Impact of Process Design on the Multiplicity Behavior of a Jacketed Exothermic CSTR

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Research on exothermic reactor operation has been based mostly on the classic two-state continuous stirred tank reactor model, implicitly assuming that the cooling jacket temperature dynamics are negligible. In this case, the cooling jacket temperature is the manipulated input instead of the cooling jacket flow rate for feedback control of reactor temperature. Adding a cooling jacket energy balance results in much more complex behavior than a simple lag effect. A stabilizing inner-loop cascade controller is assumed in the two-state CSTR model, because the three-state model incorporating cooling jacket temperature dynamics may be open-loop unstable when the two-state model is open-loop stable. The influence of design parameters on the multiplicity behavior of a three-state model is considered. Elementary catastrophe theory is used to study the effect of process parameters such as the cooling jacket flow rate, heat-transfer coefficient, heat of reaction, and cooling jacket feed temperature on the steady-state multiplicity of the three-state model. This multiplicity analysis is particularly relevant for control because the primary bifurcation parameter is the cooling jacket flow rate, the manipulated input for feedback control in the three-state model. This multiplicity analysis guides improvements in process design and/or operation to eliminate difficult operating regions associated with steady-state multiplicities; the presence of multiple steady states results in safety and operation problems due to ignition/extinction phenomena. Reactor scale-up affects the presence of these infeasible reactor operating regions. Certain design parameter changes that remove multiplicities in the two-state model cannot remove multiplicities in the three-state model.

Introduction

Motivation

Continuous stirred tank reactors (CSTRs) present challenging operational problems due to complex open-loop behavior such as input and output multiplicities, ignition/extinction behavior, parametric sensitivity, nonlinear oscillations, and perhaps even chaos. These characteristics demonstrate the need for and difficulty of feedback control system design. It is often desirable to operate CSTRs under open-loop unstable conditions since the reaction rate may yield good productivity while the reactor temperature is still low enough to prevent side reactions or catalyst degradation. CSTRs are good candidates for traditional cascade control strategies; however, cooling jacket temperature dynamics are generally neglected in academic studies of control system designs. One objective of this article is to show that the multiplicity characteristics of exothermic CSTRs change when a cooling jacket energy balance is included in the modeling equations. It is important to consider these characteristics when determining the open- and closed-loop stability properties. Multiplicity analysis gives practical guidance for process redesign to eliminate difficult operating regions associated with input and output multiplicities.

This article reviews previous studies of the steady-state multiplicity and dynamic behavior of CSTRs, and dynamic models which incorporate cooling jacket dynamics are developed. The multiplicity characteristics of the two-state CSTR model (perfectly-mixed exothermic CSTR with a single irreversible reaction) are compared to the three-state CSTR model (which includes a cooling jacket energy balance) for which global multiplicity diagrams are developed. Finally, the influence of process operation and process design parameters on multiplicity is studied in two examples.

Review of CSTR multiplicity and dynamics

Perhaps the most studied chemical reactor system is the perfectly-mixed, exothermic CSTR with a single irreversible reaction. Mathematicians and chemical engineers have subjected this system to intense research activity as a test bed of new analysis techniques for steady-state multiplicity and dynamics (Poore, 1973; Golubitsky and Keyfitz, 1980; Guckenheimer, 1986; Aris and Amundson, 1958; Uppal et al., 1974; Balakotaiah and Luss, 1981). Unfortunately, space limitations prevent a detailed literature survey of the entire body of work associated with this system notwithstanding other reactions with more complex kinetics. We note particularly relevant review articles by Razon and Schmitz (1987) concerning multiplicities and instabilities in chemically reacting systems and Bequette (1991) concerning the nonlinear control of chemical processes.

Aris and Amundson (1958) examined the stability, control, and local dynamics of the standard CSTR model using the local linearization method of Lyapunov and the phase plane analysis techniques of Poincare. Hlavacek et al. (1970) studied the stability, multiplicity, and oscillatory aspects of the standard CSTR model. They determined analytical conditions for multiplicity and found that isolas (closed, isolated steady-state branch of solutions) exist for sufficiently high heat of reaction as one varies the residence time. Uppal et al. (1974, 1976) classified the possible types of multiplicity and dynamic phenomena according to values of the system parameters. Schmitz et al. (1979) compared the theory and methods outlined in Uppal et al. with experimental studies of a second-order homogeneous reaction between sodium thiosulfate and hydrogen peroxide. They found good agreement between theory and experiment in predicting the existence of hysteresis and damped oscillations. Ray (1982) showed that small perturbations in the system parameters may result in control and operability problems when a simple proportional feedback temperature controller is used on the two-state CSTR model. Ray assumed that the inner-loop of the cascade control system was perfectly controlled (cooling jacket dynamics were neglected). He also suggested process redesign as a means to eliminate difficult operating regions.

Chang and Calo (1979) used a catastrophe theory approach in order to determine the output multiplicity behavior for an *n*th-order reaction in a CSTR. Golubitsky and Keyfitz (1980) and Balakotaiah and Luss (1981, 1983) using singularity theory (an extension of elementary catastrophe theory) found exact analytical conditions for the steady-state multiplicity behavior of the standard CSTR model. Balakotaiah and Luss were able to predict the multiplicity pattern for a given set of parameter values. They used the Damköhler number as a distinguished parameter to determine the conditions for hysteresis and isola multiplicities. Planeaux and Jensen (1986) considered the case of a CSTR with extraneous thermal capacitance caused by reactor walls and baffles. Degenerate bifurcations (when certain hypotheses of the Hopf bifurcation theorem fail) were demonstrated and tied to a variety of exotic dynamic behavior such as quasiperiodic oscillations, multiple Hopf bifurcation points, and multiple stable periodic orbits. Guckenheimer (1986) stressed the importance of better mathematical strategies for analysis. He was able to find additional dynamic phenomena by using multiple bifurcation theory. One can surmise from this review that a wealth of results exist for the standard CSTR model and other perturbations of this model. Naturally, it is important to consider other extensions to these prior results, for example, the case of two consecutive reactions $A \rightarrow B \rightarrow C$ (Farr and Aris, 1986; Moiola et al., 1990). Feinberg (1987, 1988) has developed the Deficiency Zero and the Deficiency One Theorems and used these to analyze the multiplicity behavior of a class of isothermal systems.

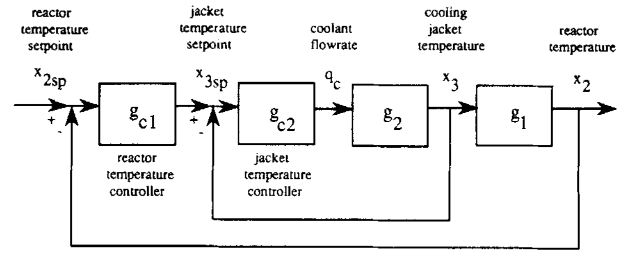

Figure 1. Cascade control scheme for exothermic CSTRs.

The previous multiplicity and control studies dealing with the standard CSTR model have assumed that the "inner-loop" of the cascade control strategy is perfectly controlled; therefore, the cooling jacket temperature is the manipulated variable for reactor temperature control (see Figure 1). In this article, we consider a three-state CSTR that includes cooling jacket temperature dynamics. The manipulated variable for reactor temperature is the cooling jacket flow rate. An objective of this work is to show that the steady-state multiplicity characteristics change with the addition of cooling jacket dynamics, and that it is important to consider this when determining the open and closed-loop stability properties. The three-state CSTR model exhibits input and output multiplicities between cooling jacket flow rate and cooling jacket temperature for certain parameter ranges which complicate the tuning of the "inner-loop" cascade controller. A crucial point is that the multiplicity analysis gives practical guidance for process redesign in order to eliminate difficult operating regions associated with input and output multiplicities.

Continuous Stirred Tank Reactor Models

The standard two-state CSTR model describing an exothermic diabatic irreversible first-order reaction ($A \rightarrow B$) is a set of two nonlinear ordinary differential equations obtained from dynamic material and energy balances (with the assumptions of constant volume, perfect mixing, negligible cooling jacket dynamics, and constant physical parameters).

$$\frac{dC_a}{dt} = \frac{Q}{V}(C_{af} - C_a) - k_0 \exp\left(\frac{-E_a}{RT}\right) C_a \tag{1}$$

Table 1. Dimensionless Variables and Parameters for Two- and Three-State CSTR Models

$x_1=\frac{C_a}{C_{af0}}$	$x_2=\frac{T-T_{f0}}{T_{f0}}\gamma$	$x_3=\frac{T_c-T_{f0}}{T_{f0}}\gamma$	$q_c=\frac{Q_c}{Q_0}$
$\gamma=\frac{E_a}{RT_{f0}}$	$\kappa(x_2)=\exp\left(\frac{x_2}{1+\frac{x_2}{\gamma}}\right)$	$\beta=\frac{(-\Delta H)C_{af0}}{\rho C_p T_{f0}}\gamma$	$\delta=\frac{UA}{\rho C_p Q_0}$
$\phi=\frac{V}{Q_0}k_0e^{-\gamma}$	$q=\frac{Q}{Q_0}$	$\tau=\frac{Q_0}{V}t$	$\delta_1=\frac{V}{V_c}$
$\delta_2=\frac{\rho C_p}{\rho_c C_{pc}}$	$x_{1f}=\frac{C_{af}}{C_{af0}}$	$x_{2f}=\frac{T_f-T_{f0}}{T_{f0}}\gamma$	$x_{3f}=\frac{T_{cf}-T_{f0}}{T_{f0}}\gamma$

$$\frac{dT}{dt}=\frac{Q}{V}(T_f-T)+\left(\frac{-\Delta H}{\rho C_p}\right)k_0\exp\left(\frac{-E_a}{RT}\right)C_a-\frac{UA}{V\rho C_p}(T-T_c) \quad (2)$$

where C_a and T are the concentration of component A and the temperature in the reactor, respectively. An additional energy balance around the cooling jacket assuming perfect mixing yields:

$$\frac{dT_c}{dt}=\frac{Q_c}{V_c}(T_{cf}-T_c)+\frac{UA}{V_c\rho_c C_{pc}}(T-T_c) \quad (3)$$

where T_c is the cooling jacket temperature. Equations 1-3 can be written in dimensionless form:

$$\frac{dx_1}{d\tau}=-\phi x_1\kappa(x_2)+q(x_{1f}-x_1) \quad (4)$$

$$\frac{dx_2}{d\tau}=\beta\phi x_1\kappa(x_2)-(q+\delta)x_2+\delta x_3+qx_{2f} \quad (5)$$

$$\frac{dx_3}{d\tau}=\delta_1[q_c(x_{3f}-x_3)+\delta\delta_2(x_2-x_3)] \quad (6)$$

where x_1, x_2, x_3, and q_c are the dimensionless concentration, reactor temperature, cooling jacket temperature, and cooling jacket flow rate, respectively. The other parameters (ϕ, q, β, and so on) are defined in Table 1. Representative values of the parameters [Cases 1-3, adapted from Ray (1982); Sistu and Bequette (1990)] are in Table 2. Case 1 is open-loop stable over the entire region of operation for the two-state CSTR model, but open-loop unstable in a certain operating region for the three-state CSTR model. Case 2 exhibits ignition/extinction behavior for the two- and three-state models, while Case 3 displays nonlinear oscillations (associated with Hopf bifurcation) for both CSTR models. Under nominal conditions $q=1.0$, $x_{1f}=1.0$, and $x_{2f}=0.0$ by definition; these variables are left in more general form, because they are possible disturbances or design parameters. We use a nominal Damköhler number (ϕ) in our analysis which separates the kinetic and flow rate effects; the traditional Damköhler number is $Da=\phi/q$. In our case studies, the residence time of the cooling jacket is on the order of one-tenth of the residence time of the CSTR.

It is well-known that the exponential relationship of reaction rate with respect to reactor temperature is one of the major nonlinearities of the CSTR. The focus during the past decade has been on the effect of more complicated kinetics on the multiplicity and dynamic behavior of CSTRs. However, we are unaware of any studies that have addressed the influence of cooling jacket dynamics on the multiplicity, stability, and dynamic behavior. Many dynamics and control studies have been based on the two-state model (Eqs. 4-5) and consider x_2 (dimensionless reactor temperature) to be the controlled variable and x_3 (dimensionless coolant temperature) to be the manipulated input. The implicit assumption with the two-state model is that x_3 can be changed very rapidly. This may be true when a boiling liquid is used as the coolant, because changing the jacket pressure has a direct effect on the cooling jacket temperature. Unfortunately, there are a large number of practical applications in industry where a single phase liquid is used as the coolant. The two-state model adequately represents the process only when the coolant flow rate can be "quickly" manipulated to obtain tight control of the coolant temperature. Absolute and velocity constraints on the cooling jacket flow rate as well as the nonlinear coupling of the reactor and cooling jacket temperatures prevent arbitrarily tight control of cooling jacket temperature in practice. We will study a three-state CSTR model (Eqs. 4-6) where x_2 (dimensionless reactor tem-

Table 2. Two- and Three-State Model Parameter Values

Set	ϕ	β	δ	γ	q	δ_1	δ_2	x_{1f}	x_{2f}	x_{3f}
Case 1	0.11	7.0	0.5	20	1.0	10	1.0	1.0	0.0	−1.0
Case 2	0.072	8.0	0.3	20	1.0	10	1.0	1.0	0.0	−1.0
Case 3	0.135	11.0	1.5	20	1.0	10	1.0	1.0	0.0	−1.0
Case 4	. . .	. . .	0.5	20	1.0	10	1.0	1.0	0.0	0.0
Case 5	0.09	7.0	0.5	20	1.0	10	1.0	1.0	0.0	0.0
Case 6	0.0377	21.467	. . .	28.444	1.0	12.468	0.602	1.0	0.0	0.0

perature) is the controlled variable and q_c (dimensionless cooling jacket flow rate) is the manipulated input.

Steady-State Multiplicity

One particularly interesting feature of nonlinear systems is their multiplicity behavior. Balakotaiah and Luss (1981), Sistu and Bequette (1990) and others have demonstrated that *input* multiplicities exist when the dimensionless feed flow rate (q) is used as the manipulated variable in the two-state CSTR. This input multiplicity behavior is one important reason why CSTRs are not generally controlled using the feed flow rate. The existence of input multiplicities in a nonlinear system implies the existence of a region where the "zero dynamics" are unstable (the corresponding linearized system has right-half-plane zeros) (Sistu and Bequette, 1995). A number of researchers (Hlavacek et al., 1970; Uppal et al., 1974; Chang and Calo, 1979; Golubitsky and Keyfitz, 1980; Balakotaiah and Luss, 1981, 1983; Guckenheimer, 1986) derive conditions for steady-state multiplicities in a two-state CSTR model. However, this work will consider the influence of the controller manipulated variables of the two and three-state CSTR models on the multiplicity behavior.

Two-state model

The necessary conditions for output multiplicity are rederived in terms of the current variable and parameter definitions. Equations 4 and 5 can be combined at steady state to give:

$$g(x_{2s},x_{3s},p)=\beta q x_{1f}\frac{\phi\kappa(x_{2s})}{q+\phi\kappa(x_{2s})}-(q+\delta)x_{2s}+qx_{2f}+\delta x_{3s}=0 \quad (7)$$

where x_2 is the "output" or controlled variable, x_3 is the "input" or manipulated variable, and p denotes a vector containing the system parameters. Most previous studies consider dimensionless reactor concentration (x_1) as the output variable; we use the dimensionless reactor temperature (x_2) because of our interest in feedback control. All of our results hold for reactor concentration as an output since there is a one-to-one relationship between dimensionless reactor concentration and dimensionless reactor temperature.

The necessary conditions for output multiplicity, input multiplicity, and the formation of isolas, respectively, are obtained from the implicit function theorem:

$$g=\frac{\partial g}{\partial x_{2s}}=0 \quad (8)$$

$$g=\frac{\partial g}{\partial x_{3s}}=0 \quad (9)$$

$$g=\frac{\partial g}{\partial x_{2s}}=\frac{\partial g}{\partial x_{3s}}=0 \quad (10)$$

Now, consider the condition $\partial g/\partial x_{3s}=0$. The result is:

$$\frac{\partial g}{\partial x_{3s}}=\delta\neq 0 \quad (11)$$

Hence, when x_3 is the manipulated variable (distinguished parameter in singularity theory) input multiplicities, isolas, transcritical bifurcations, and pitchfork bifurcations cannot occur. The presence of isolas and input multiplicities complicate controller design, since more than one manipulated variable (input) value can provide the same state variable (output) value. It is worth mentioning that when q is the manipulated variable, then input multiplicities and isolas can occur (Balakotaiah and Luss, 1981; Sistu and Bequette, 1990). In fact, if one examines the derivatives of $g(x_{2s}, x_{3s}, p)$ with respect to the other parameters, then it is easy to determine that input multiplicities and isolas can *only* occur with variations in q. Therefore, we see that q (dimensionless reactor feed flow rate) is a very important disturbance variable which warrants feedforward control action.

It is well-known that the two-state CSTR model can exhibit output multiplicities, which are physically manifested as hysteresis behavior. The appearance or disappearance of output multiplicities occurs when higher order derivatives of g with respect to the state x_{2s} are zero:

$$g=\frac{\partial g}{\partial x_{2s}}=\frac{\partial^2 g}{\partial x_{2s}^2}=\ldots=\frac{\partial^k g}{\partial x_{2s}^k}=0 \quad (12)$$

$$\frac{\partial^{k+1} g}{\partial x_{2s}^{k+1}}\neq 0 \quad (13)$$

A multiplicity of $k+1$ solutions to Eq. 7 exists around the codimension k singular point x_{2s} satisfying Eq. 12 (Stewart, 1981). Golubitsky and Keyfitz (1980) have shown that the highest-order singularity satisfying Eq. 12 for the two-state CSTR model is $k=2$, which they define to be the "hysteresis variety." We have found that the equation satisfying $\partial^2 g/\partial x_{2s}^2=0$ is given by (note that it is independent of β):

$$\phi\kappa(x_{2s})=q\,\frac{\gamma^2-2\gamma-2x_{2s}}{\gamma^2+2\gamma+2x_{2s}} \quad (14)$$

The solution of Eq. 12 when $k=2$ gives a condition for the critical value of β:

$$\beta_{\text{crit}}=\frac{4}{qx_{1f}}\,\frac{[(q+\delta)\gamma+(\delta x_{3s}+qx_{2f})]^2}{[(q+\delta)(\gamma^2-4\gamma)-4(\delta x_{3s}+qx_{2f})]} \quad (15)$$

This result is more general than previously reported, since it takes into account changes in the reactor feed temperature. Let us consider the point (if it exists) when $g=\partial^2 g/\partial x_{2s}^2=0$. If $\beta=\beta_{\text{crit}}$, then we know from Eq. 12 (when $k=2$) that $\partial g/\partial x_{2s}=0$. However, if $\beta>\beta_{\text{crit}}$ then $\partial g/\partial x_{2s}>0$ since increasing β increases $\partial g/\partial x_{2s}$. Therefore, one can conclude that in this case if $\beta>\beta_{\text{crit}}$ then we see the formation of an S shaped curve, as shown in Figure 2. Upon examination of Eq. 15 we determine that it is possible to remove output multiplicities by increasing δ so that $\beta<\beta_{\text{crit}}$. This means that output multiplicities in a two-state CSTR model can be removed by increasing the heat-transfer coefficient or increasing the heat-transfer area.

A common assumption in steady-state multiplicity studies is the positive exponential approximation for the Arrhenius temperature dependence of the reaction rate. Farr and Aris (1986) pointed out that assuming that γ is infinite is not strictly

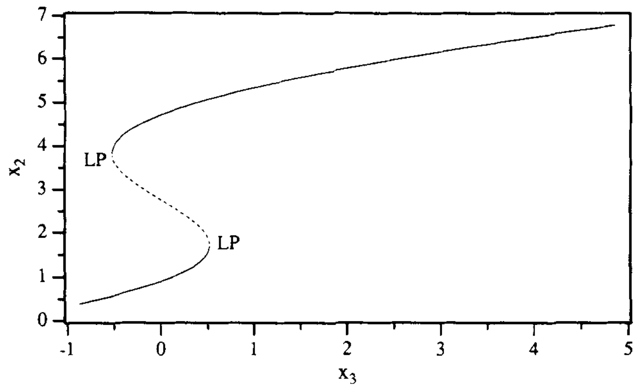

Figure 2. Case 2 output multiplicity characteristics for the two-state CSTR model.

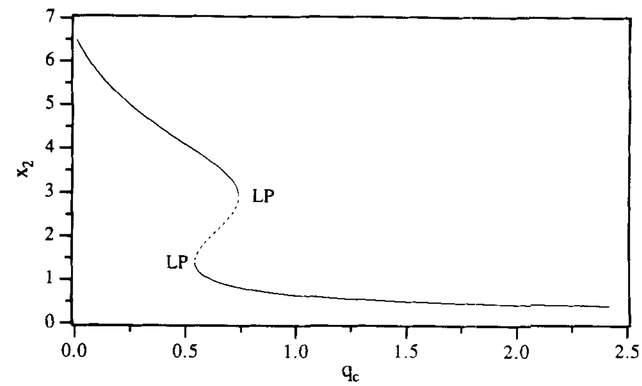

Figure 4. Case 1 multiplicity characteristics for the three-state CSTR model.

correct, since γ influences other nondimensional parameters. In fact, γ generally occurs in an exponential fashion in the denominator of the Damköhler number $(Da=\phi/q)$, hence one must be particularly careful, otherwise the system parameters have no physical meaning. We do not generally invoke the positive exponential approximation in this work other than to show that one loses information about the system behavior. When the positive exponential assumption is made, we follow Farr and Aris (1986) in stating that $\gamma \gg x_2$, so that $\kappa(x_2)$ is closely approximated by $\exp(x_2)$. In the case of the positive exponential approximation $\gamma \gg x_2$, Eq. 15 becomes

$$\beta_{\text{crit}}=\frac{4}{qx_{1f}}(q+\delta) \tag{16}$$

Three-state model

The steady-state multiplicity behavior changes with the addition of cooling jacket dynamics. For example, if we consider Case 1 parameters, we can clearly see in Figures 3 and 4 that the two-state model does not have output multiplicity between x_2 and x_3 while the three-state model does indeed exhibit output multiplicity between x_2 and q_c. These figures demonstrate that the two CSTR models can exhibit completely different multiplicity behavior for the same set of reactor parameters. Therefore, the open-loop stability may change with the addition of

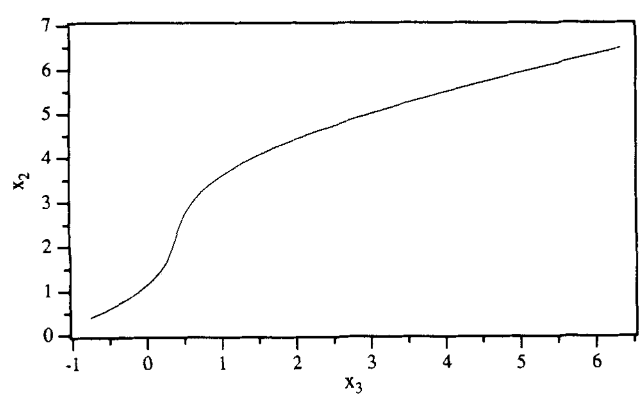

Figure 3. Case 1 monotonic relationship (no output multiplicity) between x_2 and x_3 for the two-state CSTR model.

cooling jacket dynamics in the CSTR modeling equations. We will demonstrate the effect of parameter variations [in particular q_c (dimensionless cooling jacket flow rate), ϕ (nominal Damköhler number), and β (dimensionless heat of reaction)] on the multiplicity behavior of the three-state CSTR model. ϕ and β characterize the kinetic and thermodynamic behavior of the reaction, while q_c controls the amount of external cooling. For example, small values of ϕ and β imply a low reaction rate and low heat of reaction, which are associated with low temperature operation; whereas large values of ϕ and β are characteristic of high temperature operation.

In order to understand the different steady-state multiplicity results for the two different models, we use some results from elementary catastrophe theory. Equations 4–6 can be combined at steady state to give:

$$h(x_{2s},q_{cs},p)=\beta q x_{1f}\frac{\phi\kappa(x_{2s})}{q+\phi\kappa(x_{2s})}-(q+\delta)x_{2s}+qx_{2f}+\frac{\delta q_{cs}x_{3f}+\delta^2\delta_2 x_{2s}}{(\delta\delta_2+q_{cs})}=0 \tag{17}$$

where x_2 is the controlled output, q_c is the manipulated input, and p is a vector containing the system parameters. The necessary conditions for output multiplicity, input multiplicity, and the formation of isolas, respectively, are obtained from the implicit function theorem:

$$h=\frac{\partial h}{\partial x_{2s}}=0 \tag{18}$$

$$h=\frac{\partial h}{\partial q_{cs}}=0 \tag{19}$$

$$h=\frac{\partial h}{\partial x_{2s}}=\frac{\partial h}{\partial q_{cs}}=0 \tag{20}$$

Now, we want to determine if it is possible for the three-state CSTR model to have input multiplicity or isolas. Consider the value of $\partial h/\partial q_{cs}$. The result is:

$$\frac{\partial h}{\partial q_{cs}}=\delta^2\delta_2\frac{(x_{3f}-x_{2s})}{(\delta\delta_2+q_{cs})^2}\neq 0 \tag{21}$$

Therefore, when q_c is the manipulated variable then input multiplicities, isolas, transcritical bifurcations, and pitchfork bifurcations cannot occur between x_2 and q_c. Upon examination of the derivatives of $h(x_{2s}, q_{cs}, p)$ with respect to the parameters, we have determined that q is the *only* parameter that when varied can lead to input multiplicities or isola behavior; it is therefore an important disturbance variable. The derivatives of $h(x_{2s}, q_{cs}, p)$ with respect to the other parameters remain the same sign, a useful piece of information when designing feedforward controllers. Figure 5 demonstrates that the three-state CSTR model may exhibit *input* and *output* multiplicities between cooling jacket temperature x_3 and cooling jacket flow rate q_c in certain parameter ranges. Input and output multiplicities between x_3 and q_c complicate the tuning of the inner-loop controller in a cascade control scheme. One can see that an understanding of this multiplicity behavior is particularly important for controller design and tuning.

It is well-known that the presence of an S or inverse S shaped input-output curve is associated with hysteresis (ignition/extinction) behavior, which results in a region of open-loop unstable steady states. Therefore, by characterizing this multiplicity region, one can understand how to minimize or even eliminate it in the parameter space. In particular, if multiplicity between x_2 and q_c is eliminated, then the CSTR will generally be easier to control and safer to operate, since the process gain remains the same sign over the entire operating region of interest. However, this does not guarantee that the CSTR is asymptotically stable over the entire operation region, only that ignition/extinction types of behavior are removed (for example, limit cycle behavior may occur).

We now consider the analysis of output multiplicities between x_2 and q_c. From elementary catastrophe theory, the appearance or disappearance of output multiplicities occurs when higher order derivatives of h with respect to x_{2s} are zero:

$$h=\frac{\partial h}{\partial x_{2s}}=\frac{\partial^2 h}{\partial x_{2s}^2}=\ldots=\frac{\partial^k h}{\partial x_{2s}^k}=0 \tag{22}$$

$$\frac{\partial^{k+1} h}{\partial x_{2s}^{k+1}}\neq 0 \tag{23}$$

The typical approach is to determine the highest-order singularity (the largest value of k) which satisfies Eq. 22. We have determined that the highest order singularity of Eq. 22 is $k=2$, since when $\partial^2 h/\partial x_{2s}^2=0$ then:

$$\frac{\partial^3 h}{\partial x_{2s}^3}=-\frac{q x_{1f}\beta\gamma^2(\gamma^2-2\gamma-2x_{2s})(\gamma^2+2\gamma+2x_{2s})}{8(\gamma+x_{2s})^6}<0 \tag{24}$$

The equation satisfying $\partial^2 h/\partial x_{2s}^2=0$ is exactly the same result as for the two-state model (Eq. 14). This equation defines a one-to-one relationship between ϕ and x_{2s} at the hysteresis point.

Since we are interested in the possible steady-state multiplicity from a process control viewpoint, the singularity described by Eq. 22 is no longer a point but a locus in the global parameter space. This locus is constructed over the bounds on the primary bifurcation parameter (q_c—the manipulated variable for feedback control). The minimum and maximum bounds on the cooling jacket flow rate are set as $q_c \in [0, \infty)$ without loss of generality (the methodology remains the same for arbitrary bounds on q_c).

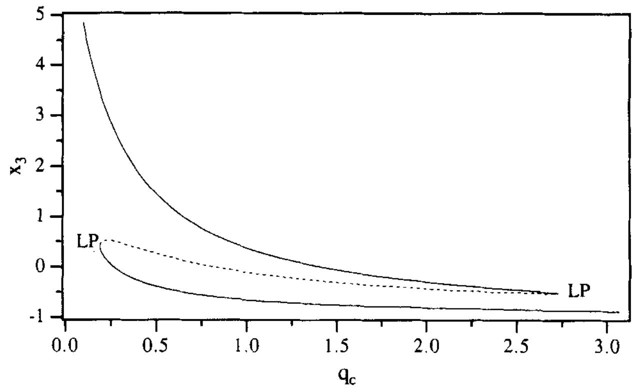

Figure 5. Case 2 input and output multiplicity characteristics for the three-state CSTR model.

Determination of Global Multiplicity Diagrams. One particularly interesting aspect of steady-state multiplicity studies is the appearance of "so-called" disjoint bifurcations (Gray, 1991). Disjoint bifurcations result in nonfeasible operating regions that separate non-closed disconnected steady-state solution branches. This type of behavior arises when there are bounds on the values of the parameters or state variables. These bounds can be either arbitrary bounds or physical bounds (certain parameters are non-negative, such as the cooling jacket flow rate). This type of behavior is shown in Figure 6. It should be made clear that disjoint bifurcations are extremely different from isola behavior, where a closed, isolated branch of solutions is either created or destroyed through a well-defined bifurcation.

Determining regions of feasible and nonfeasible operation are critical for feedback control purposes. It is generally well-known (by control researchers) that minimum and maximum bounds on the manipulated variable can lead to infeasible output regions. However, it is now clear that even with very loose bounds (in our case, only physical bounds $0 \leq q_c < \infty$) one can see disjoint bifurcations which divide the global parameter space into regions of different multiplicity behavior. These infeasible operating regions were analyzed quite nicely by Balakotaiah and Luss (1984). They describe a general method to divide the global parameter space into regions with different

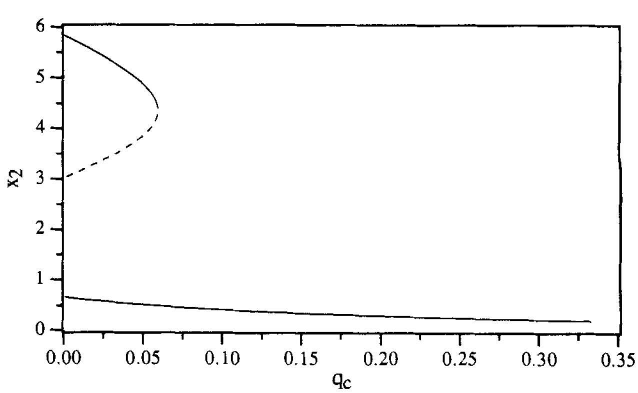

Figure 6. Case 1 (except $\phi=0.055$) "0-disjoint" multiplicity behavior.

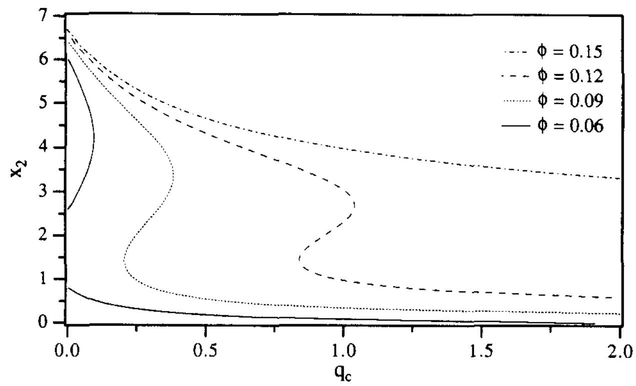

Figure 7. Effect of increasing ϕ for Case 1 conditions.

types of multiplicity diagrams (using some results of Bröcker and Lander, 1975). One possible problem is that since singularity theory is by its nature local, there can be multiple highest order singularities of equal codimension (or even a locus, or a series of loci of largest codimension), which complicate the analysis. It turns out that for our example this is not the case, hence the analysis is relatively straightforward.

The results are portrayed on the ϕ-β 2-D cross section of the parameter space. We feel that this is most appropriate since the values of ϕ (nominal Damköhler number) and β (dimensionless heat of reaction) are a direct measure of the kinetic and thermodynamic properties of the reaction. We choose to use a nominal Damköhler number (ϕ) in this analysis (unlike other researchers), because we will demonstrate that the flow rate effects are best studied separately from the kinetic effects (we note that the "traditional" Damköhler number is $Da = \phi/q$). Through all of this one must remember that we wish to characterize the multiplicity behavior in order to understand how to change the process design or process operation such that steady-state multiplicity is eliminated or minimized. Some of the process parameters are identified as important disturbance variables (therefore possible feedforward variables) because of their effect on the steady-state multiplicity diagrams. Figure 7 demonstrates that increasing ϕ (nominal Damköhler number) removes the multiplicity behavior. One can see that it is important to determine when a process operation or design change can be made to remove steady-state multiplicities.

The solution of Eq. 22 when $k=2$ (hysteresis singularity) gives a necessary condition for multiplicity on the value of β:

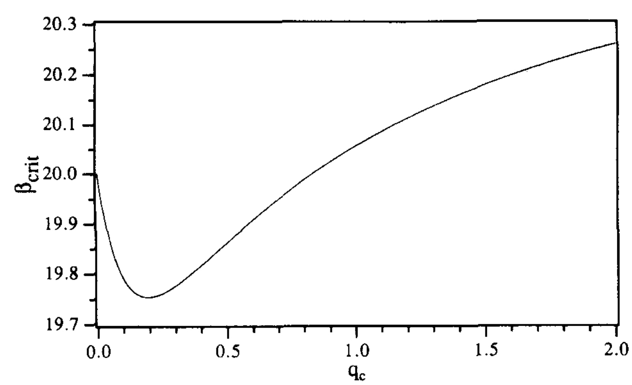

Figure 8. Nonmonotonic relationship between β_{crit} and q_c (Case 1 conditions except $\gamma = 5$).

$$\beta_{crit} = \frac{4}{qx_{1f}(\delta\delta_2 + q_{cs})} \times \frac{\{[(q_{cs} + q\delta_2)\delta + qq_{cs}]\gamma + [(q_{cs}x_{3f} + q\delta_2 x_{2f})\delta + qq_{cs}x_{2f}]\}^2}{\{[(q_{cs} + q\delta_2)\delta + qq_{cs}](\gamma^2 - 4\gamma) - 4[(q_{cs}x_{3f} + q\delta_2 x_{2f})\delta + qq_{cs}x_{2f}]\}} \tag{25}$$

We want to understand the effect of q_c on the critical value of β. There is no reason to expect a monotonic relationship between β_{crit} and q_{cs}, due to the quadratic q_{cs} terms in the numerator of β_{crit}. This is shown in Figure 8. Therefore, we take the analysis a step further in order to determine the effect of the other parameters on the monotonicity of β_{crit} with respect to q_{cs}. If it is monotone increasing or decreasing ($\partial\beta_{crit}/\partial q_{cs} > 0$ or $\partial\beta_{crit}/\partial q_{cs} < 0$) for any set of parameter values over the entire range of q_{cs}, then the minimum and maximum values of β_{crit} occur at the bounds on the manipulated variable (q_c). In the case when the cooling jacket feed temperature is equal to the reactor feed temperature ($x_{3f} = x_{2f}$), $\partial\beta_{crit}/\partial q_{cs}$ is:

$$\frac{\partial\beta_{crit}}{\partial q_{cs}} = \frac{4\delta_2\delta^2}{qx_{1f}} \frac{(\gamma + x_{2f})^2}{(\gamma^2 - 4\gamma - 4x_{2f})(\delta\delta_2 + q_{cs})^2} > 0 \tag{26}$$

In the case when the positive exponential approximation is used, $\partial\beta_{crit}/\partial q_{cs}$ is:

$$\frac{\partial\beta_{crit}}{\partial q_{cs}} = \frac{4\delta_2\delta^2}{(qx_{1f})(\delta\delta_2 + q_{cs})^2} > 0 \tag{27}$$

Therefore, under either of these cases, β_{crit} is a monotone increasing function of q_{cs}; hence, the minimum and maximum values of β_{crit} occur at the minimum and maximum values of q_{cs}, which we have taken to be 0 and ∞. Now, let us consider the general case. It can be shown quite easily that there is at most one physically meaningful minima (where $\partial\beta_{crit}/\partial q_{cs} = 0$) in the plot of β_{crit} vs. q_{cs} (there are no maxima). In addition, it is straightforward to show that the location of this minima along the q_{cs} axis is a monotone decreasing function of γ, and that this minima occurs at $q_{cs} = 0$ when $\gamma = \gamma_*$, where γ_* is the physically meaningful root of Eq. 28:

$$\gamma^3 + (-4 - x_{2f} - 2x_{3f})\gamma^2 + (-4x_{2f} - 4x_{3f})\gamma - 4x_{2f}x_{3f} = 0 \tag{28}$$

In the case when $x_{2f} = 0$, γ_* is given by:

$$\gamma_* = 2 - x_{3f} + \sqrt{(4 + x_{3f}^2)} \tag{29}$$

For example, when $x_{3f} = -1$, $\gamma_* = 3 + \sqrt{5} \approx 5.23606798$. For values of γ above γ_*, the relationship between β_{crit} and q_{cs} is monotone increasing, hence the minimum value of β_{crit} occurs when q_c is at its lowest bound ($q_c = 0$) and the maximum value of β_{crit} occurs when q_c is at its upper bound ($q_c \to \infty$).

In the limit as $q_c = 0$ (adiabatic reactor) β_{crit} is:

$$\beta_{crit} = \frac{4}{x_{1f}} \frac{(\gamma + x_{2f})^2}{(\gamma^2 - 4\gamma - 4x_{2f})} \tag{30}$$

The dimensionless reactor temperature (x_2) and nominal Damköhler number (ϕ) at the hysteresis point are:

$$x_{2s}=\frac{\gamma((2+x_{2f})\gamma+2x_{2f})}{\gamma^2-2\gamma-2x_{2f}} \tag{31}$$

$$\phi_{\text{crit}}=\frac{q(\gamma^2-4\gamma-4x_{2f})}{\kappa(x_{2s})\gamma^2} \tag{32}$$

A necessary condition for steady-state multiplicity can be derived on the dimensionless activation energy (γ), since β_{crit} and ϕ_{crit} must be nonnegative.

$$\gamma>\gamma^*=2+2\sqrt{(1+x_{2f})} \tag{33}$$

When the dimensionless reactor feed temperature is at its nominal value ($x_{2f}=0$), Eqs. 30-33 become:

$$\beta_{\text{crit}}=\frac{4\gamma}{\gamma-4} \tag{34}$$

$$x_{2s}=\frac{2\gamma}{\gamma-2} \tag{35}$$

$$\phi_{\text{crit}}=\frac{q(\gamma-4)}{\exp(2)\gamma} \tag{36}$$

$$\gamma>\gamma^*=4 \tag{37}$$

For example, when $\gamma=20$ and $q=1$, $\beta_{\text{crit}}=5$, $x_{2s}=20/9$, and $\phi_{\text{crit}}=4/5\ e^{-2}$. In the situation when the reactor feed stream is cooled ($x_{2f}<0$), $\gamma^*<4$, while when the reactor feed is heated ($x_{2f}>0$), $\gamma^*>4$. So, we can already see that how the process is operated influences the multiplicity behavior. This also indicates the effect of a feed temperature disturbance.

In the limit as $q_{cs}\to\infty$, β_{crit} is:

$$\beta_{\text{crit}}=\frac{4}{qx_{1f}}\frac{[(q+\delta)\gamma+(\delta x_{3f}+qx_{2f})]^2}{[(q+\delta)(\gamma^2-4\gamma)-4(\delta x_{3f}+qx_{2f})]} \tag{38}$$

This is the same β_{crit} as the two-state model, since as $q_c\to\infty$, $x_{3s}\to x_{3f}$. The three-state β_{crit} (for $0\le q_c<\infty$) is less than the two-state β_{crit}; therefore, the limit point instability region for the three-state model is larger than the two-state model (assuming that $\gamma>\gamma_*$). Therefore, the three-state model may be open-loop unstable when the two-state model is stable. The dimensionless reactor temperature and nominal Damköhler number at the hysteresis point are:

$$x_{2s}=\frac{\gamma[(2(q+\delta)+\delta x_{3f}+qx_{2f})\gamma+2(\delta x_{3f}+qx_{2f})]}{[(q+\delta)(\gamma^2-2\gamma)+2(\delta x_{3f}+qx_{2f})]} \tag{39}$$

$$\phi_{\text{crit}}=\frac{q[(q+\delta)(\gamma^2-4\gamma)-4(\delta x_{3f}+qx_{2f})]}{\kappa(x_{2s})(q+\delta)\gamma^2} \tag{40}$$

One can see now why it is important to separate the kinetic and flow rate effects. The traditional Damköhler number (Da) is ϕ/q, but in the case when $x_{3f}\neq x_{2f}$, using a Damköhler number in the analysis results in an implicit relationship for Eq. 40. When the feed temperatures of the cooling jacket and reactor are equal ($x_{3f}=x_{2f}$) (as is often assumed), Eqs. 38-40 become:

$$\beta_{\text{crit}}=\frac{4(q+\delta)}{qx_{1f}}\frac{(\gamma+x_{2f})^2}{(\gamma^2-4\gamma-4x_{2f})} \tag{41}$$

$$x_{2s}=\frac{\gamma((2+x_{2f})\gamma+2x_{2f})}{\gamma^2-2\gamma-2x_{2f}} \tag{42}$$

$$\phi_{\text{crit}}=\frac{q(\gamma^2-4\gamma-4x_{2f})}{\kappa(x_{2s})\gamma^2} \tag{43}$$

It is obvious that the dimensionless reactor temperature (x_{2s}) and nominal Damköhler number (ϕ_{crit}) given here when $x_{3f}=x_{2f}$ are equivalent to Eqs. 31-32. However, β_{crit} changes by a factor of $(q+\delta)/q$, therefore a larger δ (dimensionless heat-transfer coefficient) results in a larger multiplicity area in the ϕ-β parameter space. This result is counterintuitive, since we saw previously that multiplicity could be eliminated in the two-state CSTR model by increasing δ.

Upon examination of the hysteresis condition (given by Eq. 22 with $k=2$), we can determine the equations for x_{2s}, β_{crit}, and ϕ_{crit} along the hysteresis locus (connecting $q_c=0$ and $q_c\to\infty$) (Appendix 1). A codimension 1 fold bifurcates from each of the parameter bounds ($q_c\in[0,\infty)$) which separates the global multiplicity characteristics in the ϕ-β parameter space.

$$h=\frac{\partial h}{\partial x_{2s}}=0$$
$$q_{cs}=0 \tag{44}$$

$$h=\frac{\partial h}{\partial x_{2s}}=0$$
$$q_{cs}\to\infty \tag{45}$$

Equations 44-45 are satisfied along the "0-disjoint" and "∞-disjoint" loci, respectively. The dimensionless reactor temperatures (x_2) and nominal Damköhler numbers (ϕ) along the two codimension 1 folds are given in Appendix 1. The codimension 2 (cusp) hysteresis locus and codimension 1 (fold) "0-disjoint" and "∞-disjoint" loci divide the ϕ-β parameter space into five different regions (shown in Figure 9) which correspond to five different x_2-q_c bifurcation diagrams (shown in Figure

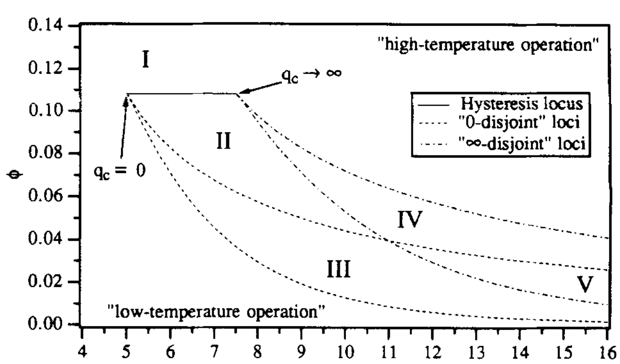

Figure 9. Global multiplicity behavior for Case 4 conditions.

Typical bifurcation diagrams for regions I–V are in Figure 10.

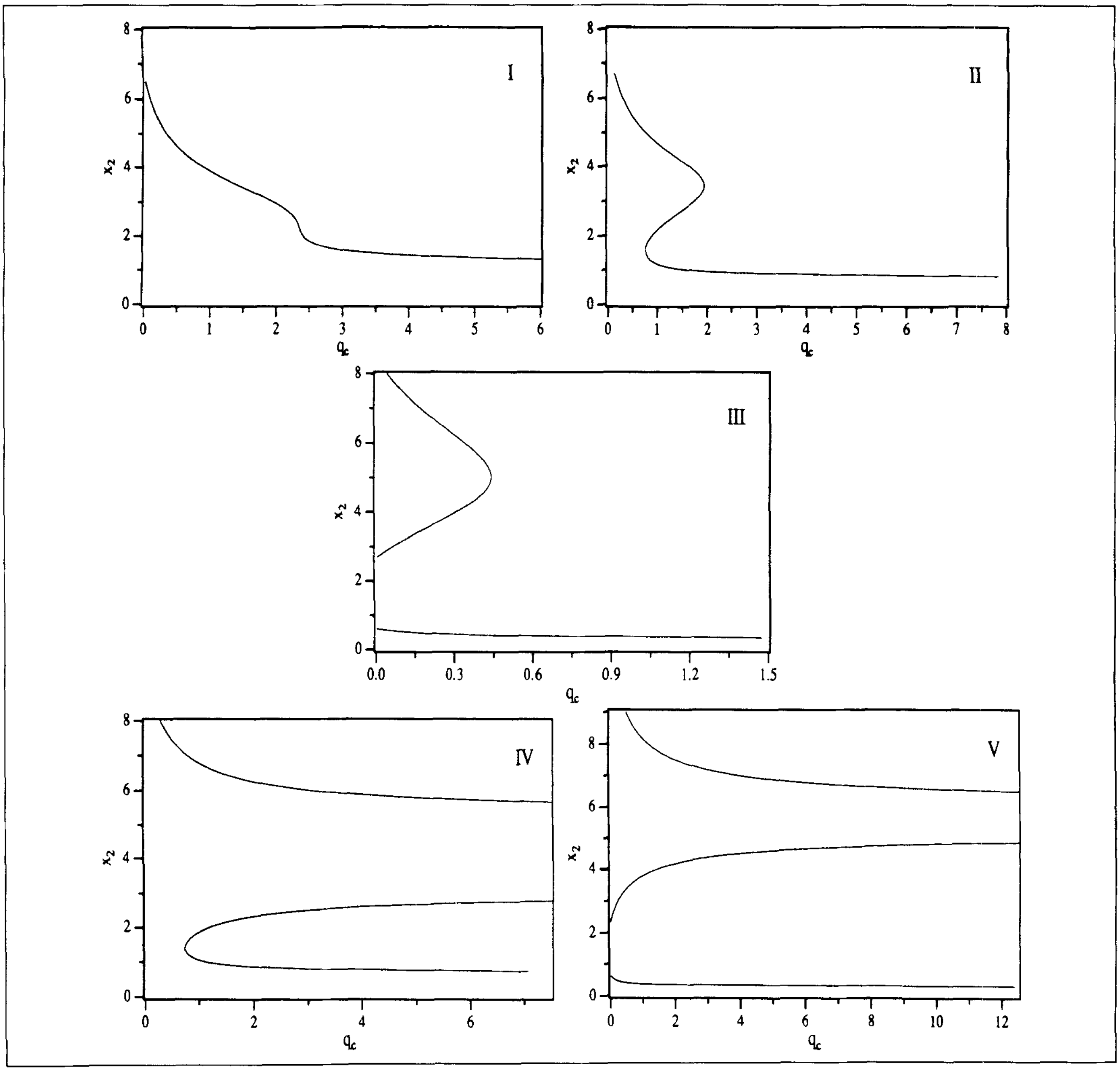

Figure 10. Bifurcation diagrams for Case 4 conditions.

10). The ϕ and β values in regions I-V of Figure 10 are given in Table 3. Region I in the ϕ-β parameter space does not exhibit output multiplicities, whereas the standard inverse S shaped curve is found in region II. Region III is an example of "0-disjoint" bifurcation (the x_2-q_c curve has a low temperature infeasibility region), while region IV is an example of "∞-disjoint" bifurcation (the x_2-q_c curve has a high temperature infeasibility region). Region V exhibits both "0-disjoint" and "∞-disjoint" bifurcations (where the codimension 1 disjoint loci intersect), resulting in very severe operation and control problems due to the multiple infeasible operating regions. If one considers the positive exponential approximation ($\gamma \gg x_2$), we see in Figure 11 that the types of global multiplicity behavior remain the same. However, the multiplicity area (regions II-V) in the ϕ-β parameter space is larger (compare Figures 9 and 11). Therefore, the use of the positive exponential approximation tends to overestimate the overall multiplicity region area.

Table 3. ϕ and β Values in Figure 10 (Case 4 Conditions)

region	ϕ	β
I	0.11	7
II	0.08	8
III	0.04	9
IV	0.06	10
V	0.03	12

Influence of CSTR Parameters on the Multiplicity Behav-

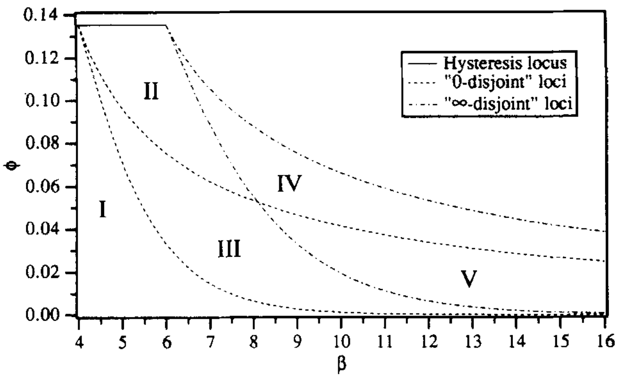

Figure 11. Global multiplicity behavior for Case 4 conditions except $\gamma \gg x_2$ (positive exponential approximation).

ior. We have seen that including an energy balance around the cooling jacket changes the multiplicity results. From a process control point of view, most of the input-output curves (shown in Figure 10) are troublesome due to the changes in the sign of the process gain and the presence of infeasible operation regions. Therefore, one would like to be able to remove steady-state multiplicities by making a design or operation change. The focus for the rest of this section is on removing the multiplicities associated with region II; multiplicities in regions III–V can be removed in a similar manner.

We have shown ϕ-β plots until now in which the hysteresis locus is horizontal. However, one can show that this is true only when $x_{3f}=x_{2f}$. For example, in Figure 12 (Case 3 conditions) the hysteresis locus has a positive slope ($\partial\phi_{crit}/\partial\beta_{crit}>0$). The derivative $\partial\phi_{crit}/\partial\beta_{crit}$ along the hysteresis locus is:

$$\frac{\partial\phi_{crit}}{\partial\beta_{crit}} = -\left(\frac{\dfrac{\partial^3 h}{\partial x_{2s}^3}\dfrac{\partial x_{2s}}{\partial q_{cs}}}{\dfrac{\partial^3 h}{\partial^2 x_{2s}\partial\phi_{crit}}\dfrac{\partial\beta_{crit}}{\partial q_{cs}}}\right) \tag{46}$$

Now, $\partial^3 h/\partial^2 x_{2s}\partial\phi_{crit}$ (when $\partial^2 h/\partial x_{2s}^2=0$) is given by:

$$\frac{\partial^3 h}{\partial^2 x_{2s}\partial\phi_{crit}} = -\frac{x_{1f}\beta\kappa(x_{2s})(\gamma^2-2\gamma-2x_{2s})(\gamma^2+2\gamma+2x_{2s})^3}{8\gamma^4(\gamma+x_{2s})^4}<0 \tag{47}$$

Therefore, the sign of $\partial\phi_{crit}/\partial\beta_{crit}$ is:

$$\operatorname{sgn}\left(\frac{\partial\phi_{crit}}{\partial\beta_{crit}}\right) = -\operatorname{sgn}\left(\frac{\dfrac{\partial x_{2s}}{\partial q_{cs}}}{\dfrac{\partial\beta_{crit}}{\partial q_{cs}}}\right) \tag{48}$$

where $\partial x_{2s}/\partial q_{cs}$ is given by:

$$\frac{\partial x_{2s}}{\partial q_{cs}} = -\frac{(x_{2f}-x_{3f})\delta_2 q\delta^2\gamma^4}{[(q\delta\delta_2+qq_{cs}+\delta q_{cs})(-\gamma^2+2\gamma)+2(\delta q_{cs}x_{3f}+qx_{2f}\delta\delta_2+qx_{2f}q_{cs})]^2} \tag{49}$$

In the case when $\gamma>\gamma_*$, $\partial\beta_{crit}/\partial q_{cs}>0$, therefore the sign of $\partial\phi_{crit}/\partial\beta_{crit}$ becomes:

$$\operatorname{sgn}\left(\frac{\partial\phi_{crit}}{\partial\beta_{crit}}\right) = -\operatorname{sgn}\left(\frac{\partial x_{2s}}{\partial q_{cs}}\right) = \operatorname{sgn}(x_{2f}-x_{3f}) \tag{50}$$

When $\gamma<\gamma_*$, $\partial\phi_{crit}/\partial\beta_{crit}\rightarrow\infty$ as $\partial\beta_{crit}/\partial q_{cs}\rightarrow 0$. The reason that Figures 9 and 11 had horizontal hysteresis loci was that the dimensionless feed temperatures of the reactor and the cooling jacket were equal (Case 4), while in Figure 12 $\gamma>\gamma_*$ and $x_{2f}-x_{3f}>0$, hence the hysteresis slope is positive.

Example I: Effect of a Process Operation Change. We want to explore the effect of x_{2f} on the steady-state multiplicity in the case when $x_{3f}=x_{2f}$ (this restriction can easily be lifted if necessary; it effectively fixes one of the parameters). If $\phi_{crit}<\phi$, then there is no multiplicity. Hence, if one understands how to change the process conditions such that ϕ_{crit} is smaller than ϕ, one can remove the multiplicity behavior. The derivative of the nominal Damköhler number (ϕ_{crit}) with respect to x_{2f} at this point is:

$$\frac{\partial\phi_{crit}}{\partial x_{2f}} = -\frac{q\exp\left\{-\dfrac{[(2+x_{2f})\gamma+2x_{2f}]}{\gamma+x_{2f}}\right\}(-\gamma^2+2\gamma+2x_{2f})^2}{\gamma^2(\gamma+x_{2f})^2}<0 \tag{51}$$

Therefore, increasing x_{2f} decreases ϕ_{crit}. ϕ_{crit} (in the case when $x_{3f}=x_{2f}$) is given by Eq. 43. Note that this equation cannot

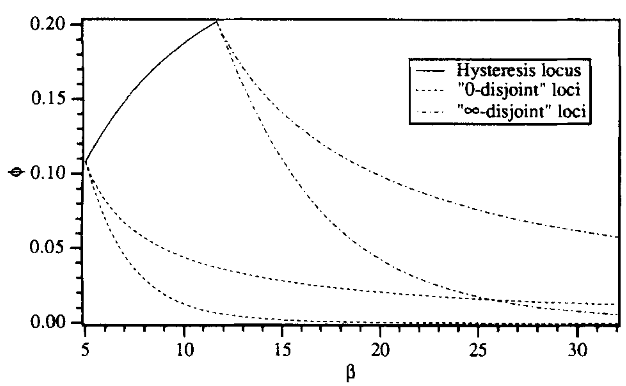

Figure 12. Global multiplicity behavior for Case 3 conditions.

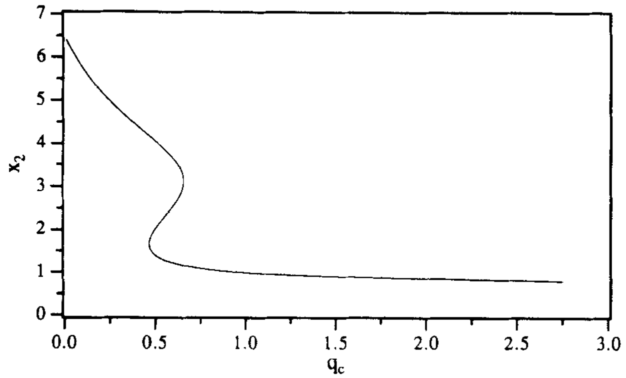

Figure 13. Case 5 output multiplicity characteristics for the three-state CSTR model.

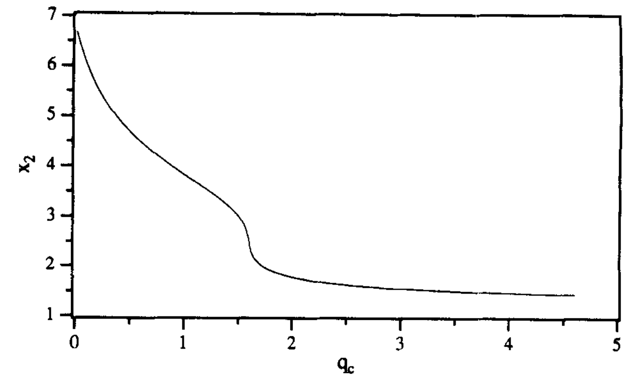

Figure 14. Case 5 (except $x_{2f}=0.2$) monotonic relationship between x_2 and q_c for the three-state CSTR model.

be solved explicitly for x_{2f} such that $\phi_{crit}<\phi$, however one can simply choose values of x_{2f} until $\phi_{crit}<\phi$ (since ϕ_{crit} is a monotone decreasing function of x_{2f}).

Let us consider Case 5 parameters (Table 2), which are actually Case 4 parameters with $\beta=7.0$ and $\phi=0.09$. This point falls in region II of Figure 9; therefore, the input-output curve is inverse S shaped, shown in Figure 13. Now, to remove multiplicity, one must increase x_{2f} so that $\phi_{crit}<\phi$ (this follows from Eq. 51). For example, in this case $x_{2f}>0.18417777$ for $\phi_{crit}<\phi$ (which removes output multiplicities). Figure 14 is a plot of x_2 vs. q_c when $x_{2f}=0.2$. The steady-state multiplicities are removed by increasing the reactor feed temperature. The same types of analyses to remove multiplicity behavior can be done for other design/operation parameters. For example, it is easy to see from Eq. 32 that decreasing q decreases ϕ_{crit}. However, this changes the steady-state relationship between x_{1s} and x_{2s}, but this can be compensated for by changing x_{1f}.

Example II: Effect of a Process Design Change. This second example shows the effect of a process design change (reactor sizing) on the bifurcation behavior of the three-state CSTR model. The reactor parameters used in this example were obtained from Devia and Luyben (1978); the dimensionless parameters (Case 6) are given in Table 2, while the physical parameters are listed in Table 4. The CSTR studied has a height to diameter ratio of 2 ($H_r=2D_r$). As pointed out by Devia and Luyben (1978), increasing the reactor size causes a reduction in the ratio of heat-transfer area to reactor volume, since it is assumed that the reactor and jacket residence times are held constant with scale-up. One therefore sees a reduction in the dimensionless heat-transfer coefficient (δ) when the reactor size is increased, since in this case $\delta \sim 1/D_r$.

Figure 15 shows the ϕ-β plot when the reactor volume is 10,000 gal (38 m^3) ($\delta=2.2793$). The reactor operation falls in region II, hence the input-output curve is inverse S-shaped. However, if the reactor volume is scaled up to 15,000 gal (57 m^3), the dimensionless heat-transfer coefficient decreases ($\delta=1.9912$). The reactor operation shifts to region IV (Figure 16), which is associated with "∞-disjoint" bifurcation. This input-output curve is shown in Figure 17. Using this analysis, one can see that if the residence time for the reactor is held constant upon scale-up, then infeasible reactor operation regions may occur. In certain cases, one may even shift into a high-temperature operation region (with no multiplicities), which is consistent with the loss in heat-transfer capacity due to scale-up.

Conclusions

We have shown that adding a third state to the classic two-state exothermic CSTR in order to account for the cooling jacket energy balance has an important effect on the steady-state multiplicity behavior. A stabilizing inner-loop cascade controller is implicitly assumed in the two-state CSTR model, since we demonstrated that the three-state model may be open-loop unstable when the two-state model is stable. We used elementary catastrophe theory in order to understand the influence of process parameters on the steady-state multiplicity behavior. We found that input multiplicities and isolas did not exist between the reactor temperature and the cooling jacket flow rate. Output multiplicities in the two-state model can be removed by increasing the heat-transfer coefficient or the heat-transfer area, yet one cannot remove output multiplicities in the three-state model by increasing the heat-transfer coefficient or heat-transfer area alone. We characterized the global input-output multiplicity behavior in terms of a nominal Damköhler number and a dimensionless heat of reaction. We have demonstrated that a detailed steady-state multiplicity analysis provides important information concerning the influence of process

Table 4. Physical Parameters in Example 2 (Devia and Luyben, 1978)

$V/Q_0=1.2$ h	Reactor holdup time
$V_c/Q_c=0.077$ h	Jacket holdup time
$U=150$ Btu/h·ft^2·°F	Overall heat-transfer coefficient
$C_p=0.75$ Btu/lb·°F	Heat capacity of feed and products
$C_{pc}=1.0$ Btu/lb·°F	Heat capacity of jacket liquid
$\rho=50$ lb/ft^3	Density of feed and products
$\rho_c=62.3$ lb/ft^3	Density of jacket liquid
$T_{cf}=70$°F	Cooling jacket feed temperature
$C_{af}=0.50$ lb·mol A/ft^3	Reactor feed concentration
$T_f=70$°F	Reactor feed temperature
$k_0=7.08\times10^{10}$ 1/h	Preexponential factor
$E_a=30{,}000$ Btu/lb·mol	Activation energy
$\Delta H=-30{,}000$ Btu/lb·mol	Heat of reaction
Heat-transfer area:	$A=2\pi D_r^2+\frac{\pi}{4}D_r^2=\frac{9}{4}\pi D_r^2$
Reactor height:	$H_r=2D_r$
Reactor volume:	$V=\frac{\pi}{4}D_r^2H_r=\frac{\pi}{2}D_r^3$

SI Conversion: W/m^2·°C = Btu/h·ft^2·°F × 5.68; kJ/kg·°C = Btu/lb·°F × 4.19; kg/m^3 = lb/ft^3 × 16.0; kJ/kg = Btu/lb × 2.33; °C = (°F − 32)/1.8.

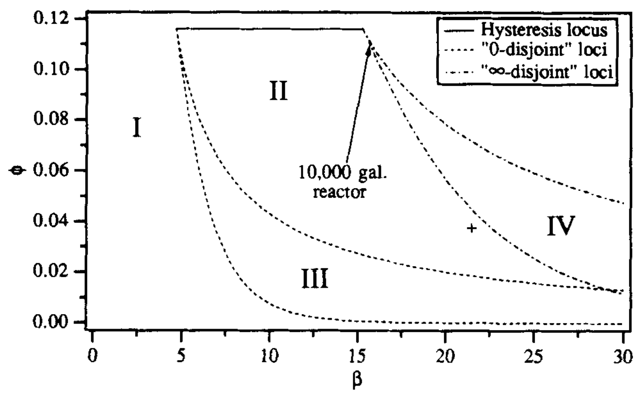

Figure 15. Global multiplicity behavior showing nominal reactor operation in region II for Devia and Luyben's example ($\delta = 2.2793$).

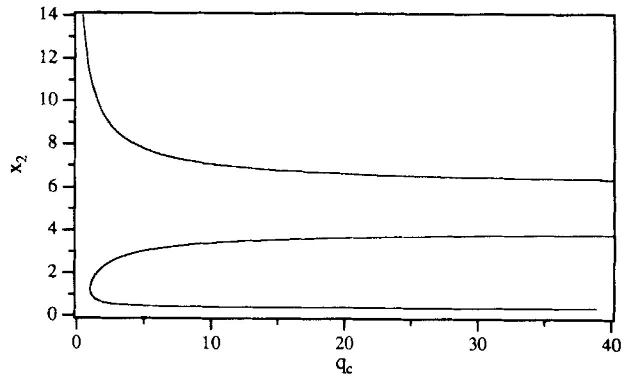

Figure 17. Case 6 output multiplicity characteristics for the three-state CSTR model when $V = 15{,}000$ gal (57 m^3).

design and operation parameters on CSTR performance. We have shown that the use of the positive exponential approximation tends to overestimate the overall multiplicity region area in the ϕ-β parameter space. We used the multiplicity analysis to remove the multiplicity behavior between reactor temperature and cooling jacket flow rate by increasing the reactor feed temperature. Reactor scale-up has an important effect on the presence of infeasible reactor operation regions. We were able to delineate important feedforward process variables such as q, x_{2f}, and x_{3f} from an analysis of the influence these variables have on the multiplicity behavior.

Acknowledgments

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Notation

A = heat-transfer area
C_{af} = concentration of reactant A in the reactor feed
C_p = heat capacity of feed and products
C_{pc} = heat capacity of jacket fluid
E_a = activation energy in Arrhenius reaction rate
ΔH = heat of reaction
k_0 = preexponential factor in Arrhenius reaction rate
Q = reactor flow rate
R = universal gas constant
T_{cf} = cooling jacket feed temperature
T_f = reactor feed temperature
U = overall heat-transfer coefficient
V = reactor volume
V_c = cooling jacket volume
x_{2f} = dimensionless reactor feed temperature
x_{3f} = dimensionless cooling jacket feed temperature

Greek letters

β = dimensionless heat of reaction
γ = dimensionless activation energy
δ = dimensionless heat-transfer coefficient
δ_1 = reactor to cooling jacket volume ratio
δ_2 = reactor to cooling jacket density heat capacity ratio
$\kappa(x_2)$ = dimensionless Arrhenius reaction rate nonlinearity
ρ = density of feed and products
ρ_c = density of jacket fluid
τ = dimensionless time
ϕ = nominal Damköhler number based on the reactor feed

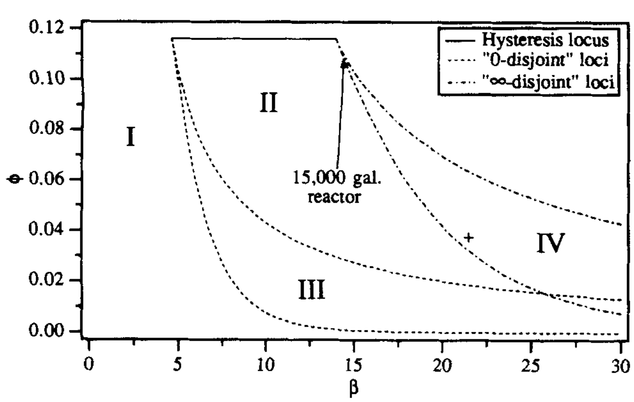

Figure 16. Global multiplicity behavior showing reactor operation in region IV when the reactor size is scaled up ($\delta = 1.9912$).

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Appendix 1: Hysteresis and Disjoint Bifurcation Formulae

The dimensionless reactor temperature (x_2), dimensionless heat of reaction (β), and the nominal Damköhler number (ϕ) along the hysteresis locus (for $q_c \in [0,\infty)$) are:

$$x_{2s}=\frac{\gamma[(\delta\delta_2+q_{cs})(q\beta x_{1f}\gamma+2qx_{2f}\gamma-2\beta qx_{1f})+2\delta q_{cs}x_{3f}\gamma]}{2[(\delta\delta_2+q_{cs})(q\gamma^2+q\beta x_{1f})+2\delta q_{cs}x_{3f}\gamma]}$$

$$\beta_{\text{crit}}=\frac{4}{qx_{1f}(\delta\delta_2+q_{cs})}\frac{\{[(q_{cs}+q\delta_2)\delta+qq_{cs}]\gamma+[(q_{cs}x_{3f}+q\delta_2x_{2f})\delta+qq_{cs}x_{2f}]\}^2}{\{[(q_{cs}+q\delta_2)\delta+qq_{cs}](\gamma^2-4\gamma)-4[(q_{cs}x_{3f}+q\delta_2x_{2f})\delta+qq_{cs}x_{2f}]\}}$$

$$\phi_{\text{crit}}=\frac{q}{\kappa(x_{2s})}\frac{\gamma^2-2\gamma-2x_{2s}}{\gamma^2+2\gamma+2x_{2s}}$$

In the case when $x_{3f}=x_{2f}$, the dimensionless reactor temperature (x_2), dimensionless heat of reaction (β), and nominal Damköhler number (ϕ) along the hysteresis locus become:

$$x_{2s}=\frac{\gamma((2+x_{2f})\gamma+2x_{2f})}{\gamma^2-2\gamma-2x_{2f}}$$

$$\beta_{\text{crit}}=\frac{4}{qx_{1f}}\frac{(\gamma+x_{2f})^2(qq_{cs}+\delta q_{cs}+q\delta\delta_2)}{(\gamma^2-4\gamma-4x_{2f})(\delta\delta_2+q_{cs})}$$

$$\phi_{\text{crit}}=\frac{q(\gamma^2-4\gamma-4x_{2f})}{\kappa(x_{2s})\gamma^2}$$

The equations for dimensionless reactor temperature (x_2) and nominal Damköhler number (ϕ) along the "0-disjoint" and "∞-disjoint" loci are given below.

The two "0-disjoint" loci (which bound region III in the ϕ-β plot):

$$(\gamma^2+\beta x_{1f})x_{2s}^2+(2\beta x_{1f}\gamma-2x_{2f}\gamma^2-\beta x_{1f}\gamma^2)x_{2s}+\gamma^2x_{2f}^2+\beta x_{1f}x_{2f}\gamma^2+\beta x_{1f}\gamma^2=0$$

where the roots of this quadratic correspond to the two "0-disjoint" curves:

$$\phi_{0-\text{dis}}=\frac{q}{\kappa(x_{2s})}\frac{(x_{2s}-x_{2f})}{(\beta x_{1f}-x_{2s}+x_{2f})}$$

The two "∞-disjoint" loci (which bound region IV in the ϕ-β plot):

$$\Lambda_2x_{2s}^2+\Lambda_1x_{2s}+\Lambda_0=0$$

where Λ_2, Λ_1, and Λ_0 are:

$$\Lambda_2=(q+\delta)[(q+\delta)\gamma^2+\beta qx_{1f}]$$

$$\Lambda_1=-(q+\delta)\gamma[(2qx_{2f}+q\beta x_{1f}+2\delta x_{3f})\gamma-2\beta qx_{1f}]$$

$$\Lambda_0=\gamma^2[(qx_{2f}+\delta x_{3f})^2+q\beta x_{1f}(q+\delta+qx_{2f}+\delta x_{3f})]$$

The two roots of this quadratic correspond to the two "∞-disjoint" curves:

$$\phi_{\infty-\text{dis}}=\frac{q}{\kappa(x_{2s})}\frac{[(q+\delta)x_{2s}-qx_{2f}-\delta x_{3f}]}{[\beta qx_{1f}-(q+\delta)x_{2s}-qx_{2f}+\delta x_{3f})]}$$

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