Fluidized Bed Polyethylene Reactor Modeling in Condensed Mode Operation

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Summary: Modeling of fluidized bed reactor for polyethylene production in the condensed mode operation is proposed in this paper. A two-phase model including the emulsion and bubble phases with the constant bubble size is employed to describe hydrodynamic behavior of the reactor. The kinetics of Ziegler-Natta polymerization is also modeled with a two active site model. The phase behavior and solubility of low molecular weight components in polyethylene are estimated with the Sanchez-Lacombe equation of state. The validation of the model is carried out with industrial data for an ethylene and 1-butene copolymerization with the isopentane as a condensable component. The simulation results are in good agreement with industrial data. The model is also used to study quantitatively the effect of the inlet stream temperature to the reactor and isopentane concentration in the reactor on the production rate. For instance, in a typical process, when the inlet stream temperature changes 10 °C, the production rate will alter about 40%. Furthermore, the change of the isopentane concentration around 1 mole percentage leads to a variation of production rate about 14%.

Keywords: condensed mode; fluidized bed reactor; modeling; polyethylene

Introduction

A large portion of polyethylene is produced by the gas-phase process in the fluidized bed reactors (FBR). This process was commercialized for the first time in the late 1970's. In a typical process, as shown in Figure 1, a gas stream comprises ethylene, co-monomer, hydrogen and nitrogen (inert gas) is fed to the reactor through a distributor. This gas stream provides the fluidization and heat transfer media as well as the supply of reactants for the growing polymer particles. Catalyst (or pre-polymer) particles are introduced to the reactor above the distributor. The fluidized particles disengage from the reactant gas in the expanded top section of the reactor. The unreacted gas mixture is removed from the top section of the reactor and passed through a cooler and compressor to remove the heat of reaction and compensate pressure drop. Then, it is combined with fresh feed and recycled to the reactor.[1]

Because of the highly exothermic nature of olefin polymerization reactions, heat removal from the reaction zone is one of the controlling factors, which limits the production rate.[2–4] The most common means of heat removal is to compress and cool the recycle gas mixture. In polyethylene reaction systems, it is possible to operate in two different modes: dry or non-condensed and condensed mode operations. In the condensed mode operation, a portion of the recycle gas mixture is condensed in the heat exchanger and the resulting liquid/vapor mixture is then returned to the reactor. As

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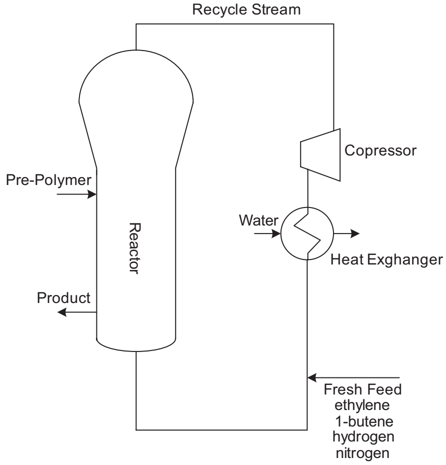

Figure 1.
Schematic of industrial fluidized bed polyethylene reactor.

a result, the cooling capacity of the recycle stream is increased because of lower temperature of the entering recycle stream and the latent heat of vaporization of condensed liquid entrained in the recycle stream. It has been shown that the heat-removal rate can be further increased by adding non-polymerizing condensable materials to raise the dew point of the recycle gas stream.[5,6] Although several models have been proposed to describe the performance of the fluidized bed reactor for olefin polymerization in the literature,[7–12] however, in all of these cases only the dry mode operation has been considered.

The aim of this research work is presenting a model for olefin polymerization in the fluidized bed reactor operating in the condensed mode to predict production capacity increasing relative to alter the operating conditions such as the temperature of inlet stream to the reactor, concentration of condensable component in the reactor and so on.

The Model Development

For modeling any reactor three aspects at least should be considered: the mechanism and kinetics of the reaction, the hydrodynamic of the reactor and the fluid phase equilibrium in the reactor. In the proposed models in the literature for the fluidized bed reactors in the dry mode operation, the most attention has been on the kinetics[13,14] and particularly on the hydrodynamic and flow regimes of the gas and powder phases in the reactor.[7–12] However, the fluid phase equilibrium has not been studied extensively. Almost in all of these proposed models, Henry's law has been assumed to consider solubility of low molecular weight components such as ethylene and hydrogen in the polyethylene powders. Actually, when higher molecular weight components such as 1-butene, 1-hexene and n-pentane are in the gas composition, solubility of the components is enhanced and Henry's law can not correctly estimate their concentration in the polymer particle.[15] This is more important in the case of FBR operating in the condensed mode. Therefore the other methods such as equations of state or activity coefficient models should be applied. In the present study, the Sanchez-Lacomb equation of state for polymer systems has been employed. In the subsequent parts, equations and relations for modeling of the kinetics, hydrodynamic and phase equilibrium aspects have been provided.

The following are the main assumptions were made to formulate the present mathematical model of the reactor:

- Two active sites model is considered in the polymerization kinetics.
- Monomers are consumed mainly in the propagation reactions (long chain approximation).
- Mass and heat transfer resistance in the polymer particles are negligible (i.e., low to moderate catalyst activity).[16]
- The fluid bed consists of the emulsion and bubble phases.
- The polymerization occurs only in the emulsion phase.
- The emulsion phase is perfectly mixed and in the minimum fluidization condition.
- The bubble phase is assumed as plug flow with constant bubble diameter.

- The liquid fraction of the inlet stream to the reactor is vaporized immediately.
- The radial concentration and temperature gradients in the reactor are negligible.
- No elutriation of solids occurs.
- A mean size is assumed for the polymer particles throughout the bed.

Kinetics Modeling

The considered mechanism to describe the copolymerization kinetics of ethylene and α-olefins are presented in Table 1.[9,13,14] This mechanism consists of the active site formation, initiation, propagation, chain transfer (to hydrogen, monomer(s), spontaneous) and active site deactivation (spontaneous) reactions. Moreover, to describe broadening molecular weight distribution and copolymer composition distribution, which commonly observed in the Ziegler-Natta polymerization, two active sites have been implemented in this model. It is also assumed that the polymerization kinetics in the condensed mode operation is the same as in the dry mode operation. It means that adding condensable components such as n-pentane to the reaction gas do not alter the kinetics of reaction.

To simplify the kinetic rate expressions the pseudokinetic rate constants were used instead of the actual kinetic constants.[13,14] By assuming the long chain approximation, that is, the monomer(s) mainly consumed in the propagation reactions, one can obtain the rate of polymerization as follows:

$$R_P = \sum_{i=1}^{\mathrm{Nm}} \sum_{j=1}^{\mathrm{Ns}} R_{p,i} = \sum_{i=1}^{\mathrm{Nm}} [M_i] \sum_{j=1}^{\mathrm{Ns}} Y_0^j k_{p,Ti}^j \quad (1)$$

where Nm and Ns are the number of monomers and types of active sites, respectively.

Table 1.
Considered mechanisms for ethylene and α-olefins copolymerization with Z-N catalysts

Description	Reaction
Site Activation	$C^j + Al \xrightarrow{k_a^j} P_0^j$
Initiation reaction with monomers	$P_0^j + M_i \xrightarrow{k_{0,i}^j} P_{1,i}^j$
Propagation	$P_{r,i}^j + M_k \xrightarrow{k_{p,ik}^j} P_{r+1,k}^j$
Transfer to monomer	$P_{r,i}^j + M_k \xrightarrow{k_{tm,ik}^j} P_{1,k}^j + D_r^j$
Transfer to hydrogen	$P_{r,i}^j + H_2 \xrightarrow{k_{th,i}^j} P_0^j + D_r^j$
Spontaneous transfer	$P_{r,i}^j \xrightarrow{k_{tsp,i}^j} P_0^j + D_r^j$
Spontaneous Deactivation	$P_{r,i}^j \xrightarrow{k_{dsp,i}^j} C_d^j + D_r^j$

The method of moment was applied to model of the copolymerization kinetics in this study. Using this method the resulting system of macromolecular differential balance equations is reduced into a lower-order system, which can easily be solved. Constructing the balance equations for the live and dead polymer chains, one can derive balance equations for zero, first and second moments of live and dead polymer chains. Solving these equations that needs determination of the components concentration in the active sites or polymer phase, the number and weight average molecular weights are calculated.[9,14]

Hydrodynamics Modeling

The most of researchers have employed the two-phase concept for modeling the gas-phase ethylene polymerization in the fluidized bed reactors.[7–12] Some of them[7–10] have employed the simple two-phase model, which assumes all of the excess gas required for the minimum fluidization passes through the bed as solid free bubbles, whereas the emulsion stays at the minimum fluidization conditions. Others[11,12] were employed the dynamic two-phase model, which takes into account that the emulsion phase does not remain at minimum fluidization condition beyond the minimum fluidization velocity of the gas stream and the bubbles may contain the polymer particles.

In the present study, we applied the simple two-phase model. Based on the mentioned above assumptions, monomer(s) and hydrogen mass balances and energy balance for a single bubble as well as mass balance for the emulsion phase have the same basis with what presented by Mcauley et al.[8] However, the energy balance for the emulsion phase because of vaporization of liquid phase, is different and is as the following equation:

$$
\begin{aligned}
&\frac{\rho_P(1-\varepsilon_{mf})}{\varepsilon_{mf}} C_{PP}\frac{dT_e}{dt} + \sum_{i=1}^{Nm}[M_i]_e C_{P,i}\frac{dT_e}{dt} + (T_e - T_{ref})\sum_{i=1}^{Nm} C_{P,i}\frac{d[M_i]_e}{dt} \\
&= \frac{U_e}{H}\sum_{i=1}^{Nm}[M_i]_{0e}^{v} C_{P,i}^{v}(T_0 - T_{ref}) + \frac{U_e}{H}\sum_{i=1}^{Nm}[M_i]_{0e}^{l} C_{P,i}^{l}(T_0 - T_{ref}) - \frac{U_e}{H}\sum_{i=1}^{Nm}[M_i]_{0e}^{l}\Delta H_i^{vap} \\
&\quad - \frac{U_e}{H}\sum_{i=1}^{Nm}[M_i]_e C_{P,i}(T_e - T_{ref}) - \frac{H_{be}\delta}{(1-\delta)\varepsilon_{mf}}(T_e - \overline{T}_b) + \frac{\sum\limits_{i=1}^{Nm}(-\Delta H r_i R_{P,i})}{AH(1-\delta)\varepsilon_{mf}} \\
&\quad - \frac{Q}{AH(1-\delta)}\sum_{i=1}^{Nm}[M_i]_e C_{P,i}(T_e - T_{ref}) - \frac{Q(1-\varepsilon_{mf})}{AH(1-\delta)\varepsilon_{mf}}\rho_P C_{PP}(T_e - T_{ref}) \\
&\quad - \frac{\pi D H}{AH(1-\delta)\varepsilon_{mf}}(T_e - T_\infty) \qquad (2)
\end{aligned}
$$

The first and second terms in the left side of this equation are accumulated energy for the polymeric and gas species because of temperature variation in the emulsion phase, respectively. Correspondingly, the third term is related to the mass variation. In the other side of the equation, the first and second terms are the inflow of enthalpy through vapor and liquid fraction of the inlet stream to the reactor. The third term is the removed heat from the emulsion phase as a result of vaporization of the liquid fraction in the inlet stream. The fourth term is the outflow of energy by the gas stream from the top of the reactor. The fifth and sixth terms are the heat transfer rate from the emulsion phase to the bubble phase and the generated heat in the emulsion phase through the polymerization. The seventh and eighth terms are also outflow of enthalpy from the reactor by the gas and polymer species in the production stream, respectively. The last term is also the convection heat transfer from the reactor to the environment.

To solve the model equations, one has to specify the values of concentrations and temperature of the materials flow entering to the reactor as initial conditions. These variables are known or assumed at the inlet of the reactor:

$$[\mathrm{M_i}]_{\mathrm{b,(0)}} = [\mathrm{M_i}]_{\mathrm{e,(0)}} = [\mathrm{M_i}]_0 \qquad (3)$$

$$\mathrm{T_{b,(0)}} = \mathrm{T_{e,(0)}} = \mathrm{T_0} \qquad (4)$$

Fluid Phase Equilibrium

Two equations of state were employed in this modeling. The first one is the Peng-Robinson equation of state for flash calculations to evaluate the liquid fraction as well as the gas and liquid composition in the inlet stream to the reactor.[17] The second one is the Sanchez-Lacombe equation of state for calculation of the concentration of monomers, hydrogen and condensable components in the polymer particles using the concentration of the components in the gas phase.

The Sanchez-Lacombe equation of state, which is a lattice-fluid model and applicable for a fluid mixture in any phases (gas, liquid or polymer), is expressed as:[18,19]

$$\tilde{\rho}^2+\tilde{P}+\tilde{T}\left[\ln(1-\tilde{\rho})+\left(1-\frac{1}{r}\right)\tilde{\rho}\right]=0 \qquad (5)$$

in which $\tilde{T}, \tilde{P}$ and $\tilde{\rho}$ are the reduced temperature, pressure and density of fluid mixture, respectively and are defined as:

$$\tilde{T}=\frac{T}{T*} \quad \tilde{P}=\frac{P}{P*} \quad \tilde{\rho}=\frac{\rho}{\rho*} \qquad (6)$$

T^*, P^* and ρ^* parameters can be calculated by the following relations:

$$T^*=\frac{\varepsilon*}{k} P^*=\frac{\varepsilon^*}{\nu^*} \rho^*=\frac{M}{r\nu^*} \qquad (7)$$

The following mixing rules can also be employed to relate mixture characteristics parameters of the model to their values of the pure components:[20]

$$\varepsilon*=\frac{1}{\nu*}\sum_i\sum_k \phi_i\phi_k\varepsilon_{ik}^*\nu_{ik}^* \qquad (8)$$

$$\nu*=\sum_i\sum_k \phi_i\phi_k\nu_{ik}^* \qquad (9)$$

$$\frac{1}{r}=\sum_i\frac{\phi_i}{r_i} \qquad (10)$$

$$\phi_i=\frac{\dfrac{w_i}{\rho_i^*\nu_i^*}}{\sum_k\left(\dfrac{w_k}{\rho_k^*\nu_k^*}\right)} \qquad (11)$$

The cross parameters are also defined by

$$\nu_{ik}^*=\frac{1}{2}[\nu_{ii}^*+\nu_{kk}^*](1-n_{ik}) \qquad (12)$$

$$\varepsilon_{ik}^*=\sqrt{\varepsilon_{ii}^*+\varepsilon_{kk}^*}](1-l_{ik}) \qquad (13)$$

Using the Sanchez-Lacombe equation of state, the following general expression for the chemical potential of the ith component in a multicomponent system can be derived:[20]

$$\begin{aligned}\frac{\mu_i(T,P,x_i)}{RT}&=\left(\ln\phi_i+1-\frac{r_i}{r}\right)+\ln\tilde{\rho}+r_i\left[-\frac{\tilde{\rho}}{\tilde{T}}+\left(\frac{1}{\tilde{\rho}}-1\right)\ln(1-\tilde{\rho})+\frac{\tilde{P}\tilde{\nu}}{\tilde{T}}\right]\\&+\frac{Z}{r}\left\{\frac{1}{\nu*}\left[2r_i\left(-\nu^*+\sum\phi_k\nu_{ik}^*\right)\right]\right\}-\frac{\tilde{\rho}}{Tp\tilde{t}}\left\{\frac{1}{\varepsilon*\nu*}\left[2r_i\left(-\varepsilon^*\nu^*+\sum\phi_k\varepsilon_{ik}^*\nu_{ik}^*\right)\right]\right.\\&\left.-\left\{\frac{1}{\nu*}\left[2r_i\left(-\nu^*+\sum\phi_k\nu_{ik}^*\right)\right]\right\}\right\}\end{aligned} \qquad (14)$$

where the compressibility factor, Z, is calculated from the equation of state as following relation:

$$\begin{aligned}Z&=\frac{P\nu}{RT}=\frac{\tilde{P}\tilde{\nu}}{\tilde{T}}r\\&=r\left[-\frac{1}{\tilde{\rho}}\ln(1-\tilde{\rho})-\left(1-\frac{1}{r}\right)-\frac{\tilde{\rho}}{\tilde{T}}\right]\end{aligned} \qquad (15)$$

At a given temperature and pressure, the criterion for equilibrium in the coexisting phases is that the chemical potential of each component should be equal in all of the phases. In our system, the phases include gas and polymer phases and following relation should be valid:

$$\begin{aligned}&\mu_i^g(T,P,\phi_1^g,\phi_2^g,\ldots)\\&\quad=\mu_i^P(T,P,\phi_1^p,\phi_2^p,\ldots)\end{aligned} \qquad (16)$$

With given the reactants concentration and temperature in the gas phase, which are calculated by hydrodynamic model, and applying Equation 25 the concentration of the components in the polymeric phase can be achieved and used in the kinetic model to calculate the production rate and molecular properties of the produced polymer.

Results and Discussion

The developed model was validated based on patent data.[21] These data, as shown in Table 2, are referred to the operating conditions of a fluidized bed polyethylene reactor to produce a copolymer containing

Table 2.
The operating conditions and input data for the simulation of fluidized bed polyethylene reactor in the condensed mode[21]

Parameter Description (Unit)	Notation	Case 1	Case 2	Case 3
Reactor Temperature (°C)	T	85.1	84.5	84.2
Reactor Pressure(KPag)	P	2173.3	2173.3	2172.5
Reactor Bed Height (m)	H	13.7	13.6	13.6
Reactor Diameter (m)	D	4.4	4.4	4.4
Superficial Gas Velocity (m/s)	U_o	0.53	0.53	0.54
Reactor Inlet Temperature (°C)	T_{in}	47.9	48.7	52.9
Polymer Average Particle Size (μ)	d_p	737	749	775
Gas Density(kg/m^3)	ρ_g	30.2	30.9	31.9
Reactor Gas Composition (mole %)				
Ethylene		53.2	52.6	52.1
1-Butene		19.8	19.71	19.71
Hydrogen		10.2	10.3	9.9
Ethane		1.2	1.1	1.1
Nitrogen		8.0	7.3	6.3
Isopentane		9.5	10.7	12.2

ethylene and 1-butene in the condensed mode using isopentane as a condensable component in three different levels of isopentane in the recycle gas stream outlet from the FBR (9.5, 10.7 and 12.2 mol%). For simulation of these cases, input data includes the pressure, temperature, bed height, diameter and superficial gas velocity of the reactor as well as the reactant gas composition in the reactor that have been considered equivalent with the composition of the recycle gas stream. The temperature of the inlet stream to the reactor is also defined as input data. The polymer production rate, composition of the inlet stream to the reactor and weight percentage of liquid therein as well as the molecular properties of polymer (Mn, Mw, comonomer content) are the simulation results. Since the catalyst feed rate has not been provided in the patent, an initial guess of its amount was used in the simulation and its final value was adjusted to meet the temperature of the reactor. The catalyst used is a complex of tetrahydrofuran, magnesium chloride and titanium chloride reduced with diethyl aluminum and tri-n-hexyl aluminum chloride impregnated on triethyl aluminum treated silicon dioxide. The co-catalyst is triethyl aluminum.[21] The active site concentration for this catalyst, which needs for the simulation, was assumed to be 0.001 moles active site per gram of catalyst, a normal value for this type of catalysts.

The kinetic rate constants for the model are derived from the literature and presented in Table 3.[14,15,22] The correlations and parameters used in hydrodynamic modeling are also derived from literature.[23–26] Furthermore, Table 4–6 show the characteristic parameters of the Sanchez-Lacombe equation of state.[18,19,27,28]

The simulation results and their corresponding patent data including the production rate, weight percentage of liquid in the inlet stream to the reactor as well as the melt flow index (MFI) and density of polyethylene resins are shown in Table 7. These results show that the model provides good agreement with the patent data. The melt flow index and density of polyethylene are regularly measured and reported in industry whereas the molecular weight and comonomer content can be calculated from by the simulation. To relate these properties the following equations were applied:[14]

$$MFI = 3.269 \times 10^{17} \overline{M}_w^{(-3.47)} \tag{17}$$

$$\rho_P = 0.966 - 0.02386(C_x)^{0.514} \tag{18}$$

where C_x is the mole percentage of 1-butene in the polymer and is calculated as the ratio of the 1-butene consumption rate to the total ethylene and 1-butene

Table 3.
The rate constants of the copolymerization of ethylene and 1-butene with a Ziegler-Natta catalyst[14,15,22]

Reaction	Unit	Site Type 1	Site Type 2	Reaction	Unit	Site Type 1	Site Type 2
Formation				Transfer			
k_a^j	s^{-1}	100	100	$k_{tm,11}^j$	m^3/kmol.s	0.0021	0.0021
E_a^j	kcal/mol	9	9	$k_{tm,12}^j$	m^3/kmol.s	0.006	0.11
				$k_{tm,21}^j$	m^3/kmol.s	0.0021	0.001
Initiation				$k_{tm,22}^j$	m^3/kmol.s	0.006	0.11
$k_{0,1}^j$	m^3/kmol.s	1	1	$E_{tm,ij}^j$	kcal/mol	8	8
$E_{0,1}^j$	kcal/mol	9	9	$k_{th,i}^j$	m^3/kmol.s	0.088	0.37
$k_{0,2}^j$	m^3/kmol.s	0.14	0.14	$E_{th,i}^j$	kcal/mols^{-1}	8	8
$E_{0,2}^j$	kcal/mol	9	9	$k_{tsp,i}^j$		0.0001	0.0001
				$E_{tsp,i}^j$	kcal/mol	8	8
Propagation				Spontaneous Deactivation			
k_{p11}^j	m^3/kmol.s	85	85				
E_{p11}^j	kcal/mol	9	9	k_{dsp}^j	s^{-1}	0.0001	0.0001
k_{p12}^j	m^3/kmol.s	2	15	E_{dsp}^j	kcal/mol	8	8
E_{p12}^j	kcal/mol	9	9				
k_{p21}^j	m^3/kmol.s	64	64				
E_{p21}^j	kcal/mol	9	9				
k_{p22}^j	m^3/kmol.s	1.5	6.2				
E_{p22}^j	kcal/mol	9	9				

consumption rates in the reactor.$\overline{M}_w$ is also the weight average of molecular weight of the copolymer.

Furthermore, the model was used to study quantitatively the effect of the inlet stream temperature to the reactor and isopentane concentration in the reactor on the production rate. These variables were changed around their values for case 1 studied in Table 2. The effect of inlet stream temperature on the production rate is shown in Figure 2. As can be seen, the production rate increases as the reactor inlet temperature decreases and in turn the

Table 4.
The pure component parameters for the Sanchez-Lacombe equation of state[19,28]

Component	T^* (K)	P^* (bar)	ρ^* (kg/m^3)
Catalyst	925	4000	867
Cocatalyst	925	4000	867
Ethylene	333	2400	631
1-Butene	397	2900	672
Hydrogen	46	1000	143
Nitrogen	141	1786	923
Ethane	315	3273	640
Isopentane	424	3040	765
Ethylene/1-butene copolymer	655	4399	900

Table 5.
Values for the binary interaction parameters n_{ik} in the S-L equation of state[27,28]

n_{ik}	Component k		
Component i	Ethylene	Hydrogen	Ethylene/ 1-butene copolymer
Ethylene	–	−0.0867	−0.1093
Hydrogen	−0.0867	–	–
Ethylene/1-butene copolymer	−0.1093	–	–

Table 6.
Values for the binary interaction parameters l_{ij} in the S-L equation of state[27,28]

l_{ik}	Component k		
Component i	Ethylene	1-Butene	Ethylene/ 1-butene copolymer
Ethylene	–	–	0.003
1-Butene	–	–	0.004
Ethylene/1-butene copolymer	0.003	0.004	–

Table 7.
Comparison of the simulation results and patent data (operating conditions of FBR are as mentioned in Table 2)

Parameter Description (Unit)	Case 1		Case 2		Case 3	
	Simul. Results	Patent Date	Simul. Results	Patent Date	Simul. Results	Patent Date
Production Rate (Ton/h)	35.9	34.7	38.0	37.3	37.2	38.1
wt % Liquid in inlet stream	23.9	24.9	26.5	27.4	26.6	27.0
PE resin MFI(g/10 min)	0.92	0.99	1.03	1.08	1.15	1.05
PE resin density (g/cc)	0.9281	0.9184	0.9279	0.9183	0.9278	0.9178

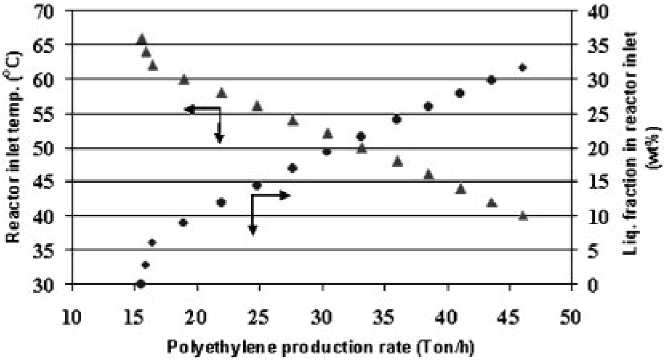

Figure 2.
Polyethylene production rate versus the reactor inlet stream temperature (▲) and liquid fraction in the reactor inlet stream (●). The isopentane concentration keeps constant at 9.5 mol%.

liquid fraction in the inlet stream to the reactor enhances whereas the recycle gas composition has been kept constant. For instance, when the inlet stream temperature changes ±10 °C from 47.9 °C, the production rate will alter between 20.9 and 48.4 Ton/h.

Figure 3 also shows the increase of the production rate versus the isopentane concentration in the reactor. The change of the isopentane concentration around 1 mole percentage in the reactor leads to a variation of the production rate about 14 percentage. For simulation of this case, when the isopentane concentration is changed in the reactor, the temperature and gas mole flow and consequently the pressure of the reactor will be altered.

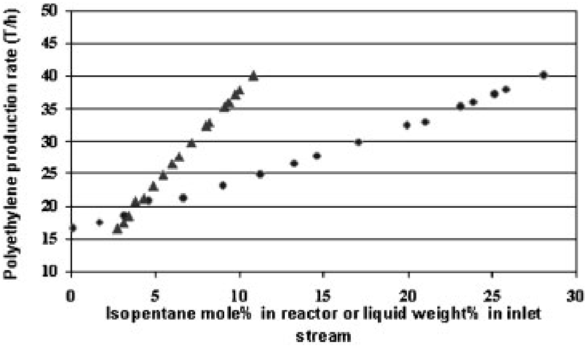

Figure 3.
Polyethylene production rate versus isopentane concentration (▲) and liquid fraction in reactor inlet stream (●). Reactor inlet stream temperature keeps constant at 47.9 °C.

However, to keep constant the physicochemical properties of polyethylene to the desired values, the temperature and pressure of FBR as well as the ethylene mole concentration, mole ratio of ethylene to hydrogen and ethylene to 1-butene should be kept invariable. The temperature is kept constant by changing the catalyst feed flow rate. Moreover, the pressure or in another word the actual gas volume flow is reserved constant by the replacement of a determined nitrogen moles with an appropriate isopentane mole, but not necessarily equal, in the reactor.

Conclusions

The fluidized bed reactor of polyethylene in the condensed mode operation has been modeled to predict the production rate versus the operating conditions of the reactor such as the reactor inlet temperature and condensable component concentration in the reactor. The developed model is based on the two-phase concept of fluidization, the two-site Ziegler–Natta polymerization kinetic and the phase equilibrium calculation upon the Sanchez-Lacombe equation of state. The Simulation results of the model showed good agreement with the available actual data in the patents.

Notation

Al	cocatalyst
C^j	potential active site of type j
C_d^j	spontaneously deactivated site of type j
C_{pg}	specific heat capacity of gaseous stream, J/kg.K
d_p	polymer particle diameter, m
D	reactor diameter, m^2
D_r^j	dead polymer chain of length r produced at site type j
H	height of the reactor, m
H_{be}	bubble to emulsion heat transfer coefficient, ($W/m^3.K$)
ΔH_i^{Vap}	latent heat of vaporization of component i, (J/kg)
$\Delta H_{r,i}$	heat of polymerization of component i, (J/kg)
k	Boltzman constant
k_{dsp}	spontaneous deactivation reaction rate constant, s^{-1}
k_a	activation reaction rate constant, s^{-1}
$k_{th,i}$	transfer to hydrogen reaction rate constant for a polymer chain with terminal monomer i,m^3/kmol.s
$k_{tm,ik}$	transfer to monomer k reaction rate constant for a polymer chain with terminal monomer i, m^3/kmol.s
$k_{tsp,i}$	spontaneous transfer reaction rate constant for a polymer chain with terminal monomer i, m^3/kmol.s
$k_{0,i}$	rate constant for initiation reaction by monomer i,m^3/kmol.s
$k_{p,ik}$	propagation reaction rate constant for a polymer chain with terminal monomer i reacting with monomer k,m^3/kmol.s
l_{ik}	binary interaction parameter in the Sanchez-Lacombe equation of state
M_i	the ith monomer
$[M_i]$	concentration of component i in the polymer particle, mol/m^3
$[M_i]_0$	initial concentration of component I in the reactor inlet, mol/m^3
$[M_i]_b$	concentration of component i in the bubble phase, mol/m^3
$[M_i]_e$	concentration of component i in the emulsion phase, mol/m^3
Mw	molecular weight, kg/kmol
n_{ik}	binary interaction parameter in the Sanchez-Lacombe equation of state
P	pressure, Pa
P^*	characteristic pressure in Sanchez-Lacombe equation of state, Pa
P_0^j	active site type j produced by activation reactions
$P_{r,i}^j$	live polymer of length r growing on site of type j with terminal monomer i
r	number of segments in the Sanchez-Lacombe equation of sytate

R_p	overall (co)polymerization rate, kmol/s
$R_{p,i}$	instantaneous rate of polymerization for monomer i, kmol/s
t	time, s
T	temperature, K
T^*	characteristic temperature in Sanchez-Lacombe equation of state, K
U_0	superficial gas velocity, m/s
U	velocity, m/s
V	volume, m^3
v^*	characteristic volume in Sanchez-Lacombe equation of state, m^3
V_p	volume of polymer inside the reactor, m^3
w_i	weight fraction of component i in a fluid mixture
Y_n^j	n-th moment of live polymer produced at site of type j

Greek Letters

δ	volume fraction of bubbles in bed
ε	void fraction of emulsion phase
ε^*	characteristic energy in Sanchez-Lacombe equation of state,
η	viscosity, Pa.s
ρ	density, kg/m^3
ρ^*	characteristic density in Sanchez-Lacombe equation of state, kg/m^3
μ	Chemical potential
φ_i	volume fraction of component i in a fluid mixture

Subscripts and Superscripts

$\sim$	Reduced property
b	bubble phase property
e	emulsion phase property
g	gas mixture property
i and k	monomer or component type
j	active site type no.
mf	minimum fluidization
p	polymer properties
r	number of repeating units in polymer chain

[1] T. Xie, K. B. McAuley, J. C. C. Hsu, D. W. Bacon, *Ind. Eng. Chem. Res.* **1994**, *33*, 449.

[2] J. M. Jenkins, R. L. Jones, T. M. Jones, U. S. Pat. 4,543,399 **1985**.

[3] J. M. Jenkins, R. L. Jones, T. M. Jones, S. Beret, U. S. Pat. 4,588,790 **1986**.

[4] Y. Jiang, K. B. McAuley, J. C. C. Hsu, *AIChE J.* **1997**, *43*, 13.

[5] Y. Jiang, K. B. McAuley, J. C. C. Hsu, *AIChE J.* **1997**, *43*, **2073**.

[6] Y. Jiang, K. B. McAuley, J. C. C. Hsu, *Ind Eng Chem Res* **1997**, *36*, 1176.

[7] K. Y. Choi, W. H. Ray, *Chem. Eng. Sci.* **1985**, *40*, 2261.

[8] K. B. McAuley, J. P. Talbot, T. J. Harris, *Chem. Eng. Sci.* **1994**, *49*, 2035.

[9] H. Hatzantonis, H. Yiannoulakis, A. Yiagopoulos, C. Kiparissides, *Chem. Eng. Sci.* **2000**, *55*, 3237.

[10] F. A. N. Fernandez, L. M. F. Lona, *J. Appl. Pol. Sci.* **2001**, *81*, 321.

[11] M. Alizadeh, N. Mostoufi, S. Pourmahdian, R. Sotudeh-Gharebagh, *Chem. Eng. J.* **2004**, *97*, 27.

[12] A. Kiashemshaki, N. Mostoufi, R. Sotudeh-Gharebagh, *Chem. Eng. Sci.* **2006**, *61*, 3997.

[13] A. B. Carvalho de, P. E. Gloor, A. E. Hamielec, *Polymer* **1989**, *30*, 280.

[14] K. B. McAuley, J. F. MacGregor, A. E. Hamielec, *AIChE J.* **1990**, *36*, 837.

[15] R. A. Hutchinson, W. H. Ray, *J. of App.l Pol. Sci.* **1990**, *41*, 51.

[16] S. Floyd, K. Y. Choi, T. W. Taylor, W. H. Ray, *J Appl Poly Sci* **1986**, *32*, 2935.

[17] J. M. Prausnitz, R. N. Lichtenthaler, E. G. De Azevedo, *Molecular thermodynamics of fluid-phase equilibria*, 3rd Ed Prentice Hall, Englewood Cliffs, NJ **1999**.

[18] R. H. Lacombe, I. C. Sanchez, *J. Phys. Chem.* **1976**, *80*, 2568.

[19] I. C. Sanchez, R. H. Lacombe, *J. Phys. Chem.* **1976**, *80*, 2352.

[20] E. Neau, *Fluid Phase Equil.* **2002**, *203*, 133.

[21] J. R. Griffin, M. L. DeChellis, U. S. Pat. 5,436,304, **1995**.

[22] C. Chatzidoukas, J. D. Perkins, E. N. Pistikopoulos, C. Kiparrisides, *Chem. Eng. Sci.* **2003**, *58*, 3643.

[23] A. Lucas, J. Arnaldos, J. Casal, L. Puigianer, *Ind. Eng. Chem. Process Des Develop.* **1986**, *25*, 426.

[24] M. Horio, A. A. Nonaka, *AIChE J.* **1987**, *33*, 1865.

[25] D. Kunni, O. Levenspiel, *Fluidization engineering*, 2nd Ed. Butterworth-Heineman, Boston, MA **1991**.

[26] D. B. Burker, C. V. Wittman, N. R. Amundson, *Chem. Eng. Sci.* **1974**, *29*, 1173.

[27] N. P. Khare, K. C. Seavey, Y. A. Liu, *Ind. Eng. Chem. Res.* **2002**, *41*, 5601.

[28] Y. Banat, Fines generation in gas-phase ethylene polymerization, Ph. D. Dissertation, University of Twente, **2006**.