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Operating zone segregation of chemical reaction systems based on stability and non-minimum phase behavior analysis

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ABSTRACT

Many chemical reaction systems exhibit input/output multiplicity characteristics and non-minimum phase behavior. These inherent characteristics are known to cause limitations in process operation, so it is useful to have some knowledge of these at the early design stage of a chemical reaction process. Focusing on inherently safer designs, this paper addresses a strategy for classifying the process operating region into distinct zones at the early stage of process design, based on stability/instability and minimum/non-minimum phase behavior analysis. The strategy is illustrated by two case studies, where the operating spaces of an isothermal CSTR and an exothermic CSTR are classified into zones with different characteristics. The results provide information that is very important for guiding process design and operation about how the inherent properties of a process change with changes in its operating conditions.

1. Introduction

A chemical reaction process is a complex physical and chemical system, often exhibiting severe nonlinear dynamic phenomena. In certain regions of the operating range, the process exhibits input/output multiplicity and non-minimum phase behavior. These inherent characteristics are known to limit process operation and have an adverse effect on the safety and/or product quality of process designs [1,2]. The importance of considering the inherent characteristics of a process early in the process design is now being widely accepted in both academia and industry, as discussed below.

Controllability is a process characteristic that describes the best achievable control quality, independent of controller design. If the achievable dynamic performance of a design is not good enough, then modifications to the plant design must be considered, such as changing inputs or outputs, adding or moving measurement points, changing operating points or even making structural changes [2]. A measure of the “closed-loop” controllability cannot be calculated early in process design because the controllers have not yet been designed. Instead, the phase behavior is used as an “open-loop” indicator of controllability. In control theory, a linear system is said to be non-minimum phase when at least one of the zeros lies on the right-half plane (RHP). For nonlinear systems, the term non-minimum phase implies unstable zero dynamics which can be characterized as the internal dynamics of a nonlinear system in the case where the output is constrained to remain constant for all times. Unstable zero dynamics are the nonlinear analogue to RHP zeros. When the process exhibits non-minimum phase behavior at one steady-state operation point, the process exhibits inverse response, that is, its initial dynamic response is in a direction opposite to the final outcome. Sistu and Bequette showed control techniques for minimum phase systems, also they mentioned the difficulty of controlling non-minimum phase systems [3]. Non-minimum phase behavior of a process limits the degree of achievable control quality in the process and complicates controller design. This limitation cannot be overcome by any causal controller.

When assessing the controllability of chemical plants, Perkins stated that controllability was one of the most important characteristics of process operability and that controllability analysis should be integrated into the early stages of chemical process design [4,5]. Lewin investigated how the selection of the optimal operating point for a continuous industrial polymerization reactor affected its controllability and resilience [6]. Bogle and Kuhlmann studied the relationship between input multiplicity and non-minimum phase behavior and between controllability and optimal operation for nonlinear single-input single-output (SISO) systems [7]. Also, Bogle presented a design method for determining the optimal design, with respect to switchability, out of a range of possible designs [8]. Kaistha took the closed-loop response as a tool for measuring the control structure controllability [9]. The latter case study showed that nonlinear dynamic phenomena, due to input multiplicity, can compromise the robustness of the control system for a reactive distillation (RD) column. Ma showed that input multiplicity can cause control difficulties when operating conditions change, such as changes in disturbances and set points [10].

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Nomenclature

Acronyms

CSTR	continuous stirred-tank reactor
DAE	differential algebraic equations
LHP	left-half plane
MP	minimum phase
NMP	non-minimum phase
RD	reactive distillation
RHP	right-half plane

Isothermal CSTR with Van der Vusse reactions

C_A	concentration of reactant A in mol/L
C_B	concentration of reactant B in mol/L
C_{Af}	concentration of reactant A in feed in mol/L
C_{0A}	steady-state concentration of reactant A in mol/L
C_{0B}	steady-state concentration of reactant B in mol/L
Q/V	dilution rate in L/h
k_1	reaction rate constant in h^{-1}
k_2	reaction rate constant in h^{-1}
k_3	reaction rate constant in L/(mol h)
y	output of model, equal to C_B
λ	eigenvalue of zero dynamics

Exothermic CSTR with reactions $A \rightarrow B \rightarrow C$

A	heat-transfer area in m^2
A_1	Arrhenius preexponential factor for first reaction in s^{-1}
A_2	Arrhenius preexponential factor for second reaction in s^{-1}
C_A	concentration of reactant A in $kmol/m^3$
C_{Af}	concentration of reactant A in feed in $kmol/m^3$
C_B	concentration of reactant B in $kmol/m^3$
C_{Bf}	concentration of reactant B in feed in $kmol/m^3$
Cp	heat capacity of reaction mixture in $kJ\,kmol^{-1}\,K^{-1}$
Cp_c	heat capacity of coolant in $kJ\,kmol^{-1}\,K^{-1}$
E_1	activation energy of first reaction in kJ/kmol
E_2	activation energy of second reaction in kJ/kmol
k_1	reaction rate of first reaction in s^{-1}
k_2	reaction rate constant in s^{-1}
q	dimensionless volumetric feed flow rate
q_c	dimensionless, cooling-medium, volumetric flow
Q	volumetric feed flow rate in m^3/s
Q_c	cooling-medium, volumetric flow rate in m^3/s
R	universal gas constant in $kJ\,kmol^{-1}\,K^{-1}$
S	ratio of rate constants
T	temperature of reactor in K
T_c	temperature of coolant in K
T_{cf}	cooling-medium feed temperature in K
T_f	feed temperature in K
U	heat-transfer coefficient in $kJ\,m^{-1}\,s^{-1}\,K^{-1}$
V	reactor volume in m^3
V_c	cooling jacket volume in m^3
x_1	dimensionless concentration of reactant A
x_{1f}	dimensionless feed concentration of reactant A
x_2	dimensionless concentration of reactant B
x_{2f}	dimensionless feed concentration of reactant B
x_3	dimensionless temperature of reactor
x_{3f}	dimensionless, reactor feed temperature
x_4	dimensionless temperature of coolant
x_{4f}	dimensionless, coolant feed temperature
y	output of model
y_1	output of model, equal to C_B
y_2	output of model, equal to T_c
y_{sp1}	set point values for controlled variable 1, x_2
y_{sp2}	set point values for controlled variable 2, x_4

Greek letter: Exothermic CSTR with reactions $A \rightarrow B \rightarrow C$

α	heat of reaction ratio
β	dimensionless heat of reaction
δ	dimensionless heat transfer coefficient
δ_1	ratio of reactor to coolant volume
δ_2	ratio of reacting mixture to coolant specific heat capacities
ρ	reaction mixture density in kg/m^3
ϕ	Damkohler number at constant volume
ξ_1	dimensionless Arrhenius preexponential factor of first reaction
ξ_2	dimensionless Arrhenius preexponential factor of second reaction
λ	eigenvalue of zero dynamics
η_1	first variable of zero dynamics equation
η_2	second variable of zero dynamics equation
ΔH_A	heat of reaction of the first reaction in kJ/kmol
ΔH_B	heat of reaction of the second reaction in kJ/kmol
τ	dimensionless time

In many applications it is important to know the behavioral features of the reactor, such as the number of possible steady states and the influence of a change in one or more operating variables on those states. Studies on the dynamic behavior of a continuous stirred-tank reactor (CSTR) were carried out by Uppal et al. [11], in this paper, the types of dynamic behavior predicted were illustrated by numerical computation of the temperature and concentration trajectories. CSTRs generally present operational problems due to complex, open-loop, nonlinear behavior in the form of multiplicity, extinction phenomena, Hopf bifurcations, isola formation and disjoint bifurcations. Some of these phenomena were discussed by Aris [12]. In the nonlinear analysis of chemical processes, singularity theory and bifurcation analysis have been used effectively to characterize regions in parameter space, over which many kinds of solution diagram exist. Methods involving the application of static and Hopf bifurcation theory to partial differential equations and a very precise determination of steady-state profiles for studying the bifurcation behavior of tubular reactors were developed by Jensen and Ray [13]. Balakotaiah illustrated that singularity theory and bifurcation theory were the most efficient and systematic tools for ascertaining the maximal number of steady-state solutions of lumped parameter systems in which several chemical reactions occur simultaneously [14]. In his work, the regions in the parameter space corresponding to these solutions were determined directly. Razon reviewed multiplicities and instabilities in chemically reacting systems [15]. Russo and Bequette showed that multiplicity patterns might depend upon modeling assumptions [16,17]. Gamboa-Torres revealed the effect of process modeling on the nonlinear behavior of CSTR reactions [18,19]. Recently, Flores-Tlacuahuac carried out an open-loop, nonlinear bifurcation analysis to address the effect of potential manipulated disturbance and design variables on reactor nonlinear behavior [20]. Seider also studied multiple steady-state solutions for reactors and showed that some of these solutions are unstable [21–23].

As can be seen above, so far, considerable attention has been paid to the analysis of the multiplicity features of reacting systems, many works have been reported on the stability analysis of reacting systems under open-loop conditions. Also, it is necessary to consider the phase behavior when studying the multiplicity features and stability of chemical processes.

Stability and controllability are important characteristics of inherently safer process designs [24]. Clearly, instability and non-minimum phase behavior limit the degree of inherent safety of a reaction system. It has been recognized that nonlinear and phase behaviors exhibited by chemical processes might have important effects on process operation and performance. However, little research has been published on considering stability and phase behavior simultaneously, while focusing on inherently safer design. Therefore, integrating stability and controllability analysis in the design of chemical processes is a topic of broad interest.

Studies in the literature have shown that the controllability and stability of a process are seriously affected by its design at the early stage. It is therefore necessary to have some knowledge of the nature of the inherent properties a process might possess, even at the early design stages. The aim of this paper is to provide a strategy for separating the operating ranges of chemical processes into distinct zones. Focusing on inherent safety, the nonlinear and phase behavior analyses are carried out simultaneously. To separate the operating ranges into distinct zones, steady states of chemical processes are then classified based on their stability or instability and minimum phase or non-minimum phase behaviors. Then, by applying this strategy to isothermal and exothermic CSTR case studies, it is shown that this strategy has great significance for process design and operation.

This article is structured as follows. In Section 2, a description of the algorithms for separating the operating ranges of a chemical reaction process is given. In Sections 3 and 4, the strategy is applied to an isothermal CSTR and an exothermic CSTR. Finally, in Section 5, the main conclusions of the paper are given.

2. Algorithm for operating zone separation

2.1. Algorithm for obtaining the zero dynamics of nonlinear systems

For nonlinear systems, the term non-minimum phase implies unstable zero dynamics. Zero dynamics can be characterized as the remaining dynamics of a nonlinear system in the case where the output keeps to be zero (constant) for all times. Different interpretations of the zero dynamics lead to differences in their computation. For the method described in this paper, the detailed algorithm for obtaining the zero dynamics of a chemical process is provided elsewhere [25–28]. Whether the zero dynamics are stable or unstable at a certain operating point can be identified by eigenvalues of the Jacobian of the zero dynamics at this operating point. When at least one eigenvalue of the Jacobian of the zero dynamics is positive, the zero dynamics is unstable. Unstable zero dynamics can cause non-minimum phase behavior. Therefore, the operating zones of the chemical reaction system can be divided into minimum phase and non-minimum phase zones, according to the zero dynamics.

2.2. Algorithm for stability analysis

Consider a nonlinear dynamic equation of the type

$$\frac{dX}{dt} = F(X, \lambda)$$

where X is the state variable and λ is a variable parameter. $X \in R^n$. Set $F_X(X, \lambda)$ as the Jacobian matrix of $F(X, \lambda)$. X_0 is the steady-state solution of $F(X, \lambda) = 0$ at $\lambda = \lambda_0$, i.e. X_0 is the solution of $F(X, \lambda_0)$.

For the system described above, the method is applied as follows. At the first step, the extended homotopy-continuation method [29], which is effective in achieving global convergence, is applied to obtain all the steady-state solutions in the parameter space of the chemical process. Then, analysis is carried out on these steady-state solutions to identify their stability characteristics, based on singularity theory. The stability characteristics of the chemical process will change with variations in the system parameters. Therefore, it is important to identify singularity points where changes to a chemical process system's stability characteristics occur. As a result, the parameter space can be divided into several subspaces, over which different characteristics, The stability of a system is determined by the eigenvalues of the *Jacobian* matrix. If all eigenvalues are in the left-half plane (LHP), the system is stable; otherwise the system is unstable.

The algorithm is described as follows:

(1) Compute all steady-state solutions of the chemical system.
Compute the solutions of $F(X, \lambda) = 0$ at different λ.

(2) Compute singular values of the chemical system's *Jacobian* matrix.
Compute the rank of the matrix $F_X(X, \lambda)$ under certain λ and the related solution of X. If $r(F_X) = n - 1$, the λ and related X are at a singularity point. The stability of the system would differ significantly between the two sides of the singularity point. Record the singularity point (X_s, λ_s).

(3) Determine the stability status on both sides of the singularity point.
Obtain one point on each side of the singularity point in the solution curve, computing all eigenvalues of $F_X(X, \lambda)$. If all eigenvalues are in the LHP, the system at the operating point is stable; otherwise the system is unstable. The stability status is continuous and often changes as it passes through the singularity point. Only a few points need to be calculated to determine the stability status.

(4) Repeat the above process to identify all the singularity points and to determine the stabilities on both sides of each singularity point.

2.3. Algorithm for zone separation, integrating stability and phase behavior

For a chemical reaction system described by differential equations, whose stability properties are determined by eigenvalues of the process Jacobian, if all eigenvalues lie in the LHP, then the system is stable; if at least one of eigenvalues lies in the RHP, the system is unstable. When eigenvalues are conjugate complex roots, the imaginary part of roots cause oscillation, if the real part of eigenvalues is below zero, the system is asymptotical stable, if the real part is up to zero, the amplitude of oscillation becomes larger and larger under disturbances, the system is unstable. When the real part is equal to zero, i.e. all eigenvalues lie on the imaginary axis, it can cause the limit cycle behavior, equiamplitude periodic oscillation will happen, although the occurrence of this situation is rare, also it is regarded as unstable.

Analysis the stability of the process zero dynamics is similar to the analysis the stability of the system. If all eigenvalues of the process zeros dynamics are in the LHP, then the zero dynamics are stable, the system exhibits minimum phase behavior. Otherwise the process exhibits non-minimum phase behavior. Based on these two rules, the operating range can be divided into sub-regions. The flowsheet for zone classification can be seen in Fig. 1.

The detailed steps are as follows:

(1) Set-up dynamic mathematical modeling of the chemical process described by differential algebraic equations (DAEs).
(2) Solve the DAE, based on the extended homotopy-continuation algorithm, to obtain all the steady states.
(3) Obtain the zero dynamics of the chemical process.
(4) Determine the characteristics of the steady states (stable or unstable), based on singularity theory and bifurcation theory.

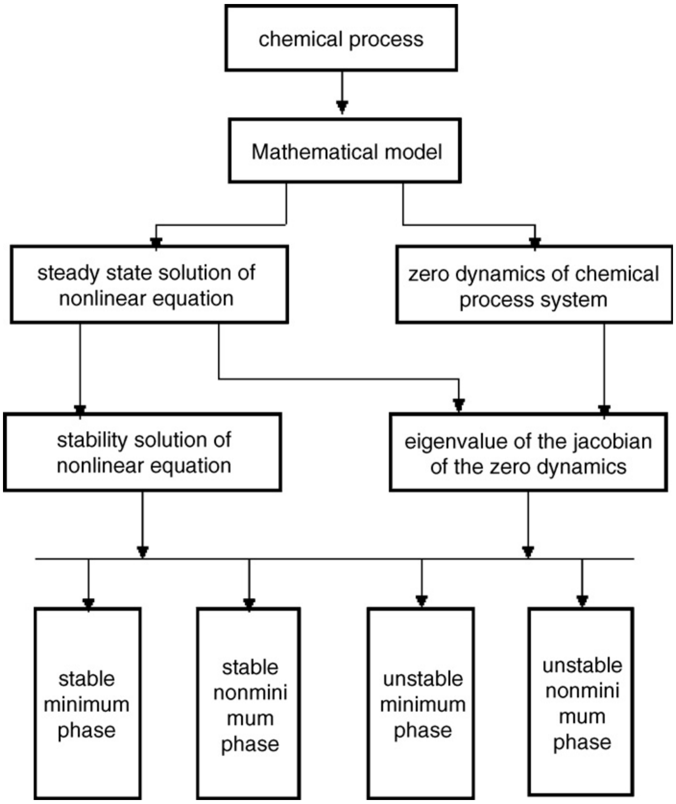

Fig. 1. A schematic diagram of zone classification.

(5) Solve eigenvalues of the *Jacobian* of zero dynamics to determine whether the zero dynamics are stable or unstable.
(6) Segregate the whole operating range into distinct zones, based on the results obtained from steps 4 and 5.

3. Example: isothermal *CSTR* with Van der Vusse reactions

Consider the following reaction network, called the Van der Vusse reaction [30], where B is the desired product:

$$A\xrightarrow{k_1}B\xrightarrow{k_2}C$$

$$2A\xrightarrow{k_3}D$$

The model equations of the process are given by

$$\frac{dC_A}{dt}=-k_1C_A-k_3C_A^2+\frac{Q}{V}(C_{Af}-C_A) \tag{1}$$

$$\frac{dC_B}{dt}=k_1C_A-k_2C_B-\frac{Q}{V}C_B \tag{2}$$

$$y=C_B \tag{3}$$

where $k_1 = 50\,\mathrm{h}^{-1}$, $k_2 = 1.5\,\mathrm{h}^{-1}$ and $k_3 = 500\,\mathrm{L/(mol\,h)}$ are the reaction rate constants $C_{Af} = 1\,\mathrm{mol/L}$ [7], is the concentration of A in the feed stream and C_A is the concentration of A in the reactor. The controlled variable is the concentration of B, C_B and the manipulated variable is the dilution rate, Q/V.

Setting the output and its derivative equal to zero in Eq. (2), solving the remaining system and substituting Q/V into Eq. (1), we can easily obtain the zero dynamics of the Van der Vusse reaction model:

$$\frac{dC_A}{dt}=-k_1C_A-k_3C_A^2+\frac{(C_{Af}-C_A)(-k_2y-k_1C_A)}{C_B} \tag{4}$$

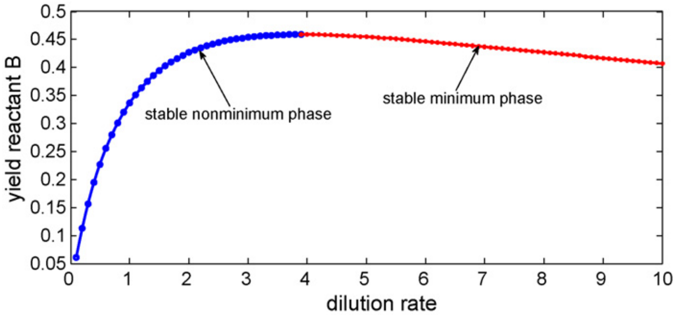

Fig. 2. Relationship between the steady states and dilution rate.

The eigenvalue, λ, of the *Jacobian* of the process zero dynamics as a function of the states is expressed by

$$\lambda=-k_1+k_2-2k_3C_{0A}+\frac{C_{Af}k_1-2k_1C_{0A}}{C_{0B}} \tag{5}$$

where C_{0A} and C_{0B} are the steady-state concentrations for the model

$$C_{0B}=\frac{k_1(-k_1-(Q/V)+\sqrt{k_1^2+2k_1(Q/V)+4C_{Af}k_3(Q/V)+(Q/V)^2})}{2k_3(k_2+(Q/V))}$$

$$C_{0A}=\frac{-(k_1+(Q/V))}{2k_3}+\frac{\sqrt{k_1^2+2k_1(Q/V)+4C_{Af}k_3(Q/V)+(Q/V)^2}}{2k_3} \tag{6}$$

Fig. 2 shows the relationship between the steady-state yield of the desired product and dilution rate. If the steady-state solution is inserted into Eq. (5), an analytical expression for the eigenvalue of the zero dynamics as a function of the input in the whole operation region is obtained. The relationship between the eigenvalue of the zero dynamics and the input is depicted in Fig. 3.

If the sign of λ is negative at a given steady state, the zero dynamics is stable at this steady state, so the system has minimum phase behavior at this steady state. Through analysis of Figs. 2 and 3 it is clear that the eigenvalue of the process zero dynamics changes from positive to negative, corresponding to a change from non-minimum to minimum phase at a certain Q/V equals to 3.9 L/h. Further, it can be seen from Figs. 2 and 3 that at the maximum yield of reactant B the eigenvalue of the process zero dynamics is equal to zero. Thus, when $Q/V < 3.9$ L/h, the process will exhibit non-minimum phase behavior, and when $Q/V > 3.9$ L/h, the process will exhibit minimum phase behavior.

Application of the algorithm described in Section 2.2 reveals that all of the steady states of the process are stable. Therefore, the whole operating region of the process can be divided into just two subzones (zone I, a stable non-minimum phase and zone II, a stable

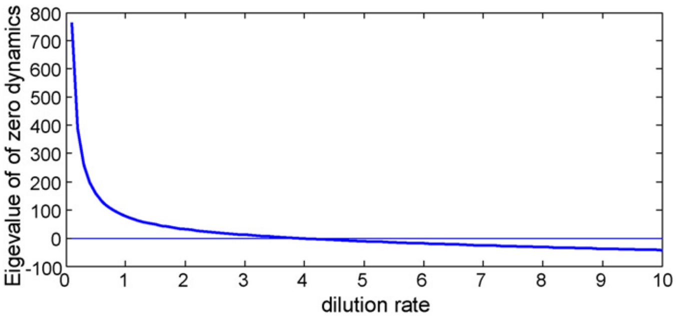

Fig. 3. Relationship between the eigenvalue of the zero dynamics and dilution rate.

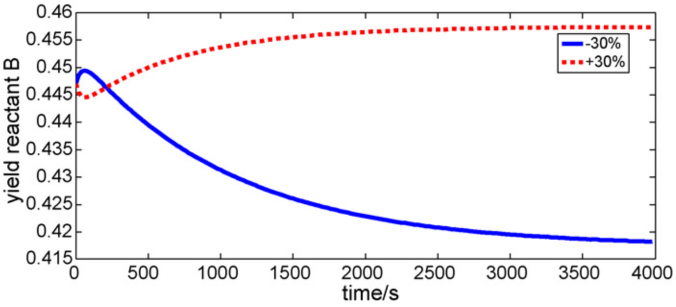

Fig. 4. Step responses of NMP zone at the steady state $Q/V = 2.6$ L/h.

minimum phase). Compared Fig. 2 with those of Kuhlmann and Bogle [7], it can be seen that they only did the phase behavior analysis, but in our paper, as shown in Fig. 2, the stability/instability and minimum/non-minimum phase behaviors are taken into account simultaneously.

For a step change at the steady state $Q/V = 2.6$ L/h in the non-minimum phase region, the responses are shown in Fig. 4. For a step change at the steady state $Q/V = 6$ L/h in the minimum phase region, the responses are shown in Fig. 5. The inverse response, caused by non-minimum phase behavior, can clearly be seen in Fig. 4. Apparently, the inverse response limits the achievable closed-loop performance, regardless of the control law used.

Because the multiple steady-state phenomenon exists in this process, its design at two Q/V values can lead to the same yield of the desired product. The input multiplicity implies that there will be a change in the sign of the steady-state gain of a process when the input varies over its range, which makes its controller design very difficult. Therefore, it is important to analyze the phase behavior of this chemical process and the result would have a significant impact on process controller design.

4. Example: exothermic CSTR with reactions $A \rightarrow B \rightarrow C$

The mathematical model which describes a CSTR in which two exothermic, irreversible, first-order reactions take place in series $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ is derived from dynamic material and energy balances. Reactor volume and physical parameters are assumed to remain constant and perfect mixing is also assumed. In addition, the dynamics of the cooling jacket are taken into account. The model consists of the following four nonlinear, ordinary differential equations [18]:

$$\frac{dC_A}{dt} = \frac{Q}{V}(C_{Af} - C_A) - k_1(T)C_A \tag{7}$$

$$\frac{dC_B}{dt} = \frac{Q}{V}(C_{Bf} - C_B) - k_2(T)C_B + k_1(T)C_A \tag{8}$$

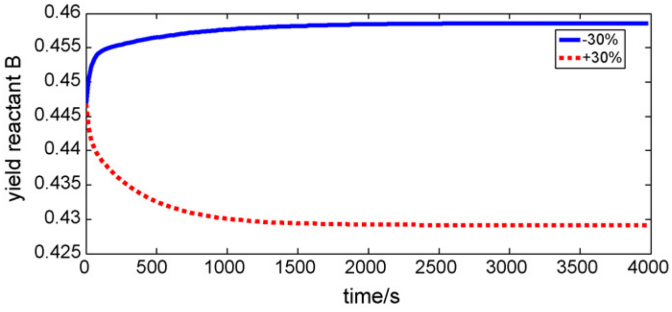

Fig. 5. Step responses of MP zone at the steady state $Q/V = 6$ L/h.

Table 1
Dimensionless variables and parameters of exothermic CSTR.

$x_1 = \frac{C_A}{C_{Af0}}$	$x_2 = \frac{C_B}{C_{Af0}}$	$x_3 = \frac{T - T_{f0}}{T_{f0}}\gamma$
$x_4 = \frac{T_c - T_{f0}}{T_{f0}}\gamma$	$x_{1f} = \frac{C_{Af}}{C_{Af0}} = 1$	$x_{2f} = \frac{C_{Bf}}{C_{Af0}} = 0$
$x_{3f} = \frac{T_f - T_{f0}}{T_{f0}}\gamma = 0$	$x_{4f} = \frac{T_{cf} - T_{f0}}{T_{f0}}\gamma = -1$	$\zeta_1(x_3) = e^{x_3/(1+(x_3/\gamma))}$
$\zeta_2(x_3) = e^{\psi x_3/(1+(x_3/\gamma))}$	$\tau = \frac{Q_0}{V}t$	$q = \frac{Q}{Q_0}$
$q_c = \frac{Q_c}{Q_0}$	$\delta = \frac{UA}{\rho C_p Q_0} = 0.78$	$\delta_1 = \frac{V}{V_c} = 10$
$\delta_2 = \frac{\rho C_p}{\rho_c C_{pc}} = 0.952$	$S = \frac{k_2(T_{f0})}{k_1(T_{f0})} = 1.015$	$\phi = \frac{V}{Q_0}k_1(T_{f0}) = 0.06$
$\beta = \frac{-\Delta H_A C_{Af0}\gamma}{\rho C_p T_{f0}} = 8$	$\alpha = \frac{-\Delta H_B}{-\Delta H_A} = 0.19$	$\gamma = \frac{E_1}{RT_{f0}} = 27.85$
$\psi = \frac{E_2}{E_1} = 0.32$		

$$\frac{dT}{dt} = \frac{Q}{V}(T_f - T) + k_1(T)C_A\frac{-\Delta H_A}{\rho Cp} + k_2(T)C_B\frac{-\Delta H_B}{\rho Cp} - \frac{UA}{\rho CpV}(T - T_c) \tag{9}$$

$$\frac{dT_c}{dt} = \frac{Q_c}{V_c}(T_{cf} - T_c) + \frac{UA}{\rho C p_c V_c}(T - T_c) \tag{10}$$

where the kinetic constants are

$$k_1(T) = A_1 e^{-E_1/RT} \tag{11}$$

$$k_2(T) = A_2 e^{-E_2/RT} \tag{12}$$

According to dimensionless parameters and variables defined in Table 1, Eqs. (7)–(10) can be written in dimensionless form as Eqs. (13)–(16):

$$\frac{dx_1}{d\tau} = q(x_{1f} - x_1) - x_1\zeta_1(x_3)\phi \tag{13}$$

$$\frac{dx_2}{d\tau} = q(x_{2f} - x_2) + x_1\zeta_1(x_3)\phi - x_2\phi\zeta_2(x_3)S \tag{14}$$

$$\frac{dx_3}{d\tau} = q(x_{3f} - x_3) + \delta(x_4 - x_3) + \beta\phi[x_1\zeta_1(x_3) + \alpha x_2\zeta_2(x_3)S] \tag{15}$$

$$\frac{dx_4}{d\tau} = \delta_1[q_c(x_{4f} - x_4) + \delta\delta_2(x_4 - x_3)] \tag{16}$$

In Eqs. (13)–(16), x_1 is the dimensionless concentration of reactant A, x_2 is the dimensionless concentration of reactant B, x_3 is the dimensionless reactor temperature and x_4 is the dimensionless cooling jacket temperature. Here, the controlled variables are the dimensionless concentration of B, x_2, and the dimensionless temperature of coolant, x_4. The manipulated variables are the dimensionless feed and coolant flow rates, q and q_c, respectively.

Set

$$\eta = \begin{bmatrix} \eta_1 \\ \eta_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_3 \end{bmatrix} \tag{17}$$

$$y_{sp} = \begin{bmatrix} y_{sp1} \\ y_{sp2} \end{bmatrix} = \begin{bmatrix} x_2 \\ x_4 \end{bmatrix} \tag{18}$$

According to the algorithm to obtain the zero dynamics of nonlinear systems, the zero dynamics equations are

$$\dot{\eta}_1 = -\frac{\zeta_1(\eta_2)(-x_{2f}+y_{sp1})\phi\eta_1-(-x_{1f}+\eta_1)(\zeta_2(\eta_2)Sy_{sp1}\phi-\zeta_1(\eta_2)\phi\eta_1)}{y_{sp1} - x_{2f}} \tag{19}$$

$$\dot{\eta}_2 = \frac{(y_{sp1} - x_{2f})\{-\beta\phi[\eta_1\zeta_1(\eta_2) + \alpha y_{sp1}\zeta_2(\eta_2)S] - \delta(y_{sp2} - \eta_2)]\}}{y_{sp1} - x_{2f}} - \frac{[\eta_1\zeta_1(\eta_2)\phi - y_{sp1}\phi\zeta_2(\eta_2)S](\eta_2 - x_{3f})}{y_{sp1} - x_{2f}} \tag{20}$$

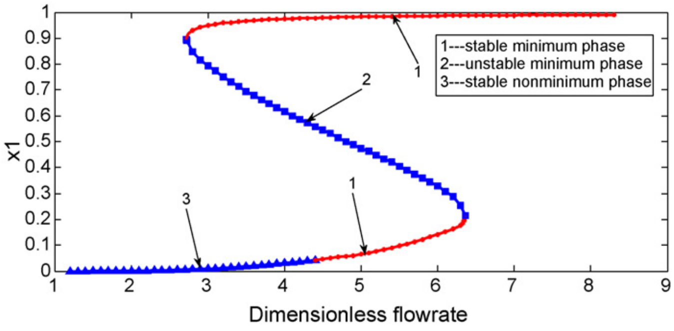

Fig. 6. Relationship between dimensionless feed q and x_1.

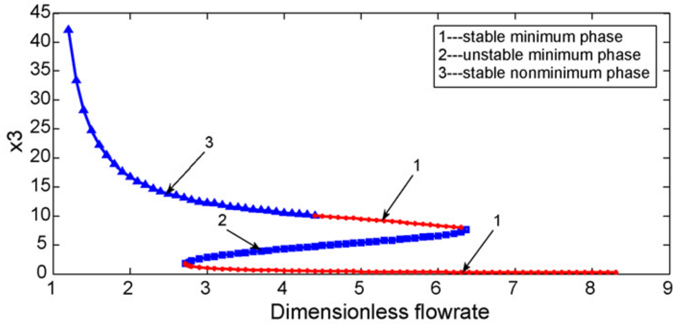

Fig. 8. Relationship between dimensionless feed q and x_3.

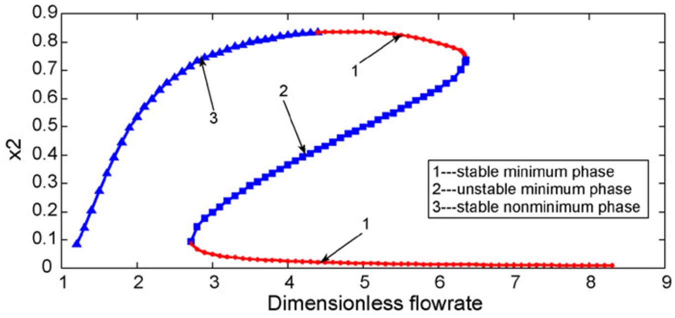

Fig. 7. Relationship between dimensionless feed q and x_2.

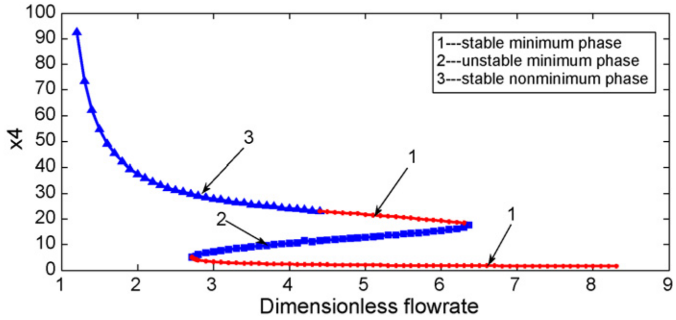

Fig. 9. Relationship between dimensionless feed q and x_4.

First, set $q_c = 0.4$, using the extended homotopy-continuation algorithm to solve the steady-state solutions of Eqs. (13)–(16). Based on the steady-state solutions, the input/output multiplicity characteristics of this chemical reaction system can be studied. Relationships between dimensionless feed q and x_1, dimensionless feed q and x_2, dimensionless feed q and x_3 and between dimensionless feed q and x_4 are shown in Figs. 6–9, respectively.

Based on the algorithm described in Section 2.2 for identifying the stable and unstable zones, the operating region can be separated into a stable zone and an unstable zone. The operating region can be divided into a non-minimum phase zone and a minimum phase zone by eigenvalues of the *Jacobian* of the process zero dynamics, as described by Eqs. (19) and (20). By integration of the above results, the entire operating region of the chemical reacting system can be separated into three distinct zones (zone I, stable minimum phase zone; zone II, unstable minimum phase zone; and zone III, stable non-minimum phase zone). The results are also shown in Figs. 6–9.

Now, consider simultaneously changing both of the manipulated variables, dimensionless feed and coolant flow rate. The results are shown in Figs. 10–13, along with the separation of the operation space into subspaces with different characteristics.

It can be seen that three subspaces exist: stable minimum phase subspace, unstable minimum phase subspace and stable non-minimum phase subspace. Within the stable minimum phase subspace, the system will run smoothly, even if some variable disturbances are encountered. Within the stable non-minimum phase subspace, the system will run smoothly only around a certain operating point and will not run smoothly if variable disturbances are encountered. Finally, within the unstable minimum phase subspace, the system may change significantly or run away even under very minor disturbances. The latter subspace is dangerous, so efforts should be made at the conceptual design stage of this reacting system to avoid selecting process operating regions in this subspace. This chemical process system is very difficult to control within the stable non-minimum phase subspace. In many cases, operation is more profitable at an unstable steady state or at a stable steady state that often involves non-minimum phase behavior. For these types of processes, controller designs are more challeng-

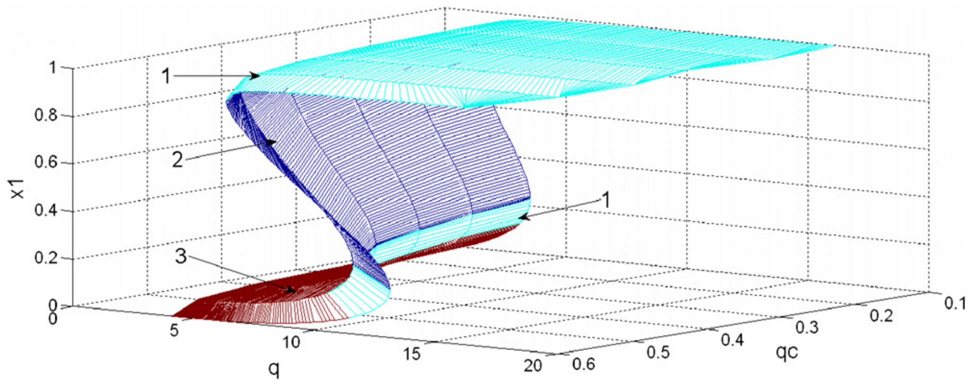

Fig. 10. Zone classification for the space surface of x_1–q–q_c. 1: stable minimum phase subspace; 2: unstable minimum phase subspace; 3: stable non-minimum phase subspace.

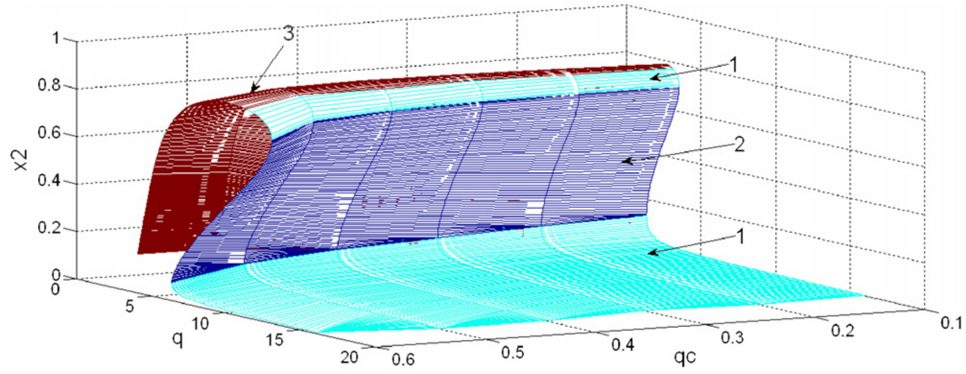

Fig. 11. Zone classification for the space surface of x_2–q–q_c. 1: stable minimum phase subspace; 2: unstable minimum phase subspace; 3: stable non-minimum phase subspace.

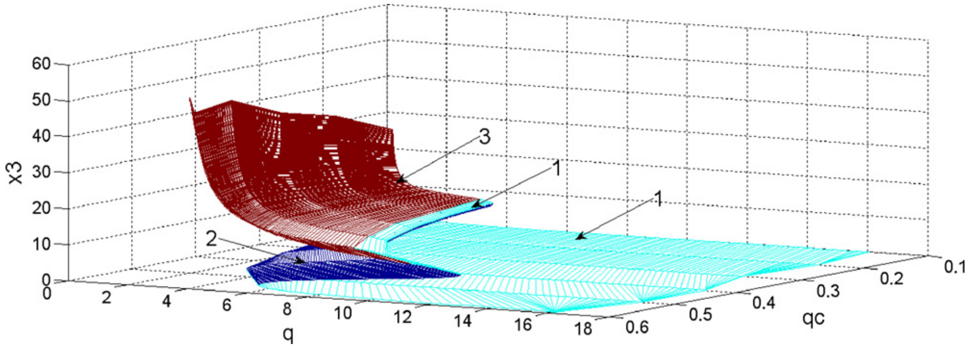

Fig. 12. Zone classification for the space surface of x_3–q–q_c. 1: stable minimum phase subspace; 2: unstable minimum phase subspace; 3: stable non-minimum phase subspace.

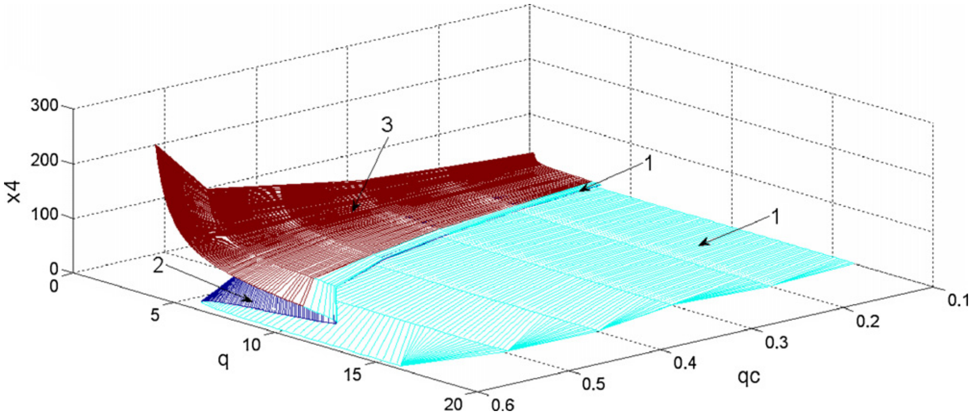

Fig. 13. Zone classification for the space surface of x_4–q–q_c. 1: stable minimum phase subspace; 2: unstable minimum phase subspace; 3: stable non-minimum phase subspace.

ing. Thus, the elimination of instability and/or non-minimum phase behavior could be achieved through changes in the operating conditions, such as inlet changes involving feed concentration and/or the cooling water flow rate.

This method can be applied for more complex reaction systems, such as industrial polymerization process and TE process. Extending this method to these complex systems and periodic solution branches will be further studied.

5. Conclusions

This paper presents a strategy for classifying the operating region into sub-zones at an early stage of chemical process design, to ensure that the designed processes are inherently safer. The strategy is applied to isothermal CSTR and exothermic CSTR examples. The results show that these systems' characteristics of stability and phase behavior varied with the process operating conditions, such as feed flow rate and cooling flow rate, providing important information for process design and operation. In many cases, operation is more profitable at an unstable state involving non-minimum phase behavior. For these types of processes, controller designs are more difficult and challenging. Consequently, it is important to account for the trade-offs between stability, controllability and product quality when selecting an appropriate chemical process design that meets practical requirements.

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