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Dynamic Evolution of the Particle Size Distribution in Multistage Olefin Polymerization Reactors

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Abstract

A wide range of polyolefins are produced in catalytic particulate polymerization reactors (e.g., loop, continuous-stirred tank, horizontal stirred bed and fluidized-bed reactors). In each of these reactor configurations, the dynamic evolution of the particle size distribution (PSD) is a key variable that affects both the reactor operability and the end-use properties of the final product. In the present study, a comprehensive population balance model is developed to predict the evolution of particle size distribution in multistage olefin polymerization reactors. Specifically, the PSD is considered to evolve in time under the combined effect of particle aggregation and growth mechanisms. Two different numerical methods (i.e., the orthogonal collocation and the Galerkin on finite elements) are employed for solving the population balance equation. The performance of the two numerical methods is assessed in terms of accuracy, stability and computational efficiency of each method. It is shown that the dynamic evolution of PSD is highly affected by the operating conditions and the selected reactor configuration. Furthermore, it is shown that particle agglomeration can significantly affect the evolution of PSD in a multistage reactor configuration.

Keywords: olefin polymerization, multistage polymerization, population balance, particle size distribution, residence time distribution.

1. Introduction

A number of particulate processes (e.g., slurry, gas-phase) are presently employed for the production of polyolefins via the catalytic (Ziegler-Natta and metallocene) polymerization of olefins. The various processes differ in both the physical state of the reaction medium and the mechanical operation of the unit (Zacca et al., 1996). In a typical solid-catalysed continuous olefin polymerization process, small catalyst particles are continuously fed into the reactor that is operated at controlled temperature and pressure. The catalyst particles react with the monomer(s) to form a broad distribution of polymer particles. The prediction of PSD in a multistage reactor configuration is of

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profound importance since it affects both the reactor operability and the end-use properties of the polyolefin product. However, this problem has not been adequately addressed in the open literature. Moreover, the effect of reactor configuration (i.e., number of compartments, presence of a recycle stream in a multistage process) on the dynamic evolution of PSD (especially during grade transition) has not been studied. Choi et al., (1994) employed a steady-state population balance approach to model the PSD in a continuous gas-phase olefin polymerization reactor. Yiannoulakis et al., (2001) applied a steady-state population balance equation to a continuous ethylene-butene copolymerization gas-phase fluidized bed reactor, to investigate the effects of reactor operating parameters (e.g., reactor temperature, relative particle to gas velocity, initial catalyst size, bulk comonomer/monomer molar ratio) on the PSD for the cases of negligible and significant particle agglomeration. Zacca et al., (1996) calculated the residence time distribution of particles for various olefin polymerization reactor configurations and predicted the corresponding PSDs. In this study, a dynamic population balance model, accounting for both particle growth and agglomeration, is formulated to predict the evolution of PSD in a multistage olefin polymerization reactor configuration. For simplification it is assumed that the catalyst feed is of uniform size, while the external and internal heat and mass transfer limitations at the particle level are negligible.

2. Particle Size Distribution Modeling

Let us assume that the operation of a solid catalyzed olefin polymerization reactor can be approximated by a perfectly backmixed, continuous flow reactor. Catalyst particles are fed into the bed at a constant rate F_c (g/s), while the mass of the solids in the bed, W(g), is kept constant by controlling the product withdrawal rate, F_p (g/s). The dynamic population balance equation, accounting for particle growth and particle agglomeration, in the reactor will be:

$$\frac{\partial n_p(D,t)}{\partial t} + \frac{\partial\left[G(D)n_p(D,t)\right]}{\partial D} = B(D,t) - D(D,t) + \frac{1}{W}\left[F_c n_c(D,t) - F_p n_p(D,t)\right] \qquad (1)$$

$$B(D,t) = \frac{D^2}{2}\int_{D_{min}}^{(D^3 - D_{min}^3)^{1/3}} \frac{K_{ag}\left(\left(D^3 - D'^3\right)^{1/3}, D'\right) n_p\left(\left(D^3 - D'^3\right)^{1/3}, t\right) n_p(D',t)\, dD'}{\left(D^3 - D'^3\right)^{2/3}} \qquad (2)$$

$$D(D,t) = n_p(D,t)\int_{D_{min}}^{\infty} K_{ag}(D,D')\, n_p(D',t)\, dD' \qquad (3)$$

where $n_p(D,t)$ and $n_c(D,t)$, expressed in ($g^{-1}cm^{-1}$), are the number density functions of the particles in the reactor and in the feed stream, respectively. The term $n_p(D,t)dD$ denotes the number of particles in the size range (D, D+dD) per mass of polymer particles. $K_{ag}(D, D')$ is a temperature and particle size dependent functional, governing

the agglomeration rate of particles of sizes D and D′. In the absence of heat and mass transfer limitations at the particle level, the particle growth rate, G(D), can be expressed in terms of the overall particle polymerization rate, R_{pp}, as follows (Hatzantonis et al. 1998):

$$G(D) = 2R_{pp} / \rho_p \pi D^2 \tag{4}$$

Moreover, one can easily show that the steady-state mass balance in the reactor in terms of the particle size distribution will be given by the following equation:

$$F_p = F_c + W \int_{D_{min}}^{\infty} G(D) n_p(D,t) d\left(\frac{\rho_p \pi D^3}{6}\right) \tag{5}$$

Notice that the second term on the right hand side of eq. (5) accounts for the total polymer production rate in the bed.

In the present study, two different numerical methods (i.e., the orthogonal collocation and the Galerkin on finite elements) were employed for the solution of the population balance model (see eqs 1 - 4) in various multistage reactor configurations. The performance of the two numerical methods was assessed in terms of accuracy, stability and computational efficiency of each method.

3. Simulation Results and Discussion

3.1 Horizontal Stirred Bed Reactor

The operation of a horizontal stirred bed reactor can be approximated by a series of stirred tank reactors (CSTRs). Mixing of the solids in the bed is effected by a series of paddles attached to a horizontal shaft. In Figure 1, a schematic representation of a horizontal gas-phase polymerization reactor is depicted. The gas-phase is assumed to be well-mixed while the solid catalyst/polymer particles in the horizontal reactor is assumed to be distributed over two backmixed CSTRs in series. The two reactors are assumed to have the same volume. To predict the PSD at the reactor exit, the dynamic PBE (see eq 1) was solved for each reactor in the series.

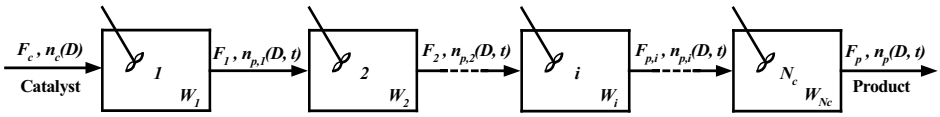

Figure 1. Schematic representation of a horizontal stirred bed reactor

In Figure 2, the steady-state PSDs at the exit of the first and second reactors in the series are depicted. It can be seen that the PSD becomes narrower and is shifted to larger sizes as the number of the reactors in series increases while the total volume of the reactors remains the same. It should be noted that the discrete points represent the numerical results for zero particle agglomeration and constant particle growth while the

continuous lines represent the analytical solution (Zacca et al., 1996). As can be seen the agreement between the analytical and numerical solutions is excellent. In Figure 3, the dynamic evolution of the PSD at the exit of the second reactor in the series is presented. The effect of particle agglomeration on the PSD is presented in Figure 4. It can be seen that in the presence of particle agglomeration, the PSD in the reactor becomes broader and is shifted to larger sizes as the particle agglomeration rate constant increases.

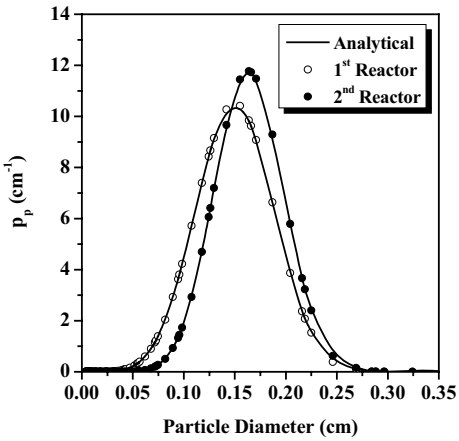

Figure 2. Comparison between analytical and numerical PSD results at the exit of the first and second CSTR in the series.

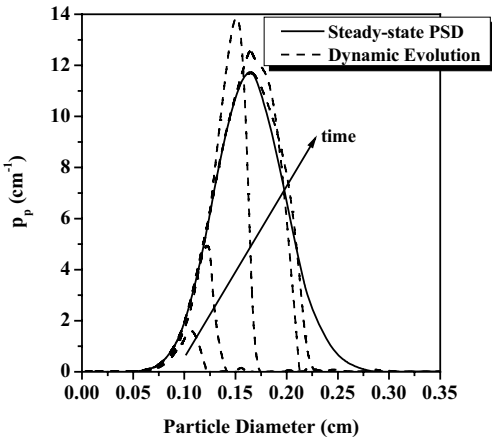

Figure 3. Dynamic evolution of the PSD at the exit of the second CSTR in the series.

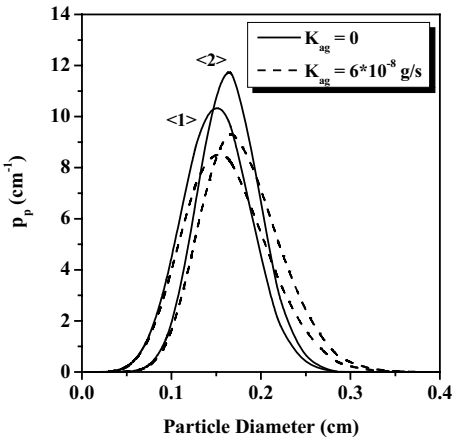

Figure 4. Effect of particle agglomeration rate constant on the PSDs at the exit of the first and second reactor in the series.

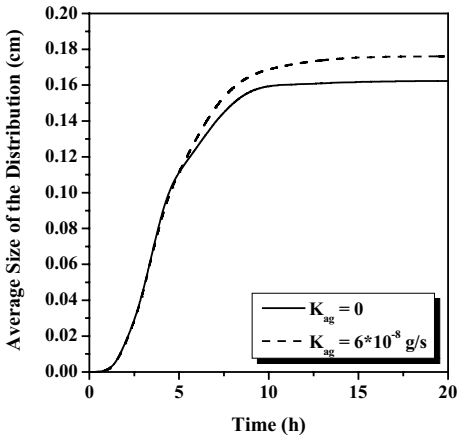

Figure 5. Dynamic evolution of the average particle size at the exit of the second reactor.

In Figure 5, the dynamic evolution of the average particle size of the distribution in the second reactor is depicted in the absence ($K_{ag} = 0$) and in the presence ($K_{ag} \neq 0$) of particle agglomeration. It is obvious that in the presence of particle agglomeration more time is required for the PSD to reach its final steady-state value.

3.3 Fluidized Bed Reactor

The mixing/circulation of solids in a gas-phase polyolefin fluidized bed reactor can be approximated by a series of CSTRs with a recycle stream (see Figure 6). In Figure 7, the effect of solids circulation rate, F_{re}, on PSD is depicted. As can be seen the individual PSDs in the first and second CSTR in the series collapse into the same distribution as the solids circulation rate increases, implying that the reactor can be approximated by a single CSTR.

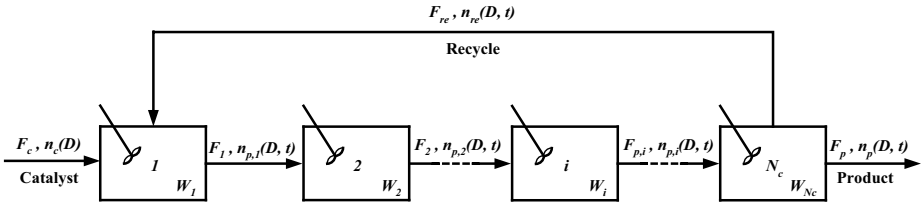

Figure 6. Schematic representation of a fluidized bed reactor.

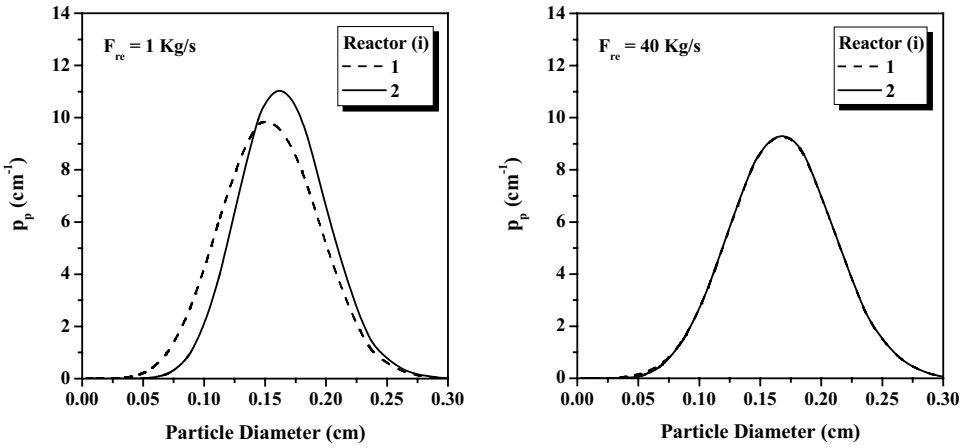

Figure 7. Effect of solids circulation rate on the PSDs in the two reaction zones.

The effect of particle agglomeration rate constant on the PSD in the second CSTR of the FBR is presented in Figure 8. As can be seen, as the value of K_{ag} increases the PSD becomes broader.

3.4 Comparison of the two Numerical Methods

The two numerical methods (i.e., the orthogonal collocation and the Galerkin on finite elements) were compared in terms of accuracy, stability and computational requirements using available analytical solutions for the PSDs at steady-state. The orthogonal collocation method exhibited faster convergence but was susceptible to numerical oscillations in the dynamic evolution of PSDs. On the other hand, the Galerkin method was more robust and slightly more accurate in the calculation of PSD moments but required more CPU time.

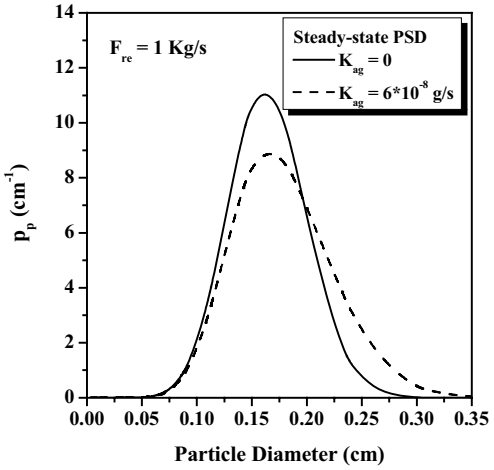

Figure 8. Effect of particle agglomeration rate constant on PSD.

4. Conclusions

In this study, a general mathematical framework has been developed for calculating the dynamic evolution of PSD in solid catalyzed olefin polymerization processes (i.e., in the horizontal stirred bed, and in the FBR). It was shown that particle agglomeration significantly affects the steady-state particle size distribution as well as its dynamic evolution. In the case of horizontal reactor it was found that the PSD becomes narrower as the number of reactors in the series increases and, thus, the reactor's behaviour approaches that of a PFR. For the FBR it was found that by increasing the solid circulation rate the PSDs in the various CSTRs become identical and the reactor's behaviour approaches that of a CSTR. Two different numerical schemes (i.e., the orthogonal collocation and the Galerkin on finite elements) were employed for the solution of the population balance equation. It was found that the Galerkin method is more robust and accurate in comparison to the OCFE, but, in general, requires more CPU time than the OCFE.

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