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Phase Behavior Analysis for Industrial Polymerization Reactors

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The production of polymer is a very important sector in the chemical processing industry as demand for polymeric materials increases, and these polymerization processes exhibit nonlinear dynamics posing difficulties on process operation and control. It is desirable to understand the relationship between open-loop controllability and process conditions. The phase behavior that is an open-loop indicator of the controllability for the methyl methacrylate and propylene polymerization reactor over the entire feasible operating region is determined, and the influences of design/operating parameters and model uncertainties on this inherent characteristic at the design stage are analyzed. Based on zero dynamics and singularity theory, directly in the nonlinear setting, a methodology for the preliminary analysis of the phase behavior over the whole feasible operating region is presented and applied into the above two reactors. The above research results demonstrate that to modify certain parameters in certain direction would improve the controllability and are expected to provide helpful guidelines for improving plant and control system design. This is desirable because it allows identification of the cause of the limitation to give an indication where to modify the design. © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 2795–2807, 2011
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Introduction

The production of polymers is a very important sector in the chemical processing industry as demand for polymeric materials increases. Polymer manufacture involves processes that can exhibit highly nonlinear dynamic behaviors, including input/output multiplicities, limit cycles, sustained oscillations, hysteresis, and chaos.[1] Nonlinearities are perceived as undesirable because they may adversely affect process operation and process controller performance and may lead to unsafe operations. Hence, there is an incentive to obtain a better understanding of the nonlinear characteristics of polymerization reactors. The open-loop steady-state and dynamic behaviors of polymerization reactors have been the focus of much research during the past several decades.

Nonlinear analysis is a tool that can reveal practical operability problems faced during process design and operation. Operability problems are normally associated with the presence of multiple input and output states, oscillatory behavior, and even chaotic dynamics, and there exists a wealth of literature on the subject. Van Heerden[2] was one of the first to study the problems of multiple steady states and instability in chemical reactors. Uppal et al.[3] addressed the complete treatment of nonlinearity and bifurcation of a continuous stirred-tank reactor (CSTR) with single reaction. Razon and Schmitz[4] provided excellent reviews of multiplicities and instabilities in chemically reacting systems. Advances obtained from early studies of single CSTRs motivated studies of more complex polymerization reactors. Complicated nonlinear bifurcation behavior in polymerization reactors has

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been reported. Ray and coworkers[5–13] performed a large amount of the multiplicity and stability research specific to polymerization reactors, providing a variety of examples illustrating the nonlinear dynamics found in polymerization processes. Recently, many articles have shown that performing detailed bifurcation and stability analysis may be very helpful for the development and implementation of nonlinear models and model-based controllers for polymerization reactors. Flores-Tlacuahuac and coworkers[14–17] addressed the open-loop nonlinear bifurcation analysis of a high-impact polystyrene system, a polyurethane polymerization reactor, and a methyl methacrylate (MMA) polymerization reactor, and the effects of potential manipulated disturbance and design variables on the stability of the polymerization reactors were analyzed.

To prevent a process from failing to meet the required performance specifications due to system inherent characteristics, it is necessary to fully identify all potential problems associated with complex process behavior and to assess the controllability when design alternatives are considered at the design stage.[18] Controllability analysis can show the influences of the design and operating parameters and disturbances on control, thus providing guidance for eliminating control difficulties by modifying the process design at an early stage when modifications of the process are still possible.

There are many existing methodologies for controllability analysis, which can be divided into two main approaches: linear model-based approaches and nonlinear model-based approaches.[19] By using relative gain array (RGA) and disturbance cost (DC), Lewin and Bogle[20] analyzed and compared the controllability and resilience of the optimal and suboptimal operating points for a continuous polymerization reactor. Kaistha[21] took the closed-loop response as a tool for measuring the controllability of control structures for a reactive distillation column, and the results showed that nonlinear dynamic phenomena can compromise the robustness of the control system. Rafael and Bogle[22] studied the stability of zero dynamics for the fluid catalytic cracking process to investigate the inverse response behavior of two common operating policies when the unit is operating either in the standard or in the ignited steady state using a full nonlinear model directly, and then Rafael and Aguilar[23] proposed a methodology for the evaluation of pairs of control and manipulated variables for nonlinear control affine systems, based on the relationship between zero dynamics and control stability; the presented method compliments the RGA analysis for nonlinear systems. Kuhlmann and Bogle[24] demonstrated the relationships between input multiplicity and nonminimum phase behavior and between controllability and optimal operation for nonlinear single-input, single-output systems, and they [25] also shown the process inherent limitation on switchability imposed by unstable zero dynamics. Meel and Seider[26] introduced a method for designing the inherently safer processes with good controllability according to the zero dynamics. Yuan et al.[27] presented a methodology for segregating the whole operating space of a CSTR into subspaces with different characteristics based on instability/stability and nonminimum/minimum phase behavior. Based on the above discussion, there are several reasons for this research work. First, to keep industrial polymerization processes such as propylene polymerization process running safety and smoothly, phase behavior analysis is of great practical importance as nonminimum phase behavior that can cause the inverse response is one of the process inherent characteristics that limit the controllability of the system and the quality of the performance achievable. Second, linearization-based methodologies such as RGA and DC may give correct information around a specified steady-state point, but they may be not satisfactory for problems with a high degree of nonlinearity over widely ranging operating regions.[28] Also, they are the time- and resource-consuming task. Third, the existing zero dynamics-based methodologies have been mostly applied to the relative simple process such as CSTR and only analyze the phase behavior for certain operating points not over wide operating region of interest. Fourth, once the process is under operation, there are many uncertainties and disturbances in the operation conditions, the process may not run at the designed operating point, a small change of some parameter in a certain direction could happen unnoticed, and it might result in a hard control problem. Therefore, it is important to analyze the effects of parameters on controllability over the process feasible operating region. And the last one, as no model provides a perfect description of reality, it would be important to investigate the effect of the model uncertainties on the phase behavior. To date, there is little work to reveal the relationship between operating/design parameters and model uncertainties and the phase behavior for the industrial polymerization process over its whole feasible operating region.

Based on the above considerations, focusing on the determination of phase behavior for a MMA polymerization reactor and an industrial polypropylene reactor, the nonlinear model is used directly. The aim of this project is to develop a methodology, based on singularity theory, for determining the phase behavior (minimum and nonminimum phase behavior) of nonlinear processes over their entire feasible operating region and analyzing the influences of design/operating parameters and model uncertainties on this inherent characteristic to provide an indication on where and how to modify the design at the early stage. The structure of this article is as follows. Initially, algorithms for proposed methodology as well as relationships between phase behavior and zero dynamics are given. This is followed by the phase behavior analysis for the MMA polymerization reactor. Phase behaviors of the industrial polypropylene reactor are then discussed, and finally, the main conclusions of the work are presented.

Methodologies Description

Zero dynamics and phase behavior

The zero dynamics of a system is the dynamics of its inverse,[29,30] which can be characterized as the remaining dynamics of a nonlinear system in the case where the output remains constant for all times.[31] For a linear system, the zero dynamics contains the same information as the zeros of the transfer function. In a nonlinear system, it is not possible to define a transfer function but it is possible to find unstable zero dynamics. According to Daoutidis and Kravaris,[32] the analysis of the zero dynamics of nonlinear system yields the same conclusions of the analysis of the zeros for linear ones. For nonlinear systems exhibiting nonminimum phase behavior, the inherent limitations imposed on controllability are analogous to the linear case. Unstable zero dynamics implies nonminimum phase behavior, which is an inherent characteristic that has some implications for controller design and control performance. Nonminimum phase behavior is related to two different characteristics of the process. One is a dynamic effect, the so-called "inverse response," and the other is the steady-state characteristics, the so-called "input multiplicity."[33]

Algorithms for obtaining zero dynamics

Different interpretations of zero dynamics lead to differences in their computation. Here, the algorithm for obtaining zero dynamics from the normal form taken from Isidori[31] is reproduced as follows.

Assuming that equations for nonlinear processes can be written as

$$\frac{dx}{dt} = f(x) + \sum_{j=1}^{m} g_j(x)u_j \qquad (1)$$
$$y_i = h_i(x), \quad i = 1, \dots, m$$

where $x = [x_1, x_2, \dots, x_n]^T \in R^n$ are the state variables, $u = [u_1, u_2, \dots, u_m]^T \in R^m$ are the inputs, and $y = [y_1, y_2, \dots, y_m]^T \in R^m$ are the outputs. *f(x)* and *g(x)* are smooth vector functions, and *h(x)* is a smooth scalar function.

Definition 1.[32] For a nonlinear multi-input, multioutput (MIMO) system described by Eq. 1, r_i, the relative order of output y_i with respect to the manipulated input u, is the smallest integer for which

$$L_g L_f^{r_i-1} h_i(x) = [L_{g1} L_f^{r_i-1} h_i(x), L_{g2} L_f^{r_i-1} h_i(x), \dots, L_{gm} L_f^{r_i-1} h_i(x)] \neq [0, 0, \dots, 0] \qquad (2)$$

where

$$L_f h(x) = \frac{\partial h(x)}{\partial x} f(x) = \sum_{i=1}^{n} \frac{\partial h(x)}{\partial x_i} f_i(x) \qquad (3)$$

$$L_f^k h(x) = L_f(L_f^{k-1} h(x)) \qquad (4)$$

Once the relative $r_1, r_2, \dots, r_m$ are defined, the first $\sum_{i=1}^{m} r_i$ elements of the nonlinear change of coordinates can be chosen as

$$\begin{aligned}
z_1 &= \phi_1(x) = h_1(x) \\
z_2 &= \phi_2(x) = L_f h_1(x) \\
&. \\
z_{r_1} &= \phi_{r_1}(x) = L_f^{r_1-1} h_1(x) \\
&. \\
z_{\sum_{i=1}^{m} r_i - r_m + 1} &= \phi_1(x) = h_m(x) \\
z_{\sum_{i=1}^{m} r_i - r_m + 2} &= \phi_2(x) = L_f h_m(x) \\
&. \\
z_{\sum_{i=1}^{m} r_i} &= \phi_{\sum_{i=1}^{m} r_i}(x) = L_f^{r_m-1} h_m(x)
\end{aligned} \qquad (5)$$

Furthermore, when $n > \sum_{i=1}^{m} r_i$, the system contains $n - \sum_{i=1}^{m} r_i$ zero dynamics,[32] and it is possible to find scalar fields, $t_1(x), \dots, t_{n-\sum_{i=1}^{m} r_i}(x)$ such that the scalar fields are linearly independent.

$$t_1(x), \dots, t_{n-\sum_{i=1}^{m} r_i}(x), h_1(x), L_f h_1(x), \dots, L_f^{r_1-1} h_1(x), \dots, h_m(x), L_f h_m(x), \dots, L_f^{r_m-1} h_m(x) \qquad (6)$$

The normal form of the nonlinear MIMO system can then be written as

$$\eta = \begin{bmatrix} \eta^{(0)} \\ \eta^{(1)} \\ .. \\ .. \\ \eta^{(m)} \end{bmatrix} = \phi(x) = \begin{bmatrix} t_1(x) \\ .. \\ t_{n-\sum_{i=1}^{m} r_i}(x) \\ h_1(x) \\ L_f h_1(x) \\ .. \\ L_f^{r_1-1} h_1(x) \\ .. \\ h_m(x) \\ L_f h_m(x) \\ .. \\ L_f^{r_m-1} h_m(x) \end{bmatrix} \qquad (7)$$

Hence, the original system is transformed into new coordinates, taking the form

$$\begin{aligned}
\frac{d\eta_1^{(0)}}{dt} &= F_1(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)}) + G_1(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)})u(t) \\
&\dots \\
\frac{d\eta^{(0)}_{n-\sum_{i=1}^{m} r_i}}{dt} &= F_{n-\sum_{i=1}^{m} r_i}(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)}) + G_{n-\sum_{i=1}^{m} r_i}(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)})u(t) \\
\frac{d\eta_1^{(1)}}{dt} &= \eta_2^{(1)} \\
&\dots \\
\frac{d\eta_{r_1-1}^{(1)}}{dt} &= \eta_{r_1}^{(1)} \\
\frac{d\eta_{r_1}^{(1)}}{dt} &= W_1(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)}) + C_1(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)})u(t) \\
&\dots \\
\frac{d\eta_1^{(m)}}{dt} &= \eta_{r_m}^{(1)} \\
&\dots \\
\frac{d\eta_{r_m-1}^{(m)}}{dt} &= \eta_{r_m}^{(m)} \\
\frac{d\eta_{r_m}^{(1)}}{dt} &= W_m(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)}) + C_m(\eta^{(0)}, \eta^{(1)}, \dots, \eta^{(m)})u(t) \\
y_1 &= \eta_1^{(1)} \\
&\dots \\
y_m &= \eta_1^{(m)}
\end{aligned} \qquad (8)$$

where

$$F_i(\eta^{(0)},\eta^{(1)},\ldots,\eta^{(m)}) = [L_f t_i(x)]_{x=\phi^{-1}(\eta)},\quad i=1,\ldots,\left(n-\sum_{i=1}^{m} r_i\right)$$

$$G_i(\eta^{(0)},\eta^{(1)},\ldots,\eta^{(m)}) = [L_g t_i(x)]_{x=\phi^{-1}(\eta)},\quad i=1,\ldots,\left(n-\sum_{i=1}^{m} r_i\right) \tag{9}$$

$$C_i(\eta^{(0)},\eta^{(1)},\ldots,\eta^{(m)}) = [L_g L_f^{r_i-1} h_i(X)]_{x=\phi^{-1}(\eta)},\quad i=1,\ldots,m$$

$$W_i(\eta^{(0)},\eta^{(1)},\ldots,\eta^{(m)}) = [L_f^{r_i} h_i(X)]_{x=\phi^{-1}(\eta)},\qquad i=1,\ldots,m$$

Therefore, the zero dynamics is

$$\frac{d\eta_1^{(0)}}{dt} = F_1(\eta^{(0)},y_{ss}) - G_1(\eta^{(0)},y_{ss})C(\eta^{(0)},y_{ss})^{-1}W(\eta^{(0)},y_{ss})$$

$$\frac{d\eta_2^{(0)}}{dt} = F_2(\eta^{(0)},y_{ss}) - G_2(\eta^{(0)},y_{ss})C(\eta^{(0)},y_{ss})^{-1}W(\eta^{(0)},y_{ss})$$

$$\ldots$$

$$\frac{d\eta^{(0)}_{n-\sum_{i=1}^{m} r_i}}{dt} = F_{n-\sum_{i=1}^{m} r_i}(\eta^{(0)},y_{ss}) - G_{n-\sum_{i=1}^{m} r_i}(\eta^{(0)},y_{ss}) \times C(\eta^{(0)},y_{ss})^{-1}W(\eta^{(0)},y_{ss}) \tag{10}$$

Algorithms for phase behavior analysis

Step 1. Compute all steady-state solutions using extended homotopy continuation.[34]

Step 2. Calculate the zero dynamics of the original nonlinear process.

Step 3. Find the singularity point of zero dynamics. Calculate the rank of the Jacobian matrix of Eq. 10 under all steady-state solutions. If the rank is less than $n-\sum_{i=1}^{m} r_i$ at a given steady-state operation point, this point is defined as the singularity point of the zero dynamics.

Step 4. Phase behavior analysis for original nonlinear processes. As the phase behavior may change when the system crosses the zero dynamics' singularity points, the whole feasible operating region can be divided into several subregions by singularity points. Select one steady-state operating point on each side of the singularity points. Then, analyze the stability of the zero dynamics at the selected operating points through the eigenvalues of zero dynamics' Jacobian matrices. If the zero dynamics is stable at a given selected operating point, then the system exhibits minimum phase behavior in the subregion where the selected operating point is located.

Step 5. Change the adjustable parameters, and repeat the above steps so that the effects of process design/operation parameters and model uncertainty on the phase behavior of the original system can be identified.

Based on the algorithm described above, the phase behaviors of two industrial polymerization reactors are investigated in the next two sections. There are two reasons for why the models for a MMA polymerization reactor and a propylene polymerization reactor are chosen in this work. First, the model for the MMA reactor discussed in the next section is the most accurate model and is widely used as a benchmark to test the various control algorithms. Second, as the first author had joined a related project of the petrochemical company, the accuracy of the model for the propylene polymerization reactor was validated by the experimental data from the company.

Phase Behavior Analysis for a MMA Polymerization Reactor

Process description and modeling

The polymerization of MMA with azo-bis-isobutyronitrile as the initiator and toluene as solvent is carried out in a jacketed CSTR. The reaction is exothermic, and a cooling jacket is used to remove the heat of reaction. Under the standard reaction mechanism[15] for the MMA free-radical polymerization and appropriate assumptions,[35] a mathematical model was developed by Daoutidis et al.[35] We use the dynamic model derived in Ref. 15 but not consider the expression of D_1. In this work, the controlled variables are the cooling fluid temperature T_j, and the molar concentration of the dead polymer chains D_0. The possible manipulated variables are the initiator volumetric flow rate F_I, the cooling water volumetric flow rate F_{cw}, and the monomer feedstream volumetric flow rate F. The major measurable disturbances come from the concentration of monomer in the inlet stream C_{Iin}, and the temperature of the inlet stream T_{in}. The kinetic/constant parameters and process design/operation parameters are as same as listed in Ref. 15.

Phase behavior analysis

Zero Dynamics. Based on the above description of the polymerization systems, set $[x_1,x_2,x_3,x_4,x_5] = [C_m,C_I,T,D_0,T_j]$, $[y_1,y_2] = [D_0,T_j]$, and $[u_1,u_2] = [F_I,F_{cw}]$. According to the form of Eq. 1, the original model of the MMA polymerization reactor is control affine and can be appropriately used for the analysis. Based on the algorithm described in the above section, the zero dynamics has the form

$$\frac{d\eta_1^{(0)}}{dt} = f_1(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)}) \tag{11}$$

$$\frac{d\eta_2^{(0)}}{dt} = f_2(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)}) + \frac{\frac{\partial f_4}{\partial x_5}(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)})}{\frac{\partial f_4}{\partial x_2}(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)})} \times f_5(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)}) - \frac{L_f f_4(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)})}{\frac{\partial f_4}{\partial x_2}(\eta_1^{(0)},\eta_2^{(0)},\eta_s^{(1)},\eta_s^{(2)})} \tag{12}$$

Effects of Manipulated Variables on Phase Behavior. Industrial polymerization reactors are normally equipped with a control device whose design and complexity rely on the control objectives. An important part of the control system design task refers to the selection of the controlled and manipulated variables and the way they are paired. Phase behavior analysis may play an important role in assessing the effect of manipulated variables on the controlled variables and helping to prevent process operation around regions with poor controllability. Based on the zero dynamics

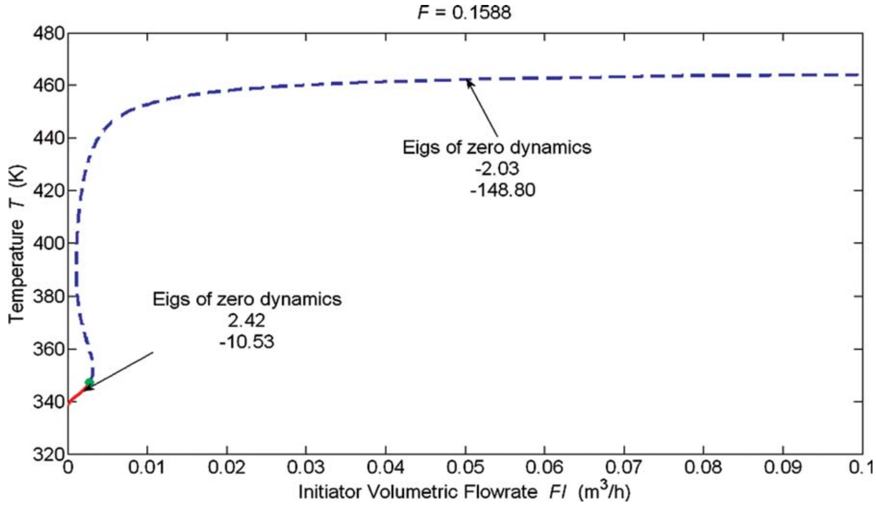

Figure 1. Relationship between the temperature *T* and initiator volumetric flow rate F_I.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

described by Eqs. 11 and 12, the phase behavior can be investigated. If the zero dynamics is asymptotically stable at a given operating point or, in other words, if all eigenvalues of the Jacobian of the zero dynamics lie in the left half-plane, the system exhibits minimum phase behavior. Otherwise, the system exhibits nonminimum phase behavior with poor controllability. Relationships between the initiator volumetric flow rate and the reactor temperature are shown in Figure 1. The solid curve represents the nonminimum phase behavior region, and the dashed curve represents the minimum phase behavior region. The system exhibits nonminimum phase behavior in the low-temperature subregion and exhibits minimum phase behavior in high-temperature subregion. Real parts of all eigenvalues for zero dynamics at several operating points are also shown in Figure 1.

The phase behavior of the polymerization reactor may differ under different manipulated variables. If the monomer volumetric flow rate and the cooling water volumetric flow rate are chosen as the manipulated variables, at this situation, the zero dynamics of the polymerization reactor then has the following form

$$\frac{d\eta_1^{(0)}}{dt} = f_1(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) + \frac{(C_{\min} - \eta_1^{(0)})}{\eta_s^{(1)}} f_4(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) \tag{13}$$

$$\frac{d\eta_2^{(0)}}{dt} = f_2(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) + \frac{\eta_2^{(0)}}{\eta_s^{(1)}} f_4(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) \tag{14}$$

$$\frac{d\eta_3^{(0)}}{dt} = f_3(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) + \frac{(T_{\text{in}} - \eta_3^{(0)})}{\eta_s^{(1)}} f_4(\eta_1^{(0)}, \eta_2^{(0)}, \eta_3^{(0)}, \eta_s^{(1)}, \eta_s^{(2)}) \tag{15}$$

Figure 2 shows the relationship between reactor temperature and monomer volumetric flow rate. From Figure 2, it is not difficult to find that when monomer volumetric flow rate and cooling water volumetric flow rate are chosen as manipulated variables, the nonlinearity of the system becomes more complex, the system exhibits multiple steady states, and there are input multiplicities in certain regions. When $T \in (345,440)$ and $T_j \in (330,400)$, there exists two steady-state manipulated variables associated with a given output, which would place a limitation on the structure of the feedback controller because input multiplicity implies a change in the sign of the steady-state gain of a system. When the sign of a process gain changes, a process with a fixed conventional controller having integral action will result in a positive feedback loop and become unstable.[35] In addition, when $F \in (0,0.6)$, the system has unstable zero dynamics and the phase behavior changes with changes in monomer flow rate. Even under minor changes in *F*, the phase behavior may change from minimum phase to nonminimum phase. These characteristics pose inherent limitations on the control performance and, potentially, internal instability problems. Therefore, such characteristics should be identified and eliminated or avoided in the process design stage for guiding control structure selection and control system design to make the system easily controllable. Focusing on inherent safety, it is desirable to choose the initiator volumetric flow rate as the main manipulated variable, based on which, the next two subsections will discuss the effects of operation/design parameters and model uncertainty on phase behavior. Only one process design/operating parameter is changed at a time.

Effects of Operating Parameters on Phase Behavior. To analyze the phase behavior over the whole feasible operation regions, first, extended homotopy continuation is used to reveal the relationships between temperatures and initiator volumetric flow rate under different parameters. From Figures 3–6, the solid line represents the nonminimum phase behavior region, and the dashed line corresponds to the minimum phase behavior region. The symbol "·"means the singularity point of the zero dynamics. The symbol "○" represents the operating point.

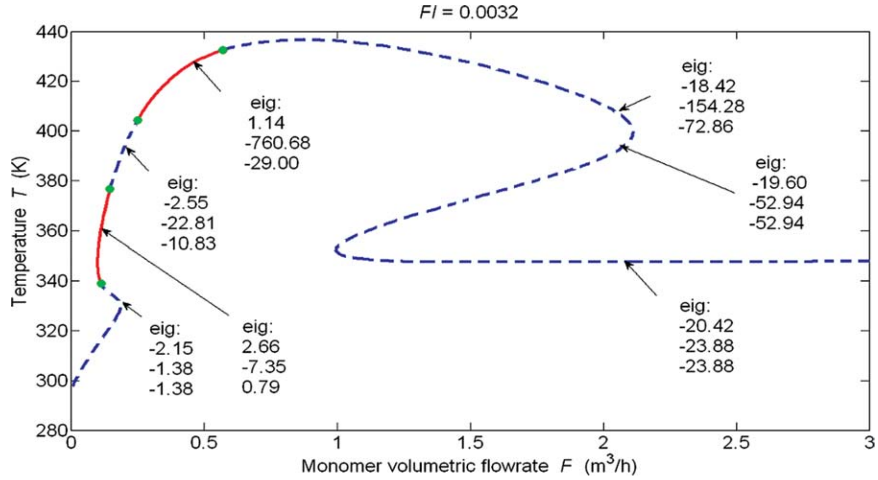

Figure 2. Relationship between the temperature *T* and monomer volumetric flow rate *F*.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figures 3 and 4 reveal relationships between temperatures T/T_j and initiator volumetric flow rate under different cooling water volumetric flow rate and monomer feed-stream volumetric flow, respectively. It can be seen that a larger nonminimum phase behavior region with stronger nonlinearities might be expected when increasing the cooling water flow rate and monomer feed-stream volumetric flow rate. The optimal nominal operating point is open-loop stable, with minimum phase behavior (shown as point A in Figure 3). If the reactor was to be operated at a higher cooling water volumetric flow rate (line 3), the reactor would be unstable (corresponding to $F_{cw} = 15$, $T \in (338,385)$), and the operating point (point B) would locate in the open-loop unstable region, which will impose difficulties on control system design. However, as shown in Figure 3, decreasing the cooling fluid flow rate will cause a rise in reactor temperature, leading to an increase in the rate of the reaction. If the reactor was to be operated at the higher monomer feed-stream volumetric flow rate (corresponding to $F = 3$ in Figure 4), the operating point (point C) would locate in the nonminimum phase region and would be located near the singularity point of the zero dynamics. Decreasing the monomer feed-stream volumetric flow rate removes the operating point from the nonminimum phase region and the region of multiplicities.

Initiator feed-stream concentration, C_{Iin}, acting as the adjustable operation parameter is shown in Figure 5. In this figure, it is not difficult to observe that the nominal operating point is practically located near the turning point of the phase behavior. In contrast to Figures 3 and 4, a decrease in the initiator feed-stream concentration would enlarge the nonminimum phase behavior region. Increasing this concentration would also lead to a rise in reactor temperature.

Figure 6 displays effects of initiator feed-stream temperature T_{in} on the phase behavior of the reactor. From Figure 6, it can be seen that the region of nonminimum phase

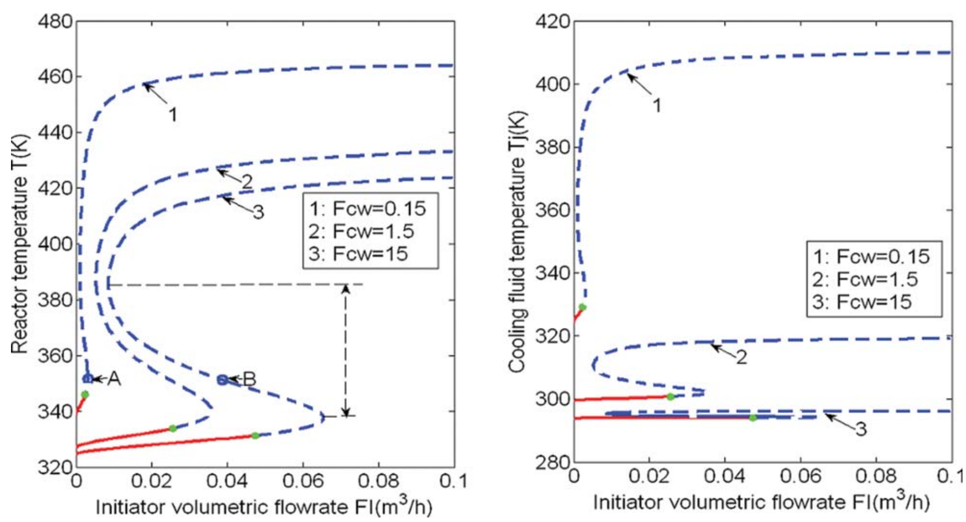

Figure 3. Relationship between the temperature and initiator volumetric flow rate.

Cooling fluid volumetric flow rate as adjustable parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

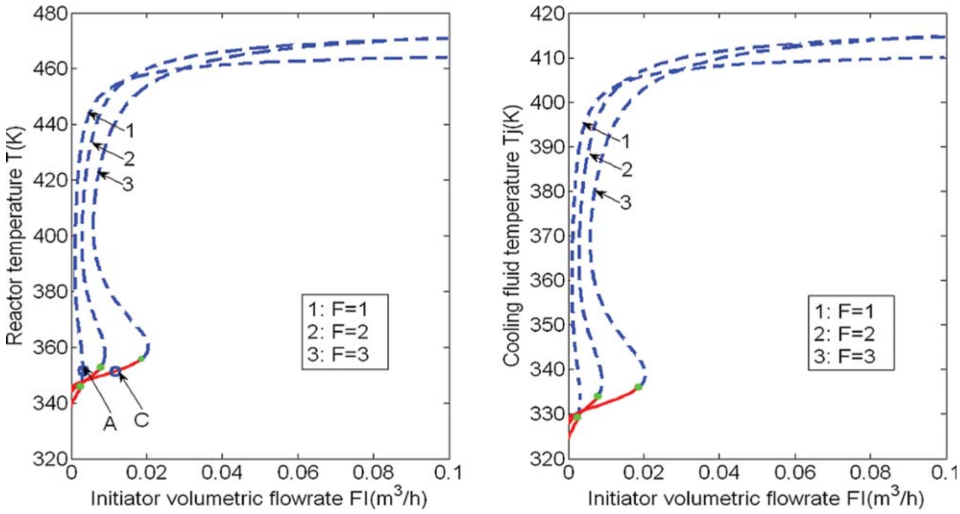

Figure 4. Relationship between temperatures and initiator volumetric flow rate.

Monomer feed-stream volumetric flow rate as adjustable parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

behavior would increase in size with decreasing initiator feed-stream temperature. Also, the nonlinearity would become more complex, if T_{in} was chosen as 330 K (line 3 in Figure 6). Under this operating condition, the reactor is unstable when $T \in (330,400)$, the operating point (point D) will locate far from the singularity point of the zero dynamics, but it would locate in the open-loop unstable steady-state region so that even a minor disturbance would affect the reactor temperature.

Figures 3–6 illustrate the effects of different operating parameters on the phase behavior of the polymerization reactor. Decreasing cooling fluid volumetric flow rate and monomer feed-stream volumetric flow rate would eliminate the nonminimum phase behavior region as well as increasing concentrations of the initiator. A decrease in feed-stream temperatures of initiator would lead to an enlarged nonminimum phase behavior region and more complex nonlinearity. Different types of operating parameters thus impose different influences on the phase behavior. From the control viewpoint, rejection of the adverse effects of disturbances on the dynamic performance of the system is one of the major challenges for closed-loop control systems. The investigation of disturbance effects on phase behavior may provide guidelines for assessing dynamic performance and control system design. Phase behavior and multiplicities are inherent characteristics determined by the process design itself. Sometimes, not only the process operating parameters but also the process design parameters impose effects on these inherent characteristics. It is, therefore, necessary to assess the influences of the design parameters on phase behavior early in design so that potential control problems associated with the inherent characteristics of the system can be eliminated or avoided.[28]

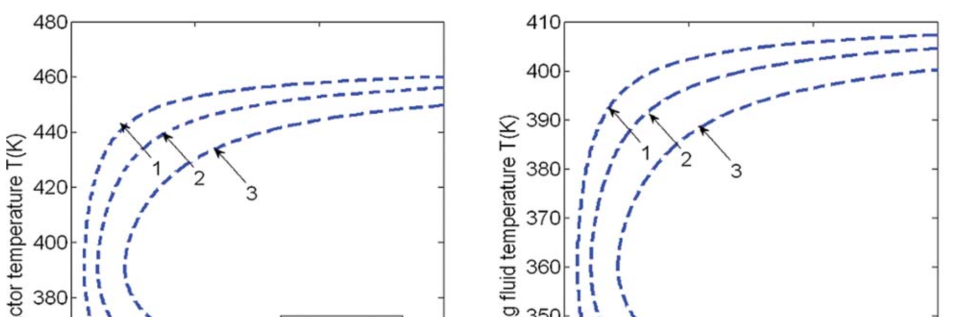

Figure 5. Relationship between temperatures and initiator volumetric flow rate.

Initiator feed-stream concentration as adjustable parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

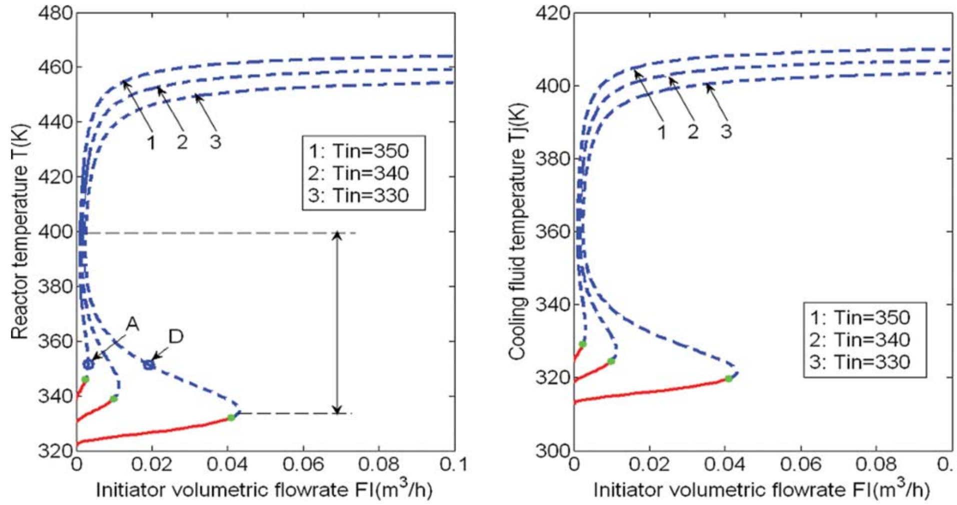

Figure 6. Relationship between temperatures and initiator volumetric flow rate.

Initiator feed-stream temperature as adjustable parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effects of Design Parameters and Model Uncertainty on Phase Behavior. Process design changes are one of the main routes for eliminating nonminimum phase behavior and multiplicities, which are perceived as a potential source of control problems. Assessing the effects of design parameters on phase behavior provides a valuable way to improve process control. In this section, heat-transfer area A and reactor volume V are chosen as adjustable design parameters, and their effects on phase behavior are discussed as follows. From Figures 7–9, the solid line represents the nonminimum phase behavior region, the dashed line corresponds to the minimum phase behavior region, the symbol "·" identifies the singularity point of the zero dynamics, and the symbol "○" represents the operating point.

Figure 7 shows the effects of different heat-transfer areas on the phase behavior. Decreasing the heat-transfer area would remove the nonminimum phase behavior and give rise to a higher reactor temperature, which would have an adverse effect on the quality of products and, furthermore, a larger parametric sensitivity region occurs. Increasing the heat-transfer area would accelerate the heat removal rate, causing a higher cooling fluid temperature. In this situation, a larger nonminimum phase behavior region and a lower reactor temperature occur simultaneously.

Figure 8 displays the effects of reactor volume on phase behavior. A larger reactor volume would relieve the nonminimum phase region and complexity of nonlinearity (line 1 in Figure 8). However, increasing the reactor volume would also increase the investment cost. If the system is operated under the assumption of $T \in (352,399)$ and $V = 0.04$ (line 3), the reactor is unstable and the operating point (point E) locates in the unstable operation region, where the system exhibits nonminimum phase behavior, proving the need for complexity in the control system design. Also, decreasing

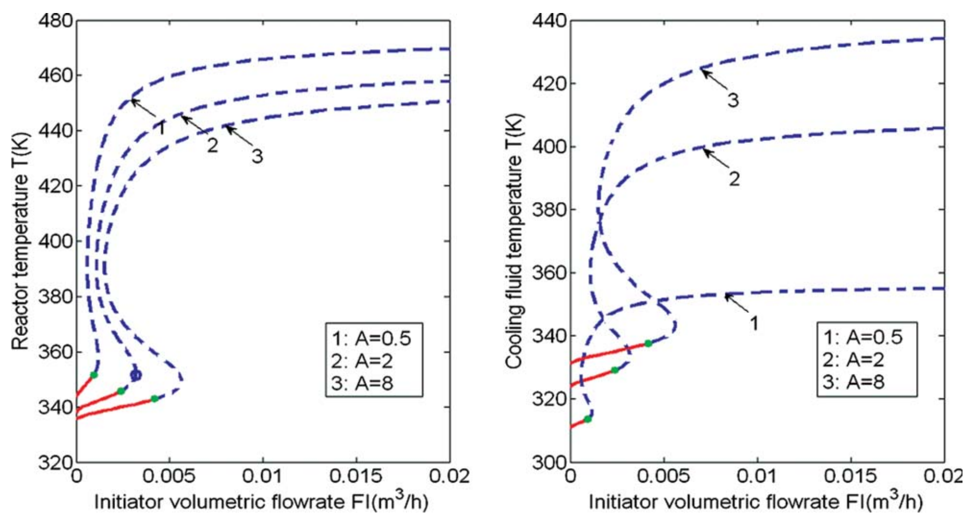

Figure 7. Relationship between temperatures and initiator volumetric flow rate.

Heat-transfer area as the adjustable process design parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

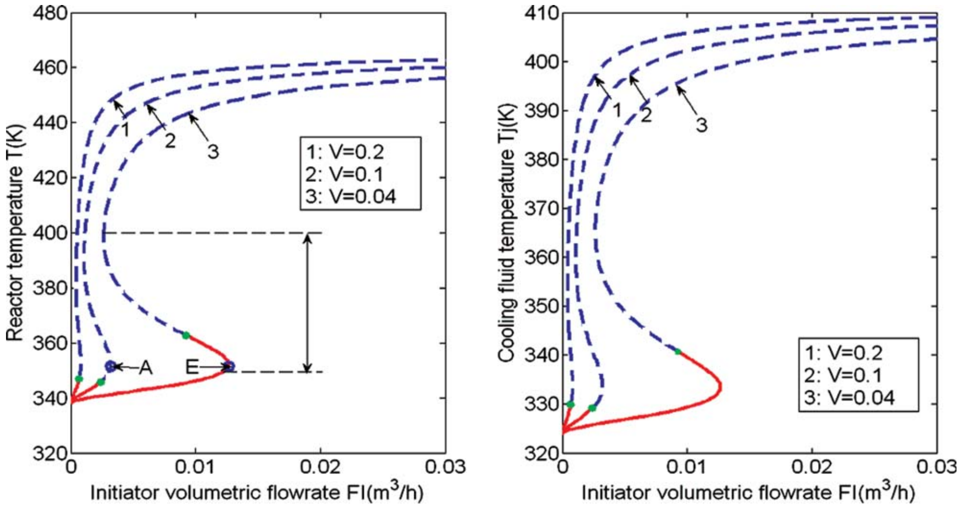

Figure 8. Relationship between temperatures and initiator volumetric flow rate.

Reactor volume as the adjustable process design parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the reactor volume would lead to more complex nonlinearity. Thus, during the process design, a tradeoff between operability and investment should be made.

As known, no mathematical model of the chemical process provides a perfect description of reality, so it is important and valuable to analyze the influences of model uncertainties on the phase behavior. Figure 9 reveals the influence of a 10 and a 25% increase of the propagation reaction activation energy E_p ($E_p = 1.8283e4$) on the phase behavior. The nonminimum phase behavior of the operating subregion becomes larger and larger with increasing in the propagation reaction activation energy E_p. On the other hand, increasing the propagation reaction activation energy will accelerate the reaction rate and enhance the complexity of nonlinearity (causing output multiplicities). According to the proposed methodology, how the other factors of model uncertainty affect the phase behavior could be analyzed easily.

Remarks

The phase behavior and multiplicities of the MMA polymerization reactor may change with changes in both process operating/design parameters, and it can also be affected by model uncertainty such as propagation reaction activation energy and heat-transfer coefficient. Changing parameters in a certain direction may have adverse effects on control performance. For example, increasing the heat removal rate or decreasing the reactor volume would give rise to a more complex nonlinearity and larger nonminimum phase behavior region. As shown in Figures 3 and 8, the operation points A and B and E correspond to the same reactor temperature ($T = 351.4$ K). Both points A and B have minimum phase behavior, but point B locates in the unstable region. Point E has nonminimum phase behavior and it also locates in the unstable region. In the case when the reactor temperature is kept constant, changing the cooling fluid flow rate in the

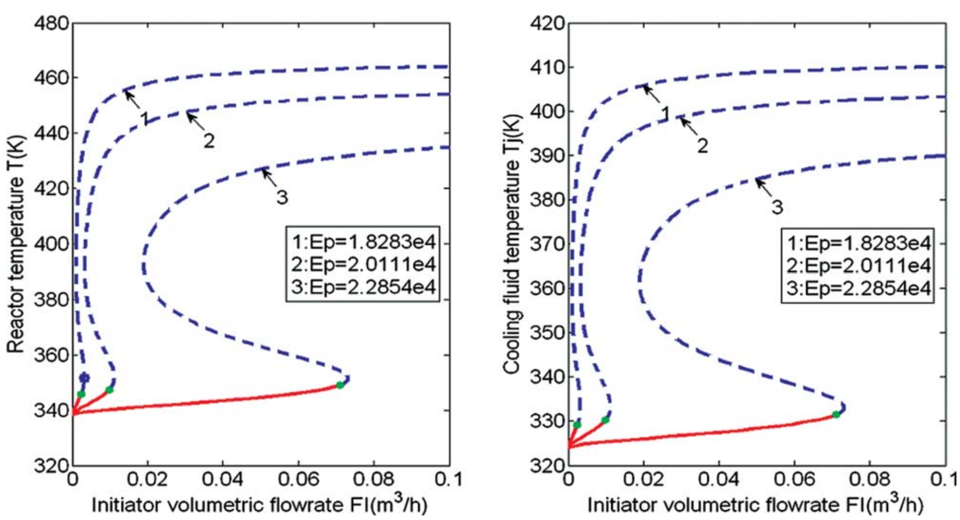

Figure 9. Effects of model uncertainty on the phase behavior of MMA polymerization reactor.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

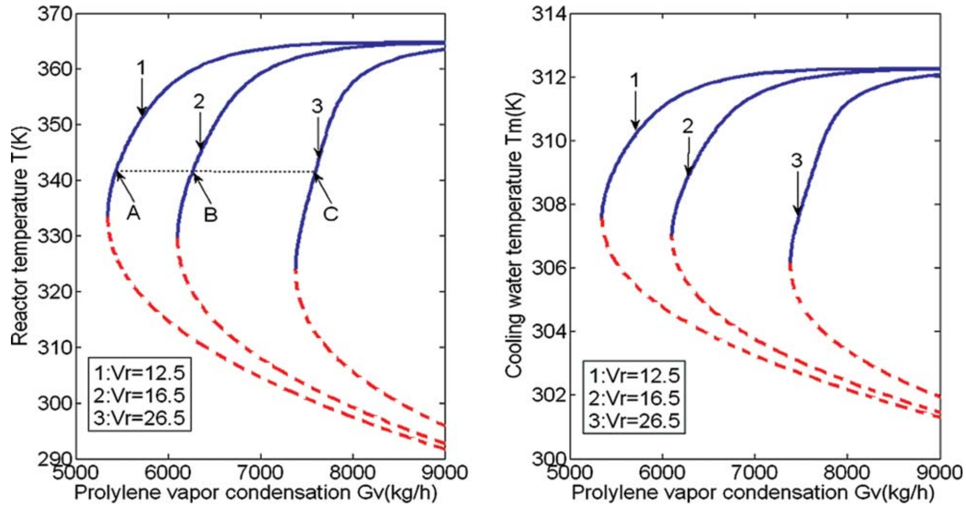

Figure 10. Relationship between temperatures and propylene vapor condensation flow rate.

Reactor volume as the adjustable process parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

positive direction may move the operation point to the unstable region, and a negative change in the reactor volume may lead to the operation point locating in the unstable nonminimum phase behavior region. On the other hand, if the manipulated variable is kept as $F_I = 0.0032$ under different cooling fluid volumetric flow rates (lines 2 and 3 in Figure 3), the reactor would exhibit nonminimum phase behavior. When the reactor is operated in the nonminimum phase behavior region, the inverse response may occur and this cannot be eliminated, irrespective of which control law is used. In particular, when the reactor is operated in the open-loop unstable region, where the system exhibits nonminimum phase behavior, the controllability is poor, so to keep the system running safety, an efficient controller is needed. Otherwise, an accident, such as runaway, may occur. Hence, assessing the influences of operating/design parameters and model uncertainty on the phase behavior may help one to identify which operating cases are easier to control and how to eliminate potentially unsafe operating factors to some extent by changing operating/design parameters or even model structure.

Phase Behavior Analysis for Polypropylene Reactor

Process description and modeling

Liquid-phase propylene polymerization is one of the most important industrial processes in polypropylene manufacture, representing about 35% of total polypropylene production.[36] The set of polymerization reactions takes place in a CSTR and the process is highly exothermic. Based on the reaction mechanism for propylene polymerization,[37] the assumptions to develop the mathematical model were (1) the contents of the reactor are perfectly mixed, (2) constant density and heat capacity of the reaction mixture, (3) the polymerization rate is equal to the propagation rate, and (4) constant reactor volume. When these assumptions are used, the mathematical model of the propylene polymerization reactor is given as shown in Ref. 37; also, its accuracy has been validated by experimental data from the petrochemical company.[38]

Phase behavior analysis

Manipulated Variables Selection. The cooling water volumetric flow rate G_w, monomer feed-stream volumetric flow rate G, propylene feed-stream volumetric flow rate G_p, hydrogen feed-stream volumetric flow rate G_h, and the volumetric flow rate of the vapor condensate of the propylene feed stream G_v, can be chosen as manipulated variables. To avoid frequent changes to the feed rate and to keep the process running smoothly, it is not desirable to select the monomer feed stream or propylene feed-stream volumetric flow rates as manipulated variables. Hydrogen is added to control molecular weight and has a minor effect on the reactor temperature. Luo[38] analyzed the effects of cooling water flow rate and vapor condensation flow rate on the reactor temperature in detail. Compared with the cooling water flow rate, vapor condensation flow rate has a greater impact on the reactor temperature, so it is desirable to select the vapor condensate flow rate as the manipulated variable for reactor temperature control.

Phase Behavior Analysis. Relationships between reactor temperature and the vapor condensation flow rate under different reactor volume V_r and cooling water feed-stream temperature T_{win} are shown in Figures 10 and 11, respectively. The influence of model uncertainty on the phase behavior is demonstrated in Figure 12.

As there are complex relationships between reactor temperature and the reactant and catalyst concentrations, the polypropylene reactor exhibits output multiplicities. In contrast to the MMA polymerization reactor, the system has only two steady states under certain operation conditions, because of the limit in the critical temperature T_{cr} of propylene ($T_{cr} = 365$ K) in the feasible operation region. In Figures 10–12, the solid curve represents the open-loop unstable steady-state region, and the dashed line corresponds to the open-loop stable steady-state region. According to the algorithms for zero dynamics, the system is known to contain five ordinary differential equations describing the zero dynamics. The Jacobian matrix of zero dynamics, therefore, has five eigenvalues. Over the whole feasible region, all five eigenvalues are located in the left half-plane, so the zero

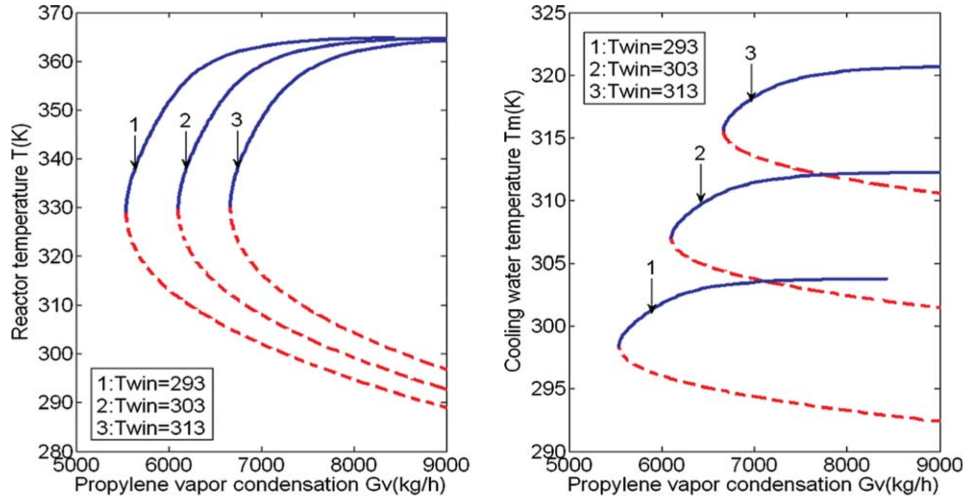

Figure 11. Relationship between temperatures and propylene vapor condensation flow rate.

Cooling water feed-stream temperature as the adjustable process parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dynamics is asymptotically stable and the system exhibits minimum phase behavior. The ways in which the reactor temperature and multiplicities change with varying process parameters will be analyzed to enable inherently safer design.

Figure 10 displays influence of the reactor volume on the reactor temperature, whereby it can be noted that the reactor temperature becomes more sensitive to the propylene vapor condensate flow rate when increasing the reactor volume. Also, the high-temperature region is open-loop unstable, which makes the closed-loop control problem more difficult. The required control action may be different because of different process gains, if the system is controlled under different reactor volumes (points A, B, and C). Figure 11 reveals how the nonlinearity changes with changes in the cooling water feed-stream temperature. The reactor is open-loop stable in the lower temperature region. We can observe that multiplicities cannot be removed by manipulating the cooling water feed-stream temperature.

Figure 12 shows effects of model uncertainties on the phase behavior and nonlinearity. Here, catalyst deactivation activation energy E_{ned} is selected as the factor of model uncertainty. As same as the above two situations, under three different values of E_{ned}, the zero dynamics is stable at all the steady states, so the original system exhibits minimum phase behavior over its whole feasible operating region. In addition, decreasing the catalyst deactivation activation energy E_{ned} would reduce the unstable region.

As can be seen from the above three figures, the propylene polymerization reactor is open-loop unstable in the higher temperature region but open-loop stable in the lower temperature region. Because of the high conversion desired, propylene polymerization reactors are usually operated in the open-loop unstable region. Although the system exhibits minimum phase behavior over the entire feasible operation region when the propylene vapor condensation flow rate is chosen as the manipulated variable, even slight variation flow rate would

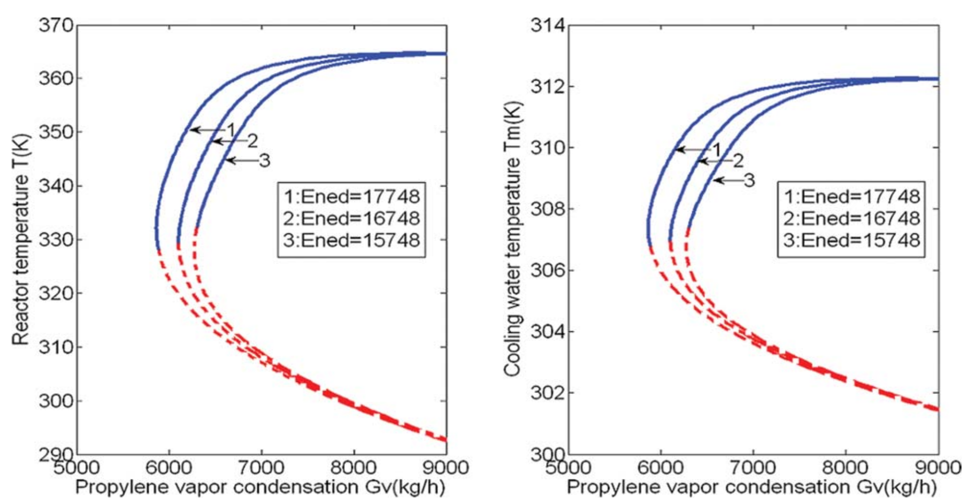

Figure 12. Effects of model uncertainty on the phase behavior of propylene polymerization reactor.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

give rise to extinction phenomena or make the system more prone to runaway to unacceptably high-temperature steady states. To make the system run safely and smoothly, efficient controller is necessary. Also, under the effects of process design/operation parameters and model uncertainty, the different sensitivities between the controlled and manipulated variables require different control actions. The results can provide important information for tuning of controller parameters.

Conclusions

Polymerization reactors usually exhibit nonminimum phase behavior and complex steady-state nonlinear multiplicities, which affect the process control performance. From a control point of view, the open-loop controllability analysis is both intellectually fascinating and of great practical importance at the early design stage.

In this article, a methodology for the preliminary analysis of the phase behavior over the whole feasible operating region of the nonlinear control affine systems was presented. The proposed method can be divided into four major steps. The first step involves calculating all the steady-state solutions using extended homotopy continuation. The second major step is to extract the expression of the zero dynamics. The third major step involves seeking the zero dynamics' singularity points, because the phase behavior may change when the original nonlinear system crosses the singularity points. The fourth and final major step deals with studying the stability characteristics of the zero dynamics at each side of the singularity points by applying Lyapunov's indirect method. Therefore, it is not necessary to detect instability/stability for zero dynamics point by point. When the zero dynamics is determined to be unstable, the original system will exhibit nonminimum phase behavior and is known to be affected by inverse response, which adversely affects the response speed of the closed-loop system to the parameter changes or disturbances. The proposed methodology was successful in identifying phase behavior and analyzing influences of process design/operating parameters and model uncertainties on the phase behavior for a MMA polymerization reactor and a polypropylene reactor.

The results obtained from the study of the phase behavior of the MMA polymerization reactor show that decreasing certain parameters (cooling water volumetric flow rate, monomer feed-stream volumetric flow rate, and heat-transfer area) to some extent dampens the nonlinearity and multiplicity behaviors and increasing certain parameters (initiator feed-stream concentration) would make the reactor more controllable. Also, a small change in some parameters (initiator feed-stream temperature and reactor volume) in a certain direction would lead to the operating point moving into the open-loop unstable region, where the system exhibits nonminimum phase behavior, causing control difficulties. In addition, the model uncertainties may have adverse effects on the phase behavior. It should be pointed out that the aforementioned results were coherent with industrial practice, rules and operators' experience. The results obtained from the study of propylene polymerization reactor exhibit minimum phase behavior over its entire feasible region, no matter how the operating conditions change. Also, in the high profitability of operating region, the reactor temperature is sensitive to the manipulated variable G_v, and it imposes difficulties on the control system design, even minor disturbance may lead to extinction phenomena or runaway. An efficient closed-loop control scheme is thus required. The aforementioned results were coherent with industrial practice, rules and operators' experience. The authors believe that identifying the presence of nonminimum phase behavior and how the operating/design parameters and model uncertainty affect the phase behavior over a large operating range, directly in the nonlinear setting, will lead to an improved plant and control system design, especially for highly exothermic process such as oxidation process. This study is desirable because it could identify the cause of the limitation so that to give an indication on where and how to modify the design. Also, the proposed methodology can be applied to the novel and complex chemical processes such as living free radicals polymerization processes and reactor-separator-recycle networks to detect their phase behavior.

In this article, phase behavior is chosen as the open-loop indicator of controllability. Many other methodologies have been developed for controllability analysis. There are two issues with chemical process controllability. First, some researchers consider that nonlinear behavior should not be moved or avoided, and controllability and nonlinear analysis is not necessary as many complex nonlinear behaviors can be efficiently dealt with and the system can be operated around optimal nonlinear operating regions by proper nonlinear control algorithms like the nonlinear model predictive control (NMPC) algorithm.[39] This may be true for controller design but is not satisfactory for analyzing the controllability of a chemical process. Second, some researchers highlight that it is important for analyzing the controllability of a system to identify and assess all potential operability problems associated with the complex behavior when the alternatives are considered during the design stage. Insisting in removing process nonlinearities to improve controllability and stability could take the operating point far away from optimal operating regions. Controllability and stability are two of the important characteristics of operability. However, profitability remains the key objective for shareholders and management in selecting design alternatives and making decision on removing process nonlinearities for improving controllability. Tradeoffs between the aforementioned objectives have been the focus of designs. This multiobjective optimization of design considering controllability, profitability, and stability simultaneously would be a very interesting future development.[19]

As discussed above, phase behavior analysis gives an open-loop indicator of controllability and provides a rough guideline for controller design at the design stage. In chemical process control, good tracking of set points is mostly of interest for lower level control tasks. Almost all of the literatures on automatic control and controller design are concerned with the task to make certain controlled variables nicely tracking given set points or dynamic set-point trajectories. From a process engineering point of view, however, a control structure that yields nice transient responses and tight control of the selected variables sometimes might be useless or even counterproductive if keeping these variables at their set points does not improve the economic performance of the process. Therefore, process control should be seen as a way to optimize plant operations rather than to just disturbance rejection and set-point tracking.[40] It is desirable to include optimality issues as well as constraints on controllability and stability when approaching the design of control systems as recent progress in numerical optimization algorithms as well as in NMPC theory.

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