper steady state in some intermediate operation domain (Cinar et al., 1987a,b). Mediating operation by feed-flow-rate manipulation can also result in a single stability or can move a stable lower steady state in the vicinity of the unstable intermediate steady state of the unforced reactor (Gol'dshtein et al., 1996).

A novel possibility for stabilizing the intermediate steady state arises from the ability to mediate the operation *to control a steady-state multiplicity*. Gol'dshtein et al. (1990) have shown that two-step periodic forcing of the intermediate mode may lead to five steady states, of which one of the intermediate steady states is stable. Hence, the mediating operation enables achievement of a stable steady state for the intermediate temperature area by creating additional multistability of CSTR. For this purpose the two-step mediating operation is examined by using singular perturbation and averaging methods. Multiplicity features of an averaged steady-state system are studied by using catastrophe theory (see, for example, Bröcker and Lander, 1975; Poston and Stewart, 1978; Golubitsky and Schaeffer, 1985).

In general, chemically reacting systems may exhibit complicated steady-state multiplicity. Steady-state multiplicity and possible types of bifurcation diagrams for CSTR as a multireaction system have been researched in detail by Balakotaiah and Luss (1982, 1983, 1984, 1988). The dynamic features of systems with widely separated time scales have been studied by Sheintuch and Luss (1987) for the limiting case. The multiplicity problem of CSTRs coupled in series has been considered by Dangenlmayr and Stewart (1985) and Retzloff et al. (1992).

This article addresses a new multiplicity problem of CSTR caused by periodic manipulation of external input as a feed flow rate. It is shown, analytically, that for the two-step control multiparameter, the CSTR problem is described by standard butterfly singularity. As a result, CSTR can exhibit at most five steady states that have a stable intermediate steady state. A systematic numerical procedure is presented for finding amplitude parameters of two-step control that provide five steady states and in this way enable stabilizing intermediate steady state. In particular, it is shown that only stroboscopical control can lead to the desired stabilization. It is also shown that correlation between a coolant temperature and a feed-flow temperature is essential in order to realize maximal multiplicity.

Reactor Model and Mediating Operation

The chemical reactor is considered to be a two-phase well-stirred tank reactor with a gas mixture reacting on the surface of a solid catalyst. A thermal equilibrium is assumed at all times between different phases in the reactor. For a single first-order reaction the heat- and mass-balance equations of the gas–solid CSTR have the form

$$(V\rho c_p + mc_s)\frac{dT}{dt'} = -\rho c_p F(T - T_f) - hA(T - T_c) + V(-\Delta H)Ck_0\exp\left(-\frac{E}{RT}\right) \quad (1)$$
$$V\frac{dC}{dt'} = -F(C - C_f) - VCk_0\exp\left(-\frac{E}{RT}\right).$$

To reduce to dimensionless form it would be desirable that F as a control variable should be a *linear* parameter of a dimensionless system as it was in the initial system (Eq. 1). So following Gol'dshtein et al. (1996) the system (Eq. 1) has the following dimensionless form:

$$\frac{d\theta}{dt} = -u\theta - \alpha(\theta - \theta_c) + B(1-\eta)k(\theta)$$
$$\gamma\frac{d\eta}{dt} = -u\eta + (1-\eta)k(\theta). \quad (2)$$

For the ratio of a gas heat capacity to the total reactor heat capacity, γ is considered to be a *small parameter*, because the solid density is 10^3 times greater than the gas density. Thus system 2 is a singularly perturbed system with a small parameter $\gamma \ll 1$. Further, following an asymptotic analysis scheme (see, for example, Gol'dshtein and Sobolev, 1988, 1992), *zero-approximation*, $\gamma = 0$, of system 2 is considered:

$$\frac{d\theta}{dt} = -u\theta - \alpha(\theta - \theta_c) + B(1-\eta)k(\theta)$$
$$0 = -u\eta + (1-\eta)k(\theta) \Rightarrow \eta = \frac{k(\theta)}{k(\theta)+u}. \quad (3)$$

Gol'dshtein et al. (1996) have shown that heat processes are approximately $1/\gamma$ times slower than concentration processes in gas–solid CSTR, $\tau_{\text{conc}} \ll \tau_{\text{temp}}$. Mediating operation is introduced as an *intermediate mode operation with respect to slow and fast reactor processes*, $\tau_{\text{conc}} \ll \tau \ll \tau_{\text{temp}}$. Taking into account the type of operation considered, the traditional averaging method (Bogoliubov and Mitropolsky, 1961) can be used with a period of averaging defined by the variable control period, τ. Note that *temperature as a slow variable can be regarded as a constant during the interval of averaging*. The averaged equations of Eq. 3 become

$$\frac{d\theta}{dt} = -\hat{u}\theta - \alpha(\theta - \theta_c) + B(1-\hat{\eta})k(\theta)$$
$$\hat{\eta} = \frac{1}{\tau}\int_0^\tau \frac{k(\theta)}{k(\theta)+u}dt. \quad (4)$$

Steady states of the averaged system (Eq. 4) are defined by the relation $d\theta/dt = 0$, which leads to

$$0 = -\hat{u}\theta - \alpha(\theta - \theta_c) + B(1-\hat{\eta})k(\theta)$$
$$\hat{\eta} = \frac{1}{\tau}\int_0^\tau \frac{k(\theta)}{k(\theta)+u}dt. \quad (5)$$

Maximal Multiplicity of the Two-Step Mediating Operation

Introducing the two-step periodic input of intermediate mode can lead to essential change of the CSTR's dynamic behavior. Gol'dshtein et al. (1990) demonstrated the existence of five steady states for the two-step mediating operation. In this part of this article we aim to show analytically that multiplicity features of system 5 are described by so-called *butterfly singularity* (see, for example, Poston and Stewart, 1978). Hence, for the two-step mediating operation CSTR may exhibit at most five steady states. It should be emphasized that for maximal (five) multiplicity of butterfly singularity at least one of three intermediate solutions is a stable one. Thus stabilization of an intermediate steady state is achieved by realizing maximal multiplicity.

A bifurcation set of butterfly singularity is a four-dimensional space described by four bifurcation parameters. Thus, we also determine four critical (bifurcation) parameters here, to which the reactor steady-state system (Eq. 5), characterized by a large number of parameters, may be reduced. For investigating the influence of the two-step mediating operation on the dynamic behavior of CSTR, it would be best to separate the two-step control parameters from other bifurcation parameters. In particular, this separation enables one to find the two-step control values for which five steady states with a stable intermediate one can be achieved (see the next section).

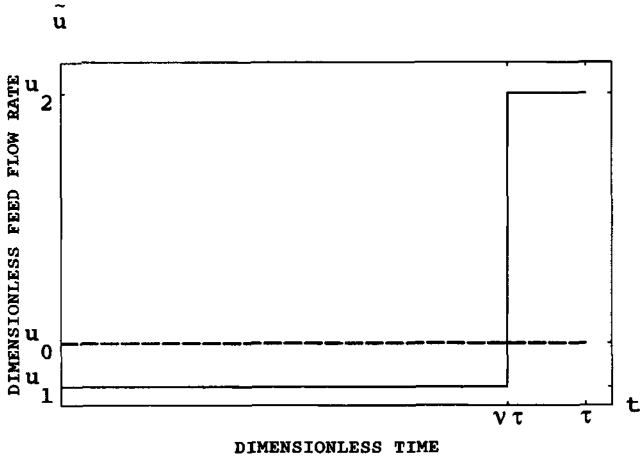

Figure 1. Two-step periodic forcing function.

Dashed line corresponds to the average value of the feed flow rate, u_0.

Let us consider zero-average oscillations of feed flow rate, $\hat{u} = u_0$ in the form of two-step periodic input (see Figure 1)

$$\tilde{u}(t) = \begin{cases} u_1 & \text{for} \quad n\tau \le t \le (n+\nu)\tau \\ u_2 & \text{for} \quad (n+\nu)\tau < t \le (n+1)\tau, \end{cases} \tag{6}$$

where ν is the duty fraction and $n = 0, 1, 2, \ldots$. Note that the selected forcing function gives the same average output as does the widely used nonsymmetric rectangular waveform (see, for example, Meerkov, 1980).

Equations describing steady states of the averaged system (Eq. 5) under two-step periodic control are

$$0 = -u_0\theta - \alpha(\theta - \theta_c) + B(1-\hat{\eta})k(\theta)$$
$$\hat{\eta} = k(\theta)(k(\theta) + u_2 + u_1 - u_0)/[(k(\theta)+u_1)(k(\theta)+u_2)]. \tag{7}$$

Equations 7 can be combined to give a single equation

$$(u_0 + \alpha)\theta - \alpha\theta_c = Bk(\theta)\frac{k(\theta)u_0 + k(\theta)u_1u_2}{(k(\theta)+u_1)(k(\theta)+u_2)}. \tag{8}$$

For reducing Eq. 8, define new variable z, new reactor parameters

$$z = \frac{\theta}{1+\beta\theta} - \frac{\alpha\theta_c}{u_0 + \alpha + \alpha\beta\theta_c} \qquad r = \frac{\alpha\theta_c}{u_0 + \alpha + \alpha\beta\theta_c}$$
$$q = B\beta\frac{u_0}{u_0 + \alpha + \alpha\beta\theta_c}$$
$$s = \frac{1}{\beta} - \frac{\alpha\theta_c}{u_0 + \alpha + \alpha\beta\theta_c} = \frac{1}{\beta}(1-\beta r) \tag{9}$$

and new forcing parameters

$$n_1 = u_1/u_0 \qquad n_2 = u_2/u_0. \tag{10}$$

The denominator of Eq. 8 is positive, so the equation can be reduced to

$$[(1+q)z - sq]e^{2(z+r)} + u_0[(n_1 + n_2 + n_1n_2q)z - n_1n_2sq]e^{z+r} + u_0^2n_1n_2z = 0. \tag{11}$$

Note that the feasible region of parameters described earlier can be determined as follows. Reactor parameters q, s, u_0 must be positive, while parameter r can be negative or positive but close to zero. Control parameters satisfy, for example, the condition, $0 \le n_1 \le 1 \le n_2$, because relative amplitudes of control pulses are symmetric variables for the averaged reactor system 7.

The presence of the nonzero mediating operation means that in Eq. 11, $u_0^2n_1n_2 = u_1u_2 \ne 0$. Under this condition Eq. 11 can be rewritten as

$$F(z,A_0,B_0,A_1,B_1) \overset{\text{def}}{=} A_1(z - A_0)e^{2z} + (B_1z - B_0)e^z + z = 0, \tag{12}$$

where

$$A_0 = A_0(s,q) = sq/(1+q)$$
$$A_1 = A_1(n_1,n_2,u_0,q,r) = \frac{1}{n_1n_2}(1+q)\frac{e^{2r}}{u_0^2}$$
$$B_0 = B_0(u_0,s,q,r) = sq\frac{e^r}{u_0}$$
$$B_1 = B_1(n_1,n_2,u_0,q,r) = \left[\left(\frac{1}{n_1} + \frac{1}{n_2}\right) + q\right]\frac{e^r}{u_0}. \tag{13}$$

The set of equations $F = dF/dz = d^2F/dz^2 = d^3F/dz^3 = d^4F/dz^4 = 0$ has a *unique solution* (for details see Appendix A)

$$\begin{aligned} & z = 3 \\ A_0 = 6 \qquad & A_1 = 1/e^6 \\ B_0 = 12/e^3 \qquad & B_1 = 4/e^3. \end{aligned} \tag{14}$$

Note that $d^5F/dz^5 \ne 0$. So, following Poston and Stewart (1978), the point (Eq. 14) is a *single butterfly point* of butterfly singularity.

By Thom's theorem (see, e.g., Poston and Stewart, 1978) the steady-state equation of CSTR (Eq. 12) defines locally butterfly singularity. Hence the maximal multiplicity of CSTR under the two-step mediating operation is 5 (see, also, Appendix B). Furthermore multidimension space of the CSTR parameters can be reduced to four-dimensional space (A_0, B_0, A_1, B_1), where bifurcation behavior is described by the classic bifurcation diagram of butterfly singularity (see, e.g., Bröcker and Lander, 1975). Below, a situation of maximal (five) multiplicity with a stable intermediate steady state is numerically investigated in detail.

Mapping of a Parameter Region Provided Five Steady States with a Stable Intermediate One

This part illustrates a successive procedure for finding control parameters, u_1, u_2, that lead to an appearance of the stable intermediate steady state. For this reason, the parameter area that has maximal multiplicity of five steady states is searched in (A_0, B_0, A_1, B_1) space. A systematic procedure for dividing parameter space into regions with a different number of solutions for standard polynomial singularities is described, for example, in Bröcker and Lander (1975) and Poston and Stewart (1978). We follow an approach that was developed by Balakotaiah and Luss (1984, 1988) for the *global parameter space* of a nonlinear CSTR problem.

First, in parametric space (A_0, B_0) we trace the locus of the swallowtail points defined by

$$F = \frac{dF}{dz} = \frac{d^2F}{dz^2} = \frac{d^3F}{dz^3} = 0. \tag{15}$$

By eliminating A_1, B_1 from Eq. 15, the next equations (parameterized by z) can be obtained

$$A_0 = 2(z^2 - 6)/(2z - 5)$$
$$B_0 = 4(3 - 3z + z^2)/e^z. \tag{16}$$

Calculation shows that the positiveness of the denominator, $2z - 5 > 0$, is required for tracing feasible A_0, B_0 values. Figure 2 shows the graph of Eqs. 16, which divides the (A_0, B_0) plane into two regions. For all A_0, B_0 values inside the cusp, Eq. 12 has a maximum of five solutions for some A_1, B_1. For all A_0, B_0 values outside the cusp, Eq. 12 has at most three solutions for some A_1, B_1.

It should be emphasized that only parameters A_1 and B_1 depend on control parameters u_1 and u_2 (see Eq. 13). So if dimensionless reactor parameters u_0, α, B, β, θ_c provide the location of the A_0, B_0 values inside the cusp in Figure 2, then control parameters u_1 and u_2 can be chosen by determining the (A_1, B_1) set that leads to five multiplicity having a stable intermediate steady state.

So secondly, for A_0, B_0 *fixed inside the cusp* in Figure 2,

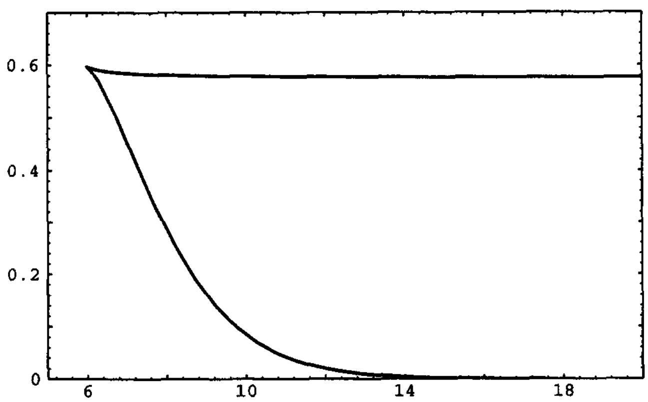

Figure 2. Locus of the swallowtail points in the (A_0, B_0) plane.

For A_0, B_0 inside cusp, 5 steady states are possible; for A_0, B_0 outside cusp, Eq. 12 may have no more then 3 solutions.

A_1, B_1 values are sought for which Eq. 12 has five solutions. For this purpose the locus of the fold points can be constructed in parametric space $(A_1(A_0/B_0)^2, B_1(A_0/B_0))$. For any A_0, B_0 inside the cusp in Figure 2 this locus separates the $(A_1(A_0/B_0)^2, B_1(A_0/B_0))$ plane into three regions that have either 1, 3, or 5 solutions. The locus of the fold points is defined by

$$F = \frac{dF}{dz} = 0. \tag{17}$$

A solution of the system in Eq. 17 gives the following equations parameterized by z (for fixed A_0 and B_0 values)

$$A_1(A_0/B_0)^2 = \frac{1}{n_1 n_2}/(1+q) =$$
$$(A_0/B_0)^2(z^2 + B_0 e^z)/[e^{2z}(A_0 - A_0 z + z^2)]$$
$$B_1(A_0/B_0) = \left[\left(\frac{1}{n_1} + \frac{1}{n_2}\right) + q\right]/(1+q) =$$
$$(A_0/B_0)[B_0(1 - A_0 + z)e^z - A_0 + 2A_0 z - 2z^2]/$$
$$[e^z(A_0 - A_0 z + z^2)]. \tag{18}$$

The calculation shows that a feasible region of A_1, B_1 corresponds to z values belonging to an interval between the roots of the denominator of Eq. 18. Figure 3 shows the locus of the fold points for various values of the A_0, B_0 parameters. In Figure 3 the locality of the five-multiplicity region can be determined, and corresponding control parameters, u_1 and u_2, can be chosen inside the region.

Thus, if dimensionless reactor parameters u_0, α, B, β, θ_c define a point, (A_0, B_0), located inside the cusp in Figure 2, then the control parameters (Eq. 10), n_1 and n_2, that give the five steady states can be determined by plotting the cusp of the fold points in the $[A_1(A_0/B_0)^2, B_1(A_0/B_0)]$ plane (e.g., Figure 3). So stabilization of the intermediate steady state can be achieved by the strategy just described.

Figure 4 shows the average steady-state characteristics obtained by applying the procedure just described. The positive slope of each curve corresponds to a stable steady state, so curves 2 and 3 demonstrate the domain of the stabilized operation in the intermediate zone. The effect is more pronounced for curve 2. It should be emphasized that Figure 4 indicates that higher reactor productivity can be expected for the intermediate steady state. The useful ability of the mediating operation for increasing the average conversion at a given temperature was researched earlier by Gol'dshtein et al. (1996) for lower and upper steady states. So Figure 4 shows that this desirable effect can also be achieved for a stable intermediate steady state.

Influence of Some Parameters on the Feasibility of a Five Multiplicity

To determine the global requirements of control parameters n_1, n_2, for which five solutions are possible, the location of the swallowtail points can be traced in the (n_1, n_2) plane. A simultaneous solution of Eq. 15 of $n_1 n_2$, $n_1 + n_2$ variables gives

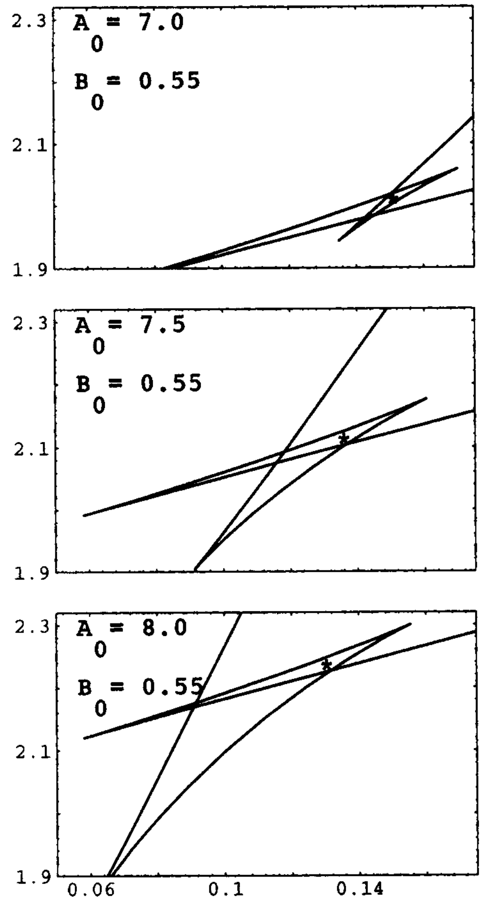

Figure 3. Locus of the fold points in the $(A_1(A_0/B_0)^2, B_1(A_0/B_0))$ plane for A_0, B_0 located inside the cusp in Figure 2.

The locus divides the $(A_1(A_0/B_0)^2, B_1(A_0/B_0))$ plane into regions having 1, 3, or 5 steady states. The * marks the region of five steady states. Inside the region control parameters n_1 and n_2 can be chosen, because for expressions $(A_1(A_0/B_0)^2 = 1/n_1n_2(1+q),\ B_1(A_0/B_0) = [(1/n_1 + 1/n_2) + q]/(1+q))$, parameter q is defined by fixing the A_0, B_0 values.

$$n_1 n_2 = 1/\left[A_1(A_0/B_0)^2(1+q)\right]$$

$$= \frac{4}{1+q}\,\frac{(2z-5)(z^2-3z+3)^2}{(z^2-6)^2}$$

$$n_1 + n_2 = [B_1(A_0/B_0) - q/(1+q)]/\left[A_1(A_0/B_0)^2\right]$$

$$= \frac{4(z^2-3z+3)}{z^2-6}$$

$$\times\left[2(z-2) - \frac{q}{1+q}\,\frac{(2z-5)(z^2-3z+3)}{z^2-6}\right]. \quad (19)$$

By fixing q, the location of the swallowtail points defined by Eq. 19 can be plotted in the (n_1, n_2) plane (see Figure 5). For all n_1, n_2 inside the cusp (of fixed q), Eq. 12 may have five solutions for some parameters r, s, u_0 (not necessarily feasible). Figure 5 illustrates that nonzero control alone can lead to five multiplicity, that is, used above the condition, $u_0^2 n_1 n_2$ $= u_1 u_2 \neq 0$, is necessary (see, also, Appendix B). Figure 5 indicates that five multiplicity can be attained, practically, by control with relative amplitude of one pulse greater than five, n_1 or $n_2 > 5$. The type of control was designated as *stroboscopical control* in Gol'dshtein et al. (1996). Thus, stroboscop-

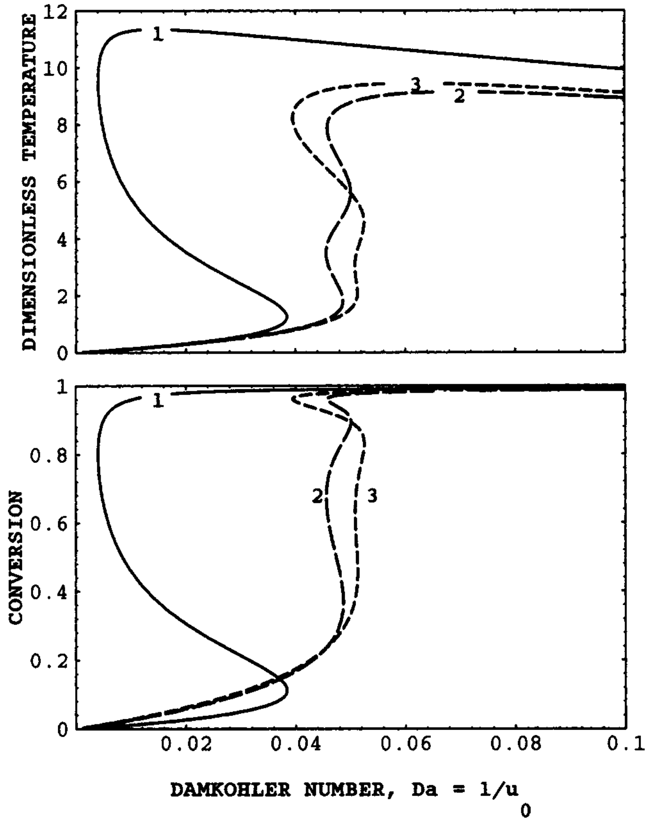

Figure 4. Steady-State characteristics vs. Damköhler number.

Reactor parameters are $\alpha = 2$, $B = 12$, $\beta = 0.04$, $\theta_c = 0$. (1) = Unforced reactor. Control parameters provided stable intermediate steady state, $n_1 = u_1/u_0$ and $n_2 = u_2/u_0$ are (2) $= u_1/u_0 = 0.42$, $u_2/u_0 = 15.6$; (3) $= u_1/u_0 = 0.385$, $u_2/u_0 = 12.8$.

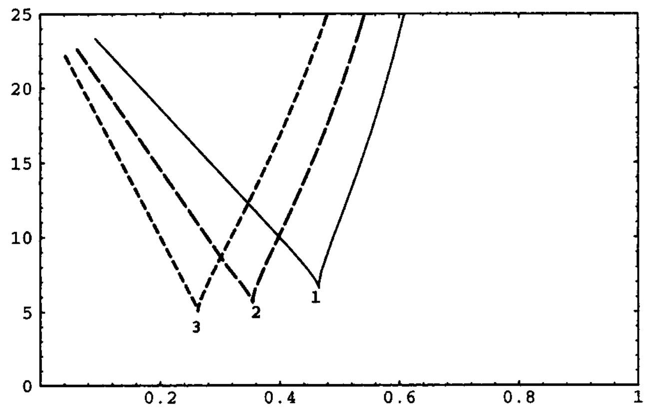

Figure 5. Influence of control parameters on a feasibility of five multiplicity.

Loci of the swallowtail points in the (n_1, n_2) plane for various reactor parameter q. For n_2, n_1 inside each cusp 5 steady states are possible. For each locus parameter q is (1) $= q = 0.3$; (2) $= q = 1$; (3) $= q = 2$.

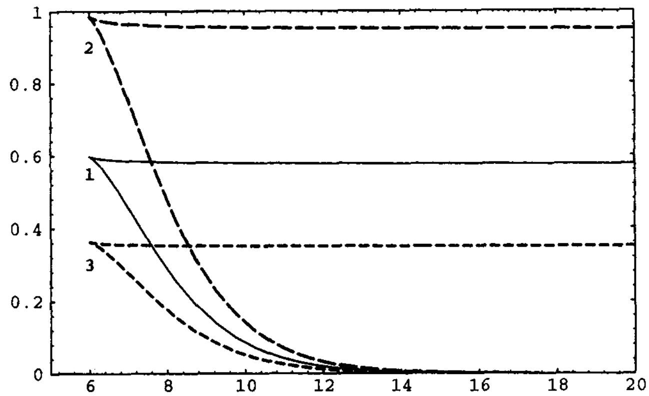

Figure 6. Influence of reactor cooling on a feasibility of the five multiplicity.

Loci of the swallowtail points in the (A_0, B_0/e^r) plane for various reactor parameters r. Inside each cusp 5 steady states are possible. For each locus parameter r is (1) $= r = 0$, ($T_c = T_f$); (2) $= r = -0.5$, ($T_c < T_f$); (3) $= r = 0.5$, ($T_c > T_f$).

ical control can be seen as a necessary control strategy for achieving stable intermediate steady state by two-step input.

Now let us estimate the influence of reactor cooling (as an internal parameter of the CSTR system) on the feasibility of maximal multiplicity. In Figure 6 the locuses of the swallowtail points defined by Eq. 16 are shown in the (A_0, B_0/e^r) plane for various fixed values r. Five steady states are possible for a (A_0, B_0/e^r) area located inside each cusp in Figure 6. For fixed r, the size of the area depends on other (internal) reactor parameters, u_0, q, s, essentially, on u_0 (see Eqs. 13 and 9). Thus, Figure 6 indicates that intense cooling with negative r ($\theta_c < 0$, i.e., $T_c < T_f$) makes possible a five multiplicity for a wider range of average feed-flow-rate values, $u_0 = 1/\text{Da}$ (i.e., for a wider Damköhler-number range, too). The opposite relation, $T_c > T_f$, decreases the feasibility of the five multiplicity.

Conclusion

In this article a novel approach for stabilizing CSTR behavior in the intermediate temperature range has been proposed. The approach is based on the introduction of the mediating operation for creating additional steady states in the intermediate temperature range. CSTR is considered to be a simple model of a gas–solid catalytic reactor with widely separated slow temperature processes and fast concentration ones. Mediating operation has been introduced as a periodic operation in the intermediate mode between fast and slow reactor processes. We analyzed here the ability of the mediating operation to control steady-state multiplicity for achieving an additional stable intermediate steady state.

It was shown, analytically, that for a two-step mediating operation, CSTR multiplicity is described by a classic butterfly singularity. Therefore, CSTR multiplicity can exhibit at most five steady states, for which at least one intermediate steady state is stable. A systematic numerical procedure for finding two control amplitude parameters corresponding to maximal multiplicity was presented in this article. Only stroboscopical control of two-step input can lead to the desired appearance of a stable intermediate steady state. Concerning the internal reactor parameters it was shown that correlation between a coolant temperature, T_c, and a feed temperature, T_f, is critical for realization of maximal multiplicity. For intense cooling, if $T_c < T_f$, five multiplicity can be attained for a wider range of average feed-flow-rate values, u_0 (i.e., Damkohler numbers). The opposite relation, $T_c > T_f$ leads to the opposite result, which avoids the unexpected appearance of additional steady states (if this situation is undesirable).

Control of steady-state multiplicity by periodic forced (external) inputs can be considered a promising novel application for stabilizing the desired steady states. Our study demonstrates the possibilities of a new mediating operation approach for this purpose. The ability to change in a wide range of dynamic behavior of a system with widely separated time scales using a single control variable can be seen as a major advantage of the mediating operation.

Acknowledgment

We are grateful to Prof. V. Balakotaiah for helpful comments.

Notation

A = heat-transfer area
$B = (-\Delta H)C_f/\rho c_p T_f(E/RT_f)$
c_p, c_s = heat capacity of the reacting mixture and solid phase, respectively
C, C_f = concentration, feed concentration
E = activation energy
F, F_0 = feed flow rate and its average value
h = heat-transfer coefficient
ΔH = heat of reaction
k_0 = reaction rate constant
$k(\theta) = \exp[\theta/(1+\beta\theta)]$
m = mass of solid catalyst
n = integer number
R = universal gas constant
t = dimensionless time $= t'\gamma k_0 \exp(-1/\beta) = t'\gamma \text{ Da } F/V$
t' = time
T = reactor temperature
u = dimensionless feed flow rate $= F/Vk_0 \exp(-1/\beta)$
V = volume of the gas reaction mixture
$\alpha = hA/V\rho c_p k_0 \exp(1/\beta)$
$\beta = RT_f/E$
η = dimensionless concentration or conversion $= (C_f - C)/C_f$
θ = dimensionless reactor temperature and its average value $= (T - T_f)/T_f(E/RT_f)$
θ_c = dimensionless coolant temperature $= (T_c - T_f)T_f(E/RT_f)$
ρ = density of the reacting mixture
$\tau_{\text{conc}}, \tau_{\text{temp}}$ = dimensionless characteristic response times of subsystems for concentration and heat processes, respectively

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Appendix A: Determination of the Singular Point Defined by Eq. 12

Equation 12 is

$$F(z,A_0,B_0,A_1,B_1) \overset{\text{def}}{=} A_1(z-A_0)e^{2z} + (B_1z-B_0)e^z + z = 0. \quad \text{(A1)}$$

The locus of the butterfly points is defined by the set of equations

$$F = \frac{dF}{dz} = \frac{d^2F}{dz^2} = \frac{d^3F}{dz^3} = \frac{d^4F}{dz^4} = 0. \quad \text{(A2)}$$

The solution of system (Eq. A2) was obtained by Gol'dshtein et al. (1990). For completeness we also reproduce here a solution that follows the procedure of Balakotaiah and Luss (1982).

Let us define new variables

$$x_0 = A_1(z-A_0)e^{2z} \quad x_1 = A_1e^{2z}$$
$$y_0 = (B_1z-B_0)e^z \quad y_1 = B_1e^z. \quad \text{(A3)}$$

Using new variables A3, system A2 can be written as a linear system of equations

$$\begin{aligned} x_0 + y_0 + z &= 0 \\ 2x_0 + x_1 + y_0 + y_1 &= -1 \\ 4x_0 + 4x_1 + y_0 + 2y_1 &= 0 \\ 8x_0 + 12x_1 + y_0 + 3y_1 &= 0 \\ 16x_0 + 32x_1 + y_0 + 4y_1 &= 0. \end{aligned} \quad \text{(A4)}$$

The solution of system A4 is

$$\begin{aligned} &z = 3 \\ &x_0 = -3 \quad x_1 = 1 \\ &y_0 = 0 \quad y_1 = 4. \end{aligned} \quad \text{(A5)}$$

Substituting Eq. A5 in Eq. A3 we can get Eq. 14.

Appendix B: Maximal Multiplicity of Eq. 11

Equation 12 was obtained from Eq. 11 under condition $u_0^2n_1n_2 = u_1u_2 \neq 0$. It was shown that Eq. 12 has a unique five-multiple solution (see Eq. 14). Here we consider Eq. 11 in a more common form for the purpose of proving that condition $u_1u_2 \neq 0$ is necessary for achieving the maximal (five) number of solutions. The existence of a five-multiple solution for Eq. 11 was proved earlier by Gol'dshtein et al. (1990).

Let us consider Eq. 11 in a common form (see also Gol'dshtein et al., 1990)

$$G(z,a_0,b_0,c_0,a_1,b_1,c_1) \overset{\text{def}}{=} (a_1z-a_0)e^{2z} + (b_1z-b_0)e^z + c_1z - c_0 = 0 \quad \text{(B1)}$$

where a_i, b_i, c_i ($i = 0, 1$) are parameters.

Proposition. If $a_1 \neq 0$ and $c_1 \neq 0$, then Eq. B1 can have five solutions as a maximum.

Proof. Let us introduce new variable $y = e^z > 0$. Equation B1 can be written

$$G(y,a_0,b_0,c_0,a_1,b_1,c_1) = (a_1 \ln y - a_0)y^2 + (b_1 \ln y - b_0)y + c_1 \ln y - c_0 = 0 \quad \text{(B2)}$$

and

$$\frac{d^3G}{dy^3} = 2a_1\frac{1}{y} - b_1\frac{1}{y^2} + c_1\frac{1}{y^3} = \frac{1}{y^3}(2a_1y^2 - b_1y + c_1).$$

If $a_1 \neq 0$ and $c_1 \neq 0$, equation $d^3G/dy^3 = 0$ has two solutions (not necessarily feasible); hence, $G = 0$ has at most five solutions in the global parameter space.

In Eq. 11 $a_1 = (1+q)e^{2r} > 0$ for all feasible values of parameter $q > 0$. Hence condition $c_1 = u_0^2n_1n_2 = u_1u_2 \neq 0$ is necessary for Eq. 11 to have maximal (five) multiplicity.

Thus the preceding condition, $u_1u_2 \neq 0$, which indicates the presence of nonzero control, is a critical condition.

Manuscript received Mar. 26, 1996, and revision received Aug. 26, 1996.