

Modeling and Simulation of Ethylene Polymerization in Industrial Slurry Reactor Series

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Abstract A five-site comprehensive mathematical model was developed to simulate the steady-state behavior of industrial slurry polymerization of ethylene in multistage continuous stirred tank reactors. More specifically, the effects of various operating conditions (*i.e.*, inflow rates of catalyst, hydrogen and comonomer) on the molecular structure and properties of polyethylene (*i.e.*, M_w , M_n , polydispersity index (I_{PD}), melt index, density, *etc.*) are fully assessed. It is shown that the proposed comprehensive model is capable of simulating the steady-state operation of an industrial slurry stirred tank reactor series. It is demonstrated that changing the catalyst flow rate, changes simultaneously the mean residence-time in both reactors, which plays a significant role on the establishment of polyethylene architecture properties such as molecular mass and I_{PD} . The melt index and density of polyethylene are mainly controlled by hydrogen and comonomer concentration, respectively.

Keywords bimodal polyethylene, multiple tanks in series, simulation, polymerization

1 INTRODUCTION

High polydispersity bimodal polyethylene products have important applications in areas such as thermoforming and blow molding. To produce this product, several reactors in series may be utilized. By suitably adjusting the temperature and concentration of chain transfer agent (*i.e.* hydrogen) in each reactor, a bimodal product can be obtained [1–4]. The molecular mass distribution of the final product may be regulated by adjusting the relative amounts of polymer produced in each reactor by changing the residence time in each stage, using different reactor temperatures.

Several processes can be used for the production of bimodal polyethylene. Ethylene can be polymerized in a variety of environments, including liquid or gaseous reactors with little restriction. Slurry polymerization of ethylene in multiple stages of continuous stirred-tank reactors (CSTR) using heterogeneous Ziegler-Natta catalysts is a common process for the commercial production of high polydispersity bimodal polyethylene.

Simulation models are important tools for the development and optimization of polymerization processes because they can describe catalyst performance and polymer properties as a function of polymerization kinetics and process conditions [5–10]. As the polyolefin industry moves towards the production of resins with more complex microstructures, these models become essential for process understanding and product design. Fontes and Mendes [5] developed a complete dynamic model for continuous slurry ethylene polymerization reactor to predict the production rates as well as the number and mass molecular mass

averages of the final polymer. Khare *et al.* [6] used a polymerization process simulator to describe the steady-state operation of an industrial slurry reactor and analyze production rates and certain key molecular properties of the final polymer material [average molecular mass and polydispersity index (I_{PD})]. The model was able to simulate the transient operation of the polymerization plant so as to suggest modifications of the operation conditions in order to increase the polymer production rate. Antonio *et al.* [7] developed a comprehensive model for the ethylene/1-butene copolymerization in an industrial slurry polymerization reactor for linear low density polyethylene synthesis. The model was able to describe the dynamic evolution of the molecular mass averages, comonomer content, particle size averages, melt index, and density of the final polymer resin. Nipun and Sunil [8] developed a model of slurry polymerization of ethylene in a multi-stage CSTR to find the effect of stagewise variation of the partial pressure of ethylene and/or hydrogen on polymer polydispersity and rate of polymerization. Only single-site type catalyst was modeled in their work.

In this paper, a five-site comprehensive mathematical model has been developed to simulate the steady-state behavior of an industrial bimodal high-density polyethylene process. In particular, the model can not only predict the properties of the polymer that is produced in each reactor but also estimate the properties of the final product. The effects of catalyst flow rate, hydrogen and ethylene molar ratio, comonomer and ethylene molar ratio on the polymer molecular structure and properties were also investigated.

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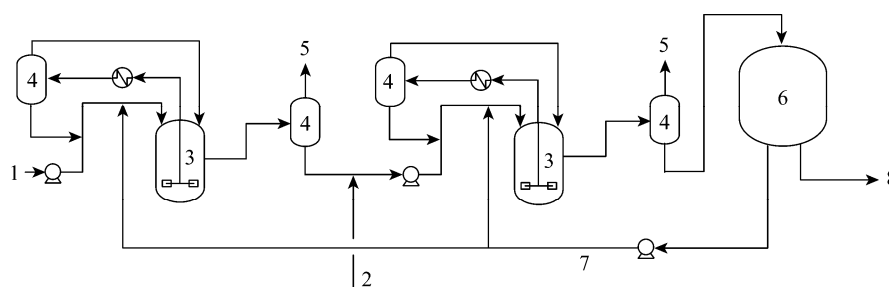


Figure 1 Process flow diagram for the series reactor

1—monomer, hydrogen and solvent; 2—monomer, comonomer, hydrogen and solvent; 3—CSTR; 4—flash drum; 5—volatile removal; 6—centrifugal separator; 7—solvent recycle; 8—oligomer separation and polymer wet cake drying

2 MODEL DEVELOPMENT

2.1 Modeled series reactor process

In Fig. 1, a schematic representation of an industrial slurry-phase olefin polymerization reactor series is illustrated. The process consists of two jacketed CSTRs, where gaseous monomer, comonomer and hydrogen diffuse in the liquid phase solvent (hexane) and react at the surface of solid catalyst micrograin, resulted in the formation of the polymer solids. Raw materials feed to the first CSTR and the slurry product is then pumped to the second CSTR, which also receives fresh monomer and solvent. The second reactor is not fed with fresh catalyst as the catalyst from the first reactor is sufficient to continue the polymerization process. The comonomer is 1-butene, and it enters as a feed stream to the second reactor only. The vapor outlet from each reactor undergoes cooling and recycles to the reactor inlet. The slurry stream leaving the second reactor enters a flash unit for removal of volatiles. The resulting stream enters a centrifugal separator, which removes and returns hexane to the reactor inlets.

The temperature in both the reactors needs not be the same. The hydrogen partial pressure is also different in two reactors, permitting the production of polymers with different average molecular mass in the two reactors. This results in a bimodal molecular mass distribution for the final polymer product. Typically, polyethylene of low molecular mass and high density are produced in the first reactor of the series, commonly operated at high hydrogen concentration. On the other hand, in the second reactor of the series, low hydrogen and high comonomer concentration result in the production of high molecular mass and low density polyethylene. Typically, industrial slurry-phase CSTRs operate at 80–85 °C, pressures of 0.2–0.9 MPa and a polymer-solids concentration of approximately 350 g polyethylene·(L hexane)⁻¹.

2.2 Kinetic modeling for Ziegler-Natta catalyst

Heterogeneous Ziegler-Natta catalyst is popular among polyolefin catalysts and used for the production over tens of million tons of polyethylene per year

[11, 12]. For heterogeneous Ziegler-Natta catalysis, even on the same catalyst particle, different active sites can have different propagation rate constants, which can give rise to very broad molecular mass distributions [13]. The mechanisms (Table 1) described here are similar to those outlined by Mcauley *et al.* [14], which has been used successfully to describe the behavior of industrial reactors. The absence of a site activation step in the proposed mechanism is explained by the assumption of the existence of a prepolymerization operational stage before the reactor feeding.

Table 1 Kinetic mechanism of ethylene/1-butene copolymerization over a Ziegler-Natta catalyst

Process	Equation
chain initiation	$P_0^k + M_i \xrightarrow{k_{ti}^k} P_{ti}^k$
chain propagation	$P_{n,i}^k + M_j \xrightarrow{k_{pj}^k} P_{n+1,j}^k$
chain transfer to hydrogen (H ₂)	$P_{n,i}^k + H_2 \xrightarrow{k_{th}^k} D_n^k + P_0^k$
spontaneous chain transfer	$P_{n,i}^k \xrightarrow{k_{ts}^k} D_n^k + P_0^k$
chain transfer to monomer	$P_{n,i}^k + M_j \xrightarrow{k_{tmj}^k} D_n^k + P_0^k$
deactivation	$P_{n,i}^k \xrightarrow{k_d^k} D_n^k + C_d^k$

2.3 Determination of kinetic parameters

We use the base set of kinetic parameters in the open literature as initial values in the model and then apply an iterative methodology to adjust them to match model predictions with plant data. Adjust the rate constants for chain propagation to match the conversions of monomer and comonomer. The primary reactions affecting monomer and comonomer conversions are those for monomer-monomer and monomer-comonomer propagations, respectively, due to the high monomer concentration relative to that of comonomer. Adjust the rate constant for spontaneous catalyst deactivation to match the production rate of high density polyethylene (HDPE). Adjust the rate constant for chain transfer to hydrogen and to monomer to match the number-average molecular mass produced at each site type. The detailed procedures were described in Ref. [6].

Gel permeation chromatography (GPC) was used to get the molecular mass distribution (MMD) of the polymer and a statistical algorithm was used to deconvolute the polymer MMD to determine the minimum number of catalyst site types that gives an accurate representation of the molecular mass distributions generated by Ziegler-Natta catalysts, as well as the mass fraction and number average molecular mass of polymer produced by each site type. The consideration of these site types, each with its respective reactivity, enables us to model the broad molecular mass distribution of the HDPE accurately. Four product grades (two parallel and two series configurations) were used for determining the kinetic parameters. Fig. 2 illustrates the MMD predicted for each site type, as well as a comparison of the prediction of the overall MMD with the experimental curve. The results indicate that a five-site model can accurately describe the molecular mass distribution of this particular sample. In Fig. 3, the effect of the number of different catalyst active sites on the percentage square error deviation of experimental and predicted MMD values is depicted. It is evident that as the number of catalyst active sites increases to five, the percentage deviation error decreases to a minimum value (*i.e.*, 0.009). Table 2 shows the results of F statistical test of the kinetic parameters. The multiple correlation index is greater than 0.9 and the F -statistic is more than ten times of the critical F -statistic in the confidence region of 99%. The final kinetic parameters for the five site model are listed in Table 3.

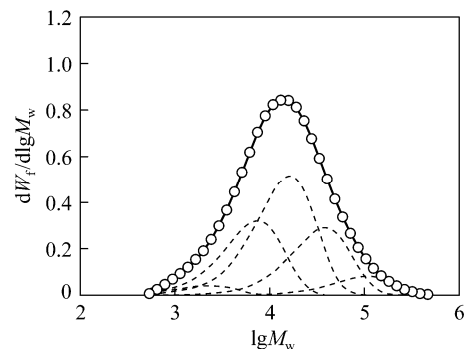


Figure 2 GPC deconvolution results for a representative HDPE sample from the parallel reactor configuration

○ plant data; M_w distribution for different sites;
— regressed curve

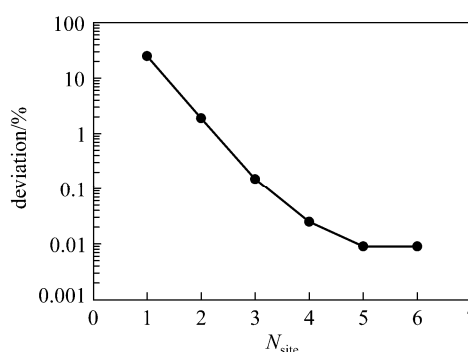


Figure 3 Effect of the number of catalyst active sites on the regressed MMD

Table 2 F statistical test of the kinetic parameters

Number of parameters	Number of degrees of freedom	Multiple correlation index	F -statistic	$10 \times F_{0.05}$	$10 \times F_{0.01}$
65	81	0.9333	51.3	15.0	17.7

Table 3 Numerical values of the kinetic rate constants (at 85 °C) for a five-site Ziegler-Natta catalyst

	Site 1	Site 2	Site 3	Site 4	Site 5
initial fraction of active sites $\mu_0^k(0)$	0.03312	0.2583	0.4158	0.234	0.06517
initiation $k_{oi}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	6478	6478	6478	6478	6478
propagation $k_{pi1}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	6478	6478	6478	6478	6478
$k_{pi2}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	605	605	605	605	605
$k_{p21}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	4983	4983	4983	4983	4983
$k_{p22}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	154	154	154	154	154
chain transfer $k_{th}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	137	41.1	19.1	8.17	3.02
$k_{tm11}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	0.00175	0.00175	0.00175	0.00175	0.00175
$k_{tm12}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	0.0045	0.0045	0.0045	0.0045	0.0045
$k_{tm21}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	0.00175	0.00175	0.00175	0.00175	0.00175
$k_{tm22}^k / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	0.0045	0.0045	0.0045	0.0045	0.0045
k_{ts}^k / s^{-1}	1.08×10^{-1}	4.05×10^{-2}	1.1×10^{-2}	3.09×10^{-3}	8.81×10^{-4}
deactivation k_d^k / s^{-1}	4.0×10^{-5}	4.0×10^{-5}	4.0×10^{-5}	4.0×10^{-5}	4.0×10^{-5}

2.4 CSTR model

The mass fraction of Ti in the catalyst is 4.8%, the total molar fraction of Ti available as active sites is equal to 40%. The rate of consumption of each monomer can be calculated by

$$R_{pi} = \left[\sum_{k=1}^{N_{\text{site}}} \sum_{j=1}^{N_{\text{mon}}} (k_{pji}^k \mu_{0,j}^k) \right] \frac{x_{\text{Ti}} w_{\text{Ti}}}{M_{w,\text{Ti}}} [M_i]_s M_{w,i} \quad (1)$$

The concentration of sites of type k having a chain ending in monomer of type 1 or 2, respectively, (*i.e.* a copolymer system) is given by

$$\mu_{0,1}^k = \mu_0^k \frac{k_{p21}^k [M_1]_s}{k_{p21}^k [M_1]_s + k_{p12}^k [M_2]_s} \quad (2)$$

$$\mu_{0,2}^k = \mu_0^k \frac{k_{p12}^k [M_2]_s}{k_{p12}^k [M_2]_s + k_{p21}^k [M_1]_s} \quad (3)$$

The concentration of active sites of type k can be found by

$$\frac{d\mu_0^k}{dt} = -k_d^k \mu_0^k \quad (4)$$

For a CSTR the residence-time distribution is

$$E(t) = \frac{1}{\tau} \exp(-t/\tau) \quad (5)$$

The mean catalyst residence time is calculated as a function of the desired solids content in the reactor, reactor volume, and catalyst feed rate according to [15]

$$\tau = \left[\frac{V_R}{\frac{w_{s,R}}{\rho_p} + \frac{1-w_{s,R}}{\rho_l}} \right] \frac{w_{s,R}}{(1+\bar{Y}_o)q_{\text{cat}}} \quad (6)$$

Yield of polymer is calculated by

$$Y = \sum_{i=1}^{N_{\text{mon}}} \int_0^t R_{pi} dt \quad (7)$$

The mean yield of homopolymer in the first reactor is calculated by

$$\bar{Y}_o^a = \int_0^\infty Y^a E(t^a) dt^a \quad (8)$$

The properties of the copolymer phase can be calculated in a similar fashion as the homopolymer phase. However, there are several additional concepts that must be included. Since the properties of the copolymer phase depend on the time the catalyst spends in the homopolymer reactor, an additional integral over homopolymer residence time, t^a , is necessary. Secondly, the kinetic rates of polymerization in the second reactor depend on the number and distribution of catalyst active sites available after the catalyst leaves the homopolymer stage. Thus, the final number of sites the catalyst possesses after the first stage (homopolymer reactor) must be the initial number of

sites for the second stage (copolymer reactor). Therefore, the mean yield of copolymer in the second reactor is calculated by a double integral:

$$\bar{Y}_o^b = \int_0^\infty E(t^a) \left(\int_0^\infty Y^b E(t^b) dt^b \right) dt^a \quad (9)$$

Under the conditions of linear addition of long polymer chains, live polymer termination by chain transfer or catalyst deactivation under constant reaction conditions (temperature and concentration), the instantaneous polymer chain length distribution at each site of a multisite catalyst is well described by the long-chain exponential approximation to the Schulz-Flory most-probable distribution [16]:

$$E(n^k) = \frac{n}{(\bar{n}^k)^2} \exp(-n/\bar{n}^k) \quad (10)$$

If the instantaneous chain length distribution is independent of residence-time, the outlet chain length distribution for a continuous reactor at steady-state is given by

$$E(n^i, o) = \frac{1}{\bar{Y}_o^i} \sum_{k=1}^{N_{\text{sites}}} [\bar{Y}_o^{k,i} E(n^{k,i})] \quad (i = a \text{ or } b) \quad (11)$$

in which “o” refers to the outlet. The outlet overall chain length distribution for a system composed of two reactors can be calculated as

$$E(n, o) = \frac{1}{(\bar{Y}_o^a + \bar{Y}_o^b)} \sum_{k=1}^{N_{\text{sites}}} [\bar{Y}_o^{k,a} E(n^{k,a}) + \bar{Y}_o^{k,b} E(n^{k,b})] \quad (12)$$

The overall molecular-mass distribution for a system composed of two reactors can be calculated as

$$E(M_w, o) = n E(n, o) \ln(10) \quad (13)$$

If the average chain lengths and compositions at each site are independent of residence-time and catalyst size, the number-average molecular mass of the polymer formed in each reactor can be calculated by

$$\frac{1}{M_n^i} = \frac{1}{\bar{Y}_o^i} \sum_{k=1}^{N_{\text{sites}}} \frac{\bar{Y}_o^{k,i}}{n^{k,i} M_{w,\text{mon}}^{k,i}} \quad (i = a \text{ or } b) \quad (14)$$

And the number-average molecular mass of the composite product after two reactors in series is

$$\frac{1}{M_n} = \frac{1}{(\bar{Y}_o^a + \bar{Y}_o^b)} \sum_{k=1}^{N_{\text{sites}}} \left[\frac{\bar{Y}_o^{k,a}}{n^{k,a} M_{w,\text{mon}}^{k,a}} + \frac{\bar{Y}_o^{k,b}}{n^{k,b} M_{w,\text{mon}}^{k,b}} \right] \quad (15)$$

If the mass-average chain length and compositions at each catalyst site is independent of residence time and catalyst size, the average mass molecular mass of the polymer formed in each reactor can be calculated according to the following equations:

$$\overline{M}_w^i = \frac{1}{Y_o^i} \sum_{k=1}^{N_{\text{sites}}} Y_o^{k,i} \overline{n}_w^{k,i} \overline{M}_{w,\text{mon}}^{k,i} \quad (i = a \text{ or } b) \quad (16)$$

And the mass-average molecular mass of the composite product after two reactors in series is

$$\overline{M}_w = \frac{1}{(\overline{Y}_o^a + \overline{Y}_o^b)} \sum_{k=1}^{N_{\text{sites}}} \left[\overline{Y}_o^{k,a} \overline{n}_w^{k,a} \overline{M}_{w,\text{mon}}^{k,a} + \overline{Y}_o^{k,b} \overline{n}_w^{k,b} \overline{M}_{w,\text{mon}}^{k,b} \right] \quad (17)$$

The polydispersity index is then calculated by [13]

$$I_{\text{PD}} = \frac{\overline{M}_w}{\overline{M}_n} \quad (18)$$

For long polymer chains the instantaneous copolymer composition is very narrow and distributed around its mean value. Therefore, for all intents and purposes, one may characterize the distribution by its mean value without significant loss of information. In this work we focus on the calculation of the ‘average copolymer composition’ in polymer particles. For a multisite Ziegler-Natta catalyst, we expect the composition of the copolymer formed at each polymerization site to remain invariant. The average copolymer composition (v_2^b = average comonomer mole fraction in the copolymer) in the second stage ‘b’ of a multistage process is calculated from the integrated yields of each monomer by

$$v_2^b = \frac{\overline{Y}_{o2}^b}{\overline{Y}_{o1}^b (M_{w2}/M_{w1}) + \overline{Y}_{o2}^b} \quad (19)$$

And the average comonomer mole fraction (v_2) in the composite product after two reactors in series is

$$v_2 = \frac{\overline{Y}_{o2}^b}{(\overline{Y}_o^a + \overline{Y}_o^b)(M_{w2}/M_{w1}) + \overline{Y}_{o2}^b} \quad (20)$$

The melt index (I_M) of polyethylene can be correlated to the mass-average molecular mass with a simple power-law function such as [7]

$$I_{Mi} = \alpha (\overline{M}_w^i)^{(-x)} \quad (i = a \text{ or } b) \quad (21)$$

where α and x are empirical constants. For bimodal polyethylene processes, the range of I_M is very large on the order of 10^{-3} – $10^3 \text{ g} \cdot (\text{10 min})^{-1}$. It is impossible to cover the whole range of I_M values with a single expression [17]. Thus, we use the same formula with different coefficients for calculating the I_M of the product produced in each reactor. The coefficients were acquired by multi-linear regression of steady-state plant data. The α and x values are 1.73×10^8 and 1.21 in the first reactor, while they are 1.63×10^{12} and 2.31 in the second reactor, respectively.

I_M of multimodal products can be obtained using a typical mixing rule with polymer mass fraction and

individual melt indexes for the polymer produced in each reactor as inputs [18]:

$$[I_M]^{-1/p} = w_a [I_{Ma}]^{-1/p} + w_b [I_{Mb}]^{-1/p} \quad (22)$$

where the exponent, p , is 3.5.

In the plant, analysis to measure the density is typically carried out only for pellets. For bimodal polyethylene processes, I_M of the polymer produced in each reactor was too high or too low for density measurements. So we only predict the density of the composite product after two reactors in series. The polymer density is calculated using the following equation [7],

$$\rho = (1 - 0.009165x_B^{0.148895}) \times [1.137247 - 0.014314 \ln(\overline{M}_w)] \quad (23)$$

where x_B is the 1-butene mole fraction and $\overline{M}_w$ is the mass-average molecular mass of the final polymer material.

3 RESULTS AND DISCUSSION

3.1 Model predictions vs. plant data

During the reaction, reaction rates are controlled by the concentration of reactants dissolved in the polymer surrounding the sites. Gaseous substances are sorbed only into the amorphous regions of the polymer [14]. For the present simulations, it is assumed that the amorphous polymer phase is in equilibrium with the liquid phase and that diffusional effects within the amorphous phase are negligible. Henry’s law was used to calculate the concentration of monomer, comonomer and hydrogen in the liquid phase, while Raoult’s law was applied to the solvent. The sorption factor η_i (solid-liquid interface) was assumed to be unity.

Base case operating conditions for production of bimodal polyethylene pipe resin M and film resin H in a series of reactors were taken from plant and shown in Table 4. The overall molecular mass distribution of the simulated products is compared to the data of plant in Figs. 4 and 5. Good agreement between our five-site model and the industrially produced bimodal polyethylene GPC curve is evident.

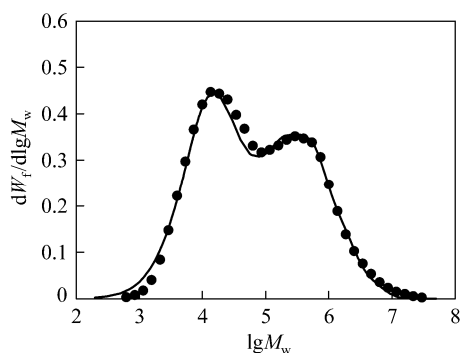
The other properties of the simulated products are compared to the data of plant in Tables 5 and 6. From a comparison of the model predictions and the industrial production rate, $\overline{M}_w$, $\overline{M}_n$, I_M and density data, it is apparent that the bulk properties of the polymer produced in the industrial reactor can largely be explained by the model.

3.2 Effect of the catalyst flow rate (residence time)

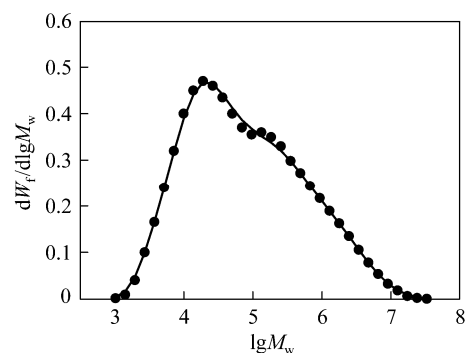
As the catalyst particle passes through the reactor

Table 4 Simulation conditions used for the base case bimodal polyethylene

Variable	Pipe resin M		Film resin H	
	First reactor	Second reactor	First reactor	Second reactor
temperature/°C	85	80	85	80
pressure/MPa	0.68	0.25	0.68	0.25
reactor volume/m ³	60	60	60	60
solids fraction/% (by mass)	32.4	32.4	32.4	32.4
n_{H_2}/n_{C_2}	8.0	0.20	8.0	0.30
n_{C_4}/n_{C_2}	0	0.012	0	0.020
catalyst flow rate/g·s ⁻¹	0.17	—	0.25	—
diameter of catalyst particle/μm	15.7	—	15.7	—
ethylene feed flow/kg·h ⁻¹	5300	5300	5300	5300
hydrogen feed flow/kg·h ⁻¹	6.10	0.18	6.8	0.26
solvent feed flow/kg·h ⁻¹	11052	11052	11052	11052
comonomer feed flow/kg·h ⁻¹		100	10	130
number-average chain length-site 1	40	1073	40	839
number-average chain length-site 2	132	3238	132	2586
number-average chain length-site 3	290	8653	290	6590
number-average chain length-site 4	684	22825	684	16868
number-average chain length-site 5	1855	64650	1855	47200

**Figure 4** Base case GPC curve fit of bimodal polyethylene pipe resin M for 2 CSTRs in series

● plant data (pipe resin M); — model prediction

**Figure 5** Base case GPC curve fit of bimodal polyethylene film resin H for 2 CSTRs in series

● plant data (film resin H); — model prediction

Table 5 Comparison of prediction results and plant data for pipe resin M

Item	First reactor		Second reactor		After two reactors	
	Plant data	Simulated value	Plant data	Simulated value	Plant data	Simulated value
mean residence time/h	2.500	2.498	1.250	1.241	—	—
production/t·h ⁻¹	5.300	5.296	5.400	5.366	10.7	10.6
$\overline{M}_w$	24850	24480	—	792082	395670	410786
$\overline{M}_n$	6300	6109	—	166165	11372	11826
I_{PD}	3.94	4.01	—	4.76	34.8	34.7
comonomer content/% (by mole)	—	—	—	0.94	0.46	0.46
$I_M/g \cdot (10 \text{ min})^{-1}$	820	846	—	0.039	0.36	0.36
density/g·cm ⁻³	—	—	—	—	0.9479	0.9483

Table 6 Comparison of prediction results and plant data for film resin H

Item	First reactor		Second reactor		After two reactors	
	Plant data	Simulated value	Plant data	Simulated value	Plant data	Simulated value
mean residence time/h	2.24	2.235	1.150	1.141	—	—
production/t·h ⁻¹	5.300	5.276	5.430	5.426	10.730	10.702
$\overline{M}_w$	21350	22430	—	581090	307850	301360
$\overline{M}_n$	5418	5617	—	143834	10652	9979
I_{PD}	3.94	3.99	—	4.04	28.9	30.2
comonomer content/% (by mole)	—	—	—	1.26	0.62	0.62
$I_M/\text{g} \cdot (10 \text{ min})^{-1}$	950	941	—	0.079	0.68	0.68
density/g·cm ⁻³	—	—	—	—	0.9485	0.9486

Table 7 Summary of simulation for the effect of catalyst flow rate

$q_{\text{cat}}/\text{g} \cdot \text{s}^{-1}$	Mean residence time/h		Mean yield (polyethylene)/g·(g cat.) ⁻¹		$\overline{M}_w$	$\overline{M}_n$	I_{PD}
	First reactor	Second reactor	First reactor	Second reactor			
0.01	16	10	22850	13986	315920	9606	32.9
0.05	5.2	2.7	14054	12713	389054	11231	34.6
0.10	3.4	1.7	10775	10505	403401	11617	34.7
0.17	2.5	1.24	8654	8768	410786	11826	34.7
0.25	2.0	0.98	7330	7585	414851	11944	34.7
0.50	1.4	0.66	5378	5720	420090	12100	34.7
1.00	0.94	0.45	3903	4230	423685	12209	34.7

system, monomer polymerizes causing polymer to encapsulate the catalyst which expands and grows into the resultant polymer particle. In this section, the two stage reactors were simulated at catalyst flow rate from 0.01 to 1.0 g·s⁻¹. The other operating conditions in Table 4 for production of bimodal polyethylene pipe resin M were kept the same in each stage, that is, we assume the mass fraction of solids in the solvent, polymerization temperature, pressure, hydrogen/ ethylene mole ratio and comonomer/ethylene mole ratio to be constant. As the catalyst flow rate increases, the flow rates of ethylene, hydrogen, commoner and solvent have to increase in order to maintain the reactor pressure and mass fraction of solids in the solvent. This leads to the reduction of the residence time. Table 7 shows the changes of catalyst mean residence time, catalyst mean yield, mass average molecular mass ($\overline{M}_w$), number average molecular mass ($\overline{M}_n$) and polydispersity with increasing the flow rate of catalyst. The effect of catalyst flow rate on the GPC curves was shown in Fig. 6. It can be seen that when $q_{\text{cat}} > 0.05$ g·s⁻¹, the polydispersity, $\overline{M}_w$, $\overline{M}_n$ and MMD of bimodal polyethylene changed little. On the other hand, increased catalyst flow rate results in lower catalyst mean residence time and catalyst mean yields.

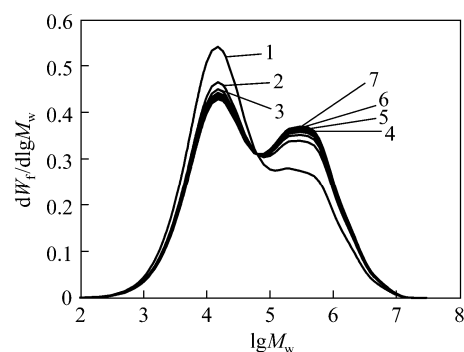


Figure 6 Effect of catalyst flow rate on the GPC curves of bimodal polyethylene produced in 2 CSTR series
catalyst flow rate/g·s⁻¹: 1—0.01; 2—0.05; 3—0.1; 4—0.17; 5—0.25; 6—0.5; 7—0.1

The reaction rate of polymerization is dependent on several parameters such as monomer concentration, temperature and active site concentration. It is apparent that as the catalyst flow rate increases, active site concentration increases and so does the polymerization rate. Since the kinetic rates of polymerization in the second reactor depend on the number and distribution of catalyst active sites available after the catalyst leaves the homopolymer stage, the properties of the copolymer phase depend on the time the catalyst spends in the homopolymer reactor. The catalyst mean

Table 8 Effect of hydrogen to ethylene molar ratio on the molecular mass, I_{PD} and I_M of polyethylene produced after two reactors in series

Number	Hydrogen/ethylene (molar ratio)		$\overline{M}_w$	$\overline{M}_n$	I_{PD}	I_M
	First reactor	Second reactor				
1	4	0.25	364789	22890	15.9	0.43
2	6	0.25	356455	15640	22.8	0.45
3	8	0.20	408281	11785	34.6	0.36
4	10	0.15	496976	9738	51.0	0.24

residence time in the first reactor for catalyst flow rate of $0.01 \text{ g}\cdot\text{s}^{-1}$ is 3 times as long as that for catalyst flow rate of $0.05 \text{ g}\cdot\text{s}^{-1}$, the effects of catalyst deactivation may be important, which can cause the change of number and distribution of catalyst active site. As the mean residence-time is progressively decreased (total flow rate increases), catalyst deactivation becomes less important and the polydispersity changes little. However, when catalyst feed rate is changed from 0.01 to $1.0 \text{ g}\cdot\text{s}^{-1}$, the catalyst mean yield ratio of the first reactor to the second reactor decreases from 1.63 to 0.92. It means that the mass fraction of the low molecular mass homopolymer within the final product after two reactors in series decreases, while the mass fraction of the high molecular mass copolymer increases. This causes the slow increase of $\overline{M}_w$ and change of GPC curves of the final product.

3.3 Effect of the hydrogen inflow rate

It is well known that, in Z-N catalytic olefin polymerization, the hydrogen concentration is employed to control the melt index of polyolefin, which is related to its molecular mass [19]. In this section, the two stage reactors were simulated at hydrogen/ethylene molar ratio in the first and second reactors of the series changed from 4.0 to 10 and from 0.15 to 0.25, respectively. The other operating conditions in Table 4 for production of bimodal polyethylene pipe resin M were kept the same in each stage, that is, we assume the mass fraction of solids in the solvent, polymerization temperature, pressure, catalyst flow rate and comonomer/ethylene molar ratio to be constant. We also assume that the mean yield of homopolymer in the first reactor is equal to that of copolymer in the second reactor. The effect of hydrogen to ethylene molar flow rate ratio on the molecular mass, I_{PD} , I_M and MMD of polyethylene produced after two reactors was shown in Table 8 and Fig. 7.

As hydrogen is the chain transfer agent, the average molecular mass decreases with the increase of hydrogen concentration. However, when hydrogen/ethylene molar flowrate ratio increases in the first reactor and decreases in the second reactor at the same

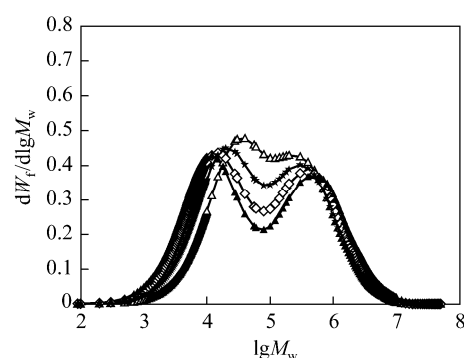


Figure 7 Effect of hydrogen to ethylene mol flow rate ratio on bimodal polyethylene produced in 2 CSTR series
 $\triangle$ 1st reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 4$; 2nd reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 0.25$; $\star$ 1st reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 6$; 2nd reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 0.25$; $\circ$ 1st reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 8$; 2nd reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 0.20$; $\blacktriangle$ 1st reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 10$; 2nd reactor, $\text{H}_2/\text{C}_2\text{H}_4 = 0.15$

time, $\overline{M}_w$ of bimodal polyethylene increases, while $\overline{M}_n$ and I_M of bimodal polyethylene decrease. It demonstrates that the mass average molecular mass and melt index of copolymer produced in the second reactor plays a significant role on the mass average molecular mass and melt index of bimodal polyethylene and the number average molecular mass of homopolymer produced in the first reactor makes contribution to the number average molecular mass of bimodal polyethylene. Additionally, when hydrogen/ethylene molar flowrate ratio increases in the first reactor and remains unchanged in the second reactor, $\overline{M}_w$ and $\overline{M}_n$ of bimodal polyethylene decrease, and I_M of bimodal polyethylene increases due to an intensification of hydrogen chain transfer. The higher the hydrogen/ethylene mol ratio of the first reactor to the second reactor is, the broader is the MMD of bimodal polyethylene.

3.3 Effect of the comonomer inflow rate

Another simulation is carried out varying the

Table 9 Summary of simulation for the effect of comonomer flow rate

1-butene/ethylene (molar ratio)	$\overline{M}_w^b$	$\overline{M}_n^b$	I_{PD}^b	$v_2^b/\%$ (by mole)	$v_1^b/\%$ (by mole)	$\rho/\text{g}\cdot\text{cm}^{-3}$
0.00326	862579	183157	4.71	0.25	0.13	0.9552
0.00977	836791	176871	4.73	0.77	0.39	0.9492
0.0195	810657	170571	4.75	1.5	0.76	0.9436
0.0326	798611	167710	4.76	2.48	1.25	0.9378
0.0651	790372	165749	4.77	4.76	2.43	0.9277
0.0977	784716	164399	4.77	6.89	3.55	0.9201

1-butene inlet concentration. The results are depicted in Table 9. It was observed that the average 1-butene mole fraction in the copolymer produced in the second reactor and in the composite product increased with higher 1-butene to ethylene molar ratio (*i.e.*, the comonomer concentration increases). As expected, polyethylene density decreases with the addition of 1-butene. In industrial practice, this is the main variable manipulated to control polymer density. Increasing 1-butene concentration in the second reactor gives higher 1-butene incorporation in the copolymer. Also the copolymer molecular mass is seen to be decreased by increasing 1-butene concentration. The comonomer enhances transfer reaction rate. The small effect of the comonomer concentration on the polydispersity index can be attributed to the simultaneous reduction in both mass-average molecular mass and number-average molecular mass.

4 CONCLUSIONS

A five-site comprehensive mathematical simulation model for the polymerization of ethylene with multiple site coordination catalysts at steady state in a process with two CSTRs operating in series has been developed. The predictions for molecular mass and polydispersity, melt index, density and average comonomer incorporation are in good agreement with plant data. On this basis, the effects of catalyst flow rate, ethylene and hydrogen mol ratio and comonomer inflow rate on the molecular mass, polydispersity and polymer properties such as melt index and density were simulated using this model.

(1) As the catalyst flow rate increases, catalyst mean residence time and catalyst mean yield decrease, $\overline{M}_w$ and $\overline{M}_n$ increase, the mass fraction of the low molecular mass homopolymer decreases, while the mass fraction of the high molecular mass copolymer increases.

(2) When hydrogen/ethylene molar flow rate ratio increases in the first reactor and decreases in the second reactor at the same time, $\overline{M}_w$ of bimodal polyethylene increases, while $\overline{M}_n$ and I_M of bimodal

polyethylene decrease. When hydrogen/ethylene molar flow rate ratio increases in the first reactor and doesn't change in the second reactor, $\overline{M}_w$ and $\overline{M}_n$ of bimodal polyethylene decrease, and I_M of bimodal polyethylene increases. The higher the hydrogen/ethylene molar ratio of the first reactor to the second reactor is, the broader is the MWD of bimodal polyethylene.

(3) The copolymer molecular mass is decreased with increasing 1-butene concentration. The addition of 1-butene results in the decrease of polyethylene density.

NOMENCLATURE

C_d	normalized concentration of dead sites
D_n^k	normalized concentration of dead chains of length n at site k
E	generic distribution representation
I_M	melt index, $\text{g}\cdot(10\text{ min})^{-1}$
k	rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$[M_i]_s$	sorbed concentration of monomer i at the catalyst sites, $\text{mol}\cdot\text{L}^{-1}$
M_w	molecular mass, $\text{g}\cdot\text{mol}^{-1}$
$\overline{M}$	average molecular mass, $\text{g}\cdot\text{mol}^{-1}$
N_{site}	number of sites
N_{mon}	number of monomers
n	chain length
$\overline{n}^k$	number-average chain length at site k
$\overline{n}_w^k$	mass-average chain length at site k
P_0^k	normalized concentration of vacant sites of type k
$P_{n,j}^k$	normalized concentration of sites of type k and chain length n ending in monomer j
q_{cat}	catalyst mass flow rate to reactor, $\text{g}\cdot\text{s}^{-1}$
R_{Pi}	kinetic rate of mass consumption of monomer i , $\text{g}\cdot(\text{g cat.})^{-1}\cdot\text{s}^{-1}$
t	chronological time, s
V_R	reactor volume, m^3
w_F	mass fraction of polymer with different molecular mass
w_{Ti}	mass fraction of titanium in the catalyst
$w_{s,R}$	solids mass fraction in reactor
w_i	polymer mass fraction produced in reactor i
x_{Ti}	fraction of titanium atoms that are catalyst sites, dimensionless
Y	polymer polyethylene yield, $\text{g}\cdot(\text{g cat.})^{-1}$
$\overline{Y}_0$	mean yield of polymer polyethylene, $\text{g}\cdot(\text{g cat.})^{-1}$
$\overline{Y}_{01}, \overline{Y}_{02}$	yield of monomer 1,2 in polymer
μ_0^k	normalized zeroth moment of all polymer chains at site k
v_2	average comonomer content in polymer (molar fraction)

ρ	density of polymer produced after two reactors in series, g·cm ⁻³
ρ_l	liquid density in the reactor, kg·m ⁻³
ρ_p	polymer density in the reactor, kg·m ⁻³
τ	catalyst mean residence time, s

Superscripts

a	first reactor
b	second reactor
k	site type

Subscripts

d	deactivation
i or j	monomer type
n	number-average
p	propagation
Ti	titanium
ts	spontaneous chain-transfer
th	chain transfer to hydrogen
tm	chain transfer to monomer
w	mass-average
0	initiation
1	ethylene
2	1-butene

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