Refereed Proceedings

The 12th International Conference on Fluidization - New Horizons in Fluidization Engineering

Engineering Conferences International *Year* 2007

Role of Intrinsic Kinetics and Catalyst Particle Size Distribution in CFD Simulations of Polymerization Reactors

Rong Fan* Rodney O. Fox†
Michael E. Muhle‡

*Iowa State University, fanrong99@yahoo.com
†Iowa State University, rofox@iastate.edu
‡Univation Technologies, michael.e.muhle@exxonmobil.com

ROLE OF INTRINSIC KINETICS AND CATALYST PARTICLE SIZE DISTRIBUTION IN CFD SIMULATIONS OF POLYMERIZATION REACTORS

Rong Fan*, Rodney O. Fox * and Michael E. Muhle**
*Chemical and Biological Engineering Dept. 2114 Sweeney Hall,
Iowa State University, Ames, IA, 50011
**Univation Technologies, 5200 Bayway Drive, Baytown, TX 77520

ABSTRACT

Fluidized-bed reactors are widely used in the production of polyethylene. In this work, the quadrature method of moments (QMOM), a chemical reaction engineering (CRE) model, and computational fluid dynamics (CFD) are combined to investigate the role of intrinsic kinetics and the catalyst particle size distribution (PSD) in a gas-phase fluidized-bed reactor. The catalyst PSD is represented by a few nodes using the QMOM and an intrinsic rate model based on the age of particles is used to solve the evolution of particle temperature, particle size, and catalyst sites with age. Assuming the particle age distribution is well mixed, the moments of the polymer PSD are calculated and compared with experimental data. It was found that the CRE model predicts slightly larger particles as compared to the experimental data. However, the general shape of the PSD is well represented. The overall predictions were quite good, indicating that combining the reaction kinetics with QMOM is a promising method for predicting the polymer PSD in a gas-phase polymerization reactor. It was also found that the initial particle temperature rise is strongly correlated to the initial catalyst PSD: the larger the catalyst particle size, the larger the polymer particle size and the higher the peak temperature in the solid phase. Hence it is very crucial to use QMOM to represent the larger particles in the upper tail of the catalyst PSD. Segregation and hot spots in the fluidized bed are investigated using CFD simulations.

INTRODUCTION

Commercial gas-phase reactors are critically dependent upon good mixing for heat removal and prevention of polymer agglomerates. It has been found that to a large extent, good mixing is related to the polymer particle size and the distribution of these particle sizes in the bed [1]. The polymer particle size distribution (PSD) is governed by the particle size of the catalyst feed and the reaction kinetics. The catalyst particles grow by a factor of 15-20 at a rate determined by the intrinsic kinetics of the polymerization. This time-dependent process generates the resulting polymer PSD in the fluidized-bed reactor. The polymer represents as much as 99.99% of the total bed mass. Most previous CFD models have represented the catalyst particles by a single particle size. However the large particles produced by the polymerization reaction can not be predicted using such an assumption and more importantly the assumption underestimates particle overheating in the reactor [2, 3].

In this work, QMOM is used to represent the catalyst PSD by a summation of Dirac delta functions. The PSD is approximated by a number of specific particle size classes, and tracked by the development of the moments. According to the previous work [4, 5], only a few (3 or 4) size classes are needed to represent the PSD accurately, so this method has a significant computational advantage over conventional methods. The QMOM is combined with a chemical reaction engineering (CRE) model to study the effect of the catalyst PSD on the overheating and final PSD of the polymer. A flow chart of the modeling process is shown in Fig. 1. First, moments of the catalyst PSD are calculated from a known experimental PSD $f(L)$. In order to consider the effect of the catalyst PSD, two or three nodes can be used to represent the PSD using QMOM, and each node has its own diameter and weight. The CRE model is applied to each node by assuming that the initial particle size L_{s0} has the diameter of the node.

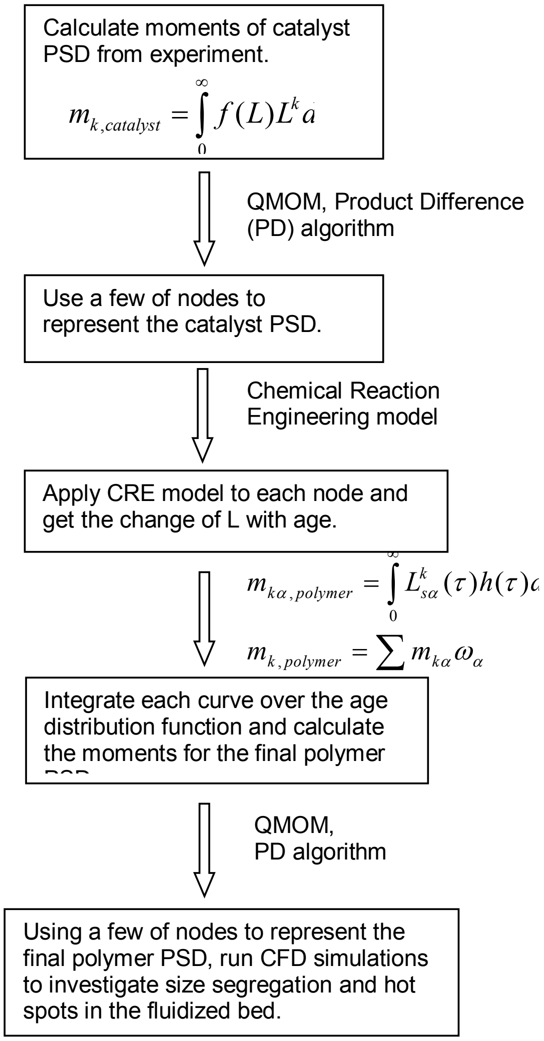

Fig. 1 Flow chart for combining QMOM with the CRE model to initialize the CFD simulations for investigating the effect of catalyst PSD on particle overheating and the polymer PSD.

From the CRE model, the evolution of particle diameter with age for each node is obtained. According to the definition of the solids age distribution in a well-stirred reactor, the moments of the polymer PSD for each node can be obtained by integrating each curve over the age distribution function. If there is no aggregation or breakage, the number of particles will not change so the weight for each node will be constant. Thus the moments of the polymer PSD can be calculated as a sum of the weighted moments of each node. More information on this method and results will be presented in the following. Once the moments of the polymer PSD are known, two or three nodes can be used to represent the PSD of the polymer using QMOM in the computational fluid dynamics (CFD) model. Moreover the CRE model is able to predict the particle temperature associated with each of the nodes. Thus CFD simulations can be conducted to investigate size segregation and hot spots that occur in the fluidized-bed reactor.

CRE MODEL

The solid phase residence time for a polyethylene polymerization reactor is on the order of hours, and the time scales of the fluid dynamics in a fluidized bed are on the order of seconds. In order to separate the time scales of the fluid dynamics and reactor residence time, a CRE model based on the age of particles was developed. The CFD simulations are initialized with a polymer PSD and particle temperature found from the CRE model. During the CFD simulation (on the order of seconds), because the polymerization reaction is relatively slow, we can assume that the particles will not grow significantly and that the particle temperatures will not change due to reaction, the ubiquitous pseudo steady-state assumption.

The equations for the CRE model are as follows [6]:

$$\rho_s \frac{d\varepsilon_s}{d\tau} = M_{gs} M_w \qquad \text{External mass transfer}$$

$$\frac{d}{d\tau}(\varepsilon_s [c]) = -\varepsilon_s k_i [c] \qquad \text{Potential active site balance}$$

$$\frac{d}{d\tau}(\varepsilon_s [c^*]) = \varepsilon_s k_i [c] - \varepsilon_s k_d [c^*] \qquad \text{Active site mass balance}$$

$$\frac{d}{d\tau}(\varepsilon_s [c^0]) = \varepsilon_s k_d [c^*] \qquad \text{Deactivated site mass balance}$$

$$\varepsilon_s \rho_s C_{ps} \frac{dT_s}{d\tau} = H_{gs} + \Delta H_{rs} \qquad \text{Solid phase heat balance}$$

$$\rho_s \frac{d}{d\tau}(\varepsilon_s X_{sM}) = M_{gs} M_w - \eta \varepsilon_s k_p \rho_s X_{sM} [c^*] \qquad \text{Solid phase mass transfer}$$

The mass-transfer and heat-transfer terms M_{gs} and H_{gs} are given by $M_{gs} = \varepsilon_s k_c a_v (c_g - c_M) M_w$ and $H_{gs} = -\varepsilon_s h_f a_v (T_s - T_g)$. τ is the residence time (or age) of a particle in the reaction. In the absence of aggregation and breakage, the local solid void fraction is related to the particle size by a constant: $\varepsilon_s = c L_s^3$. The parameters used in the CRE model are listed in Table 1.

Table 1: Gas and Solid properties used in the CRE model.

Gas properties	
Gas Pressure P_g, (bar)	10~30
Gas Temperature T_g, (°K)	300~400

Particle properties	
Particle Density ρ_s, (g/cc)	0.843
Catalyst Heat Capacity C_{ps}, (cal/g K)	0.168
Ave. Catalyst Particle Size ($\mu\mathrm{m}$)	10~100
Ave. Polymer Particle Size ($\mu\mathrm{m}$)	1000
Monomer Bulk Diffusivity D_b, (cm^2/s)	$2\sim6\times10^{-3}$
Monomer Effective Diffusivity D_{eA}, (cm^2/s)	$1\sim5\times10^{-4}$
Thermal Conductivity of Particle λ_f, (cal/cm s °K)	$3\sim7\times10^{-5}$
Heat of Polymerization - ΔH_r, (cal/mol)	25000

The CRE model is used to fit the experimental data and obtain the kinetic rate parameters. A set of experiments was conducted around a center point for different feed flow ratios of comonomer/monomer and hydrogen/monomer in an industrial lab reactor. Generally speaking, a two-site model fit the curves with a high degree of accuracy. It was found that the first site had a fast decay rate, and the second site had a much slower rate of decay. Based on this, the rate parameters can be used to model the single particle temperature rise and to investigate hot spots in the fluidized-bed reactor using CFD simulations.

RESULTS AND DISCUSSION

Effect of Catalyst PSD on Overheating and Polymer PSD

The catalyst PSD from experimental data is plotted in dimensionless form in Fig 2. The PSD is close to log-normal but contains a small "bump" at the low end. The average particle size is in the range 10-100 μm and will be denoted by d_{ave}.The normalized moments of the catalyst PSD can be calculated from the definition:

$$m_{k,catalyst} = \int_0^{+\infty} f(L)L^k dL \qquad (1)$$

Using QMOM, two or three nodes can be used to represent the catalyst PSD. If two nodes are used, one is located at 0.91 d_{ave} and the second at 1.71 d_{ave}. The weight percentage of these nodes are 63.87% and 36.13%. If three nodes are used to represent the PSD, the three nodes are 0.69 d_{ave}, 1.25 d_{ave} and 2.03 d_{ave}. The percentage of the weight for each node is 24.57 %, 63.81% and 11.62%.

The kinetic data for a case with significant particle overheating are used in the following discussions and only the results for three nodes are shown. The evolution of the PSD and temperature increase with age is shown in Fig. 3 and Fig. 4 respectively. The moments of this distribution can be calculated as

$$m_{k,polymer} = \omega_1 m_{k1} + \omega_2 m_{k2} + \omega_3 m_{k3} \qquad (2)$$

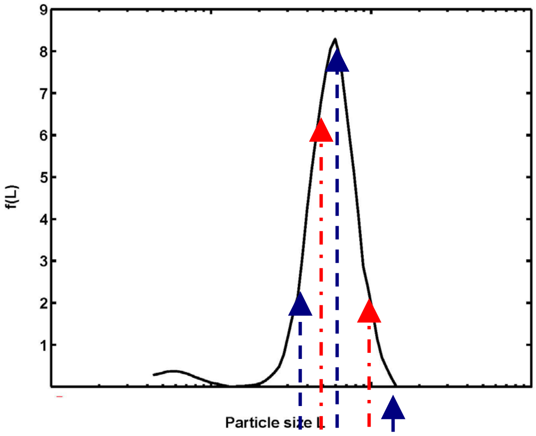

Fig. 2 Catalyst particle size distribution. (Red: two nodes; Blue: three nodes)

By integrating over the three curves in Fig. 3 weighted by the age distribution, the normalized moments of the predicted polymer PSD can be obtained.

The standard deviation (σ) of the polymer PSD and the width represented by the coefficient of variation (*c.v*) of the distribution can be calculated from those moments and are given by:

$$\sigma = \sqrt{(m_2 - m_1^2)} = 0.04497 \text{ cm}, \quad c.v = \sigma/\overline{L} = \sqrt{(m_2 - m_1^2)}/m_1 = 0.34472.$$

Presumably, using more nodes should yield higher accuracy by giving a better representation of the log-normal distribution of the catalyst PSD. We have found that the highest temperature using three nodes is much higher than the highest temperature using two nodes. Hence, representation of the underlying distribution with one or two nodes underestimates the overheating problem in the bed.

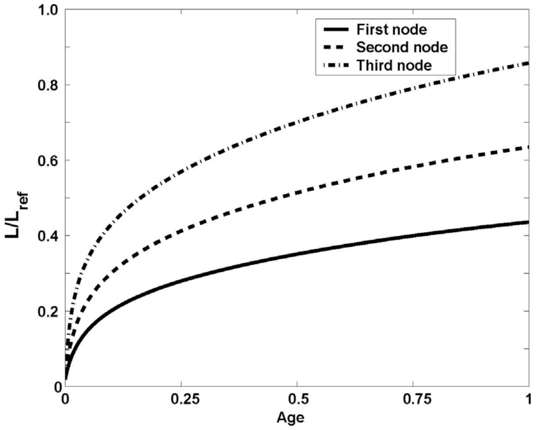

Fig. 3 Evolution of particle diameter with age.

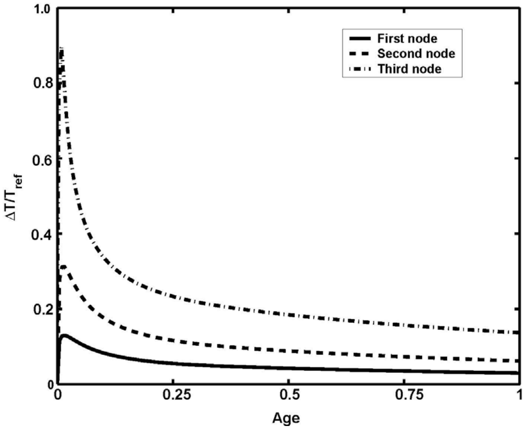

Fig. 4 Evolution of particle temperature with age.

The moments predicted from the CRE model are compared with the PSD data obtained from a Malvern Mastersizer laser-based particle size analyzer. The probability plots for the catalyst PSD and the polymer PSD are shown in Fig. 5.

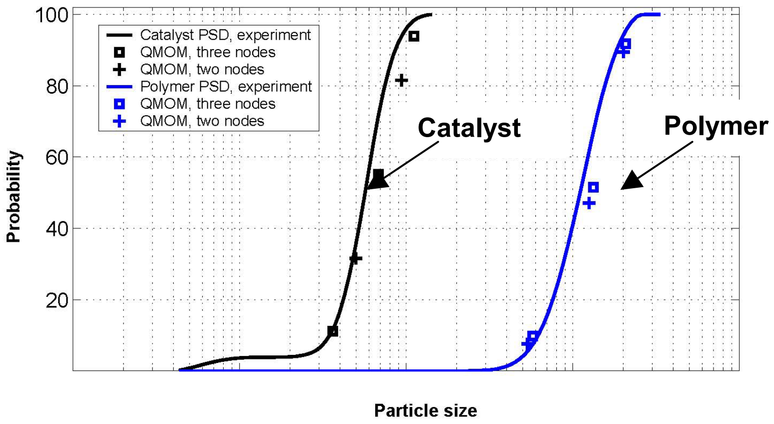

Fig. 5 Comparison of experimental PSD of catalyst and polymer with predicted PSD.

The cumulative percents estimated from QMOM using two or three nodes are also shown in Fig. 5. The overall predictions agreed well with experimental data, but the simulations have a higher standard deviation and larger width. This difference may be due to the assumption that the particles are well mixed (i.e., no segregation due to size), or how the experimental PSD sample was obtained (i.e., at the outlet located lower down in the bed). The model predicts slightly larger particles as compared to the experimental data. The results demonstrate that the CRE model in combination with QMOM is a promising method for predicting the polymer PSD. The moments calculated from the catalyst PSD (either using 2 or 3 nodes) are very similar. However, the use of three nodes to represent the catalyst PSD results in a higher temperature increase for the larger node. The temperature profile in the reactor is affected by the catalyst PSD. The larger the catalyst size, the larger the polymer particle and the higher the peak temperature increase in the solid phase. Also the breadth of catalyst PSD is important, since when the dispersion increases, the nodes are more widely distributed; the largest node has a higher probability of overheating. Thus, in order to investigate the hot spots in the reactor, it is very crucial to represent the upper tail of the catalyst PSD.

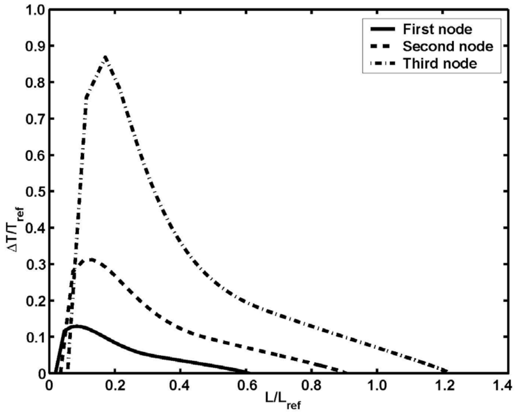

Fig. 6 Evolution of particle temperature with particle size.

Effect of Chemical Kinetics on Overheating

Combining the CRE model and QMOM, it is possible to study the effect of chemical kinetics on the temperature rise of a growing polymer particle. The evolution of particle temperature rise with particle size using three nodes is plotted in Fig 6. The relative temperature rise is around 0.9 for the largest node.

Simulation of Particle Segregation and Hot Spots with CFD

After successfully predicting the polymer PSD, the moments are known and, using QMOM, the PSD of the polymer particles can be represented by two or three nodes in the CFD code and be utilized to investigate segregation and hot spots. Using QMOM, three nodes can be used to represent the polymer PSD. For each node, a maximum temperature is associated with the particle diameter using the curve for each node in Fig. 6. A CFD simulation of a pilot-scale fluidized-bed reactor was run with these three nodes, and the average particle size along the bed height has been calculated. Not much segregation was observed at the bottom of the reactor, and the average particle size at the bottom was only about 1.1 times of the average size for the whole reactor. However, more size segregation was observed in the expansion and dome area. The average particle size at the top of the fluidized bed was only 50%-60% of the average particle size. The numbers of particles for each size are plotted in Fig. 7. From the graph, it is clear that small particles are over represented in the expansion area. Although the number of small particles per unit volume is very small (less than 50), small particles are likely to have high temperatures and thus hot spots are more likely to be observed. The particle temperature rise profile for the CFD simulation is shown in Fig. 8 where the average solid temperature T_s is defined by

$$T_s = \frac{T_{s1}\omega_1 + T_{s2}\omega_2 + T_{s3}\omega_3}{\omega_1 + \omega_2 + \omega_3}. \qquad (3)$$

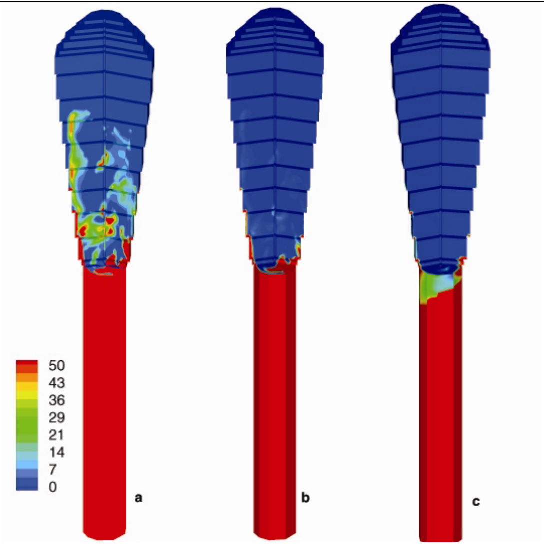

Fig. 7 Relative number of particles for each size: a: small, b: medium, c: large.

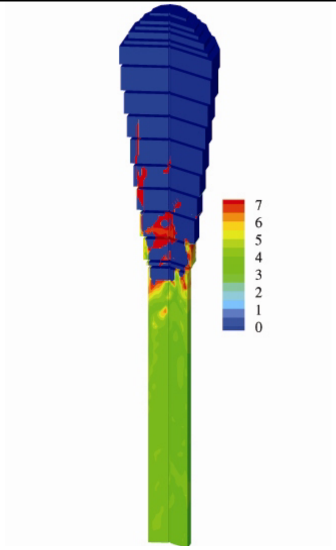

Fig. 8 Average particle temperature rise

From the figure, we can see that in the bulk of the fluidized bed, the temperature is more uniform without hot spots. However, in the expanded section, the average particle temperature is much higher. This information will help us to locate possible hot spots and agglomeration in the reactor. Incorporating electrostatics into the CFD model is also expected to influence the location of the hot spots.

CONCLUSIONS

Due to the different time scales for the chemical reactions and fluid dynamics, the polymerization reactions can be solved outside of the CFD simulation using a CRE model. The particle size, age, and temperature distribution can be determined from the CRE model. The catalyst PSD is represented by a few nodes using QMOM. Combining the CRE model and QMOM, the polymer PSD can be predicted with a high degree of accuracy [7].

Using the results from the CRE model, a CFD simulation was conducted to investigate size segregation and hot spots in a pilot-scale fluidized-bed polymerization reactor. In future work, the CFD simulation will be extended to incorporate agglomeration and breakage of polymer particles. In a later stage, the electrical force component will also be incorporated into the CFD model to determine the effect of particle triboelectric charging on the PSD and overheating. Once the work on validation of pilot-scale polymerization reactor is completed, validation of the CFD model for the commercial-scale reactor will be undertaken.

REFERENCES

[1] I. D. Burdett, R. S. Eisinger, P. Cai and K. H. Lee, Gas-phase fluidization technology for production of polyolefins, Fluidization X, Engineering Foundation, New York, 2001.

[2] V. Mathiesen, T. Solberg and B. H. Hjertager, Predictions of gas/particle flow with an Eulerian model including a realistic particle size distribution, Powder Technology **112** (2000) 34-45.

[3] J. A. Debling and W. H. Ray, Heat and mass transfer effects in multistage polymerization process: Impact polypropylene, Industrial and Engineering Chemical Research, **34** (1995) 3466-3480.

[4] D. L. Marchisio, D. R. Vigil and R. O. Fox, Quadrature method of moments for aggregation-breakage process, Journal of Colloid Interface Science **258** (2003) 322-334.

[5] R. Fan, D. L. Marchisio and R. O. Fox, Application of the direct quadrature method of moments to poly-disperse, gas-solid fluidized beds. Powder Technology **139** (2004) 7-20.

[6] H. Song, Bounds on operating conditions leading to melting during olefin polymerization, Ph. D. thesis, University of Houston, 2004.

[7] R. Fan, Computational fluid dynamics simulation of fluidized bed polymerization reactors, Ph. D. thesis, Iowa State University, 2006.