

Nonlinear Behaviour of a Low-Density Polyethylene Tubular Reactor-Separator-Recycle System

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Abstract

The aim of this work is to analyse the nonlinear behaviour of a low-density polyethylene reactor-separator-recycle system. A simplified dynamic model is derived based on the detailed model presented in Häfele (2004). A numerical bifurcation and stability analysis is performed to predict the region of stable operation. As a result multiple steady states and oscillatory behaviour were found. The implications of these findings for practical process operation are discussed.

Keywords: polymerisation, tubular reactor, low-density polyethylene(LDPE), nonlinear dynamic model, nonlinear analysis

1. Introduction

A distributed parameter dynamic model of an industrial scale low-density polyethylene process was developed by Häfele (2004). The resulting set of partial differential and algebraic equations were transformed into a DAE system with order of 30000 using an adaptive method of line approach (Häfele et al., 2004). Dynamic simulations demonstrated that the mass recycle has strong influence on the process dynamics such that it increases the time constant of the overall process significantly and gives rise to intricate nonlinear behaviour including thermal runaway phenomena. In practice the reactor is stabilized under this condition using suitable means of control. Since open loop operation is also of major practical interest, a further investigation of the nonlinear dynamic behaviour is presented in this study.

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Recent studies on the nonlinear behaviour of coupled reactor-separator-recycle networks have shown that multiple steady states and instabilities have their origins in mass recycles alone where energy feedback was excluded by means of heat exchangers (Pushpavanam and Kienle (2001); Kiss et al. (2003)). Pushpavanam and Kienle (2001) studied a first order exothermic reaction in a CSTR-separator network with mass recycle. It was found that the behaviour of such a system strongly depends on the mode of operation whether the feed flow rate or recycle flow rate is controlled. Severe operational problems including monotonic and oscillatory unstable steady states were found for fixed feed flow rates. It was concluded that fixed recycle flow rates should be preferred for feasible steady state plant operation.

Nonlinearity analysis for a plug flow reactor-separator-recycle polymerisation system with a fixed feed flow rate was presented by Kiss et al. (2003). They found that state multiplicity is a common feature of consecutive-autocatalytic reactions. In an application study considering a low density polyethylene process, they predicted the existence of multiple steady states and that a large range of conversion corresponded to an unstable point. However, their analysis was based on a steady state model. Hence, the stability and dynamic behaviour in the region of multiple steady states was not studied.

In the present study, first a simplified model is presented and compared to the detailed dynamic model of Häfele (2004). A numerical bifurcation and stability analysis is performed to predict the region of stable operation. As a result multiple steady states and oscillatory behaviour were found. The implications of these findings for practical reactor operation are discussed.

2. Process description

A simplified flow diagram of the low-density polyethylene plant is shown in Figure 1. It consists of a tubular reactor, a flash unit and a recycle stream. A detailed flow sheet of the LDPE plant is given in Häfele (2004).

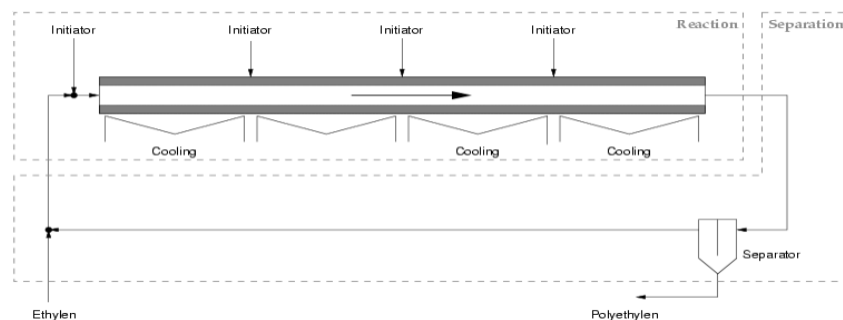


Figure 1. Simplified flow sheet of the LDPE plant

The polymerization process is carried out at pressures up to 3000 bar. The tubular reactor considered in this study has a length of 1000 m. Despite the length of the reactor, conversion is kept low, about 20-30% due to the high exothermic reaction of the polymerisation. Unreacted monomer is separated from the product in the flash unit and recycled to the inlet of the reactor. The reaction is started by the addition of different initiators, which selectively decompose into radicals at different temperatures. The radicals start the chain growth by forming longer radicals. The excess heat is removed by means of cooling jackets around the reactor. Moreover a distributed injection of the initiator distributes the reaction along the tube.

3. Mathematical Model

The reactor model takes account of the main reactions which are common for free radical polymerisation as shown in Table 1. These are decomposition of the initiator, initiation of the chain growth, chain growth reaction and termination by either combination or disproportionation. In Table 1, I represents the initiator, I^* is the initiator radical, M is the monomer, R is the growing or live polymer radical, P is the dead polymer, n and m denote the degree of polymerization. Kinetic rate expressions in Table 1 are taken from the literature.

Table 1. Reaction mechanism

Initiator decomposition	$I \xrightarrow{k_{dl}} 2I^*$	$k_{dl} = 1.35 \times 10^{13} \exp\left(\frac{-117476 - 0.2805 \times 10^{-5} P}{R_g T}\right)^a$	(1/s)
		$k_{dH} = 2.89 \times 10^{14} \exp\left(\frac{-138237 - 1.012 \times 10^{-5} P}{R_g T}\right)^a$	(1/s)
Initiation	$I^* + M \xrightarrow{k_i} R_i$	$k_i = k_p$	
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$	$k_p = 5.88 \times 10^4 \exp\left(\frac{-29704 + 2.325 \times 10^{-5} P}{R_g T}\right)^b$	(m ³ /gmol s)
Termination by combination	$R_n + R_m \xrightarrow{k_c} P_{n+m}$	$k_c = 1.075 \times 10^6 \exp\left(\frac{-1247 + 1.422 \times 10^{-5} P}{R_g T}\right)^b$	(m ³ /gmol s)
Termination by disproportionation	$R_n + R_m \xrightarrow{k_{dt}} P_n + P_m$	$k_{dt} = k_c$	

^a reference: Kim and Iedema (2004)

^b reference: Lee and Marano (1979)

The dynamic model of the LDPE process is based on the mass and energy balances. The following assumptions hold : one phase flow (supercritical); no axial dispersion; constant pressure drop; constant coolant temperature; constant physical properties; negligible time delay and constant temperature in the recycle; negligible energy balance on the coolant medium and the reactor wall; ideal separation in the flash unit. Two types of initiators are used by employing the low temperature initiator at the first injection point and the high temperature initiator at later injection points.

The dynamic model of the tubular reactor is developed for one section of the reactor which comprises one coolant cycle; hence the whole reactor consists of four sections. The general structure of the model equations as follows:

$$\frac{\partial \underline{x}}{\partial t} + v \frac{\partial \underline{x}}{\partial z} = \underline{S}[\underline{x}] + U[\underline{x}], \quad 0 < z < L \quad (1)$$

$$BC : \underline{x}(0, t) = \underline{x}_{in}(t); \quad IC : \underline{x}(z, 0) = \underline{x}_0(z)$$

Where v is the axial velocity of flow; z is the axial coordinate; L is the total length of a reactor section and t is the time. The state vector $\underline{x}$ consists of the temperature and concentrations of monomer, initiators, initiator radicals, moments of living and dead polymer chains. $\partial \underline{x} / \partial t$ is the rate of accumulation, $\partial \underline{x} / \partial z$ is the rate of convection. $\underline{S}[\underline{x}]$ represents sources and sinks due to chemical reactions. $U[\underline{x}]$ is the heat transfer term.

$$S[x] = \sum_{j=1}^J v_{ij} r_j, \quad i=1, \dots, NC \quad (\text{for the mass balances}) \quad (2)$$

$$S[x] = \Delta H_r \sum_{j=1}^J r_j \quad (\text{for the energy balance}) \quad (3)$$

$$U[\underline{x}] = u(T - T_c) \quad (4)$$

Where v is the stoichiometric coefficient, j is the index for reaction, u is the heat transfer coefficient, ΔH_r , is the heat of reaction. In Equation (3) equal heat of reaction for propagation, initiation and termination reactions is assumed. Furthermore the method of moments is used to represent the progress of the reaction in terms of the leading moments of the chain length distribution of the “live” and “dead” polymer chains. These moments are defined by the following equations:

$$\lambda_i = \sum_{k=1}^{\infty} k^i [R_k] \quad \text{and} \quad \mu_i = \sum_{k=2}^{\infty} k^i [P_k] \quad (5)$$

where λ_i and μ_i are the i^{th} moment of the living polymer and the dead polymer respectively. The moments will close for the considered reaction mechanism. For the purpose of stability analysis only zeroth moments are employed in the model. Mass and energy balances for both flash and mixer are assumed to be quasi-stationary. Hence the simplified model results in a system of partial differential and algebraic equations (PDAE) with 24 PDE. Subsequently it is transformed into a DAE system (with the order of 1200) by using a finite difference approximation on equidistant grid. Then it is solved within the simulation environment DIVA which also provides continuation methods for the numerical bifurcation analysis as explained in Mangold et al. (2000).

4. Results

In this section, the results of the steady state and dynamic simulations and numerical bifurcation analysis are presented. First of all the simplified model is validated by

comparing to the detailed model. In Figure 2 it is shown that the temperature profile of the simple model agrees reasonably well with the detailed model. A constant heat transfer coefficient used in the simple model is the main reason for the large deviation through the end of reactor. The agreement between two models can be improved by correlating the heat transfer coefficient to the polymer concentration along the reactor in order to take account decreasing heat transfer due to increasing polymer chain lengths.

Dynamic simulations of the detailed model demonstrated that the mass recycle has strong influence on the process dynamics such that it gives rise to intricate nonlinear behaviour including thermal runaway phenomena (Häfele, 2004), which can be prevented by proper control actions in practice. Transient behaviour of the simple model also agrees with this result. Figure 3 shows the response of the reactor temperature to a 10 % and 20 % decrease in the fresh feed flow-rate, indicated with the dashed and continuous lines respectively. For the later case the system temperature runs away. This phenomenon may be explained by means of stability analysis in the following paragraph.

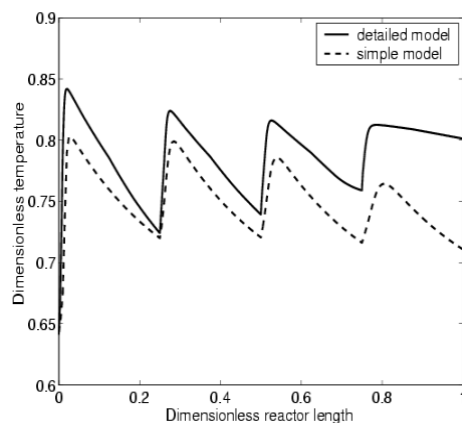


Figure2. Steady state temperature profile

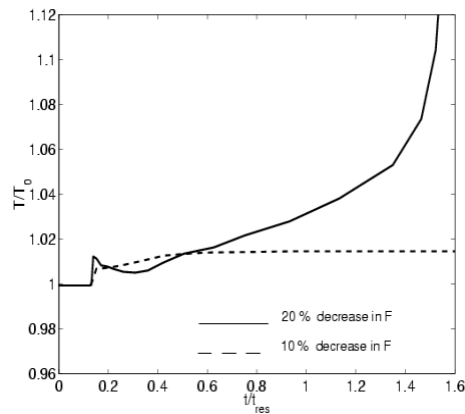


Figure3. Dynamic temperature response

Next, the stability analysis is carried out to predict the multiple steady states, unstable or oscillation regions of operation. The important parameters that influence the stability are the feed flow-rate (residence time), heat transfer coefficient and initiator concentrations. In this study we present the results that were obtained if the residence time is considered as a continuation parameter. As shown in Figure 4a the simplified model predicts typical S-shaped multiplicities. The branches of stable and unstable solutions are represented by the solid and dashed lines respectively. The current nominal operating point is illustrated as a circle on the lower stable branch. The bifurcation diagram shows five fold points corresponding to three nested hysteresis loop. It is worth noting that no steady state solution exists for very low residence times, which is in agreement with the results of Kiss et al. (2003). Stable branches above the conversion level of 0.26 are not feasible because of corresponding high temperature

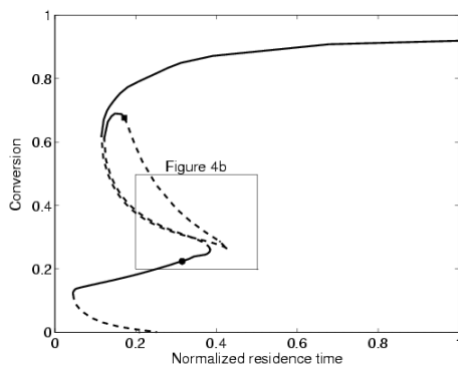


Figure 4a. Bifurcation diagram

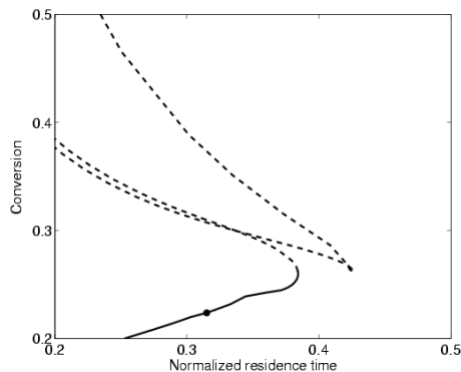


Figure 4b. Bifurcation diagram

values. The highest conversion achievable for economically reasonable operation is found to be 0.26 whereas in commercial plants it is more than 0.30. However, at this operating point a small increase of the residence time may drive the reactor to the upper stable branch where the temperature is far above its upper limit for a safe operation. This behaviour is also demonstrated in the dynamic simulation results in Figure 3. At the Hopf bifurcation point (shown as a filled square in Figure 4a) one gets large amplitude oscillations of temperature and concentrations but because of very high temperatures this branch is not feasible as mentioned above. Furthermore multiplicity regions in a two dimensional cross-section of the parameter space can be mapped out by the two parameter continuation of the limit points of Figure 4 by using DIVA.

5. Conclusions

In this study the nonlinear behaviour of the tubular reactor-separator-recycle system was investigated. The simplified model takes account only the main features of the detailed model. Nevertheless it was shown that the simple model agrees at least qualitatively well with the detailed model. As a result of stability analysis multiple steady states and oscillatory behaviour were found. The implications of these findings for practical reactor operation were discussed. In the future the influence of the other important parameters such as overall heat transfer coefficient and initiator feed concentration will be studied.

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