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A CFD-PBM coupled model with polymerization kinetics for multizone circulating polymerization reactors

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ABSTRACT

An Eulerian–Eulerian two-fluid coupling the population balance model (PBM) is developed to describe the gas–solid two-phase flow in a multizone circulating polymerization reactor (MZCR). The polymerization kinetics is also incorporated into the coupled model by using a user-defined function (UDF). The model is first used to predict the entire field in the MZCR with considering the polydispersity of solid phase. Furthermore, the temperature field is obtained numerically with considering polymerization reaction, and the effect of inlet gas temperature on the temperature field is also investigated. Finally, the model is adopted to distinguish between the flow behaviors in a circulating fluidized bed reactor (CFBR) and a MZCR. The simulated results show that the flow behavior in the MZCR with polydisperse solid phase is different from that with uniform particle size and the inlet gas temperature has great effects on the temperature distribution. Moreover, the simulation results also show that the differences in between CFBR and MZCR are mainly embodied in the temperature distribution.

1. Introduction

The multizone circulating reactor (MZCR) technology, which is similar to circulating fluidized bed (CFB) [1,2], is a newly announced reactor design for solid-catalyzed gas-phase polymerization to be used for producing polymers with an onion ring structure. Recently, a computational fluid dynamics (CFD) model was applied to describe the gas–solid two-phase flow in the MZCR by our group [1]. Interesting flow behaviors in the MZCR were observed, such as solid holdup distribution and solid velocity vector. Note that the small catalyst particles with certain particle size distribution are first encapsulated with thin polymer layer in pre-polymerization reactor before they are introduced into the riser of MZCR. Accordingly, polymer particle size varies in a large range and can be characterized by particle size distribution (PSD) in olefin polymerization reactors including the MZCR. Meanwhile, the PSD can be directly related to polymerization particle kinetics, *i.e.* polymerization kinetics, particle growth, aggregation and breakage dynamics [3–8], which was not considered in our previous work [1]. However, Polymerization kinetics as well as the PSD of polydisperse system is critically important for CFD modeling [5,9–11] and their influences on the flow fields in reactors require further investigation in the aspect of proper scaling-up and design of reactors [12–14].

On the other hand, recently, many attentions have been paid to the fact of polydisperse reactors and the influences of particle kinetics on the flow behaviors in multiphase reactors [5,9,15–22], particularly in gas–solid/gas–liquid reactors. Some hybrid CFD-PBM coupled models, were put forward to describe the two-phase flow fields in reactors via solving the CFD model to obtain the entire flow field as well as the particle population balance equation (PBE) for the PSD. For instance, Olmos et al. [21] tried to couple PBE with an Eulerian–Eulerian two-fluid model to simulate bubble-column reactors. Other researchers have also tried to solve the PBE with the Eulerian–Eulerian two-fluid model simultaneously. However, most previous works were still limited to gas–liquid systems [17,18,22–25]. Refer to Fan et al. [5,9,15,16], Yang et al. [26–28], Mahecha-Botero et al. [29–33], Nijemeisland et al. [34–36], Ranade et al. [37–40], Zhang et al. [41,42] and Luo et al. [43–45] for a survey on flow fields in reactors, studies on the flow fields in multizone circulating polymerization reactors are limited, especially for polydisperse systems considering polymerization reaction between the gas phase and solid phase [5,23–25,41,42]. More recently, we suggested a CFD model based on the Eulerian–Eulerian approach to describe the gas–solid two-phase flow in fluidized bed polymerization reactors [44,46]. Considering that the solid phase can be characterized by a particle size distribution (PSD), we also developed a CFD model coupled with population balance model to describe gas–solid two-phase flows in polydisperse fluidized bed propylene polymerization reactors [2,4]. Unfortunately, most of past studies including our previous works were still concentrated on the application of CFD to the gas–solid FBRs. What is more, the polymerization reaction is a highly exothermic reaction [7,43,47–49], and it can lead to the appearance of hot spots in the two-phase system if the heat of polymerization cannot be efficiently removed from the reactor. These hot spots can influence the reactor safety and polymer properties.

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From previous study on modeling of MZCR[1], it can be found that the object is a pilot-plant scale polypropylene reactor at cold-flow state, and it is assumed that there is a monodisperse solid phase in the reactor. Therefore, from the point of view of understanding, mastering, and optimizing a chemical process, how to simulate the heat transfer problem in polydisperse system is of a great importance. In order to design a more efficient multizone circulating polymerization reactor, it is needed to obtain a fundamental understanding of the dynamic gas–solid two-phase flow behavior with particle polydispersity taken into consideration as well as the heat release due to the polymerization.

On the other hand, the flow behaviors of solid particles in the riser and downer were deeply investigated in the past. For instance, Liu et al. [6] and Wei et al. [50–52] investigated the flow behavior of solid particles in the riser and downer of CFB. Comparisons are made in a circulating fluidized-bed riser/downer system between respective riser and downer based on the measurements of the radial distributions of the local solid holdups and local particle velocities along the two columns by Zhang et al. [53]. Parssinen et al. investigated the axial and radial solids distribution in a long and high-flux CFB riser [54]. Bi and Zhu revealed the importance of unit structure in improving the performance of CFBs by simulation approach and they suggested the concept of a high-density CFB [55]. A comparison of flow dynamics and flow structure in a riser and a downer was also investigated by Wu and Zhu [56]. Lehner and Wirth [57] investigated the flow pattern in a downer reactor with different gas/solid distributors on the top of downer and different solids (glass beads, $d_p = 60$ and 130 μm). Based on the above description, the above works are not regarding the CFD model for MZCRs and the flow field behaviors in MZCRs can not be obtained in above works, whereas corresponding studies can still throw some light on this work. Furthermore, from the above description, the main difference between the above MZCR and a common CFB (such as FCC) is that the reaction only takes place in the riser for a common CFB. Its downer is used to implement the circulation and separation of catalyst particles or serve as a heat exchanger and catalyst regenerator. However, the reaction occurs not only in the riser but also in the downer for a MZCR.

In this work, a CFD-PBM coupled model is developed for the description of distribution of polydisperse particles in multizone circulating propylene polymerization reactor. Quadrature Method of Moments (QMOM) is used to simplify the PBE so as to realize the combination of the CFD model and PBE, which are then both solved interactively by the commercial CFD code FLUENT 6.3.26. The temperature fields are calculated with consideration of polymerization reaction. The polymerization reaction kinetics is incorporated into the model in this work. Particular attention is paid to distinguish the difference between MZCR and CFB through investigating the effects of polymerization reaction of downer. Therefore, the current work can be used to analyze the flow behavior in MZCR and potentially benefit the design of polymerization MZCR, such as avoiding agglomeration of polymer and hot spots in the reactor and optimizing the operation conditions.

2. Multi-fluid model description

In this work, the multi-fluid model based on the Eulerian–Eulerian approach is employed to describe gas–solid two phase flow in a MZCR. For polydisperse solid phase, a PBE is needed and the QMOM is used to represent the continuous PSD. The polymerization kinetics and heat transfer are also considered using the energy equations.

2.1. Polymerization kinetics

To describe the kinetics of propylene polymerization on the Ziegler–Natta catalysts, a simple kinetics model is employed, which is the same as that used in our previous work [58]. The polymerization kinetics scheme comprises of a series of elementary reactions, namely, site activation, propagation, site deactivation, chain transformation, and chain transfer reactions. For simplicity, in this work, the temperature distribution changes only due to heat release of propagation reaction and heat transfer between gas and solid, and the wall of MZCR is assumed to be adiabatic. In addition, we also assume that the polymerization kinetic mechanisms in the MZCR including its two legs as described in Fig. 1 are the same. The mainly elementary reactions and corresponding kinetics equations are listed below.

$$\text{Propagation rate}: R_p = k_p[\mathrm{M}][\mathrm{C}^*], \tag{1}$$

where, [M] is the concentration of monomer, [C*] is the concentration of active catalyst site, k_p is the rate constant, which can be described as:

$$k_\mathrm{p} = k_\mathrm{p}^0 \exp\left(-E_\mathrm{A}/\mathrm{R}_\mathrm{gas}T\right). \tag{2}$$

Because propylene is consumed mainly by the propagation reaction, the polymerization rate is given by Eq. (1) in this study.

2.2. CFD model

Numerical simulations are based on a three-dimensional (3D) two-fluid Eulerian–Eulerian model. The theory of granular flow, which considers the conservation of solid fluctuation energy, is used for the closure of solid stress terms. In this work, the 3D two-fluid model, involving continuity and momentum equations, is identical to that reported in our previous works except for heat transfer equations [1,3–5,44,46]. Here, due to limited space, most of the model equations are listed as Supplementary data. The main equations regarding the heat transfer equations, which are not considered in our previous work [1], are summarized as follows:the energy balance equations for gas and solid phases are characterized as:

$$\frac{\partial}{\partial t}\left(\alpha_g\rho_g h_g\right) + \nabla\cdot\left(\alpha_g\rho_g v_g h_g\right) = -\alpha_g\frac{\partial P_g}{\partial t} + \overline{\overline{\tau}}_g : \nabla\vec{v}_g - \nabla\cdot\vec{q}_g + \sum_{p=1}^{n} Q_{gs}, \tag{3}$$

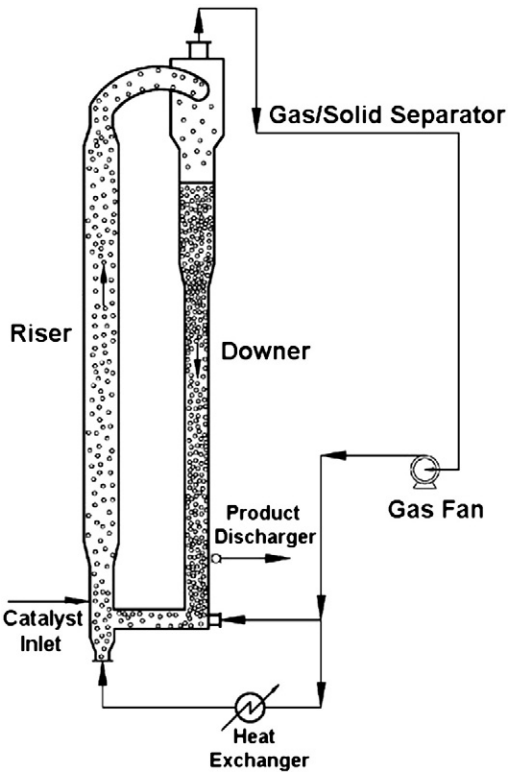

Fig. 1. Multizone circulating polymerization reactor.