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Nonlinear Analysis and Design of High-Impact Polymerization Reactors Using a Bifunctional Initiator

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Abstract

In this work the steady-state multiplicity analysis of a complete and detailed high-impact polymerization system carried out in a non-isothermal continuous stirred tank reactor is addressed. The potential effect of manipulated, disturbance and design variables on the reactor control is discussed. It is shown that high sensitivity dependence problems cannot be removed by making changes in the analyzed design parameters.

1. Introduction

Polymer manufacture involves processes which can exhibit highly nonlinear behavior including phenomena such as input/output multiplicities, limit cycles, sustained oscillations, hysteresis, chaos, etc.[1] Nonlinear analysis tools are useful to locate the range of design parameters over which complex operating regimes may occur.[2] They also permit, for instance, to set up control schemes able to address issues embedded by intrinsic nonlinear behavior.[3] Since process plants are now required to be more flexible, a consideration of nonlinearities is necessary in order to have confidence in model predictions concerning plant operation over a wide range of operating conditions. Commonly, nonlinearities are perceived as an undesired phenomenon, because they may adversely affect product quality, process control and lead to unsafe operations.[3] It is widely accepted that processes must be designed and operated not only to optimize static performance, but also to impart the system with accepted levels of controllability and resiliency. Thus, nonlinear analysis is potentially helpful on early design stages. Initial efforts to take into account nonlinear behavior in an optimization design framework have been recently reported.[4] Even when nonlinearities are commonly considered harmful to process operation, there might be cases when optimal static design calls for operation around highly nonlinear regions. It is a common rationale that, although feasible operation of open-loop unstable systems is possible by adequate feedback control, such a situation is usually undesirable, because of operability and safety reasons and should be avoided by proper design.

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The analysis of the nonlinear dynamics of polymerization reactors has been a very important research area. In particular, polymerization processes are of great interest because they usually present complicated steady-state nonlinear bifurcation behavior. This knowledge is important because the nonlinear behavior of chemical reactors has an important effect on operation difficulties.[2] Furthermore, the knowledge of their behavior might help to optimize the process by the elimination of nonlinearities.

The aim of this work is to address the operability difficulties faced by HIPS reactors. The steady-state operability problem is addressed by using nonlinear bifurcation techniques. Even when the industrial production process involves a series of connected reactors, only one CSTR was chosen to perform the analysis to avoid mathematical modelling complexities. We extend some previous results published by our research group[5] by including a more sophisticated model description of the HIPS reactor that includes branching and crosslinking reactions. High-impact polystyrene is an important commodity material which combines the ease of processing of polystyrene with increased mechanical resistance.

2. Mathematical Model

In the open literature there are only a few references on the modelling of the HIPS process. The model used here has been developed by the authors as part of a project aimed at the detailed modelling of the HIPS and the GPPS (general purpose polystyrene) processes. The general model, which is to be published elsewhere,[6] describes the populations of linear polystyrene (which forms the bulk of the continuous phase), grafted polybutadiene and crosslinked polybutadiene, and that description has been kept here for the sake of completeness, although some of the populations (grafted and crosslinked polybutadiene) are not relevant for the dynamics of the bulk and therefore not discussed in this paper. At this point it is important to clarify that this paper will focus on the dynamics of the continuous phase for two reasons: i) the variables of the continuous phase (conversion, molecular weight) are the most important ones from the point of view of the dynamics of the process and ii) the variables of the continuous phase are those more easily measured and therefore more amenable of being controlled variables in a control scheme. The properties of the dispersed phase, such as gel content and swelling index, are also important parameters for the quality of the product. However, their dynamics are mostly driven by the dynamics of the bulk phase and therefore their study is not of primary importance in this work. It is worth mentioning that in industrial practice, given the high operating temperatures used in the second and third reactors, all the dispersed phase is trapped as crosslinked material and it is separated from the continuous (linear polystyrene phase) before analysis in the laboratory. The molecular weight measured in the laboratory corresponds only to the continuous linear phase. This determines that the only population considered for calculations of molecular weight in this paper is that corresponding to the continuous linear phase. The model, however, is also able to estimate the properties of the dispersed phase. Due to space limitations the full description of the mathematical model will not be given here, but it can be consulted elsewhere.[6]

3. Results and Discussion

Feedstream Temperature. Figure 1 displays the steady-state multiplicity maps employing the feedstream temperature as the main bifurcation parameter and the feedstream flowrate as secondary parameter. The nominal operating point is denoted by the symbol "*o*", and, as usual, stable steady states are drawn as a solid line and unstable steady states by a dashed line. Figure 1(a) displays an interesting fact. It shows that monomer conversion could be raised by dropping the feedstream temperature. For instance, by decreasing the feedstream temperature down to 300 K, the monomer conversion raises around 40%. Normally, operation problems associated to the gel effect onset should not matter around this conversion region. Figure 1(a) also shows that the process output rate could be increased by operating along branch 3 of this figure. In fact, without changing additional operating conditions, except the monomer feedstream flowrate, the process will turn out to be more profitable in terms of increased monomer conversion and polymer output rate. Moreover, an additional feedstream temperature drop, so the final reactor temperature is around 300 K, will lead to a 50% monomer conversion where, hopefully, operability problems due to the gel-effect onset are not yet important. On the other hand, branch 1 of Figure 1(a) shows that reducing the monomer feedstream flowrate will lead to a reduction in both monomer conversion and polymer output rate. This discussion highlights the fact that the feedstream temperature may be used as a manipulated variable for monomer conversion control. However, industrially on-line monomer conversion is not normally available for process control purposes. However, as figure 1(d) displays, monomer conversion closed-loop control could be forced by controlling the reactor temperature. However, the control of reactor temperature by manipulating the feedstream temperature should be tight, otherwise the process may end up running around the high conversion region where gel effects are important. From figures 1(b) and (c), it is clearly seen that number-average (M_n) and weight-average (M_w) molecular weights exhibit a smooth dependence on both bifurcation parameters.

Residence Time. Figure 2 displays the steady-state multiplicity maps using the residence time and the feedstream flowrate as the main and secondary bifurcation parameters, respectively. Such continuation diagrams were included to analyze the effect of residence time as an important design parameter. From figure 2, it is clear that the nominal design point corresponds to a high sensitivity point in relationship to residence time. Moreover, any tiny decrease in residence time would result in the reactor running into the gelation region. Actually, such design point represents true operating condition of the industrial HIPS process. It might have occurred that, when designed, the reactor was highly optimized. The problem seems to stem from the fact that the nominal design point represents probably the point of maximum monomer conversion that might be achieved without gelation problems. From figure 2(a) it is clear that due to the nonlinear behavior exhibited by the reactor, increasing the residence time will lead to a decrease in reactor conversion. This is the opposite of what one normally would expect from a well behaved (i.e., non-multiplicity steady-state pattern) reaction system. From this same figure, one might get the feeling that nothing can be done to operate the HIPS reactor further away from the high sensitivity region. This is not completely true. As the previous discussion on other

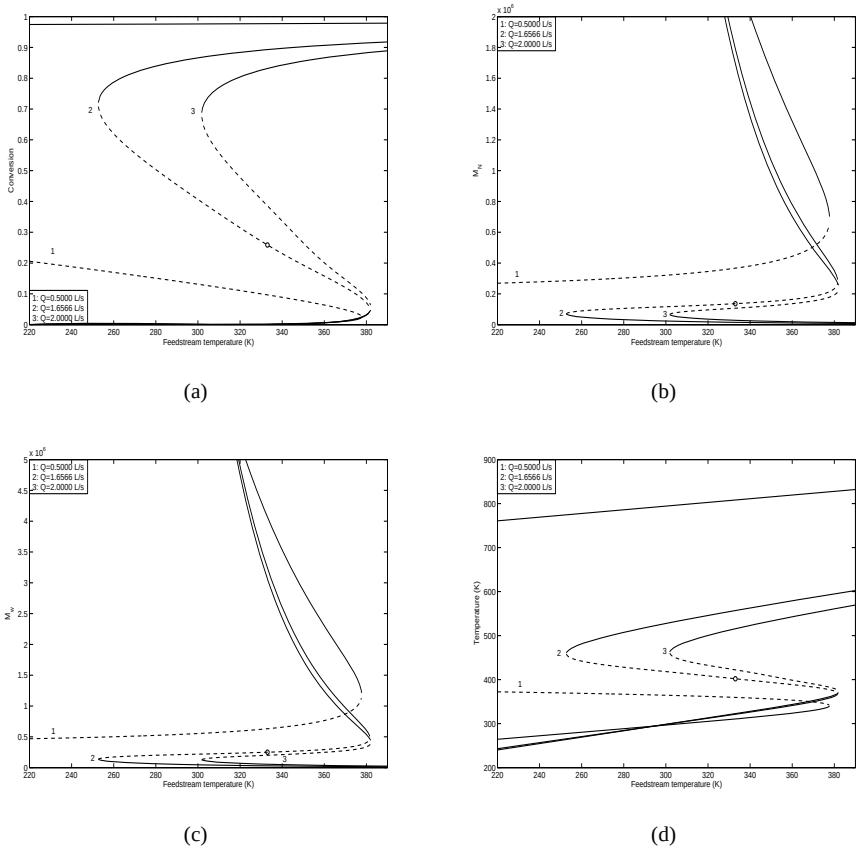

Figure 1: Continuation diagrams using the feedstream temperature and the feedstream flowrate as the main and secondary bifurcation parameters.

parameters effect on the multiplicity maps, have clearly shown that it should be possible to do so.

4. Conclusions

In this work a steady-state multiplicity analysis of a complete and detailed model of the HIPS polymerization system has been carried out. The effect on the closed-loop control of the reaction system of potential manipulated, disturbance, and design variables has been addressed. Moreover, when analyzing the multiplicity behavior in the face of residence time variations, a major finding was the realization about how close the HIPS reactor is to run into gelation problems. This highly sensitive behavior was probably embedded into the HIPS reactor when designed, looking for optimal design conditions. Such highly sensitive dependence cannot be removed by simple changes in the residence time. The use of nonlinear analysis tools would allow to reveal potential operability problems and take corrective action to try to reduce them. With the advent of higher computing facilities it turns out to be feasible to analyze large and complex systems like the one addressed in this work. It should be stressed that our results are based on a steady-state mathematical model previously subject to partial verification.[5] Therefore, we hope that some of the

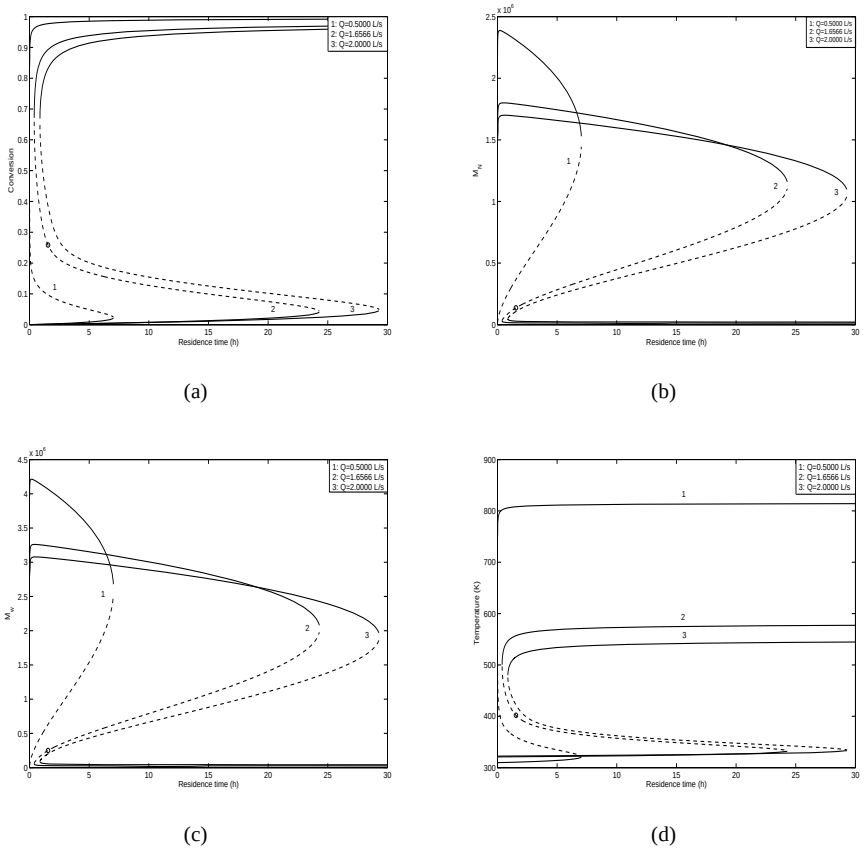

Figure 2: Continuation diagrams using the residence time and the feedstream flowrate as the main and secondary bifurcation parameters.

reported process response curves should be observed in a real industrial setting. Although there are in the open literature reported works on the modeling and dynamic simulation of HIPS processes,[7] neither of these works deal with the nonlinear and bifurcation analysis of the HIPS reaction system.

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