Dynamic Evolution of the Particle Size Distribution in Gas-Phase Olefin Polymerization Fluidized Bed Reactors

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Abstract

In the present study, a comprehensive mathematical model is developed to predict the evolution of particle size distribution (PSD) in a gas-phase olefin polymerization fluidized bed reactor (FBR). To calculate the particle growth and the spatial monomer and temperature profiles in a particle, the random pore polymeric flow model (RPPFM) is employed. The RPPFM is solved together with a dynamic population balance model, accounting for both particle growth and agglomeration, to predict the PSD in the bed. To evaluate the extent of particle agglomeration in the bed, a new agglomeration kernel is developed in terms of the individual particle surface temperatures, the polymer softening temperature and a size dependent function, describing the mechanism of dual particle collisions. The effects of bulk polymerization temperature and propylene toethylene molar ratio on the extent of particle agglomeration in an FBR are thoroughly analyzed.

Keywords: fluidized bed reactor, particle size distribution, olefin polymerization, particle agglomeration.

1. Introduction

In fluidized bed solid catalyzed gas-phase olefin polymerization, small catalyst particles are continuously fed into the reactor at a point above the gas distributor and react with the incoming fluidizing monomer gas mixture to form a broad distribution of polymer particles. During their stay in the bed, the polymer particles grow in size due to polymerization, can be entrained by the fluidizing gas or/and undergo particle agglomeration when the reactor operates close to the polymer softening temperature (Hatzantonis et al., 1998). It should be pointed out that, at the particle level, external and internal mass and heat transfer limitations can become significant, especially, in the presence of highly active catalysts or/and small but very active particles. This can greatly affect the development of particle size distribution (PSD) in a catalyzed olefin polymerization fluidized bed reactor (FBR). Thus, in order to predict the PSD in an FBR the monomer(s) and energy balances have to be solved together with a population balance equation (PBE), governing the development of PSD. In the present study, a

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non-isothermal dynamic polymeric flow model (RPPFM), accounting for both internal and external mass and heat transfer resistances, is employed to calculate the growth rate of individual polymer particles. A dynamic population balance model accounting for both particle growth and agglomeration, is formulated to describe the PSD developments in an olefin polymerization FBR.

2. Single Particle Growth Modeling

To simulate the growth of a single polymer particle, the random pore polymeric flow model (RPPFM) (Kanellopoulos et al., 2003) was employed. It should be pointed out that internal mass and heat transfer resistances can often become significant at the particle level. Thus, one has to solve the monomer(s) and energy balances in each particle in order to predict the individual particle growth rate and particle overheating. To calculate the overall particle polymerization rate, the local monomer incorporation rate is integrated over the particle volume.

In Figure 1, the effect of the initial catalyst size on the polymerization rate-time histories is illustrated. As can be seen from Figure 1, as the initial catalyst size increases the polymerization rate initially decreases due to mass transfer limitations. That is, the rate of monomer transfer from the bulk gas phase to the active catalyst sites becomes the limiting step in the polymerization. However, despite the fact that the polymerization rate decreases as the catalyst size increases, particle overheating increases due to heat transfer limitations (see Figure 2). The results of Figure 2 can be better explained in terms of the particle heat removal rate, $Q$, and the polymerization heat rate, $\dot{Q}_p$. As the polymerization continues and the particle’s surface area increases, the heat removal rate asymptotically approaches the polymerization heat rate. As a result, the particle temperature approaches that in the bulk gas phase.

3. Particle Size Distribution Modeling

Let us assume that the operation of a solid catalyzed olefin polymerization FBR 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 FBR will be:

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

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

$$D(D,t) = n_p(D,t) \int_{D_{\min}}^{D_{\max}} K_{ag} \left( D, D' \right) n_p(D',t) dD' \quad (3)$$

where $n_p(D,t)$ and $n_c(D,t)$, expressed in (g cm\(^{-1}\)), are the corresponding number density function of the particles in the bed 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 $D'$. To calculate the overall particle polymerization rate, $R_{pp}$, one has to integrate the local monomer consumption rates over the particle volume (Yiannoulakis et al. 2001), using spatial monomer and temperature profiles obtained from the solution of RPPFM. According to Hatzantonis et al. (1998), the particle growth rate, $G(D)$, can be expressed in terms of the overall particle polymerization rate, $R_{pp}$, as follows:

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

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

$$F_p = F_c + W \int_{D_{\min}}^{D_{\max}} G(D)n_p(D,t) dD \frac{\rho_p \pi D^3}{6} \quad (5)$$

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

3.1 Numerical Solution

In the present study, the adjustable geometric discretization method of Litster et al. (1995) was employed for solving the general PBE, eq. (1). Following the original
developments of Litster et al. (1995), the volume domain is first divided into a number of discrete elements according to the geometric discretization rule:

\[ V_{i+1}/V_i = 2^{1/q} \quad ; \quad i = 1, 2, ..., N_p + 1 \]  

(6)

where \( q \) is an integer equal or greater than one, controlling the number of elements in the discretized domain. Assuming a constant value for the number density function, \( n_{p,i} \) within each element “i”, a discrete particle number distribution, \( N_{p,i} \), can be defined:

\[ N_{p,i} = \frac{D_{pi}}{D_i} \int_{D_i} n_{p,j} \, dV \equiv \frac{n_{p,j} (D_{i+1} - D_i)}{r - 1} \]  

(7)

where

\[ r = D_{pi+1}/D_i = \sqrt[2]{2^{1/q}} \]

(8)

Accordingly, an equivalent to eq. (1) discretized PBE can be derived:

\[
\sum_{k=2}^{q} N_{p,i-k} \sum_{j=1}^{q} C_2 K_{ag}(D_{i-k}, D_j) N_{p,j} + \sum_{k=2}^{q} N_{p,i-k+1} \sum_{j=1}^{q} C_3 K_{ag}(D_{i-k+1}, D_j) N_{p,j} + 1/2 \sum_{k=1}^{q} C_4 K_{ag}(D_{i-k}, D_j) N_{p,j}^2 + \sum_{j=1}^{q} \left( a \frac{G_p(D_{i-1})}{D_i} + \sum_{j=1}^{q} C_{ag}(D_{i-j}, D_j) N_{p,j} \right) N_{p,i-j} + \left( b \frac{G_p(D_{i})}{D_i} - \frac{1}{\tau} \sum_{j=1}^{q} C_4 K_{ag}(D_{i}, D_j) N_{p,j} - \frac{c}{\tau} \sum_{j=1}^{q} K_{ag}(D_{i}, D_j) N_{p,j} \right) N_{p,i} + c \frac{G_p(D_{i+1})}{D_i} N_{p,i+1} + \frac{F_p}{W} N_{c,i} = \frac{dN_{p,i}}{dt}, \quad i > 1
\]

(9)

For \( i=1 \), the following boundary condition will hold true:

\[
\left( \frac{1}{\tau} + \sum_{j=1}^{q} C_4 K_{ag}(D_{1}, D_j) N_{p,j} \right) N_{p,1} + \frac{G_p(D_2)}{(r-1)D_2} N_{p,2} - \frac{F_p}{W} N_{c,1} = \frac{dN_{p,1}}{dt},
\]

(10)

where,

\[
a = \frac{2r}{(1+r)(r^2 - 1)} \quad ; \quad b = \frac{2}{1+r} \quad ; \quad c = a \quad ; \quad C_1 = \frac{2^{(j+1)/q}}{2^{2/q} - 1}
\]

(11)

\[
C_2 = \frac{2^{(j+1)/q} - 1 + 2^{(i-k)/q}}{2^{2/q} - 1} \quad ; \quad C_3 = \frac{2^{1/q} - 2^{(j-1)/q} - 2^{(i-k)/q}}{2^{2/q} - 1} \quad ; \quad C_4 = \frac{2^{(j+1)/q}}{2^{2/q} - 1}
\]

(12)
\[ \lambda = i - S(q + k + 2) - k + 1 \quad ; \quad \mu = i - S(q + k + 1) - k \quad ; \quad S(q) = q(q + 1)/2 \]  
(13)

Notice that the derived discretized population balance equation (9) guarantees the accurate estimation of the zero moment (i.e., total number of particles) and first moment (i.e., total polymer mass) in the reactor. It should be pointed out that from the discrete values of \( N_{p,i} \), one can calculate an equivalent continuous distribution using a cubic-spline approximation.

4. Simulation Results Discussion

The particle agglomeration rate can be expressed in terms of the diameters of the colliding particles, using the following equation (Yiannoulakis et al. 2001):

\[ K_{ag} = K_0 \exp\left( E_g \left( \frac{T_{s1} + T_{s2}}{T_{sf}} \right) \left( \frac{D_1^4}{D_2^4} + \frac{D_2^4}{D_1^4} \right) \right) \]  
(14)

where \( K_0 \) is an agglomeration rate constant in (g/cm/s), \( T_{s1} \), \( T_{s2} \) are the surface temperatures of particles of sizes \( D_1 \) and \( D_2 \) respectively, \( T_{sf} \) is the average polymer softening temperature of particles \( D_1 \) and \( D_2 \), and \( K_0 \), \( E_g \) are proportionality constants. In Figure 3 the effect of agglomeration rate constant, \( K_0 \), on the PSD is shown. It is can be seen that the PSD in the bed becomes broader as the value of \( K_0 \) increases. In fact, PSDs with longer tails are obtained whereas their respective peak positions are shifted to larger sizes (Yiannoulakis et al. 2001).

To investigate the effect of polymerization temperature on the extent of particle agglomeration, the gas-phase polymerization of ethylene was considered. The PE softening temperature was assumed to be equal to 117.2 °C while the agglomeration kernel was assumed to follow eq. (14). To calculate the PSD in the bed, the full RPPFM/PBE model was numerically solved. In Figure 4, the effect of the bulk gas phase temperature (e.g., 40-100 °C) on the PSD is depicted. As can be seen, the PSD becomes broader as \( T_b \) increases due to the increased rate of particle agglomeration.
Numerical simulations were also carried out to investigate the effect of propylene to ethylene molar ratio, $[C_3]/[C_2]$, on the particle agglomeration in a gas-phase ethylene-propylene copolymerization FBR. The particle agglomeration kernel followed the general form of eq. (14). In Figure 5, the effect of copolymer composition on the copolymer softening temperature is depicted. In Figure 6, the calculated PSDs are shown for different values of $[C_3]/[C_2]$. It is apparent that the PSD becomes broader while its peak position is shifted to larger particle sizes as the propylene to ethylene molar ratio increases (i.e., the copolymer softening temperature decreases).

5. Conclusions

A dynamic population balance model, accounting for particle agglomeration and growth, was developed to predict the PSD in catalyzed gas-phase olefin polymerization FBRs. A single particle growth model was employed to calculate the overall particle polymerization rate with respect to particle size. A new agglomeration kernel was identified in terms of the particle’s surface temperature, copolymer softening temperature and particle collision function. The effect of the functional form of the particle collision function on the PSD was theoretically investigated. Furthermore, the effect of polymerization temperature and propylene to ethylene molar ratio on the extent of particle agglomeration in the bed were examined.

References