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The bifurcation behavior of a polyurethane continuous stirred tank reactor

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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.

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

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(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 formulation 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