WHY ARE FREE-RADICAL LOOP POLYMERIZATION REACTORS NOT LIKELY TO OSCILLATE?

Príamo A. Melo, Evaristo C. Biscaia Jr., José Carlos Pinto*

Programa de Engenharia Química/COPPE – Universidade Federal do Rio de Janeiro
Cidade Universitária CP 68502, Rio de Janeiro, RJ 21945-970 – Brazil
**E-mail address: pinto@peq.coppe.ufrj.br*

Abstract

The so-called loop reactors are of particular interest for the polymerization industries. Due to the high degrees of mixing that may be attained and enhanced heat transfer capabilities, these reactors offer very special advantages for carrying out polymerization reactions. Recently, Melo *et al.* (2001a,b) characterized the residence time distribution and thermal behavior of a lab-scale loop polymerization reactor and observed that the dynamics induced by the recycling pump is of major relevance for the proper description of the process behavior. Besides, they showed that the thermal capacitance of this equipment should not be neglected during the modeling of industrial scale reactors. In the present communication, a bifurcation analysis of the loop polymerization reactor is presented. It is shown that due to the thermal capacitance of the reactor externals, both lab scale and industrial scale loop polymerization reactors are not likely to present periodic oscillations. The free-radical solution polymerization of vinyl acetate was chosen as a case study.

Introduction

Increasingly, plastics are replacing other materials in the automobile, packing, electronics, appliances, and building industries. As for the year of 1995, the overall world plastics production was estimated to be about 100 million tons (Kiparissides, 1996), moving figures of hundreds of billions of U.S. dollars. Because demand for polymeric materials as well as enhanced end-use product quality continues to grow, chemical and polymer engineers are continuously expected to come up with improvements to the operation of current plants and conceive new, state-of-the-art polymerization processes.

Originally, most polymeric materials were manufactured in batch processes, using specially well-stirred tank reactors. Among the advantages for carrying out polymerization reactions in batch tank reactors, one may point to the flexibility of producing several types of polymers using the same system. As disadvantages, one may point to the low yield capacity and possible batch-to-batch product quality fluctuations (Schork *et al*., 1993).

The increase in the demand for polymers prompted the development of continuous processes by adapting, initially, the stirred batch tanks. Compared to the batch reactors, continuous stirred tank reactors presented lower operability costs. However, due to pronounced viscous effects found in most polymerization reactions, perfect mixing is usually unattainable and efficient heat transfer rates are very difficult to establish.

Continuous tubular reactors were expected to be a feasible alternative to the continuous stirred tank reactors. Tubular reactors present a large production capacity and exhibit enhanced heat transfer capabilities. However, tubular reactors are vulnerable to deposit of polymeric material on the internal walls, which may result, ultimately, in the reactor plugging. Besides, distortions of the radial velocity profile may produce steep temperature gradients that may lead to ineffective reactor and product quality control (Schork *et al*., 1993).

Loop reactors appeared in this scenario as a potential alternative to carry out polymerization reactions. Loop reactors are tubular reactors in which the ends of the tube are connected to each other. Most applications of loop reactors consists of continuous processes, although batch mode of operation is also possible. The internal recycling of material takes places through an axial pump, responsible for establishing the operating recycle ratio. High internal flow rates prevent the deposit of polymeric material on the reactor walls and, together with the enhanced reactor area/volume ratio, permit efficient heat transfer rates to be attained.

Industrial applications of loop reactors are notoriously restricted to the polymerization of α-olefins (such as polyethylene and polypropylene) in the well-known slurry (Phillips Co.) and liquid pool (Montell Co.) processes (Zacca, 1995). Regarding free-radical emulsion and solution polymerization systems, loop reactors applications have been studied since the early 70s (see, for instance, Lanthier, 1970, Lynn and Huff, 1971, Meyer and Renken, 1990, Abad *et al*., 1994, Araújo, 1997, and Cabral, 1998). Recently, BASF Co. patented a process for the free-radical copolymerization reaction of styrene and acrylonitrile in a loop reactor (Fischer and Baumgartel, 1998). Seemingly, this is the first industrial application of loop reactors for free-radical polymerization reactions.

It is clear from the above paragraphs that loop reactors have potential to play an increasingly role on the polymer industries. But in order to conceive new processes and/or improve current ones, design and process engineers must be concerned with stability issues associated with the system being considered. By stability issues it is meant, basically, problems involving multiplicity of steady-states and onset of periodic oscillations. Steady-state multiplicity is not convenient at an industrial site because of the possible, unexpected occurrence of ignition-extinction phenomena. Oscillations are not desired because they modify continuously the quality of the final material. In general, the reactor stability problem may be posed as follows: *Given the reactor operational parameters and their range of validity, what kind of steady-state and dynamic behavior is expected?*

Regarding the modeling of loop polymerization reactors, Zacca (1991) showed that during the slurry polymerization of ethylene using Ziegler-Natta catalysts, self-sustained oscillatory behavior may be developed. Later, Zacca (1995) showed that as many as five steady-states are possible in the loop reactor and that travelling waves may be found for some process conditions.

More recently, Melo *et al.* (2000) showed that for a wide range of the operational parameters, free-radical loop reactors are likely to present multiple steady-states and oscillatory behavior. Using the reactor average residence time as the main free parameter, they observed the induction of oscillatory behavior by varying the recycle ratio and that the lower the overall heat transfer coefficient the greater are the chances for nonlinear behavior to arise. Besides, it was shown that although steady-state multiplicity region lies in a narrow range of residence times, impurities in the feed may widen this region.

Both Zacca (1991, 1995) and Melo *et al.* (2000) did not pay attention to the role played by the recycling pump on the reactor steady-state and dynamic behavior. However, Melo *et al.* (2001a,b) characterized the residence time distribution and thermal behavior of a lab-scale loop polymerization reactor and observed that the dynamics induced by the recycling pump is of major relevance for the proper description of the process. In addition, Melo *et al.* (2001b) showed that the external thermal capacitance factors of both the reactor and the recycling pump should not be neglected during the modeling of industrial scale reactors.

In the present communication, a bifurcation analysis of the loop polymerization reactor including the axial recycling pump is presented. It is shown that due to the thermal capacitance of the reactor externals, both lab scale and industrial scale loop polymerization reactors are not likely to present periodic oscillations. The free-radical solution polymerization of vinyl acetate in methanol was chosen as a case study.

Polymerization Kinetics & Reactor Modeling

The polymerization mechanism and the reactor mathematical model equations are not presented in this communication due to the lack of space. However, in what follows, a few comments regarding the polymerization chemistry and reactor modeling are made.

The classical free-radical mechanism was used to describe the polymerization reaction chemistry. The basic steps of initiation, propagation and termination (by combination only for vinyl acetate) were considered. In addition, chain transfer to monomer, solvent, polymer and terminal double bond polymerization steps were also taken into account.

The general reactor configuration in sketched in Figure 1. The reactor consists of two tubular sections interconnected by an axial pump. The axial pump is responsible for setting-up the recycle ratio during reactor operation. The recycle ratio (Rec) is defined as the ratio between the flow rate in tubular section 2 and the feed flow rate. Large internal flow rates improve the macroscopic mixing in the reactor.

Each tubular section is described according to the axial dispersion model while the recycling pump is regarded as a continuous stirred tank reactor. In order to solve the model, the method of lines was used to discretize the space coordinate in the model equations and boundary conditions. The resulting set of differential-algebraic equations was solved using the well-known DASSL code (Petzold, 1982).

In addition to the reactor recycle ratio, other reactor model parameters of fundamental importance are the reactor average residence time, the heat transfer coefficients and the external thermal capacitance factors for both the reactor and the recycling pump (ε_r and ε_p, respectively). The external thermal capacitance factors represent the ratio of the thermal capacitance of externals (e.g., tube walls, connections, valves, recycling pump, *etc.*) to that of the reaction mixture. As it will be presented below, the larger the magnitude of these factors, the greater is their effect on the steady-state and dynamic behavior of the system.

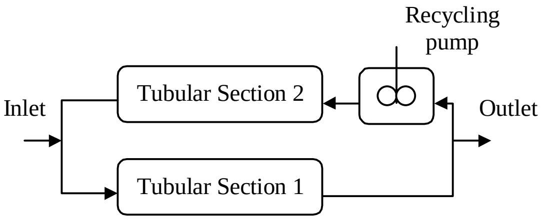

Figure 1 – Loop reactor flowsheet.

In the following section, the reactor average residence time is used as the main free-continuation parameter. It is intended to show the effect of both the heat transfer coefficients and the external thermal capacitance factors on the structure of the bifurcation diagrams. In order to perform the analysis, the continuation package AUTO (Doedel *et al.*, 1997) was used. Throughout the rest of this communication the following notation (——), (----), and (■) will be used to represent stable and unstable branches of steady-state solutions, and Hopf bifurcation points, respectively.

Results & Discussion

Table 1 provides the simulation data used in this work. The values presented in Table 1 are in accordance to the experimental lab-scale loop reactor described by Melo *et al.* (2001a,b). Figure 2 presents a typical bifurcation where the effect of the heat transfer coefficient in the recycling pump ($(UA)_p$) is varied. It may be observed that for lower values of this coefficient, there is a large region of residence times in which self-sustained periodic oscillations are possible. This is the region located between the pair of Hopf bifurcation points. As $(UA)_p$ increases, oscillations are no longer expected because the pair of Hopf bifurcation points coalesces and vanishes.

Table 1 – Reactor operational parameters.

Definition	Value	Unit
Total length of tubular sections	317.2	cm
Diameter of tubular sections	1.7272	cm
Feed temperature	42	^oC
Coolant temperature	55	^oC
Heat of polymerization	21	kcal/gmol
Feed monomer concentration	7.3×10^{-3}	$gmol/cm^3$
Feed solvent concentration	7.3×10^{-3}	$gmol/cm^3$
Feed initiator concentration	3.0×10^{-5}	$gmol/cm^3$
Mass Peclet number	10	-
Thermal Peclet number	0.1	-
Reactor heat transfer coefficient	2.0×10^{-4}	cal/cm^2sK

In Figure 3, it is presented the effect of the external thermal capacitance factors on the bifurcation diagram. Figure 3a shows that, when the external thermal capacitance factors for both the reactor and the pump are not considered, oscillatory behavior in the loop reactor may be expected within a large region of residence times, as long as the reactor and pump heat transfer coefficients are chosen conveniently. In Figure 3b, the external thermal capacitance for the pump remains zero while ε_r is set to 0.25. In this case, oscillations are no longer expected. Figure 3c shows that when ε_p is set to 6.0 while keeping ε_p equal to 0.0, again the possibility of reactor oscillatory behavior is annihilated.

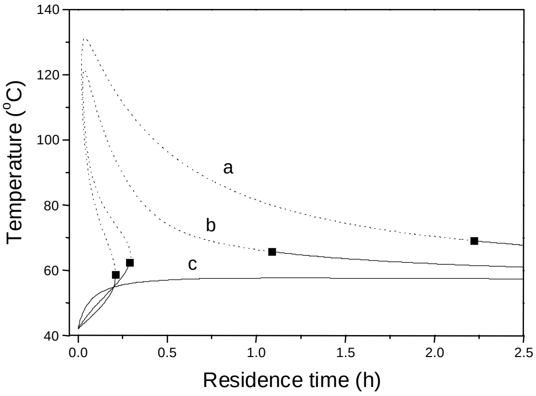

Figure 2 – Bifurcation diagram of the loop reactor – effect of the heat transfer coefficient in the recycling pump (Rec=50, a: $(UA)_p$=0.2cal/sK, b: $(UA)_p$=2.0 cal/s/K, and c: $(UA)_p$=10.0cal/sK).

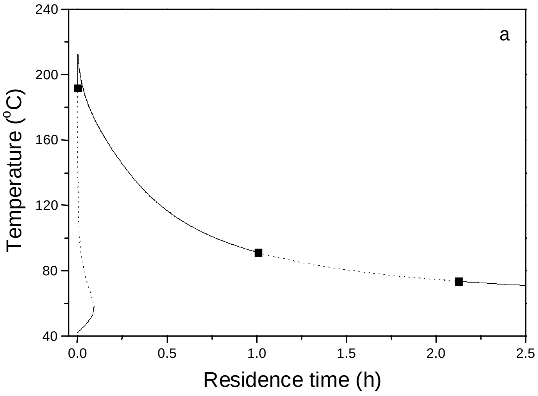

Figure 3 – Bifurcation diagram of the loop reactor – effect of the external thermal capacitance factors (Rec=50, $(UA)_p$=0.2cal/sK, a: ε_r=0.0, ε_p=0.0).

Experimental values for the recycling pump heat transfer coefficient and the external thermal capacitance factors were obtained by Melo *et al.* (2001b). Melo *et al.* (2001b) ran thermal experiments in the absence of chemical reaction in a lab-scale loop reactors, at conditions similar to the those presented in Table 1. They found that the heat transfer coefficient in the pump may be as large as 71.6cal/sK and that the external thermal capacitance factors values (ε_r=26.13 and ε_p=1161.98) are extremely high. Based on these values and the diagrams presented above, it may be concluded that at lab-scale, self-sustained oscillatory behavior is not expected in loop reactors.

Now, considering a loop reactor with industrial dimensions (e.g., length and diameter of tubular sections equal to 178m and 0.6m, respectively), Melo *et al.* (2001b) evaluated that for a wall thickness of 0.635cm then ε_r=0.37 and a wall thickness of 6.35cm results in ε_r=4.1. These estimates may be said to represent minimum values for ε_r because only the reactor walls were considered in the calculation.

Therefore, proper estimation of ε_r for an industrial scale loop reactor would to lead to much larger values. Again, based on the diagrams and analysis presented above, it may be conjectured that even industrial scale loop reactors are not likely to present oscillatory behavior.

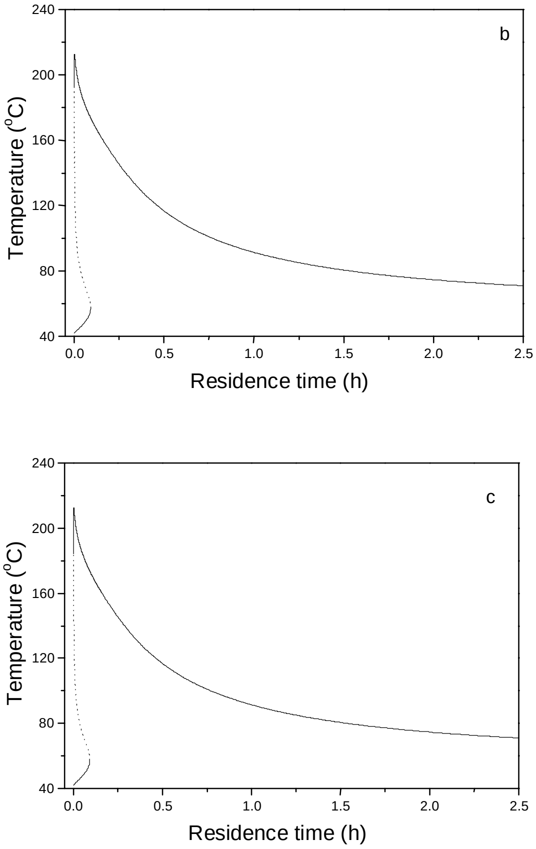

Figure 3 – Continuation (Rec=50, $(UA)_p$=0.2cal/sK, b: ε_r=0.25, ε_p=0.0, and c: ε_r=0.0, ε_p=6.0).

Conclusions

Novel results regarding the bifurcation behavior of loop reactors have been presented in this communication. Because the recycling pump was considered during the stability analysis of the reactor, it was possible to show that a large heat transfer coefficient in this piece of equipment may eliminate the possibility of self-sustained, periodic reactor behavior. In addition, the same effect was observed when the external thermal capacitance factors are also considered. The external thermal capacitance factor for an industrial scale reactor considering only the reactor walls was found to be up to one order of magnitude greater than the minimum value necessary to extinguish the oscillations in the lab-scale reactor. Thus, considering that the external thermal capacitance factor for the industrial scale loop reactor may increase significantly when other pieces of equipment (valves, connections, recycling pump, *etc.*) are accounted, also in these reactors periodic oscillations are not likely to occur.

Future Work

It is believed that the conclusions drawn here are valid for olefin loop polymerization reactors. The mathematical model developed here has been extended in order to describe the polymerization of propylene in a loop reactor. Currently, a full bifurcation analysis of this system in under investigation.

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