SHORT COMMUNICATION

PARTICLE SIZE DISTRIBUTION AND ITS EFFECT ON THE OLEFIN POLYMER REACTOR DYNAMICS OVER OLEFIN POLYMERIZATION CATALYSTS WITH MULTIPLE ACTIVE SITES

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Abstract – Mass and energy balances in a reactor have been derived to study the effect of particle size distribution for multiple active site catalyst systems on the reactor dynamics. It was found that multiple active sites in a Ziegler-Natta catalyst affect neither the reactor dynamics nor the particle size distribution, as opposed to a system which uses single site catalysts. It was discovered that a simple reaction model with a single type of active site dominant adequately explains the reactor dynamics and the particle size distributions for a continuous stirred-bed reactor for polymerization of propylene over a Ziegler-Natta catalyst.

Key words : Particle Size Distribution, Reactor, Dynamics, Catalyst, Active Site

INTRODUCTION

Gas phase olefin polymerization processes have been developed in the past two decades towards minimizing capital investment in the process, by eliminating separation processes needed for hydrocarbons and polymer products in slurry or solution processes. Continuous stirred-bed reactors (CSBR) and fluidized bed reactors are widely used in gas phase polymerization. The mathematical modeling of gas phase olefin polymer reactors is complicated by the mechanics of growing polymer particles and the characteristics of the catalysts used. Very little information has been published on the dynamics of gas phase olefin polymerization reactor systems. Brockmeier and Rogan [1976] modeled a semibatch stirred-bed reactor for gas phase propylene polymerization and obtained the polymer yield and particle size from their model. Choi and Ray [1988] modeled a CSBR for the solid catalyzed gas phase polymerization of propylene. They observed a single unstable steady state at normal operation conditions. However, they assumed the PSD in the reactor to be uniform and ignored the effect of the PSD on the reactor dynamics.

The structure of CSBRs is the following. Injected active catalyst is mixed uniformly with polymer particles by a U-shaped anchor agitator. Liquid propylene is injected at the bottom of the reactor and instantaneously absorbs the heat of reaction and is vaporized. In order to regulate the molecular weight of polymer products, a small amount of hydrogen is added to the reactor. The unreacted propylene gas is sent to a condenser and liquefied. This liquefied propylene is recycled to the reactor. Product is withdrawn continuously from the reactor in a cyclone, separating solid polymer from the gas-solid mixture, which is shown in Fig. 1. Since the principal

mechanism for the removal of the heat of polymerization is the vaporization of propylene, the reactor must be operated so as to preclude the condensation of propylene. For an equation of state relating the pressure, temperature and monomer concentration in the reactor, Choi and Ray [1988] used the ideal gas law. This, however, has several limitations and does not represent the state of a real gas. The Redlich-Kwong equation has been used in this work. The vapor pressure expression for propylene [Reid et al., 1987] has been used to
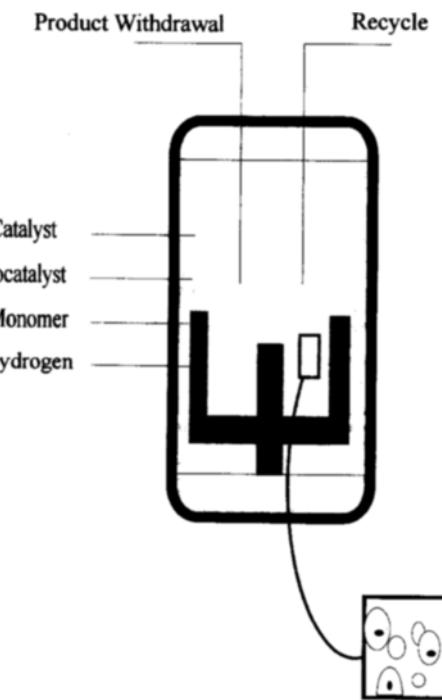

Fig. 1. Schematic diagram of continuous stirred-bed reactor for olefin polymerization.

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calculate a phase diagram of propylene. It shows the state of propylene at a given temperature and pressure, which are calculated from the macroscale equations governing the reactor.

Kim et al. [1997] show the effect of PSD over single-site Ziegler-Natta catalysts on the dynamics of olefin continuous stirred-bed polymer reactors. They observe that bed height and particle volume are affected by the PSD whose form depends on both the reaction mechanism and residence time. Here, their work is extended to the system using Ziegler-Natta catalysts which have multiple active sites and show whether the PSD affect the reactor dynamics.

THE EQUATIONS GOVERNING THE POLYMERIZATION

The several assumptions taken in this model of a CSBR propylene polymerization are the same as those used in Kim et al. [1997]. With these assumptions, the mass and energy balances have been derived for a gas phase polymerization of propylene in a CSBR.

$$(1 - \delta) V_R \frac{dC_M}{dt^*} = q_{Mf} + \frac{C_M}{\rho_{par}} q_{cf} - C_M Q + r_M \left(1 - \frac{C_M}{\rho_{par}}\right) \quad (1)$$

$$(1 - \delta) V_R \frac{dC_H}{dt^*} = q_{Hf} + \frac{C_H}{\rho_{par}} q_{cf} - C_H Q + r_{trH} - r_M \frac{C_H}{\rho_{par}} \quad (2)$$

$$\rho_{par} V_R \frac{d\delta}{dt^*} = q_{cf} - \rho_{par} (1 - \varepsilon) Q - r_M \quad (3)$$

$$\rho_{par} V_R \delta \frac{d\phi_c}{dt^*} = (1 - \phi_c) q_{cf} + \phi_c r_M \quad (4)$$

$$[V_R(1 - \delta) C_M C_{pM} + V_R \delta(1 - \phi_c) \rho_{par} C_{pp}] \frac{dT}{dt^*}$$
$$= -(q_{Mf} + q_R) C_{pM} (T - T_{ref}) - (\Delta H_v)(q_{Mf} + q_R)$$
$$+ C_{pMl} q_R (T_R - T_{ref}) + C_{pMl} q_{Mf} (T_{fM} - T_{ref})$$
$$- (- \Delta H_{rxn}) r_M - (C_{pM} - C_{pp}) (T - T_{ref})r \quad (5)$$

where $r_M = -V_R \delta M_{wM} \int_{V_c}^{\infty} k_p [M]_p \bar{i} \, f(V) \, dV$

Here the definitions of δ and ε are as follows.

$$\delta = \frac{V_{par}}{V_R} = \frac{V_{par}}{V_{par} + V_g} = \text{Fractional Volume of Stirred-Bed}$$

$$\varepsilon = \frac{v_g}{Q} = \frac{v_g}{v_g + v_{par}} = \frac{\text{Gas Withdrawal Rate}}{\text{Product Withdrawal Rate}}$$

Hutchinson and Ray [1990] showed that Stern correlation fits experimental data very well for light hydrocarbons such as ethylene and propylene and deviates slightly for heavier hydrocarbons. In this work, Stern's correlation is used to calculate monomer concentration at the particle.

$$[M]_p = k_H^* P_M$$

$$\log (k_H^*) = -5.38 + 1.08 \left(\frac{T_{cr}}{T}\right)^2 \quad (6)$$

where k_H^* is Henry's constant.

Floyd et al. [1986a,b, 1987] found resistances are negligible except for a highly active and larger initial volume of catalyst. Hutchinson and Ray [1987] studied the possibility

Table 1. Dimensionless variables and parameters

$t = \dfrac{t}{t_R}$	$t_R = \dfrac{V_R \rho_{Ml}}{q_{Mf}}$	$X_1 = \dfrac{C_M}{\rho_{Mr}}$	$X_2 = \dfrac{C_H}{\rho_{Hr}}$
$X_3 = \delta$	$X_4 = \phi_c$	$X_{1p} = \dfrac{[C_M]_p}{\rho_{Mr}}$	
$A_1 = \dfrac{\rho_{Mr}}{\rho_{par}}$	$A_2 = \dfrac{\rho_{Hr}}{\rho_{par}}$	$A_3 = \dfrac{\rho_{cf}}{\rho_{par}}$	$\theta = \dfrac{V_R}{Q}$
$B_1 = \dfrac{\rho_{Ml}}{\rho_{Mr}}$	$B_2 = \dfrac{\rho_{Ml}}{\rho_{par}}$	$D_{ap} = t_R k_p [N^*]_0$	
$f_c = \dfrac{q_{cf}}{\rho_{cf} V_R}$	$f_H = \dfrac{q_{Hf}}{\rho_{Hr} V_R}$	$f_I = \dfrac{\gamma_I}{k_{dU}}$	$\gamma_I = k_I [CO]$
$\gamma_H = \dfrac{k_{trH}}{k_p} \sqrt{\dfrac{M_{wM}}{\rho_{Hr}}}$	$\delta_1 = \dfrac{k_{dM}}{k_{dU}} \dfrac{\rho_{Mr}}{M_{wM}}$	$\delta_2 = \dfrac{k_{dH}}{k_{dU}} \sqrt{\dfrac{\rho_{Hr}}{M_{wH}}}$	
$\mu_1 \dfrac{k_{HM}^* M_{wM}}{\rho_{Mr}}$	$\mu_2 = k_{HM}^* RT$	$\mu_3 = \dfrac{B \rho_{Mr}}{M_{wM}}$	$\mu_4 = \dfrac{M_{wM} T^{1/2}}{A \rho_{Mr} k_{HM}^*}$
$X_5 = \dfrac{T}{T_{ref}}$	$f_R = \dfrac{q_R}{q_{Mf}}$	$X_{SR} = \dfrac{T_R}{T_{ref}}$	
$A_4 = \dfrac{C_{ppar}}{C_{pM}}$	$A_5 = \dfrac{C_{pMl}}{C_{pM}}$	$X_{SR} = \dfrac{T_{fM}}{T_{ref}}$	
$BH_R = \dfrac{(-\Delta H_{rxn})}{C_{pM} T_{ref}}$	$BH_v = \dfrac{(\Delta H_v)}{C_{pM} T_{ref}}$	$T_d = \dfrac{T_{cr}}{T_{ref}}$	

of particle ignition and extinction phenomena for olefin polymerization on a heterogeneous catalyst. Overheating was observed at the start of the reaction for gas phase polymerization, when the polymer particle has a high volume to surface area ratio. They observed that as catalyst activity increases, the overheating problem becomes more severe. This result may be important during a start-up of the reactor or grade transition. In this study, it is presumed that there is no particle overheating.

These governing equations may be made dimensionless using the adimensional variables and parameters defined in Table 1. The kinetic data depend on which catalyst is used and what is composition of a catalyst. The use of different cocatalysts in a given Titanium compound gives rise to different propagation rate and activation energy [Choi and Ray, 1988]. Though no published paper contains all necessary kinetic data, the use of kinetic data on similar Ziegler-Natta catalysts selected from several sources in the open literature enables a quantitative study of reactor dynamics. Physical properties and operating parameters are shown in Table 2.

Choi and Ray [1988] modeled propylene polymerization over a conventional Ziegler-Natta catalyst in a CSBR. Their operating parameters are used in this work with minor modification of some parameters, e.g., the reference pressures. Rincon-Rubio et al. [1990] used slurry lab-scale reactor to polymerize propylene with a highly active magnesium supported Ziegler-Natta catalyst, which included several deactivation rate constants. There are no published kinetic data for the deactivation steps. Consequently, those values for the deactivation rate constants used in this research are assumed constant. Chen [1993] measured the kinetics of propylene polymerization in a gas phase lab-scale reactor with magnesium chloride-supported Ziegler-Natta catalyst similar to Rincon-Rubio et al. [1990]. These

Table 2. Physical properties and operation parameters

Parameter	Value	Reference
ρ_{Mr}	0.093 (g/cm^3)	
ρ_{par}	0.9103 (g/cm^3)	Choi and Ray [1988]
ρ_{Ml}	0.4 (g/cm^3)	Choi and Ray [1988]
ρ_{Hr}	1.625×10^{-4} (g/cm^3)	
ρ_{cf}	2.84 (g/cm^3)	Chen [1993]
V_0	6.545×10^{-8} (cm^3)	Chen [1993]
V_R	1.0×10^6 (cm^3)	Choi and Ray [1988]
$[N^*]_0$	6.0×10^{-6} (mol/cm^3 cat)	
$[CO]$	1.0×10^{-5} (mol/cm^3)	
k_p	3.948×10^9 (cm^3/mol hr)	Rincon-Rubio et al. [1990]
k_l	7.094×10^{10} (cm^3/mol hr)	Chen [1993]
k_{trH}	3.0525×10^5 (cm$^{3/2}$/mol$^{1/2}$ hr)	Rincon-Rubio et al. [1990]
k_{dU}	0.066 (1/mol)	Rincon-Rubio et al. [1990]
k_{dM}	23.7 (cm^3/mol hr)	Rincon-Rubio et al. [1990]
k_{dH}	4.773 (cm$^{3/2}$/mol$^{1/2}$ hr)	Rincon-Rubio et al. [1990]
ε	0.25	Choi and Ray [1988]
T_r	300.15 (K)	Choi and Ray [1988]
T_f	328.15 (K)	Choi and Ray [1988]
P_{Mr}	22 (atm)	
P_{Hr}	2 (atm)	Srinivasan et al. [1988]

data are used in our model. No one, however, has measured the activation energy for chain transfer to hydrogen, k_{trH}. Though the amount of hydrogen injected to the reactor is small and the main purpose of hydrogen is molecular weight control, the rate change of the hydrogen concentration in the reactor is important because of the hydrogen-assisted deactivation at the particle. An estimate of the rate constant and activation energy for k_{dH} was obtained from the ratio, k_{trH}/k_p, calculated from several experimental data (Table 3).

Algebraic manipulation of the governing equations leads to the solution. The principal parameter of the olefin polymerization model is not the residence time of monomer, but the catalyst injection rate.

$$X_1 = \frac{B_1 + \dfrac{t_R}{A_1}\left(A_3 f_c - \dfrac{1-\varepsilon}{\theta}\right)}{\dfrac{t_R \varepsilon}{\theta}} \qquad (7)$$

$$f_H - \frac{X_2 \varepsilon}{\theta} + \frac{X_2^{1/2}}{A_1 X_{1p}}\left(A_3 f_c - \frac{1-\varepsilon}{\theta}\right) = 0 \qquad (8)$$

$$X_3 = \frac{\dfrac{t_R}{A_3}\left(-A_3 f_c + \dfrac{1-\varepsilon}{\theta}\right)}{D_{ap} X_{1p} \displaystyle\int_{V_c}^{\infty} \dfrac{\overline{i} \, f}{[N]_0^*} dv} \qquad (9)$$

$$X_4 = \frac{A_3 f_c}{(1-\varepsilon)/\theta} \qquad (10)$$

$$X_5 = \frac{L_f - \dfrac{t_R A_3}{B_1 A_1}[BH_R + (A_4 - 1)]f_c}{\left(1 + f_R - \dfrac{t_R(1 - A_4)(1-\varepsilon)}{B_1 A_1 \theta}\right) + \dfrac{t_R A_3(1 - A_4)}{B_1 A_1}f_c} \qquad (11)$$

where $L_f = (1 + f_R)(1 - BH_v) + A_5[f_R(X_{5R} - 1) + (X_{5f} - 1)]$

$$+ \frac{t_R BH_R(1 - \varepsilon)}{B_1 A_1 \theta} - \frac{t_R(1 - A_4)(1 - \varepsilon)}{B_1 A_1 \theta}$$

Since mass and heat transfer resistances are negligible and bed height is a variable, the governing equations can be combined. Inserting the total PSD function derived in Kim et al. [1997a] into the solution, the reactor dynamics and the effect of PSD can be recovered for the multiple active site catalysts systems. The feasible region and constraints for feasible polymer reactor operations are shown in Kim et al. [1997b].

RESULTS AND DISCUSSION

The existence of multiple active sites has been debated since Ziegler-Natta catalysts were discovered. In order to explain the broader molecular weight distribution of the polymer, two theories, that is, diffusion limitations and multiple active sites, have been developed. The concept of diffusion limitation was used by Ray's group [Floyd et al., 1986a,b, 1987]. They studied microparticle, macroparticle and external file mass and heat transfer resistance phenomena using a multigrain model. It was discovered that even though there is diffusion limitation between monomer and polymer particle, a more important role in determining molecular weight distribution is

Table 3. Chain transfer rate constants and the ratio of chain transfer constant to propagation rate constant

	k_{trH} $\left(\dfrac{cm^{3/2}}{mol^{1/2} \, hr}\right)$	Reaction temperature	Catalyst	$\dfrac{k_{trH}}{k_p}$
Yuan et al. [1982]	$2.95 \times 10^{13*}$		A	2.24×10^2
Bosworth [1983]	1.138×10^6		Supported catalyst	6.33×10^{-4}
Rincon-Rubio et al. [1990]	3.0525×10^5	70 °C	B	0.77×10^{-4}
Sarkar and Gupta [1992, 1993]	6.69×10^5	70 °C	A	3.72×10^{-4}
Choi [1984]	2.41×10^9	87 °C	δ TiCl$_3$ type	1.1×10^4
Kuo [1985]	1.59×10^4	50 °C	C	0.59×10^{-4}
Galvan [1986]	3.60×10^6		TiCl$_4$/MgCl$_2$ type	1.0×10^{-4}

where A: δ TiCl$_3$/AlCl$_3$/TEA, B: TiCl$_4$/MgCl$_2$/TEA/DMS, C: TiCl$_4$/MgCl$_2$/EB/PC/DMS
*This value is a pre-exponential factor (Activation Energy=12 kcal/mol)

played by multiple active sites. In this study, we assume no diffusion limitation. Galvan [1986] used two active sites to show that these are responsible for a broad MWD. McAuley et al. [1990] assumed that there are two active sites of catalyst and showed that results of their model agreed well with experimental data. Rincon-Rubio et al. [1990] also used two active sites to develop a kinetic model for evaluating continuous changes in polymerization rate and polymer properties with time. Here, in order to study the effect of the existence of the multiple active site centers on the PSD, we assumed two types of active sites.

1. Active Site Reduction Mechanism (TASR)

The active site reduction mechanism leads to a bed height relation as follows.

$$X_3 = \frac{\left(-A_3 f_c + \dfrac{1-\varepsilon}{\theta}\right)}{f_c} \cdot \frac{1}{\displaystyle\int_1^\infty \left(\dfrac{1+\alpha}{\sqrt{\bar{V}}+\alpha}\right)^{\beta-1} \exp\left[-\pi_2(\sqrt{\bar{V}}-1)\right]\, d\bar{V}} \tag{12}$$

where the definition of all dimensionless groups is in Table 1. Gonzalez [1990] developed the kinetic model of MMA polymerization using the continuous approximation, i.e., the difference terms in polymer chain length are expanded in a Taylor series, to estimate molecular weight distribution. He assumed that the infinite chain length domain be replaced with a finite one having a large upper bound and used a log-arithmic transformation and normalization to transform chain length interval to cover the range 0 to 1. The normalized integrand was discretized by Radau quadrature. This procedure is generally used to integrate an unbounded integrand. However, the solution is sometimes very sensitive to the approximated upper bound. Another method of integration of an unbounded integrand is the use of the inverse of the integration variable. It also replaces an unbounded domain with a normalized range from 0 to 1. The integrand, however, must not contain a singular point after the substitution. Since the governing equation and particle size distribution functions have no singular points, the substitution $\bar{V} \to 1/\bar{V}$ is done and the Simpson method is used to integrate the expressions. Since each type of active centers has a different rate of chain transfer to hydrogen, the rate of hydrogen consumption is given by

$$\frac{r_{trH}}{q_{Mf}}\frac{\rho_{Ml}}{\rho_{Hr}} = -\frac{t_R\, \gamma_H\, X_2^{1/2}\left(-A_3 f_c + \dfrac{1-\varepsilon}{\theta}\right)}{X_{1p}\, A_1}$$

$$\frac{\displaystyle\int_1^\infty \left(\dfrac{\sqrt{\bar{V}}+\gamma_{H2}\,\alpha}{1+\alpha}\right)\left(\dfrac{1+\alpha}{\sqrt{\bar{V}}+\alpha}\right)^\beta \exp[-\pi_2(\sqrt{\bar{V}}-1)]\, d\bar{V}}{\displaystyle\int_1^\infty \left(\dfrac{1+\alpha}{\sqrt{\bar{V}}+\alpha}\right)^{\beta-1} \exp[-\pi_2(\sqrt{\bar{V}}-1)]\, d\bar{V}} \tag{13}$$

where $\gamma_{H2} = \dfrac{k_{p1}}{k_{p2}}\dfrac{k_{trH2}}{k_{trH1}}$

If $k_{p1}/k_{p2} = 10$ and the ratio (k_{trH1}/k_{trH2}) is also 10, the two in-

tegrands of the right hand side in Eq. (13) become identical. Note that Rincon-Rubio et al. [1990] and McAuley et al. [1990] used similar values of the ratios.

2. Simple Reaction Mechanism (TASS)

For the simple reaction mechanism with two types of active sites, bed height can be expressed by

$$X_3 = \frac{\dfrac{t_R}{A_I}\left(-A_3 f_c + \dfrac{1-\varepsilon}{\theta}\right)}{\dfrac{D_{ap}\, X_{1p}\, Z\, f_c\, \theta}{[N^*]_1^0\, V_0\, N_A}} \tag{14}$$

Since the two types of active sites have no relation to each other in this model, only Z is involved in Eq. (14). The hydrogen mass balance for TASS is derived as the following.

$$f_H - \frac{X_2\,\varepsilon}{\theta} - \frac{X_2^{1/2}\,\gamma_{H1}\,\omega_1}{A_1\,X_{1p}\,\omega}\left[\frac{1-\varepsilon}{\theta} - A_3 f_c\right] = 0 \tag{15}$$

where $\omega_1 = \dfrac{1}{(1+\gamma_{t1}\,\theta)(1+\delta_{11}X_{1p}+\delta_{12}X_2^{1/2})}$

$$+\frac{\eta}{(1+\gamma_{t2}\,\theta)(1+\delta_{21}X_{1p}+\delta_{22}X_2^{1/2})}$$

$$\omega_1 = \frac{1}{(1+\gamma_{t1}\,\theta)(1+\delta_{11}X_{1p}+\delta_{12}X_2^{1/2})}$$

$$+\frac{\gamma_{H2}}{(1+\gamma_{t2}\,\theta)(1+\delta_{21}X_{1p}+\delta_{22}X_2^{1/2})}$$

$$\eta = \frac{f_{l2}}{f_{l1}}\frac{D_{ap2}}{D_{ap1}} \qquad \gamma_{H2} = \frac{k_{trH2}\,[N^*]_2^0\, f_{l2}}{k_{trH1}\,[N^*]_1^2 f_{l1}}$$

3. Comparison of Two Models

Few kinetic data have been published for two types of active sites. Rincon-Rubio et al. [1990] used the propagation rate constant and potential site concentration of the second type of active sites as one order of magnitude lower than those of the first type of active sites. McAuley [1990] assumed that type 2 active sites have larger kinetic constants than type 1 active centers approximately by a factor of 3 to 5 for ethylene polymerization. Kuo [1985] measured kinetic parameters in propylene polymerization and showed that one type of active site may have a propagation rate constant an order of magnitude greater than the other. Since deactivation mechanisms are not well understood and the kinetic rate constants depend on which catalysts are used, we assume that the ratio of kinetic data of one type of active site to the second is 10. This simplifies the governing equations. In general, most Ziegler-Natta catalysts used industrially for polymerization of propylene contain largely one type producing isotactic polypropylene and a small portion of a second which produces atactic polymer. In order to increase the number of isotactic active centers and to eliminate atactic ones, an electron donor is usually used. The isotactic index, the factor of isotactic polypropylene is over 95 % for widely used Ziegler-Natta catalysts.

Monomer and hydrogen concentrations, bed height, catalyst residue and pressure are depicted in Fig. 2 in the active site reduction mechanism with two types of active site centers. The monomer concentration profile is the same as that for the simple reaction model with a single type of active centers.
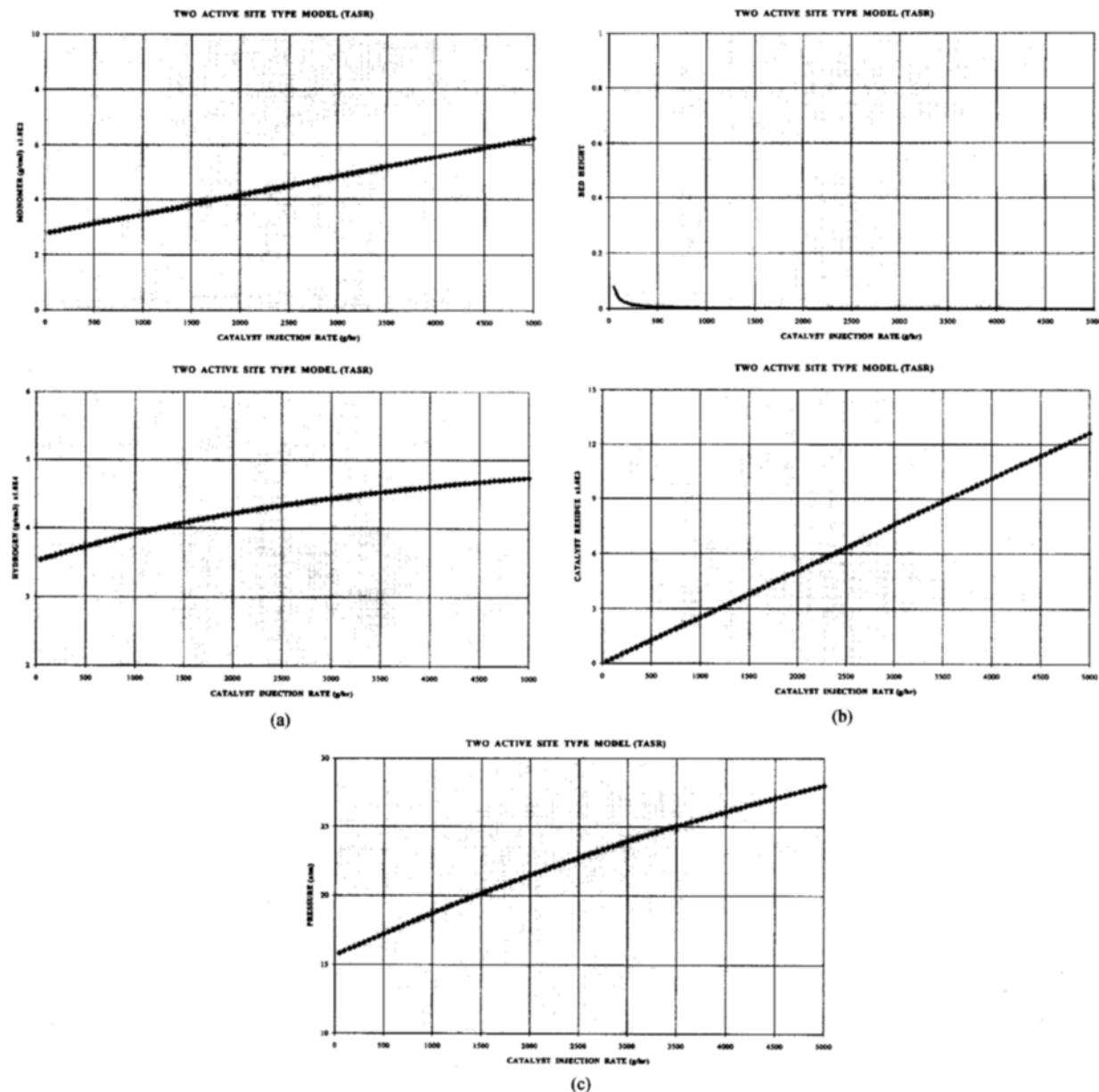
Fig. 2. Steady state profiles for active site reduction mechanism with two types of active sites (TASR).

Since the potential site concentration and propagation rate contant of the type 2 active sites are an order of magnitude lower, the contribution of the second active sites is minimal. The hydrogen concentration in the reactor, on the other hand, is somewhat smaller than that with single type active sites, because the chain transfer to a hydrogen occurs between both types of active site centers. Bed height is slightly lower at smaller catalyst injection rates and the same at higher rates when compared to a single type active-site case. Since the monomer concentration in the reactor for the case of two types of active centers is the same as in a single type, the pressure profile has the same shape. Mean number and total particle size distribution do not change with the addition of another type of active sites. The predicted value of mean diameter is much larger than the size of commercial products.

Therefore, this mechanism may not be acceptable for prediction of the PSD and the number mean diameter of products.

Similar phenomena are observed in simple reaction mechanism model with two types of active sites. Monomer concentration in the bulk is almost identical to that of the single type active site case. Hydrogen concentration is slightly lower due to the chain transfer reaction at both active sites. Bed height, catalyst residue, and pressure in the reactor are almost the same for a simple reaction mechanism with single type of active site. Mean particle volume and the total PSD change slightly with the addition of another type of active site. This follows from the assumption that the second type active site concentration is much smaller and the order of magnitude of kinetic constants of the second is one order lower. These results are shown in Fig. 3.
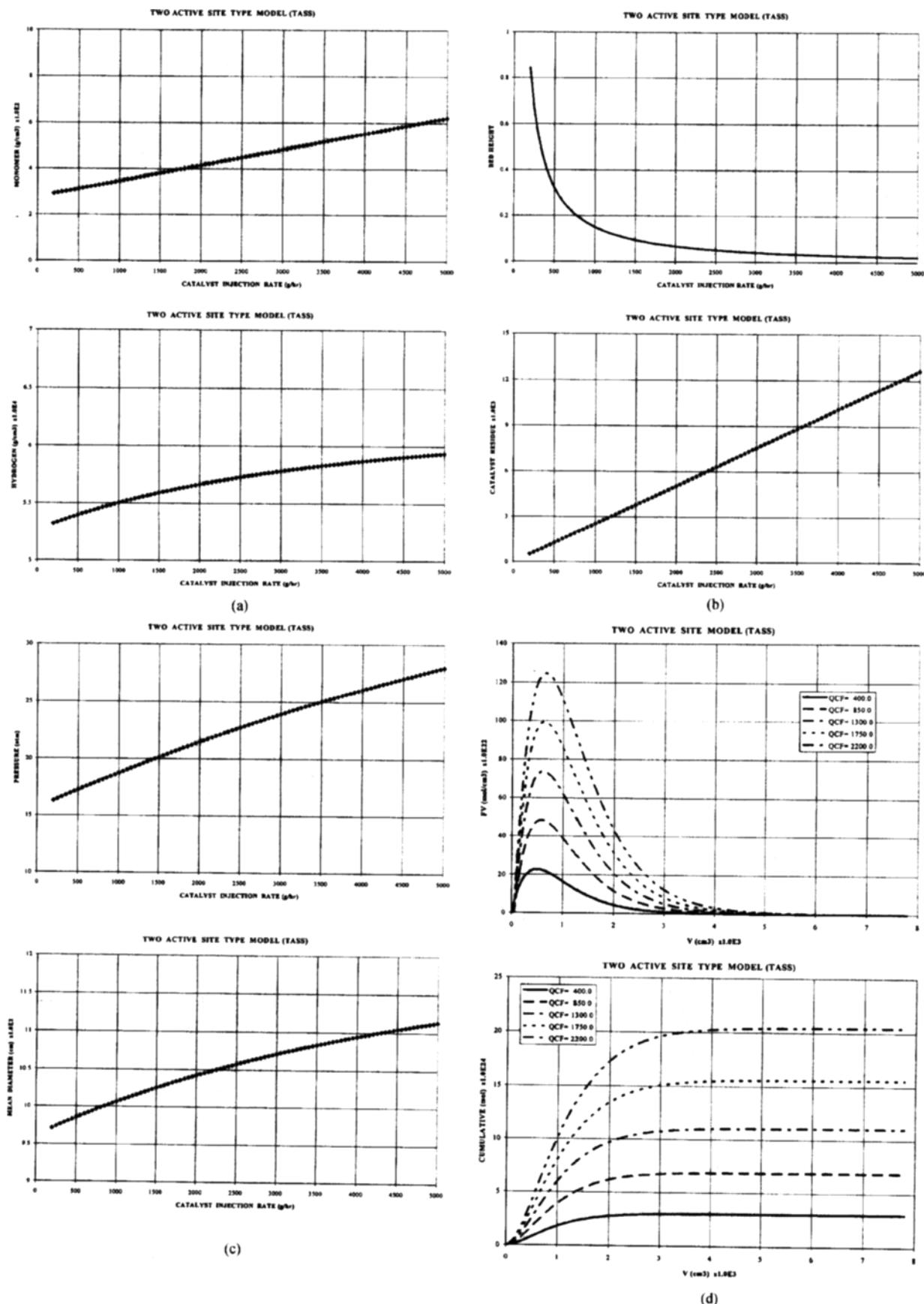
Fig. 3. Steady state profiles for simple reaction mechanism with two types of active sites (TASS).

CONCLUSION

Mass and energy balances were derived for a gas-phase polymerization of propylene in a continuous stirred-bed reactor. The Redlich-Kwong equation was used to calculate monomer pressure at a given concentration. The general solutions for nonisothermal reactors with multiple active site catalysts systems were developed. We observe that multiple active sites in a Ziegler-Natta catalyst affect neither the reactor dynamics nor the particle size distribution. Without loss of generality, we conclude that a simple reaction model with a single type of active site dominant explains adequately the reactor dynamics and the particle size distributions for a continuous stirred-bed reactor for polymerization of propylene over a Ziegler-Natta catalyst.

NOMENCLATURE

C_i : concentration of species i [mol/cm^3]
C_{pi} : heat capacity of species i [cal/g K]
$C_{pM\ell}$: heat capacity of liquid propylene [cal/g K]
D_{ai} : Damköhler number, i=d, p, t
i : average number of active sites
k_H : Henry's constant
k_p : rate constant for propagation [cm^3/mol hr]
k_{trH} : rate constant for chain transfer to hydrogen [cm$^{3/2}$/mol$^{1/2}$ hr]
M_{wM} : molecular weight of monomer [g/mol]
Q : volumetric withdrawal rate [cm^3/hr]
q_{cf} : catalyst injection rate [g/hr]
q_r : recycle rate [g/hr]
r_M : rate of monomer consumption
r_{trH} : rate of hydrogen chain transfer
T : reaction temperature [K]
t : dimensionless time
V : particle volume [cm^3]
V_R : reactor volume for olefin polymerization [cm^3]

Greek Letters

δ : fractional volume of stirred-bed
ε : ratio of gas withdrawal rate to product withdrawal rate
ϕ_c : catalyst residue
ρ_{cf} : catalyst density [g/cm^3]
ρ_i : density of species i [g/cm^3]
ρ_{par} : particle density [g/cm^3]

Subscripts

c : catalyst
f : feed
H : hydrogen
M : monomer
o : initial
p : particle
R : recycle

Superscript

* : initial condition

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