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Modelling and Simulation of High Pressure Industrial Autoclave Polyethylene Reactor

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High-pressure technology for polyethylene production has been widely used by industries around the world. A good model for the reactor fluid dynamics is essential to properly set the operating conditions of the autoclave reactor. The high-pressure autoclave reactor model developed in this work is based on a non-isothermal dynamic model, where PID control equations are used to maintain the operation at the unstable steady state. Kinetic mechanisms to describe the polymerization rate and molecular weight averages are presented. The model is capable of computing temperature, concentration gradients and polymer characteristics. The model was validated using industrial data, presenting good representation of the behavior of the autoclave reactor used in ethylene homopolymerization.

1. Introduction

Low density polyethylenes are used in a large variety of applications. Generally they are produced in either autoclave type or tubular reactors. This work develops a mathematical model for the production of low density polyethylene in an industrial high-pressure autoclave reactor. The system modeled in this work consist of a series of two autoclave reactors with a length to diameter ratio of 15.2. Mixing in both reactors is provided by a shaft running down the center of the reactor with several impeller blades.

The mixing pattern in the high-pressure reactor makes it behave more like a continuous stirred tank reactor (CSTR) rather than a tubular reactor. In the first reactor a baffle is placed near the end of the reactor as to reduced the backmixing of the product at the last part of reactor 1. Heat transfer through the walls is limited, so that the reactor is essentially adiabatic and cooling is provided by the inflow of cold monomer. The inflow of initiator at several points down the reactor provides control of the temperature which may vary down the length of the reactor. A scheme of the modeled high-pressure reactor is shown in Figure 1.

Ethylene free radical polymerization mechanism and kinetics has been outlined by Zabisky et al. (1992) and the outlines of the mixing model for the high-pressure autoclave reactor has been proposed by Chan et al. (1993). The autoclave reactor presents several complications such as nonideal mixing, presence of unstable steady states, possibility of gel formation and reaction in two phases (monomer rich phase and polymer rich phase).

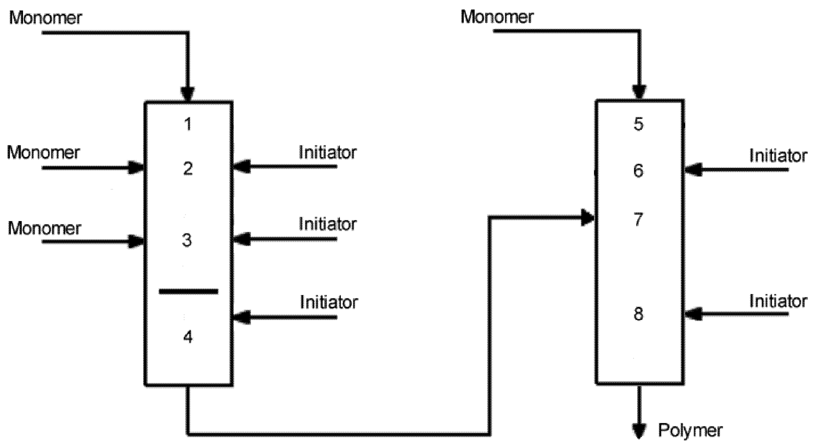


Figure 1. Industrial high-pressure reactor.

2. Mixing Model

The mixing pattern in an autoclave type reactor tends to be of a recirculating nature. The effect of mixing on reactor performance is very important, especially since an imperfectly mixed vessel requires more initiator per unit of polymer produced than does a more perfectly mixed reactor under the same conditions (Georgakis & Marini, 1982). The initiator tends to decompose near the feed points, and not in the bulk of the reactor, thus not promoting as much polymerization as if the initiator was uniformly distributed throughout the reaction mixture. The temperature gradients down the reactor also suggest imperfect mixing (Chan et al, 1993).

In order to account for the imperfect mixing in the reactor, the autoclave reactor can be subdivided into several sections which can be represented by a series of small reactors consisting of a CSTR segment followed by a plug-flow segment to account for the temperature gradients down the reactor. This plug-flow segment can be transformed into a series of small volume CSTRs in order to avoid solving partial differential equations. To account for the back mixing promoted by the impeller blades, each main CSTR segment of the reactor is allowed to recycle part of its volume back to the previous CSTR main segment (Figure 2).

The model developed for the reactor is a dynamic model and includes temperature controller equations to maintain the operation point at the desired steady state. This is needed because the industrial reactor normally operates at an unstable steady state in which the operation can either cause the temperature to rise or cool down the reactor until no polymerization occurs.

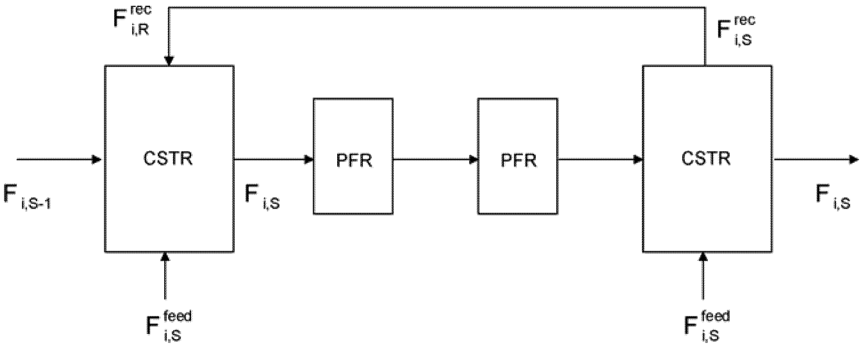


Figure 2. Mixing model.

The mass balance for a species in a volume segment of the reactor is given by:

$$\frac{dN_{i,S}}{dt} = F_{i,S}^{feed} + F_{i,S-1} + F_{i,R}^{rec} - F_{i,S} - F_{i,S}^{rec} + r_{i,S} \cdot V_{i,S} \quad (i, S \geq 1) \tag{1}$$

The plug-flow segments have no feed streams nor have any stream leaving as recycle to other segments. To investigate the effect of the macromixing parameters on the reactor fluidodynamics, two main parameters are defined: volume fraction of the CSTR segment to the total volume of the section ( ) and the recycle ratio ( ).

$$\theta = \frac{V_{S,CSTR}}{V_{S,TOTAL}} \tag{2}$$

$$\beta = \frac{Q_S^{rec}}{Q_S + Q_S^{rec}} \quad (S \geq 1) \tag{3}$$

These parameters have to be estimated for each reactor and for each section in the reactor. Larger   denotes the more the section resembles an ideal CSTR, while larger   denotes higher axial mixing of contiguous sections.

The energy balance for the reactor requires to account for the inflows, outflows, recycles and the reaction in each segment. The reactor was assumed to be adiabatic and cooling is supplied by cold monomer feed. Heat generation is considered to come from the propagation reaction only.

$$\begin{aligned}(\rho_S \cdot C_{p_S} \cdot V_S)\frac{dT_S}{dt} = {} & \rho_S^{feed} \cdot Q_S^{feed} \cdot Cp_S^{feed} \cdot (T_S^{feed} - T_{ref}) + \rho_{S-1} \cdot Q_{S-1} \cdot Cp_{S-1} \cdot (T_{S-1} - T_{ref}) \\ & + \rho_R^{rec} \cdot Q_R^{rec} \cdot Cp_R^{rec} \cdot (T_R^{rec} - T_{ref}) - \rho_S \cdot Q_S \cdot Cp_S (T_S - T_{ref}) \\ & - \rho_S^{rec} \cdot Q_S^{rec} \cdot Cp_S^{rec} \cdot (T_S^{rec} - T_{ref}) - \Delta H \cdot r_S \cdot V_S \end{aligned} \tag{4}$$

Temperature control is done by manipulating the initiator feed based on the actual temperature in some measured segments of the reactor and on the temperature set point. The controller applied to the reactor was a continuous proportional-integral-derivative type and 5 controllers were used to control the initiator feed into the segments 2, 3, 4, 6 and 8.

$$\Delta F_I = K_c \cdot \left[(E_n - E_{n-1}) + \frac{\Delta t}{\tau_i} \cdot E_n + \frac{\tau_d}{\Delta t} \cdot \left(E_n - 2 \cdot E_{n-1} + E_{n-2} \right) \right] \tag{5}$$

Ethylene free radical polymerization mechanism and kinetics has been outlined by Zabisky et al. (1992) and Chan et al. (1993) for a two phase kinetic mechanism where a monomer and a polymer rich phase exist in the reaction mixture. Herein, a homopolymer that presents only one phase in the reactor (monomer rich phase) was studied and therefore the momentum equations to account for the molecular weight of the polymer were adapted from Zabisky et al. (1992) for a one phase kinetic mechanism.

The kinetic mechanism considers the initiation of radical by thermal decomposition of the initiator, chain propagation, termination by combination and disproportionation, transfer to monomer and to polymer, -scission of terminal radicals and backbiting.

The transfer to polymer reaction leads to polymer moment equations that are not closed, where the ith moment depends on the (i+1)th moment. To solve this problem, the closure technique of Hulburt and Katz (1964) was used in the model to calculate the third moment of the polymer distribution, as recommended by Zabisky et al. (1992). The kinetic parameters used in the simulations are based on the data published by Zabisky et al. (1992) and Chan et al. (1993). The full dynamic mathematical model was comprised of 308 ordinary differential equations to calculate the material balance of all components, the energy balance and the population balance (via method of moments). The model was solved using a 5th order Runge-Kutta integration method with variable integration step.

3. Results

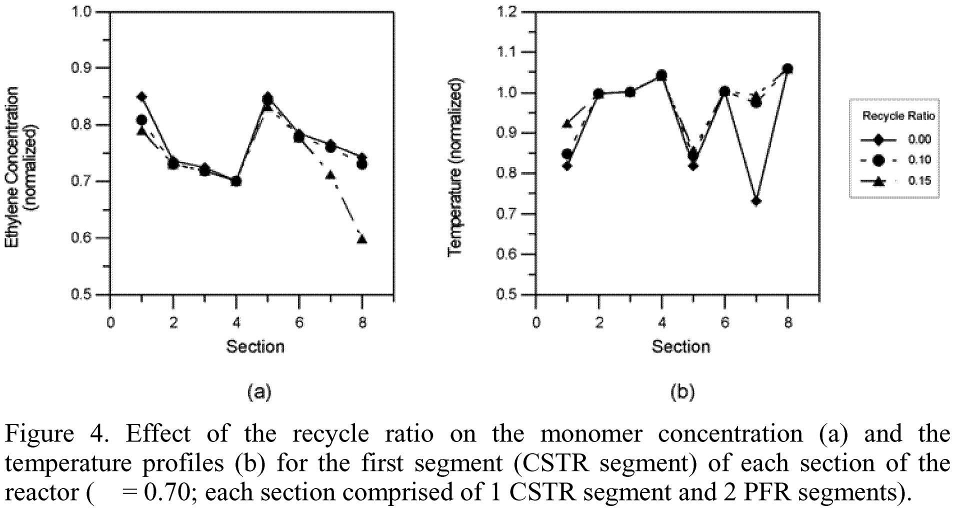
Industrial production recipes from Politeno (Brazil) were used for simulation. Validation of the model were done by comparing the values predicted by the model with observed industrial steady-state values for monomer profile, initiator flow rates, temperature profile and final product characteristics. The industrial reactor was divided into eight sections to be simulated. The volumes of the reaction sections were 16.8, 13.7, 12.8, 13.3, 16.8, 8.3, 15.3 and 3.0% of the total volume of the reactor. The monomer feed distribution assumed that 12.5, 25.0, 50.0 and 12.5% of the total monomer feed entered the first segment of sections 1, 2, 3 and 5 respectively. The initiator was fed into the first segment of sections 2, 3, 4, 6 and 8. The reactor operated at pressure of 1600 atm and the temperature of the ethylene feed was of 353 K. The temperature at the third segment of sections 2, 3, 4 and 6 and 8 were controlled at 513, 513, 537, 513 and 531 K, respectively. Temperature control is a key factor for the operation of the autoclave reactor and it is very important that the controller manages to control the temperature within a short time spam. The PID controller implemented in the model and the control parameters found were able to control the temperature within a few residence time showing the efficiency of the model and it control system.

The mixing parameters, and , are a second key factor for the model and must be throughly studied. Several simulations were done as to find the best set of mixing parameters for the industrial autoclave reactor that is being simulated. Figure 3 shows the effect of the recycle ratio on the reactor behaviour.

Comparing the profiles obtained in Figure 4 to actual reactor profiles have showed that none of the profiles obtained with simulations that were carried out with constant recycle ratios (all sections using the same recycle ratio) have displayed a satisfactory fit to the actual reactor data. Analyzing the configuration of the reactor and the fraction of ethylene feed in each section, we could establish that not all sections would display the same recycle ratio and that this parameter has to carefully set for each reactor design. For the design shown in Figure 1, the recycle ratio of section 4 (towards section 3) was set to zero since the baffle between sections 3 and 4 minimizes the recycle and backmixing of the reaction mixture. The recycle ratio of section 3 (towards section 2) was increased since the flow rate of ethylene fed into section 3 is larger and as such a better mixing can occur near this feeding point. The best configuration found for the mixing parameters of the model was: volume fraction of the CSTR segment to the total volume of the section ( ) of 0.70 for all sections; and recycle ratio ( ) of 0.15, 0.30, 0.15, 0.15 and 0.05 for the sections 2, 3, 6, 7 and 8, respectively. A comparison with industrial data is shown in Figure 4. The results found in Figure 4 are quite good and the largest relative error of the predicted values was less then 5% and as such we can state that the model truly represents the industrial reactor behavior.

4. Conclusions

A comprehensive model describing the high-pressure autoclave reactor for polyethylene production was developed, accounting for the mixing pattern in the reactor, the mechanistic polymerization reaction and temperature control. The model was proven satisfactory and has fitted homopolymer recipes for initiator flow rates, temperature profiles and final polymer characteristics.



(a) (b)

Figure 4. Effect of the recycle ratio on the monomer concentration (a) and the temperature profiles (b) for the first segment (CSTR segment) of each section of the reactor (= 0.70; each section comprised of 1 CSTR segment and 2 PFR segments).

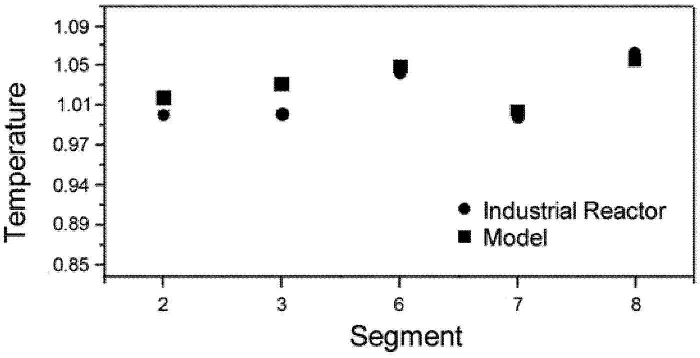


Figure 5. Comparison of temperature profiles between the proposed model and actual industrial data for polyethylene homopolymerization.

Acknowledgments

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