

AHMAD SHAMIRI^{1,2}
M.A. HUSSAIN¹
F.S. MJALLI³
NAVID MOSTOUFI⁴

¹Department of Chemical Engineering, University of Malaya, Kuala Lumpur, Malaysia

²Training Center, Razi Petrochemical Company, Bandar Imam, Iran

³Petroleum & Chemical Engineering Department, Sultan Qaboos University, Muscat, Oman

⁴Process Design and Simulation Research Center, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

SCIENTIFIC PAPER

UDC 678.742.3

DOI 10.2298/CICEQ111214038S

COMPARATIVE SIMULATION STUDY OF GAS-PHASE PROPYLENE POLYMERIZATION IN FLUIDIZED BED REACTORS USING ASPEN POLYMERS AND TWO PHASE MODELS

A comparative study describing gas-phase propylene polymerization in fluidized-bed reactors using Ziegler-Natta catalyst is presented. The reactor behavior was explained using a two-phase model (which is based on principles of fluidization) as well as simulation using the Aspen Polymers process simulator. The two-phase reactor model accounts for the emulsion and bubble phases which contain different portions of catalysts with the polymerization occurring in both phases. Both models predict production rate, molecular weight, polydispersity index (PDI) and melt flow index (MFI) of the polymer. We used both models to investigate the effect of important polymerization parameters, namely catalyst feed rate and hydrogen concentration, on the product polypropylene properties, such as production rate, molecular weight, PDI and MFI. Both the two-phase model and Aspen Polymers simulator showed good agreement in terms of production rate. However, the models differed in their predictions for weight-average molecular weight, PDI and MFI. Based on these results, we propose incorporating the missing hydrodynamic effects into Aspen Polymers to provide a more realistic understanding of the phenomena encountered in fluidized bed reactors for polyolefin production.

Keywords: polypropylene polymerization, Ziegler-Natta catalyst, Aspen polymers, mathematical modeling.

Due to the advantages of fluidized-bed reactors, such as their ability to carry out polymerization reactions, good particle mixing and the high rate of mass and heat transfer, many research works have been devoted to this technology [1-11]. Various modelling strategies have been proposed to simulate and explain the steady state, dynamic and phase interactions of olefin polymerization in fluidized-bed reactors due to the complex mixing and contacting patterns of the phases. McAuley *et al.* [1] considered the fluidized-bed polyolefin reactor as a well-mixed (CSTR) reactor. Choi and Ray [2] presented a simple model with two distinct phases, namely “bubble” and “emul-

sion” phases, where the polymerization reaction takes place only in the emulsion phase. Fernandes and Lona [3] proposed a three-phase model that considers bubble, emulsion and particulate phases with plug-flow behavior. Ibrehem *et al.* [4] proposed a fluidized-bed represented by four phases, i.e. bubble, cloud, emulsion and solid phases and considered that the polymerization reactions occur in the emulsion and solid phases.

Aspen Polymers, which is built on top of Aspen Plus[®] as a layered product, is a process modeling software package that can simulate polymer manufacturing processes and characterize polymer properties such as molecular weight, melt flow index (MFI) and production rate. It can be used to model multi-site Ziegler-Natta catalysts to predict their characteristically broad molecular-weight distributions [6]. Khare *et al.* [5] and Luo *et al.* [6] developed their model by using fundamental chemical engineering principles and advanced software tools, Aspen Polymers and

Corresponding author: A. Shamiri, Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.

E-mail: ahmadshamiri@gmail.com

Paper received: 14 December, 2011

Paper revised: 20 April, 2012

Paper accepted: 24 April, 2012

Aspen Dynamics. They considered the important issues of physical properties and thermodynamic model selections, polymer properties, catalyst characterization and reactor model, in addition to the traditional Ziegler-Natta polymerization kinetics. Khare *et al.* [5] presented a model for steady-state and dynamic gas phase polypropylene process using stirred-bed reactors while Luo *et al.* [6] developed a model for a commercial bulk polypropylene process for the Hypol Technology. Khare *et al.* [5] characterized a Ziegler-Natta catalyst by assuming the existence of multiple catalyst site types. Their model contains a single set of kinetic and thermodynamic parameters that accurately predicts the polymer production rate, molecular weight and polydispersity index. They proposed procedures to develop and validate the polypropylene process model, considering physical and thermodynamic model selections, catalyst characterization, reactor model and Ziegler-Natta polymerization kinetics.

A flow diagram of the gas-phase fluidized bed polypropylene production process is shown in Figure 1. In the present work, a method is suggested to model and simulate the gas-phase propylene polymerization in the fluidized bed catalytic reactor using Aspen Polymers and the two-phase concept of fluidization. Comparative simulation studies were carried out in order to investigate the effect of important polymerization parameters, namely catalyst feed rate and

hydrogen concentration on the product properties such as production rate, molecular weight and MFI.

Reaction mechanism with nominal kinetic parameters

Several models have been proposed in the literature to describe the kinetic scheme for a heterogeneous Ziegler-Natta catalyst [1,12-15]. The Ziegler-Natta catalyst, considering multiple active sites as well as heat- and mass-transfer resistance, tends to produce a polymer with a broad molecular weight distribution. The effect of multiple site types is more significant than the effect of heat- and mass-transfer resistances. The single-site kinetic model is incapable of describing the kinetic behavior, production rate and molecular weight distribution of propylene homopolymerization. The added complexity of using more sites may limit the model's use for simulation purposes, and the estimation of the large number of kinetic parameters may be restrictive [12]. Therefore, a two-type active site was considered in the present study to describe polymer properties for both models. Using similar methodology to McAuley *et al.* [1], Carvalho de *et al.* [12] and Kissin [13], the kinetic model was developed for Ziegler-Natta catalysts containing multiple active sites to describe the homopolymer production rate, molecular weight and its distribution.

The reaction rate constants used in this work were taken from different published works on similar reactive systems [1,6,15]. This is mainly due to the lack of a unique source that covers all the kinetic

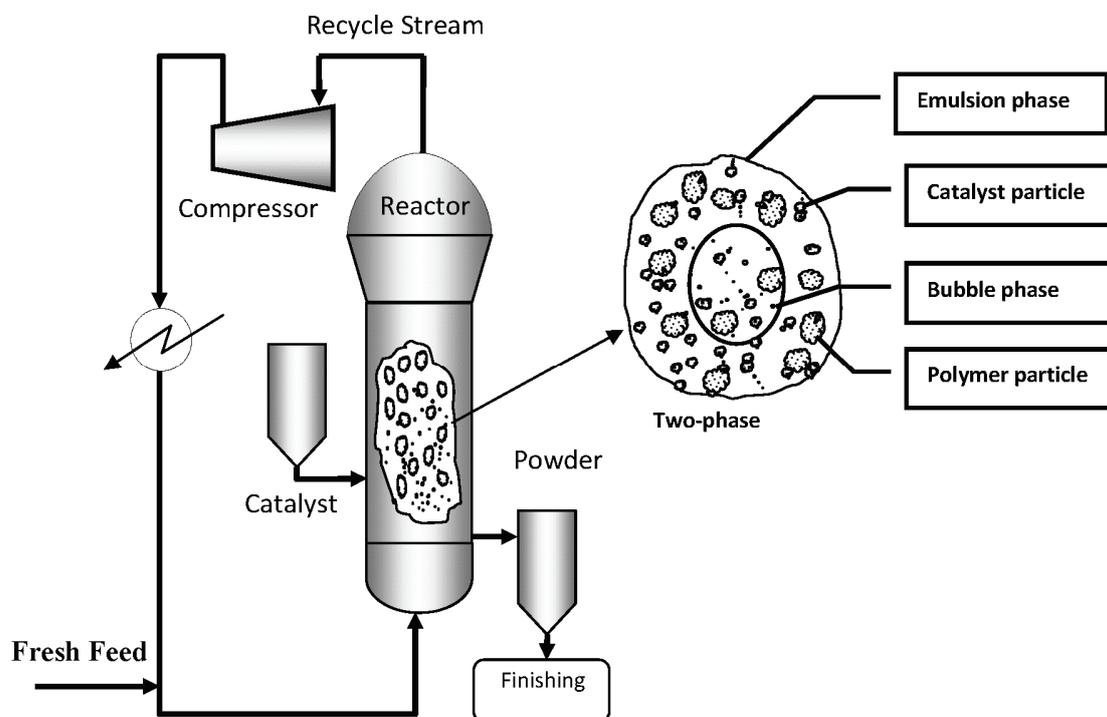


Figure 1. Schematic diagram of an industrial gas phase fluidized bed polypropylene production reactor.

parameters for propylene polymerization. Characterization of polymer properties was modeled using population balances and method of moments. The kinetic scheme comprising of a series of elementary reactions and the rate parameters, used for the two phase model and Aspen Polymers simulator, are listed in Tables 1 and 2, respectively. Aspen Polymers and the two-phase model were standardized to use the same components in the input flow and kinetic parameters.

Process modeling methodology using two-phase model

The kinetics of propylene homo-polymerization over a Ziegler-Natta catalyst based on the model de-

veloped by Shamiri *et al.* [14] and the dynamic two-phase flow approach proposed by Cui *et al.* [16,17] were combined to provide a more realistic understanding of the phenomena faced in the bed hydrodynamics. The kinetic model consists of mass balances on the species present in the reactor written as a series of algebraic and differential equations. Characterization of polymer properties was modeled using population balances and method of moments which were used to predict the polymer production rate, weight average molecular weight and MFI. The set of moment equations are given in Table 3.

The parameters used for the two-phase model are those reported by Cui *et al.* [16]. Jafari *et al.* [18]

Table 1. Elementary chemical reactions of propylene homo-polymerization used for the two phase model

Reaction	Description
$N^*(j) + \text{Cocatalyst} \xrightarrow{k_{\text{act}}(j)} N(0, j)$	Formation of active sites
$N(0, j) + M \xrightarrow{k_{\text{ini}}(j)} N(1, j)$	Initiation of active sites
$N(r, j) + M \xrightarrow{k_p(j)} N(r+1, j)$	Propagation
$N(r, j) + M \xrightarrow{k_{\text{tm}}(j)} N(1, j) + Q(r, j)$	Chain transfer to monomer
$N(r, j) + H_2 \xrightarrow{k_{\text{th}}(j)} N_H(0, j) + Q(r, j)$	Transfer to hydrogen
$N_H(0, j) + M \xrightarrow{k_h(j)} N(1, j)$	-
$N_H(0, j) + AlEt_3 \xrightarrow{k_{\text{hr}}(j)} N(1, j)$	-
$N(r, j) + AlEt_3 \xrightarrow{k_{\text{tco}}(j)} N(1, j) + Q(r, j)$	Transfer to co-catalyst
$N(r, j) \xrightarrow{k_{\text{fs}}(j)} N_H(0, j) + Q(r, j)$	Spontaneous transfer
$N(r, j) \xrightarrow{k_{\text{ds}}(j)} N_d(j) + Q(r, j)$	Deactivation reactions
$N(0, j) \xrightarrow{k_{\text{ds}}(j)} N_d(j)$	-
$N_H(0, j) \xrightarrow{k_{\text{ds}}(j)} N_d(j)$	-

Table 2. Kinetic rate constants used for the two phase model and the Aspen Polymers model

Reference	Site Type 2	Site Type 1	Unit	Rate constant	Reaction
[1]	1	1	s^{-1}	$k_{\text{act}}(j)$	Formation
[6]	54.93	22.88	$L \text{ mol}^{-1} s^{-1}$	$k_{\text{ini}}(j)$	Initiation
[1]	0.1	0.1	$L \text{ mol}^{-1} s^{-1}$	$k_p(j)$	
[1]	20	20	$L \text{ mol}^{-1} s^{-1}$	k_{hr}	
[14]	34.28	342.8	$L \text{ mol}^{-1} s^{-1}$	$k_p(j)$	Propagation
[6]	0.2171	0.0865	$L \text{ mol}^{-1} s^{-1}$	$k_{\text{tm}}(j)$	Transfer
[6]	7.5	7.5	$L \text{ mol}^{-1} s^{-1}$	$k_{\text{th}}(j)$	
[1]	0.12	0.024	$L \text{ mol}^{-1} s^{-1}$	$k_{\text{tco}}(j)$	
[1]	0.0001	0.0001	$L \text{ mol}^{-1} s^{-1}$	$k_{\text{fs}}(j)$	
[6]	0.00034	0.00034	s^{-1}	$k_{\text{de}}(j)$	Deactivation

Table 3. Moment equations

$$\begin{aligned} \frac{dY(0,j)}{dt} &= [M]\{k_{ini}(j)N(0,j) + k_h(j)N_H(0,j)\} + N_H(0,j)k_{hr}(j)[AlEt_3] - \\ &\quad - Y(0,j)\{k_{th}(j)[H_2] + k_{fs}(j) + k_{ds}(j) + \frac{R_V}{V_p}\} \\ \frac{dY(1,j)}{dt} &= [M]k_{ini}(j)N(0,j) + N_H(0,j)\{k_h(j)[M] + k_{hr}(j)[AlEt_3]\} \\ &\quad + Y(0,j)\{k_{tm}(j)[M] + k_{tco}(j)[AlEt_3]\} + [M]k_p(j)Y(0,j) - \\ &\quad - Y(1,j)\{k_{tm}(j)[M] + k_{tco}(j)[AlEt_3] + k_{th}(j)[H_2] + k_{fs}(j) + k_{ds}(j) + \frac{R_V}{V_p}\} \\ \frac{dY(2,j)}{dt} &= [M]k_{ini}(j)N(0,j) + N_H(0,j)\{k_h(j)[M] + k_{hr}(j)[AlEt_3]\} \\ &\quad + Y(0,j)\{k_{tm}(j)[M] + k_{tco}(j)[AlEt_3]\} + [M]k_p(j)\{2Y(1,j) \\ &\quad + Y(0,j)\} - Y(2,j)\{k_{tm}(j)[M] + k_{tco}(j)[AlEt_3] + k_{th}(j)[H_2] + k_{fs}(j) + k_{ds}(j) + \frac{R_V}{V_p}\} \\ \frac{dX(n,j)}{dt} &= Y(n,j)\{k_{tm}(j)[M] + k_{tco}(j)[AlEt_3] + k_{th}(j)[H_2] + k_{fs}(j) + k_{ds}(j)\} - X(n,j)\frac{R_V}{V_p} \end{aligned}$$

$n = 0, 1, 2$

showed that using the parameters reported by Cui *et al.* [16], for either Geldart A or B particles, provide results that are in good agreement with the experimental data involving fluidized bed reactors for both the bubbling and turbulent fluidization regimes.

The assumptions considered in developing the model are summarized below:

- The fluidized bed comprises of two phases: bubble and emulsion.
- The emulsion phase is not at the minimum fluidization condition and the bubble phase contains solid particles.
- Reactions occur in both bubble and emulsion phases.
- There is negligible resistance to heat and mass transfer between the gas and polymer particles due to small catalyst particles, low to moderate catalyst activity or polymerization rates [19].
- Constant mean particle size is assumed throughout the bed.
- A two-site kinetic scheme is assumed.
- Side reactions with poisons are neglected.

In a fluidized bed reactor, upward motion of the gas bubbles causes enough mixing of solid particles in the emulsion phase. Therefore, concentrations of various species and temperature are nearly uniform in the emulsion phase. Consequently, a pseudo-homogeneous CSTR is a valid assumption and can be applied to the modelling process [1]. The bubbles travel up through the bed at constant velocity and the par-

ticles within the bubbles present a downward flow, growing in size and weight as they flow downwards which makes the assumption of plug flow valid for such a regime in the bubble phase. This two-phase model is based on the principles of fluidization and the experimental findings on the significance of solid particles present in the bubble phase and the excess gas in the emulsion phase [16,17]. The correlations needed for estimating the void fractions of the bubble and emulsion phases from the dynamic two-phase model are summarized in Table 4.

Assuming that the only significant consumption of monomer is by the propagation reaction and that consumption of hydrogen is by the transfer to hydrogen reaction, the following expression for the consumption rate of component (monomer and hydrogen) can be obtained:

For monomer:

$$R_i = \sum_{j=1}^{NS} [M_i]Y(0,j)k_p(j), \quad i = 1 \quad (1)$$

For hydrogen:

$$R_i = \sum_{j=1}^{NS} [M_i]Y(0,j)k_m(j), \quad i = 2 \quad (2)$$

The total polymer production rate for each phase can be calculated from:

$$R_p = \sum_{i=1}^2 Mw_i R_i \quad (3)$$

Table 4. Empirical correlations used in the two phase model

Formula	Reference
$Re_{mf} = \left[(29.5)^2 + 0.357 Ar \right]^{1/2} - 29.5$	[24]
$Ar = \frac{\rho g (\rho_s - \rho_g) g d_p^3}{\mu_g^2}$	-
$\delta = 0.534 \left[1 - \exp \left(-\frac{U_0 - U_{mf}}{0.413} \right) \right]$	[16]
$\varepsilon_e = \varepsilon_{mf} + 0.2 - 0.059 \exp \left(-\frac{U_0 - U_{mf}}{0.429} \right)$	[16]
$\varepsilon_b = 1 - 0.146 \exp \left(-\frac{U_0 - U_{mf}}{4.439} \right)$	[16]
$V_{pe} = Ah(1 - \varepsilon_e)(1 - \delta)$	-
$V_{pb} = Ah(1 - \varepsilon_b)\delta$	-

in which R_i is the instantaneous rate of reaction for monomer and hydrogen.

The volumetric outflow rate of the polymer, R_v , can be determined from the consumption rates of the monomers and the rate of change of the weight of polymer in the reactor:

$$R_v = \frac{M_w R}{\rho_s} - \frac{dB_w / dt}{\rho_s} \quad (4)$$

Control of MFI is an important issue for producing the needed polypropylene grade. The MFI of a polymer is a function of its molecular weight (\overline{M}_w), which is related to the operating conditions of the reactor and the feed composition. The relation between MFI and the weight average molecular weights of polypropylene is given by [20]:

$$MFI = \left(\frac{\overline{M}_w}{111525} \right)^{-0.288} \quad (5)$$

Process simulation methodology using aspen polymers

Developing an accurate simulation of propylene polymerization in fluidized-bed reactors using Aspen Polymers requires special expertise. Predicting reliable physical and thermodynamic properties of a chemical system is important in process simulation for simulating chemical unit operations such as reactors and separators. Unfortunately, creating thermophysical properties for polymers, as well as polymerization reaction models, is especially challenging and requires attention to detail.

Thermodynamic phase equilibrium models are categorized as either activity-coefficient or equation-of-state (EOS) based models. In the present work, EOS models were selected for the polypropylene process due to the nature of the species and high operating pressure involved. EOS models are suitable for systems at moderate to high pressures and reactor pressure for this gas-phase polypropylene process ranges from 20 to 30 bar [5]. According to Gross and Sadowski [20], a model based on the perturbed-chain statistical associating fluid theory (PC-SAFT EOS), is the best for describing physical and thermodynamic properties of a polymeric systems. Therefore, PC-SAFT EOS was used to model the physical and thermodynamic properties for the polypropylene process. The PC-SAFT model is an extension of the prestigious SAFT EOS model. The main difference between these models is that the PC-SAFT model considers hard sphere chains while SAFT model accounts for hard spheres. This allows PC-SAFT EOS to include the connectivity of segments that comprise the chains when considering the attractions between species. This improvement shows a more realistic description of the thermodynamic behavior of chainlike molecules [5,21,22]. The PC-SAFT EOS also shows superior prediction for vapor-liquid equilibrium and binary mixtures of small molecules compared to SAFT and Peng-Robinson models, respectively [5,6].

Table 5 lists the components included in the model. The applied pure-component parameters for the PC-SAFT equation of state model (EOS) are listed in Table 6 [6]. The data listed in these tables were integrated into the Aspen Polymers simulator associated with the built-in PC-SAFT EOS model.

Table 5. Component used for polypropylene gas phase polymerization

Species	Function
Propylene (C ₃ H ₆)	Monomer
Polypropylene (PP)	Polymer
Propylene Segment (C ₃ H ₆ -R)	Polymer segment
Hydrogen (H ₂)	Chain transfer agent
Titanium Tetrachloride (CAT)	Catalyst
Triethyl-Aluminium (COCAT)	Co-catalyst
Nitrogen (N ₂)	Inert
Water (H ₂ O)	Cooling Water

Table 6. Pure-component parameter for the PC-SAFT EOS [6]

Component	m	$\sigma / \text{\AA}$	uk_6^{-1} / K	$r / \text{mol g}^{-1}$
Hydrogen	0.8285	2.973	12.53	-
Propylene	1.960	3.536	207.2	-
Polypropylene	-	4.147	298.6	0.0253
Catalyst	25	2.668	198.8	-
Co-catalyst	25	2.668	198.8	-

Based on the thermodynamic model and the component parameters that are suitable for the reaction conditions involved in the present process [5, 6], a RCSTR module within Aspen Polymers was selected to model the gas-phase fluidized polymerization reactor. Furthermore, the characterization of the Ziegler-Natta catalyst and a set of two-site kinetic schemes with reaction rate constants were incorporated

into the model. The emulsion phase can be simply presented by a single RCSTR model which takes gaseous feed that includes the propylene gas, hydrogen gas and the nitrogen gas as an inert and 88% of the solid feed which is Ziegler-Natta catalyst [14]. For modeling the bubble phase, which accounts for the gaseous feed and 12% of the solid feed, there are two options in Aspen Polymers: a single RPlug or a series of RCSTR. Since the behaviour of a plug-flow reactor can be approximated by that of a multistage CSTR [23], a series of four equal-volume RCSTR modules was chosen to represent the bubble phase due to an impractical low polypropylene production using an equivalent RPlug module.

A major problem faced during the process simulation was the convergence of the recycle stream which was not solved in a previous work [6]. In the present study, according to the calculation procedure of the process flow sheet, the problem was addressed and solved with some difficulty. From this angle, this work can be regarded as the first of its kind to be able to estimate the real gas-phase fluidized bed polymerization system which considers both the emulsion phase and bubble phase for predicting the polymer production rate, weight average molecular weight, number average molecular weight, PDI and MFI with Aspen Polymers. The flow sheet for the complete gas phase catalytic propylene polymerization fluidized-bed reactor is shown in Figure 2.

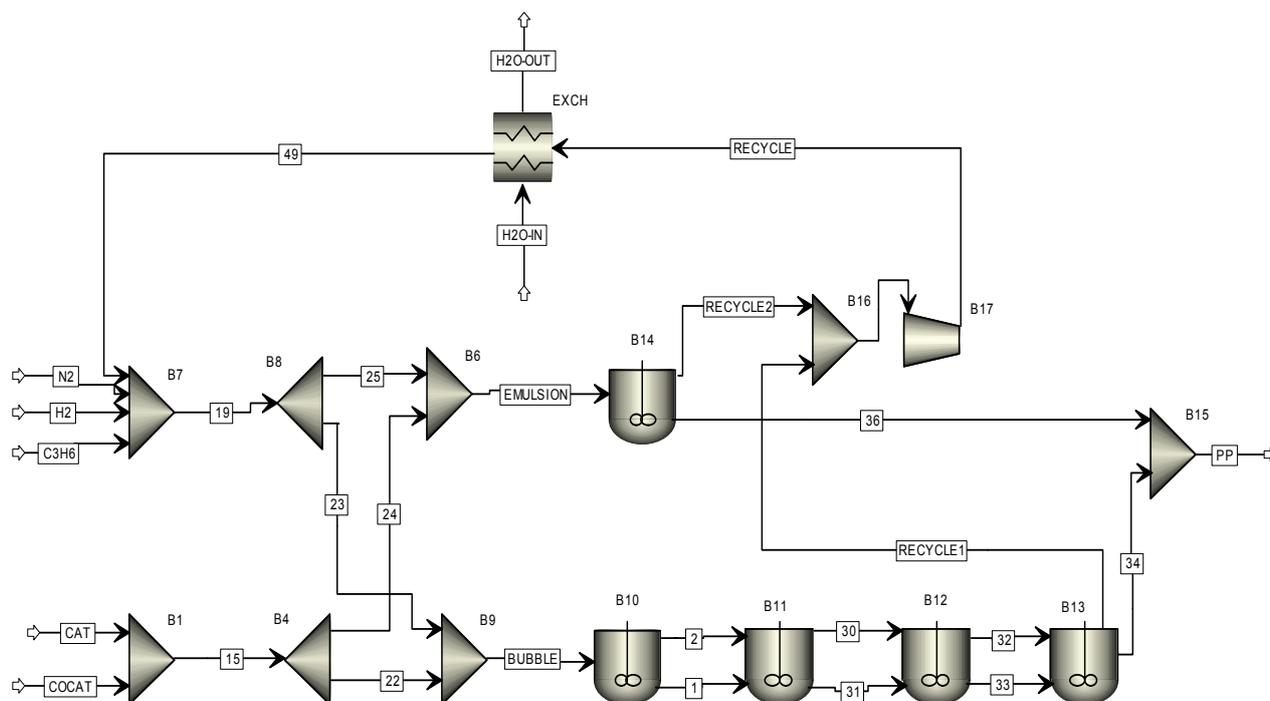


Figure 2. Gas phase catalytic propylene polymerization fluidized bed reactor simulation scheme. (B14: reactor emulsion phase, B10, B11, B12, B13: reactor bubble phase).

RESULTS AND DISCUSSION

A series of comparative simulation studies were carried out using the two-phase model and the Aspen Polymers simulator for gas-phase propylene polymerization in a fluidized-bed reactor along with a two-site kinetic scheme of Ziegler-Natta catalyst. To realistically represent the real fluidized-bed reactor, both emulsion and bubble phases in the fluidized-bed reactor were considered in this model. A comparison between this two-phase model with previous models was carried out by Shamiri *et al.* [14] who showed that there is a good agreement between this model and previously reported models in terms of overall polymer production in the reactor. However, this two-phase model has the advantage of being able to account for the production of the polymer in the bubble phase as well.

Comparison between the two methods of obtaining the models was carried out based on the effect of varying catalyst feed to the polypropylene production rate and the effect of hydrogen molar percentage in the feed to the weight-average molecular weight and MFI. The standardized component inlet flow rates and operating conditions and physical parameters used in the models are given in the Tables 7 and 8.

Figure 3 shows the effect of catalyst feed rate on the polypropylene production rate predicted by both models. This figure reveals that the polymer production rate is directly proportional to the catalyst feed rate. As the catalyst feed rate increases, the polymer production rate increases due to increase in available active sites. Clearly, both models are closely in agreement with each other to some extent with small deviation. The results also show that the series RCSTR model for the bubble phase in the fluidized bed can be used to estimate the performance of a real fluidized bed.

Controlling the average molecular weight and performing grade transition of polypropylene product is directly related to the hydrogen concentration in the reactor. The polymer molecular weight and its distribution govern the MFI and affect the quality of the polymer product. Figure 4 shows the effect of hydrogen concentration on the polymer molecular weight predicted by the two models. As the hydrogen molar fraction in the feed to the reactor increases from 0.7% to 1.1%, the weight average molecular weight decreases and consequently the chain length and the degree of polymerization decreases due to increase in chain transfer reaction rate. Both models predict similar trends, but with different values. At hydrogen molar fraction of 0.9% both models predicted the same polymer weight average molecular weight of around 1.95×10^5 .

The effect of hydrogen mole fraction in the feed on the MFI of the polymer is shown in Figure 5. The MFI of the polymer increases with increasing hydrogen mole fraction in the feed. An agreement between the predictions of the two models can be observed at the hydrogen mole fraction of 0.9%. But below this concentration, the Aspen Polymers simulator over-predicts the MFI while beyond this concentration, it under-predicts the MFI.

The effect of hydrogen mole fraction in the feed on the number-average molecular weight and PDI of the polymer are shown in Figures 6 and 7. As shown in these figures, number-average molecular weight and PDI of the polymer decreases by increasing the hydrogen mole fraction of the feed. It can be seen that by increasing the hydrogen concentration, the molecular weights decrease which results in decreasing the chain length and the degree of polymerization due to the increase of chain transfer reaction rate. These figures demonstrate that there is a clear mismatch between the predicted values of number-average mo-

Table 7. Component inlet flow rate

Species	Function	Inlet flow rate, kg/h	Gas phase mole fraction
Propylene (C ₃ H ₆)	Monomer	319627.44	0.730
Hydrogen (H ₂)	Chain transfer agent	186.12	0.009
Titanium Tetrachloride (CAT)	Catalyst	0.72	-
Triethyl-Aluminium (COCAT)	Co-catalyst	0.72	-
Nitrogen (N ₂)	Inert	76186.44	0.261

Table 8. Operating conditions and physical parameters

Physical parameter	Operating condition
$\mu = 1.14 \times 10^{-4}$ Pa.s	$V = 50$ m ³
$\rho_g = 23.45$ kg/m ³	$T = 70$ °C
$\rho_s = 910$ kg/m ³	$P = 25$ bar
$dp = 500 \times 10^{-6}$ m	$\epsilon_{mf} = 0.45$

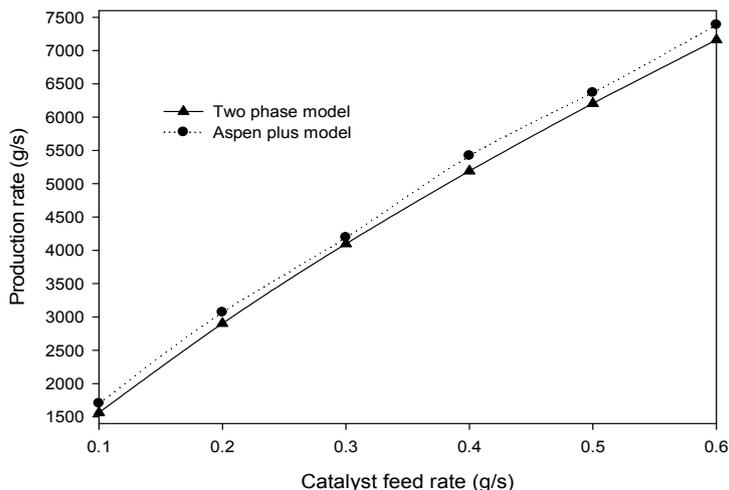


Figure 3. Comparison between the two phase model and the Aspen Polymers model for the effect of variation of catalyst feed on polymer production rate.

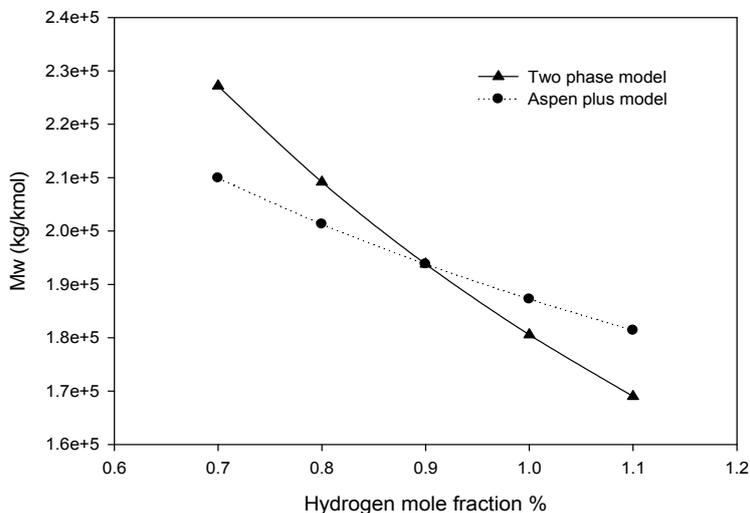


Figure 4. Comparison between the two phase model and the Aspen Polymers model for the effect of variation of hydrogen feed molar fraction on weight average molecular weight.

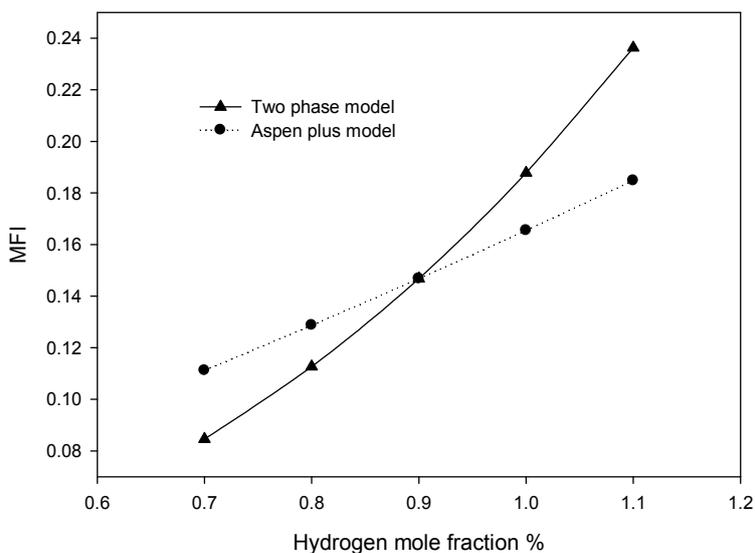


Figure 5. Comparison between the two phase model and the Aspen Polymers model for the effect of variation of hydrogen feed molar fraction on melt flow index.

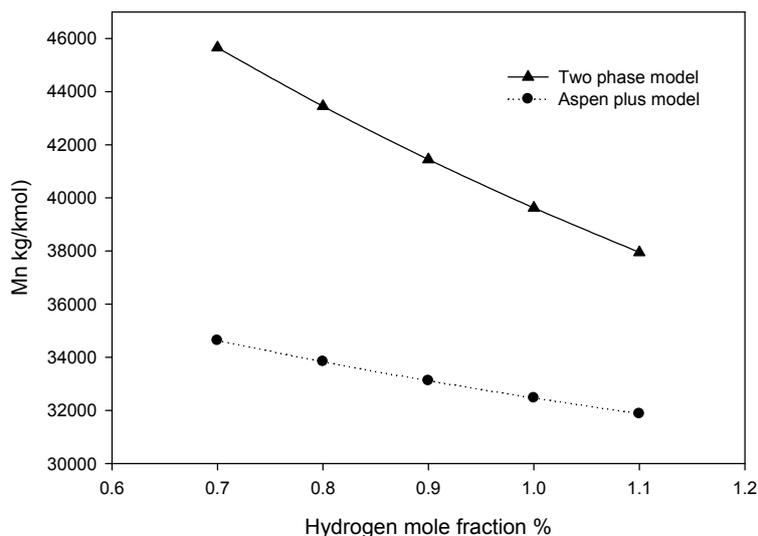


Figure 6. Comparison between the two phase model and the Aspen Polymers model for the effect of variation of hydrogen feed molar fraction on number average molecular weight.

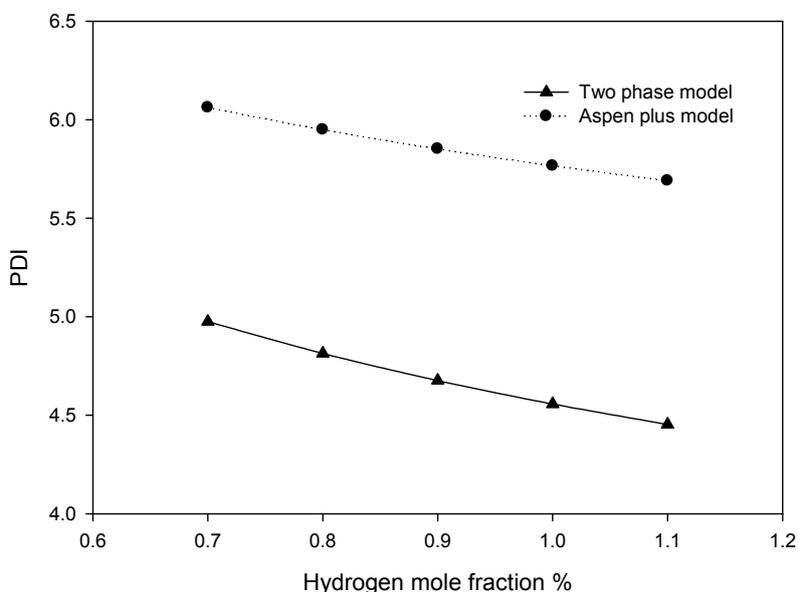


Figure 7. Comparison between the two phase model and the Aspen Polymers model for the effect of variation of hydrogen feed molar fraction on PDI.

lecular weight and PDI by the two-phase and Aspen Polymers models. The Aspen Polymers model shows very small change in number average molecular weight which may be impractical.

Distributions of gas and solid particles in the fluidized bed depend strongly on the superficial gas velocity and gas-solid distribution can have a significant effect on the reaction and heat and mass transfer rates in the fluidized beds. Therefore, it is very important to investigate the effect of the superficial gas velocity on the process variables. The effect of superficial gas velocity on polypropylene product rate predicted by the two-phase model is illustrated in

Figure 8. This figure shows that increasing the superficial gas velocity results in decreasing the polymer production rate. In fact, by increasing the superficial gas velocity, gas passes faster through the bed. As a result, some monomers may bypass the catalyst, therefore, the monomer contact with growth sites is reduced, resulting in decreasing the monomer conversion and polymer production rate.

In the two-phase model, the hydrodynamic sub-model was combined with comprehensive kinetic model to evaluate the effect of key process parameters such as superficial gas velocity on the polymer production rate and polymer properties. The model from

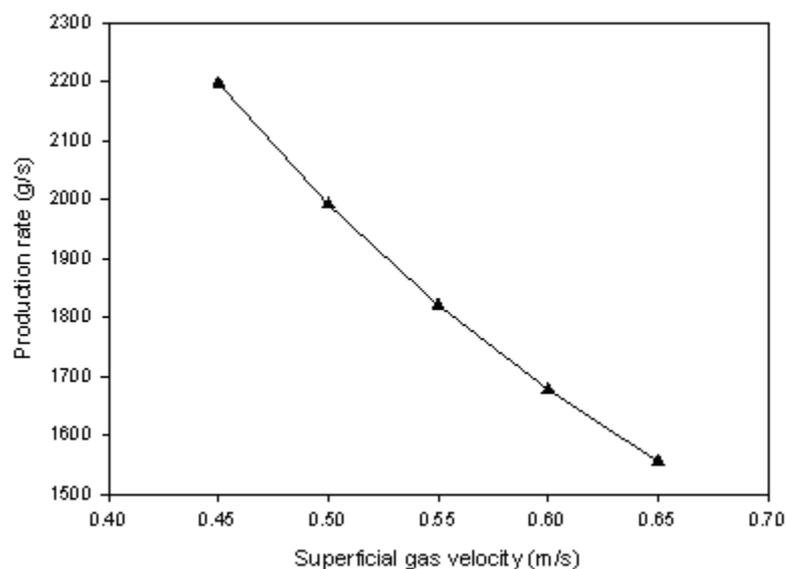


Figure 8. Effect of superficial gas velocity on polypropylene product rate predicted by the two phase model.

the Aspen Polymers simulator is an oversimplification of what actually happens in the fluidized bed, since the effect of hydrodynamics (the correlations required for estimating the void fractions of the bubble and emulsion phases from the dynamic two-phase model which are summarized in Table 4) is ignored. Prediction from this simplified model can be used for qualitative predictions (since it predicted correct variables trends). However, due to the many assumptions involved in this model, it is incapable of explaining the effect of the key process parameters such as superficial gas velocity on the polymer production rate and polymer properties in the polypropylene fluidized-bed reactor.

CONCLUSION

A comparative simulation study was carried out using Aspen Polymers and the two-phase model in order to determine the influence of key operating parameters, namely catalyst feed rate and hydrogen concentration, on production rate, molecular weight and MFI. By comparing the predictions of polymer production rate, we show that both models produce similar predictions. A moderate deviation was observed by comparing the effect of increasing the hydrogen feed fraction on the weight-average molecular weight, PDI and MFI due to the difference in the basic kinetic model used in the two models. However, the Aspen Polymers model is only an approximation to the fluidized bed reactor since there is no fluidized bed module in this simulator. Despite the similarity in the general trends described by these two models, some deviation was observed especially for the

weight-average molecular weight, PDI and MFI. Due to the many assumptions involved in the Aspen Polymers model, this model is incapable of predicting the effect of the key process parameters such as superficial gas velocity on the polymer production rate and polymer properties in the polypropylene fluidized bed reactor. The rigorous details of the two-phase model suggest that it is more realistic than the corresponding Aspen Plus model and it can be concluded that the two-phase model provides more acceptable predictions. To improve the predictions of the simulator, it is recommended that the hydrodynamic correlations used in the proposed two-phase model be incorporated in the simulator via a Visual Basic macro or an attached spreadsheet. This is expected to improve the accuracy of the simulator package.

Notations

AlEt_3	triethyl aluminum co-catalyst
A_r	Archimedes number
B	moles of reacted monomer bound in the polymer in the reactor
B_w	mass of resin in the reactor (kg)
d_p	particle diameter (m)
F_{cat}	catalyst feed rate (g/s)
H_2	hydrogen
J	active site type
$k_{act}(j)$	formation rate constant for a site of type j
$k_{ds}(j)$	spontaneous deactivation rate constant for a site of type j
$k_{fs}(j)$	spontaneous transfer rate constant for a site of type j with terminal monomer M
$k_h(j)$	rate constant for reinitiating of a site of type j by monomer M

$k_{hr}(j)$	rate constant for reinitiating of a site of type j by cocatalyst
$k_{ini}(j)$	rate constant for initiation of a site of type j by monomer M
$k_p(j)$	propagation rate constant for a site of type j with terminal monomer M reacting with monomer M
$k_{tco}(j)$	transfer rate constant for a site of type j with terminal monomer M reacting with $AlEt_3$
$k_{th}(j)$	transfer rate constant for a site of type j with terminal monomer M reacting with hydrogen
$k_{tm}(j)$	transfer rate constant for a site of type j with terminal monomer M reacting with monomer M
M	monomer (propylene)
MFI	melt flow index (g/10 min)
\overline{M}_w	weight average molecular weight of polymer (kg/kmol)
Mn	number average molecular weight of polymer (kg/kmol)
Mw	monomer molecular weight (kg/kmol)
$N^*(j)$	potential active site of type j
$N(0,j)$	uninitiated site of type j produced by formation reaction
$N(1,j)$	living polymer chain of type j with length one
$N(r,j)$	living polymer molecule of length r , growing at an active site of type j , with terminal monomer M
$N_H(0,j)$	uninitiated site of type j produced by transfer to hydrogen reaction
NS	number of active site types
P	pressure (Pa)
PDI	polydispersity index
r	number of units in polymer chain
R	instantaneous consumption rate of monomer (kmol/s)
$R(j)$	rate at which monomer M is consumed by propagation reactions at sites of type j
Re_{mf}	Reynolds number of particles at minimum fluidization condition
R_p	production rate (kg/s)
R_v	volumetric polymer outflow rate from the reactor (m^3/s)
t	time (s)
T	temperature (K)
U_0	superficial gas velocity (m/s)
U_{mf}	minimum fluidization velocity (m/s)
V	reactor volume (m^3)
V_b	volume of bubbles
V_p	volume of polymer phase in the reactor (m^3)
V_{pb}	volume of polymer phase in the bubble phase (m^3)
V_{pe}	volume of polymer phase in the emulsion phase (m^3)

$X(n,j)$	n th moment of chain length distribution for dead polymer produced at a site of type j
$Y(n,j)$	n th moment of chain length distribution for living polymer produced at a site of type j

Greek letters

δ	volume fraction of bubbles in the bed
ε_b	void fraction of bubble for Geldart B particles
ε_e	void fraction of emulsion for Geldart B particles
ε_{mf}	void fraction of the bed at minimum fluidization
μ	gas viscosity (Pa s)
ρ_g	gas density (kg/m^3)
ρ_s	polymer density (kg/m^3).

Acknowledgment

The authors would like to thank the support of the Research Council of the University of Malaya under research grant UM.C/HIR/MOHE/ENG/25.

REFERENCES

- [1] K.B. McAuley, J.F. MacGregor, A.E. Hamielec, *AIChE J.* **36** (1990) 837-850
- [2] K.Y. Choi, W.H. Ray, *Chem. Eng. Sci.* **40** (1985) 2261-2279
- [3] F.A.N. Fernandes, L.M.F. Lona, *Chem. Eng. Sci.* **56** (2001) 963-969
- [4] A.S. Ibrehem, M.A. Hussain, N.M. Ghasem, *Chem. Eng. J.* **149** (2009) 353-362
- [5] N.P. Khare, B. Lucas, K.C. Seavey, Y.A. Liu, A. Sirohi, S. Ramanathan, S. Lingard, Y. Song, C.-C. Chem, *Ind. Eng. Chem. Res.* **43** (2004) 884-900
- [6] Z.-H. Luo, P.-L. Su, D.-P. Shi, Z.-W. Zheng, *Chem. Eng. J.* **149** (2009) 370-382
- [7] A. Shamiri, M. Azlan Hussain, F. Sabri Mjalli, N. Mostoufi, M. Saleh Shafeeyan, *Chem. Eng. Sci.* **66** (2011) 1189-1199
- [8] A. Shamiri, M.A. Hussain, F.S. Mjalli, *Def. Diff. Forum.* (2011) 1079-1084
- [9] A. Shamiri, M.A. Hussain, F.S. Mjalli, N. Mostoufi, *Comp. Chem. Eng.* **36** (2012) 35-47
- [10] M. Ali, E. Ajbar, K. Alhumaizi, *Korean J. Chem. Eng.* **27** (2009) 364-372
- [11] N. Ghasem, W. Ang, M. Hussain, *Korean J. Chem. Eng.* **26** (2009) 603-611
- [12] A.B. Carvalho de, P.E. Gloor, A.E. Hamielec, *Polymer* **30** (1989) 280-296
- [13] Y.V. Kissin, *Isospecific polymerization of olefins with heterogeneous Ziegler-Natta catalysts*, Springer-Verlag, New York, 1985
- [14] A. Shamiri, M.A. Hussain, F.S. Mjalli, N. Mostoufi, *Chem. Eng. J.* **161** (2010) 240-249
- [15] J.J. Zacca, J.A. Debling, W.H. Ray, *Chem. Eng. Sci.* **51** (21) (1996) 4859-4886

- [16] H. Cui, N. Mostoufi, J. Chaouki, Chem. Eng. J. **79** (2000) 133-143
- [17] H. Cui, N. Mostoufi, J. Chaouki, Powder Technol. **120** (2001) 12-20
- [18] R. Jafari, R. Sotudeh-Gharebagh, N. Mostoufi, Chem. Eng. Technol. **27** (2004) 123-129
- [19] S. Floyd, K.Y. Choi, T.W. Taylor, W.H. Ray, J. Appl. Polymer Sci. **32** (1986) 2935-2960
- [20] [K.B. Sinclair, Characteristic of linear LPPE and description of UCC gas phase process, SRI International, Menlo Park, CA, 1983
- [21] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. **40** (2001) 1244-1260
- [22] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res. **30** (1991) 1994-2005
- [23] N. Watanabe, H. Kurimoto, M. Matsubara, Chem. Eng. Sci. **39** (1984) 31-36
- [24] A. Lucas, J. Arnaldos, J. Casal, L. Puigjaner, Ind. Eng. Chem. Proc. Des. Dev. **25** (1986) 426-429.

AHMAD SHAMIRI^{1,2}
M.A. HUSSAIN¹
FAROUQ SABRI MJALLI³
NAVID MOSTOUFI⁴

¹Department of Chemical Engineering,
University of Malaya, Kuala Lumpur,
Malaysia

²Training Center, Razi Petrochemical
Company, Bandar Imam, Iran

³Petroleum & Chemical Engineering
Department, Sultan Qaboos University,
Muscat, Oman

⁴Process Design and Simulation
Research Center, School of Chemical
Engineering, College of Engineering,
University of Tehran, Tehran, Iran

NAUČNI RAD

KOMPARATIVNA SIMULACIONA STUDIJA POLIMERIZACIJE PROPILENA U GASNOJ FAZI U REAKTORIMA SA FLUIDIZOVANIM SLOJEM KORIŠĆENJEM ASPEN POLYMERS I DVOFAZNIH MODELA

U ovom radu je predstavljena komparativna studija koja opisuje polimerizaciju propilena gasnoj fazni u reaktorima sa fluidizovanim slojem uz korišćenje Ziegler-Natta katalizatora. Ponašanje reaktora je objašnjeno dvo-faznim modelom (zasnovanim na principima fluidizacije), kao i simulacijom pomoću procesnog simulatora Aspen Polymers. Model dvo-faznog reaktora uzima u obzir emulzionu i mehurastu fazu sa različitim količinama katalizatora pri čemu se polimerizacije odigrava u obe faze. Oba modela predviđaju brzinu proizvodnje, molekulsku masu, polidisperzni indeks (PDI) i indeks tečenja polimera (MFI). Oba modela su korišćena prilikom ispitivanja uticaja važnih parametara polimerizacije, tačnije brzina napajanja katalizatorom i koncentracija vodonika, na osobine dobijenog polipropilena, kao što su brzina proizvodnje, molekulska masa, PDI i MFI. Oba dvo-fazna modela i Aspen Polymers simulator su pokazali dobro slaganje u pogledu brzine proizvodnje. Međutim, modeli se razlikuju u svojim predviđanjima kad je u pitanju prosečna molekulska masa, PDI i MFI. Rezultati pokazuju da je neophodno uvesti i hidrodinamičke efekte u Aspen Polymers, kako bi se obezbedilo realnije razumevanje fenomena koji se javljaju u reaktorima sa fluidizovanim slojem za proizvodnju poliolefina.

Ključne reči: polimerizacija polipropena, Ziegler-Natta katalizator, Aspen polimeri, matematičko modelovanje.