

# The bifurcation behavior of a polyurethane continuous stirred tank reactor

Víctor Zavala-Tejeda<sup>a</sup>, Antonio Flores-Tlacuahuac<sup>b,\*</sup>,<sup>1</sup>, Eduardo Vivaldo-Lima<sup>c,2</sup>

<sup>a</sup>Departamento de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880, México DF, 01210, México

<sup>b</sup>Department of Chemical Engineering, Carnegie-Mellon University, 5000 Forbes Av., Pittsburgh 15213, PA, USA

<sup>c</sup>Department of Chemical Engineering, Institute for Polymer Research (IPR), University of Waterloo, Waterloo, Ont., Canada N2L 3G1

Received 12 May 2005; received in revised form 8 August 2006; accepted 13 August 2006

Available online 30 August 2006

## Abstract

In this work the open-loop nonlinear bifurcation analysis of a continuous stirred tank reactor where polyurethane polymerization reactions take place is carried out. The effect of potential manipulated, disturbance and design variables on the reactor nonlinear behavior is addressed. Moreover, the impact of cascade feedback control on the steady-state multiplicity pattern is also discussed. It is shown that cascade control introduces new nonlinearity patterns increasing closed-loop sensitivity.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Polyurethane; Nonlinear behaviour; Polymerization reactor; Bifurcation; Control

## 1. Introduction

It has been recognized that nonlinear behavior (i.e., input/output multiplicities, hysteresis, limit cycles, etc.) exhibited by chemical processes might have an important role on their operation and performance (Seider et al., 1990). Owing to complex embedded nonlinearities and system size, most of nonlinear analysis problems do not have analytical solutions. Therefore, before the advent of numerical bifurcation methods, system simulation was used for finding nonlinear behavior. However, the information that simulation provides is rather limited. Moreover, simulation strategies may impose strong time and computational demands. Bifurcation and continuation methods provide an effective way to analyze global nonlinear behavior. Continuation methods are employed to address the nonlinear behavior response of a given system in presence of parameters variation (Ray and Villa, 2000). Bifurcation theory and continuation methods permit the numerical detection of

input multiplicities, output multiplicities, isolas, limit cycles (Hopf Bifurcations), etc. It does so by appending the model equations with the theoretical conditions that enable the computation of singularities (Dhooge et al., 2003). One of the uses of bifurcation results is in assessing ways of removing nonlinearities. Commonly, the presence of nonlinearities might lead to severe operation and closed-loop control problems, particularly when the process features open-loop instabilities or when it exhibits nonlinear oscillations.

In particular, continuous stirred tank reactors (CSTRs) have long been the subject of intensive research (Aris and Amundson, 1958) and they continue to attract the attention of researchers (Antoneli and Astolfi, 2003). CSTRs present challenging operational problems owing to complex open-loop behavior such as input/output multiplicities, ignition/extinction phenomena, parametric sensitivity, nonlinear oscillations and even chaos. These characteristics demonstrate the need for and difficulty of control systems design. However, it is often desirable to operate CSTRs around nonlinear regions. In particular, operation under open-loop unstable conditions might be required. There the reaction rate may yield good productivity, while the reactor temperature is still low enough to prevent side reactions, or a rapid molecular weight and viscosity increase leading to the gel effect onset (in the case of polymerization reactors).

The advances and challenges that emerged from studies on the nonlinear behavior of simple chemical reaction systems

\* Corresponding author. Tel.: +52 55 5950 4074; fax: +52 55 5950 4279.

E-mail addresses: antonio.flores@uia.mx, aflores2@andrew.cmu.edu

(A. Flores-Tlacuahuac).

URL: <http://200.13.98.241/~antonio>.

<sup>1</sup> On leave from Universidad Iberoamericana.

<sup>2</sup> On research leave from Universidad Nacional Autónoma de México (UNAM), Facultad de Química, Departamento de Ingeniería Química, Conjunto E, Ciudad Universitaria, CP 04510, México D.F., México.

(Aris and Amundson, 1958; Uppal et al., 1974) naturally motivated further studies on systems featuring more complex behavior. Polymerization reactions fall in this category of complex behavior systems. There, reaction mechanisms tend to be composed of several competing reactions. Moreover, mass and energy balances are strongly coupled through Arrhenius kinetic rate temperature dependence. In addition, the onset of the gel effect has been related to the emergence of highly complex nonlinear and oscillatory behavior. A recent review on the nonlinear dynamics of polymerization reactors can be found elsewhere (Ray and Villa, 2000). The polymer industry represents an important segment of the chemical processing industry with around 100 million tons/year produced worldwide (Ray and Villa, 2000). The growth of the European polymer market is reported in the range from 1% to 8% depending on the type of polymer (Moen, 2004).

In this work, the steady-state nonlinear bifurcation analysis of a CSTR for the production of a nonlinear polyurethane is performed. Polyurethanes have been in the market for over 60 years. Their uses and applications are quite diverse. Created initially to rival polyamide (nylon) fibers, they are now important in fields such as flexible and rigid foams, elastomers, coatings, and adhesives, as well as in medical applications. In the open literature there are several works on the modelling of step-growth (including polyurethane production) and chain-growth polymerization. Those models usually work well for linear polymers, but their direct application to the production of nonlinear polymers is at most an approximation to the actual behavior of these systems. The more rigorous models for nonlinear polymerization (see, for instance, Kuchanov et al., 2004, for a very complete and updated review on the quantitative theory of step-growth polymerization) require using procedures and methods which make them unattractive for control, optimization or other computationally demanding studies. There are few recent works on the modelling of polyurethane production, taking into account crosslinking reactions in a simple, yet theoretically sound way, which can enhance the predictive power of the models.

Several polymerization processes and reactor types, both for batch and continuous production, have been proposed for step-growth polymerization. The batch reactor is the most versatile reactor type and is used extensively for specialty polymers at low production volumes. Examples of step-growth polymers produced in batch reactors include nylon 6, phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde (Hamielec and Tobita, 1992). On the other hand, newer high-capacity plants often use continuous processes. The first approximation to a continuous process is a model that consists of plug flow reactors (PFR) and CSTRs, in various combinations (Hamielec and Tobita, 1992). Some step-growth polymers produced in CSTRs include nylon, polyesters, epoxy polymers, and formaldehyde polymers (Gupta and Kumar, 1987).

Polyurethanes can be produced by the one-shot process (mixing all the components directly, including auxiliaries or additives), prepolymer processes (for instance, NCO prepolymers), reactive one-pack systems (storage-stable, ready-to-use formu-

lation of a polymer precursor that may contain several components), or other processes (e.g., polycondensation methods) (Dietrich and Uhlig, 1992). The formation of urethane polymers is usually fast enough without the use of catalysts, but important applications like reaction injection molding (RIM) require very fast reactions, for which catalysts must be used (Gupta and Kumar, 1987; Macosko, 1989). The liquid monomers (diisocyanates and macroglycols) used in polyurethane formation are suitable for bulk polymerization processes. The reaction can be conducted in a mold (casting, reaction injection molding), continuously on a conveyor (block and panel foam production), or in an extruder (thermoplastic polyurethane elastomers and engineering thermoplastics) (Ulrich, 1997).

The early technologies for polyurethane production included solution (in organic solvents) polymerization processes in stirred tank reactors, and the reaction times could be in the order of hours, if relatively low temperatures and no added catalysts were used. The more recent technologies, like RIM (Gupta and Kumar, 1987; Macosko, 1989), which take advantage of the high reaction rates (in the order of minutes, or less than a minute) favored by the use of catalysts (Draye and Tondeur, 1999; Schwetlick et al., 1994), and the possibility of combining reaction and processing at the same time, explain in part why CSTRs are not of much use and interest to the modern polyurethane industries. Although most chemical companies worldwide have replaced or abandoned technologies intensive in the use of organic solvents, due to environmental and health concerns, some small polymer producing companies in less developed or less environmentally regulated countries still use old solvent-based technologies, like the first solution polymerization processes for polyurethane production. For those companies, the study of CSTR-based processes, and optimization studies can be helpful. On the other hand, some continuous processes, such as reactive extrusion (used to produce polyurethanes elastomers and engineering thermoplastics (Ulrich, 1997)), can be modelled using series of CSTRs. Therefore, the analysis of polyurethane production in CSTRs using organic solvents, is a topic of interest.

The aim of this work is to provide a first look into the operability problems faced by polyurethane reactors. A highly complex reaction system (i.e., cross-linking reactions), studied by Vivaldo-Lima et al. (2002) is addressed in this paper. The steady-state operability problems are addressed by using nonlinear bifurcation techniques. In this initial work about polyurethane polymerization reaction systems only codimension one bifurcations were searched for (Kusnetzov, 1998). Thereby, only the presence of limit points and Hopf bifurcation points singularities was examined. There are not published reports, to the authors' knowledge, on the nonlinear analysis of polyurethane reactors. Even when industrial polyurethane processes involve several kinds of reaction systems, only a single CSTR was selected to perform the bifurcation analysis, in order to keep things as simple as possible. All of the nonlinear bifurcation diagrams were generated using the *Matcont* continuation software (Dhooge et al., 2003).

The outline of this paper is as follows. Section 2 contains the description of the model and parameter values. In Section 3

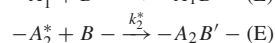
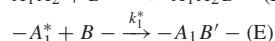
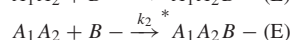
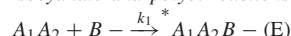
the effect of potential manipulated variables on the reactor non-linear behavior is analyzed. In Sections 4 and 5 the impact of disturbance and design variables on the steady-state non-linear behavior is addressed, respectively. In Section 6 the effect of cascade feedback control on the onset of nonlinearities is analyzed. Finally, Section 7 contain the conclusions of this work.

## 2. Mathematical model

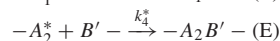
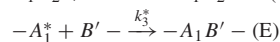
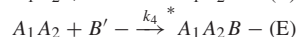
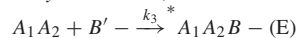
In this part the mathematical model of a nonlinear step-growth copolymerization of a mixture of low- and high-molecular weight diols, and a low-molecular-weight diisocyanate using a kinetic model is described (Vivaldo-Lima et al., 2002). The set of polymerization reactions is carried out in

Table 1  
Polyurethane kinetic mechanism

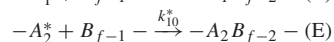
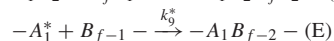
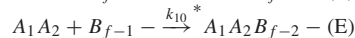
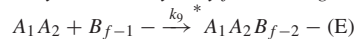
### Isocyanate and polyol reactions



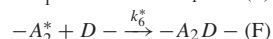
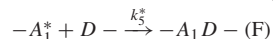
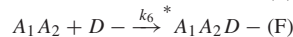
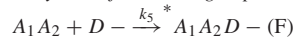
### Isocyanate and 1,4 butanediol reactions



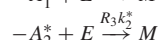
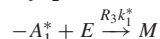
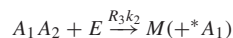
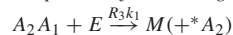
### Isocyanate and hydroxylfunctional groups reactions



### Isocyanate functional groups and amine functional groups



### Allophanate functional groups production



### Isocyanate and urea functional groups reactions

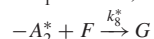
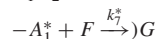
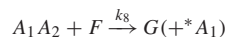
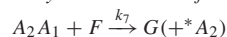


Table 2  
Reactor design and operation parameters

Reactor volume	10000 L
Jacket volume	300 L
Reactor residence time	120 min
Jacket residence time	5 min
Total volumetric flow rate	400 L/min
Diisocyanate feedstream conc.	3.04 mol/L
Polyol feedstream conc.	0.6 mol/L
1,4 Butanediol feedstream conc.	2.4 mol/L
Feedstream temperature	303 K
Cooling water temperature	293 K
Heat-transfer area	27.2 m <sup>2</sup>
Heat of reaction	-22.1 Kcal/mol
Global heat-transfer coefficient	1.15 Kcal/(m <sup>2</sup> min K)
Feedstream density	1.22 Kg/L
Feedstream heat capacity	0.1 Kcal/(Kg K)
Cooling water density	1 Kg/L
Cooling water heat capacity	1 Kcal/(Kg K)

Table 3  
Reaction rate constants (L/(mol - min)), T(K)

$R_3 = 0.00263$
$k_1 = 5.1 \times 10^3 e^{-4900/T}$
$k_3 = 1.43523 \times 10^7 e^{-6475/T}$
$k_1^* = 1.205810^8 e^{-8135/T}$
$k_3^* = 1.486 e^{-1500/T}$
$k_2 = k_1$
$k_4 = k_3$
$k_5 = 2k_3$
$k_6 = k_5$
$k_7 = R_3k_1$
$k_8 = k_7$
$k_2^* = k_1^*$
$k_4^* = k_3^*$
$k_5^* = 2k_3^*$
$k_6^* = k_5^*$
$k_7^* = R_3k_1^*$
$k_8^* = k_7^*$
$k_9 = 0$
$k_{10} = 0$
$k_9^* = 0$
$k_{10}^* = 0$

a nonisothermal CSTR assuming perfect mixing and constant physical properties. Since there is no condensate being produced in polyurethane production and no blowing agents (like water) are being considered, constant volume in the reactor has also been assumed.

Changes on the density of the monomer-polymer mixture have been neglected. The kinetic model allows for the calculation of the concentrations of all species. Different reactivities for isocyanate functional groups located in different positions of the monomer and polymer molecules, as well as the hydroxyl functional groups of different molecules are allowed. Number average molecular weight is calculated from its definition, as the ratio of moles of molecules at initial reference conditions to moles of molecules at a given time. The model

Table 4  
Polyurethane CSTR mathematical model

$$\frac{d[A_1]}{dt} = \frac{Q}{V}(A_{1o} - A_1) - k_1[A_1](B + R_3E) - k_3[A_1][B'] - k_9[A_1][B_f] - k_5[A_1][D] - k_7[A_1][F]$$

$$\frac{d[A_2]}{dt} = \frac{Q}{V}(A_{2o} - A_2) - k_2[A_2](B + R_3E) - k_4[A_2][B'] - k_{10}[A_2][B_f] - k_6[A_2][D] - k_8[A_2][F]$$

$$\begin{aligned} \frac{d[A_1^*]}{dt} = & \frac{Q}{V}(A_{1o}^* - A_1^*) + k_2[A_2][B] \\ & + k_4[A_2][B'] + k_6[A_2][D] + R_3k_2[A_2][E] \\ & + k_8[A_2][F] + k_{10}[A_2][B_f] \\ & - k_1^*[A_1^*][B] - R_3k_1^*[A_1^*][E] - k_3^*[A_1^*][B'] \\ & - k_5^*[A_1^*][D] - k_7^*[A_1^*][F] - k_9[A_1^*][B_f] \end{aligned}$$

$$\begin{aligned} \frac{d[A_2^*]}{dt} = & \frac{Q}{V}(A_{2o}^* - A_2^*) + k_1[A_1][B] + k_3[A_1][B'] \\ & + k_5[A_1][D] + R_3k_1[A_1][E] + k_7[A_1][F] \\ & + k_7[A_1][B_f] - k_2^*[A_2^*][B] - R_3k_2^*[A_2^*][E] \\ & - k_4^*[A_2^*][B'] - k_6^*[A_2^*][D] - k_8^*[A_2^*][F] - k_{10}[A_2^*][B_f] \end{aligned}$$

$$\begin{aligned} \frac{d[B]}{dt} = & \frac{Q}{V}(B_o - B) - (k_1[A_1] + k_2[A_2])[B] \\ & - k_1^*[A_1^*][B] - k_2^*[A_2^*][B] \end{aligned}$$

$$\begin{aligned} \frac{d[B']}{dt} = & \frac{Q}{V}(B'_o - B') - (k_3[A_1] + k_4[A_2])[B'] \\ & - k_3^*[A_1^*][B'] - k_4^*[A_2^*][B'] \end{aligned}$$

$$\frac{d[B_f]}{dt} = \frac{Q}{V}(B_{fo} - B_f) - (k_9[A_1] + k_{10}[A_2])[B_f] - k_9^*[A_1^*][B_f] - k_{10}^*[A_2^*][B_f]$$

$$\frac{d[D]}{dt} = \frac{Q}{V}(D_o - D) - (k_5[A_1] + k_6[A_2])[D] - k_5^*[A_1^*][D] - k_6^*[A_2^*][D]$$

$$\begin{aligned} \frac{d[E]}{dt} = & \frac{Q}{V}(E_o - E) + (k_1[A_1] + k_2[A_2])[B] + k_1^*[A_1^*][B] + k_2^*[A_2^*][B] \\ & + (k_3[A_1] + k_4[A_2])[B'] + k_3^*[A_1^*][B'] \\ & + k_4^*[A_2^*][B'] - R_3[E](k_1[A_1] + k_2[A_2]) + k_1^*[A_1^*] + k_2^*[A_2^*] \end{aligned}$$

$$\begin{aligned} \frac{d[F]}{dt} = & \frac{Q}{V}(F_o - F) + (k_5[A_1] + k_6[A_2])[D] + k_5^*[A_1^*][D] \\ & + k_6^*[A_2^*][D] - [F](k_7[A_1] + k_8[A_2]) + k_7^*[A_1^*] + k_8^*[A_2^*] \end{aligned}$$

$$\frac{d[M]}{dt} = \frac{Q}{V}(M_o - M) - R_3[E](k_1[A_1] + k_2[A_2]) + k_1^*[A_1^*] + k_2^*[A_2^*]$$

$$\frac{d[G]}{dt} = \frac{Q}{V}(G_o - G) - [F](k_7[A_1] + k_8[A_2]) + k_7^*[A_1^*] + k_8^*[A_2^*]$$

$$\frac{dT}{dt} = \frac{Q}{V}(T_o - T) + \frac{\Delta H_r Grr}{\rho_m C p_m} - \frac{UA(T - T_j)}{\rho_m C p_m V}$$

$$\frac{dT_j}{dt} = \frac{Q}{V}(T_{jo} - T_j) + \frac{UA(T - T_j)}{\rho_w C p_w V_j}$$

developed by Vivaldo-Lima et al. (2002) used the Macosko-Miller recursive probabilistic approach to calculate the weight average molecular weight, and the gelation point. That model is strictly valid for batch and plug flow reactors. In the case of CSTRs for AB step growth polymerization, the polydispersity index increases more rapidly than in a batch reactor (Dotson et al., 1996). Therefore, the gelation point might occur sooner in a CSTR. That is why calculation of weight average molecular weight and the gelation point were not carried out in this paper, except in one case, for illustrative purposes. The possibility of getting the gelation point sooner than the values obtained in the calculations carried out by Vivaldo-Lima et al. (2002) for nonlinear polyurethane batch reactors should be kept in mind, in the analysis of the following sections of this paper. That means that safe operation of the CSTR should be carried out at even lower conversion levels than the ones observed in the subsequent sections of this paper.

Although calculation of the weight average molecular weight was suppressed, allophanate and biuret ramification reactions, are still considered by the model. The model was validated experimentally by Vivaldo-Lima et al. (2002) for the batch reaction of 4, 4'-diphenylmethane diisocyanate (MDI) with a mixture of a polyester and 1,4-butanediol. The kinetic mechanism is summarized in Table 1. Design and operation parameters are shown in Table 2. Reaction rate constants are shown in Table 3, while Table 4 contains the mathematical model involving material balances for all species as well as energy balances for both reactor contents and cooling jacket.

The estimate of allophanate formation ( $k_7$  in Table 3) was obtained by Vivaldo-Lima et al. (2002), using experimental data in the range of 30 to 90 °C. Since the calculations may reach temperatures as high as 200 °C, the amount of allophanate formation could be underestimated. A more precise estimate of  $k_7$  could be obtained using experimental data in a higher temperature range, such as the experimental data reported by Heintz et al. (2003).

### 3. Effect of manipulated variables

In an industrial environment polymerization reactors are normally equipped with a control device whose design and complexity relies on the control objectives. Part of the control system design task refers to the selection of the controlled and manipulated variables and the way they are paired. Nonlinear analysis tools may have an important role in assessing the impact of manipulated variables on the controlled variables and helping to prevent process operation around high parametric sensitivity regions. Therefore, in this part of the work the problem of examining such nonlinear input/output behavior, with the aim of learning how to approach both pairing and operability issues, is addressed.

Figs. 1–5 display the effect of potential manipulated variables on key product relevant output variables: Diisocyanate and 1-4-butanediol conversions, number average molecular weight ( $M_n$ ) and reactor temperature. Weight average molecular weight,  $M_w$ , is a very important output variable, since it provides a criterion, when the value diverges, of the gelation point onset. However,

as explained before, the calculation procedure for  $M_w$  used by Vivaldo-Lima et al. (2002) for nonlinear batch polyurethane reactors, based on the recursive probabilistic Macosko-Miller approach, is not adequate for CSTRs. Therefore, all the information related to molecular weight development in this paper is analyzed through the number average molecular weight,  $M_n$ . Calculations of  $M_w$  will be presented in some specific cases, in Fig. 6, with illustrative purposes only. In a multi-loop control system structure, cooling water flowrate would be employed for reactor temperature control either as simple feedback or in a cascade control structure. On other hand, monomer flowrate may be used for monomer conversion control and the initiator flowrate for (MWD) regulation. It should be noticed that, in a true multivariable control environment, the use of figures such as Figs. 1–5 would be difficult to assess, due to the fact that the control system drives all the manipulated variables in presence of control error and such behavior is graphically difficult to represent.

It is shown in Fig. 1 that, under nominal operating conditions (denoted by the “o” symbol), the polyurethane CSTR model features output multiplicity behavior. There are three multiple steady-state branches giving rise to low, medium and high monomer conversion regions (open loop stable points are denoted by the continuous line, while open-loop unstable steady-states are denoted by the dashed line). In order to avoid high viscosities due to gelation, the single CSTR is commonly operated around the medium conversion region. Moreover, high monomer conversion demands the use of a sequence of reactors (either CSTR or tubular). There is also a risk of reaching the gelation point at upper intermediate and high conversions, a situation that might be undesired. Under nominal operating conditions, the steady state is open-loop unstable, a situation that should not impose serious demands on the control system, since a major goal of control system design is to regulate open-loop unstable plants. However, there are some researches (Kokossis and Floudas, 1994; Blanco et al.), that claim that process design should completely avoid open-loop unstable operating points. It can be realized from Fig. 1 that, regardless of the cooling water flowrate, there is no way to avoid operating around the steady-state multiplicity region. From a practical point of view, the medium and high conversion branches can be considered disconnected, since probably they joint but at large unfeasible cooling water flowrates. Interestingly, Hopf bifurcation points (denoted by the “•” symbol) only emerge at the high temperature region. This observation has an important operational significance, since it means that around the nominal operating region undesired oscillatory behavior will not appear. Moreover, for a given SIR value, the four reactor output variables are almost constant, except close to the turning point. Although operation around the high temperature region should probably be avoided, it is interesting to note that both high temperature Hopf points lead to stable oscillatory behavior as shown in Fig. 2. Commonly, operation around oscillation regions has been avoided because of production and safety reasons. However, in polymerization reaction engineering there has been some interest in taking advantage of periodic reactor operation through input forcing (Spitz et al., 1977). However,



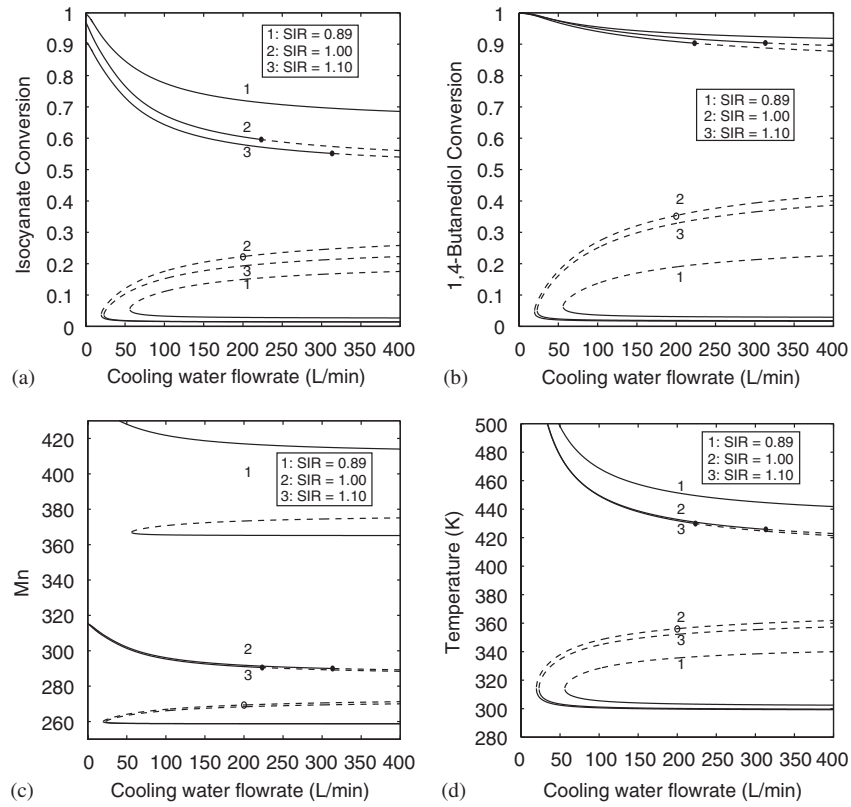


Fig. 1. Continuation diagrams using the cooling water flowrate and SIR as continuation parameters.

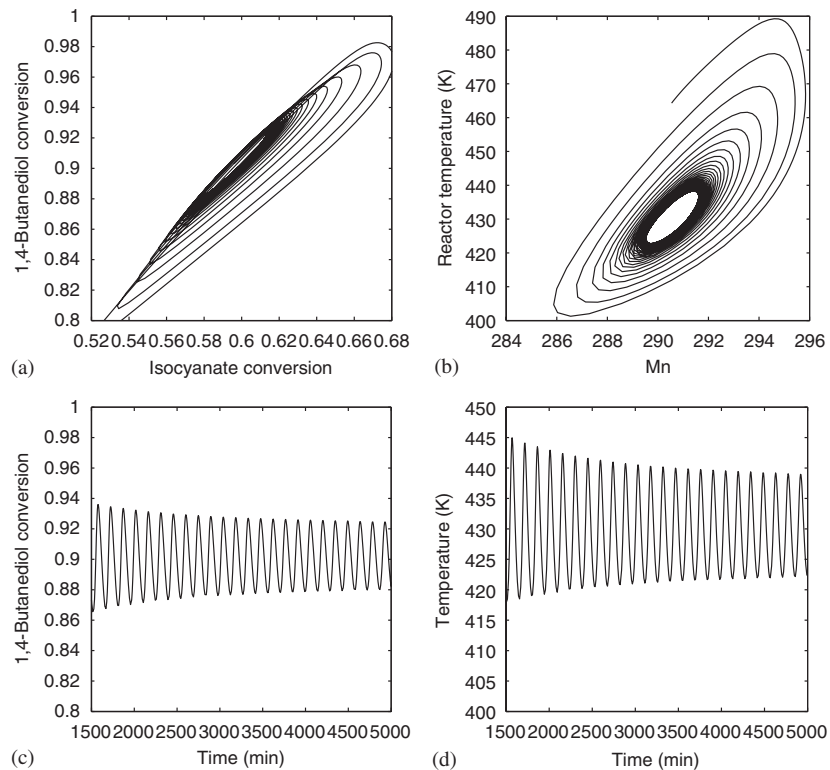


Fig. 2. Oscillatory behavior around the high temperature region.

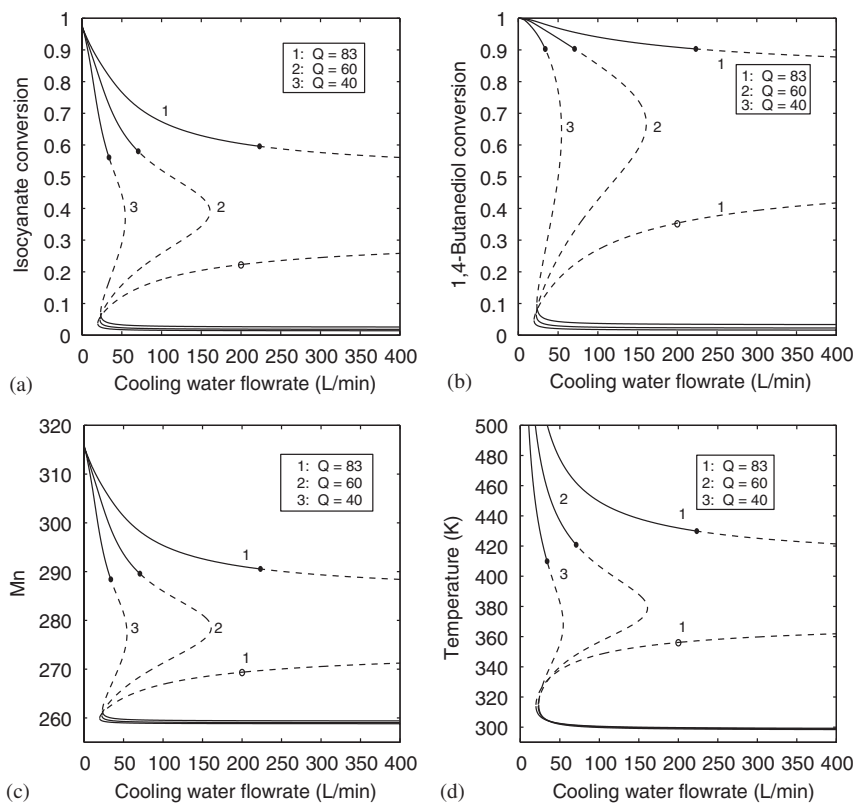


Fig. 3. Continuation diagrams using the cooling water flowrate and feedstream volumetric flowrate as continuation parameters.

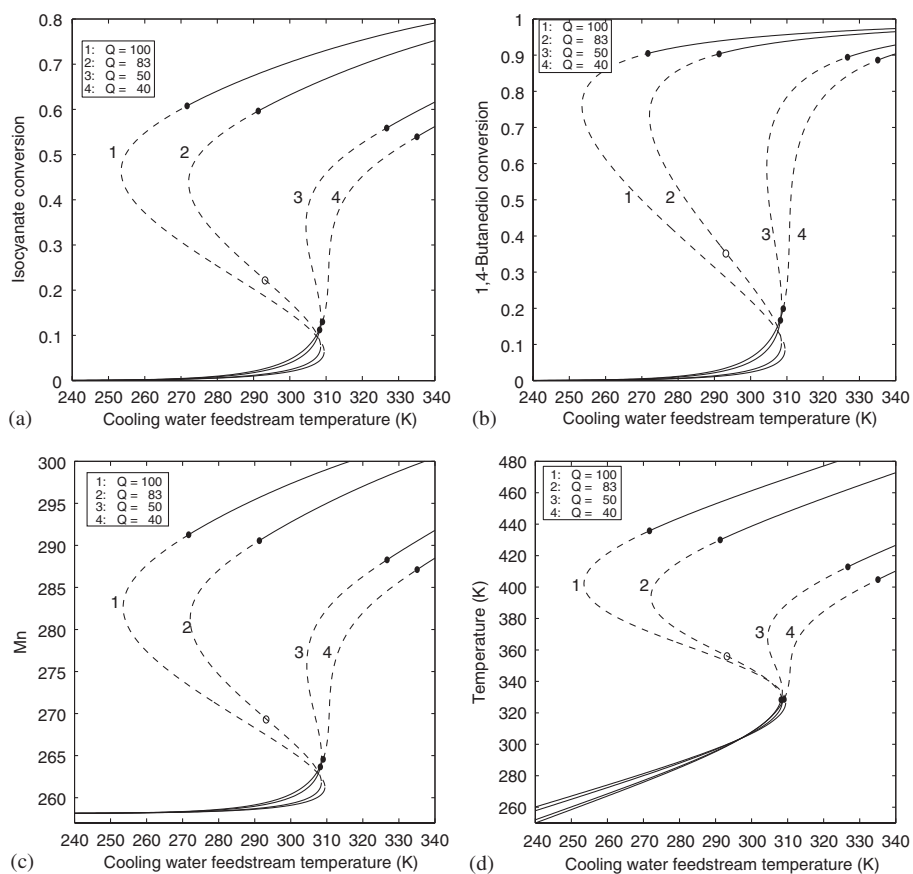


Fig. 4. Continuation diagrams using the cooling water feedstream temperature and feedstream volumetric flowrate as continuation parameters.

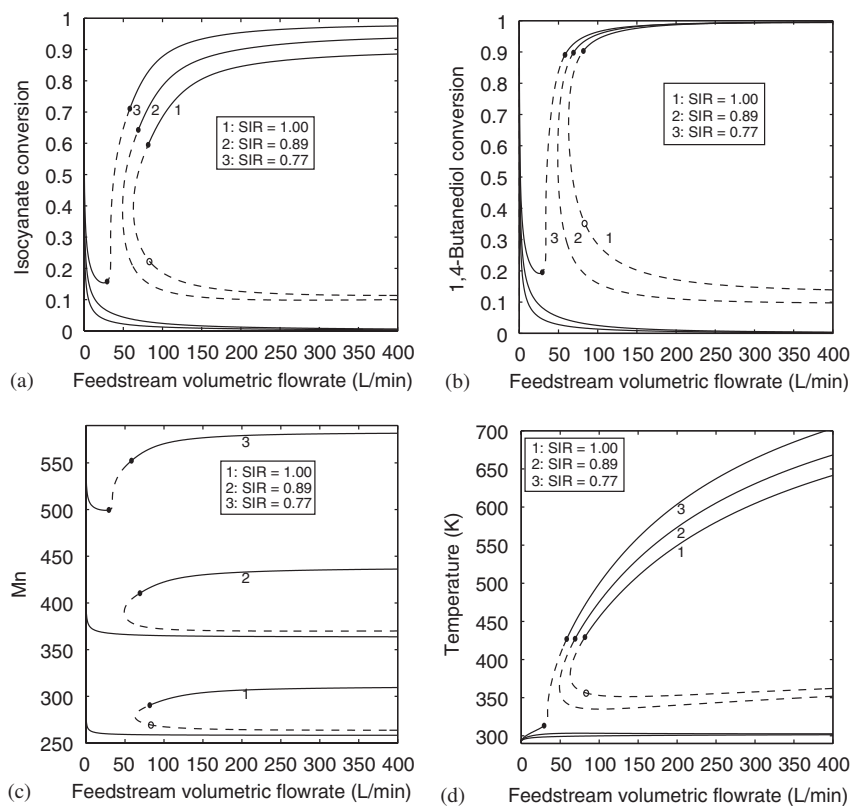


Fig. 5. Continuation diagrams using the feedstream volumetric flowrate and SIR as continuation parameters.

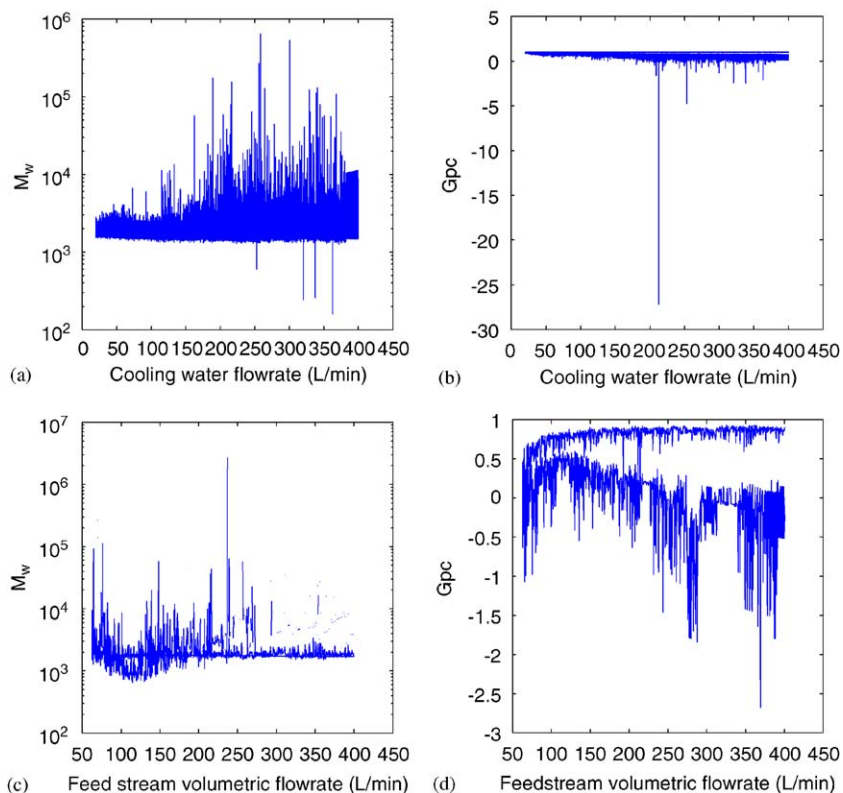


Fig. 6. Molecular weight distribution ( $M_w$ ) and polymer gel point ( $G_{pc}$ ) using the cooling water and feed stream flow rates as continuation variables.



an idea not fully explored in polymerization systems, deals with the intentional introduction of oscillatory behavior through the use of feedback nonlinear controllers (Chen et al., 2000). Accordingly, the desired location and amplitude of the oscillatory behavior might be regulated. It remains as a pending task to determine if such theoretical developments might have a practical implication in polymerization systems. Therefore, it can be concluded from Fig. 1, that only mild nonlinearities emerge under cooling water flowrate and SIR variations.

In contrast, harder nonlinearities might be expected when the cooling water flowrate is employed as the manipulated variable and the monomer flowrate acts as upset, as shown in Fig. 3. However, large variations in the monomer flowrate might be difficult to occur because usually such monomer flowrate comes from storage tanks that act as filters, smoothing the upset. It should be noticed that the largest parametric sensitivity region occurs when both flowrates are reduced down to small values (line 3), a situation that may happen during reactor shut-down. However, for safer operation, it is probably better to just impose a grade transition down to the low conversion branch, without modifying the monomer flowrate. Once there, the cooling water and monomer flowrate control valves may be simply turned off. Hence, the nonlinear bifurcation maps help one to get rid of a potentially unsafe operation policy.

The steady-state reactor response, when the feedstream cooling water temperature is employed as the manipulated variable and the monomer flowrate acts as disturbance, is shown in Fig. 4. It should be stressed that in practical terms the cooling water flowrate, and not the feedstream water temperature, is actually used as the manipulated variable simply because it is easier to manipulate. However, in academic studies it is common to find the feedstream water temperature as manipulated variable. This case is mainly analyzed in order to find out what might occur to the CSTR response, subject to variations in water temperature because of periodic season weather temperature conditions. Thus, for instance, an increase of around 17 K in feedstream water temperature, might give rise to hysteresis behavior: any additional small increment in water temperature beyond 310 K will cause a large increase in reactor temperature. The highly sensitivity behavior is, of course, originated due to the presence of the limit point bifurcation seen clearly in Fig. 4(d). On the other hand, high parametric sensitivity is not present around the low temperature region. However, operation of the CSTR around such operating region is uncommon. The onset of oscillatory behavior at the low temperature region should be noticed.

So far, nonlinear behavior has emerged through multiple steady-states, limit point and Hopf bifurcations. Fig. 5 features, in addition to these nonlinearities, the presence of input multiplicities. The onset of such multiplicities has been associated to the presence of complex competing factors (Kopel, 1982) and the employment of recycle structures. In closed loop control, they are sometimes related to the use of integral action (Chen and Chang, 1985). The presence of input multiplicities is more clearly seen in both, isocyanate and in butanediol conversions. Fig. 5(d) seems to indicate that input multiplicities are absent, if only reactor temperature is considered. Actually,

there is a small temperature range, around 350 K, where input multiplicities arise, but it is too small to be of practical importance. It should be noticed that, contrary to the output multiplicities case, input multiplicities can arise only in a subset of the system states. Since in this case, input multiplicities do not occur at the branch of the nominal operating point, it is difficult to take advantage of its presence to improve reactor performance.

As explained before, calculations of  $M_w$  using the Macosko-Miller approach (Vivaldo-Lima et al., 2002) (as an approximation, since this model is not strictly applicable for CSTRs) were carried out for illustrative purposes. The results obtained are shown in Fig. 6. Fig. 6(a) shows the steady-state reactor response ( $M_w$  in this case) when the cooling water flow rate is used as manipulated variable, at the conditions of profile 1 of Fig. 1. It is observed that huge oscillations of  $M_w$  are predicted by the model, with some values (at some values of  $Q_w$ ) reaching very high values of  $M_w$ , which may indicate that a polymer network could have been produced, or that the operation is close to the gelation point. Since the model for  $M_w$  used to carry out these calculations, based on the equations proposed in Vivaldo-Lima et al. (2002), is valid only for the pre-gelation period, and the predictions obtained with the model during the post-gelation period are meaningless (Vivaldo-Lima et al., 2002), then calculations of the “gelation point criterion” ( $G_{pc}$ ) were also carried out (Fig. 6(b)). When  $G_{pc} = 0$ , it means that the gelation point has been reached. If  $G_{pc} < 0$ , it means that the polymerization is taking place during the post-gelation period (Vivaldo-Lima et al., 2002). In other words, the model for  $M_w$  used to carry out these calculations is only valid for the pre-gelation period, when  $G_{pc} > 0$ . Fig. 6(b) clearly shows that a polymer network is produced when the cooling water flow rate is greater than approximately 130 L/min. That explains many of the sudden and frequent reductions (oscillations) on  $M_w$  observed in Fig. 6(a).

Fig. 6(c) shows a similar profile as in Fig. 6(a), only that this time the manipulated variable is the feed stream flow rate ( $Q_f$ ). The operating conditions correspond to those of line 1 in Fig. 5. Two steady states are possible at all the values of feed stream flow rate analyzed. Although not as severe as in the previous case, oscillations on  $M_w$  are also observed in this case. Once again, the corresponding diagram of  $G_{pc}$  versus  $Q_f$  is shown in Fig. 6(d). Once more it is observed that polymer networks can be produced in most of the possible operating values of  $Q_f$ , in one of the steady states.

The results shown in Fig. 6, although approximate, confirm that the feasible operating conditions (to avoid producing a polymer network in the tank reactor) should be chosen in the low conversion and low temperature regions considered in these analysis.

#### 4. Effect of disturbances

Rejection of the effect of disturbances on process behavior is one of the major challenges for the closed-loop control of processing systems. The acquaintance of disturbance effects

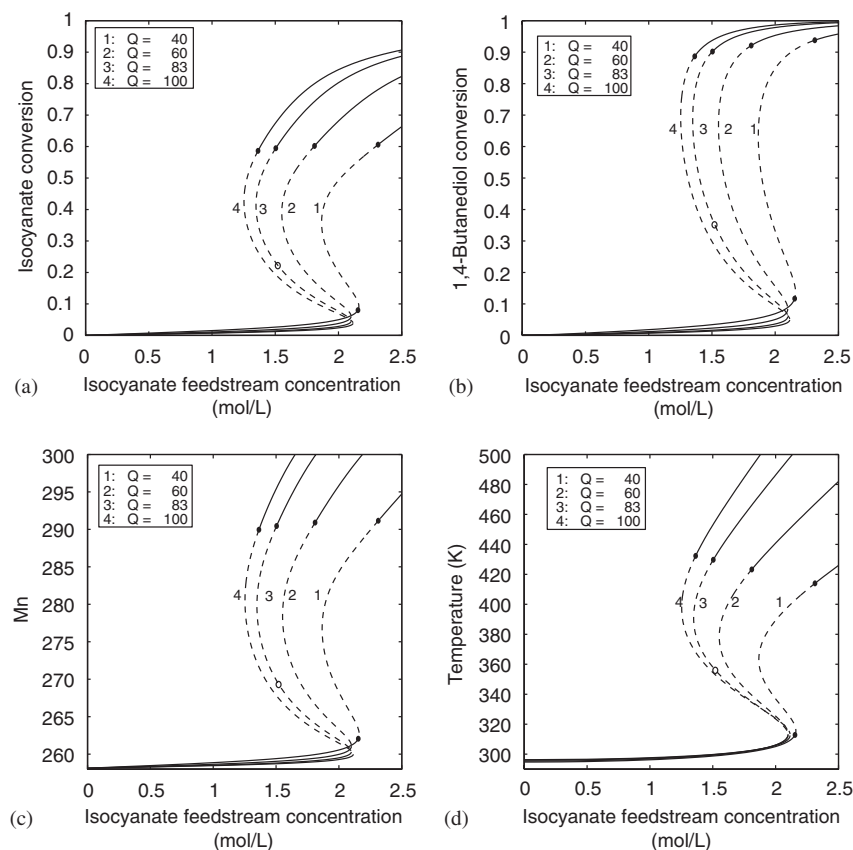


Fig. 7. Continuation diagrams using the isocyanate feedstream concentration and feedstream volumetric flowrate as continuation parameters.

may influence the control system design, in such a way to decide whether or not such upsets should be on-line measured and employed in a feedforward control structure.

Fig. 7 displays the open loop behavior of the polyurethane CSTR in presence of diisocyanate feedstream concentration disturbances. The secondary variable in this case is monomer flowrate. The first thing to notice from this figure is the extremely high sensitivity of the reactor response, in face of small variations of the diisocyanate feedstream concentration. This is specially true for the response in the 1,4-butanediol conversion. Only output multiplicities emerged. However, in Fig. 7, it is clearly noticed that, tiny diisocyanate feedstream concentration reductions, lead to large increases in diisocyanate and butanediol conversions. On the other hand, increases of the same order of magnitude do not have the same effect. Therefore, reactor operation might be enhanced in terms of product conversion by slightly decreasing the diisocyanate concentration. A similar effect is observed on the number average molecular weight response. Most of the calculations of  $M_n$  shown in the figures of this work produced fairly low values. However, these values are of the same order of magnitude as those obtained by Vivaldo-Lima et al. (2002) for polyurethane production in batch reactors. It should be kept in mind that, although not calculated here, weight average molecular weights are much higher. Therefore, the MWD is broad. From Fig. 7, it turns out

that the on-line measurement of the isocyanate functional group concentration is convenient for feedforward control purposes, thus enhancing disturbance rejection capabilities. However, the on-line measurement of this variable may turn out to be difficult or time delayed.

## 5. Effect of process design

Process design changes are one the main routes to get rid of nonlinearities whenever they are perceived as harmful. In fact, nonlinearities tend to emerge as the result of highly economical optimized processes (Seider et al., 1990), giving rise to tightly interconnected processes. Moreover, operating conditions of highly optimized systems tend to lie near strong sensitivity regions. Therefore, under such scenario, process control turns out to be a complicated and difficult task. Bifurcation analysis provides a valuable tool to realize the way process design changes might help to improve process operation (Bildea and Dimian, 1998). Recently, a new optimization formulation has been proposed to address explicitly nonlinear issues during process design (Marquardt and Monnigmann, 2004). This formulation is an example of the way bifurcation theory may be embedded within optimization formulations, addressing simultaneous design and control problems. In this section, the effect of process design changes on the nonlinear reactor

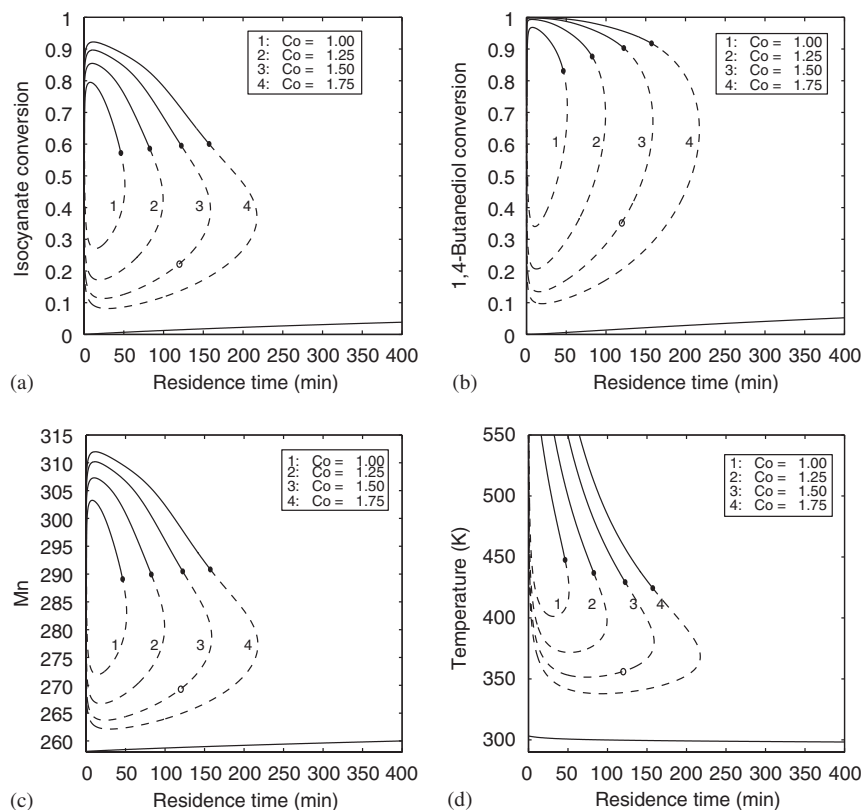


Fig. 8. Continuation diagrams using the residence time and isocyanate functional group feedstream concentration as continuation parameters.

behavior is analyzed. Specifically, the way in which residence time changes affect the system response are considered. In bifurcation analysis studies, residence time has been frequently used as the main continuation parameter (Uppal et al., 1974), mainly because it is a parameter easy to modify in practical situations. Normally, in design situations, residence time changes are carried out through changes in reactor volume.

Figs. 8–11 display the open loop behavior of the polyurethane CSTR, when the residence time is changed. The secondary variables are diisocyanate and 1,4-butanediol feedstream concentrations, feedstream temperature and cooling water flowrate, respectively. Globally speaking, these four figures exhibit some of the most critical nonlinear phenomena issues, since they feature high sensitivity, input and output multiplicities, instabilities, isolas and oscillatory behavior. From Fig. 8 an interesting situation is noticed. Since the reactor exhibits input multiplicities, one might would lead to conclude that the same reactor response might be achieved by reducing the residence time. This is not true since input multiplicities do not occur at the same residence time value. For instance, by decreasing the residence time down to around 50 min, an input multiplicity for temperature is found. But, there are not input multiplicities on the rest of the variables. Therefore, the same reaction yield would not be obtained at reduced residence time values.

Fig. 9 shows again input multiplicities and isola behavior. It is noticed that, if the monomer flowrate is increased up to

100 L/min, with a simultaneous increase in reactor volume to keep constant the residence time, then the reactor will end up operating along the fourth branch. This is an undesirable situation since, even with large increments in the residence time, the reactor response seems to be completely settled down. Hence, in a sense, the gain between reactor output and residence time is almost null for a large residence time range. In Fig. 10, similar reactor response patterns as those discussed before, are observed. Since polyurethane reactors are sometimes fed from holding tanks, seasonal temperature fluctuations should not worsen the reactor operation issue. Finally, Fig. 11 also exhibits input multiplicities and isola behavior. This figure shows that the polyurethane polymerization reaction system almost quenches if the cooling water flowrate decreases down to 25 L/min. Eventually, the reaction system will reach an open-loop stable branch. Therefore, this behavior highlights a potential safe route for reactor shutdown.

## 6. Effect of feedback control

Due to the fact that, under nominal operating conditions, the steady state of the polyurethane reactor turns out to be open-loop unstable, feedback control is required in order to stabilize the system. Even if the process was open-loop stable, modelling errors and upsets would demand the use of closed-loop control. Even when advances in the theory and on-line applications of nonlinear model predictive techniques have been

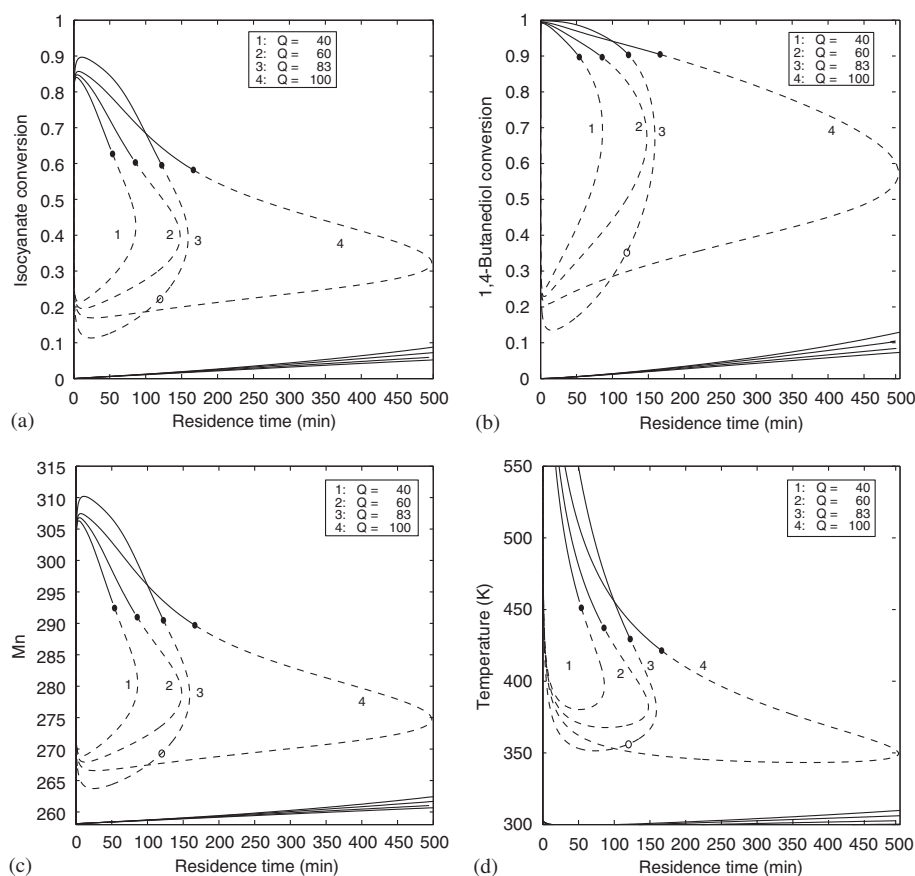


Fig. 9. Continuation diagrams using the residence time and feedstream volumetric flowrate as continuation parameters.

reported (Maciejowski, 2002), most chemical processes are still controlled by PID controllers. It is a common practice that such controllers exploit the natural dynamic behavior embedded in the process, thus leading to advanced control structures that extend the scope of the traditional feedback loop. Cascade control is one of the most widely industrially used advanced control schemes. It relies on the use of two manipulated variables (as determined by the master and slave control loops) to regulate the value of the controlled variable. Successful implementation of cascade control demands that the dynamic behavior of the slave loop performs faster than the corresponding one from the master loop.

There are some works in the literature that address the impact of pure feedback PID control on the closed-loop nonlinear behavior (Chen and Chang, 1985; Cook, 1985; Alvarez and Curiel, 1997). It has been reported (Alvarez and Curiel, 1997) that even linear plants controlled with a linear controller, subject to input saturation constraints, may lead to complex dynamic behavior. From these studies, it can be concluded that linear PID control tends to introduce nonlinear behavior that was not previously present. In fact, one of the worst effects of PID control is the possibility of losing global stability, because of the introduction of additional steady states (Chen and Chang, 1985). Therefore, in this part of the work, an analysis of

the potential effects of the cascade control configuration on the closed-loop behavior of the polyurethane CSTR, is carried out. One of the aims of the analysis is to highlight the fact that hard nonlinearities will tend to increase in PID closed-loop control systems.

The controlled variable is the reactor temperature. The slave control loop manipulates the cooling water flowrate to control the jacket temperature, while the master control loop sets the set-point of the jacket temperature. Both, the slave and master controllers are pure gain proportional controllers. The pure gain cascade control system was implemented using the following form of a feedback multistate control law:

$$Q_{cw} = Q_{cw}^{bias} + k_2(T^{sp} - T) + k_3(T_j^{sp} - T_j),$$

where  $k_3$  is the gain of the slave controller whose purpose is to control the reactor jacket temperature ( $T_j$ ),  $k_2$  is the gain of the master controller whose aim is to control the reactor temperature ( $T$ ). As usual *bias* stands for the steady-state value of the manipulated variable ( $Q_{cw}$ ).

Just for discussion purposes a gain of 20 for the slave controller was selected. In Fig. 12, the closed-loop bifurcation diagrams of the cascade control system are displayed. The bifurcation parameter is the gain of the master loop. The hollow

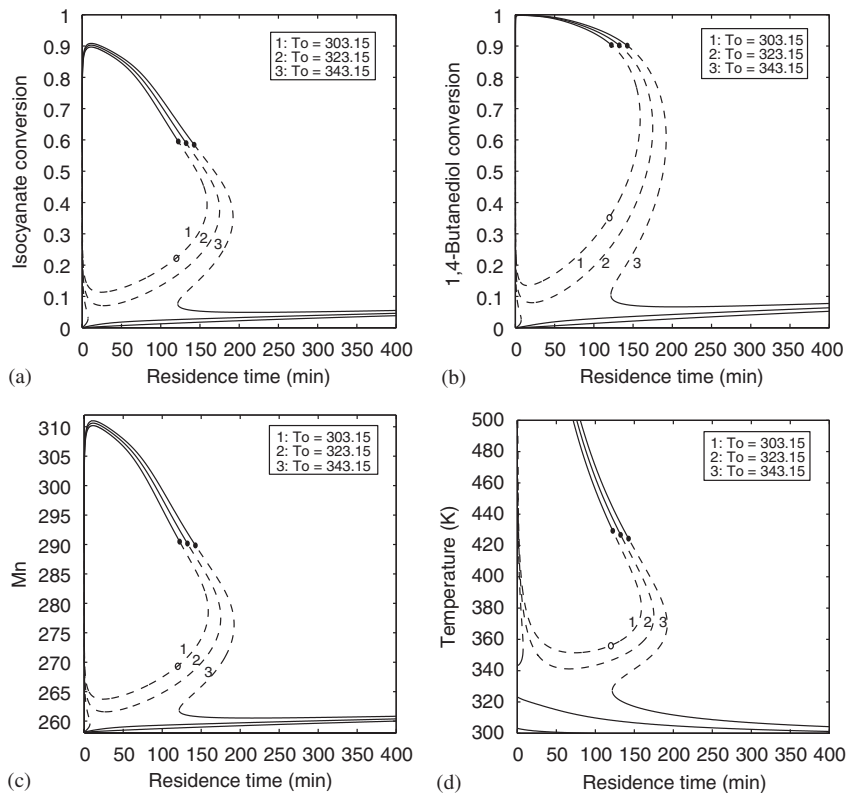


Fig. 10. Continuation diagrams using the residence time and feedstream temperature as continuation parameters.

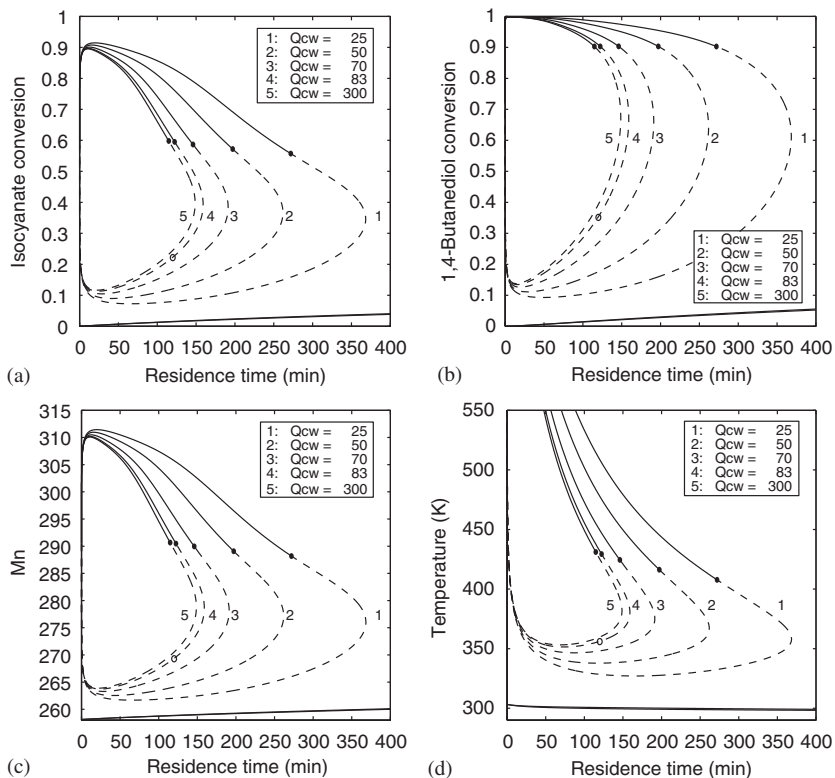


Fig. 11. Continuation diagrams using the residence time and cooling water flowrate as continuation parameters.

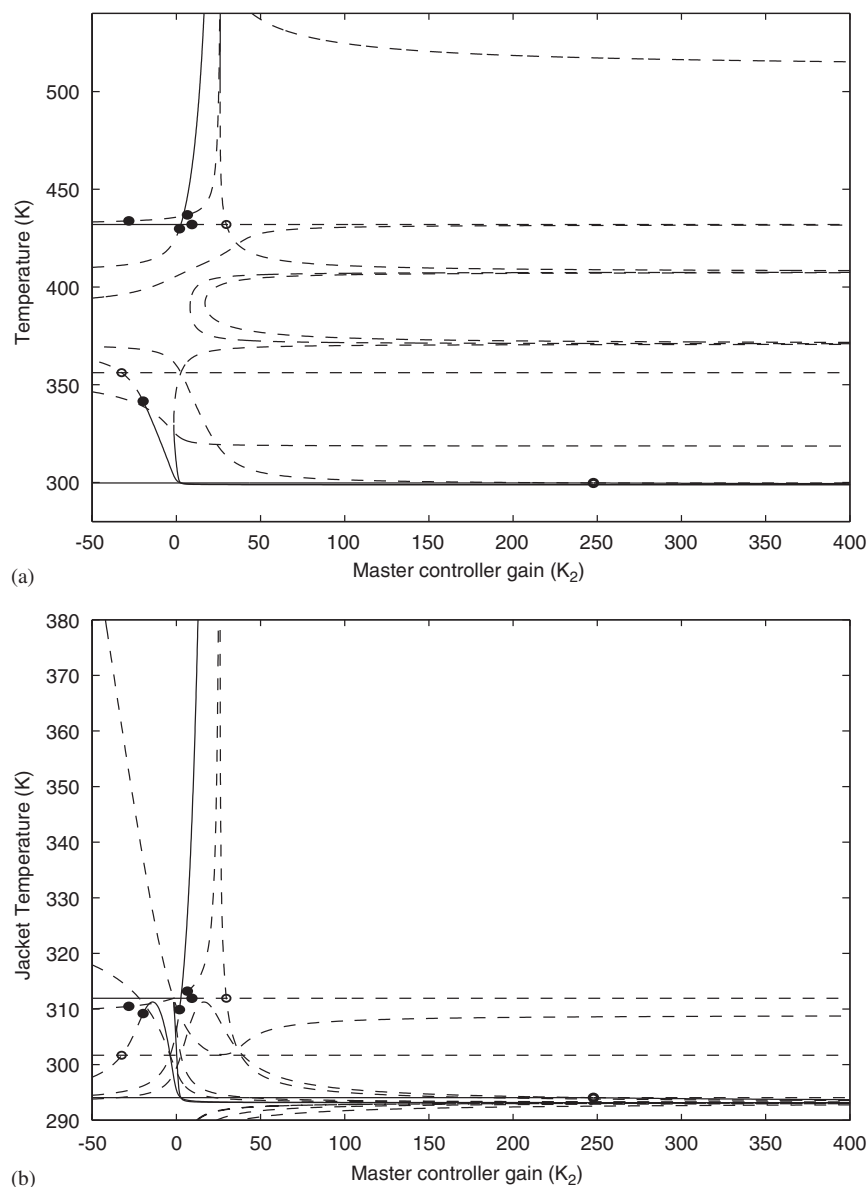


Fig. 12. Continuation diagrams using the master controller gain as continuation parameter.

circle represents a branching point, while the filled one means a Hopf bifurcation point. The three horizontal lines stand for the three steady states that were originally present under open-loop conditions. All the other points and lines were introduced by the pure gain cascade control system. As it can be noticed, at the high temperature region, there is a narrow range of master loop gains for assuring closed-loop stability. At the middle temperature range, the simple pure gain cascade system is unable to closed-loop stabilize the system, for any value of the master loop gain. On the other hand, at the low temperature region control is easier to achieve. There, the closed-loop control system remains stable practically with any master loop gain. Of course, the gain value will be constrained by the final control element capacity. However, as it was previously discussed, operating the process around the low temperature region may not

be attractive, since the rate of polymerization may not be high enough. Fig. 12 provides another clue, in addition to the possible gel formation onset, to avoid operating around the high temperature region. Such region has embedded some Hopf bifurcation points. If oscillatory behavior is to be avoided, then the reactor should not probably be operated at this region. It can be noticed that, global stability issues become more relevant, if the polyurethane CSTR is operated around the low temperature region. Around this region the control system introduces a new stable steady-state branch. The same problem appears to be less relevant at the high temperature region. There, the stable steady–steady branch quickly drifts away. An interesting point to highlight is the fact that around the medium temperature region, one might be able to get oscillatory behavior using positive feedback. This is one of the suggested approaches to



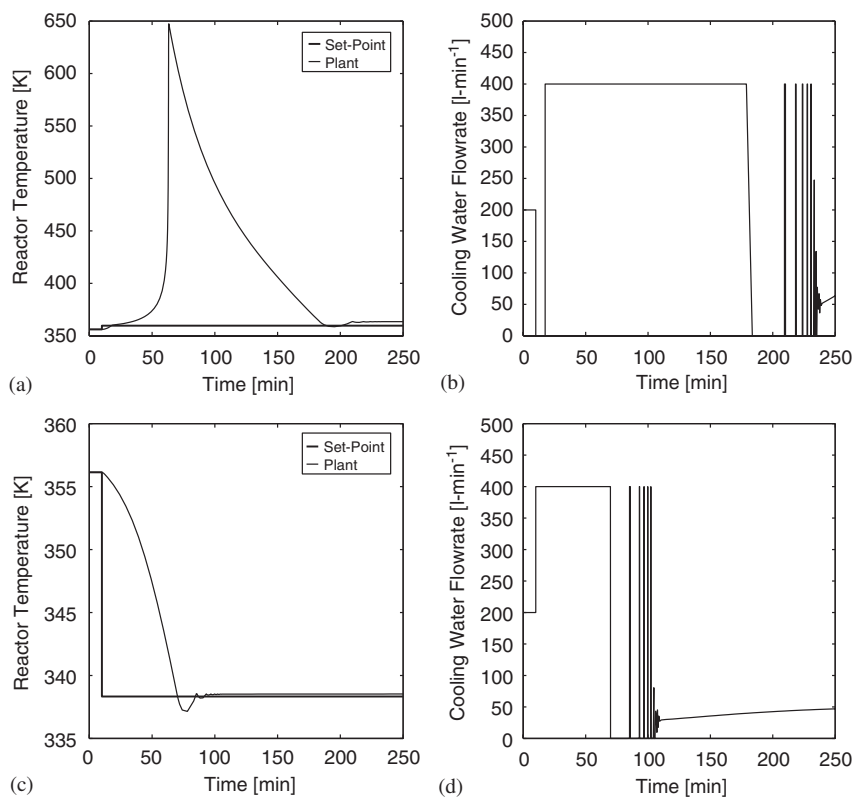


Fig. 13. Servo closed-loop response for +10% (a,b) and -10% (c,d) set-point change. Gain and integral time PI controller tuning parameters were  $-1000\text{L}/(\text{min} - \text{K})$  and 20 min, respectively.

introduce oscillatory behavior in feedback control systems (Mukesh and Rao, 1977). Globally speaking, the analysis shows that nonlinearities should be taken into account when selecting a control configuration and its tuning parameters. The nonlinear bifurcation analysis might reveal some ways to enhance closed-loop control.

It is a well-known fact that the closed-loop performance of PID controllers tend to worsen as system nonlinearities get higher. Since PIDs are linear control laws aimed to the closed-loop control of linear or mildly nonlinear systems, this result does not come as a surprise. In fact, PIDs applied to highly nonlinear systems tend to demand large control actions (because of system sensitivity) even for small disturbances hitting the system or set-point changes. To illustrate this point, we tuned a PI control system both for set-point tracking and disturbance rejection scenarios (the controlled variable is the reactor temperature, while the cooling flow rate is the manipulated variable). Because of the embedded nonlinearities, traditional empirical tuning rules tend to produce unreliable parameter settings (leading, for instance, to closed-loop unstable systems) when addressing the closed-loop control of highly nonlinear systems. Therefore, the tuning of the PI controller was done using a trial and error procedure until the best closed-loop response was achieved. The gain and integral time control parameters were  $-1000\text{L}/(\text{min} - \text{K})$  and 20 min, respectively. Fig. 13 displays the closed-loop response for  $\pm 10\%$  changes

in reactor temperature set-point. As noticed in Fig. 13(a), the control system is unable to avoid thermal runaway conditions due to control valve saturation. Even when eventually the desired set-point is reached, it is clear that the large temperature peak might lead to unsafe reactor operation. As depicted in Fig. 13(c), the reactor system is easier to control when lowering the reactor temperature set-point. The bifurcation diagram shown in Fig. 1 can be used to explain the emergence of the temperature peak: under nominal conditions there is a large upper temperature steady state, while lower steady states are closer to the nominal one. Notice that in both cases, the control actions are aggressive, leading to control valve saturation for a while, regardless the direction of the set-point change. As displayed in Fig. 14, the situation looks similar under disturbance rejection conditions when compared to the set-point tracking scenario. Here the disturbance was taken as  $\pm 10\%$  variation in the feed stream temperature. As before, a large temperature peak emerges when the disturbance hits the system in the direction of reactor temperature increase. As mentioned before, the reactor closed-loop response might lead to unsafe operation. Again, disturbance rejection is relatively easier to handle (although the control valve hits its bounds), a situation that we should expect looking at the bifurcation diagram of Fig. 1.

From the analysis performed, it can be concluded that the closed-loop control of the polyurethane CSTR will impose serious demands on feedback controllers. In order to achieve

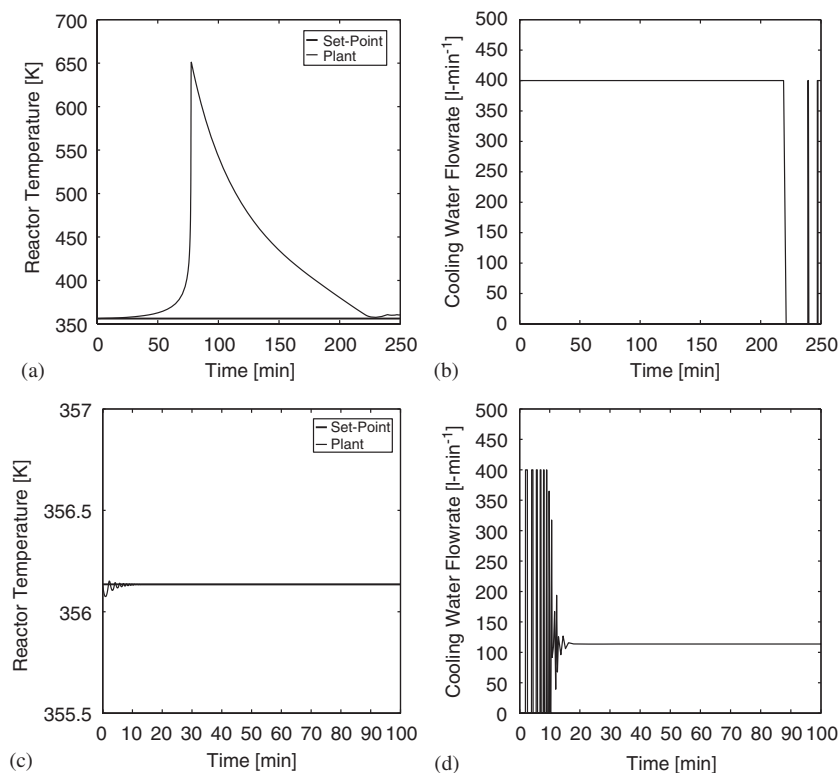


Fig. 14. Disturbance rejection closed-loop response for +10% (a,b) and -10% (c,d) feed stream temperature change. Gain and integral time PI controller tuning parameters were  $-1000 \text{ L}/(\text{min} \cdot \text{K})$  and 20 min, respectively.

satisfactory levels of performance and stability robustness properties, nonlinear control techniques (i.e., MPC) will be required. This is one of the advantages of carrying out bifurcation studies. The use of advanced control techniques might be justified on the grounds of the highly nonlinear patterns that were found. Without undertaking bifurcation studies it would not be clear whether or not PID control was enough to keep running the process.

## 7. Conclusions

In this work the bifurcation behavior of a polyurethane CSTR has been addressed. A steady-state model, that has been previously experimentally validated, was used to carry out the full nonlinear and bifurcation analysis of an industrial scale polyurethane reactor. Because of the complexity and nonlinearities embedded in the mathematical model, numerical continuation techniques, augmented to detect singularities, were used to trace the branches of both stable and unstable steady-state solutions. Several combinations of potential manipulated, disturbance and design variables were examined. For some of these combinations, patterns of multiplicity and oscillatory behavior were observed. Due to limitations imposed by the need to operate at low and intermediate monomer conversions, in order to avoid reaching the gelation point (appearance of a gel polymer network), the nominal operating point was open-loop unstable.

The complex nonlinear behavior displayed by the polyurethane CSTR can be explained on the grounds of the highly complex kinetic relations, mass and heat-transfer interactions, the occurrence of the gelation point and heat transfer withdrawal limitations. Thereby, removing nonlinearities will not be an easy task by any means. A closed-loop cascade controller was used to depict some of the limitations that linear controllers impose on the control of highly nonlinear systems. It was found that the cascade controller contributed to increase nonlinearity and destroy global stability properties. It was also found that simple PID controllers might not provide acceptable closed-loop control response and that advanced control techniques are worth to be explored for this kind of highly nonlinear polymerization systems.

We would like to stress that the practical benefits of nonlinear studies, like the one addressed in this work, have not been fully realized in industry. This is partially due to the fact that, although bifurcation diagrams are easy to compute for small scale systems, they tend to require large computer times as the system dimension gets higher. Moreover, medium and large scale systems require specialized software (Doedel and Tuckerman, 2000). From a process control point of view, bifurcation diagrams might be used to learn how nonlinearities might worsen PID closed-loop control performance, as it was shown in this work, leading to the justification of advanced control techniques.

## Notation

$A$	heat-transfer area, $m^2$
$A_1, A_2$	isocyanate functional groups concentration, mol/L
$B$	concentration of hydroxyl functional groups bound to the polyol, mol/L
$B_p$	concentration of hydroxyl functional groups bound to the 1,4-butanediol molecule, mol/L
$C_o$	isocyanate functional group concentration in the feed stream, mol/L
$C_{pm}$	feedstream heat capacity, Kcal/Kg K
$D$	amine functional group concentration, mol/L
$D_2$	diamine molecule
$E$	urethane concentration, mol/L
$F$	urea functional group
$G$	biuret functional group concentration, mol/L
$G_{rr}$	global reaction rate, mol/L min
$k_i, k_i^*$	kinetic rate constants, where superscript * indicates reactivity of a functional group bound to a polymer molecule, L/mol min
$k_2$	master controller gain
$k_3$	slave controller gain
$M$	allophanate functional group concentration, mol/L
$M_n$	number average molecular weight, kg/kmol
$Q$	feedstream volumetric flow rate, L/min
$Q_{cw}$	cooling water flowrate, L/min
$R_3$	proportionality constant between rates of allophanate and urethane formation
$SIR$	stoichiometric imbalance ratio
$T$	reactor temperature, K
$T_j$	jacket temperature, K
$T_{jo}$	jacket feedstream temperature, K
$T_o$	reactor feedstream temperature, K
$U$	global heat-transfer coefficient, Kcal/ $m^2$ min K
$V$	reactor volume, L
$V_j$	jacket volume, L
<i>Greek letters</i>	
$\Delta H_r$	heat of reaction, Kcal/mol
$\rho_m$	feedstream density, Kg/L
$\theta$	reactor residence time, min

## Acknowledgments

E.V.-L. acknowledges financial support from the Science and Technology National Council of Mexico (CONACYT), Projects 31170-U and U40259-Y; DGAPA-UNAM (PASPA Program), and the Department of Chemical Engineering of the University of Waterloo (UW), for funding his research stay at UW.

## References

- Alvarez, J., Curiel, L.E., 1997. Bifurcations and chaos in a linear control system with saturated input. *International Journal of Bifurcation and Chaos* 7 (8), 1811–1822.
- Antoneli, R., Astolfi, A., 2003. Continuous stirred tank reactors: easy to stabilise? *Automatica* 39, 1817–1827.
- Aris, R., Amundson, N.R., 1958. An analysis of chemical reactor stability and control. *Chemical Engineering Science* 7, 121–130.
- Bildea, C.S., Dimian, A.C., 1998. Stability and multiplicity approach to the design of heat-integrated PFR. *A.I.C.H.E. J.* 44 (12), 2703–2712.
- Blanco, A.M., Bandoni, J.A., Biegler, L., Re-design of The Tennessee eastman challenge process: an eigenvalue optimization approach. in: *Proceedings of Foundations of Computer Aided Process Design*, manuscript accepted for publication.
- Chen, G., Muiola, J.L., Wang, H.O., 2000. Bifurcation control. Theories, methods and applications. *International Journal of Bifurcation and Chaos* 10 (3), 511–548.
- Chen, L.-H., Chang, H.-C., 1985. Global effects of controller saturation on closed-loop dynamics. *Chemical Engineering Science* 40, 2191–2205.
- Cook, P.A., 1985. Simple feedback systems with chaotic behaviour. *Systems and Control Letters* 6, 223–227.
- Dhooge, A., Govaerts, W., Kuznetsov, Y., 2003. MATCONT: a matlab package for numerical bifurcation analysis of ODEs. *ACM Transactions on Mathematical Software* 29, 141.
- Dietrich, D., Uhlig, K., 1992. Polyurethanes. *Ullmanns Encyclopedia of Industrial Chemistry*, vol. A21. VCH Publishers Inc., pp. 665–716.
- Doedel, E., Tuckerman, L.S., 2000. *Numerical Methods for Bifurcation Problems and Large-Scale Dynamical Systems*. Springer, Berlin.
- Dotson, N.A., Galvan, R., Laurence, R.L., 1996. *Polymerization Process Modeling*. VCH Publishers Inc., New York. p. 267.
- Draye, A.-C., Tondeur, J.-J., 1999. Kinetic study of organotin-catalyzed alcohol isocyanate reactions Part 1: inhibition by carboxylic acids in toluene. *Journal of Molecular Catalysis A: Chemical* 138, 135–144.
- Gupta, S.K., Kumar, A., 1987. *Reaction Engineering of Step Growth Polymerization*. Plenum Press, NY.
- Hamiel, A.E., Tobita, H., 1992. *Polymerization Processes*. Ullmanns Encyclopedia of Industrial Chemistry, vol. A21. VCH Publishers Inc., pp. 305–428.
- Heintz, A.M., Duffy, D.J., Hsu, S.L., 2003. Effects of reaction temperature on the formation of polyurethane prepolymer structures. *Macromolecules* 36, 2695–2704.
- Kopel, L.B., 1982. Input multiplicities in nonlinear multivariable control systems. *A.I.C.H.E. J.* 28 (6), 935–945.
- Kokossis, A.C., Floudas, C.A., 1994. Stability in optimal design: synthesis of complex reactor networks. *A.I.C.H.E. J.* 40 (5), 849.
- Kuchanov, S., Slot, H., Stroeks, A., 2004. Development of a quantitative theory of polycondensation. *Program Polymer Science* 29, 563–633.
- Kuznetsov, Y., 1998. *Elements of Applied Bifurcation Theory*. second ed. Springer, Berlin. p. 1998.
- Maciejowski, J.M., 2002. *Predictive Control with Constraints*. Prentice-Hall, Englewood Cliffs, NJ.
- Macosko, C.W., 1989. *RIM, Fundamentals of Reaction Injection Molding*. Hanser Publishers,
- Marquardt, W., Monnigmann, M., 2004. Constructive Nonlinear Dynamics in Process System Engineering. In: Barbosa, A., Matos, H. (Eds.), *Escape-14*. Elsevier, Amsterdam, pp. 99–116.
- Moen, O., 2004. Machine Means for Design, Control and Economic Optimisation of Polyolefin Production Processes and Their Products. In: Barbosa, A., Matos, H. (Eds.), *Escape-14*. Elsevier, Amsterdam, pp. 117–122.
- Mukesh, D., Rao, C.D.P., 1977. Stability and dynamics of cascade reactors with control only on the first reactor. *Industrial Engineering and Chemical Process. Design and Development* 16 (2), 186–192.
- Ray, W.H., Villa, C., 2000. Nonlinear dynamics found in polymerization processes—a review. *Chemical Engineering Science* 55, 275.
- Schwetlick, K., Noack, R., Stebner, F., 1994. Three fundamental mechanisms of base-catalysed reactions of isocyanates with hydrogen-acidic

- compounds. *Journal of the Chemical Society, Perkin Transactions 2* (3), 599–608.
- Seider, W.D., Brengel, D.D., Provost, A.M., Widagdo, S., 1990. Nonlinear analysis in process design: why overdesign to avoid complex nonlinearities? *IEC Research* 29 (5), 805–818.
- Spitz, J.J., Laurence, R.L., Chappellear, D.C., 1977. An experimental study of a polymerization reactor in periodic operation. *A.I.C.H.E Symposium Series* 72 (160), 86–101.
- Vivaldo-Lima, E., Luna-Barcenas, G., Flores-Tlacuahuac, A., Cruz, M.A., Manero, O., 2002. Modeling of nonlinear polyurethane production in batch reactors using a kinetic-probabilistic approach. *Industrial & Engineering Chemistry Research* 41, 5207–5219.
- Ulrich, H., 1997. Urethane Polymers. in: Kroschwitz, J.I., Howe-Grant, M., (Eds.), *Kirk-Othmer Encyclopedia of Chemical Technology*, fourth ed., vol. 24, Wiley, New York, NY, 695–726.
- Uppal, A., Ray, W.H., Poore, A.B., 1974. On the dynamic behavior of continuous stirred tank reactors. *Chemical Engineering Science* 29, 967–985.