

Modeling of metallocene catalyzed propylene polymerization in fluidized bed reactors

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Abstract. A study was performed to improve the model for metallocene catalyzed polyolefin polymerization in fluidized bed reactor by adapting multi-scale modeling approach. Monomer concentration and reactor temperature was predicted using kinetic model of polypropylene homopolymerization coupled with well mixed reactor models of fluidized bed reactor. Well mixed model typically used for Ziegler-Natta was selected as supported homogeneous metallocene exhibited heterogeneous property similar to ZN catalyst. Result of simulation showed that model was able to predict reaction temperature accurate with around 3% over-prediction of reactor temperature, which is more accurate than previous model. Model predicted decrease in final monomer concentration from 0.9929 mol/s to 0.986 mol/s when initial reactor was raised from 25C to 75C.

1 Introduction

Polyolefin are considered to the most important commodity polymers today with increasing application in household and the industries. metallocene has been center of many studies since because of the advantages it poses against such as conventional Ziegler Natta and Phillips catalyst. The solution process was the pioneering commercial process to use metallocene catalyst to produce polyethylene. Gas phase and Slurry process will utilize heterogeneous catalyst where metallocene catalysts will need to be supported.

Reactor configuration of polyolefin polymerization includes tubular reactor, fluidized bed, continuous/ semi-continuous CSTR, reaction columns and reactors in series. Polymers properties will be impacted by different mixing conditions. In addition, the formed structure of the polymer affects the flow of the complex fluid. Reactor configuration used in modeling studies conducted for metallocene catalyze polyolefin reactor include fluid bed reactor [1], loop reactors [2-5], fixed bed reactor [6]; stirred tank [7-13], and continuous stirred tank reactor with semi-segregation [14].

Modeling of metallocene catalyst system in this study will enable the establishment of relationship between physical reactor parameter such as pressure, temperature and carrier gas velocity with properties of end polymer product. Optimization of final polymer product properties will then be achieved through control of physical reactor condition.

Modeling polymerization of metallocene in fluidized bed reactor was attempted by Meier et al, 2010 [1]. The monomer concentration in the polymer has been calculated with the Flory-Huggins equation in kinetic where the

kinetic parameters have been determined by fitting the reaction rate curves with the model. Meier et al., 2010 has developed a compartment model to describe the general in stationary temperature profiles in the reactor and related molecular weight distribution of the polymer. The studies reach a conclusion that the under prediction of the temperature gradient by the model over the annulus is likely caused by the inaccuracies in the input data for the solids circulation rate.

Modeling of polymerization process can be classified to three scales depending on specific properties of process. Micro-scales include polymerization kinetic, and Meso-scales include physical transport phenomena of reaction such as phase heat and mass transfer. The macro-scale modeling of polymerization process focused reactor modeling. This study has adapted multi-scale modeling approach for modeling polymerization of metallocene in fluidized bed. Mechanisms of addition polymerization were modeling and solve using method of moment method in kinetic modeling. Well mixed model establish by McAuley et al has taken into account both meso and macro - scale of modeling by factor in as inter/intra phase mass and heat transfer and semi-batch nature of fluidized bed reactor. Purpose of this study is to establish an accurate model for polymerization of metallocene in fluidized bed reactor based on well mixed model by utilizing more robust kinetic model to improve accuracy the modeling.

Section 2.0 covered the development of multi-scale model, where as Section 3.0 discussed the result and discussion for the studies. Section 4.0 is the Conclusion of the studies.

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2 Modeling development

This study focused on developing model for 2 t scale of metallocene catalyzed homopolymerization of polypropylene which are the micro scale (kinetic model) and macro scale (reactor model) reaction. Kinetic modeling in this study was adapted from model developed by Nikhil Prakash, 2013 [15]. For reactor modeling, well mixed model was selected as the reaction behavior of a supported homogenous metallocene catalyst would match the characteristic of a heterogeneous Ziegler-Natta and Phillips catalyst process, in a gas phase fluidized bed reactor.

2.1 Kinetic model

Kinetic modeling of approach for metallocene catalyzed homopolymerization of polypropylene in this study was adapted from model developed by Nikhil Prakash, 2013 [15]. Prakash applied method of moment as the discretion method in the modeling of metallocene polymerization. Mechanism of reaction is show in **Table 1**. The reaction rate constants were taken from literature.

Table 1. Mechanism of Polypropylene Polymerization

Reaction	Stoichiometry	Description
1.	$Cat + Cocat \longrightarrow P(0)$	Instantaneous catalyst activation
2.	$P(0) + M \xrightarrow{k_1} P(1)$	Chain initiation
3.	$P(i) + M \xrightarrow{k_2} P(i+1)$	Chain propagation
4.	$P(i) \xrightarrow{k_3} P_p(0) + D(i)$ {chain}	Spontaneous catalyst deactivation
5.	$P(0) \xrightarrow{k_4} P_p(0)$ {site}	
6.	$P(i) + M \xrightarrow{k_5} D(i) + P(1)$	Chain transfer to monomer
7.	$P(i) \xrightarrow{k_6} D(i) + P'_H(0)$	β -Hydride elimination
8.	$P'_H(0) + M \xrightarrow{k_7} P(1)$	Reinitiation after β -H elimination
9.	$P(i) + M \xrightarrow{k_8} R(i+1)$	Secondary (2, 1) insertion
10.	$R(i) + M \xrightarrow{k_9} P(i+1)$	Propagation after (2, 1) insertion
11.	$R(i) + M \xrightarrow{k_{10}} D(i) + P(1)$	Chain transfer after (2, 1) insertion
12.	$P(i) + Cocat \xrightarrow{k_{11}} D(i) + P'_{Mc}(0)$	Chain transfer to cocatalyst
13.	$P'_{Mc}(0) + M \xrightarrow{k_{12}} P(1)$	Reinitiation after transfer to cocatalyst

2.2 Reactor model

In the present study, a well mixed model was adapted to describe the dynamic behavior of the metallocene catalyzed polypropylene gas phase fluidized bed reactor. McAuley et al. [16]. concluded the well-mixed model which consider bubbles are small with unrestricted mass and heat transfer between the emulsion and bubbles phases and that the composition and temperature are uniform in the gas phase throughout the bed.

Assumption used in proposed model includes a) Mass and heat transfer resistance between the solid polymer

particles and emulsion are negligible due to low to moderate catalyst activity, b) Voidages of bubble and emulsion phase as well as their fractions in the bed can be determine through dynamic two phase structure of gas-fluidized beds, c) isothermal reaction operation, d) continuously catalyst fed into the reactor, and e) Constant mean particle size is assumed throughout the bed.

Based on the above assumptions, dynamic material and energy balance equations can be written for the monomer and hydrogen based on the previously mentioned assumptions [17]. The mole balance is shown in **Eq. 1**.

$$(V \varepsilon_{mf}) \frac{d[M_i]}{dt} = U_0 A ([M_i]_{in} - [M_i]) - R_v \varepsilon_{mf} [M_i] - (1 - \varepsilon_{mf}) R_i \quad (1)$$

where V = reactor volume (m^3), M_i = concentration of component I in the reactor ($kmol/m^3$), U_0 = superficial gas velocity (m/s), A = cross sectional area of reactor (m^2), $[M_i]_{in}$ = concentration of component I in the inlet gaseous stream ($kmol/m^3$), R_v = volumetric polymer phase out flow rate from the reactor (m^3/s), ε_{mf} = void fraction of bed at minimum fluidization, R_i = instantaneous rate of reaction of monomer I.

The energy balance is derived in **Eq. 2**.

$$\left[\sum_{i=1}^m [M_i] C_{pi} V \varepsilon_{mf} + V (1 - \varepsilon_{mf}) \rho_{pol} C_{p,pol} \right] \frac{dT}{dt} = U_0 A \sum_{i=1}^m [M_i] C_{pi} (T - T_{ref}) - U_0 A \sum_{i=1}^m [M_i] C_{pi} (T - T_{ref}) - R_v \left[\sum_{i=1}^m [M_i] C_{pi} \varepsilon_{mf} + (1 - \varepsilon_{mf}) \rho_{pol} C_{p,pol} \right] (T - T_{ref}) + (1 - \varepsilon_{mf}) \Delta H_R R_p \quad (2)$$

where M_i = concentration of component I in the reactor ($kmol/m^3$), C_{pi} = specific heat of capacity of component (J/kgK), V = reactor volume (m^3), ε_{mf} = void fraction of bed at minimum fluidization, ρ_{pol} = density of polymer, $C_{p,pol}$ = specific heat capacity of solid product (J/kgK), T_{in} = temperature of inlet gaseous stream (K), T_{ref} = temperature at reference condition (K), U_0 = superficial gas velocity (m/s), A = cross sectional area of reactor (m^2), R_v = volumetric polymer phase out flow rate from the reactor (m^3/s), ε_{mf} = void fraction of bed at minimum fluidization, R_p = production rate (kg/s), H_R = reactor height (m).

The set of model equations from kinetic model and reactor model which are comprised of stiff, nonlinear and coupled ordinary differential equations are solved numerically using MATLAB 7.0.1 software and the implicit numerical differentiation formulas of ode15s.

3 Results and discussion

A comparative simulation on temperature profile of reaction was conducted to test predictive capability of proposed model. Simulated Temperature profile by model was compared with 1) modeling result from literature and 2) experiment result source from literature, this served to verify the accuracy of the model developed, seen in **Figure 1**. Modeling result from literature refers to studies conducted by Meier et al, which Meier developed was based on Flory-Higgins equation. The studies conclude that simple well mixed model was not able to describe vertical temperature gradients because no segregation and no mixing phenomena have been taken into account.

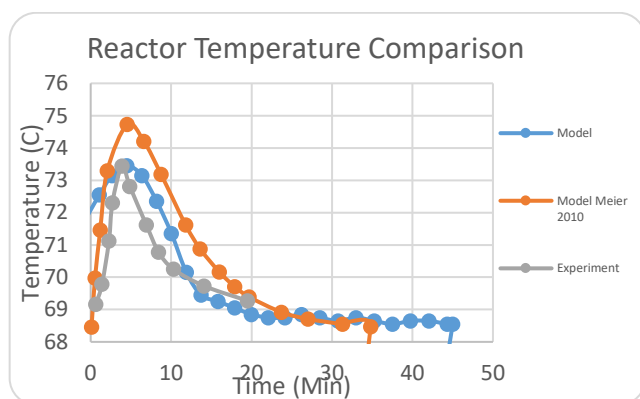


Fig. 1. Reactor Temperature Profile Metallocene catalyzed polymerization in FBR.

It is shown that reactor temperature is proportional to time, until a peak temperature within 10 min of reaction before decline back to starting reactor temperature. Modeling result showed that reactor temperature rises to 76.2 °C in 5.7 min, reactor temperature from literature model rise to 74.7 °C within 4.54 min whereas maximum temperature of 73.44 °C was attained within 3.9 min by experiment studies.

The development multi-scale model was able to predict reactor profile more accurately as compared to Model developed by Meier et al, 2010, this is mainly contributed by the incorporation of a robust kinetic model into solving of reactor model. A dynamic rate of polymerization and active site numbers $p(0)$ over course of reaction was provided by the kinetic model, corresponding to development in reactor including changes caused by mixing phenomena and segregation.

Both model shared similarities in terms of the energy effects due to absorption and desorption of propylene have been neglected, the gas and solids velocities in the reactor are assumed to be constant. Main difference between the two model which explain the difference in the result of modeling is that in well mixed model, the polymerization reactor is considered to be a single phase (emulsion phase) where uniform temperature and composition exists throughout the bed. In Meier model, the reactor is divided in three sections which is the annulus, draft tube and cone section, with equilibrium assumed in each compartment and no heat transfer from the annulus to the draft tube section takes place.

The validated reactor model is used to predict the evolution of reactor behavior, which is the monomer concentration against time, under varying inlet reactor temperature, as shown in **Fig. 2**.

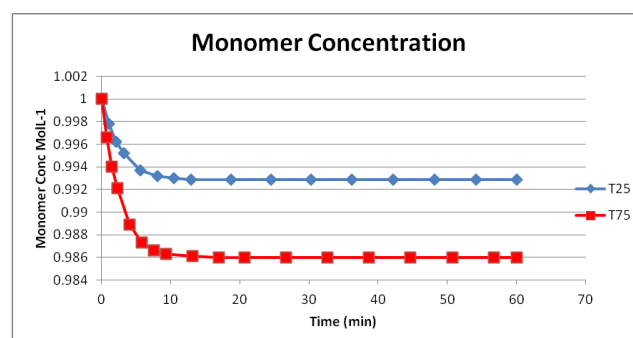


Fig. 2. Evolution of Reactor Behavior Monomer concentration against time predicted by model at temperature 25°C and 75°C.

Figure 2 showed that at 25°C inlet temperature, the monomer concentration declined sharply from starting concentration to minimum concentration of 0.9929 mol/s after 12.95 min, whereas at 75°C inlet temperature, the monomer concentration reduce greatly from point of initiation to minimum concentration of 0.986 mol/s after 16.93 min.

The observation indicates higher monomer consumption at higher temperature, especially at the initiation of reaction. This is supported by steep increase of polymerization rate at higher temperature simulated in kinetic modeling. This observation can be explained as propagation rate constant K_p , spontaneous deactivation and chain transfer to monomer is directly proportional to reactor temperature. Reduction of monomer concentration can also be cause by dip in solubility of propylene in solvent with increase in temperature at constant pressure.

4 Conclusion

A dynamic multi-scale model was developed for metallocene catalyzed polyolefin polymerization in fluidized bed reactor. Result of simulation matches with temperature profile of modelling result from literature and experiment data, with around 0.04% differences in maximum temperature reach during polymerization, even though previous studies that suggested simple well mixed model was not able to predict vertical temperature gradients because no segregation and no mixing phenomena have been taken into account. This problem was treated by incorporating kinetic behaviour into reactor modelling. Deviation of reactor temperature simulated by model is likely due to the assumption used where energy is transferred between the phases due to existence of temperature gradient between bubbles and emulsion as well as by the diffusing gas. Model predicted decrease in final monomer concentration from 0.9929 mol/s to 0.986 mol/s, when initial reactor was raised from 25°C to 75°C. This is due to higher monomer consumption at higher temperature, especially at the initiation of reaction.

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