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Gas-phase Polyethylene Reactors – A Critical Review of Modelling Approaches

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1 Introduction

Polyethylene (PE) is the most common thermoplastic in the world, with current annual on-line capacity reaching over 100 million tonnes. Industrial processes for polyethylene (PE) production can be divided into different categories according to the phase in which the polymerization takes place: solution, slurry or gas-phase processes, with the latter two being more significant in terms of production volumes. While slurry phase processes are commercially important for high density polyethylene (HDPE), gas-phase processes were responsible for 40% of the total PE production in 2018, meaning that is the most widely used process. Due to their versatility, gas-phase processes can be used to make products with a full range of densities, from linear low density polyethylene (LLDPE) to high density polyethylene (HDPE) in the same reactor [1][2]. Up until recently, all PE plants operated fluidized bed reactors (FBR), since this was the only reactor configuration that allowed enough heat evacuation in order to achieve commercially pertinent rates of polymerization [1]–[3]. However, as of 2017 a new PE plant has been under construction with a new reactor configuration. This novel process, termed Hyperzone, is made of a FBR reactor followed by a multi-zone circulating reactor (MZCR) to make bimodal HDPE. In the MZCR, one can observe two distinct hydrodynamic zones. Thus, the growing polymer is kept in continuous circulation between “fast fluidization” and “packed bed” zones [4]. Nevertheless, virtually all other plants use FBRs for their gas phase polymerization, and so the focus of this review will be exclusively on this type of reactor.

A diagram of a typical FBR for PE production is shown in Figure 1. This scheme is based on the Unipol process, but other processes (such as Spherilene) are licensed worldwide [3].

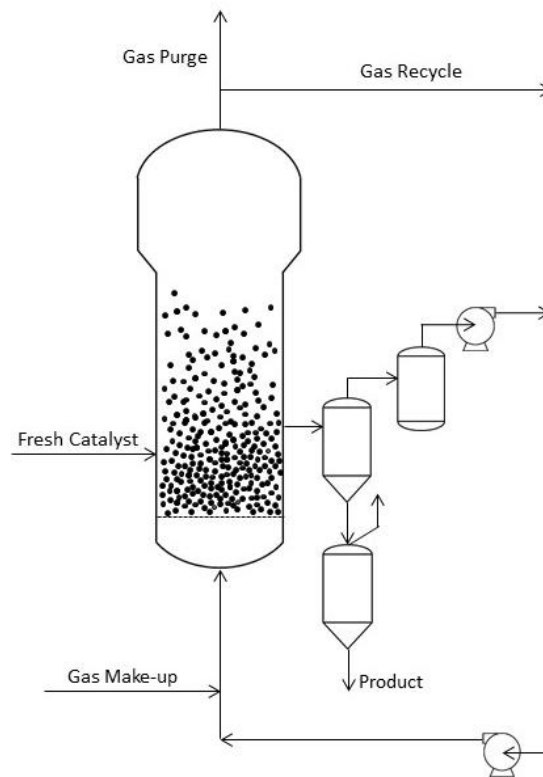


Figure 1. Scheme of typical fluidized bed reactor.

The reactor is essentially an empty cylinder with an expansion zone at the top (to reduce the gas velocity and help prevent any fine particles from flowing out of the reactor and into the recycle compressor), and a distributor plate at the bottom. Heterogeneous Ziegler-Natta or metallocene catalyst (or prepolymerized catalyst) particles are continually introduced into the reactor, ready to react with the fresh monomer(s) being fed at the bottom of the bed. Active species diffuse to the particle, through the pores, and then into and through polymer covering the active sites. The highly exothermic polymerization occurs at the active sites (see section 2.1). Continual accumulation of polymer causes the particles to grow from an original diameter on the order of 10-50 microns to a diameter of several hundred microns when they are removed through a product discharge valve. From there, they go into a series of degassing tanks to separate the unreacted monomers. The gaseous recycle stream is compressed, cooled and afterwards mixed with fresh monomers, hydrogen and eventually other compounds, then fed back into the reactor.

Over the years, advances in catalyst technology have made it possible to produce several kilograms of polymer per gram of supported catalyst. Heat transfer can be a challenge because as the space time yield of the bed improves due to faster polymerization, the quantity of heat that needs to be removed increases proportionally. The principal means of removing the heat generated by polymerization is convective heat transfer between solid particles and the gas phase. FBRs are the best option for maximizing heat transfer, as the gas flows through the bed at reasonably high speed (between 0.5 and 1 m/s), much higher than in stirred beds. Of course, convective heat transfer improves as the relative gas-particle velocities improve, but this is not a parameter that one can choose arbitrarily. If the velocity is too low, the bed will not be fluidized, but if the velocity is too high the particles will be blown out of the bed, which can cause problems downstream. Another option to relieve the reactor of excessive heat is to manipulate the inlet gas temperature, but this is also limited because one cannot have very large temperature gradients in the reactor either. Perhaps the most common way of improving the heat removal from the reactor is to alter the physical nature of the feed stream. Chemically inert compounds such as ethane or higher alkanes can be introduced into the reactor in the place of nitrogen to increase the heat capacity of the gas stream [1], [5], [6]. When these alkanes are added as uncondensed vapors, the reactor is working under what is called “super dry mode”.

Even more heat can be removed when these compounds are (partially) condensed in the feed stream. When this happens, the FBR is said to be operating in “condensed mode”. In this case the recycle stream is compressed, and then cooled by passing it through at least one external heat exchanger to a temperature below that of the dew point of the gas mixture. The resulting stream is then fed into the lower zone of the reactor in such a way that the liquid is sprayed into the reacting zone, and the droplets of liquid are vaporized by the heat of reaction [5]. Alkanes such as isomers of butane, pentane or hexane are most commonly used to this end. In the case of super dry mode, or condensed mode, the added inert alkanes can be referred to as induced condensing agents (ICA). Monomers such as 1-butene or 1-hexene can also be liquefied and contribute to energy evacuation as well. In normal condensed mode, it has been shown that the liquid droplets evaporate rapidly, and that the clear majority of the powder bed in a typical reactor contains only solid particles and a continuous gas phase [7], [8]. On the other hand, adding an ICA has a much more significant effect on the observed rate of polymerization that cannot be exclusively explained by better heat evacuation. It turns out that the well-known co-solubility effect implies

that the concentration of ethylene in the polymer amorphous phase is increased by the presence of a heavier hydrocarbons [9]–[13]. However, only very recently has this effect been taken into consideration in the development of processes models.

Given the importance of the gas-phase production of PE, significant efforts have been made to model this process over the years. As it has been discussed many times, modelling a complex chemical process such as this involves integrating models that describe physical and chemical phenomena that are occurring over numerous different length and time scales; from the active site on the supported catalyst surface all the way up to the complex flow patterns in a bubbling FBR. In order to better frame the problem, it is useful to implement a multiscale approach as shown schematically in Figure 2 [1], [14]–[16]. The three length scales we choose to define here are:

- microscale – Polymerization kinetics;
- mesoscale – Particle morphology, thermodynamics (including sorption and diffusion), intraparticle mass and heat transfer;
- macroscale – Mixing, overall mass and heat balances, particle population balances, residence time distribution.

In a multiscale approach, each phenomenon should be appropriately modelled at its specific level. The relevant information is then transmitted to the models at other scales.

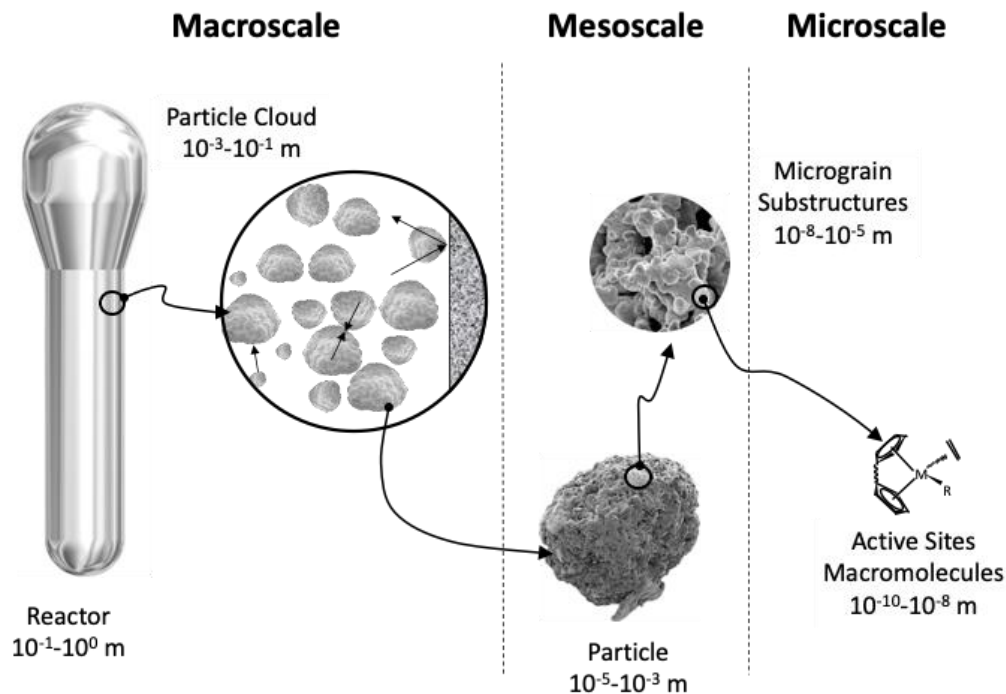


Figure 2. Possible different length scales to be considered for reactor modelling. © 2012 Wiley-VCH Verlag & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany. Reproduced with permission.

A few authors have already published reviews to guide us through the different modelling approaches in gas phase polyolefin polymerization. For instance Xie *et al.* [17], Kiparissides [18], and Hamielec and Soares [19] discussed the catalysts used and reaction kinetics, as well as the main mathematical models available at the time the articles were written. Xie *et al.* [17] and Kiparissides [18] focused on the reactor modelling, while Hamielec and Soares [19] concentrated on mathematical modelling of the polymerization kinetics and polymer properties. Nevertheless, all of these papers, either implicitly or explicitly involve the concept of multiscale models. Abbasi *et al.* [15] and Zhu *et al.* [16] explicitly invoked the need for multiscale models for gas phase olefin polymerization. While the latter group focused on polypropylene rather than PE and defined 5 scales rather than the 3 proposed above, they made it clear that regardless of the model one chose for the reactor scale, intraparticle gradients of heat and mass transfer will influence how the particles behave in the reactor. Sun *et al.* [20] looked more at mesoscale phenomena in FBRs, compared different types of Computational Fluid Dynamics (CFD) and Discrete Element Method (DEM) modelling approaches for PE and clearly demonstrated that mesoscale and

macroscale phenomena are connected. Kaneko *et al.* [21] also used a DEM-based approach to demonstrate the interaction between macroscale mixing and mesoscale particle overheating. There are of course many other studies in the open literature that support this multiscale concept (either implicitly or explicitly), that might use different numerical approaches and assumptions, but they all show the fact that the more a model takes into account the interaction between phenomena occurring at different scales, the more information one can obtain from it. Of course, important questions to ask at this point include “how much information do we want from our model?”; and “which model should we choose?” The main purpose of this review is to attempt to answer this last question rather than to present an exhaustive review of all of the modelling papers in the literature. Furthermore, in order to move forward with future modelling studies, it is also important to identify what information is still lacking for us to be able to write and solve comprehensive, *a priori* models of ethylene polymerization in fluidized bed reactors. However, given the complexity of the interactions between the phenomena that occur at different length scales in the reactor, it is useful to quickly review the micro- and mesoscale models currently used for heterogeneously catalyzed ethylene polymerization.

2 Conclusions

For non-CFD models, 3 main approaches have been discussed and comparative studies show that they all have specific uses: one-phase, well-mixed models; two-phase constant bubble growth or variable bubble growth models with a single emulsion phase, and one or more bubble phases; and fully compartmentalized models.

The one-phase, well-mixed approach is of mathematical simplicity, and when coupled with a kinetic model, can be used to obtain basic results such as production rate, monomer conversion, and depending on the kinetic model, molecular weight and composition distributions. The biggest downsides of this model are the lack of rigor when describing the heat and mass transfer between gas and solid phases, the fact that it does not allow for any temperature or concentration gradients in the reactor, and the inability to describe phenomena such as bed segregation. These weaknesses can be overcome by fitting model parameters to data available for each specific case should they be available. While this procedure would result in strongly system-dependent parameter values, if such data is available, the one phase approach can be used for process

control purposes. Of course, if one relies on existing data to fine tune model parameters, the values thus obtained can mask certain effects, and this in turn can negatively affect the predictive capability of the model for different process conditions. In the absence of data for the fine tuning of model parameters, this approach can be used to understand global reactor behavior, and capture overall tendencies (*e.g.*, the impact of ICA on productivity) reasonably well. Furthermore, this reactor modeling approach can be adapted to include population balances, and it is easy to understand and solve.

The two-phase approach is divided into constant and variable bubble size models. The first is not physically accurate, and comparative studies show little to no improvement in terms of fitting reactor data, with respect to the well-mixed approach. The second allows one to impose a temperature gradient on the gas phase rising through the bed, but not on the emulsion phase. Thus, it is slightly more realistic, but nevertheless shows little difference in terms of predicting reactor behavior than the single-phase models. Furthermore, it is important to point out that the two-phase models depend extensively on the use of empirical or semi-empirical correlations for key reactor parameters, such as the bubble volume fraction, the bubble size, interphase mass and heat transfer coefficients, etc. It appears to be possible to fine tune such parameters if process data are available, but it should be reiterated that this makes a model very process-specific and limits its predictive capability.

Finally, in exchange for a certain level of complexity (and increased computational times) fully compartmentalized models offer the most effective non-CFD choice for describing the FBR at a certain level of detail. On one side, it is simple enough to easily account for the complex particle morphology, with all the relevant transport phenomena, as well as for distributed polymer properties, such as the particle size and the molecular weight or composition. On the other side, a few, selected fluidization experiments could be used to assess the reliability of the prediction in terms of reactor fluid dynamics, making the tool reliable and asking for very reasonable computational effort. Once again, one can include only emulsion compartments, or emulsion and bubble (or even emulsion, plus bubble, plus wake) phases. Including the bubbles once again requires heat and mass transfer correlations for interphase transfer phenomena, and choices to be made about bubble growth in the reactor. It appears to us that the best compromise is to use a fully compartmentalized emulsion-only model as this reduces reliance on a plethora of

parameters that are challenging to reliably estimate *a priori*, and allows one to capture variations of temperature, concentration and even number of phases in the reactor.

Finally, it should be mentioned that most studies found in the literature (until very recently) focus on dry-mode or dismiss co-solubility effects all together, which goes against what is practiced in the industry. This implies that all models that do not explicitly account for the complex involved thermodynamics will rely on kinetic parameters that mask or implicitly lump composition-dependent solubilities in polymer phase as well as variable diffusion coefficients. A model that lacks an accurate thermodynamic description has not only a limited predictive capability but also neglects phenomena that strongly influence reactor behavior and material properties.

As an alternative to conventional modelling efforts, CFD modeling for fluidized bed reactors represents an emerging tool, at least in the open scientific literature. The reason lies in the high level of detail provided by simulation outcomes. In principle, it is possible to characterize the velocity field in every point of the vessel with a frequent temporal sampling, providing information that is challenging or impossible to achieve solely with experimental activity.

Despite the increasing number of studies that appear in the literature, the application of CFD-based tools to the simulation of olefin FBR is still at its infancy.

First, although the availability of computational resources as well as efficient and robust algorithms is steadily increasing, comprehensive three-dimensional simulations of a whole industrial scale FBR are still currently out of reach. The unique example provided in this review required external high-performance parallel computing resources and should be considered a proof of concept rather than a routine approach. On top of that, only 25 seconds of physical time could be simulated, which are not enough for practical purposes. For this reason, most CFD simulations are carried out considering two dimensional geometries.

Second, for the sake of computational efficiency CFD simulations still require some simplifications concerning the description of the physical phenomena occurring in the reactor. Such simplifications must be carefully assessed through an experimental validation or with plant data. Along with the reactor geometry represented through a two-dimensional domain, solid phase is described as a continuum rather than a discrete phase (*i.e.*, by tracking each single particles), which would result in a prohibitive computational cost due to the amount of solid

present in the reactor. Moreover, empirical and semi-empirical correlations are still employed (*e.g.*, for drag coefficients) and the population balances for the calculation of solid PSD are solved with efficient but approximated algorithms based on the method of the moments. Therefore, CFD models still require some validation with experimental data, which is commonly performed through the comparison of pressure drops and/or bed height for semi-batch systems, where the gas can circulate but neither inlet nor outlet solid flow is present. To the best of our knowledge, comparisons involving experimental and predicted solid PSD as well as molecular weights are an exception rather than a common course of action.

A third aspect for the routine implementation of CFD-based tools is the availability of *ad hoc* expertise for this kind of modeling techniques.

Even though the knowledge of current limitations is an essential requirement for an aware use of CFD models, their application provides not only challenges but also new possibilities. The first one, although obvious, is the detailed description of the fluid dynamics, even when semibatch systems are accounted for. Contrary to the simplified fluid dynamic description implemented in one phase and in multiphase compartmentalized models, CFD simulations naturally consider solid recirculation and thus provide a better evaluation of segregation effects, as well as elutriation. Second, multiphase simulations intrinsically account for the mutual interactions between solid and gas phase in every position of the reactor, despite the required but assessed (and accepted) simplifications for the sake of computational efficiency. This implies that there is no need to evaluate *a priori* or through a trial-and-error approach the number of phases and the number of compartments to include into the model: the presence and the importance of gradients naturally arises from the simulation outcomes. Therefore, CFD simulations can be employed as a useful tool to guide in a rational way the choice of a compartmentalized model.

Given the proven potential of CFD and the continuous advancements concerning both hardware and software, an increased implementation of CFD-based tools, an ever-growing descriptive capability for FBR simulations and a careful experimental validation that involves also the solid phase are envisaged in the near future. Currently, a combination of both types of models, compartmentalized including all kinetic and transport details, combined with selected CFD simulation, represents a very effective approach both in scientific and industrial applications.

Acknowledgments

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