

Three-Dimensional CFD-PBM Coupled Model of the Temperature Fields in Fluidized-Bed Polymerization Reactors

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A three-dimensional (3-D) computational fluid dynamics model, coupled with population balance (CFD-PBM), was developed to describe the gas–solid two-phase flow in fluidized-bed polymerization reactors. The model considered the Eulerian–Eulerian two-fluid model, the kinetic theory of granular flow, the population balance, and heat exchange equations. First, the model was validated by comparing simulation results with the classical calculated data. The entire temperature fields in the reactor were also obtained numerically. Furthermore, two case studies, involving constant solid particle size and constant polymerization heat or evolving particle-size distribution, polymerization kinetics, and polymerization heat, were designed to identify the model. The results showed that the calculated results in the second case were in good agreement with the reality. Finally, the model of the second case was used to investigate the influences of operational conditions on the temperature field. © 2011 American Institute of Chemical Engineers AICHE J, 57: 3351–3366, 2011

Keywords: fluidized-bed polymerization reactor, computational fluid dynamics (CFD), population balance model (PBM), polymerization kinetics, temperature field

Introduction

Fluidized-bed reactor (FBR) is one of the most widespread commercial reactors to produce polyolefin because of its simple construction and excellent heat and mass transfer capabilities.¹ Various technologies, such as Hypol technology, Innovene technology, Unipol technology, and Spheripol technology, are designed to produce polypropylene (PP). Among them, even though there are different reactor arrangements in essence,^{2–4} FBR, which is generally used to produce high-impact PP,⁴ is usually the key portion in different reactor arrangements. In fluidized-bed olefin polymerization reactor, small catalyst particles are continuously fed into

the bed and react with the incoming gaseous monomer to produce polymer particles with a broad size distribution. Because of the distribution in polymer particle sizes, segregation occurs, and the fully grown polymer particles migrate to the bottom where they are removed from the reactor. Meanwhile, the small particles and fresh catalyst particles tend to migrate to the upper room of reactor and continue to react with the monomer.^{2–5} Therefore, the reaction system is considered as a gas–solid two-phase system, and the solid phase can be characterized by particle-size distribution (PSD). The gas phase consists of monomer and hydrogen, and the solid phase consists of polymer or catalyst particles (the catalyst particles can entirely transfer into the polymer particles). Moreover, the PSD can directly relate to polymerization and particle kinetics, i.e., polymerization kinetics, particle growth, aggregation, and breakage dynamics as shown in Figure 1.^{6,7} For olefin polymerization, the particles

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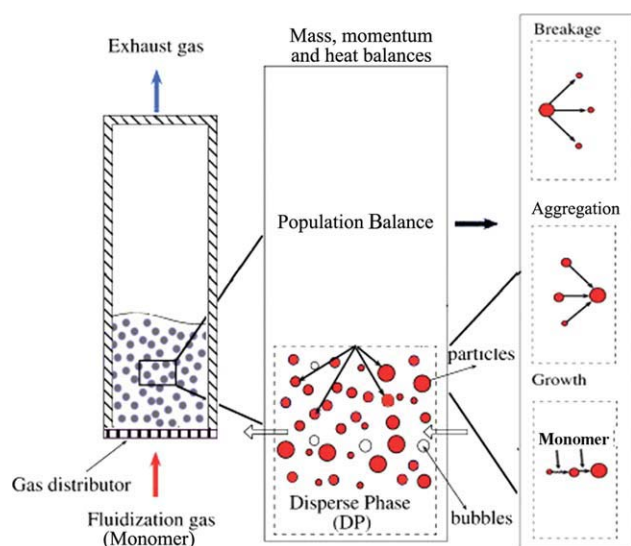


Figure 1. The evolution of particle-size distribution in the fluidized-bed olefin polymerization reactor.

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can break into small fragments if the temperature in the reactor is too low or agglomerate to bigger ones if the temperature approaches to the melting temperature of the polymers. To maintain reasonably high production rate, the gas-phase fluidized bed is usually operated at a relatively high temperature. However, the olefin polymerization is a highly exothermic reaction, so particles in the reactor are mostly affected by aggregation. It has been reported that the agglomeration of polymer particles can lead to reactor runaway and production shutdowns in the commercial production of polyolefin resins.^{6,7} Our study focuses on investigating the effect of aggregation on the hydrodynamics in FBRs.

To operate FBR more effectively, it is important to obtain a fundamental understanding of the gas–solid two-phase flow behaviors considering PSD in the solid phase as well as the temperature fields in the FBR.^{8–17} As mentioned, the polymerization is highly exothermic^{5–7} and may lead to the appearance of hot spots in the two-phase system if the polymerization heat cannot be efficiently removed from the reactor.^{18,19} These hot spots can downgrade the reactor safety and polymer properties.^{20,21} Therefore, ideal mixing and heat transfer are required to ensure efficient gas–solid contact and uniformity of temperature in FBR. In this respect, computational fluid dynamics (CFD) is becoming more and more an engineering tool to predict flow and temperature fields in various types of apparatus of industrial scale.^{22–24} CFD is also an emerging technique and holds great potential in providing detailed information on complex fluid dynamics.^{22–25} In addition, to describe the gas–solid two-phase flow behaviors of a polymerization system with solid PSD, the CFD model has to be solved together with the particle population balance model (PBM).

Generally, there are two categories of CFD models studied: the Lagrangian and the Eulerian models.^{22–27} The Lagrangian model describes equations of motion of each particle by taking into account particle–particle collisions and the forces acting on the particle, whereas in the Eulerian–Eulerian model, the two phases are both considered as con-

tinuous and fully interpenetrating. In recent years, considerable attention has been focused on the application of CFD to gas–solid FBRs.^{22–27} A comprehensive review on these CFD models applied to FBRs has been published.²⁸ Most authors used Eulerian models, including continuity and momentum equations for two interpenetrating continua, one representing the gas and the other for solid. In addition, different authors have adopted different assumptions with boundary conditions, interphase momentum transfer (drag) relationships, and parameters in the Eulerian model. As a whole, these CFD models can provide reasonably quantitative agreement with limited experimental findings with the help of fitting parameters.^{29–31} However, previous studies mainly focused on predicting the gas/solid holdup distributions via CFD model just by simplifying the flow field as a two-dimensional (2-D) field.^{29–34} Less effort is paid to the three-dimensional (3-D) CFD modeling of gas–solid fluidized-bed polymerization reactors.³⁵ Recently, we suggested a 3-D CFD model based on the Eulerian–Eulerian approach to describe the gas–solid two-phase flow in fluidized-bed polymerization reactors.³⁶ The entire flow behaviors in the FBRs, such as the solid holdup distributions, the bubble behaviors, and the solid velocity vectors, were obtained. In the modeling of FBRs mentioned above, studies on the temperature distributions/fields were not reported. Furthermore, preceding CFD models including our previous model³⁶ have assumed the solid particles of single size and ignored (polymerization) particle kinetics.

On the other hand, in olefin polymerization field, there are many publications on PSD by using particle balance equation (PBE). For instance, Zacca et al.⁶ presented a PBM for multi-stage olefin polymerization processes using catalyst residence time as main coordinate. Hatzantonis et al.³⁷ developed a generalized steady-state PBM rigorously accounting for the integrated effects of particle growth, attrition, elutriation, and aggregation in a gas-phase FBR. Harshe et al.³⁸ developed a comprehensive model for the propylene polymerization in a FBR, and the need for coupling the reaction-engineering model with the PBE was demonstrated. These models can be used to predict polymer molecular structure and morphology, including PSD. Recently, Yiannoulakis et al.⁴ developed a steady-state PBM, in which the polymeric flow model is used to predict the PSD in an ethylene copolymerization FBR and to calculate the growth rate of a single particle. More recently, our group developed a coupled single-particle and particle PBM to predict the PSD of PP produced in loop reactors.³⁹ Although these PBE-based models can be used to predict PSD of polyolefin produced in reactors including FBR, they still cannot be used to describe the flow behaviors in reactors.

Recently, more attention^{40–48} has been paid to the fact of polydisperse reactors and the influences of particle kinetics on the flow behaviors in gas–solid reactors, especially in gas–solid fluidized-bed polymerization reactors. Some hybrid CFD models that described the gas–solid flow fields in reactors via solving the CFD model to calculate the entire flow field, as well as the particle PBE for PSD, namely the CFD–PBM coupled model, were put forward.^{40–48} Olmos et al.⁴⁰ tried to couple the PBE with an Eulerian–Eulerian two-fluid model to simulate bubble-column reactors. In their work, the dispersed phase was represented by 10 different-size groups. However, to reduce the computing time significantly, only the momentum balance for the mixture was considered.

Thus, the 10 different classes were converted into the computational domain with the same mean algebraic velocity. Their results showed good agreement with experiments for some hydrodynamic variables; however, it underestimated the global holdup. Besides, the work was done in gas–liquid systems instead of gas–solid systems.⁴¹ Other researchers also tried to solve the PBE with multifluid code simultaneously; however, most works were still constrained within gas–liquid systems.^{42–44} Fan et al.⁴⁵ suggested a CFD-PBM coupled model to simulate polydisperse gas–solid FBRs. The direct quadrature method of moments (DQMOM) was used to solve the PBE and was implemented in a multifluid model to simulate polydisperse gas–solid FBRs. However, their model was a 2-D model, and several other features (e.g., heat and mass transfer, and chemical reaction) were not considered in the model. Fan et al.^{46–48} applied the CFD modeling approach developed in the above to fluidized-bed polyolefin reactors, which were used to produce high-density polyethylene and other polymers. In Ref. 46, quadrature method of moments (QMOM), chemical reaction engineering (CRE) model, and CFD were combined to investigate roles of intrinsic kinetics and the PSD of catalyst in a gas–solid FBR, wherein polymer PSD and flow fields including temperature field were also predicted. However, the aggregation and breakage were ignored. In addition, in their work, the polymerization reactions were solved outside of the CFD simulation using a CRE model. Based on the above discussions, it is obvious that PBE was not incorporated into the CFD model authentically as in previous CFD-PBM coupled models. Previous works also prove that the method of moments (DQMOM and QMOM) could be used to solve the PBE and realize the combination of the CFD model and PBE embedded with the particle kinetics. For QMOM and DQMOM, Mazzei et al.⁴⁹ pointed out that owing to numerical diffusion, QMOM and DQMOM, albeit theoretically equivalent, did not yield the same numerical results, and the QMOM was the only accurate method. Moreover, to the best of our knowledge, thus far there is no open report regarding the application of CFD-PBM coupled model in modeling the temperature field in the fluidized-bed olefin polymerization reactor. However, as described above, obtaining the temperature field is very important to operate the reactor more effectively, especially for considerations of operating safety and consistent polymer properties.

In this work, a 3-D CFD-PBM coupled model for the description of the gas–solid two-phase flow in fluidized-bed propylene polymerization reactor is developed. Based on an Eulerian–Eulerian two-fluid model, the coupled model incorporates the kinetic theory of granular flow (KTGF), the PBE embedded with the particle kinetics, and the heat-exchange coefficient equation. The QMOM is used to solve the PBE and realize the combination of the CFD model and PBE. The PBE and CFD models are both solved by the commercial CFD code FLUENT 6.3.26 in which the essential combination of PBE and CFD models is implemented. To the best of our knowledge, our work is the first one that aims at realizing the combination of PBE and CFD models in the fluidized-bed polymerization reactor. Two case studies, (1) with constant solid particle size and constant polymerization heat and (2) with evolving solid PSD, polymerization kinetics, and polymerization heat, are designed to confirm the suggested model.

Multifluid Model Description

A 3-D two-fluid model based on the Eulerian–Eulerian approach was used to describe the gas–solid two-phase flow in fluidized-bed polymerization reactor. The two-fluid model incorporated the KTGF, the PBE, and the heat-exchange coefficient equation. The QMOM was used to solve the PBE and implement the combination of the CFD model and PBE. The polymerization kinetics and the aggregation of polymer particles were also considered via the PBE embedded with the particle kinetics.

The population balance model and quadrature method of moments

The population balance concept was first presented by Hulburt and Katz,⁵⁰ which is a well-established method in computing the size distribution of the dispersed phase and well accounting for the breakage and aggregation effects in multiphase flows. A general form of the population balance equation can be expressed as follows⁵¹

$$\frac{\partial n(L; x, t)}{\partial t} + \nabla \cdot [\bar{u}n(L; x, t)] = -\frac{\partial}{\partial L} [G(L)n(L; x, t)] + B_{\text{ag}}(L; x, t) - D_{\text{ag}}(L; x, t) + B_{\text{br}}(L; x, t) - D_{\text{br}}(L; x, t) \quad (1)$$

where $n(L; x, t)$ is the number density function with particle diameter (L) as the internal coordinate, $G(L)n(L; x, t)$ is the particle flux due to molecular growth rate, $B_{\text{ag}}(L; x, t)$ and $D_{\text{ag}}(L; x, t)$ are the birth and death rate of particles diameter (L) due to aggregation, respectively, and $B_{\text{br}}(L; x, t)$ and $D_{\text{br}}(L; x, t)$ are the birth and death rate of particles diameter (L) due to breakage, respectively. In Eq. 1, the first term on the left hand is the transient term, the second term is the convective term, and the terms on the right hand are the source term describing particle growth, aggregation, and breakage dynamics, respectively.

In this study, QMOM is used to track the particle-size evolution by solving a system of differential equations in lower order moments. The moments of the PSD are defined as follows

$$m_{kk}(x, t) = \int_0^\infty n(L; x, t)L^{kk}dL \quad kk = 0, 1, \dots, N-1 \quad (2)$$

where kk is the specified number of moments and some moments have special meanings, such as m_0 , m_1 , m_2 and m_3 , which are related to the total number, length, area, and volume of solid particles per unit volume of mixture suspension, respectively. In addition, the Sauter mean diameter (L_{32}) is usually recognized as the mean particle size and is defined according to Eq. 3.

$$L_{32} = \frac{m_3}{m_2} \quad (3)$$

Applying the moment transformation into Eq. 1 results in

$$\frac{\partial m_{kk}}{\partial t} + \nabla \cdot (\bar{u}m_{kk}) = -\int_0^\infty kL^{k-1}G(L)n(L; x, t)dL + \bar{B}_{\text{ag}}(L; x, t) - \bar{D}_{\text{ag}}(L; x, t) + \bar{B}_{\text{br}}(L; x, t) - \bar{D}_{\text{br}}(L; x, t) \quad (4)$$

where $B_{ag}(L;x,t)$, $D_{ag}(L;x,t)$, $B_{br}(L;x,t)$, and $D_{br}(L;x,t)$ are given by

$$B_{ag,kk} = \frac{1}{2} \int_0^\infty n(\lambda; x, t) \int_0^\infty \beta(\lambda, L) (\lambda^3 + L^3)^{kk/3} n(\lambda; x, t) dL d\lambda, \quad (5)$$

$$D_{ag,kk} = \int_0^\infty L^{kk} n(L; x, t) \int_0^\infty \beta(\lambda, L) n(\lambda; x, t) dL d\lambda, \quad (6)$$

$$B_{br,kk} = \int_0^\infty L^{kk} \int_0^\infty a(\lambda) b(L|\lambda) n(\lambda; x, t) dL d\lambda, \quad (7)$$

$$D_{br,k} = \int_0^\infty L^{kk} a(L) n(L; x, t) dL \quad (8)$$

where $\beta(\lambda, L)$ is the aggregation kernel, $a(L)$ is the breakage kernel, the frequency of disruption of a particle of length L , and $b(L|\lambda)$ is the fragment distribution function that contains the information of fragments produced by a breakage event.

The QMOM uses a quadrature approximation as follows

$$m_{kk} = \int_0^\infty n(L; x, t) L^{kk} dL \approx \sum_{i=1}^N w_i L_i^{kk} \quad (9)$$

where the weights (w_i) and abscissas (L_i) are determined through the product-difference algorithm from the lower order moments.⁵² After applying the quadrature approximation, the transformed moment PBE can be written as

$$\begin{aligned} \frac{\partial m_{kk}}{\partial t} + \nabla \cdot (\vec{u} m_{kk}) &= k \sum_{i=1}^N L_i^{kk-1} G(L_i) w_i \\ &+ \frac{1}{2} \sum_{i=1}^N w_i \sum_{j=1}^N w_j (L_i^3 + L_j^3)^{kk/3} \beta(L_i, L_j) \\ &- \sum_{i=1}^N L_i^{kk} w_i \sum_{j=1}^N w_j \beta(L_i L_j) + \sum_{i=1}^N w_i \int_0^\infty L_{kk} a(L_i) b(L|L_i) dL \\ &- \sum_{i=1}^N L_i^{kk} w_i a(L_i) \quad (10) \end{aligned}$$

The PBE in Eq. 10 is solvable via the quadrature method of moments by following the evolution of w_i and L_i as well as m_{kk} . The moments are related to the weights and abscissas by Eq. 9.

The local value of growth rate $G(L)$ is related to the polymerization reaction rate, which can be calculated as

$$G(L_i) = \frac{d(L_i)}{dt} = \frac{R_p L_0^3}{3 \rho_s L_i^2} \quad (11)$$

The polymerization reaction rate is defined as the rate of propagation reaction rate and is shown as Eq. 12

$$R_p = k_p [C][M] \quad (12)$$

The aggregation kernel, which represents the effect of the particle aggregation on the particle temperature, proposed by Hatzantonis et al. is used as³⁷

$$\beta(L_i, L_j) = KK(L_i^2 + L_j^2) \left(\frac{1}{L_i L_j} \right)^4 \quad (13)$$

where KK is a function of fluidizing temperature that can be expressed as⁴

$$KK = kk_1 \exp(kk_2 T_s / T_{sf}) \quad (14)$$

where T_s is the average temperature of the two aggregating particles (the solid-phase temperature) and T_{sf} is the average polymer melting temperature of particle size L_i and L_j .

CFD model

Numerical simulations are based on the two-fluid model Eulerian–Eulerian approach. The KTGF, which considers the conservation of solid fluctuation energy, is used for the closure of solid stress terms. The governing equations are summarized as follows.^{53–56}

Eulerian–Eulerian Two-Fluid Equations. The continuity equations for phase q ($q = g$ for gas, s for solid phases) can be written as

$$\frac{\partial}{\partial t} (\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \vec{v}_q) = \dot{m}_{sp}, \quad \dot{m}_{sp} = \frac{1}{2} \rho_s \pi G m_2 \quad (15)$$

The momentum balance equations for gas and solid phases can be expressed as

$$\begin{aligned} \frac{\partial}{\partial t} (\alpha_g \rho_g \vec{v}_g) + \nabla \cdot (\alpha_g \rho_g \vec{v}_g \vec{v}_g) &= -\alpha_g \nabla p + \nabla \cdot \bar{\tau}_g \\ &+ K_{gs} (\vec{v}_s - \vec{v}_g) + \alpha_g \rho_g g \quad (16) \end{aligned}$$

$$\bar{\tau}_g = \alpha_g \mu_g (\nabla \vec{v}_g + \nabla \vec{v}_g^T) \quad (17)$$

$$\begin{aligned} \frac{\partial}{\partial t} (\alpha_s \rho_s \vec{v}_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \vec{v}_s) &= -\alpha_s \nabla p - \nabla p_s + \nabla \cdot \bar{\tau}_s \\ &+ K_{gs} (\vec{v}_q - \vec{v}_s) + \alpha_s \rho_s g \quad (18) \end{aligned}$$

$$\bar{\tau}_s = \alpha_s \mu_s (\nabla \vec{v}_s + \nabla \vec{v}_s^T) + \alpha_s \left(\lambda_s - \frac{2}{3} \mu_s \right) \nabla \cdot \vec{v}_s \vec{I} \quad (19)$$

The energy balance equations for gas and solid phases are characterized as

$$\begin{aligned} \frac{\partial}{\partial t} (\alpha_g \rho_g h_g) + \nabla \cdot (\alpha_g \rho_g \vec{v}_g h_g) &= -\alpha_g \frac{\partial p_g}{\partial t} + \bar{\tau}_g : \nabla \vec{v}_g - \nabla \cdot q_g \\ &+ \sum_{p=1}^n (Q_{gs} + \dot{m}_{gs} h_{gs} - \dot{m}_{sg} h_{sg}) \quad (20) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} (\alpha_s \rho_s h_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s h_s) &= -\alpha_s \frac{\partial p_s}{\partial t} + \bar{\tau}_s : \nabla \vec{v}_s - \nabla \cdot q_s \\ &+ \sum_{p=1}^n (Q_{sg} + \dot{m}_{sg} h_{sg} - \dot{m}_{gs} h_{gs}) + \Delta Q_{rsz} \quad (21) \end{aligned}$$

where

$$h_i = \int_{T_{ref}}^T c_{p,i} dT \quad i = g \text{ or } s_i \quad (22)$$

$$q_i = -\alpha_i \kappa_i \nabla T_i \quad (i = g \text{ or } s) \quad (23)$$

Kinetic Theory of Granular Flow. The two-fluid model requires constitutive equations to describe the rheology of the solid phase. When the particle motion is dominated by collision interaction, the concepts from fluid kinetic theory can be introduced to describe the effective stresses in the solid phase resulting from particle streaming (kinetic contribution and direct collisions) collisional contribution. Furthermore, these constitutive relations for the solid-phase stress based on the kinetic theory concepts were derived by Lun et al.⁵⁵ and have been widely accepted. Accordingly, they were also used in this work as follows

$$p_s = \alpha_s \rho_s \Theta_s [1 + 2g_0 \alpha_s (1 + e_s)], \quad (24)$$

$$\lambda_s = \frac{4}{3} \alpha_s^2 \rho_s d_s g_0 (1 + e_s) \sqrt{\frac{\Theta_s}{\pi}} \quad (25)$$

where

$$g_0 = \frac{1}{1 - (\alpha_s / \alpha_{s,max})^{1/3}} \quad (26)$$

$$\Theta_s = \frac{1}{3} \overline{\mu'_s \mu'_s} \quad (27)$$

Besides Eqs. 24–27, the transport equation for granular temperature that is essential in this work is according to Ding and Gidaspow's model⁵³

$$\frac{3}{2} \left[\frac{\partial}{\partial t} (\rho_s \alpha_s \Theta_s) + \nabla \cdot (\rho_s \alpha_s \vec{v}_s \Theta_s) \right] = (-p_s \vec{I} + \overline{\tau_s}) : \nabla \vec{v}_s + \nabla \cdot (k_{\Theta_s} \nabla \Theta_s) - \gamma_{\Theta_s} + \phi_{gs} \quad (28)$$

where the diffusion coefficient for granular energy, k_{Θ_s} , is given by Syamlal et al.⁵⁶

$$k_{\Theta_s} = \frac{15 \rho_s d_s \alpha_s \sqrt{\pi \Theta_s}}{4(41 - 33\eta)} \left[1 + \frac{12}{5} \eta^2 (4\eta - 3) \alpha_s g_0 + \frac{16}{15\pi} (41 - 33\eta) \eta \alpha_s g_0 \right] \quad (29)$$

where

$$\eta = \frac{1}{2} (1 + e_s) \quad (30)$$

The collision dissipation of energy, γ_{Θ_s} , is modeled using the correlation by Lun et al.⁵⁵

$$\gamma_{\Theta_s} = \frac{12(1 - e_s^2)g_0}{d_s \sqrt{\pi}} \rho_s \alpha_s^2 \Theta_s^{1.5} \quad (31)$$

$$\phi_{gs} = -3K_{gs} \Theta_s \quad (32)$$

In this study, the granular energy was assumed at steady state and dissipated locally. The convection and diffusion were also

neglected. Accordingly, Eq. 28, which is a complete granular temperature transport equation, can be rewritten to an algebraic equation, and the simplified equation is as follows

$$0 = (-p_s \vec{I} + \overline{\tau_s}) : \nabla \vec{v}_s - \gamma_{\Theta_s} - 3K_{gs} \Theta_s \quad (33)$$

As selected in our previous work,³⁶ here, the same models for the solid-phase dynamic viscosity are adopted as follows

$$\mu_s = \mu_{s,col} + \mu_{s,kin} + \mu_{s,fr} \quad (34)$$

where

$$\mu_{s,col} = \frac{4}{5} \alpha_s \rho_s d_s g_0 (1 + e_s) \sqrt{\frac{\Theta_s}{\pi}} \quad (35)$$

$$\mu_{s,kin} = \frac{10 d_s \rho_s \sqrt{\Theta_s \pi}}{96 \alpha_s (1 + e_s) g_0} \left[1 + \frac{4}{5} (1 + e_s) \alpha_s g_0 \right]^2 \quad (36)$$

$$\mu_{s,fr} = \frac{p_s \sin \theta}{2 \sqrt{I_{2D}}} \quad (37)$$

Drag Force Model. In this work, the transfer of forces between the gas and solid phases was described by an empirical drag law proposed by Gidaspow,³¹ which is the same that applied in our previous reports.³⁶ Corresponding equations are described as follows

$$\text{at } \alpha_g > 0.8, \quad K_{sg} = \frac{3}{4} C_D \frac{\alpha_s \alpha_g \rho_g |\vec{v}_s - \vec{v}_g|}{d_s} \alpha_g^{-2.65} \quad (38)$$

where

$$C_D = \frac{24}{\alpha_g Re_s} \left[1 + \left(\frac{3}{20} \alpha_g Re_s \right)^{0.687} \right] \quad (39)$$

$$Re_s = \frac{\rho_g d_s |\vec{v}_s - \vec{v}_g|}{\mu_g} \quad (40)$$

$$\text{at } \alpha_g \leq 0.8, \quad K_{sg} = 150 \frac{\alpha_s (1 - \alpha_g) \mu_g}{\alpha_g d_s^2} + \frac{7 \alpha_s \rho_g |\vec{v}_s - \vec{v}_g|}{4 d_s} \quad (41)$$

Turbulent Model. A standard $k - \varepsilon$ model was used to solve the transport equations for k and ε .^{57,58} The $k - \varepsilon$ model is written as follows

$$\nabla \cdot (\rho_m k \vec{v}_m) = \nabla \cdot \left(\frac{\mu_{t,m}}{\sigma_k} \nabla k \right) + G_{k,m} - \rho_m \varepsilon \quad (42)$$

$$\nabla \cdot (\rho_m \varepsilon \vec{v}_m) = \nabla \cdot \left(\frac{\mu_{t,m}}{\sigma_\varepsilon} \nabla \varepsilon \right) + \frac{\varepsilon}{k} (C_{1\varepsilon} G_{k,m} - C_{2\varepsilon} \rho_m \varepsilon) \quad (43)$$

also, the assumption of excellent mixing in the reactor

$$\rho_m = \sum_{i=1}^N \alpha_i \rho_i \quad (44)$$

$$\vec{v}_m = \frac{\sum_{i=1}^N \alpha_i \rho_i \vec{v}_m}{\sum_{i=1}^N \alpha_i \rho_i} \quad (45)$$

$$\mu_{t,m} = \rho_m C_\mu \frac{k^2}{\varepsilon} \quad (46)$$

Heat-Exchange Coefficient. The rate of energy transfer between phases is assumed to be a function of the temperature difference and is described as follows

$$Q_{gs} = \kappa_{gs}(T_s - T_g) \quad (47)$$

$$\kappa_{gs} = \frac{6\kappa_g \alpha_g \alpha_s Nu_s}{d_s^2} \quad (48)$$

The Nusselt number is typically determined from one of the many correlations reported in the literature. Here, we applied the correlation of Ranz and Marshall as follows⁵⁹

$$Nu_s = 2.0 + 0.6 Re_s^{1/2} Pr^{1/3}, \quad Pr = \frac{c_{p,g} \mu_g}{\kappa_g} \quad (49)$$

The CFD-PBM coupled model

Particles in the fluidized-bed polymerization reactor have a size distribution due to the polymerization reaction. In two-phase CFD simulations, generally a two-fluid model is applied with particles of a constant diameter instead of different sizes in the dispersed phase. However, if the PSD is wide or multimodal, this approach is more likely to fail.⁶⁰ The CFD-PBM coupled model can overcome this drawback.

Figure 2 shows the schematic of CFD-PBM coupled model suggested in this work. The solid volume fraction, particle velocity, and temperature calculated from the Navier–Stokes transport equations by CFD are used to solve the PBM, because they are related to the particle growth, aggregation, and breakage. Once the population balance equation is solved, moments of PSD can be used to calculate the Sauter diameter to further modify the interphase force in the two-fluid model and hence update the information of solid volume fraction, particle velocity, and temperature for PBM. Thus, an integrated coupling between CFD and PBM is achieved. Both CFD and PBM can improve each other in the coupled model.

Simulation Conditions and CFD Modeling Method

The 3-D simulations based on the coupled CFD-PBM model were performed with the industrial CFD code FLU-

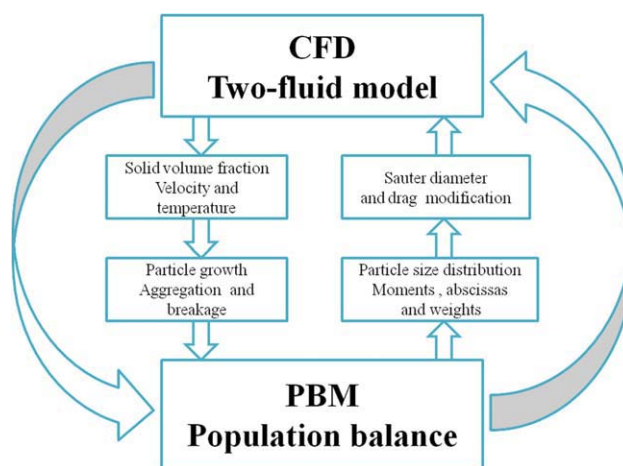


Figure 2. Coupled model in the CFD-PBM coupled model.

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ENT 6.3.26 (Ansys, USA) in double precision mode. The simulated reactor has an inner diameter of 0.33 m, a height of 0.90 m, and an initial bed height of 0.2 m. In addition, to simulate the 3-D reactor, a commercial grid-generation tool, GAMBIT 2.3.16 (Ansys, USA), was used to generate the 3-D geometries and the grids. Grid sensitivity was carried out initially, and the results indicated that a total amount of 89,010 cells was adequate to conserve the mass of solid phase in the dynamics model. The phase-coupled SIMPLE algorithm was used to couple pressure and velocity. Equations and source terms of the reaction kinetics and PBM were defined via external user-defined scalars and functions. A two-stage calculation was implemented. First, the flow field was simulated without the reaction and aggregation process until the fully fluidized flow field reached. Afterward, the reaction process was simulated within FLUENT by activating the energy and PBE model. This two-stage calculation method is already applied in other processes and is proved to be accurate and computationally efficient (the feasibility of the two-stage calculation method was validated by Öncül et al.⁶¹). In addition, as to the above solution, reconstruction of PSD must be used, and it is automatically accomplished within FLUENT 6.3.26 (Ansys, USA) (the reconstruction principle can be found in Ref. 62). Furthermore, the simulations were performed in a platform of Intel 2.83 GHz Xeon with 8 GB of RAM.

Table 1. Model Parameters^{22–36,49–70}

Descriptions	Values	Descriptions	Values
Gas density	21.56 kg m ⁻³	Particle density	900 kg m ⁻³
Gas viscosity	1.081 × 10 ⁻⁵ Pa s	Particle heat capacity	2104 J kg ⁻¹ K ⁻¹
Gas heat capacity	1817 J kg ⁻¹ K ⁻¹	Restitution coefficient	0.9
Inlet gas velocity	0.3 m s ⁻¹	Granular viscosity	Gidspow
Inlet gas temperature	313 K	Granular bulk viscosity	Lun et al. ⁵⁵
Bed width	0.33 m	Frictional viscosity	Schaeffer
Bed height	0.9 m	Angle of internal friction	30°
Wall boundary condition	No slip for air and free slip for solid phase, ^{36,69,70} the adiabatic heat-transfer equation	Initial solid packing	0.6
Operating pressure	1.40 × 10 ⁶ Pa	Convergence criteria	1 × 10 ⁻³
Maximum iterations	50	Time step	1 × 10 ⁻³ s

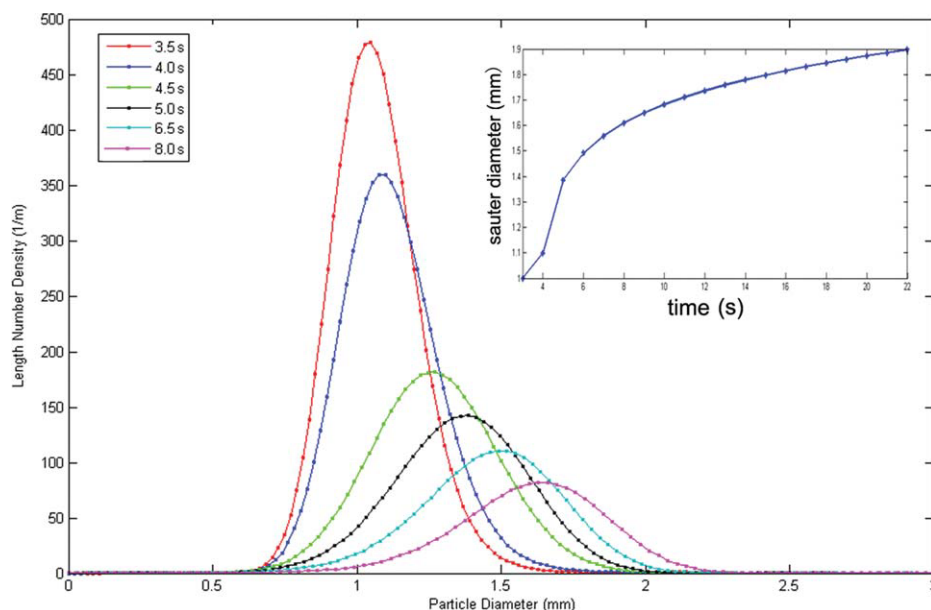


Figure 3. The evolution of particle-size distribution with time due to aggregation ($KK = 1E - 18$).

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On the other hand, the simulated results depend on the range of parameter values presented in Eqs. 1–49. Most of the parameters are directly linked to the properties of the gas and solid phases in the reactor. The properties of the typical gas and solid phases are listed in Table 1. In addition, as described above, many researchers^{22–36,40–66} studied the gas–solid/liquid–solid two-phase flow, a set of reference values of these parameters can be selected. In our previous study,³⁶ two important parameters including the restitution coefficient (e_s) and the specularity coefficient (ϕ) were investigated. We find that a little change of ϕ would lead to a significant change of pressure drop in the loop reactor (here, no results are given and please refer to our previous study³⁶). However, the pressure drop is not sensitive to the changes of the restitution coefficient. Therefore, the default value of 0.9 for the restitution coefficient in FLUENT was chosen. Furthermore, our foregone sensitivity analysis of specularity coefficient shows that with the increase of ϕ , the difference between

the predicted pressure drop at the corresponding flow velocity and flow time and that obtained via the classical Newitt model increases.^{67,68} A good prediction of pressure drop when ϕ equals to 0 can be obtained. Meanwhile, the value of 0 for ϕ is also that at the free-slip boundary condition for the solid-phase wall boundary condition and can be found in typical literatures.^{69,70} Therefore, the value of 0 for the specularity coefficient was chosen and shown in Table 1. Finally, the detailed settings in the software are listed in Table 1. Unless otherwise noted, the parameters used for the following simulations were exactly as listed in Table 1.

Results and Discussion

This section comprises three subsections, namely, the coupled CFD-PBM model testing, identification, and application. The model is preliminarily validated by comparing the predicted results with the classical calculated/experimental

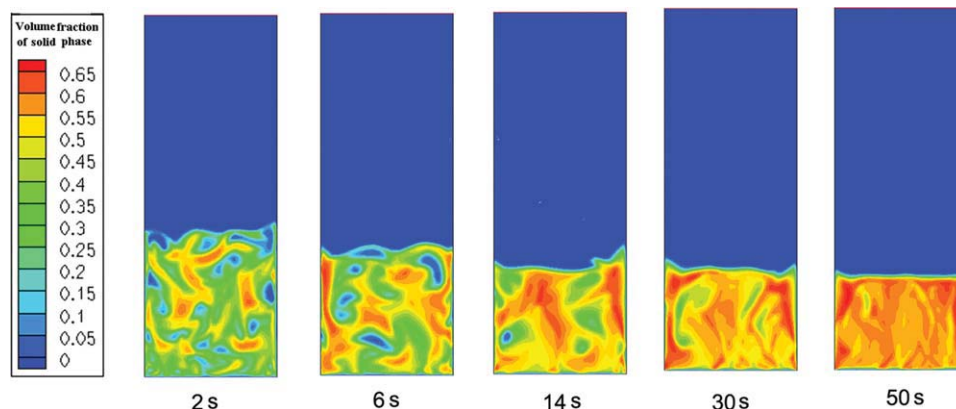


Figure 4. The evolution of defluidization with time due to aggregation ($KK = 1E - 18$).

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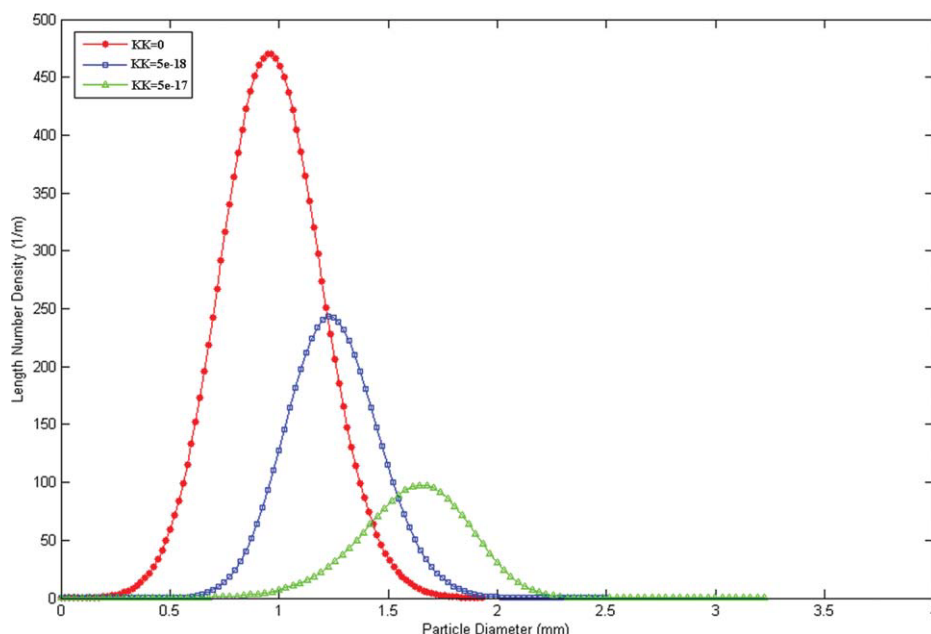


Figure 5. Effect of KK on particle-size distribution ($t = 4$ s).

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results. Two case studies, (1) with constant solid particle size and constant polymerization heat and (2) with evolving solid PSD, polymerization kinetics, and polymerization heat, were designed to identify the suggested model. The coupled model was used to investigate the influences of some operational conditions on the temperature fields. Furthermore, the temperature data shown in Figures 10–12 and 16–19 represent the mean temperature value of a plane in the reactor.

Model testing

Compared to our previous model,³⁶ the coupled CFD-PBM model suggested in this work incorporates the PBM and the heat-exchange coefficient equations. In addition, in the fluidized-bed olefin polymerization reactor, the polymer particles can break into many small fragments if the polymerization temperature is too low or agglomerate to bigger ones if the temperature approaches to the melting temperature of polymers. To maintain reasonable polymerization rate in industry, the gas-phase fluidized bed is usually operated at a relatively high temperature. Furthermore, the olefin polymerization is a highly exothermic reaction. Therefore, the particles and their size distribution in the reactor are dominated by aggregation. As described earlier, the PBM incorporated in the CFD can be used to compute the aggregation-dominated PSD. Therefore, in this work, we testified the aggregation kernel and its effect on the flow hydrodynamic.

Since Arastoopour et al.⁶³ experimentally investigated the agglomeration of inert polyethylene particles in a fluidized bed. Their experimental results showed that the aggregation kernel turns out to favor the agglomeration of large-size particles. On the basis of Arastoopour et al.'s work,⁶³ Hatzantonis et al. proposed a modified particle aggregation kernel (Eq. 13) to account for the high aggregation rate of small-size particles.³⁷ In Eq. 13, KK is an aggregation rate constant and is not related to the fluidizing temperature. However, in

practice, the fluidizing temperature has a great impact on the aggregation rate. In the CFD-PBM coupled model, KK was used as a functional form of fluidizing temperature suggested by Yiannoulakis et al. and shown in Eq. 14.⁴ Meanwhile, the results obtained by Arastoopour et al.,⁶³ Hatzantonis et al.,³⁷ and Yiannoulakis et al.⁴ are used to testify the aggregation kernel coupled in our CFD-PBM coupled model.

To compare our model with that suggested by Hatzantonis et al.,³⁷ we first used a constant aggregation rate ($KK = 1E - 18 \text{ m}^{-6} \text{ s}^{-1}$), and the simulated results are shown in Figures 3 and 4. Figures 3 and 4 illustrate the evolution of PSD with fluidizing time and the evolution of defluidization

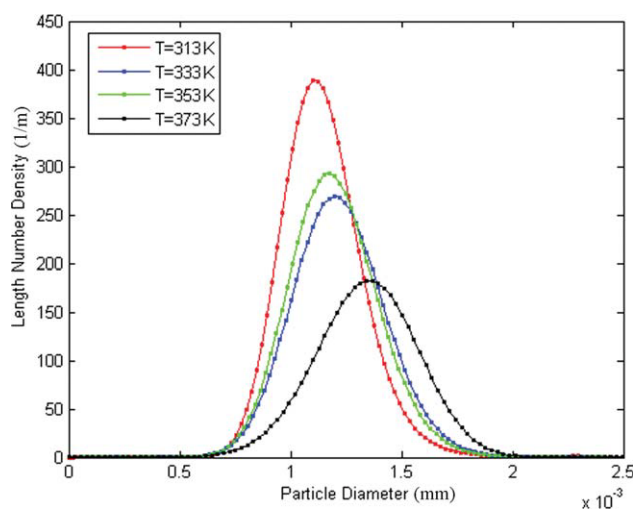


Figure 6. Effect of particle temperature on particle-size distribution ($t = 4$ s).

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Table 2. Major Differences for the Input Conditions at the Two Cases^{2-7,18,19}

Cases	PSDs	Polymerization Heats	Equations
Case 1	Monodisperse	The assumption of constant ΔQ_{rsz} is applied, namely, ΔQ_{rsz} is independent on the particle size and the polymerization kinetics.	$Q_{rs} = C_{p,g} \bar{m}_{g,inlet} (T_{g,outlet} - T_{g,inlet})$ $\Delta Q_{rsz} = \frac{Q_{rs}}{V_s} = 4.8 \text{ Wm}^3$ $T_{g,inlet} = 313 \text{ K}, T_{g,outlet} = 349 \text{ K}$
Case 2	Polydisperse	ΔQ_{rsz} is dependent on the particle size and the polymerization kinetics. Supplementary data regarding to the Case 2 are given in Appendix.	$\Delta Q_{rsz} = R_p \cdot \Delta H$ $R_p = k_{p0} \exp\left(-\frac{E}{R(273.15+t)}\right) [M][C^*]$ $G(L_s) = \frac{L(L_s)}{dt} = \frac{R_p L_0^3}{3\rho_s L_s^2}$ $\dot{m} = \frac{1}{2}\pi\rho_s G(L_s) m_1$ $\Delta H = 100 \text{ kJ/mol}^{-1}$

due to the aggregation, respectively. From Figures 3 and 4, the aggregation rate decreases with the increase of the Sauter mean particle size, and a fully fluidized flow field can be formed at 3.4 s in the presence of aggregation kernel. In addition, from Figures 3 and 4, as the particles begin to aggregate, the Sauter mean diameter continues to increase, whereas the height of the bed decreases until the defluidization phenomenon appears. Furthermore, the simulated results shown in Figure 3 are in qualitative agreement with the results obtained by Hatzantonis et al.³⁷ (please refer to Figure 12 in Ref. 27).

For further validation, the effect of KK on the PSD was also obtained by using the CFD-PBM coupled model, and the simulated results were compared with those obtained by

Arastoopour et al.,⁶³ Hatzantonis et al.,³⁷ and Yiannoulakis et al.⁴ The simulated results are shown in Figures 5 and 6. Figure 5 illustrates the simulated effect of KK on the PSD at 4 s. The results are in qualitative agreement with the simulated results obtained by Hatzantonis et al.³⁷ and Yiannoulakis et al.⁴ Figure 6 illustrates the simulated effect of particle temperature on the PSD at 4 s in which the temperature of particle is assumed to be constant, namely, for Eq. 14, $kk_1 = 5e - 10$ and $kk_2 = 2.5$. The simulated results show that the aggregation rate increases exponentially with particle surface temperature, and as the particle surface temperature approaches the melting point of the polymer, the particles' aggregation tendency increases, which is consistent with the experimental results obtained by Arastoopour et al.⁶³

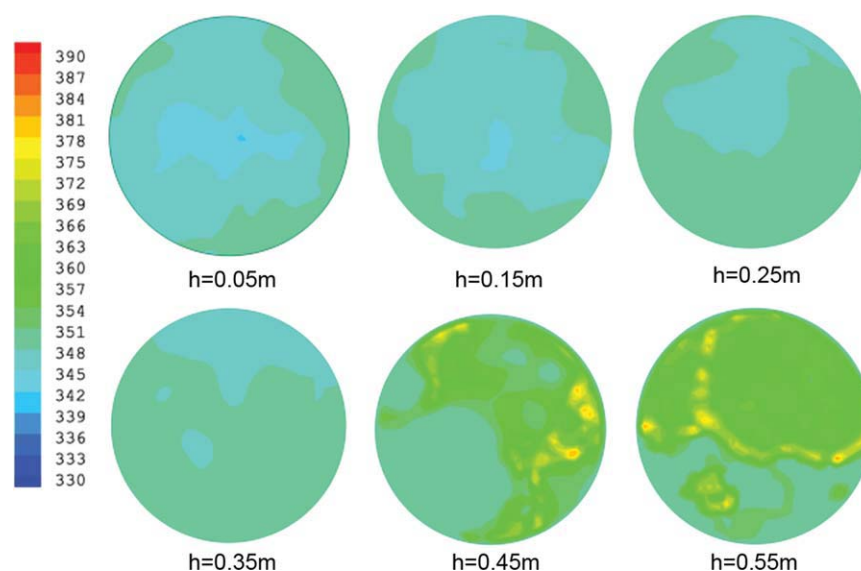


Figure 7. Temperature distributions of solid phase in FBR in Case 1.

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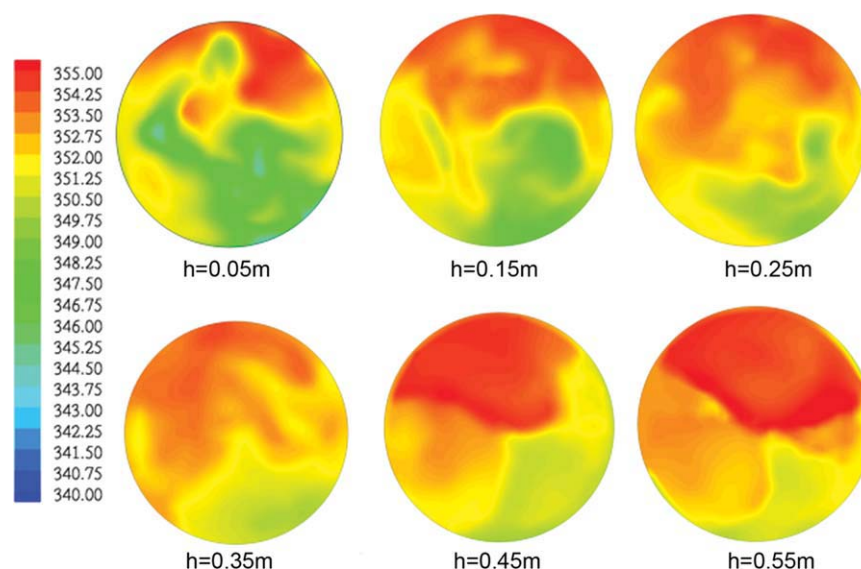


Figure 8. Temperature distributions of solid phase in FBR in Case 2.

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Model identification

In this work, two case studies, (1) with constant solid particle size and constant polymerization heat and (2) with evolving solid PSD, polymerization kinetics, and polymerization heat, were designed to distinguish the suggested model. For the two cases, except those listed in Table 1, corresponding simulated conditions are shown in Table 2. In addition, the simulated results and their comparisons at the two cases are described as follows step by step.

The simulated temperature distributions of solid phase in the reactor at Case 1 are shown in Figure 7. In Case 1, the temperature in the whole bed is about 348 K, and some hot spots ($T > 370$ K) appear at the section where height is larger than 0.45 m. It is well known that the heat-transfer

coefficient of gas–solid two-phase increases proportionally with the increase of the product of volume fraction of liquid phase and volume fraction of solid phase. In addition, because of the gas entrainment, little amount of solid particles in the top of bed leads to the generation of a few fraction of solid phase there. Hence, the amount of heat release in the interphase is little. Meanwhile, in Case 1, both the solid particle size and the polymerization heat in the bed are assumed to be constant. It means that the heat release in any position of solid phase is the same. The same heat release in the top of bed leads to the appearance of hot spots. However, the above results would not be observed in that position in industry because of the little fraction of solid phase. To overcome the limitation in Case 1, the heat release

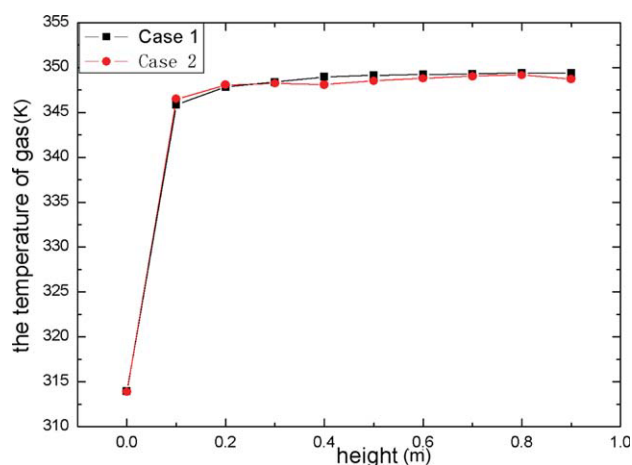


Figure 9. Comparison of temperature of gas phase in different cases.

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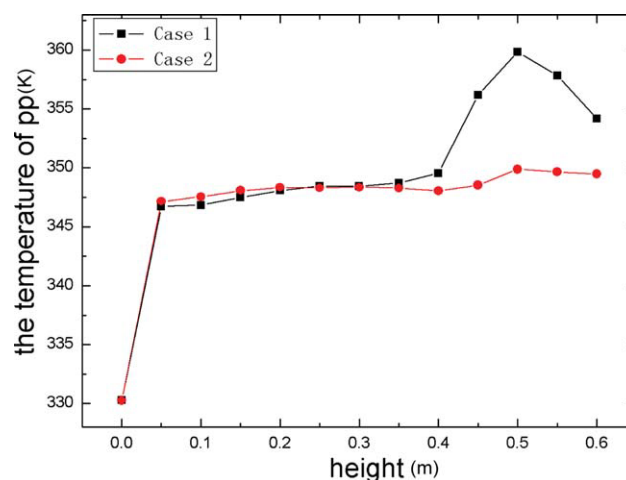


Figure 10. Comparison of temperature of solid phase in different cases (at steady fluidization).

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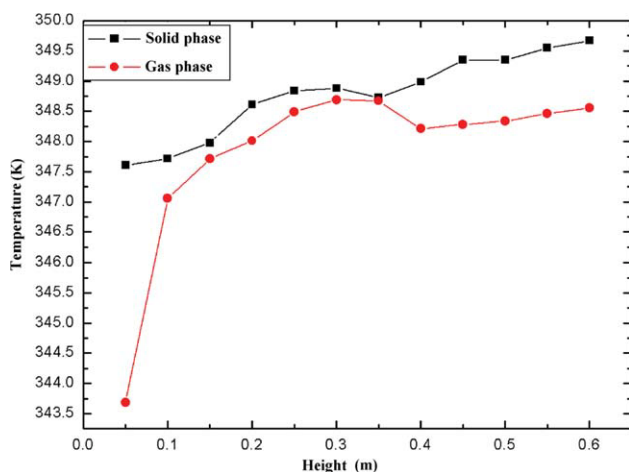


Figure 11. The evolution of temperatures of gas and solid phases with axial direction from the bottom to top of the reactor in Case 2 (at steady fluidization).

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amount in the solid phase was related to the volume fraction of solid phase in Case 2; the PSD and polymerization kinetics were considered based on Case 1. The corresponding simulated temperature distributions of solid phase in the reactor are shown in Figure 8, where an uneven temperature distribution but no hot spot ($T > 370$ K) was observed in the bed. In practice, the uneven temperature distribution in the bed is due to the presence of PSD and polymerization kinetics. Based on Figures 7 and 8 and the above discussions, the simulated temperature distributions in the bed in Case 2 are closest to the reality.^{64,65} To further demonstrate this claim, comparisons of the temperature fields of gas and solid phases at steady-state conditions in the two cases are listed in Figures 9 and 10. In Figures 9 and 10, the obtained temperature fields of gas phase in the bed in the two cases are similar, and the temperature fields of solid phase in the bed in Case 2 greatly differ from that in Case 1. Based on the collected plant data,^{65,66} the appearance of hot spots in Case 1 cannot represent the actual flow fields

in the bed. It is well known that the polymer particles and polymerization heat in industry are changed during the polymerization process.^{37,38} Furthermore, the simulated results in Case 2 are closer to the actual flow fields in the bed because of the consideration of PSD in Case 2. Namely, the simulated results in Case 2 agreed better with the fact. Therefore, the suggested model in Case 2 was used to investigate the influences of some operational conditions on the temperature fields.

Model application

Temperature Distributions in the Entire FBR. The CFD-PBM coupled model in Case 2 is for the first time used to predict the temperature distributions in the entire FBR. The results are shown in Figure 11 (the results are also listed in Figures 9 and 10). From Figure 11, both the temperatures of gas and solid phases increase in total along the axial direction from the bottom to the top of the FBR. In addition, Figure 11 also shows that the change of the temperature of gas phase tags along with that of solid phase, and both their change are small (< 5 K). Regarding to the small changes of temperature, it is noted that first the cool fresh gaseous monomers are fed into the bottom of the FBR and react with the solid catalyst instantaneously. Accordingly, much heat is released because of the highly exothermic reaction of olefin polymerization, which causes the heating up of gas phase in the bottom of FBR. Second, the released heat is removed promptly by gaseous monomers because of FBR's excellent mass and heat transfer characteristics. Therefore, the total change of temperature of gas and solid phases along the axial direction is little.

On the other hand, although the total change along the axial direction is little, the temperature changes of the same plane in the FBR are about 10 K. To illustrate this point, the flow fields including the solid holdup and the temperature distributions of any plane were obtained in the FBR. The simulated flow fields of the planes at 0.05 and 0.10 m in height are shown in Figures 12 and 13, respectively. From Figure 12, the temperature distributions of gas and solid phases are related to the volume fraction of solid phase, and the three distribution profiles shown in Figure 12 are similar. In addition, as shown in Figure 12, the

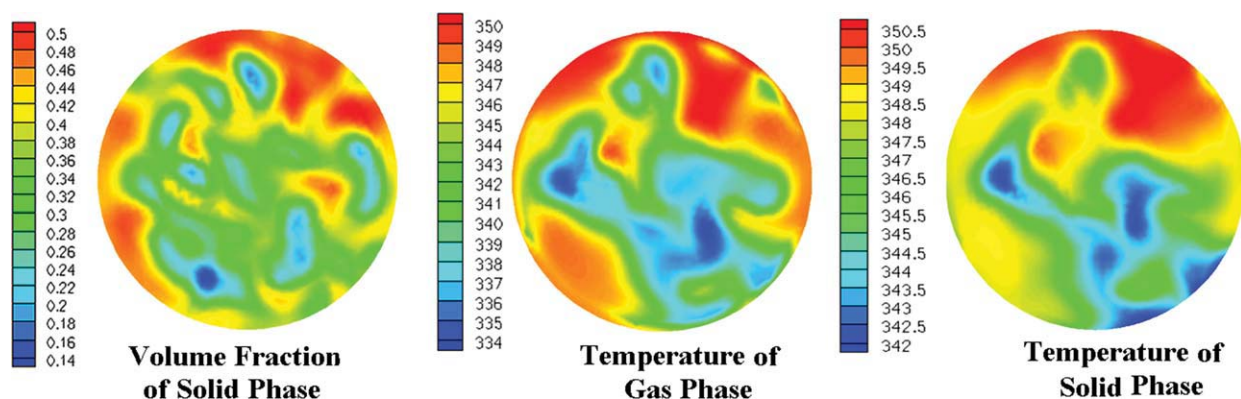


Figure 12. Flow fields of the plane in which height is 0.05.

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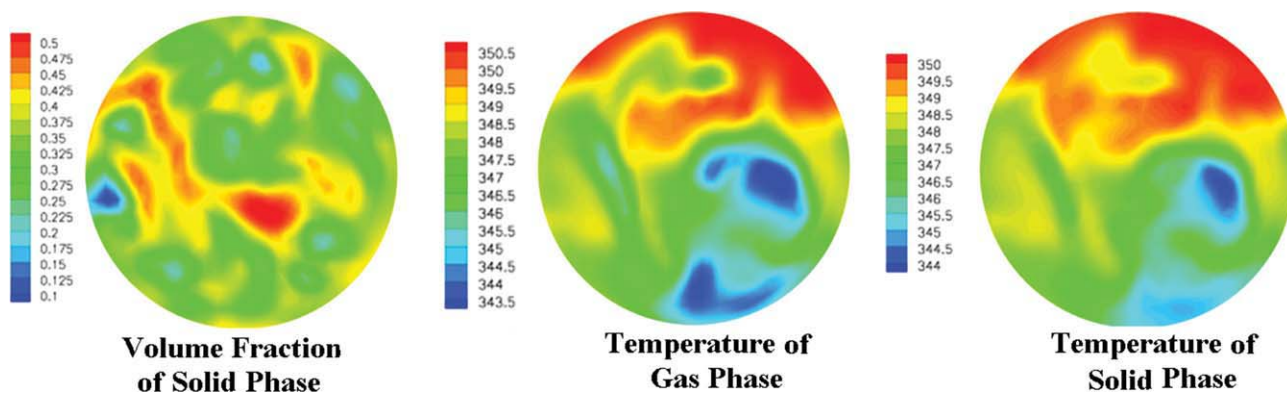


Figure 13. Flow fields of the plane in which height is 0.10 ($t = 73.5$ s).

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particles near the wall of reactor are easy to aggregate, and correspondingly, the temperature values near the wall are the highest in the plane. According to Figure 13, the profile of volume fraction of solid phase is greatly different from the other two profiles. In practice, the temperature distributions are not only related to the volume fraction of solid phase in the plane but also depended on the temperature of gaseous monomers rising from the bottom in FBR. Because the rising gaseous monomers near the wall are not fully cooled, the temperature near the wall is the highest in the plane.

Based on the above discussion, the temperature of solid phase increases along the axial direction from bottom to top

for any plane of FBR, and the temperature of solid phase near the wall is higher than that in the other position. Figure 14 is the simulated temperature distribution profile when the volume fraction of solid phase is 0.2, which shows that the highest temperature position indeed appears at the top or near the wall section of the FBR.

The Inlet Gas Velocity on the Temperature Fields. To investigate the effect of the inlet gas velocity on the temperature fields in the FBR, three inlet gas velocities are studied, i.e., 0.25, 0.30, and 0.40 m s^{-1} . The simulated results are shown in Figures 15 and 16.

Figures 15 and 16 illustrate that the inlet gas velocity is an important factor in controlling the reactor temperature fields. In a low velocity, the released heat by the solid particles due to polymerization cannot be removed from solid phase in time, which results in the increase of temperature of solid phase, then consequently, the increase of the temperature of gas phase. Therefore, the high inlet gas velocity is helpful to remove the polymerization heat. However, an excessive high inlet gas velocity may greatly influence the fluidization quality of FBR. At an unreasonably high inlet gas velocity, the amount of entrainment of the

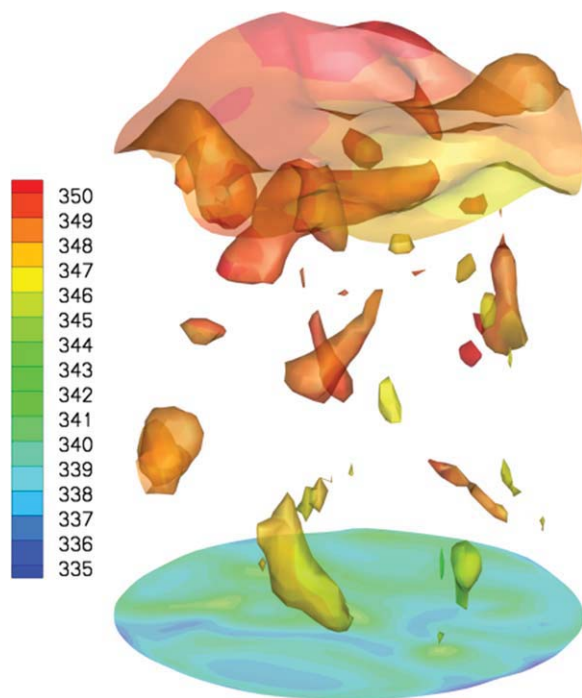


Figure 14. Temperature distributions of solid phase at the solid volume fraction of 0.2 ($t = 73.5$ s).

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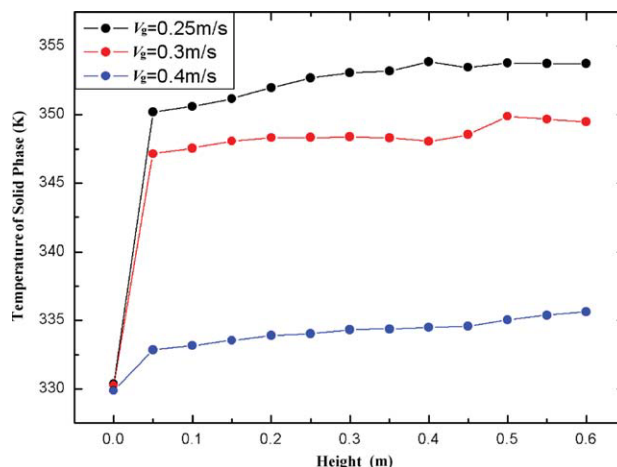


Figure 15. Effect of inlet gas velocity on temperature of solid phase.

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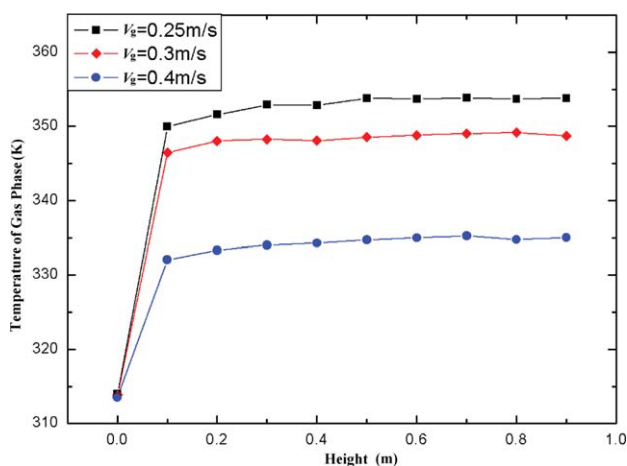


Figure 16. Effect of inlet gas velocity on temperature of gas phase.

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active polymer particles increases, which results in the blockage of circular pipe and distributor. Therefore, the practical inlet gas velocity is always within an appropriate range.

The Inlet Gas Temperature on the Temperature Fields. The effect of the inlet gas temperature on the temperature fields in the FBR is also investigated via the above CFD-PBM coupled model. The simulated temperature field is shown in Figures 17 and 18.

Figures 17 and 18 illustrate that the decrease of inlet gas temperature can lead to the decrease of the reactor temperature. In practice, the inlet gas temperature is to sustain the polymerization temperature. Furthermore, similar reason related to heat transfer and PSD as well as what is described above can well explain this result.

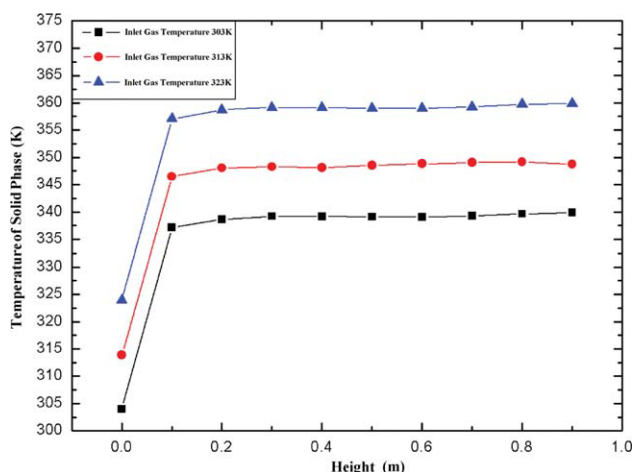


Figure 17. Effect of inlet gas temperature on temperature of solid phase.

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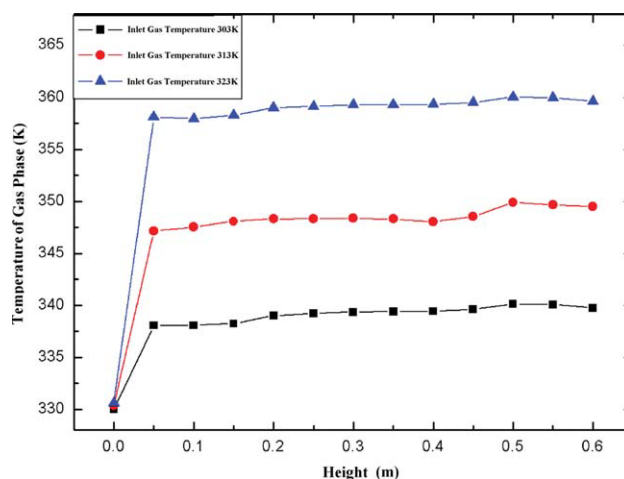


Figure 18. Effect of inlet gas temperature on temperature of gas phase.

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Conclusions

In this study, a 3-D CFD-PBM coupled model using an Eulerian–Eulerian two-fluid model was developed to describe the gas–solid two-phase flow in fluidized-bed polymerization reactors. The 3-D CFD-PBM coupled model incorporates the KTGF, the population balance, and the heat-exchange coefficient equations. The 3-D CFD-PBM coupled model was preliminarily tested by comparing simulated result with the classical calculated data. In addition, two case studies, (1) with constant solid particle size and constant polymerization heat and (2) with evolving solid PSD, polymerization kinetics, and polymerization heat, were designed to distinguish the suggested model. Finally, the distinguished model was used to investigate the influences of some operational conditions on the temperature field.

The simulated results show that the 3-D CFD-PBM coupled model is more appropriate to simulate the flow field in the fluidized-bed polymerization reactors. The temperature of solid phase increases along the axial direction from the bottom to the top of FBR, and for the same plane of FBR, the temperature of solid phase near the wall is higher than that in the other positions of the reactor. The simulated results also show that the inlet gas velocity is an important factor in controlling the reactor temperature fields. Furthermore, with the decrease of the temperature of inlet gas, the temperature of gas and solid phases in the FBR also decreases. Further studies on the CFD-PBM coupled model for the gas–solid two-phase flow in FBR are in progress in our group.

Acknowledgments

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Notation

C_{μ} , $C_{1\varepsilon}$, $C_{2\varepsilon}$ = coefficients in turbulence model
 C_d = drag coefficient
 $C_{p,g}$ = heat-capacity coefficient of gas phase ($\text{kJ kmol}^{-1} \text{K}^{-1}$)
 $C_{p,i}$ = heat-capacity coefficient of the i th phase ($\text{kJ kmol}^{-1} \text{K}^{-1}$)
 $C_{p,s}$ = heat capacity of solid phase ($\text{kJ kmol}^{-1} \text{K}^{-1}$)
 e_s = particle-particle restitution coefficient
 e_w = particle-wall restitution coefficient
 g_0 = gravitational acceleration (m s^{-2})
 G = particle-size growth rate (m s^{-1})
 $G_{k,m}$ = production of turbulent kinetic energy
 h_i = specific enthalpy of the i th phase ($\text{kJ kg}^{-1} \text{K}^{-1}$)
 $\bar{I}$ = identity matrix
 k = turbulence kinetic energy tensor
 k_p = propagation rate related to the temperature of particle ($\text{L mol}^{-1} \text{s}^{-1}$)
 kk = specified number of moments
 kk_1 = proportionality constants in Eq. 14
 kk_2 = proportionality constants in Eq. 14
 KK = an aggregation rate constant, which is a function of fluidizing temperature defined according to Eq. 14 ($\text{m}^{-6} \text{s}^{-1}$)
 K_g = gas-phase heat-exchange coefficient ($\text{kg m}^2 \text{s}^{-1}$)
 K_s = solid-phase exchange coefficient ($\text{kg m}^2 \text{s}^{-1}$)
 K_{gs} = interphase exchange coefficient ($\text{kg m}^2 \text{s}^{-1}$)
 κ_{gs} = thermal conductivity of liquid phase of interphase ($\text{W m}^{-1} \text{K}^{-1}$)
 L , L_s = particle diameter (m)
 L_0 = initial particle diameter (m)
 L_{32} = the Sauter mean diameter (m)
 $m_{g,\text{inlet}}$ = inlet gas flow (kg m^{-3})
 m_{kk} = the kk th moment of number density function (m^{kk})
 $\dot{m}$, $\dot{m}_{sp}$ = mass transfer between the gas and solid phases
 $\bar{m}_{g,\text{inlet}}$ = inlet gas flow change rate ($\text{kg m}^{-3} \text{s}^{-1}$)
 n = axial distance (m)
 Nu_s = Nusselt number of solid phase, dimensionless
 p = pressure (Pa)
 Pr = Prandtl number of liquid phase
 p_s = particulate phase pressure (Pa)
 q_i = heat flux (W m^{-2})
 Q_{gs} = intensity of heat exchange between gas and solid phases ($\text{W s}^{-1} \text{m}^{-3}$)
 Q_{rs} = total polymerization heat of solid phase in reactor (W)
 R_p = polymerization reaction rate ($\text{mol L}^{-1} \text{s}^{-1}$)
 Re_s = particles Reynolds number
 t = flow time (s)
 T_g = gas temperature (K)
 $T_{g,\text{inlet}}$ = inlet gas temperature of reactor (K)
 $T_{g,\text{outlet}}$ = outlet gas temperature of reactor (K)
 T_s = solid temperature (K)
 U_{mf} = minimum fluidization velocity
 U_t = particle terminal velocity
 u = particle growth rate vector due to processes other than interaction with other particles (m s^{-1})
 v_g = gas velocity (m s^{-1})
 v_m = velocity vector of system m (m s^{-1})
 v_s = solid velocity (m s^{-1})
 $v_{s,w}$ = solid velocity at wall (m s^{-1})
 x = spatial coordinate (m)
 α_g = volume fraction of gas phase
 α_i = volume fraction of phase i
 α_s = volume fraction of solid phase
 $\alpha_{s,m}$ = maximum volume fraction of solid phase
 ε = turbulence dissipation rate ($\text{m}^2 \text{s}^{-3}$)
 ϕ = specular factor
 μ_g = viscosity of gas phase (Pa s)
 μ_s = solid shear viscosity (Pa s)
 $\mu_{s,\text{col}}$ = solid collisional viscosity (Pa s)
 $\mu_{s,\text{kin}}$ = solid kinetic viscosity (Pa s)
 $\mu_{s,\text{fr}}$ = solid frictional viscosity (Pa s)
 $\mu_{t,m}$ = frictional viscosity of system m (Pa s)
 σ_e = granular kinetic theory parameter (kinetic viscosity) (Pa s)
 θ = angle of internal friction ($^\circ$)

Θ_s = granular temperature ($\text{m}^2 \text{s}^{-2}$)
 γ_{Θ} = the collisional dissipation of energy ($\text{m}^2 \text{s}^{-2}$)
 $\bar{\tau}_g$ = shear stress of gas phase (N m^{-2})
 $\bar{\tau}_s$ = shear stress of solid phase (N m^{-2})
 λ_s = solid bulk viscosity (Pa s)
 ρ_g = gas density (kg m^{-3})
 ρ_i = density of phase i (kg m^{-3})
 ρ_m = density of system m (kg m^{-3})
 ρ_s = solid density (kg m^{-3})
 $[C]$ = catalyst concentration (mol L^{-1})
 $[C^*]$ = active catalyst concentration (mol L^{-1})
 $[M]$ = monomer concentration (mol L^{-1})
 ΔQ_{rsz} = heat produced from polymerization reaction (kJ kmol^{-1})
 ΔH = polymerization heat capacity (kJ mol^{-1})

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Appendix: Supplementary Data Regarding to Case 2

In Case 2, we assume that the initial PSD is a normal distribution and its mean diameter is 1 mm. The detained PSD is shown in Figure A1. In addition, the i th moments of number density function are as follows: $m_0 = 1.14 \times 10^9$, $m_1 = 1.14 \times 10^6$ m, $m_2 = 1.14 \times 10^3$ m², and $m_3 = 1.14$ m³. Correspondingly, the normalized moments are as follows: $m_0 = 1$, $m_1 = 1 \times 10^{-3}$, $m_2 = 1 \times 10^{-3}$, and $m_3 = 1 \times 10^{-9}$.

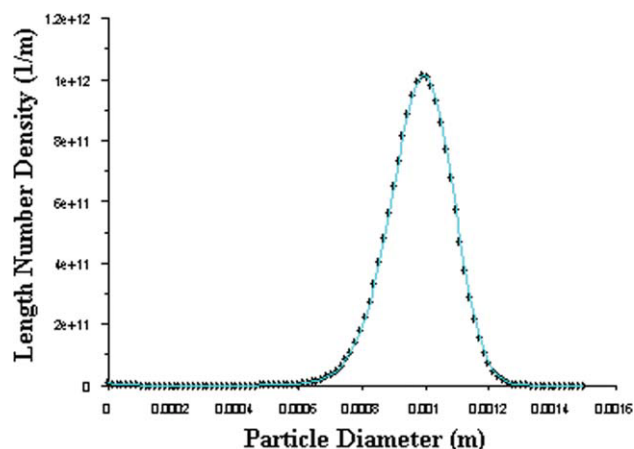


Figure A1. Length number density of initial PSD in Case 2.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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