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Development of a Multi-compartment Dynamic Model for the Prediction of Particle Size Distribution and Particle Segregation in a Catalytic Olefin Polymerization FBR

George Dompazis, Vassilis Kanellopoulos, Costas Kiparissides

Department of Chemical Engineering and Chemical Process Engineering Research Institute, Aristotle University of Thessaloniki, PO Box 472, Thessaloniki, Greece 541 24

Abstract

In the present study a comprehensive multi-scale, multi-compartment model is developed for the prediction of morphological (i.e., particle size distribution (PSD), particle segregation) and molecular (i.e., molecular weight distribution (MWD)) distributed polymer properties in a catalytic olefin polymerization FBR. The multi-scale description of the FBR utilizes models at four different levels, namely, a kinetic model, a single particle model, a population balance model and a multi-compartment reactor-mixing model. At the molecular level, a two-site Ziegler-Natta catalytic copolymerization model is employed to describe the copolymerization of ethylene with propylene. To calculate the particle growth and the spatial monomer and temperature profiles in a particle, the random pore polymeric flow model (RPPFM) is utilized. The RPPFM is solved together with a dynamic discretized particle population balance model, to predict the PSD. Moreover, overall dynamic mass and energy balances in the reactor level are derived, in order to calculate the monomer(s) concentration and temperature profiles along the reactor height. The effects of various fluidized bed operating conditions (e.g., fluidization gas velocity, temperature, catalyst feed rate) on the morphological and molecular distributed polymer properties and reactor operability are analyzed.

Keywords: Multi-compartment model, Multi-scale reactor model, particle segregation, particle size distribution, polymer distributed properties.

1. Introduction

High and medium density polyoelfins are commercially manufactured in gas phase fluidized bed olefin polymerization reactors using high activity transition metal catalysts such as Ziegler-Natta catalysts, Phillips-Chromium oxide catalysts and supported metallocene catalysts. Although polymer particles are assumed to be very well-mixed, particle segregation may occur in large industrial fluidized bed reactors. This means that the polymer particle size distribution at the reactor exit may differ from the PSDs at different locations along the bed height. In a fluidized bed reactor, strong segregation can occur if the bed contains particles of different densities. Density differences and particle size differences are common reasons for particle segregation.

Despite its inherent importance, a limited number of papers have been published on the modeling of the particle-size distribution in gas-phase catalytic olefin polymerization processes. Zacca, et al. (1994), developed a population balance model using the catalyst residence time as the main coordinate, to model particle-size developments in multistage olefin polymerization reactors, including vertical and horizontal stirred beds

and fluidized-bed reactors. Choi, et al. (1994), incorporated an isothermal simplified multigrain particle model, by neglecting the external particle mass and heat transfer resistances, into a steady-state PBE to investigate the effect of catalyst deactivation on the PSD and average molecular properties for both uniform and size distributed catalyst feeds. Yiannoulakis, et al. (2001), extended the model of Choi, et al. (1994), to account for the combined effects of internal mass and heat transfer resistances on the PSD for highly active catalysts. In a recent publication Dompazis, et al. (2005), developed a comprehensive integrated model, accounting for the multi-scale phenomena taking place in a continuous gas-phase ethylene copolymerization FBR to describe the molecular and morphological properties of the particulate polymer. Kim and Choi, (2001) presented a steady state multi-compartment population balance model using the concept of size-dependent absorption/spillage model to investigate the effects of fluidization and reaction conditions on the reactor performance.
In what follows, a dynamic multi-scale, multi-compartment model is developed. Extensive numerical simulations are carried out to investigate the effect of critical reactor operating parameters (e.g., fluidization gas velocity, catalyst feed), on the dynamic evolution of the molecular and morphological polymer distributed properties (PSD, MWD etc.), particle segregation, and temperature in the reactor.

2. Kinetic Modeling at the Molecular Level

To describe the molecular weight developments over a heterogeneous Ziegler-Natta catalyst, a generalized two-site kinetic model is employed (Hatzantonis et al., 2000). The kinetic mechanism comprises a series of elementary reactions, including site activation, propagation, site deactivation and site transfer reactions.

3. Modeling at the Particle Level

To simulate the growth of a single polymer particle, the random pore polymeric flow model (RPPFM) of Kanellopoulos, et al. (2004) was employed. The equations to be solved for the calculation of spatial ethylene and propylene concentrations and temperature profile in a growing polymer particle, as well as the overall particle growth rate, $G(D)$, (cm/s) are presented elsewhere (Kanellopoulos, et al., 2004).

4. Calculation of PSD in a Reactor Compartment

To calculate the dynamic evolution of PSD in a gas-phase FBR a dynamic population balance model needs to be solved together with the system of differential equations describing the radial monomer(s) concentration and temperature profiles in a single particle (Kanellopoulos, et al., 2004) and the overall mass and energy balances in the reactor level. Accordingly, the bed is divided into N compartments of equal volume (see Figure 1). Each reactor zone is assumed to consist of an emulsion phase compartment and a bubble phase compartment. Polymer particles can be transferred from the emulsion to the bubble phase and vice versa. In all cases, the total mass of solids in each compartment remains constant. The dynamic population balance equation and the overall mass balance in the jth reactor zone can take the following form:

Emulsion Phase:

$$\frac{\partial n_j(D,t)}{\partial t}+\frac{\partial\left[G(D)n_j(D,t)\right]}{\partial D}=\frac{1}{W_{e,j}}\left[F_{j-1}n_{j-1}(D,t)-F_j n_j(D,t)+F_{tr,j}^{we}n_{tr,j}^{we}(D,t)-F_{tr,j}^{ew}n_{tr,j}^{ew}(D,t)\right] \quad (1)$$

$$F_{i-1} + F_{tr,j}^{we} + W_{e,j} \int_{D_{\min}}^{D_{\max}} G_j(D) n_j(D,t) d\left(\rho_p \pi D^3/6\right) - F_j - F_{tr,j}^{ew} = 0 \tag{2}$$

Bubble Phase:

$$\frac{\partial n_{w,j}(D,t)}{\partial t} = \frac{1}{W_{w,j}} \left[F_{re,j+1} n_{w,j+1}(D,t) - F_{re,j} n_{w,j}(D,t) - F_{tr,j}^{we} n_{tr,j}^{we}(D,t) + F_{tr,j}^{ew} n_{tr,j}^{ew}(D,t) \right] \tag{3}$$

$$F_{re,j+1} - F_{re,j} + F_{tr,j}^{ew} - F_{tr,j}^{we} = 0 \tag{4}$$

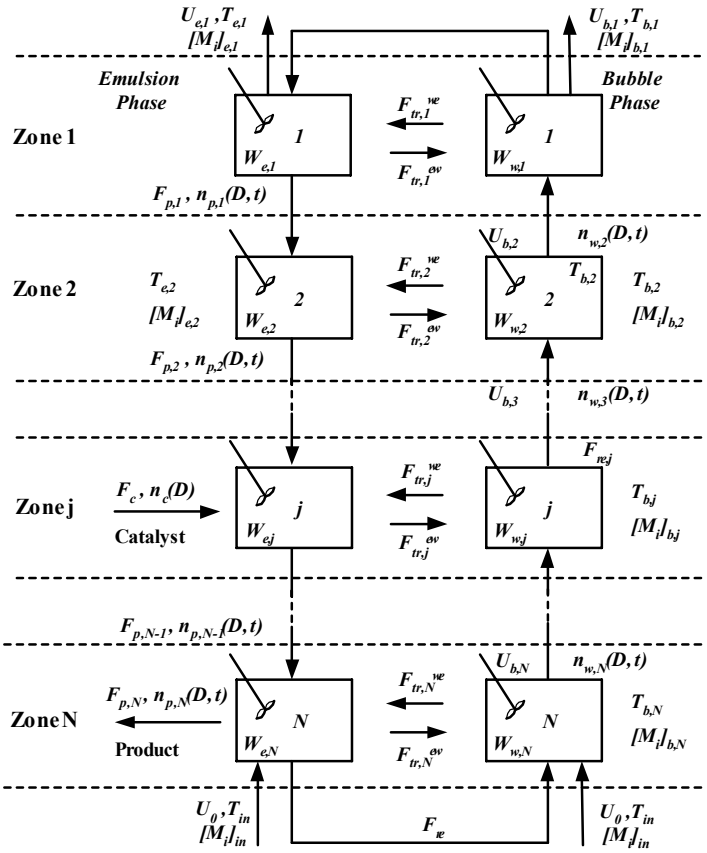

Figure 1. Schematic representation of the multi-compartment model.

where $n_j(D,t)$ and $n_{w,j}(D,t)$, expressed in (#/g/cm), denote the number diameter density functions of particles in the " j " emulsion phase and in the " j " wake phase of the bubble phase compartment, respectively. W_e and W_w is the mass of solids in the emulsion phase and in the wake phase of the bubbles, respectively and F_{re} is the particle circulation rate (Baeyens and Geldart 1986).

5. Overall Monomer and Energy Balances

Based on the above multi-compartment model (see Figure 1), the mass and energy balance equations for the bubble and emulsion phases can be derived to describe the temporal-spacial variation of monomer concentration and temperature in the bubble and emulsion phases, respectively (Dompazis et al., 2006).

6. Results and Discussion

Extensive numerical simulations were carried out by using the proposed model (see Figure 1) to investigate the effects of various reactor operating conditions on the distributed molecular and morphological polymer properties in a catalyzed, gas phase, ethylene propylene copolymerization FBR.

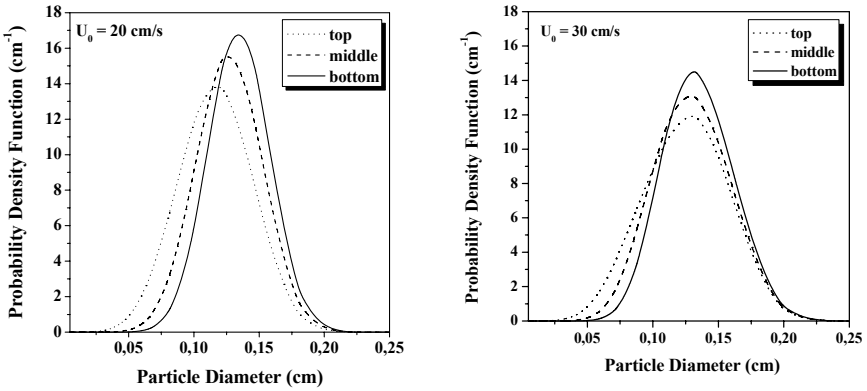

Figure 2. Effect of fluidization gas velocity on the PSD in the emulsion phase.

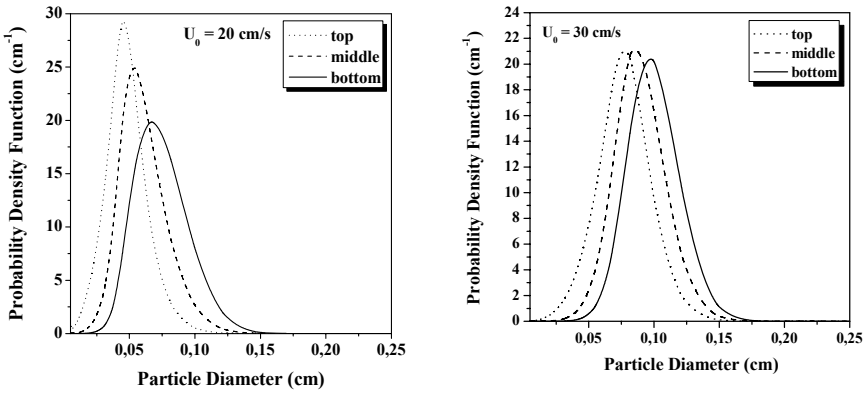

Figure 3. Effect of fluidization gas velocity on the PSD in the bubble phase.

In Figures 2 and 3, the effect of fluidization gas velocity on the particle size distribution in the reactor compartments is shown for a catalyst feed rate equal to 0.1 g/s. In the present multi-compartment model the number of compartments was set equal to three in all model simulations. As can be seen, at low gas velocities, the PSD is shifted to larger sizes from the top to the bottom compartment. As the gas velocity increases, the individual PSDs in each compartment collapse into the same distribution, implying that

the FBR can be approximated by a single CSTR. The particle size distributions in the wake phase of bubbles are shown in Figure 3. As expected, the amount of small particles in the wake phase of bubbles is substantially larger than that in the emulsion phase. Thus, as a bubble rises in the reactor the PSD of particles in the wake shifts to smaller sizes.

Figure 4 depicts the effect of fluidization gas velocity on the temporal spatial variation of temperature in the FBR for a catalyst feed rate equal to 0.1 g/s. Notice that in the first case the fluidization gas velocity is equal to 30 cm/s (segregation mode), while in the second one the corresponding fluidization gas velocity is equal to 70 cm/s (well-mixed operation). As can be seen, at low fluidization gas velocities the reactor temperature increases with respect to its axial position. As the gas fluidization velocity increases, the reactor temperature is almost constant along the bed height.

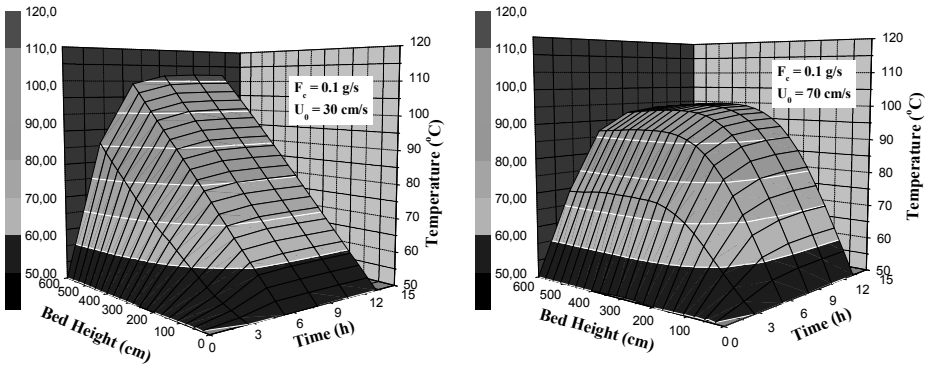

Figure 4. Effect of fluidization gas velocity on reactor temperature.

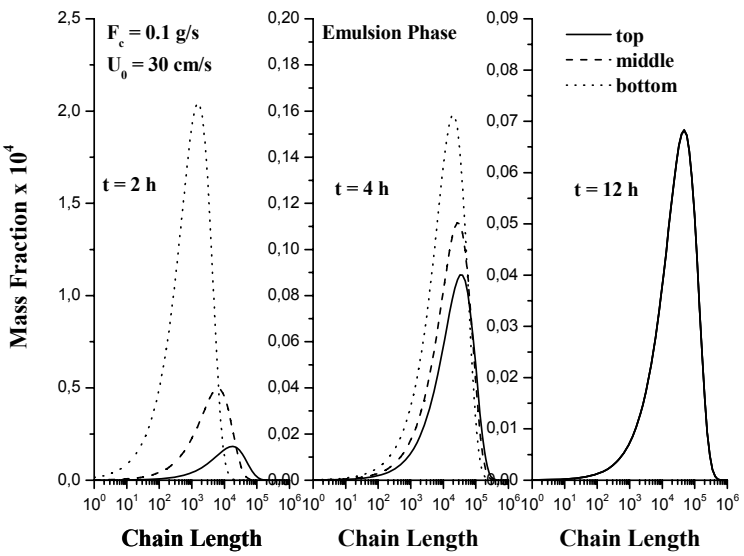

Figure 5. Dynamic evolution of MWD of polymer particles along the bed height.

In Figure 5, the dynamic evolution of MWD of polymer particles in the emulsion phase is illustrated along the bed height. As can be seen, the MWD of particles is shifted to larger chain lengths as we move from the bottom to the top of the bed. This can be explained by the fact that the polymerization time of the polymer particles in the top compartment is smaller than the corresponding time of the particles in the bottom compartment. As a result, the molecular weight of the polymer particles in top compartment will be higher due to the higher polymerization rate.

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