

Simulation and Nonlinear Analysis of the Stagnant Polymer Layer in a LDPE Tubular Reactor

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Abstract

The formation of polymer rich layers close to the wall of a LDPE tubular reactor is studied. A CFD simulation of a detailed single-phase reactor model reveals the coexistence of two steady states, a polymer-lean one and a polymer-rich one. A bifurcation analysis of a strongly simplified version of the reactor model indicates that diffusion effects may be responsible for the bistability.

Keywords: LDPE, polymerization, reactor fouling, CFD simulation, bifurcation analysis.

1. Introduction

Low-density polyethylene (LDPE) is one of the most widely used thermoplastics. It is often produced in tubular reactors of several thousand meters length under high pressure. One problem that occurs during operation of these reactors is the formation of a highly viscous, polymer-rich layer at the reactor walls, the so-called reactor fouling (Mähling et al., 2000; Zhou et al., 2001; Buccelli et al., 2005). The polymer layer impedes the heat transport and therefore has to be removed periodically. In practice this is done based on empirical rules, either mechanically by opening an exit valve and using the sudden pressure drop to blow out the foulant (“reactor bumping”) or thermally by increasing the wall temperature. A deepened understanding of the foulant layer formation and a more systematic defouling strategy, based on a process model and feedback control, is desirable.

In this work the formation of a stagnant polymer layer close to the reactor wall is analyzed by two model variants. The first model is a detailed single-phase CFD model comprising compressible Navier-Stokes equations for the flow field, component mass balances for the relevant reacting species, and an energy balance. The second variant is a simple isothermal one-dimensional model, which is meant to capture the interactions between flow velocity, varying viscosity, diffusion and chemical reaction in a qualitative way.

The models indicate a possible coexistence of two steady states, one with a foulant layer and one without. To our knowledge, this effect has not been reported before and adds to the knowledge on nonlinear effects in LDPE tubular reactors provided by other authors like Kiparissides et al. (1993), Tsai and Fox (1996), Häfele et al. (2005), Häfele et al. (2006), Disli and Kienle (2011).

2. Detailed LDPE Reactor Model

This contribution studies fouling effects in a single-phase high-pressure tubular reactor with free-radical LDPE polymerization. The model geometry is a two-dimensional axisymmetric cylinder with the diameter of 4 cm and a length of 32 m. The left tube orifice has inlet boundary conditions with a constant inflow velocity of 10 m/s, the right one is an outlet with a fixed outlet pressure. No-slip boundary conditions are applied at the interface to the reactor wall. The reactor wall is further attached to a cooling system.

The model governing equations are balance equations for mass, momentum, energy and species with non-constant thermodynamic properties. Empirical expressions for the density, specific heat capacity, thermal conductivity and viscosity of the ethylene-polyethylene mixture are taken from (Bucchelli et al., 2005). The balance equations result in the compressible Reynolds-averaged Navier-Stokes equations with the $k-\omega$ SST turbulence model (Menter, 1994). Turbulent momentum, heat and mass transfers are related with help of Reynolds analogy that introduces turbulent fluxes in mass and energy balance equations. The reaction kinetics are based on a simplified LDPE reaction scheme (Häfele et al., 2006) and contain reactions for initiator decomposition, chain initiation, initiation by modifier, chain propagation, terminations by coupling and disproportion, and chain transfer to modifier. The partial mass balance equations are written in terms of mass fractions of initiator, initiator radical, modifier, modifier radical, monomer, living and dead polymers. The polymer mass fractions are zero moments of the mass fraction distributions summed up over all chain lengths. Diffusion fluxes are modelled by the Fickian approach with constant diffusion coefficients. The cooling system is assumed to have a constant cooling temperature and a constant heat transfer coefficient.

Numerical analysis of the detailed model has been performed in the OpenFOAM CFD toolbox (Jasak, 1996). The aim of the analysis is to show that the formation of the fouling layer near the reactor wall may be described by a single-phase model. Figure 1 presents typical profiles for the dead polymer mass fraction ω_D and the temperature T of steady-state solutions coexisting for a set of identical model parameters. Profiles on the left-hand side correspond to a polymer-lean mode in the reactor, and profiles on the right-hand side correspond to a polymer-rich mode. In the polymer-rich mode the turbulent heat transfer is reduced and this leads to a deterioration of cooling and consequent increase of the temperature in the reactor. The dependency of stable steady-state solutions on model parameters can be obtained by slowly varying a parameter and doing a dynamic simulation until the model settles to a new steady state. Such kind of analysis has been applied to the detailed LDPE reactor model. The initiator mass fraction ω_R at the inlet has been used as a bifurcation parameter. Results are presented in Figure 2. The existence of a region with multiple steady states can be seen clearly.

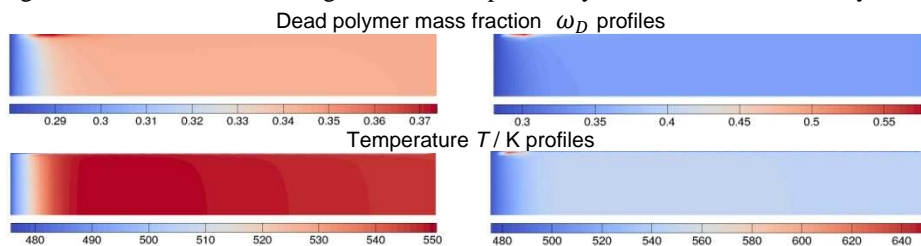


Figure 1: Coexisting steady-state profiles of a polymer-lean (left) and a polymer-rich (right) solution for $\omega_R = 1.5 \times 10^{-4}$ at the inlet

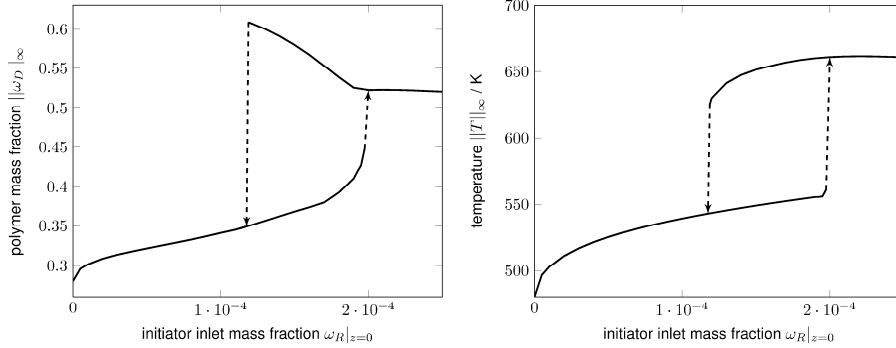


Figure 2: Norms of steady-state solutions as a function of ω_R at the inlet

3. Simplified Model and Nonlinear Analysis of the Stagnant Layer

In the following an attempt is made to give a qualitative physical explanation of the nonlinear behaviour found in the numerical studies of the previous section. We introduce a simple isothermal one-dimensional model of a polymerization reactor, which is meant to capture the interactions between flow velocity, varying viscosity, diffusion and chemical reaction in a qualitative way. This simple model enables us to study basic principles of foulant layer formation and its dependency on key model parameters. We consider one-dimensional flow in a channel between two parallel plates and assume that there are separate flow layers, a center flow layer and a wall flow layer. The center layer represents the bulk flow of the fluid, while the wall layer captures a possibly polymer rich layer. Using symmetry assumptions we can reduce our considerations to a half-channel spanning from one wall to the center plane of the channel (see Figure 3).

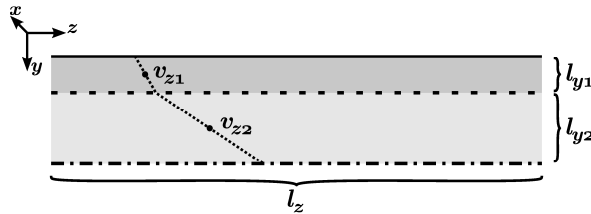


Figure 3: Geometry of a half-channel with wall, wall flow layer and center flow layer (from top to bottom). The flow direction is from left to right.

The following assumptions are used to obtain the simplified model. Each flow layer is ideally mixed in all directions but the flow direction. Mass exchange between the flow layers is only due to diffusion. Mass transport in flow direction is caused only by convection. The convective flow is driven by a constant mass flow and assumed to be quasistationary. The flow velocity has zero gradient in flow direction and is piecewise linear in the direction perpendicular to the wall plates. There is momentum transfer by laminar friction between the wall and the wall layer as well as between the two flow layers. The temperature and the density of the fluid are taken as constant. The viscosity

of the fluid and the reaction rates are determined, assuming constant pressure, by the same correlations as used in Section 2. The reaction mixture mainly consists of the primary components polymer and monomer, as well as some minor secondary components. If we assume the diffusion to be independent on the chain-length of the polymer, we can treat the polymer as a single pseudo-component. The mixing of the two primary (pseudo-)components is described by Fickian diffusion in this model. We also use Fickian diffusion for the diluted minor components. The diffusion coefficients are constant to further simplify the diffusion mechanism. We use the same reaction scheme as in Section 2.

The simple model is able to predict a bistable behaviour similar to what was found in the detailed model in Section 2. Typical steady-state profiles with and without the formation of a polymer-rich, stagnant wall layer are shown in Figure 4 and Figure 5, respectively. These figures correspond to different steady-state solutions for the same parameter set, as can also be seen from the bifurcation diagram in Figure 6 (a).

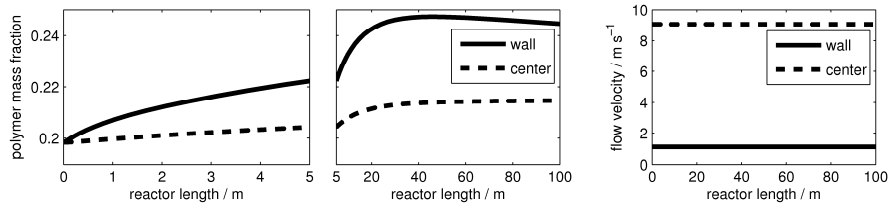


Figure 4: Mass fractions of polymer along and flow velocities in layer 1 and 2 for steady state A in Figure 6 (a). The wall flow layer has a slightly increased polymer mass fraction. There is no distinctive foulant layer.

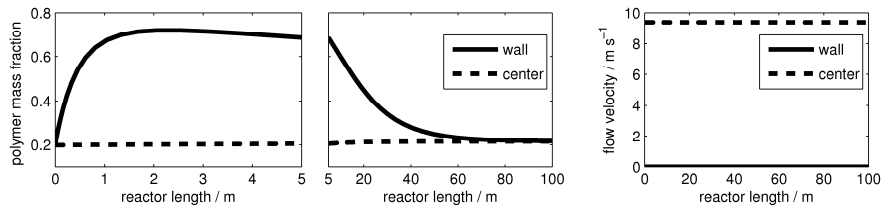


Figure 5: Mass fractions of polymer and flow velocities in layer 1 and 2 for steady state B in Figure 6 (a). The wall flow layer has a high polymer mass fraction and is almost stagnant.

Based on the results with the simple model we propose a self-accelerating process as a potential source of the bistability. A lower flow velocity close to the reactor wall leads to a higher residence time, a higher monomer conversion, and hence a higher polymer concentration near the wall. This leads to an increased viscosity that slows down the flow velocity further. The diffusion of the initiator into the region close to the wall sustains this mechanism, while the interdiffusion of polymer and monomer counteracts this mechanism by dissolving the polymer “clog”.

To understand the dependence of the steady-state multiplicity on diffusion effects in more detail, the diffusion coefficient for the primary components is taken as an additional bifurcation parameter, as it determines how fast excess polymer is transported from the wall layer to the bulk flow. The resulting multiplicity region is depicted in Figure 6 (b). For high inlet concentrations and low diffusion coefficients, there are steady-state solutions with a polymer-rich, stagnant wall layer. For low inlet

concentrations and high diffusion coefficients, the difference between the wall layer and the bulk flow is much smaller. For parameter values in between, the two cases either coexist or are not clearly distinguishable any more. The steady-state multiplicity is restricted to a parameter region at low initiator inlet concentrations and low primary component diffusion coefficients. In the case of steady-state multiplicity, the diffusion coefficient of the primary components is significantly lower than that of the initiator. This presumes a very low mobility of the polymer chains compared to the mobility of the diluted initiator molecules in the mixture, which seems quite realistic due to the large differences in size of the initiator and of the polymer molecules.

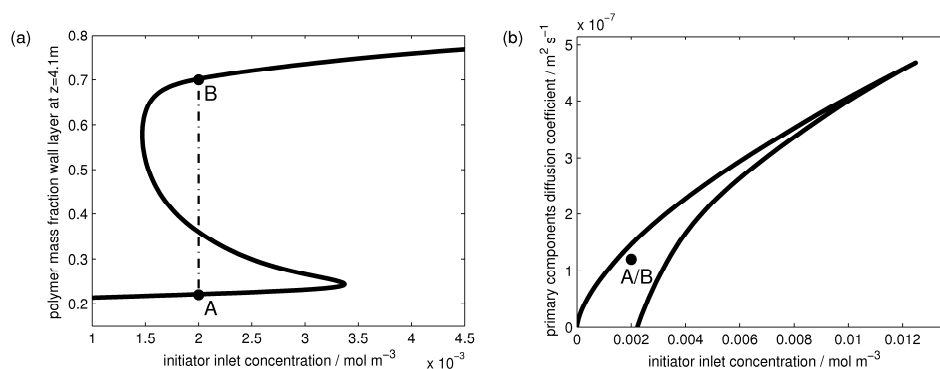


Figure 6: (a) Steady-state solutions of the simplified model with initiator inlet concentration as bifurcation parameter. A and B are the steady-state solutions shown in Figure 4 and 5. (b) Multiplicity region in the parameter space with initiator inlet concentration and diffusion coefficient of the primary components as bifurcation parameters.

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