Review

CFD simulation of fluidized bed reactors for polyolefin production – A review

M.J.H. Khan, M.A. Hussain, Z. Mansourpour, N. Mostoufi, N.M. Ghasem, E.C. Abdullah

ABSTRACT

This literature survey focuses on the application of computational fluid dynamics (CFD) in various aspects of the fluidized bed reactor. Although fluidized bed reactors are used in various industrial applications, this first-of-its-kind review highlights the use of CFD on polyolefin production. It is shown that CFD has been utilized for the following mechanisms of polymerization: governing of bubble formation, electrostatic charge effect, gas–solid flow behavior, particle distribution, solid–gas circulation pattern, bed expansion consequence, mixing and segregation, agglomeration and shear forces. Heat and mass transfer in the reactor modeling using CFD principles has also been taken under consideration. A number of softwares are available to interpret the data of the CFD simulation but only few softwares possess the analytical capability to interpret the complex flow behavior of fluidization. In this review, the popular softwares with their framework and application have been discussed. The advantages and feasibility of applying CFD to olefin polymerization in fluidized beds were deliberated and the prospect of future CFD applications was also discussed.

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Keywords:
CFD
Fluidized bed
Polyolefins
Reactors

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Article history:
Received 15 November 2013
Accepted 25 January 2014
Available online 7 February 2014

Keywords:
CFD
Fluidized bed
Polyolefins
Reactors

ARTICLE INFO

Article history:
Received 15 November 2013
Accepted 25 January 2014
Available online 7 February 2014
5. Modeling of agglomeration in fluidized bed reactors.

6. Summary

Acknowledgements

References

Notation

- $A$ : cross sectional area of the fluidized-bed (m$^2$)
- $A_r$ : pre-exponential factor (consistent unit)
- CFD : computational fluid dynamics
- $D$ : diameter of the fluidized-bed reactor (m)
- $D_v$ : the electric displacement vector
- DEM : discrete element method
- DPM : discrete particle model
- $E$ : electric field (V/m)
- $E_a$ : Activation energy for the reaction (J/K mol)
- EDC : eddy dissipation concept
- FBR : fluidized bed reactor
- GFM : granular flow model
- $H$ : total enthalpy (J/kg, J/mol)
- $H_b$ : bed height
- IPSA : inter phase slip algorithm
- KTGF : kinetic theory of granular flow
- MGM : multi grain model
- $P$ : induced polarization
- PEA : partial elimination algorithm
- TFM : two fluid model
- VOF : volume of fluid
- $N_i$ : apparent order of reaction
- $P_n$ : bulk partial pressure of gas (Pa)
- $D_{0,r}$ : diffusion coefficient for reaction (m$^2$/s)
- $C_p$ : heat capacity at constant pressure (J/k)
- $H_{rea}$ : heat released by surface reaction (°C)
- $Y_j$ : mass fraction of species $j$ in particle
- $T_p$ : particle temperature (°C)
- $R_p$ : radius of particle (m)
- $R_{1,r}$ : rate of particle species depletion (kg/s)
- $R_{kin,r}$ : rate of reaction (units vary)
- $R_{s,r}$ : rate of species reaction per unit area (kg/m$^2$s)
- $S_{g}$ : source term in gas phase scalar equation
- $T_{f,Ω}$ : local temperature of fluid (°C)
- $A_p$ : surface area of particle (m$^2$)
- $D_b$ : bubble diameter (m)
- $H_a$ : Hamaker constant (erg)
- $J_s$ : dissipation of granular energy (m$^2$/s$^2$)
- $N_C$ : Courant number
- $Pr$ : Prandtl number
- Re : particle Reynolds number
- $T_{∞}$ : system temperature (°C)
- $q_{i,wall}$ : conductive heat flux between particle $i$ and wall (W/m$^2$)
- $q_{i,f}$ : conductive heat flux between particles $i$ and $f$ (W/m$^2$)
- $q_{i,j}$ : conductive heat flux between particles $i$ and $j$ (W/m$^2$)
- $k_e$ : effective fluid thermal conductivity ((K-m)/W)
- $q_{i,rad}$ : flux between particle $i$ and its local surrounding environment (W/m$^2$)

Greek letters
- $ε$ : the void volume of the fluidized bed
- $Σ$ : surface tension (N/m)
- $θ$ : porosity of the polymer particle
- $η_r$ : effectiveness factor
- $α_s$ : volume fraction of solid
- $ρ$ : density of fluid (kg/m$^3$)
- $ρ_s$ : solid density (kg/m$^3$)
- $θ_s$ : granular temperature (m$^2$/s$^2$)
- $κ_s$ : thermal conductivity (W/m K)
- $λ_s$ : solid bulk viscosity (kg/m$^2$s$^{-1}$)
- $α_g$ : volume fraction of gas
- $α_s,max$ : maximum volume fraction of solid phase
- $φ$ : sphericity
- $Μ$ : dynamic viscosity (Pa s)
- $γ$ : shear rate (1 s$^{-1}$)
- $μ_0$ : zero shear viscosity (Pa s)
- $γ_s$ : dissipation due particle–particle collision (m$^2$/s$^3$)
- $ϕ$ : electric potential (V)
- $Γ_g$ : gas phase diffusion coefficient
- $ρ_g$ : density of gas phase (kg/m$^3$)
- $ρ_f$ : density of fluid (kg/m$^3$)
- $ε_0$ : permittivity of vacuum (F/m)
- $x_e$ : electric susceptibility (m/V)$^n-1$
- $ε_m$ : relative permittivity of mixture (F/m)
- $ε_s$ : relative permittivity of solid phase (F/m)
- $ε_g$ : relative permittivity of gas mixture (F/m)
- $Δt$ : time step in simulation (s)
- $Δp$ : pressure drop (Pa)
- $Δx$ : dimension of the grid

Subscripts
- $Kn$ : kinetic
- $Eff$ : effective
1. Introduction

1.1. The process of fluidization and fluidized bed reactors

The physicochemical phenomenon called, 'fluidization', conveys the idea of converting a bed of fine particulate materials into a fluid-like state by passage of a gas or liquid through it. Transport phenomena in fluidized beds have several complex features which can be utilized to great benefit in various processes. If a fluid is passed through a bed of fine particles, at lower velocities the fluid simply percolates through the void spaces between particles and this is known as a fixed bed. When displacement of particles occurs by increasing the flow rate of the fluid, it is known as an expanded bed. Particles are suspended at a higher velocity in the fluid. The buoyancy force acts as the balancing force between gravitational and drag forces when the bed is in suspended form. When the pressure drop across the bed becomes equal to the weight of particles, the bed is considered as fluidized and the superficial fluid velocity at which this situation is observed is called the minimum fluidization velocity. This phenomenon can be expressed mathematically by the following equation [1–3]:

$$\Delta p = H_b (1 - e)(\rho_s - \rho_f) g$$

(1)

The section with a clear surface or upper limit of the fluidized bed is regarded as the dense phase. Further increment of velocity of the fluid may cause the surface to lose its distinct character. There are a number of influential factors for controlling the quality of fluidization. In general, properties of solids and fluid determine the smoothness of fluidization. Moreover, solids mixing, bubble size, bed geometry, gas flow rate, particle size, distributor type and vessel interiors are other factors affecting fluidization.

Fluidized bed reactors (FBRs) have been frequently used in various processes. Implementation of fluidization technology can be categorized into chemical and physical processes. Olefin polymerization (propylene and ethylene), a wide range of synthesis reactions, manufacturing of silicon, gasoline synthesis (Fischer-Tropsch), coking (Fluid and Flexi), combustion, gasification and catalytic cracking of heavy hydrocarbons are examples of chemical processes. Physical processes involving fluidization include heat exchange, drying, coating, granulation, solidification and purification of gases with adsorbent [4,5].

Different types of reactors, like continuous stirred tank reactor (CSTR) [6], tubular loop, autoclave and fluidized bed reactor (FBR), have been used to produce polyolefins. However, recently FBRs have drawn the attention of engineers, scientists and researchers. As a result, gas–solid fluidized-bed reactors are broadly used for producing polyolefin as well as other petrochemical products.

Employing gas phase fluidized beds in polyolefin production processes is beneficial due to its low investment requirement and low operating cost compared to other processes. This technology also provides some significant engineering advantages. For example, it involves no solvent separation, has great heat exchange potential and has ability to utilize various types of catalysts to manufacture a wide range of products [7]. Diverse benefits of fluidized bed reactors, like their capabilities to carry out a wide range of multiphase chemical reactions, excellent mixing performance of particles, significant mass and heat transfer, as well as their ease of operation in both batch and continuous states have established this type of reactors as one of the most extensively used reactors for polyolefin production.

Union Carbide can be credited as the first commercial user of the fluidized bed polymerization reactor for producing high density polyethylene (HDPE) in 1968. The same manufacturer extended its production line for production of linear low density polyethylene (LLDPE) in 1975 and for polypropylene (PP) in 1985. Several simulation and experimental studies have been accomplished in order to understand the observable fact of fluidization for improving and optimizing their design [8]. Effective fluidization ensures proper gas–solid contact, homogenous temperature profile and minimum gas bypassing [9]. Consequently, Hypol, Innoven, Unipol, Spheripol, which are widely used commercial technologies, have been producing polyolefin through fluidization [10,11].

1.2. Scope of the review

Polyolefin reaction mechanism models are classified based on several factors. Constant bubble size model [9], well-mixed model [2,12], bubble growth model [13], catalyst phase model [14], well-mixed and constant bubble size dynamic model [15] and multiple active sites model [16] are significant types of models for describing olefin polymerization phenomena in many studies. Numerous references are available for mathematical modeling and simulation of gas-phase olefin polymerization in fluidized condition. In this type of reactor, mechanism of reaction, physical transport methods, reactor design and operating conditions have great influence on the quality of the polymer product. In most cases, polymerization processes are widely categorized into heterogeneous and homogeneous processes. Homogeneous reaction method implies that the polymerization occurs within a single phase while in heterogeneous systems reactants and polymerization reaction are presented in different phases [13]. Pseudo-homogeneous models of polyolefin production are simple and can be used in catalytic batch reactors. In this model it is assumed that only a single (liquid or gas) phase exists in the reactor. On the other hand, heterogeneous models are mostly practical for simulation of gas phase semi-batch reactors. Such models are widely used in olefin polymerization reactors. Due to the multi-phase nature of polymerization (liquid–solid phase or gas–solid phase), the heterogeneous catalyst reaction model should be solved simultaneously with a hydrodynamic model describing inter-phase heat transfer, mass transfer and mixing.

It is well established that a fluidized bed should be considered as a two-phase system. These phases are emulsion and bubble, also known as the dense and lean phases, respectively. Although bubbles are often assumed to be solid-free, they usually carry a small quantity of solids. Each gas bubble carries a considerable amount of solids behind it which is called wake. Solids in the wake are dragged up with the bubble, consequently, the rest of solids within the emulsion phase flow downward. Each bubble is surrounded by a cloud which is also rich in solids and moves with the same velocity as the bubble. Polyolefin reaction modeling is illustrated schematically in Fig. 1. This figure illustrates the expositions of multiphase reactions in a fluidized bed reactor for olefin polymerization reaction.

Reactant gases, blown into the bed from the bottom, form bubbles in a fluidized bed. While bubbles rise in the bed, mass transfer of reactant gases takes place between cloud and bubble as well as cloud and emulsion. After transfer of reactant gases from bubble to emulsion, chemical reaction takes place in the emulsion and on the surface of the catalyst particles. The rate of mass transfer of reactants from bubble to emulsion diagnostically affects the polymer production rate. Many researchers have mentioned that reactor modeling should be done based on the type of the catalyst and the value of porosity [14,17,18]. The superficial gas velocity, as well as the catalyst dosing rate, can severely affect the molecular weight of polymer in the emulsion phase, concentration of monomer and temperature inside the emulsion phase [19–21].

In a gas-phase polymerization process, monomers in the gas phase react with the solid catalyst in the emulsion phase to form polymer particles [22]. Since the reaction takes place in a mixture
of gas and solid phases, a two phase model was considered in many cases for describing this process. Reports about simulation of industrial scale or even pilot scale polymerization process are limited in the open literature. Gobin et al. [23] simulated large polymerization reactors and mainly focused on the ability of the simulator to explain the complex flow behavior of the large-scale reaction system.

Advanced process modeling and simulation tools, like the CFD approach, are required to understand the effect of numerous changes that are required for the scale-up process such as bed diameter, rising of bed height and fluidization velocity, distributor types and adding of in-bed heat exchanger tubes along with baffles, as well as experimental data for validation. Therefore, several research groups have been involved in developing non-intrusive measurement techniques in the laboratory scale polymerization reactors to obtain statistically and mathematically significant data for validation of CFD models [24].

Earlier models of FBRs were not capable of being used for scale-up purposes but to a certain extent were proposed for interpretation of experimental data [7,25–27]. The use of CFD analysis is also in its initial stage, especially in the field of polyolefin reactions. Although, there are broad applications of the CFD in recent studies of chemical reactors, current CFD simulations include too much simplification and paid inadequate attention to the multi scale structure (e.g., homogenous assumption in hydrodynamics, mass transfer and reaction models and 2D instead of 3D models). These simplified treatments may miss the real mechanisms underlying the complex states of motion. To conquer this problem, CFD with consideration of meso-scale structures has been proposed in recent years. This method can help to understand the structure-oriented coupling between flow, heat/mass transfer and reactions. This combination, the so-called multi-scale CFD (MSCFD), characterizes the sub-grid meso-scale structure with stability criteria in addition to conservation equations. This approach is demonstrated by the energy minimization multi-scale (EMMS) model and its extensions, e.g., EMMS/matrix for flow modeling and EMMS/mass for reaction modeling and can be a promising approach in industrial and scale up simulations [28].

In this paper, the background of these computational models, considering various aspects involved in polyolefin reactions in a fluidized bed reactor, are discussed.

2. Computational modeling of fluidized bed reactor

2.1. Theoretical framework

Development of CFD, which can be used to solve conservation and momentum equations in multiphase flows [29], is an advanced research area for visualizing fundamental phenomena without carrying out real-time experiments [30]. In case of a polymerization reactor, an extra advantage of CFD is that it can provide information on turbulent zones. Information in these zones is vital because the reactants are mostly introduced to these areas and the reaction yield is higher. Although, experimental analysis of the flow pattern in polymerization reactors remains vital, the irregular mechanism of mixing of reactive fluids makes the flow visualization more complex. CFD studies had been initially criticized for their limitations in adequate analyzing the polymerization process. A mentionable drawback of the CFD modeling of a polymerization procedure is its high computational time. Since transport equations in a polymerization reaction are highly coupled in nature, it is extremely challenging to solve the related equations and simplification of the reaction mechanism as well as dependency of the transport properties on the variables is essential [31].

Although initial CFD studies have limitations in analyzing different polymerization processes, this approach was able to provide dynamic simulation of FBRs. Continuous development of supercomputers and invention of computer units with continually increasing power have facilitated solving these complicated equations numerically. The effort required for experimental design and data acquisition have been significantly reduced by the CFD analysis. Recent developments in the research field of multiphase flow of gas–solid modeling suggest substantial process developments that have the potential to advance plant operations significantly. Forecasting of gas–solid flow pattern in certain production systems, such as pneumatic transport lines, fluidized bed reactors, hoppers and precipitators, is critical to control the operation parameters of a majority of process plants. The lack of ability to precisely model these fluidization regimes has slowed down the progress of simulations for these operations. Hence, in recent years, researchers involved in the development of CFD softwares have been paying attention to significant points to
propose updated modeling techniques for simulating gas–solid flows with a higher level of consistency. Implementation of CFD for analyzing multiphase flows have been widely accepted and have directed researchers to develop CFD codes for simulating fluidized beds. Consequently, engineers involved in olefin polymerization industries are beginning to use these latest methods to make significant upgrading by considering alternatives although it would be too expensive or time consuming to obtain the real plant size results [32].

Although gas–solid flow modeling techniques are based on conservation equations, but it has also been reported that conventional methods are not yet adequately improved to be effective tools for the design of industrial FRBs. The reason for this drawback remains first in the complexity of the gas–solid flow pattern in reacting systems which makes computations very difficult and time consuming. Adding chemical reactions to this complexity requires additional computational resources and particularly handling of large geometries of industrial reactors. Therefore, for large systems, parallel computing can be utilized to reduce computational time [33–35]. Furthermore, to provide comprehensive information on more systems, parallel computing can be utilized to reduce computational time and be used if the system media is dilute. The Eulerian–Eulerian approach is applicable to determining the hydrodynamics of multiphase flows with a higher level of consistency. Implementation of CFD for analyzing multiphase flows have been widely accepted and have directed researchers to develop CFD codes for simulating fluidized beds. Consequently, engineers involved in olefin polymerization industries are beginning to use these latest methods to make significant upgrading by considering alternatives although it would be too expensive or time consuming to obtain the real plant size results [32].

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Two forms of CFD models, i.e., Lagrangian and Eulerian methods, are generally used to describe gas–solid fluidized reactors. The Lagrangian model solves equations of motion (Newton’s second law) for every particle in the system in which particle–particle collisions and various forces acting on the particle are taken into account. In the Eulerian model, both phases (solids and gas) are counted as continuum (fluid) and momentum and continuity equations are considered for both phases [39–41]. The Eulerian–Lagrangian approach, which is also recognized as discrete particle model (DPM) or discrete element method (DEM), considers the fluid as a continuum while the solids are considered as the dispersed phase. The DPM uses the Eulerian framework to model the continuous phase and the trajectories of particles are simulated in the Lagrangian framework. The continuous phase can be modeled by averaging its properties over a wide range of trajectories. However, to obtain a momentous average of all quantities, an abundant of particle trajectories is suggested to be simulated. In some software packages, such as ANSYS FLUENT, the Eulerian–Lagrangian approach is capable of modeling dispersed multiphase flow surrounded by a low volume fraction of solid particles [42]. Gas and emulsion phases are assumed to be continuous in the Eulerian–Eulerian approach while is considered entirely interpenetrating in every control volume. Three different Euler–Euler multiphase models are accessible to explain fluidized bed olefin polymerization: the Eulerian model, the mixture model and the volume of fluid (VOF) model as described in the following section.

2.1.1. The Eulerian model

In the Eulerian model, both phases are considered as continuum and momentum and continuity equations for multi-phase flow are solved. A single pressure field is considered for all phases. Interphase exchange coefficient and pressure are important parameters for coupling these equations. Based on the relevant phases, different types of coupling methods are available. Fluidized beds, risers, bubble columns and particle suspensions can be covered by the Eulerian multiphase model. For calculation of the fluid-solid momentum exchange coefficient, ANSYS FLUENT suggests utilizing Syamlal–O’Brien and Gidaspow [43] correlations for use in the granular flow while Wen and Yu [44] correlation can be used if the system media is dilute. The Eulerian–Eulerian approach is applicable to determining the hydrodynamics of fluidized beds in which volume fraction of phases are of the same order. This computationally cost effective approach is also convenient where body forces (like gravity) act to split the phases or interact within and between the phases. This method is limited by hardware memory constraints and convergence issues.

2.1.2. The mixture model

The mixture model is simpler than the Eulerian model. This approach was developed for modeling of two or more phases (interpenetrating continua). Momentum equations are solved by this model and evaluate relative velocities to describe the flow of dispersed phases. Cyclone separator, sedimentation, particle-laden flow with low loading and bubbly flow are examples of application of the mixture model. Homogeneous multiphase flows can also be modeled without relative velocities for the dispersed phase by the mixture model.

2.1.3. The VOF model

The VOF approach is applied to model multi immiscible fluids. In this model, momentum equations, equations of continuity for all fluids through the flow field and tracking the volume fraction of each of fluids are considered. Calculation of motion of large bubbles in a liquid, motion of fluid through a system, jet breakup and steady or transient movement of multi fluid phases are typical applications of this model. There are, however, some limitations in application of the VOF model. For instance, all control volumes are required to be filled with either a single fluid or a combination of phases, that is, void regions where no fluid is present and cannot be defined in this model and only a single phase can be described as a compressible ideal gas. The VOF cannot model the streamwise periodic flow including specified mass flow rate and specified pressure drop. User-defined function of ANSYS FLUENT is the option to explain compressible fluids behavior with the help of VOF model. However, if a system is highly sensitive to pressure, then the VOF approach is not advisable. The VOF model also cannot be used with the DPM model for gas–solid reaction modeling in which particles are analyzed in parallel.

2.1.4. Combined approaches

Although the Eulerian–Eulerian model has become the primary choice of most researchers to investigate the performance of the polymerization reaction fluidized beds, some researchers combined the Eulerian–Eulerian approach and the granular flow model (GFM) [45–47]. In this approach, both phases are governed by conservation equations of mass and momentum. Describing interphase forces, i.e., drag, lift and virtual mass forces, is important to couple momentum balances of two phases. It has been shown that due to the large difference between densities of emulsion and fluid phases, the lift force and the virtual mass force are less significant and can be neglected [48,49]. Consequently, in most CFD analyses of fluidization, only drag force was considered [39].

In the gas–solid flow, particles are considered as exaggerated molecules with the intention that an analogy of their behavior with gas molecules can be stipulated. The GFM approach typically does not provide the trajectory of particles and its averaging in a computational cell but can be perfectly accomplished at a hypothetical level which requires extensive modeling efforts. Formulation of the governing equations involves various averaging issues. As a result, the Eulerian–Eulerian model is applicable to multiphase flow processes containing large volume fractions of the dispersed phase [50,51]. Conversely, the 2D Eulerian-Eulerian model extended with the kinetic theory of granular flow (KTGF) was applied by Lu et al. [52] to simulate the behavior of bubbles in a gas–solid FBR. Their simulated results were compared with bubble sizes obtained from the equation of Darton et al. [53] and the model of Davidson [16]. Several studies on behavior of bubbles in a free and agitated gas–solid FBR via 2D and 3D Eulerian models were also carried out [54]. Vegendla et al. [55] performed a...
comparative study of Eulerian–Eulerian and Eulerian–Lagrangian method on two-phase gas–solid riser flow behavior by considering gas phase as a continuous phase and the solid phase as a dispersed phase. Solids volume fraction, solids velocity, gas phase turbulent kinetic energy and its dissipation were elaborately studied at certain operating conditions. They concluded that the simulation results, when applying Eulerian–Lagrangian method, fits better to the experimental data whereas the Eulerian–Eulerian method showed more deviation from the experimental data. A combined CFD approach using DEM along with Navier–Stokes equations has been suggested to explain multiphase flow behavior and heat transfer amid particles and between the gas and the particles for methanol-to-olefins (MTO) production in FBR [56]. The same study claimed that this hybrid approach can provide real-time particle activity by tracing the movement vector of the catalyst particle coupled with heat transfer equations.

However, some CFD studies have been reported recently on the flow structure of phases in fluidized bed polymerization reactors [57–60], since there are many important parameters in the modeling which can notably influence the simulation results [61]. Chen et al. [62] applied a CFD model to describe the gas–solid two-phase flow in fluidized bed polymerization reactors. They considered complete hydrodynamics of the FBR, such as solid hold-up distribution, behavior of bubbles and solids velocity. Many researchers also performed advanced investigations on the influence of operation conditions and geometry of the reactor, like type of distributor, size of solid particles, gas velocity and operating pressure on the hydrodynamics of the reactor, for accurate scale-up and design of reactors [63–66].

2.2. CFD software packages

Among different CFD software packages, only a few are capable of modeling complex multiphase flows. Phenics, Fluent, CFX, Star–CD, Ester–Astrid, COMSOL and MFIx are some common software packages that have been used in CFD analysis of olefin polymerization since the last decade. These softwares can be used for interfacing the user-defined function (UDF) to enhance the modeling and to get more realistic simulation results. Preprocessing is considered as the first step for developing and analyzing the flow model. The prerequisite for preprocessing is to propose the model with the support of a computer aided design (CAD) package, generating a mesh and entering the data. For this purpose, GAMBIT is well accepted by researchers as a preprocessing tool. The CFD solver is capable of performing the calculations and generates the results after preprocessing. Among several CFD packages, ANSYS FLUENT has been used in most industrial simulation practices. Moreover, Flow Wizard is the earliest wide-ranging function of CFD product for designers introduced by ANSYS FLUENT. Some particular industrial sectors, like material processing industries, also use specific CFD packages such as FIDAP and POLYFLOW for their process development and scale up purposes [67–70].

In the recent years, the commercial CFD package ANSYS FLUENT seems to be the first choice for a number of researchers for modeling fluidized bed reactors. In fact, ANSYS FLUENT is one of the most inclusive softwares offered to the CFD community because of its wide range of industrial applications, from airflow over aircraft wings to the modeling of gas–solid flows in fluidized beds. A large number of research articles have been published in recent years on the application of ANSYS FLUENT in the CFD analysis of fluidized bed reactors of polyolefin production. Table 1 shows some of significant researches on CFD approach applied to polyolefin production in the fluidization research field [71–93]. ANSYS FLUENT has shown its excellent potential on solving the governing equations for the fluid flow as well as heat and mass transfer since launched in 1983. A wide range of models on incompressible and compressible as well as laminar and turbulent fluid flows can be efficiently solved by this software in either steady or transient state [94,95]. ANSYS FLUENT is capable of modeling transport phenomena (including heat and mass transfer) with chemical reaction in complex geometries which is essential for analysis of fluidized bed reactors of polyolefin production. The set of free surface and multiphase flow models is one of the very constructive group of models in ANSYS FLUENT that can be used for analysis of gas–liquid, gas–solid, liquid–solid and gas–liquid–solid flows. This option also covers the volume-of-fluid (VOF), mixture, Eulerian and DPM approaches. Different types of heat transfer mechanisms can be modeled by ANSYS FLUENT, including natural, forced and mixed convection, with or without conjugate heat transfer, porous media, etc. Additional physical phenomena, for instance buoyancy and compressibility, can be broadly modeled in addition to the turbulence model. Extended wall functions and zonal models can address the issues of near-wall accuracy with more precision.

Conservation equations of mass and momentum for flows related to fluidization can be solved by ANSYS FLUENT including heat transfer or compressibility to the problem requires addition of a supplementary equation of energy conservation. For modeling the turbulent flow, additional transport equations should be solved. Both incompressible and compressible turbulent flows can be described by this general form of equation. Mixing and transport of chemical species can be modeled through convection, diffusion and reaction sources for each component. Various concurrent chemical reactions can be modeled, including reactions occurring in the bulk phase (volumetric reactions) and/or on wall or particle surfaces and in the porous region. ANSYS FLUENT has both pressure-based and density-based solvers with options for convection and diffusion components. The user should specify mass fraction of inlet species to determine the convection component of the rate of mass transfer. On the other hand, diffusion term can be evaluated from the gradient of inlet species. In the pressure-based solver, both convection and diffusion components are considered for evaluating the net rate of transport of species at the inlet.

ANSYS FLUENT (version 14.5) provides three models for generalized finite-rate formulation reaction modeling:

- **Laminar finite-rate model**: Arrhenius kinetic expression is used to determine reaction rates by ignoring the effect of turbulence. This kinetic expression is computationally expensive.
- **Eddy-dissipation model**: In this model, Arrhenius kinetic calculations can be avoided as the rate of reaction is assumed to be controlled by the turbulence. As a result, this model is computationally inexpensive. This model also requires products to initiate reaction which is one of the main steps in of the polymerization catalytic reaction.
- **Eddy-dissipation-concept (EDC) model**: The EDC model can integrate detailed Arrhenius chemical kinetics with turbulent flames. Consequently, featured chemical kinetic calculations are computationally expensive [96].

Since polymerization of olefins is a pressure dependent reaction, known as the “fall-off” reaction, one of these three methods can be used to represent the rate expression [96–98]. The method introduced by Magnussen and Hjertager in ANSYS FLUENT has been suggested to be the basis to model turbulence-chemistry interactions [99]. Catalytic polymerization is an exothermic reaction and ANSYS FLUENT affords to solve directly this exothermic reaction modeling in a fluidized bed.

Polymerization reaction involves more than one type of gas reactant, including carrier (N₂), polymer chain cutting (H₂) and
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<tr>
<td>of bubble coalescence (size and frequency), bubble rise velocity, and pressure drop</td>
<td>GAMBIT</td>
<td></td>
<td>Corrugated wall offered more stable gas–solid fluidization operation than flat wall</td>
<td>[72]</td>
</tr>
<tr>
<td>Effect of nature of reactor wall (flat- and corrugated)</td>
<td>FLUENT 6.3.26 &amp; GAMBIT-generated grid structure</td>
<td>3-D transient Euler–Euler CFD simulations</td>
<td>The obtained results gave a close comparison of the simulated factors</td>
<td>[73]</td>
</tr>
<tr>
<td>Solid volume fraction, axial solid velocity, radial solid velocity, power spectrum, normal Reynolds stresses, turbulent kinetic energy, granular temperature and energy spectrum</td>
<td>FLUENT 6.3.26</td>
<td>Eulerian approach with KTFG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interchange due to gas advection between the emulsion phase and bubbles</td>
<td>MFree code with the KTFG</td>
<td>Two-fluid modeling approach with classical potential flow theory</td>
<td>Suitable for high gas velocity rates</td>
<td>[74]</td>
</tr>
<tr>
<td>Physical values of fluid and particle phases</td>
<td>In-house CFD/DEM code (DEMET) and MATLAB</td>
<td>Euler–Lagrange approach combined discrete element Method (DEM)</td>
<td>This combined model can predict accurately the particles motion and the pressure gradients in the bed. But only applicable in small scale with relative large particles</td>
<td>[75]</td>
</tr>
<tr>
<td>Fluid–particle interaction (porosity and momentum transfer)</td>
<td>DEM program “DEMET” and MATLAB codes</td>
<td>Euler–Lagrange approach in combination with a deterministic collision model</td>
<td>Is able to simulate the highly complex hydrodynamic behavior of the dense gas–solid flow in the fluidized bed</td>
<td>[76]</td>
</tr>
<tr>
<td>Electrostatic charges on single bubble</td>
<td>MFree</td>
<td>Two Fluid Model (TFM) coupled with the Srivastava and Sundaresan frictional model [208]</td>
<td>This model showed that electrostatic charges are predicted to cause the bubble to elongate and rise more quickly</td>
<td>[77]</td>
</tr>
<tr>
<td>Hydrodynamic behavior of binary particle mixtures</td>
<td>Fluent 6.3.26 and high-order discretization scheme-QUICK</td>
<td>Multi-fluid Eulerian model incorporating the kinetic theory of granular flow</td>
<td>Particle–wall restitution coefficient only plays a minor role in predicting the segregation and mixing of binary particle mixtures in bubbling fluidized beds</td>
<td>[78]</td>
</tr>
<tr>
<td>differing in size and density and effect of wall boundary condition</td>
<td></td>
<td>Multi-fluid Eulerian–Eulerian and KTFG in combination with stochastic collision frequency method and conductive heat transfer theory</td>
<td>This model considers gas phase as the primary phase, whereas the particle phases are considered as secondary or dispersed phases</td>
<td>[79]</td>
</tr>
<tr>
<td>Particle–particle heat transfer between different particle classes in a dense gas–solid fluidized bed of binary particles</td>
<td>FLUENT 6.3.26 and SIMPLE algorithm</td>
<td>Full three-dimensional two-fluid Euler framework with standard per-phase k–ε turbulence model and RNG dispersed modes</td>
<td>KTGF model yielded better prediction of gas holdup profile; RNG dispersed modes predicted better flow pattern of three-phase fluidized beds; no significant improvement was observed with the laminar flow model</td>
<td>[80]</td>
</tr>
<tr>
<td>Solid wall boundary conditions and granular temperature models</td>
<td>FLUENT 13.0.0 for CFD simulation and the 3D geometrical meshing was achieved using the GAMBIT (version 2.4.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas–solid flow, solid-phase properties, Momentum exchange coefficients, Pressure drop and bed expansion ratio, time-average local voidage and velocity profiles</td>
<td>Fluent version 6.3; MFree, Open-FOAM; two phase Euler Pimple Foam</td>
<td>Eulerian–Eulerian model, KTGF</td>
<td>The flow fields showed a very good agreement between the MFree and Fluent simulations, but did not conform to those of Open FOAM (Open Source Field Operation and Manipulation)</td>
<td>[81]</td>
</tr>
<tr>
<td>Mixing of gas and solids phases, inlet gas velocity and solids circulation rate, particle properties (i.e., density and diameter), the residence time distribution (RTD)</td>
<td>FLUENT with the SIMPLE algorithm</td>
<td>2D Eulerian–Eulerian model based on the KTFG coupled with a k–ε turbulent model</td>
<td>The developed model can predict the hydrodynamic behavior including the solids volume fraction and the gas and solids velocities. Comparisons with available experimental results showed good matching</td>
<td>[82]</td>
</tr>
<tr>
<td>Flow behavior and conversion, solid phase viscosity and pressure of fluid, cohesive inter-particle forces and heat transfer</td>
<td>In-house code FLOTARCS-MP-3D in Cartesian coordinate system</td>
<td>Eulerian–Eulerian approach and KTFG</td>
<td>The model is fairly successful in bringing forth the effect of hydrodynamics on conversion in a bubbling bed of Geldart A particles and in the process highlights the strength of computational fluid dynamics in capturing vital details of complex flow patterns in fluidized beds</td>
<td>[83]</td>
</tr>
<tr>
<td>Gas phase turbulence, diffusive species transfer, rate of conversion</td>
<td>FLUENT 12.1, coupled with SIMPLE algorithm and QUICK scheme</td>
<td>Eulerian-granular framework; 2D planar model employing the KTFG</td>
<td>The model could predict the correct trend when a much less reactive carrier gas is injected. In this case, reaction rate was the limiting factor and the accurate hydrodynamic resolution of the gas–emulsion interface was of lesser importance</td>
<td>[84]</td>
</tr>
<tr>
<td>Bubble properties such as aspect ratio, diameter and rise velocity as well as bed expansion</td>
<td>ANSYS FLUENT 12.1; SIMPLE algorithm, QUICK and second order upwind scheme were also employed</td>
<td>Eulerian–Eulerian Two-Fluid Model (TFM) with closure equations based on the kinetic theory of granular flow (KTFG)</td>
<td>3D simulations were in better agreement with experiments than the corresponding 2D simulations while bubble aspect ratio showed that the deviation of the predicted bubble properties using 2D simulations were more pronounced at higher bed height and higher superficial velocities</td>
<td>[85]</td>
</tr>
</tbody>
</table>
### Table 1 (Continued)

<table>
<thead>
<tr>
<th>Factors studied</th>
<th>CFD package and algorithm</th>
<th>CFD approach</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various bed thicknesses with respect to particle packing, bed expansion, bubble behavior, solids velocities, and particle kinetic energy</td>
<td>Open-source code, MFIX-DEM.</td>
<td>Eulerian–Lagrangian simulations with the discrete element method (DEM)</td>
<td>Due to the inherent limitations of CFD-DEM approach, a direct numerical simulation (DNS) is advised to be preferable to accurately investigate the transition from 2D flow to 3D flow</td>
<td>[86]</td>
</tr>
<tr>
<td>Random motion of particles, solid pressure, conductivity of fluctuating energy and viscosity, tangential restitution coefficient and normal restitution coefficient</td>
<td>KTRS-FIX code [161] (Kinetic Theory of Rough Spheres-Flow with Interphase eXchange),</td>
<td>Two-fluid model with a kinetic theory of rough spheres (KTRS), implicit continuous Eulerian (ICE) approach and KTGF</td>
<td>An agreement between numerical simulations and experiments by was achieved by using this model with the consideration of particle rotation where kinetic theory is applicable</td>
<td>[87]</td>
</tr>
<tr>
<td>Particulate systems consisting of a compressible gas and solid particles with complex and/or moving boundaries</td>
<td>SIMPLE algorithm</td>
<td>Immersed boundary method (IBM) [220] incorporated into the coupled discrete element method and computational fluid dynamics (DEM-CFD) approach</td>
<td>DEM-CFD-IBM approach is capable to handle large objects or arbitrary shaped boundaries</td>
<td>[88]</td>
</tr>
<tr>
<td>Gas distributor plate angles, presence of a heat exchange tube bundle, superficial fluidizing velocities and initial solid packing heights</td>
<td>ANSYS Fluent 12.1, SIMPLE™ algorithm, and QUICK scheme</td>
<td>Eulerian–Eulerian model (EEM) with KTGF</td>
<td>This model can capture the key features of a fluidized bed system, fast fluidization, bubbling fluidization in the reactor and solid circulation between the various parts of reactor column</td>
<td>[89]</td>
</tr>
<tr>
<td>Simulation and characterization of bubble behavior and bed dynamics</td>
<td>Fluent 6.3 and SIMPLE</td>
<td>Eulerian–Eulerian three dimensional (3-D), KTGF and maximum entropy method (MEM) and Eulerian-Eulerian approach coupled with KTGF</td>
<td>The bubble behavior in a cylindrical fluidized bed in the bubbling regime is characterized and explained in this simulation study</td>
<td>[90]</td>
</tr>
<tr>
<td>Effect of inlet boundary conditions, solids acceleration process and flow, the effects of particle size on the flow</td>
<td>Fluent 6.3, Gambit 2.4. SIMPLE algorithm and QUICK</td>
<td>Energy Minimization Multi-Scale (EMMS) interphase exchange coefficient model with Eulerian model and KTGF</td>
<td>This model is effective to specify the inlet boundary conditions for the simulations of gas–solids two-phase flows in a circulating fluidized bed</td>
<td>[91]</td>
</tr>
<tr>
<td>Bed height, the bed expansion ratio and solid volume fraction, turbulent granular temperature</td>
<td>FLUENT 6.2.16,</td>
<td>Multi-fluid Eulerian–Eulerian model along with finite volume method and KTGF</td>
<td>To evaluate the third dimension of the system and compare the results with the corresponding data obtained from the 2-D analysis for validation, the use of this model is highly efficient</td>
<td>[92]</td>
</tr>
<tr>
<td>Effect of using different inter-phase drag model, solid volume fractions, expansion height, and pressure drop inside the fluidized bed at different superficial gas velocities</td>
<td>FLUENT 6.3 and Phase-Coupled Semi-Implicit Method for Pressure Linked Equations (PC-SIMPLE) algorithm</td>
<td>Multi-fluid Eulerian–Eulerian model along with finite volume method and KTGF</td>
<td>Although three-dimensional simulation takes more time and computing processors than two-dimensional simulation, this simulation gives more accurate results when the models are compared with experimental data</td>
<td>[93]</td>
</tr>
</tbody>
</table>
Table 2
Equations used for CFD analysis in ANSYS FLUENT for polyolefin fluidized bed reactors [96].

<table>
<thead>
<tr>
<th>Type of equations used</th>
<th>Mathematical expression</th>
<th>Significant factors</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conservation of mass or continuity equation</td>
<td>( \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = S_m )</td>
<td>Is valid for incompressible as well as compressible flows</td>
<td>Mass added to the continuous phase from the dispersed phase</td>
</tr>
<tr>
<td>Continuity equation for 2D axisymmetric</td>
<td>( \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho v_x) + \frac{\partial}{\partial z} (\rho v_z) = \rho \nabla \cdot \vec{v} - S_m )</td>
<td>Incompressible, compressible flows and any user-defined sources</td>
<td>Both axial and radial velocity are considered</td>
</tr>
<tr>
<td>geometries</td>
<td></td>
<td></td>
<td>Brainforces</td>
</tr>
<tr>
<td>Momentum conservation equations</td>
<td>( \frac{\partial (\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = \nabla \cdot (\Gamma \nabla \vec{v}) + \vec{F}_e + \vec{F}_t )</td>
<td>Static pressure, stress tensor, external body forces</td>
<td>Momentum vector considers porous-media and user-defined sources</td>
</tr>
<tr>
<td>Stress tensor</td>
<td>( \vec{F}_t = \mu \left( \nabla \vec{v} + \nabla \vec{v}^T \right) - \frac{2}{3} \nabla \cdot \vec{v} )</td>
<td>Effect of volume dilation</td>
<td>Molecular viscosity and unit tensor is very effective</td>
</tr>
<tr>
<td>2D axisymmetric geometries momentum</td>
<td>( \frac{\partial (\rho v_x)}{\partial t} + \frac{1}{\Gamma} (\rho v_x v_x) + \frac{1}{\Gamma} (\rho v_x v_z) = -\frac{\partial p}{\partial x} + \frac{1}{\Gamma} \left( \mu \frac{\partial v_x}{\partial x} + \frac{2}{3} (\nabla \cdot \vec{v}) \right) )</td>
<td>Axial and radial momentum</td>
<td>Swirl velocity is main concern</td>
</tr>
<tr>
<td>conservation equations</td>
<td>+ \frac{1}{\Gamma} \left( \mu \frac{\partial v_z}{\partial z} + \mu \right) + \vec{F}_e )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>User-defined scalar (UDS) transport equations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single phase flow</td>
<td>( \frac{\partial \phi_k}{\partial t} + \nabla \cdot (\alpha_k \rho \vec{v} \phi_k) - \alpha_k D_i^{<em>} \nabla \phi_k^2 - \delta_k^</em> ) ( k = 1, \ldots, N )</td>
<td>Arbitrary scalar, diffusion coefficient</td>
<td>In the case of anisotropic diffusivity tensor may change</td>
</tr>
<tr>
<td>Multiphase flow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Periodic flows</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressible flow equation</td>
<td>( \rho = \frac{p_0 + p}{RT} )</td>
<td>Operating pressure, local static pressure, molecular weight,</td>
<td>For 3D problems no particular inputs required throughout the problem setup</td>
</tr>
<tr>
<td></td>
<td></td>
<td>temperature, Energy factor, conservative vectors</td>
<td>Follow ideal gas law</td>
</tr>
<tr>
<td>Energy conservation equation</td>
<td>( \frac{\partial (\rho E)}{\partial t} + \nabla \cdot (\vec{v} (\rho E + p)) = -\nabla \left( \sum_i \delta_i \right) + S_h )</td>
<td></td>
<td>For inviscid flows energy conservation equations are reduced because of the absence of molecular diffusion</td>
</tr>
<tr>
<td>Mass diffusion equation (Laminar flow)</td>
<td>( \delta_i = -\rho \delta_{i,m} \nabla Y_i - D_i \frac{\nabla Y_i}{T} )</td>
<td>Diffusion flux, concentration gradients, Schmidt number, turbulent viscosity, turbulent diffusivity</td>
<td>Fick’s law is used for modeling</td>
</tr>
<tr>
<td>Mass diffusion equation (turbulent flow)</td>
<td>( \delta_i = -\rho \delta_{i,m} \frac{\mu_k}{S_c} \nabla Y_i - D_i \frac{\nabla Y_i}{T} )</td>
<td>Turbulent diffusion generally overwhelms laminar diffusion</td>
<td>Only applicable for a non-reversible reaction</td>
</tr>
<tr>
<td>Laminar finite-rate model equation</td>
<td>( R_i = \frac{\mu}{T} (\nabla Y_i - \nabla Y_{Sil}) ) ( k_i \Delta \frac{1}{f_i} ) ( (1 + \phi_i) \left( k_i \Delta \frac{1}{f_i} \right) )</td>
<td>Rate exponent for product species, reactant species and molar concentration of species</td>
<td></td>
</tr>
<tr>
<td>Eddy-dissipation model equation</td>
<td>( R_i = \phi_i M_{Rev} A_i \rho_k \Delta \min \left( \frac{v_{Y_i}}{v_{\Delta_i \rho_k \Delta \min}} \right) )</td>
<td>Mass fraction of any product species and particular reactant</td>
<td>ANSYS FLUENT permits multi-step reaction mechanisms with the eddy-dissipation and finite-rate/eddy-dissipation models</td>
</tr>
</tbody>
</table>
reaction closure (CO\textsubscript{2}) gases. In the case of multiple gas phase reactants, ANSYS FLUENT suggests that the reaction stoichiometry must be extended as follows:

\begin{equation}
\text{Particlespecies} + \text{gasspecies (1)} + \text{gasspecies (2)} + \text{gashpecies (n)} \rightarrow \text{Products}
\end{equation}

Gas–solid catalyzed reaction is widely used for industrial scale polymer production. For example, Ziegler–Natta catalyst is used in polypropylene and polyethylene production. The reactant gases (propylene/ethylene, nitrogen and hydrogen) are converted on the polymer particles to produce a broad distribution of polymer molecules. The porous catalyst particles, composed of small sub fragments which includes active metal. Polymerization occurs on the active sites of the catalyst surface by diffusion through the porous catalyst [15,100]. Table 2 [96] shows the necessary properties of ethylene and nitrogen gas are also available in COMSOL. The feed to the reactor was considered to be a mixture of ethylene, propylene, nitrogen and hydrogen. The following equations for the surface reaction rate and mass fraction of the surface species calculation:

\begin{equation}
\text{Rate of reaction:}\quad \bar{R}_{ij} = A_p n_y R_{ij, r}
\end{equation}

\begin{equation}
R_{ij, r} = R_{kin, r} \left( \frac{p}{\bar{R}_{ij, r}} \right)^N
\end{equation}

\begin{equation}
\text{Kinetic rate of reaction:}\quad R_{kin, r} = A_r T_p \beta_r e^{-\left( \frac{E_r}{R T_p} \right)}
\end{equation}

\begin{equation}
\text{Rate of particle surface species depletion for reaction order } N_{e,n} = 1:\quad \bar{R}_{ij, r} = A_p n_y Y_r P_{kin, r} \frac{D_{0, r}}{D_{0, r} + R_{kin, r}}
\end{equation}

\begin{equation}
\text{For reaction order } N_e = 0:\quad \bar{R}_{ij, r} = A_p n_y Y_r R_{kin, r}
\end{equation}

Another CFD software, COMSOL also provides effective simulations to study the gas phase fluidization. Material, energy and momentum balance equations of ethylene polymerization process can be found in the literature [101–103]. The following equations below are applicable for gas phase polymerization process specially used in COMSOL. The feed to the reactor was considered primarily of ethylene as the monomer and nitrogen as the carrier gas (homo-polymerization).

\text{Material balance}

The steady state material balance for ethylene through the fluidized bed reactor is given by:

\begin{equation}
D_i \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial C_i}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial z} \left( \frac{\partial C_i}{\partial z} \right) \right] + r_{c_i H_4} = \frac{\partial}{\partial z} (v_z C_i) + \frac{1}{r} \frac{\partial}{\partial r} (v_r C_i)
\end{equation}

where the subscript “\text{i}” indicates ethylene species. The reaction rate of ethylene is given by:

\begin{equation}
r_{c_i H_4} = -k_r C_i C_{c_i H_4}
\end{equation}

where the reaction rate constant is:

\begin{equation}
k_r = 0.085 \exp \left[ \left( \frac{9000}{T \text{K}} \right) \left( \frac{1}{7} - \frac{1}{360} \right) \right]
\end{equation}

Eq. (8) should be solved according to the following boundary conditions:

\text{Reactor walls: } \langle r = R \rangle; -\frac{\partial C_i}{\partial r} = 0
\end{equation}

\text{Ethylene initial feed concentration: } \langle z = 0 \rangle; C_{c_2 H_4} = C_{c_2 H_4}
\end{equation}

\text{Convective flux: } \langle z = L \rangle; -\frac{\partial C_i}{\partial z} = 0
\end{equation}

\text{Energy balance}

The energy balance inside the FBR can be obtained by employing conduction and convection heat transfer equations:

\begin{equation}
\rho_g C_p \left( v_r \frac{\partial T}{\partial r} + v_z \frac{\partial T}{\partial z} \right) = \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (r p T) \right) + \frac{\partial^2 T}{\partial z^2} + r_{c_i H_4} \Delta H_{\text{rnx}}
\end{equation}

This equation should be solved according to the following boundary conditions:

\text{Symmetry: } r = 0, \frac{\partial T}{\partial r} = 0
\end{equation}

\text{Symmetry: } r = R, T = T_w
\end{equation}

\text{Inlet temperature: } z = 0, T = T_0
\end{equation}

\text{Convective heat flux: } z = L, \frac{\partial T}{\partial z} = 0
\end{equation}

\text{Momentum balance}

At steady state condition, velocity profiles in the \text{r} and \text{z} directions can be obtained from:

\text{r-Direction:}

\begin{equation}
\rho_g \left( v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} \right) = -\frac{\partial p}{\partial r} + \mu_g \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial v_r}{\partial r} \right) + \frac{\partial^2 v_r}{\partial z^2} \right]
\end{equation}

\text{z-Direction:}

\begin{equation}
\rho_g \left( v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial p}{\partial z} + \mu_g \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial v_z}{\partial r} \right) + \frac{\partial^2 v_z}{\partial z^2} \right]
\end{equation}

These equations should be solved subject to the following boundary conditions:

\text{No slip at reactor walls: } r = R, v_r = 0, v_z = 0
\end{equation}

\text{Symmetry: } r = 0, \frac{\partial v_z}{\partial r} = 0, \frac{\partial v_z}{\partial z} = 0
\end{equation}

\text{Inlet velocity: } z = 0, v_z = v_0, v_r = 0
\end{equation}

\text{Reactor exit: } z = L, \frac{\partial v_z}{\partial z} = 0, v_z = 0
\end{equation}
At the present time, numerous general-purpose CFD codes are available. The choice of number of governing equations to be used and selection of codes solely depends on the purpose of the model. Three types of gas–solid regimes are considered to be handled by ANSYS FLUENT: (i) particle-laden flow (ii) pneumatic transport (iii) fluidized bed (both fluidized bed reactors and circulating fluidized beds). Application of CFX-4 commercial code for simulating of gas–solid fluidized beds has been detailed by Lettieri et al. [117]. The particle-bed model and the Eulerian granular model were their main considerations. Taghipour et al. [119] conducted both experimental and simulation studies on a gas–solid fluidized bed system. They used a 2D fluidized bed column to provide a meaningful understanding of the hydrodynamics of the reactor. It is worth mentioning that, compared to Taghipour et al. [119], Herzog et al. [81] carried out their simulations with a more recent version of Fluent and achieved results that match much better with the numerical results of MFIX. Their analysis showed that the Eulerian–Eulerian model of OpenFOAM (Open Source Field Operation and Manipulation) has not been fully developed until now; whereas, Londono et al. [120] made initiatives to benchmark the OpenFOAM module based only on global values. However, this module is an addition to the development of Passalacqua and Fox [121].

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The first set of gasifier task. Syamlal et al. carried out an elaborated case study on verification of a complex software is a critical and difficult computational science and engineering and stated that the main reason is the ‘effectiveness’ along with the ‘sustainability’ of the OS development. The theory manual of MFIX contains equations while the user’s manual contains code architecture, numerical technique and user instructions. The first set of gasifier simulations by OS codes were carried out in 1995. Gas–solids flow models in MFIX are continuing development process like other recognized mathematical models and numerical techniques. Hydrodynamics, heat transfer and chemical reactions in fluid–solids systems can be described directly by MFIX general-purpose computer code. This code can solve commonly recognized set of partial differential equations for conservation of mass, momentum, species and energy for multiple phases. Table 3 illustrates the applicable categories of MFIX and shows the multicategorical applications of MFIX as a CFD tool.

2.4. Supporting tools for CFD software

GAMBIT (widespread as a preprocessor) is an additional potential software package designed for quick geometry modeling as expert meshing is essential for CFD analysis. This combined tool can be merged with ANSYS FLUENT and offers various advantages. GAMBIT possesses single interface for geometry design and meshing that transports jointly all FLUENT preprocessing technologies in one setting. Sophisticated tools can be used for revising and replaying model development orientations for parametric studies. GAMBIT is also capable of importing geometry from any CAD/CAE software in Para solid, STEP, ACIS, or IGES set-up. A broad spectrum of modeling of gas–solid fluidized bed reactions and healing capabilities are routinely provided with its solid geometry during import to the solver of GAMBIT. Geometry based modelings can be carried out through GAMBIT. Repairing and systematic grouping of the geometry for high quality granular polymer meshing are also appropriately achieved with GAMBIT semi-automatic cleanup tools. Some geometric properties, like sharp corners, small features, overlapping faces and holes can be identified fast and are easily accessible in GAMBIT. As a single package, GAMBIT preprocessor provides different types of mesh required to solve CFD problems. Ample meshing toolkit of GAMBIT can be used to decompose geometries for structured meshing or execute programmed meshing with control over clustering. This package includes tetrahedral volume meshes and triangular surface meshes.

Fig. 4 illustrates the classical meshing applied for simulation of a fluidized bed. Fluid circulation in the emulsion phase just above the fluidized part of the bed may considerably alter the pressure of the solid phase and influence the fluidization pattern and velocity vectors. As a result, researchers generate a moderately coarse mesh (Fig. 4a) at the initial stage to optimize the computational prerequisites. Usually, a refined mesh (Fig. 4b) is then considered for simulation of the complex expanded fluidized bed and more precise meshing can be explored through special mesh refinements.

3. Aspects and mechanisms in fluidized bed reaction

3.1. Modeling of hydrodynamic behavior of fluidized bed reactor

Profound knowledge of fluidized bed hydrodynamics is important for proper gas–solid reaction modeling and, thus, a proper fluidization processes design. Modeling of gas–solid flow patterns, together with the volume, size and velocity of bubbles is a challenging issue. Uniform gas distribution in the reaction zone of the reactor with a desirable interfacial surface area between the gas and solids is important to achieve better conversion. Higher gas velocity is a must for higher production rate and for balancing purposes staging and baffling is also considered. Furthermore, strong control over heat exchange is essential to avoid potential dead spots.

Development of hydrodynamic models for describing fluidization process started in early 1960s. The precedent studies mainly focused on the stability of fluidization as well as formation and motion of bubbles. Literature survey disclosed that researchers have attempted to obtain a better understanding of the hydrodynamics of FBRs by carrying out laboratory scale experiments. However, laboratory scale data are not necessarily enough for accurate scale up. For clear understanding of the hydrodynamics in a commercial scale fluidized bed reactor, the study on a vessel of that size is a must. As such, computational modeling is needed to decrease the capital cost and attain featured engineering design guidance. Most of designs of FBRs have been performed based on the data from the laboratory scale or pilot scale units. Accurate hydrodynamic models, considering fundamental laws of mass, energy, momentum and species conservation, can link the

Table 3

<table>
<thead>
<tr>
<th>Sector</th>
<th>Considered factors</th>
<th>Fraction of usages in percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>Coal gasification and combustion, Biomass combustion</td>
<td>28%</td>
</tr>
<tr>
<td>Fluidization</td>
<td>Bubbling fluidized beds, risers, particle flow, gas–solids flow</td>
<td>20%</td>
</tr>
<tr>
<td>Chemical reactors</td>
<td>Fluid catalytic cracking, fluid bed reactors and polymerization</td>
<td>12%</td>
</tr>
<tr>
<td>Multiphase flows</td>
<td>Multiphase, micro-fluidics, slurry flow, gas–liquid</td>
<td>14%</td>
</tr>
<tr>
<td>Geophysical</td>
<td>Volcanic granular flows</td>
<td>8%</td>
</tr>
<tr>
<td>Other applications</td>
<td>Micro-channel heat exchanger, Powder flow</td>
<td>18%</td>
</tr>
</tbody>
</table>

Fig. 4. Typical mesh (a) original mesh performing using GAMBIT and (b) refined mesh in FLUENT only for the height of fluidized section. Reproduced with permission from Elsevier.
gap between laboratory scale experimental data and industrial scale reactors [119]. Although polyolefin systems have been the focus of numerous researchers since the last three decades, the nonideality of the particle behavior makes it difficult to utilize a CFD model to study effects of its parameters on the system behavior.

3.2. Fluid flow modeling

Small number of studies are available on the dynamics of fluid flow in fluidized bed polymerization reactors, especially for influences of modeling parameters and operation/reactor conditions on the flow behavior [62,130–132]. Two dimensional Eulerian–Eulerian model, combined with the KTGF approach, was applied to simulate the flow fields in a gas–solid FBR [54,133–137].

CFD has become a very attractive option besides experimental techniques. However, this numerical method needs a very effective and careful validation procedure. Eulerian–Eulerian model and Eulerian–Lagrangian approaches are two approaches that are frequently used for formulation of multi-fluid flow and motion of dispersed phase, respectively [138,139]. CFD models for various systems, like solid–liquid, gas–solid and particle–fluid, have been used since two decades ago [140–142]. The two-fluid model (TFM), based on the Eulerian–Eulerian approach, has been adopted to solve various multiphase flow problems. The TFM requires a package of empirical or physical models for closing the conservation equations [143]. Nowadays, the KTGF has become the top choice for the closure law to explain solid phase dynamics (solid viscosity, solid pressure, solid shear stress) along with the TFM [144]. However, some researchers considered a drag force model to obtain precise simulation results. Recently, some researchers applied drag force model combined with the KTGF-based TFM model for calculation of dynamic parameters and simulation hydrodynamics of gas–solid fluidized bed [145,146]. Several momentum exchange coefficients in the gas–solid flow were also developed [147,148]. Hosseini et al. [149] examined different drag models at high gas velocities using combined 2D Eulerian-Eulerian approach and the KTGF. They showed that particles motion and bubbles behavior are satisfied by experimental data.

In the gas phase olefin polymerization, porosity and effect of temperature on performance of the reactor is significant [150]. Ding and Gidaspow [45] pioneered the study on prediction of instantaneous porosity and evaluation of the porosity distribution in fluidized beds experimentally. Jung et al. [151] analyzed various types of granular temperature in a 2D model fluidized bed with a combination of KTGF-based code and MFIX and showed that the results are in agreement with their earlier experimental study. Energy spectrum of particle turbulence, phase dispersion, granular temperature, Reynolds stresses and phase dispersion have been evaluated in risers of fluidized bed [152,153]. However, very few researchers have focused on the organized analysis of fluidization dynamic parameters with complete investigation on the multi-phase gas–solid flow. Nevertheless, the TFM (Eulerian–Eulerian model) integrated with the KTGF is accepted by many researchers to simulate the flow behavior in the gas–solid fluidized bed. Since the RNG–k–ε model requires an impractical higher turbulent viscosity and is hard to converge, the typical k–ε turbulence model with high computation speed and acceptable speed of convergence is normally chosen to solve the transport equations of $k$ and $ε$. FLUENT offers double precision option and can provide a better solution for these complexities. In this case, discretization of the momentum equation can be done by the second order upwind scheme in the ANSYS FLUENT package [154,155].

Turbulence is an important phenomenon in gas–solid fluidized beds. This phenomenon can affect mixing as well as heat and mass transfer. Proper knowledge of turbulent energy power spectrum is required to simplify and investigate the turbulent flow [156]. According to the cascade theory of turbulence, the turbulent energy spectrum is divided into energy-containing range, inertial range and dissipation range. Reynolds number and the Kolmogorov-5/3 law are key tools for calculation and classification of flow behavior. For instance, a flow with a high Reynolds number is categorized under inertial range which also can be observed by the Kolmogorov-5/3 law [143,147,157,158]. Flow at lower Reynolds numbers, inhomogeneous and irregularity is observed for the spatial and temporal distribution of instantaneous turbulent dissipation. For a flow with lower Reynolds number, Kolmogorov-5/3 law is not suitable whereas the Levy–Kolmogorov law can be considered [159–162] while constitutive equations are applied in the TFM to explain the rheology of the solid phase (pressure gradient and viscosity) [163–165].

Concepts of fluid kinetic theory can be introduced to explain the functional stresses in the solid phase follow–on from particle streaming collision contribution if the particle motion is enough to be dominated by particle collision interaction [166–168]. Concepts of kinetic theory developed by Lun et al. [169] were adopted in some studies for explanation of constitutive functions for the solid-phase stress. Moreover, some significant KTGF equations for study of flow behavior have been accepted widely as follows:

$$p_i = \alpha_i p_i(1 + 2g_0(1 + e_i))$$ (25)

$$\lambda_s = \frac{4}{3} \alpha^2_s d_sg_0(1 + e_i) \sqrt{\frac{\bar{e}}{\tau}}$$ (26)

where

$$g_0 = 1 - \left(\frac{\alpha_s}{\alpha_{s,\text{max}}}\right)^{1/4}$$ (27)

It is also necessary to consider transport equation for the granular temperature [45]:

$$\frac{\partial}{\partial t}(\rho_s \bar{e}_s \Theta_s) + \nabla \cdot (\rho_s \bar{e}_s \bar{v}_s \Theta_s) = \frac{2}{3} \left[ (-\rho_s \bar{I} + \bar{t}_e) \nabla \bar{v}_s + \nabla (k \nabla \Theta_s) - \rho \Theta_s + \psi_s \right]$$ (28)

Lun et al. [169] provided the following correlation for the collision dissipation of energy:

$$\eta_{\Theta_s} = 12(1 - \frac{e_s^2}{d_s}) \frac{p_c \rho_s \bar{v}_s^{1.5}}{d_s \sqrt{\pi}}$$ (29)

Double precision mode of ANSYS FLUENT can be applied to solve the stated equations. For coupling of velocity and pressure, SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) algorithm with phase-coupled mode can be used. GAMBIT is convenient for grid generation and 3D geometries visualization in different system environments.

3.3. Mixing models

Fluidized beds are generally useful devices for various applications of particle mixing. Motion of bubbles is considered as the main driving force for particle mixing. On the other hand, segregation also occurs at certain conditions. In gas–solids olefin polymerization reactor, perfect mixing is always advisable. To initiate polymerization, mixing of granulated polymer particle, reactant gas, carrier gas and polymer chain cutting gas is mandatory [15,170]. Mixing and segregation take place simultaneously and at the equilibrium state when a moderately homogeneous distribution of particles is desired [171]. During
fluidization, bubbles move from the bottom toward the top of the bed which results in both mixing and segregation of particles. These phenomena are fully supported by the two-phase theory of fluidization [172].

Due to traveling of bubbles up throughout the bed, particles are drawn into a sluggish zone trailing the bubbles, known as the wake [173,174]. Particle penetration in the wake causes axial mixing and consequently fresh particles permeate from the dense adjoining region. Particles adjacent to the wake will be deposited at the surface of the bed due to the upward movement of bubbles. As a result, particles at the bottom of the bed can be mixed with the particles at the top. The adjoining fluid surrounding the rising bubble is considered as the main motive of particle mixing [175]. In the intervening time, the bubble at its rising moment leaves a void behind [176]. Mixing of solids in a bubbling fluidized bed is highly affected by collision and coalescence of bubbles. Bubbles and emulsion can be considered as source and sink of kinetic energy for particles, respectively. Energy transfer from source to sink occurs through the drift region. This energy transfer produces circulation of solids, in the scale of bubble diameter, in the drift zone. Therefore, both gross and internal circulations are the cause of solids mixing in the bed [177–179].

Norouzi et al. [177] investigated the behavior of the solid phase in fluidized beds using a 2D CFD-DEM simulation to get more information on mixing and motion of solids. Their typical results are shown in Fig. 5 which demonstrates evolution of void fraction contours and solids flux vectors in a fluidized bed with a porous plate distributor at superficial gas velocity of 1 ms$^{-1}$. Formation of bubbles at the vicinity of the distributor, growth of bubbles, their coalescence and breakage can be seen in this figure. Norouzi et al. [177] showed that the bubble breakage affects internal circulation of particle which develops in rapid local mixing of particles.

Heat of polymerization reaction is mainly removed through mixing. It has been found through experiments in polymerization reactors that the quality of mixing in a specific reactor has a significant influence on the rate of polymerization as well as product properties. CFD has the advantage that it is capable of presenting precise information on turbulent zones in the reactor. These information can help to obtain a better reaction yield by introducing reactants into regions with intense turbulence.

The non-linear behavior of reactive fluids can further complicate the formulation of quantitative analysis along with flow visualization during lab scale experiments. Hence, although experimental investigation of the flow behavior in polymer reactors is very important, every parameter related to the mixing process is not manageable with experimental analysis, especially for the desired spatial resolution [180–182]. In spite of successful efforts to solve various problems on the effect of mixing on kinetics of polymerization, there are also difficulties identifiable on modeling of mixing in polymerization reactors. On the other hand, improvement of CFD methods has provided the opportunity to visualize the mixing dynamics such that the necessity to carry out real-time experiments can be bypassed [30,183]. To make simulation faster, Wells and Ray [184] proposed a CFD model in combination with a compartment model while ignoring back mixing. Kolhapure and Fox [185] performed a CFD simulation of ethylene polymerization in a tubular reactor and showed that uneven mixing reduces the polymer conversion but increases the polydispersity index. However, their modeling approach can be criticized for using randomly defined mixing parameters that limited the application of the model. Substantial effect of bubble motion on different aspects of mixing, such as wake, cross solid mixing, interaction and coalescence of adjacent bubbles, dispersion of particles in the wake and eruption of the bubble were explained through the CFD approach [186]. The CFD-DEM technique was applied for investigation of mixing and the particle motion in the flat-bottom spout bed. Both mixing and segregation phenomena were explained with clear justifications with the help of CFD-DEM [187,188]. Wu and Zhan [189] investigate the mixing of particles for various configurations in

![Fig. 5. Void fraction contours and solid flux vectors of the bed with a porous plate distributor. Reproduced with permission from Elsevier [155].](image)
the reactor inlet by employing hard-sphere DEM. Effect of mixing of polydisperse fluidized inert powders was studied with the support of multifluid model option of ANSYS FLUENT by Mazzei et al. [190]. In their study, they proposed and applied a novel quadrature method of moments (Q MOM) into ANSYS FLUENT code considering all particles possess different velocity.

The population balance equation (PBE) is one of the widely accepted methods to explain mixing based on variation of particle size. The change of particle size distribution (PSD) with respect to time and space can highly influence physical and chemical phenomena of the gas phase polymerization processes. Variation of the PSD can be linked to significant segregation which can cause uneven mixing of particles in the bed. For analysis of the mixing performance, particle population can be categorized by diameter and velocity. Consequently, two internal coordinates, a scalar and a vector, should be used for this purpose [191]. To explain the population of particles, a volume density function (VDF) has been proposed. Since, the PBE and the moments are linear in the VDF, mixing is also a linear process and these values may be accurately calculated through their transport equations in the numerical code. To solve this problem, ANSYS FLUENT correlates user defined scalars either with a specific phase (the fluid or any granular phase) or with the mixture of all phases [192].

To reduce the computational time in simulation of a fluidized bed polymer reactor, a vessel may be considered whose height is double the static height of the powder. This height possibly is enough to let small size particles to fall back into the dense bed. In this case, these particles bypass the computational domain and are irreversibly lost [193].

It has been reported that polymerization requires an extremely viscous medium which can affect flow pattern in a polymerization system [87,194,195]. Therefore, the mass viscosity is highly recommended to be considered for polymerization reactor modeling. The apparent viscosity of the mixture can be calculated from [196,197]:

\[
\mu = \frac{\mu_0}{\left(1 + \mu_0 \gamma^{1/2} / 35,000\right)^{0.6}}
\]  (30)

and the density of the mixture can be calculated from [198]:

\[
\rho = \left(1174 - 0.918T\right)(1 - wp) + \left(1250.0 - 0.605T\right)wp
\]  (31)

3.4. Bubble modeling

Bubbling is involved in most gas fluidized beds. Therefore, to understand the governing phenomena of bubble formation, it is highly important to understand the fluidization features in the olefin polymerization process. Complete fluidization of the bed is required for bubble formation which spreads throughout the bed in the form of high void fraction regions. Generally, the shape of a bubble depends on its velocity, not the bed dimension. A slow bubble is spherical and starts to deform by increasing its velocity. The size of a bubble can be determined by an effective spherical radius which includes the wake region [199]. The nature of bubble formation and movement in fluidized beds can influence the hydrodynamics of fluidization. Thus, bubble diameter, distribution of bubbles and their collision are considered as significant parameters [200]. A number of comprehensive studies have been carried out on various bubble properties. It has been found that the bubble wake is one of the influential aspects accountable for inherent transport properties in the system. Therefore, investigating the bubble wake have drawn attention of researchers for many years. Ever-increasing computer power along with employment of CFD approach has gained considerable attention for investigating bubble behavior in polymerization process through CFD modeling [201–204].

However, still inadequate understanding of multiphase flows has been gained due to complex phenomena involving fundamental interactions between phases, for instance, particle–bubble interaction or particle–particle collision [205]. Geldart and Kelsey [206] investigated the bubble motion in two-dimensional and three-dimensional beds with different thicknesses in an effort to show a relationship between three and two dimensional bubble sizes for the first time. For quantitative comparison, some successful CFD simulations, e.g., Syamlal–O’Brien [207], Laux-Johansen [208] and many other cases can be considered [209]. Time step, partitioning schemes, solid stress closure equations and frictional stress are influential parameters on bubble properties. Boemer et al. [168] conducted experiments on various bubble parameters like size of bubble, bubble velocity, angle of wake, pressure distribution and voidage. Although they obtained useful results, not much data points were reported for bubble properties. Particle velocity is one of the most significant parameters on the formation of bubble and it is possible, through CFD-DEM, to provide information on the velocity profile of particles in bubbles [210,211]. The comparison on particle velocity and bubble shape is shown in Fig. 6 for both simulation and experimental runs. Fig. 6(a) illustrates the significant interface between bubble and emulsion phase, which is also predicted through the CFD model. Experimental results achieved by the model are also shown in Fig. 6(b). Electrostatic effect between particles, diameter of bubble and solids diffusivity was also considered in this study.

Bubbles can be identified from the void fraction images produced by ANSYS FLUENT. Example of such images can be seen in Fig. 7. In addition, a specific program is required to track the bubbles from a frame to another. It is advised that discontinuation of void fraction to be fixed by the user in order to compare the simulation results.

Setting up the time step has an important effect on the accuracy of bubble simulation. In order to obtain transient simulations, the governing equations should be solved to propagate the solution at specific time steps. Computational time and convergence are usually affected by the time step. ANSYS FLUENT offers the ‘first order semi-implicit’ real time solution technique, thus, a smaller time step is appropriate for a more precise solution. Since computational time is a major issue in studying of bubbles in the gas phase polymerization process, prolonged simulation of a few real seconds becomes key consideration as simulation of bubble dynamics in a fluidized bed can take more than 1 week for a simple geometry. For comparing different times steps, the dimensionless Courant number can be used [212]. The Courant number reflects the part of a cell that the fluid traverses by advection in a time step:

\[
N_c = \frac{\gamma^T \Delta t}{\Delta x}
\]  (32)

When advection is dominant over dispersion, the Courant number should be kept small to reach a better accuracy and minimize the numerical dispersion. It is recommended to set the Courant number to 0.3 for obtaining convergence at a proper calculation speed for continuing “good” behavior in the computations [212].

The differencing scheme is another parameter that affects properties of bubbles in the simulation of an olefin polymerization reactor. There are first-order upwind and second-order upwind options available in ANSYS FLUENT. It is shown in Fig. 8 that bubbles appear at the beginning of simulation, but fade away at longer times since the bubbles cannot be detected when the differencing scheme was changed from the second-order upwind to the first-order upwind. Discretization of voidage derivatives by
the second-order differencing scheme is preferred since it does not assure cell uniformity and calculate a gradient between the cell nodes, thus, bubble boundaries can be determined distinctively. If the cell value is kept constant as in first order differencing scheme the solution would become fundamentally smoothed in successive time steps as shown in Fig. 8.

Van Wachem et al. [213] established a CFD model in conjunction with the Eulerian-Eulerian gas–solid model for a freely bubbling fluidized bed using the commercial CFX package. Renzo et al. [214] carried out CFD simulation of a bubbling FBR by considering the chemical kinetic aspects and focused on multi-phase fluid dynamics, polydisperse particle distributions, intra-particle heat and mass transfer rates.

Bed height is another important parameter for bubble modeling. Height of the bed increases due to formation of bubbles. Coalescence of bubbles takes place during their rise and produce larger bubbles. At the same time, deformation of bubble occurs due to wall effects and interaction with other bubbles. Experiments have indicated that small bubbles are formed near the bottom of the bed and they grow larger as a result of coalescence when rising in the bed [215]. Modified Sitnai’s methodology has also been used to give details on the fundamental procedure for the analysis of hydrodynamic properties of bubbles [216]. Based on this model, it was concluded that for the hypothetical transient pressure field created by the theoretical Davidson model [16] for a single noninteracting bubble in a bed with no internals, the time lag, $\tau_a$, determined from autocorrelation yields the ratio of the bubble diameter, $D_b$, to the vertical bubble velocity, $V_b$, given by:

$$\tau_a = \frac{D_b}{V_b}$$

(33)

This equation can be used to calculate the ratio of bubble diameter to bubble velocity from the time lag obtained from the experimental and computed autocorrelations. The bubble diameter may then be determined from:

$$D_b = \nu_b \tau_a$$

(34)

where the bubble velocity can be determined from the well-known equation of Davidson and Harrison [16]:

$$\nu_b = \frac{0.71}{\sqrt{gD_b}}$$

(35)

The type of the gas distributor influences bubble formation and motion which in turn affects the mixing in fluidized bed of olefin

Fig. 6. Comparison between experiment [190] and model results in terms of (a) bubble shape and (b) particle velocity profile of polyethylene. The unit vector above particle velocity profile plot corresponds to a particle velocity of 1 m/s and minimum fluidization velocity 1.25 m/s. Reproduced with permission from Elsevier [147].
polymerization. Particle size distribution in the axial direction is affected by circulation of solids. There are two possible flow paths in a fluidized bed in the upper zone and the bottom zone. Most of the small particles move in the upper part of the bed while large particles flow around in the bottom section. It is noticeable that the number of gas bubbles occurring steadily during the fluidization changes when the geometry of the gas distributor is changed. The gas bubbles merge to grow in size and proceed to the center of the fluidized bed steadily. Bigger bubbles complete their circulation cycle as they burst adjacent to the bed surface. Correspondingly, intense upward flow trend is observed in the case of smaller particle which also proceed to the center progressively [217]. Flow pattern of bubble and emulsion phases in a fluidized bed for various types of gas distributor is shown in Fig. 9. It can be seen in this figure that the path of the emulsion phase is more complex than the gas phase. Bubbles are formed as the gas passes through the distributor. Coalescence of bubbles occurs as they flow up and gradually inclined toward the center and burst at the surface of the bed. In a same way, particles at the bottom of the bed flow up and shift to the center through movement of bubbles. Once the particles reach the top surface of the bed, they mainly move downward gradually in the region close to the wall. Two circulation zones are virtually of the same dimensions and the gas flows evenly in these zones [Fig. 9(a)]. Particle motion and bubble formation are shown in Fig. 9(b) and (c) in which the gas is injected through the core and annulus regions, respectively, of the distributor.

3.5. Elevated pressure processes

Since the polymerization process occurs at elevated pressure, there is a need for fundamental knowledge of variation of the flow structure against pressure. Li and Kuipers [218] numerically investigated the influence of pressure on the regime transition in dense gas fluidized bed using the DEM. Their results showed that increasing the pressure decreases the incipient of fluidization, increases the homogeneity of the bed and the bed height and leads to a quick transition to turbulent regime of fluidization. They also found that particle–particle collision, compared to particle–fluid interaction, is reduced at elevated pressures. Godlieb et al. [219] considered the relationship between operating pressure and granular temperature by performing a full 3D DEM-CFD simulation. They found that the granular temperature increases by increasing the pressure and that the pressure has influences the granular temperature mainly in the vertical direction. Zhang et al. [220] investigated motions of bubble and particle in a three-phase fluidized bed at elevated pressures. The Eulerian volume-averaged method, the Lagrangian dispersed particle method and the VOF method were used to describe the motion of liquid, solid particles and gas bubbles, respectively. Furthermore, bubble-induced force model, continuum surface force (CSF) model, Newton's third law and close distance interaction (CDI) model were applied to illustrate, respectively, the coupling effect of particle–bubble, gas–liquid, particle–liquid interactions and the particle–particle collision analysis. Their simulation results indicated that the bubble trajectory is more tortuous at high pressure than at low pressure. Mansourpour et al. [221] studied the effect of pressure on the bubble dynamics (i.e., bubble diameter, rise velocity and its path of rise) in a gas fluidized bed based using the DEM-CFD technique. Their results showed that at elevated pressure, bubbles rise slower and become smaller while bubble break-up rate increases. Consequently, the bed homogeneity enhances at higher pressures. Furthermore, the bubble path becomes twisty through the bed at elevated pressures. Norouzi et al. [178] developed a

![Fig. 7](image_url) Void fraction of solids at specific cutoff for different time steps. Reproduced with permission from ACS [24].

![Fig. 8](image_url) Simulation with time step of 0.00025s, first order up-wind (Courant number was below 0.15, at constant cell value). With condition of gas velocity 12.6 cm/s, gas density 1.21 kg/m³, pressure 101,325 Pa and minimum fluidization velocity 0.093 m/s. Reproduced with permission from ACS [21].
3.6. CFD study on heat transfer phenomena and modeling of polyolefin reaction

Design of a gas phase polymerization reactor is generally based on considering an arrangement of single or multiple pseudo-homogeneous phases in which mass and heat transfer between phases are taken into account. High rate of the polymerization reaction (normally in the order of 5–50 kg of polymer per gram of catalyst per hour) and its exothermic nature (heat of reaction of 100 kJ/mol) makes removing the generated heat at increased yields difficult in industrial reactors. This problem is more serious in gas-phase reactions since the heat transfer characteristics of gas-phase particles are poor [222].

It is well known that heat transfer problems in fluidized beds are related to particle–particle interactions [223] and researchers can provide knowledge of this local phenomena through modeling. Fitting the model for a polyolefin reactor involves the combination of a wide range of particle growth models [224]. Therefore, researchers have investigated effect of local deviations in flow rate, gas composition and initiation temperature of reaction on both particle growth and reactor performance. Coupling heat transfer and reaction kinetics in modeling polyolefin reactors is unavoidable and academic and industrial communities have encountered difficulties inherent in this problem. For example, the DEM was used in simulation of both ethylene and propylene polymerization process in a lab scale reactor [225,226]. Kaneko et al. [227] verified temperature of particles and gas in a fluidized bed reactor for polyolefin production by the DEM. In their study, the reaction rates were simplified to zero-order kinetic expressions. In this model the reaction rate depends only on the temperature profile in the reactor, but the effect of reactant concentration on the reaction rate was not considered. Karimi et al. [228] developed a DEM-CFD technique combined with equations of conservation of mass and energy to study the behavior of a gas-phase polyethylene reactor. The comprehensive reaction mechanism of McAuley et al. [104] and the corresponding kinetics was employed in their model.

Effect of operating conditions of the reactor on temperature distributions of gas and solids was also investigated to examine the possibility of hot spot formation. Their simulations showed that temperature of particles decreases by increasing the gas velocity due to an increase in the heat transfer rate. It was also shown that increasing the pressure results in a higher bed homogeneity and more efficient contact between reactants and the catalyst.

Many researchers have attempted to couple mass and energy balances for a single particle through a modified two-dimensional mass, momentum and energy balance equations in a FBR [229]. They showed that there is a need for more accurate explanation of the FBR hydrodynamics in order to obtain a full-scale integrated reactor model and to present practical information about heat transfer and its relationship with particle growth and fluidization conditions. By applying the direct QMOM, CFD packages can solve PBES in the reactor [230]. For a laboratory scale fluidized bed, temperature distribution and void fraction can be calculated by CFD softwares. Rapid heat generation among the multiphase environment (gas, solid, emulsion, etc.) causes the overheating of bigger particles which would likely result in hot spots in the reactor. Consequently, multigrain model (MGM) is the model which has attracted several research groups to explain the hot spot phenomena. The MGM considered agglomeration of concentric layers of micro particles, in which the reaction occurs inside the polymer particles. Considerable results can be achieved from modeling studies by the MGM approach. For instance, it can be shown that intraparticle temperature gradients and external heat transfer resistances can be neglected for low active catalyst or small extent of the reaction and that heat transfer resistances are much more important at early stages of polymerization. However, McKenna et al. [223] pointed the disadvantages of the MGM approach such as its deficiency to calculate changes in rapidly evolving particles with physically impractical predictions, for example melting of particle cores. In addition, they demonstrated that conventional heat transfer models, such as empirical correlation of Ranz-Marshall, may contain assumptions which give rise to physically unrealistic results, especially when applying to highly dynamic polymerization processes. Therefore, McKenna et al. [223] used the CFD approach to analyze the heat transfer and geometric scale effects at the same time in the gas-phase olefin polymerization for complex operating conditions.

Since measurements in industrial reactors are not easy to carry out, the CFD technique has been used as a useful tool for displaying details that cannot be obtained directly from the experiment [231]. However, only a limited number of successful CFD modeling of fluidized bed hydrodynamics including heat transfer have been reported. Studies on hydrodynamics of two dimensional
non-reactive gas–solid fluidized bed reactor with heat transfer, both experimentally and computationally, can be found which are mainly focused on the influences of temperature and particles size on the hydrodynamic condition of the bed and gas–solid heat transfer[232]. A multifluid Eulerian model, integrated with the kinetic theory of solid particles, can be used to simulate the gas–solid flow in a wide range of superficial gas velocity and diverse particle sizes. Ranz-Marshall equation is widely applied to calculate particles gas heat transfer coefficient and can provide reasonable results for particle and gas temperatures during bubble formation and rise in gas–solid fluidized beds. Another challenge is detecting formation of hot spots which mainly occurs due to nonlinear exchanging of heat at the distributor and near the wall of the fluidized bed [146].

A multifluid Eulerian model, associated with the KTGF approach, was applied by Huilin et al. [233] to describe hydrodynamics of bubbling fluidized beds. They demonstrated, with simulation results, that the hydrodynamics of a bubbling fluidized bed is severely affected by distribution of particle size as well as the magnitude of energy dissipation in particle–particle interactions. It was shown by Mickley and Fairbanks [234] that the particle–wall contact time is an important factor in calculating the heat transfer coefficient between wall and fluidized bed. Although their theoretical work is reasonably verified with the experimental data, their correlation is applicable only to limited operating conditions. Di Natale et al. [235] presented an experimental study on heat transfer coefficients between a fluidised bed of fine particles and a submerged surface using different shapes of immersed tubes within the fluidized bed. Their findings highlighted the strong influence of the surface shape on the heat transfer coefficient in addition to thermal properties of the gas and solid.

Dong et al. [236] employed the TFM for simulation of gas–solid two-phase flow in fluidized beds. Conservation of mass, momentum and energy for both solid and gas phases were considered. Their model also utilized the KTGF for describing solid properties such as solids shear stresses and solids viscosity based on the granular temperature that determines the oscillating behavior of the particles. Interaction between particles can be represented by solids pressure and bulk viscosity to obtain normal forces and the shear viscosity for tangential forces, respectively, in collisions. The collisions probability is adjusted with the radial distribution function. The CFD package ANSYS FLUENT was used for simulation purposes which offers the energy equations on the basis of enthalpy balance. For calculating the rate of energy transfer between solid and gas phases, the rate was considered as the function of average particle diameter, gaseous thermal conductivity, temperature difference, Nusselt number and volumetric fraction. The interphase heat transfer coefficient of Gunn [237] was exercised which is associated by particle Reynolds number and Prandtl number. For determination of the local instantaneous heat transfer coefficient, $h$, the operative thermal conductivity of both phases is considered which can be calculated by correlations of Kuipers et al. [134] and Patil et al. [238] as follows:

\[
K_g^{eff} = \left(1 - \frac{\alpha_s}{\alpha_g}\right) K_g
\]  
\[
K_g^{eff} = \frac{1}{\alpha_g} K_g \left(\omega A + (1 - \omega) \Gamma\right)
\]  
\[
\Gamma = \frac{2}{1 - B/A} \left[ \frac{A - 1}{(1 - B/A)^2} \ln \left(\frac{A}{B}\right) - \frac{B - 1}{1 - B/A} + \frac{B + 1}{2} \right]
\]  
\[
A = \frac{K_s}{K_g}, \quad B = 1.25 \left(\frac{\alpha_s}{\alpha_g}\right), \quad W = 7.2 \times 10^{-3}
\]

The grid refinement technique suggested by Kuipers et al. [5] is usually employed for mesh generation to subdivide the region near heated surfaces as a substitute of the uniform sub cell dimensions proposed by Syamlal and Gidaspow [239].

Detailed heat transfer study on particle level in fluidization with CFD validation is very rare. Brown and Lattimer [240] studied heat transfer characteristics of fluidized particles. Their study included both CFD simulation and experimental data. They showed that the apex surface of the bed usually exhibits the maximum particle temperatures due to higher bed-to-wall heat flux, lower residence time of bed particle in gas channel and convective gas-to-particle heat transfer at the top of the bed. Fig. 10 illustrates the time dependent fluctuations of particles within the fluidized state. It is noticeable that entrainment of the fluidized bed particles occurs above the temporal outlines. Upward movement above the jet zone and downward movement in the moving section is the main cause for these phenomena. The escalating surface temperature of particle restraints the heat exchange rate of gas-to-particle. At the fluid inlet point, a greater heat flux was noticed from bed to wall that also caused energy loss.

Many researchers discussed about the reports on CFD simulation of individual particles and their interactions in the system and

![Fig. 10. Instantaneous particle time line temperature distribution in a fluidized regime at minimum fluidization velocity 1.6 ms⁻¹. Reproduced with permission from Elsevier [219].](image-url)
the few models to describe overall behavior of the reactor [241]. Dehnavi et al. [242] investigated the hydrodynamics and heat transfer of the fluidized bed of polyethylene particles based on the Eulerian–Eulerian approach. Their findings proved that the Eulerian–Eulerian model is good fitting for scale up of industrial fluidized bed reactors for polyethylene production.

Various commercial softwares have been suggested by researchers for CFD simulation of heat transfer in a bed of polylefin particles. The calculation domain provided by ANSYS FLUENT is divided into a finite number of non-overlapping control volumes. The main grid points, positioned in the center of each control volume, consist of certain significant scalars, like pressure, volume fraction, density, and granular temperature, while velocity components are stored at the cell surfaces. A simple discretization for governing equations can be carried out with the help of a staggered grid to ease numerical instabilities. Integration of conservation equations are carried out in time and space. The integration is executed by applying the first order upwind differencing in space and complete implicit techniques in time. For solving the discretized equations, a specialized phase coupled algorithm, called PC-SIMPLE (Phase-Coupled Semi-Implicit Method for Pressure-Linked Equations) was used.

Drag force is one of the dominant hydrodynamic parameters in heat transfer analysis of olefin polymerization reactors. Due to the strength of the drag force, the two-phase partial elimination algorithm (PEA) was simplified for the gas–solid flow and was used to decouple the drag forces. The interphase slip algorithm (IPSA) was applied for ensuring the coupling between velocity and the continuity equation. The feed gas/gases (ethylene/propylene) were considered as the continuous phase. It was shown that particle shape in the case of inter-particle heat transfer is significant. The dispersed phase surrounding spherical particles, whose average diameter is presumed to be uniform and constant, showed comparatively linear changes of heat transfer fluctuations [243,244]. Researchers [56,245] investigated heat transfer characteristics of powders with diverse properties in gas–solid fluidization by means of the combined CFD-DEM approach incorporated with a heat transfer model. They extended the model of Zhou et al. [246] by applying a cohesive force model.

In order to apply the heat transfer equation, most researchers commonly have considered three modes: conduction between the wall and particles, convection between fluid and particles and radiation between particles and their local surrounding environment. For instance, according to the heat balance, the governing equation for particle numbered as \( i \) can be written as [246]:

\[
M_p C_p \frac{dT}{dt} = \sum_j q_{i,j} + q_{i,f} + q_{i,rad} + q_{i,wall}
\]  

(42)

This is widely known as the lumped formulation in which thermal resistances inside the particle are neglected. Equations required for calculating the heat fluxes are listed in Table 4.

Inter particle and amid fluid heat transfer elaborately can be portrayed by the CFD approach with combination of the DEM. Fig. 11 shows the evolution of temperature of a fluidized bed at various operating conditions. It can be seen in this figure that temperature of the bed increases as the hot gas flows upward. At the initial stage of heating, no considerable transform of bed structure is detected when \( u_f < u_{memb} \) (Fig. 11a). When \( u_{memb} < u_f < u_{memb} \), the bed is transformed from a fixed bed to a static expanded bed (Fig. 11b). A small change can be noticed in the expanded bed frame-up during the heating process. Alteration of gas properties, which depend on local temperature and forces acting on particles, is the cause of this change. Particles move faster in the fluidized bed when \( u_f > u_{memb} \) and rapid and homogeneous heating can be noticed (Fig. 11c). Consequently, rapid heat transfer occurs between fluid and particles, thus, the bed temperature increases rapidly.

### 4. Electrostatic modeling of polymerization

Regular collision between particles is frequent in fluidization. Therefore, generating electrostatic charge is unavoidable in fluidized bed of nonconducting materials. In the olefin polymerization process, finding particles sticking to the wall, also recognized as wall sheeting, is very common. The wall sheeting also causes formation of large aggregated particles and alteration of the hydrodynamics [247]. Solids circulation and fines entrainment are also affected by electrostatics. Electric charge in polymer particles is produced by particle–particle and particle–wall contacts as well as gas–solid friction. The polymerization reaction is exothermic and wall sheeting causes a decrease in the heat dissipation. As a result, solids attached to the wall become molten and form sheets. Consequently, electrostatic charge minimization in industrial scale fluidized bed reactors is required for which injection of antistatic chemical agents to fluidized beds can be suggested [248,249]. However, controlling the dose of the antistatic agent is vital since an excessive dose can affect the catalyst activity. It has been reported that the charge dissipation occurs due to increasing the relative humidity in the fluidizing system. Addition of fine particles to large dielectric particles can neutralize the electric charge of the system [250].
It has been proven that the fines particles are largely positively charged, whereas large particles and the system wall are mostly negative in nature [251]. As a result, fine particles adhere to the wall due to their positive charge. Griffin et al. [251] and Sowinski et al. [252] conducted experiments in fluidized beds packed with polyethylene particles and measured charges of particles by the Faraday cup. Some researchers found that certain the electrostatic charge in a fluidized bed may increase by increasing the static bed height and the gas velocity since solids motion and rate of solids collision are affected by these two parameters. In a fluidized bed of polymer, the electrostatic charge increases as the temperature is increased which directs particle for agglomeration [253,254]. As agglomerate formation is a cause of extra overhead cost in polymer production, it is essential to recognize the charge arrangement, dissipation progression and entrainment to manage electrostatic effects. Numerous research projects have been conducted form industrial and academic point of view on the effect of electrostatic forces in fluidized beds, especially in fluidized polymerization reactors. Significant amount of entrainment was observed in the neutral bed while in a fluidized bed of fine polymer, elutriation was decreases in gas phase polyethylene production. Adhesion of fine particles to larger particles forms a polymer layer on the reactor wall due to slow entrainment [255]. Failure to control electrostatic charges may also cause wall fouling in fluidized bed polymer reactor. Wall fouling may take place just above the bed surface on the reactor wall which is caused by induction charging and deposits [256]. Desired fluidization achieved by boosting the scale of electrification with the rise of system pressure and temperature [257]. The scheme of the charging mechanism and transport is shown in Fig. 12.

Desired fluidization state can be achieved by boosting the scale of electrification with the rise of system pressure and temperature [239]. From the above discussion, it is clear that the modeling of electrostatics in gas–solid fluidized beds, particularly in the polymerization process, is extremely important. Therefore, some researchers have focused on incorporating electrostatic phenomena in modeling of gas–solid fluidized beds by either Eulerian–Lagrangian or Eulerian–Eulerian approach which are especially suitable for fluidized bed catalytic polymerization reactor. Al-Adel et al. [258] studied gas–particle flow by fixing the charge for the entire particles and neglecting hydrodynamic segregation in the riser fluidized bed. They carried out two fluid modeling and simulations to explain the effect of electric field on size and shape of bubbles considered fixed charge on particles. The electrostatic model combined with the multi-fluid CFD code for studying the polydispersity by computing electric field at each grid point and time step was proposed by Rokkam et al. [7] where the QMOM was applied for relating it to the distribution of polymer particle size. The particle charge is a function of its size and is considered as an input to the electrostatic model whereas charge dissipation and charge generation are not usually considered for this type of CFD modeling [259].

Lim et al. [260] numerically studied pneumatic transport of granular materials through inclined and vertical pipes in the presence of an electrostatic field using a coupled DEM-CFD technique and a simple electrostatic field model. They showed that in the presence of a mild electrostatic field, reversed flow of particles can be found in the dense region close to the bottom wall of the inclined conveying pipe and forward flow in a more dilute region in the region above. At sufficiently strong electrostatic field, complete backflow of solids in the inclined pipe may occur and applying a higher inlet gas velocity is necessary to maintain a net positive flow along the pipe. Hassani et al. [210] added inter-particle electrostatic forces among charged particles and between charged particles and the wall to their 3D DEM-CFD code. They investigated effects of electrostatic forces on hydrodynamics of fluidization in terms of bubble behavior, probability distribution of porosity, solids diffusivity and solids circulation in beds filled with mono-charged and bipolar-charged particles. They explored the effect of existence of mono-charged particles on bubble properties by comparing fluidized bed with and without charged particles. Their results are shown in Fig. 13 which demonstrates that by increasing the charge of particles, a significant change in the bed hydrodynamics should be expected. Bubbles become smaller and the sharp interface between emulsion and bubble phases vanishes when charge of particles increases from 0 to 30 pC due to the effect of repulsive forces between charged particles in the emulsion phase.

Prediction of hot spots, chemical reactor modeling, polymer particle size distribution and variation of reactor temperature have also been carried out by the Eulerian–Eulerian approach combined with the QMOM [261]. Multiphase CFD model, based on the Eulerian–Eulerian approach, can be used for describing segregation of polymer particles caused by charge and/or size. ANSYS FLUENT 6.3 provides options for electrostatic modeling and verification. A set of equations should be introduced for describing of electrostatic effects in the CFD study of fluidized bed polymerization reactors which can be solved by the user defined scalar (UDS) in ANSYS FLUENT 6.3 and onward versions. The UDS for a multiphase system in ANSYS FLUENT is in the form [7]:

$$\frac{\partial \left( \varepsilon_g \rho_g \varphi \right)}{\partial t} + \nabla \cdot \left( \varepsilon_g \rho_g \mu_g \varphi - \varepsilon_g \Gamma_g \nabla \varphi \right) = S_g$$

(43)

This Poisson equation is coupled with the multi-fluid CFD model through the volume fractions of the gas and solid phases, thus, must be solved at every time step during the simulation. Gauss’s law was used to evaluating the force acting on a charged particle in the gas–solid flow. This law in the differential form is:

$$\nabla \cdot D = \rho$$

(44)

The relationship between the electric displacement and the electric field is:

$$D_t = \varepsilon_0E + P$$

(45)
The following constitutive relation was used to relate the induced polarization and electric field for an isotropic medium:

\[ P = \varepsilon_0 \chi_e E \]  

(46)

where \( \chi_e \) is the electric susceptibility of the medium. The value of \( 1 + \chi_e \) is the relative permittivity which can be measured and its value can be found in the literature [7]. The electric field is related to the charge density as follows:

\[ \nabla \cdot \varepsilon_m \varepsilon_0 E = \rho \]  

(47)

The relative permittivity \( \varepsilon_m \) for a gas–solid mixture can be obtained from the Bruggeman equation:

\[ \varepsilon_g = \left( \frac{\varepsilon_g - \varepsilon_m}{\varepsilon_g - \varepsilon_s} \right) \left( \frac{\varepsilon_g}{\varepsilon_m} \right)^{1/3} \]  

(48)

Finding out the location of the density electrostatic forces in the reaction system is very important. The electric field in radial and axial directions in a reactor is shown in Fig. 14. Highly dense electric field can be founded close to the wall and near the distributor plate. The electric potential gradient seems to be greater in the radial direction compared than in the axial direction. As mentioned earlier, fine particles are attracted toward walls of the reactor by the electrostatic forces. It is clear in Fig. 14 that the strongest electric field effect is located in the axial direction close to the distributor plate.

Fouling of the reactor wall due to electrostatic charges was analyzed through CFD modeling in the industrial scale by Sowinski et al. [262]. They argued that smaller particles create more wall fouling as they possess higher charge. Particle sizes from 600 to 710 \( \mu \)m show an affinity to stick to the column wall. At high gas velocity, there is a tendency for particles to either adhere to the column wall or to be dislodged with the tapping of the column and remain within the dropped particles by the influence of the quantity of generated electrostatic charge inside the fluidized bed.

Since interaction of particles is highly influenced by the electrostatics and the hydrodynamics is directly related to the particle interaction, it is important to figure out how to control the...
electrostatic potential distribution in a gas–solid fluidized bed [263–265]. The electrostatic effect makes the particles to form coherent structures and reminds one of the continuous behavior of the liquid. Fig. 15 shows the electrostatic effect on the particles in a quasi-2D fluidized bed. The degree of electrostatic effect can be clearly recognized in this figure, where the electrostatic effect can be clearly observed in the measurement, the particles form coherent structures and exhibits liquid like behavior [266]. Zhou et al. [217] also found different flow patterns inside the fluidized bed when considering electrostatic field distribution where tuning of gas velocity for individual zone and adjustment of gas bubbling and particle motion usually is reformed.

5. Modeling of agglomeration in fluidized bed reactors

Occurrence of agglomeration is one of the most important technical difficulties in industrial fluidized polymerization reactors. Among different adhesive forces (including liquid bridging force, van der Waals force and solid bridging force), agglomeration of polymer particles in fluidized bed reactors is usually caused by solid bridge force at high temperatures. Therefore, a sufficient knowledge of agglomeration and related phenomena, such as segregation, is vital for studying fluidized beds reactors. Experiments in these systems are tedious and expensive while numerical simulation provides a powerful tool for investigating the agglomeration phenomenon. A variety of modeling tools, such as population balance in the Eulerian framework and DEM in the Lagrangian framework, have been used to predict the dynamic evolution of particle size distribution in fluidized bed reactors. Population balance was utilized to simulate the particle size distribution by many researches [86,267–273]. The DEM was addressed in a number of previous studies to simulate the agglomeration phenomenon. Mikami et al. [274] developed a model for wet powder fluidization. To take into account the liquid bridge force between particles, a regression expression for the liquid bridge force was developed as a function of dimensionless liquid bridge volume and the separation distance based on numerical solutions of the Laplace–Young equation. Fluidization behavior of wet particles is completely different from that of dry particles and the minimum fluidization velocity, the bed voidage and pressure fluctuations in a wet fluidized bed are higher than those in a dry fluidized bed. Kuwagi et al. [275] developed a two-dimensional DEM to study the mechanism of fine particles agglomeration in which van der Waals interaction was taken into account as the cohesive force. They showed that agglomerates are formed in the bubble wake region while they break in the upper region of bubbles. Wet granulation processes were conducted in a rotating drum with the DEM approach by Mishra et al. [276]. By applying this technique, steady state size distribution of agglomerates was obtained. Groger et al. [277] performed a cohesive DEM to investigate the internal tensile strength and shear strength. Inter-particle cohesion was taken into account by modeling the liquid bridge. Their results showed that the surface roughness has a great influence on the stresses in wet particle systems.

A mechanistic study of de-fluidization based on the DEM-CFD simulation was conducted by Wang and Rhodes [278]. They applied an artificial cohesive force between particles and investigated effect of a wide range of inter-particle forces as well as mobility of individual particles on the fluidization condition of the bed. They found that transition from free-bubbling to de-fluidization state by increasing the inter particle force is gradual and de-fluidization occurs more gradually at higher excess velocities. A mathematical model based on the DEM was developed by Limtrakul et al. [279] to simulate the hydrodynamics of a vibrated fluidized bed. Effects of vibration, particle type, amplitude and frequency of vibration and superficial gas velocity on improvement of fluidization quality were studied in their work. Their results showed that the fluidization state can be observed by enough total forces of vibration and fluid provided to the particles. Yang et al. [280] presented a numerical study based on the DEM in which the agglomeration of fine particles was considered with van der Waals attraction. Agglomerate structure, packing density, coordination number and tensile strength were analyzed with particular reference to the effect of particle size associated with the van der Waals attraction. Their results showed that the spherically formed agglomerates were not homogenous, but had the packing density and coordination number decaying exponentially with the agglomerate radius. Li et al. [281] reviewed recent advancement of the DEM technique in adhesive particulate flows and compared the DEM approach with other similar Lagrangian methods.

Although many reports exist on simulating the agglomerating phenomenon in fluidized beds by evaluating the cohesive force between particles through liquid bridging and interaction of particles with van der Waals force, a few reports exists on simulation of the whole mechanism of agglomeration in fluidized beds at high temperature. Kuwagi et al. [275] developed a model for metallic solid bridging by the surface diffusion mechanism, including the effect of surface roughness, by the DEM-CFD technique in a fluidized bed with uniform temperature distribution. They described the agglomeration process of particles and observed a decrease in the pressure fluctuations. Mansourpour et al. [282] proposed a model to improve the simulation of agglomeration process at high temperature compared to previous models. They used a DEM-CFD approach in which agglomerates were tracked as real objects and their translational and rotational motions were calculated according to the multi-sphere method. In simulations of Mansourpour et al. [283], particles stick together and form agglomerates with an irregular shape, instead of clusters of primary particles as defined in previous researches. Their model included the energy balance equations for both gas and particles in
order to consider the effect of temperature distribution on the agglomeration phenomenon. The cohesive force employed by Mansourpour et al. [282, 283] was based on a time dependent model, developed for solid bridging by the viscous flow. The surface of the particle becomes sticky when its temperature increases to a value greater than the softening point. Colliding particles with sticky surfaces join together and form larger agglomerates by forming permanent solid bridges. Applying these improvements resulted in gradually de-fluidization of the bed in simulations of Mansourpour et al. [283].

Fig. 16 illustrates snapshots of agglomerate formation in a fluidized bed of polyethylene particles [282]. The agglomerates are colored according to the number of particles in agglomerates. This figure demonstrates gradual defluidization of the bed by the progress of agglomeration of particles. At early stages of fluidization ($t = 1$ s), agglomerates have not been formed and the bed is completely fluidized. Formation of bubbles at the distributor, their rise and grow through the bed and their burst at the bed surface can be seen in this figure. After elapsing 6 s of fluidization, small agglomerates (containing two or three particles) are formed in the dense regions as well as the vicinity of the distributor. Increasing the number of agglomerates in the bed boosts the possibility of particle-agglomerate and agglomerate-agglomerate contacts. When these agglomerates grow in size, their movement becomes more restricted. Consequently, bed expansion and size if bubbles are reduced ($t = 20$ s). In this situation, the gas passing through the bed cannot exert enough drag force on the agglomerates to compensate their weight. On the other hand, large agglomerates hinder the movement of smaller species in the bed. Therefore, the majority of the gas injected to the bed passes through the channels formed by agglomerates. It can be seen in Fig. 16 that at ~50 s, massive agglomerates are accumulated at the bottom and a de-fluidized layer is formed on the distributor. Nevertheless, in this situation particles and agglomerates at a
higher level are still fluidized and the height at which bubbles are formed is shifted to the top of the de-fluidized layer. De-fluidization due to agglomeration occurs as a consequence of two different mechanisms: agglomeration and segregation. Formation of large agglomerates which have minimum fluidization velocities higher than the gas velocity leads to accumulation of a large fraction of agglomerates at the bottom of the bed. This is likely to be the cause of beginning of segregation with worsening of the fluidization quality and eventually occurrence of de-fluidized zones at the bottom of the bed. It is worth noting that the agglomeration is probably promoted by a reduction in momentum of particles which is a result of segregation. Moreover, segregation influences the hydrodynamics of the fluidized bed as it influences the bubble characteristics.

In order to gain more insight in the effects of segregation on the fluidization behavior, several numerical investigations based on the CFD concepts were conducted. Dahl and Hrenya [284] investigated segregation of particles with Gaussian and log-normal size distributions by the DEM technique. Annaland et al. [285] calculated the rate of particle segregation in a bi-disperse freely bubbling fluidized bed with both a novel multi-fluid model (MFM) based on the KTFG for multi-component mixtures and the DEM. The granular temperature of the segregating system, as calculated with the MFM, agrees reasonably well with the granular temperature found in the DEM simulation. Fan and Fox [286] integrated the direct QMOM into the multi-fluid model to represent the PSD with a finite number of nodes in MFIX. They compared their simulation results with results of Dahl and Hrenya [284] and showed that the multi-fluid model can capture occurrence of segregation along the bed height while this model cannot detect horizontal segregation. Tagami et al. [287] used CFD-DEM to investigate the fluidization behavior of binary and ternary mixtures. They indicated that momentum transfer is enhanced when the size ratio of particles is increased in polydisperse systems. It was also shown that a wide size distribution enhances bubble growth and rise velocity of bubbles through the bed. Norouzi et al. [178] conducted a numerical study for investigating size segregation of particles in the presence of fines in a bubbling gas–solid fluidized bed based on the DEM technique. They investigated the effect of adding fines at different concentrations and with various sizes and showed that segregation is enhanced by adding fine particles. Furthermore, reducing the size of fines initially enhances the final extent of segregation while further decrease in size of fines diminishes the segregation.

6. Summary

The incredible advancement in the computer hardware engineering, upshot in boosted memory with capability of high performance computing workstations, has facilitated solving equations of momentum, heat and mass transfer with a wide range of numerical methods. These progresses inspired the beginning of more practical numerical techniques resulting the arrangement of a sequence of CFD codes. Due to the well-built accomplishment achievement in single phase flow simulation, CFD is regarded as a significantly promising tool for modeling multiphase flow. Nevertheless, CFD is still being considered at the level of verification and validation for modeling multiphase flows for modeling multiphase flow systems such as fluidized beds and more progress concerning the flow dynamics and computational models are needed to make it a standard tool in designing large scale industrial reactors. The up to date issues in the CFD modeling and its applications in fluidized bed of olefin polymerization system design and various reaction parameters have been shown in this paper. The hydrodynamic behavior in fluidized beds was found to be non-linear and complex as well. It was shown that conventional mathematical modeling and hypothesis of these hydrodynamic are not convenient enough for pilot to large industrial-scale reactors. The cost effectiveness and prompt solution capability have made the CFD approach as the best choice option for researchers and industrial users. Therefore, CFD models seem to be properly fitted to scale up the full-scale reactor with detailed reaction mechanism. Availability of wide-ranging and multipurpose CFD commercial softwares has the proven track record to fulfill the requirements of giving details on complete fluidization factors. These are adequate to put up to any kind of analysis condition from prediction of fluid flow behavior, mixing effect, bubble phenomena, mass and momentum incident, inter-particle charging and so on to integrated reactor design and optimization. Among these softwares, ANSYS FLUENT has been most widely employed for simulating fluidized bed polymerization reactors, reaction mechanism and production optimization studies. Moreover, CFD simulation of a bubbling fluidized bed reactor has been carried out by several research groups who also included the chemical kinetics, bed dimensions and bubble formation confrontations into multiphase fluid dynamics. The axisymmetric nature of the reactor has given way to chaotic transient generation of bubble formation within certain time durations. Exothermic nature of the polymerization reaction causes heat transfer problems in particle–particle interactions and requires a full scale modeling approach. More detailed CFD investigations can provide results about the effect of gas temperature and particle size on gas–solid heat transfer and bed hydrodynamics. A more clear understanding of effect of electrostatic charge on polymeric systems through a numerical implementation can be carried out in ANSYS FLUENT.

CFD modeling is more feasible to obtain criteria for regulating the distribution of electrostatic potential by changing and observing its effect on the hydrodynamics of the gas–solid fluidized bed. Using porous media models for simulating the gas phase catalytic reaction through a multi-phase reacting system is common in mathematical modeling of such reactors. These models can be modified based on the scale and requirements of the simulation as well as the accuracy associated with their numerical implementation. It was also pointed out in this review that there is still a gap between experimental and CFD results in pilot and industrial scale systems. Experimental validations are extremely necessary to ensure that CFD simulations are more than just theoretical exercises. In the recent years, some studies have been carried both in the laboratory, closely resembling that in the industry. New technologies, such as particle image velocimetry, have also shown to provide valuable data for validating CFD predictions. Nevertheless, successful validation has been reported in many cases and even where there are discrepancies, deficiencies in the model or measurement technique were readily identifiable.

Acknowledgements

The authors are grateful to the University of Malaya and the Ministry of Higher Education of Malaysia (MOHE) for supporting this research project via the research grant UM.C/HIR/MOHE/ENG/25 which made possible for publishing of this paper.

References
