PARTICLE SIZE DISTRIBUTION IN OLEFIN CONTINUOUS STIRRED-BED POLYMERIZATION REACTORS

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Abstract – The control of polymer particle size and PSD is of industrial importance. Very fine particles pack poorly, thereby limiting reactor capacity, and present a dust explosion hazard. In olefin polymerization, a particle size distribution (PSD) in the polymerization reactor has been derived using population balances. Three reasonable reaction mechanisms for Ziegler-Natta catalysts, i.e., a simple reaction model, an active site reduction model, and a two sites model, have been used to derive the average number of active sites. It was observed that the PSD depends not only on residence time, but also on the reaction mechanism. It was also found that multiple active sites change the PSD slightly. The PSD, however, does not depend on initial catalyst volume.

Key words: Particle Size Distribution, Olefin, Polymerization, Reactor, Population Balance

INTRODUCTION

Ziegler and Natta discovered that ethylene can be polymerized at normal pressures and temperatures to yield a linearly structured solid polymer of high molecular weight by an aluminum alkyl compound acting on transition metals in a hydrocarbon medium. Many modified catalysts and so-called "new generation" catalysts have been developed and continue to be improved. Though many catalysts having greater activity and regularity have been developed, the reaction mechanisms remain not well understood. If one of the catalyst components is changed or the composition modified, the polymerization rate and product yield also change. This implies that the reaction mechanisms depend on the type of catalyst, its components, and composition. The nature of the reaction steps is, however, independent of the catalyst used. For example, catalyst initiation, propagation, chain transfer, and deactivation steps do happen during polymerization. From the micromolecular point of view, each step may not be identical for each catalyst. Chien [1989], for example, showed many possible mechanisms for initiation.

The solid polymer product is not monodisperse in size as it exits the reactor. Yet, it is understood that particles of different sizes may have differing activities. The control of polymer particle size and PSD is of industrial importance. Very fine particles pack poorly, limiting reactor capacity, and present a dust explosion hazard [Carson, 1988]. Population balances have been developed for particulate systems such as crystallization and emulsion polymerization. Min [1976], Kiparissides et al. [1979], and Rawlings [1985] applied population balance analysis to emulsion polymerization reactors.

The concentration of polymer particles is considered to be a function of time and of both external and internal coordinates. External coordinates are normally the three macroscopic spatial coordinates describing the reactor system, and internal coordinates are microscopic coordinates describing catalyst and polymer properties. There are many possible choices for internal coordinates: particle radius, surface area, volume, mass of polymer in the particle, time that the particle has spent in the reactor, etc. In emulsion polymerization, birth mechanisms include the nucleation of particles by radical entry into micelles, micelle initiation, and homogeneous nucleation. Death mechanisms are particle-particle coalescence and termination by polymer chain combination and disproportionation. These phenomena are similar to those occurring during olefin polymerization. In olefin polymerization, birth and death phenomena depend on the catalyst. Catalyst deactivation also occurs during polymerization and should be included in death terms. A population balance described in the next section has been used to derive particle size distribution.

In this work, generally accepted reaction mechanisms will be used to derive an expression for the particle size distribution and to understand the reactor dynamics. In section 2, a most probable set of reaction mechanisms is discussed. In section 3, population balances and the particle size distribution (PSD) for each reaction mechanism are derived and compared. We describe in section 4 the conclusion of our work.

REACTION MECHANISMS

Polymerization reaction mechanisms depend on the catalysts used in a polymerization reactor. A consistent and realistic explanation of each reaction step remains elusive, but Kissin [1985, 1989] and Tait and Watkins [1989] have explained several issues, such as active site center formation and have compared some early models. They focused their attention on microscopic reaction chemistry and emphasized the link

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between the polymerization rate measured in laboratory-scale batch reactor and the reaction kinetics.

1. A Simple Model

Four basic reaction steps included here are chain initiation, propagation, transfer to a chain transfer agent, and catalyst deactivation steps. These are widely accepted for most Ziegler-Natta catalyst systems. The initial stages of a polymerization depend strongly on specific catalysts. Many supported highly active Ziegler-Natta catalysts exhibit an initially high polymerization rate decreasing abruptly or rising rapidly to a maximum and then decreasing rapidly with time. A chain initiation reaction occurs between transition metal compounds and organometallic cocatalysts. McAuley et al. [1990], de Carvalho et al. [1989] derived general reaction mechanisms for ethylene polymerization and copolymerization. They assumed that cocatalyst concentrations are in excess and showed that the formation of propagation centers may be written as two reactions. First, initiation sites are formed by a reaction of potential sites on the catalyst particle and the cocatalyst. These initiation centers, then, react with monomers to form propagation centers. Our definition of an active site center is the locus at which monomer insertion and polymer chain growth may happen but monomer units are not yet attached. Consequently, chain initiation in this work is confined to the reaction of potential sites with the cocatalysts.

The propagation step is the addition of a monomer to an active site center with a growing polymer chain. Eirich and Mark [1956], Saltman [1960] and Vesley et al. [1961] used an adsorption model to derive a general kinetic scheme for Ziegler-Natta polymerization. They assumed that the propagation reaction occurs on adsorbed metal alkyl species. The active site centers are, however, not alkyl species, but alkylated transition metal compounds. Although all active site centers of a given catalyst do not have equal reactivity, that is, the propagation rate constants are not same [Kissin, 1985], in this work, they are assumed independent of their location on the catalyst and of the length of the growing polymer chain. Chain transfer reactions may happen with a given monomer, co-catalyst, a chain transfer agent. The order of magnitude of chain transfer to a chain transfer agent is much greater than chain transfer to monomer. Hydrogen is a chain transfer agent widely used to control the molecular weight of polymer product. In this model, we assume that chain transfer of hydrogen to growing polymer chain is half order as do Rincon-Rubio et al. [1990] and Kuo [1985]. It is shown in Table 1.

The destruction of active site centers by organometallic compounds is especially important in the case of highly active, supported catalysts. The main role of organometallic compounds is, however, the formation of active site centers with transition metal complex. These are also effective scavengers of impurities in reaction media. Though organometallic compounds do take part in the destruction of active site centers, we have omitted this step in this model, since the role of activation of active centers by these compounds is superior to the deactivation role.

From the ideas expressed above, the simple reaction mechanism of olefin polymerization system is shown in Table 1. This model may be extended with the addition of other reaction steps not included here.

2. An Active Site Reduction Mechanism

Chien and Kuo [1985] developed a high-mileage Ziegler-Natta catalyst and studied the decay and transformation of active sites. They showed that the decrease in the rate of polymerization follows a second order kinetics, suggesting a bimolecular transformation of initially active sites to a second type of active site. Second order termination was found at higher and lower aluminum/titanium ratio. A site transformation step important in propylene polymerization was introduced in the kinetic models of Rincon-Rubio et al. [1990]. Soga et al. [1981] discovered that if T_i^{+3} is involved, the catalyst is active for the polymerization of both propylene and ethylene; and if T_i^{+2} is involved, the catalyst is active only for the ethylene polymerization. During the polymerization, the valence of titanium is reduced from +4 to +3 by organometallic compounds and then reduced from +3 to +2 by termination. Schnauß and Reichert [1990] modeled the kinetics of ethylene polymerization with Ziegler-Natta catalysts assuming that reduction occurs between vicinal active species fixed to the surface. Rincon-Rubio et al. [1990] included a spontaneous site transformation mechanism different from those of Chien and

Table 1. A simple reaction mechanism of olefin polymerization system

Initiation		
$N^* + CO$	$\rightarrow$	N_0
Propagation		
$N_0 + M$	$\rightarrow$	P_1
$P_j + M$	$\rightarrow$	P_{j+1}
Chain Transfer		
$P_j + \frac{1}{2}H_2$	$\rightarrow$	$N_H + Q_j$
Deactivation		
P_j	$\rightarrow$	$N_d + Q_j$
$P_j + M$	$\rightarrow$	$N_d + Q_j$
$P_j + \frac{1}{2}H_2$	$\rightarrow$	$N_d + Q_j$

Table 2. A model reaction mechanism including active site reduction step in olefin polymerization system

Initiation		
$N^* + CO$	$\rightarrow$	N_0
Propagation		
$N_0 + M$	$\rightarrow$	P_1
$P_j + M$	$\rightarrow$	P_{j+1}
Termination		
$P_j + P_k$	$\rightarrow$	Q_{j+k}
Chain Transfer		
$P_j + \frac{1}{2}H_2$	$\rightarrow$	$N_H + Q_j$
Deactivation		
P_j	$\rightarrow$	$N_d + Q_j$
$P_j + M$	$\rightarrow$	$N_d + Q_j$
$P_j + \frac{1}{2}H_2$	$\rightarrow$	$N_d + Q_j$

Kuo [1985] and Schnauß and Reichert [1990]. In this model, the step suggested by Chien and Kuo is used as an active site center transformation. If the step used by Rincon-Rubio et al. is important for a specific catalyst system, one may extend a previous simpler reaction model. Any other reaction steps are the same as in the simple reaction mechanism. Table 2 summarizes this model mechanism.

3. A Model for Two Types of Active Sites

Ever since the Ziegler-Natta discovery, a debate has continued as to the reason for a broad molecular weight distribution (MWD) for polymerization. There are two principal arguments. One argues that broad MWD is a consequence of diffusion limitations. Another proposes that it follows from catalyst heterogeneity.

The diffusion-limitation theory depends on the fact that the growing polymer breaks the catalyst particle at an early stage of the polymerization. The subparticles are encapsulated, providing a diffusion limitation by the restriction of monomer transport through the semicrystalline polymer. The catalyst heterogeneity theory stems from the existence of multiple active sites having different propagation rates and activation energies. Floyd et al. [1986a,b, 1987] used a multigrain model to show the effects of heat and mass transfer resistances between bulk and catalyst. They showed that microparticle and macroparticle heat and mass transfer resistances are significant only for highly active and initially large catalysts in gas phase olefin polymerization. They concluded that external film heat transfer resistance is often significant during initial stage of polymerization and that mass transfer resistance is negligible in gas phase olefin polymerization. Floyd et al. [1987] also examined the effect of diffusion limitation on polymer properties such as MWD. They concluded that diffusion resistance affects the polymerization rate more strongly than the polymer properties. Though catalyst heterogeneity theory can explain a broad MWD, the effect on particle size distribution is still unknown. In this work, two types of active sites in a catalyst are assumed to exist. The reaction mechanism is shown in Table 3.

Table 3. Mechanism for olefin polymerization with two types of active sites

Initiation		
$N^*(i) + CO$	$\rightarrow$	$N_0(i)$
Propagation		
$N_0(i) + M$	$\rightarrow$	$P_1(i)$
$P_j(i) + M$	$\rightarrow$	$P_{j+1}(i)$
Termination		
$P_j(1) + P_k(1)$	$\rightarrow$	$Q_{j+k}(1)$
Chain Transfer		
$P_j(i) + \frac{1}{2}H_2$	$\rightarrow$	$N_H + Q_j(i)$
Deactivation		
$P_j(i)$	$\rightarrow$	$N_d + Q_j(i)$
$P_j(i) + M$	$\rightarrow$	$N_d + Q_j(i)$
$P_j(i) + \frac{1}{2}H_2$	$\rightarrow$	$N_d + Q_j(i)$

where $i=1, 2$

PARTICLE SIZE DISTRIBUTIONS

In this section, we develop a description of the particle size distribution for gas phase olefin polymerization in a continuous-stirred bed tank reactor. Rawlings [1985] derived a general method for population balances and showed that there is freedom regarding the choice of internal coordinates and external coordinates (three spatial coordinates). If the mixing of reaction mixture is ideal, the particle coordinates do not depend on the spatial coordinates. Several choices exist for internal coordinates and these depend not only on the reaction and physical processes, such as agglomeration, but also on the convenience of simplifying the equations governing the system.

Hutchinson and Ray [1990] discovered that the coalescence between particles may occur during initial stage of polymerization for mildly active catalysts and over specific ranges of catalyst volume. Particle coalescence in gas phase polymerization depends not only on the agitation speed and particle growth, but also particle surface temperature. These phenomena present a complication, but are important only in the initial stages of polymerization; consequently, these are not included in this work. Rawlings [1985] showed that the choice of polymer size as internal coordinate might be better if there is no coalescence between the particles. In this work, polymer size, especially polymer volume, is used as an internal coordinate.

There is no agglomeration between particles and the mixing of the system is ideal, so distribution of the n active sites is described as follows:

$$\frac{\partial\{f_i(V, t)V_R\}}{\partial t} + \frac{\partial}{\partial V}\{V_R \, r_{vi} \, f_i(V, t)\} = \sum_{i=1}^{4} r_i \tag{1}$$

where V_R is the reactor volume, r_{vi} is the volume growth rate, and r_i contains death and birth mechanisms. The right hand side terms in Eq. (1) contain deactivation, initiation, catalyst-injection and flow terms. The deactivation mechanism may be partitioned as

$$r_1 = \sum_{i=1}^{3} r_{li} \tag{2}$$

The net rate of change of the number of active sites by unassisted deactivation is given by

$$r_{11} = V_R \, k_{dU} \left\{ f_{i+1}(V, t) \sum_{N=1}^{Nd} g_n(i+1, V, t) - f_i(V, t) \sum_{N=1}^{Nd} g_n(i, V, t) \right\} \tag{3}$$

where g_n (i, V, t) is the number of active sites of chain length n in a particle of size.

Eq. (3) allows only active site centers of length up to N_d to deactivate. If all centers are assumed to deactivate, the sum $\sum_{N=1}^{Nd} g_n$ (i+1, V, T) is equal to (i+1). Therefore, Eq. (3) can be described by

$$r_{11} = V_R \, k_{dU} \{(i+1) \, f_{i+1} - i \, f_i\} \tag{4}$$

The rest of the deactivation terms are similar. The net rate of

change of active site centers by monomer-assisted deactivation and by hydrogen-assisted deactivation are given by

$$r_{12} = V_R \, k_{dM} \, [M]_p \, \{(i+1) \, f_{i+1} - i \, f_i\} \tag{5}$$

$$r_{13} = V_R \, k_{dH} \, [H_2]_p^{1/2} \, \{(i+1) \, f_{i+1} - i \, f_i\} \tag{6}$$

The net rate of change of active centers by the initiation reaction is given by

$$r_2 = V_R \, k_I \, [N^*] \, V \, N_A \, [CO]_p \, (f_{i-1} - f_i) \tag{7}$$

If all catalysts are assumed to have the same size initially, the rate of change of active site centers due to catalyst injection is expressed by delta function.

$$r_3 = \frac{q_{cf}}{V_0 \, \rho_{cf} \, N_A} \, \delta(V - V_0) \tag{8}$$

The last term on the right hand side of Eq. (2) involves the flow into and from the reactor.

$$r_4 = V_R \left\{ \frac{Q_f}{V_R} f_{if} - \frac{Q}{V_R} f_i \right\} \tag{9}$$

Other mechanisms such as impurity-assisted deactivation may be included without loss of generality.

RESULTS AND DISCUSSION

1. The Effect of Model Reaction Mechanisms
1-1. Simple Reaction Mechanism Model

In emulsion polymerization, Rawlings [1985] assumed that radical entry, desorption, and termination terms are much faster than volume growth and outflow from the reactor. The Smith-Ewart recursion relation can be derived using this assumption. Since Soga et al. [1983] and Kissin [1985] have shown that the life-time of active sites is shorter than residence time of the reactor, an assumption similar to that made for emulsion polymerization is used here. We assume that the initiation and deactivation events are rapid compared to the volumetric growth rate and the rate of withdrawal from the reactor. If the reactor system operates at steady state,

$$A\{(i+1) \, f_{i+1} - i \, f_i\} + C \, (f_{i-1} - f_i) = 0 \tag{10}$$

Here A and C are defined as below.

$$A = k_{dU} + k_{dM} \, [M]_p + k_{dH} \, [H_2]_p^{1/2} \tag{11a}$$

$$C = k_I \, [N^*] \, V \, N_A \, [CO]_p \tag{11b}$$

The average number of active site centers is needed in the derivation of a total particle size distribution. In order to solve Eq. (10), we introduce a generating function $\psi(V)$ defined by the equation

$$\psi(V) = \sum_{i=0}^{\infty} f_i \, \xi^i \tag{12}$$

where ξ is a complex number defined within the unit circle $|\xi| \leq 1$. The average number of active site centers may be found from

$$\bar{i} = \frac{\sum_{i=0}^{\infty} i \, f_i}{\sum_{i=0}^{\infty} f_i} = \frac{\left(\frac{\partial \psi}{\partial \xi}\right)_{\xi=1}}{(\psi)_{\xi=1}} \tag{13}$$

Blackley [1982] derived the relationship between the population summaries, such as $\sum_{i=0}^{\infty} i \, f_i$ and the distribution function, ψ (ξ, t) for the emulsion polymerization systems. From the definition in Eq. (12) and the relationship derived by Blackley [1982], the following equation is derived.

$$(1 - \xi) \left[A \, \frac{d\psi}{d\xi} - C\psi \right] = 0 \tag{14}$$

Since $\xi=1$ is a trivial solution, the second bracket should vanish. It is a first order linear differential equation and can be integrated. The final form of the average number of active site centers is given by Eq. (13):

$$\bar{i} = \frac{C}{A} = \frac{\text{Initiation Reaction Term}}{\text{Deactivation Reaction Term}} \tag{15}$$

If deactivation events are more numerous than the initiation, the active sites are reduced during polymerization.

The total particle size distribution may be obtained by summing Eq. (1) over all numbers of active sites. Initial particles are supplied by catalyst injection, and the reactant inflow term does not contain any polymer particle, that is, f_{if} is zero.

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V}(r_v \, f) = \frac{q_{cf}}{V_R \, \rho_{cf} \, N_A \, V_0} \, \delta(V - V_0) - \frac{Q}{V_R} \, f \tag{16}$$

Rawlings [1985] showed that the equation containing a delta function term may be written in the classical formulation with the impulsive terms included as boundary conditions.

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V} (r_v \, f) = - \frac{Q}{V_R} \, f$$

$$\text{at} \quad V = V_0 \qquad f = \frac{q_{cf}}{V_R \, \rho_{cf} \, N_A \, V_0 \, r_v} \tag{17}$$

The rate of particle mass increase in a particle containing i active site centers is given by

$$r_{pi} = \frac{dm_{pi}}{dt} = \frac{k_p \, i \, [M]_p \, M_{wM}}{N_A} \tag{18}$$

The units of r_{pi} (g/hr) differ from those of Choi and Ray [1988] and Brockmeier [1979]. The definition they used was the rate of particle mass increase per unit volume, that is, g/(hr cm^3). Since they assumed that all particle sizes are the same and considered the macroscopic rate expression involving bulk density of the particle and catalyst residue concentration, the unit, g/(hr cm^3), offers a natural description. In this case, however, the number of active site centers may differ in each particle and the number of active sites i are obtained from reactions, such as initiation and deactivation. Given that ρ_{par} is constant during polymer growth and $[M]_p$ does not depend on particle volume, the rate of particle growth, r_v, may be obtained from average polymer mass growth rate, r_p by summing over all active site centers.

$$r_p = \frac{\sum_{i=0}^{\infty} r_{pi}\, f_i}{\sum_{i=0}^{\infty} f_i} = \frac{k_p \bar{i}\, [M]_p\, M_{wM}}{N_A} \tag{19a}$$

$$r_v = \frac{dV_{par}}{dt} - \frac{1}{\rho_{par}}\, r_p = \frac{k_p \bar{i}\, [M]_p\, M_{wM}}{N_A\, \rho_{par}} \tag{19b}$$

For a completely homogeneous particle, the rate of change of potential sites in the particle, which do not react with co-catalyst and do not become active sites, may be expressed as

$$\frac{d([N^*]V)}{dt} = -k_I\, [N^*]\, V\, [CO]_p$$

$$\text{at} \quad t=0 \quad [N^*]V = [N^*]_0\, V_0 \tag{20}$$

Unlike emulsion polymerization, there is no active site entry to the particle nor desorption from the particle. Consequently, the total number of potential sites is conserved. The integration of Eq. (20) with the residence time distribution of particles leads to the following relation:

$$[N^*]V = \frac{[N^*]_0\, V_0}{1 + k_I [CO]_p\, V_R/Q} \tag{21}$$

If the residence time of particles is small or the initiation rate is small, the number of active site centers would be the same as potential sites.

Combining Eq. (19b), (20) and Eq. (17) at steady state, the total particle size distribution can be written as:

$$f(V) = \frac{q_{cf}\, A}{V_R\, \rho_{cf}\, V_0\, \alpha_v\, C N_A} \exp\left[-\frac{A}{\theta\, \alpha_v\, C}(V - V_0) \right] \tag{22}$$

$$\text{where} \quad \alpha_v = \frac{k_p\, [M]_p\, M_{wM}}{\rho_{par}\, N_A}, \quad \theta = \frac{V_R}{Q}$$

Since $f(V)$ is the total particle size distribution per unit volume (mol/cm^3 cm^3), the total particle size distribution, F (mol/cm^3), can be obtained from $f(V)$ times particle volume, V:

$$F(V) \equiv f(V) \cdot V = \frac{q_{cf}\, A\, V}{V_R\, \rho_{cf}\, V_0\, \alpha_v\, C N_A} \exp\left[-\frac{A}{\theta\, \alpha_v\, C}(V - V_0) \right] \tag{23}$$

The cumulative particle size distribution is derived by the integration of total PSD. Only available experimental data for PSD in open literature is a cumulative PSD [Karol, 1984; Tait, 1989].

$$CUM = \frac{\pi_1 V_0^2}{\pi_2} \left\{ \left(1 + \frac{1}{\pi_2}\right) - \left(\bar{V} + \frac{1}{\pi_2}\right) \exp[-\pi_2(\bar{V}+1)] \right\} \tag{24}$$

$$\text{where} \quad \pi_1 = \frac{f_c\, A}{V_0\, k_p\, A_1\, X_{1p}\, C}, \quad \pi_2 = \frac{V_0\, N_A\, A}{\theta\, k_p\, A_1\, X_{1p}\, C}$$

$$\bar{V} = \frac{V}{V_0}, \quad X_{1p} = \frac{[M]_p\, M_{wM}}{\rho_{Mr}}, \quad A_1 = \frac{\rho_{Mr}}{\rho_{par}}$$

The number average particle volume and diameter are defined by the following relations:

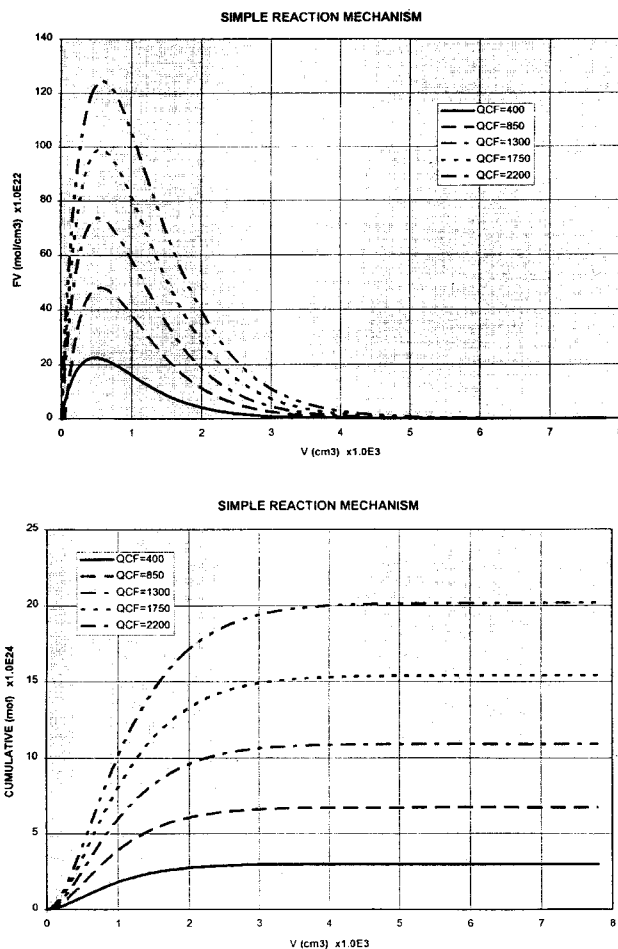$$<V> = \frac{\int_1^{\infty} fV\, dv}{\int_1^{\infty} f\, dv} = V_0\left(1 + \frac{1}{\pi_2}\right)$$

Fig. 1. Particle size distribution curves for a simple reaction mechanism.

$$<D> = \left(\frac{6}{\pi}<V>\right)^{1/3} \quad \text{(if the particles are spherical)} \tag{25}$$

The particle volume is increased because of the propagation reactions, as shown by $1/\pi_2$.

The total particle size distribution is shown in Fig. 1. When the catalyst injection rate, q_{cf}, increases, as expected, more particles are made and the total PSD becomes much broader. The peak of each PSD slightly shifts to a larger size for an increase in q_{cf}. Since the reactor is assumed to be well stirred, the shape of the total PSD resembles that of the residence time distribution, an exponential decay. However, the curves describing a normalized distribution (the total PSD divided by q_{cf}) do not superpose. The PSD curve depends not only on the residence time distribution, but also on the reaction. We can also see that the PSD is a function of average number of active sites which depends on the reaction mechanism and the residence time distribution. The cumulative PSD is drawn in Fig. 1. The slope of cumulative curve is steep for higher q_{cf}. Tait [1989] and Karol [1984] plotted the cumulative distribution using experimental data and showed that a mean value of the diameter is approximately 0.1 cm. The cumulative PSD calculated in this model also shows that a mean diameter of the particle is about 0.1 cm. The average number of active

SIMPLE REACTION MECHANISM (TR=4hr)

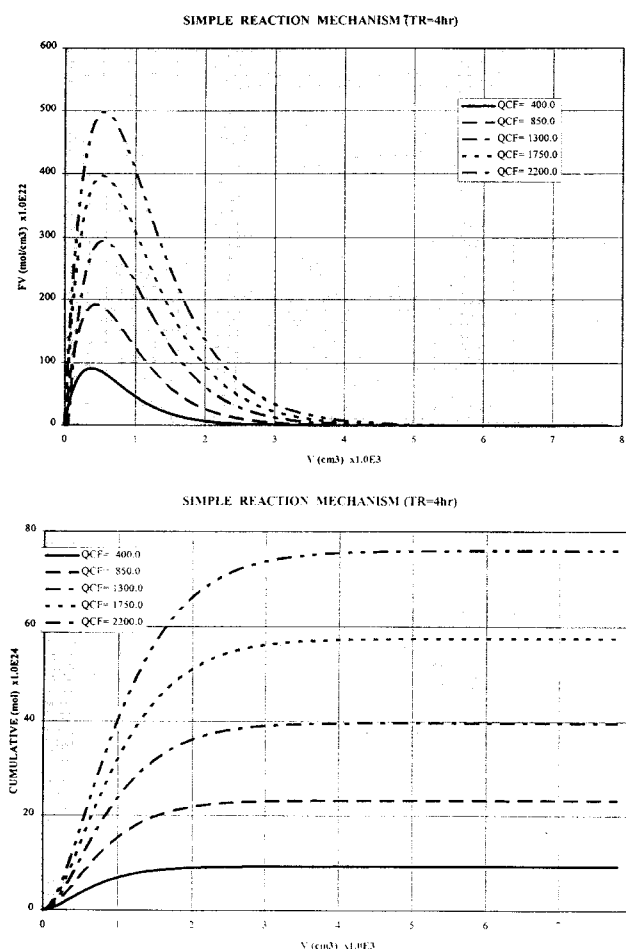SIMPLE REACTION MECHANISM (TR=4hr)

Fig. 2. Particle size distribution curves for a simple reaction mechanism with 4 hr residence time.

sites, the ratio of initiation step to deactivation step, is inversely proportional to the monomer concentration. Therefore, it decreases for higher catalyst injection rate.

The shapes of total PSD and the cumulative curve for a longer residence time, which is drawn in Fig. 2, are quite different from those of the 1 hour case (Fig. 1). The number of particles per unit volume increases for all q_{cf}, because the total particle distribution function depends on the reciprocal of number average active sites. More potential sites at the particles can be converted to active sites by the initiation reaction in a longer stay in the reactor. Consequently, for a longer residence time, the total number of particles increases and most have a small size which narrows the width of total PSD. As the total number of particles in the reactor depends strongly on the catalyst injection rate, the normalized curve (total PSD divided by q_{cf}) shifts to larger sizes with larger q_{cf} when compared to the one hour case.

1-2. Active Site Reduction Mechanism Model

The case including active site reduction introduces an additional death term to Eq. (1). Kuo [1985] observed that the two growing polymer particles may react and die. The net rate of change of active site centers by this reaction is given by

$$r_5 = \frac{k_t}{V N_A}\{(i+2)(i+1) f_{i+2} - i(i-1)f_i\} \tag{26}$$

An assumption, similar to those used in the simple model to derive the number average active site centers, leads to the Eq. (27), given that initiation, deactivation and termination steps are much faster than volume outflow and growth.

$$A[(i+1) f_{i+1} - i f_i] + B[(i+2)(i+1) f_{i+2} - i (i-1) f_i]$$
$$+ C(f_{i-1} - f_i) = 0 \tag{27}$$

The generating function defined by Eq. (12), transforms Eq. (27) into a second order differential equation:

$$\left(1 + \xi\right)\frac{d^2\psi}{d\xi^2} + \frac{A}{B}\frac{d\psi}{d\xi} - \frac{C}{B}\psi = 0 \tag{28}$$

Stockmayer [1957] and O'Toole [1965] solved Eq. (28) by transforming it to a modified Bessel equation of order $(1 - A/B)$. A and B contain kinetic constants and reactant concentrations. The ratio (A/B) may not be an integer, because neither A nor B can be integer-valued. The general solution form of a modified Bessel equation, except when $(1 - A/B)$ is exactly an integer or zero, can be expressed as

$$Y = C_1 I_{1-\alpha}(X) + C_2 I_{\alpha-1}(X) \tag{29}$$

where $\alpha = A/B$, $X = 2\sqrt{\beta(1 + \xi)}$
     $\beta = C/B$, $Y = \psi(\xi)/X^{1-\alpha}$

O'Toole [1965] noted that the second term of the right-hand side in Eq. (29) alternates in sign and the first term is clearly dominant for large i. Therefore, the number average active site centers can be obtained from Eq. (29) and the boundary condition $\psi(\xi=1)=1$.

$$\bar{i} = \frac{h}{4}\frac{I_\alpha(h)}{I_{\alpha-1}(h)}, \qquad h = 2\sqrt{2\beta} \tag{30}$$

Blackley [1982] refers to the term $I_\alpha(h)/I_{\alpha-1}(h)$ as the *subdivision factor*. It quantifies that the extent to which the overall number of active site centers in the particles as a whole is enhanced by compartmentalization of the propagation steps into a large number of small reaction loci. Comparing the order α and $\alpha-1$ with available data from the literature [Kuo, 1985; Rubio-Rincon et al., 1990], the value of α is much greater than 1. Thus, the subdivision factor is close to 1 and the number average active site centers can be written approximately as

$$\bar{i} = \frac{h}{4}\sqrt{\frac{k_I[CO]_p N_A^2 [N^*]_0 V_0}{2 k_t(1 + k_I[CO]_p V_R/Q)}}\sqrt{V} \equiv G\sqrt{V} \tag{31}$$

The total particle size distribution, cumulative PSD and number mean volume can also be derived following the procedure described above.

$$f = \frac{q_{cf}}{N_A V_R \rho_{cf} \alpha_v G V_0^{3/2}}\left(\frac{V_0}{V}\right)^{1/2}\exp\left[-\frac{2}{\theta \alpha_v G}(\sqrt{V} - \sqrt{V_0})\right] \tag{32}$$

$$F \equiv fV = \frac{q_{cf} V}{N_A V_R \rho_{cf} \alpha_v G V_0^{3/2}}\left(\frac{V_0}{V}\right)^{1/2}$$
$$\exp\left[-\frac{2}{\theta \alpha_v G}(\sqrt{V} - \sqrt{V_0})\right] \tag{33}$$

$$CUM = \frac{2\pi_1 V_0^2}{\pi_2}\left[1 + \frac{2}{\pi_2} + \frac{2}{\pi_2^2} - \left(\overline{V} + \frac{2\sqrt{\overline{V}}}{\pi_2} + \frac{2}{\pi_2^2}\right)\right.$$

$$\left. \exp\{-\pi_2(\sqrt{\overline{V}}-1)\}\right] \tag{34}$$

$$\langle V\rangle = V_0\left[1 + \frac{2}{\pi_2}\left(1 + \frac{1}{\pi_2}\right)\right] \tag{35}$$

where $\quad \alpha_v = \dfrac{k_p X_{1p} A_1}{N_A}, \quad \pi_1 = \dfrac{q_{cf}}{N_A V_R \rho_{cf}\alpha_v GV_0^{3/2}}, \quad \pi_2 = \dfrac{2\sqrt{V_0}}{\theta\alpha_v G},$

$\theta = \dfrac{V_R}{Q}$

In this case, the total PSD is inversely proportional to the square root of particle volume. For the simple model, the total PSD does not depend on particle volume. If termination is greater than other deactivation processes, the total PSD would be broader and the average particle volume large. However, if termination is less important, the total PSD and the average particle volume approach those values obtained us-

ACTIVE SITES REDUCTION MECHANISM

ACTIVE SITES REDUCTION MECHANISM

Fig. 3. Total and cumulative particle size distribution curves for an active site reduction mechanism.

ing the simple mechanism. The total particle size distribution and cumulative total PSD are shown in Fig. 3. Note that the peak maximum is lower than that in the simple model for all given q_{cf} values and the distribution is broader.

Since the termination reaction occurs between two growing polymers in the particles [Kuo, 1985], the sizes of the particles differ, each having a different growth path. The average number of active sites does not change with catalyst injection rate. These depend on not only particle volume, but also the termination rate constant. In contrast with a simple model case where the average number of active sites is constant, the average number of active sites in this model is proportional to the square root of the particle volume. This is a consequence of the termination step. Min [1976] and Rawlings [1985] studying emulsion polymerization showed that the average number of radicals in the particles can be obtained from the Stockmayer-O'Toole equation, which consists of the termination mechanism and radical entry into the particle and radical exit from the particle. Unlike the radical transfer step in emulsion polymerization, all active sites remain in the particle, and the total number of sites involving potential and dead sites is conserved in olefin polymerization.

1-3. Two-Active-Site Model

When two types of active sites are found in a particle, the definition of a distribution function must differ necessarily from that used in the simple model.

It becomes a bi-variate distribution.

$f_{r,i-r}dV$: Number of particles with r active sites (type-1) and i-r active site (type-2) in a volume V to V+dV at time t

The number active site population balance can then be written as.

$$\frac{\partial f_{r,i-r}}{\partial t} + \frac{\partial}{\partial V}(r_{v,-}f_{r,i-r}) = \sum_{k=1}^{5} r_{r,i-r,k} \tag{36}$$

The two active sites model with active site reduction mechanism (TASR) along with a two sites model with simple reaction mechanism (TASS) has been studied. The population balance and PSD for TASS is a special case of TASR, eliminating the termination reaction term. The expression for the net rate of change of the number of active site centers by deactivation, such as unassisted, monomer-assisted and hydrogen-assisted deactivation, is given by

$$r_{r,i-r,11} = k_{dU1}\{f_{r+1,i-r}\cdot(r+1) - f_{r,i-r}\,r\}$$
$$+ k_{dU2}\{f_{r,i-r+1}\cdot(i-r+1) - f_{r,i-r}\,(i-r)\} \tag{37a}$$

$$r_{r,i-r,12} = k_{dM1}[M]_p\{f_{r+1,i-r}\cdot(r+1) - f_{r,i-r}\,r\}$$
$$+ k_{dM2}[M]_p\{f_{r,i-r+1}\cdot(i-r+1) - f_{r,i-r}\,(i-r)\} \tag{37b}$$

$$r_{r,i-r,13} = k_{dH1}[H_2]_p^{1/2}\{f_{r+1,i-r}\cdot(r+1) - f_{r,i-r}\,r\}$$
$$+ k_{dH2}[H_2]_p^{1/2}\{f_{r,i-r+1}\cdot(i-r+1) - f_{r,i-r}\,(i-r)\} \tag{37c}$$

The net rate of change of active sites by transformation from one type to another and by site reduction can be derived using Table 2:

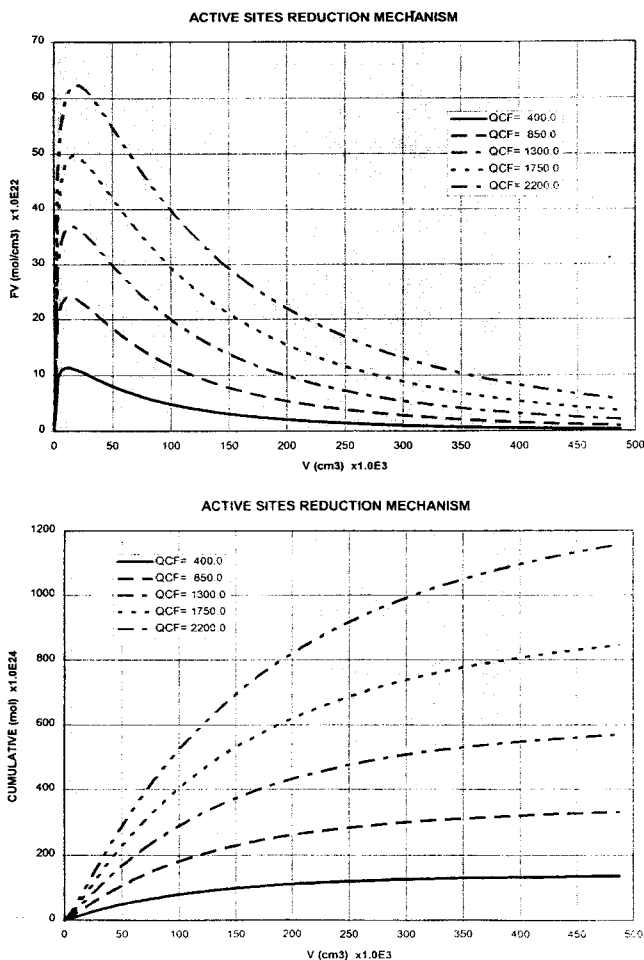$$r_{r,i-r,2} = k_{st}\{f_{r+1,i-r}\cdot(r+1) - f_{r,i-r}\,r\} \tag{38}$$

$$r_{r,i-r,3} = \frac{k_t}{N_A V}\{f_{r+2,i-r}(r+2)(r+1) - f_{r,i-r}\,r(r-1)\} \qquad (39)$$

The net rate of change of the number of active sites due to the initiation reaction and the volume outflow from the reactor is expressed by.

$$r_{r,i-r,4} = k_{I1}[N^*]_1[CO]_p\{f_{r-1,i-r} - f_{r,i-r}\}$$
$$+ k_{I2}[N^*]_2[CO]_p\{f_{r,1-r-1} - f_{r,i-r}\} \qquad (40)$$

$$r_{r,i-r,5} = \frac{Q_f}{V_R}f_{r,i-r,f} - \frac{Q}{V_R}f_{r,i-r} \qquad (41)$$

Since there are two types of active sites, the bivariate generating function may be defined as follows.

$$\psi(\zeta,\xi,t) = \sum_{i=0}^{\infty}\sum_{r=0}^{i} f_{r,i-r}\,\zeta^r\,\xi^{i-r} \qquad (42)$$

Giannetti [1989] summarized the relationship between population summations and the generating function, $\psi(\zeta,\xi,t)$ in the development of emulsion copolymerization kinetics. Using an assumption similar to that used in simple reaction case and the relationship shown by Giannetti, the following partial differential equation may be derived, and it describes the evolution of the generating function.

$$A\left(\frac{\partial\psi}{\partial\zeta} - \zeta\frac{\partial\psi}{\partial\zeta}\right) + B\left(\frac{\partial\psi}{\partial\xi} - \xi\frac{\partial\psi}{\partial\xi}\right) + C(\zeta\psi - \psi)$$
$$+ D(\xi\psi - \psi) + E\left(\frac{\partial^2\psi}{\partial\zeta^2} - \zeta^2\frac{\partial^2\psi}{\partial\zeta}\right) = 0 \qquad (43)$$

where
$A = k_{dU1} + k_{st} + k_{dM1}[M]_p + k_{dH1}[H_2]_p^{1/2}$
$B = k_{dU2} + k_{dM2}[M]_p + k_{dH2}[H_2]_p^{1/2}$
$C = k_{I1}[N^*]_1 V N_A[CO]_p,$
$D = k_{I2}[N^*]_2 V N_A[CO]_p, \quad E = \dfrac{k_t}{N_A V}$

Two limiting cases may be obtained by setting, E = 0 (TASS) and E≠0 (TASR). In the case of TASS, Eq. (43) reduces to a 1st order linear partial differential equation which is solved by separation of variables. The solution of the TASS case is of the form:

$$\psi(\zeta,\xi) = \sum_{k=1}^{\infty} Z_k(1-\xi)^{-\frac{\lambda}{A}}\exp\left(\frac{C}{A}\zeta\right)(1-\xi)^{\frac{\lambda}{B}}\exp\left(\frac{D}{B}\zeta\right) \qquad (44)$$

where Z_k is constant of integration. The superposition principle applied to the partial differential equation requires that the complete solution is the sum of all solutions, $\psi(\zeta,\xi)$, for all physically acceptable values of λ. The only plausible eigenvalue, however, is zero, because the solution becomes indefinite as ζ and ξ approach unity, regardless of the value λ [Giannetti, 1989]. The final solution form for the TASS case and number average active sites for this case are given by the generating function and Eq. (45b, c).

$$\psi(\zeta,\xi) = \exp\left\{\frac{C}{A}(\zeta-1)\right\}\exp\left\{\frac{D}{B}(\xi-1)\right\} \qquad (45a)$$

$$\bar{r} = \frac{\left(\frac{\partial\psi}{\partial\zeta}\right)_{\zeta,\xi=1}}{(\psi)_{\zeta,\xi=1}} = \frac{C}{A}$$

$$= \frac{\text{Initiation Reaction Term of Active Sites for Type-1}}{\text{Deactivation Reaction Term of Active Sites for Type-1}} \qquad (45b)$$

$$\overline{i-r} = \frac{\left(\frac{\partial\psi}{\partial\xi}\right)_{\zeta,\xi=1}}{(\psi)_{\zeta,\xi=1}} = \frac{D}{B}$$

$$= \frac{\text{Initiation Reaction Term of Active Sites for Type-2}}{\text{Deactivation Reaction Term of Active Sites for Type-2}} \qquad (45c)$$

These results (TASS) show that the number average active site centers for each type are determined by their own initiation and deactivation mechanisms independently. Since two active sites do not contact or collapse, there is no contribution of coupling to the average number of active sites.

In the case of TASR, that is, E is non-zero, the second partial differential equation is solved using separation of variables. An observation similar to the TASS case indicates that the only physically acceptable eigenvalue is zero. The final form of generating function and the average active sites are written as

$$\psi(\zeta,\xi) = \exp\left\{\frac{D}{B}(\xi-1)\right\}2^{\frac{\alpha-1}{2}}(1+\zeta)^{\frac{1-\alpha}{2}}\frac{I_{\alpha-1}\{2\sqrt{\beta(1+\zeta)}\}}{I_{\alpha-1}(2\sqrt{2\beta})} \qquad (46a)$$

$$\bar{r} = \frac{\left(\frac{\partial\psi}{\partial\zeta}\right)_{\zeta,\xi=1}}{(\psi)_{\zeta,\xi=1}} = \frac{h}{4}\frac{I_\alpha(h)}{I_{\alpha-1}(h)}$$

$$\overline{i-r} = \frac{\left(\frac{\partial\psi}{\partial\xi}\right)_{\zeta,\xi=1}}{(\psi)_{\zeta,\xi=1}} = \frac{D}{B}$$

$$= \frac{\text{Initiation Reaction Term of Active Sites for Type-2}}{\text{Deactivation Reaction Term of Active Sites for Type-2}} \qquad (46c)$$

The summation of the number distribution leads to the total particle size distribution.

$$f = \sum_{i=0}^{\infty}\sum_{r=0}^{i} f_{r,i-r} \qquad (47)$$

The form of population balance for total PSD is the same as in Eq. (17) except for the different form of volume growth rate. The average polymer mass growth rate contains two terms involving the propagation reactions of the two active site species and can be written as

$$r_p = \frac{\sum_{i=0}^{\infty}\sum_{r=0}^{i}(r_{p_r} + r_{p_{sr}})f_{r,i-r}}{\sum_{i=0}^{\infty}\sum_{r=0}^{i} f_{r,i-r}} = \frac{k_{p1}[M]_p M_{wM}}{N_A}\bar{r}$$
$$+ \frac{k_{p2}[M]_p M_{wM}}{N_A}\overline{i-r} \qquad (48)$$

Given that polymer particle density is constant during polymerization, the polymer volume growth rate is given by

$$\frac{k_{p1}[M]_p M_{wM}}{\rho_{par}N_A}\bar{r} + \frac{k_{p2}[M]_p M_{wM}}{\rho_{par}N_A}\overline{i-r} \equiv \alpha_{v1}\bar{r} + \alpha_{v2}\overline{i-r} \qquad (49)$$

The total particle size distribution function, the cumulative PSD and the number average particle volume are derived by

solving Eq. (17) and Eq. (49). The results are summarized in Table 4. If the number of type-1 active sites is greater than that of type-2, the number average active sites of type-2 are negligible (that is, $P_1 \to \infty$). Therefore, the total PSD in Table 4 can be reduced to the same form of the total PSD in the single site active site reduction mechanism by substituting $P_1 \to \infty$. The subdivision factor in average number of active site centers of type-1 is unity since the difference in the order of the modified Bessel functions is negligible.

In the case of TASS, each average number of active sites contains only the ratio of the initiation to deactivation term occurring at each site, similar to the simple model. Since the particle volume growth rate is the sum of propagation rate at each site, the following relation can be written.

$$r_v = \alpha_{v_1} \frac{C}{A} + \alpha_{v_2} \frac{D}{B} = \alpha_{v_1} \left(\frac{C}{A} + \frac{\alpha_{v_2}}{\alpha_{v_1}} \frac{D}{B} \right) \equiv \alpha_{v_1} Z \qquad (50)$$

The total PSD function and its integral, the cumulative PSD are derived and number average particle volume may also be evaluated using the result.

$$f = \frac{q_{cf}}{V_R \, \rho_{cf} \, V_0 \, k_{p1} \, X_{1p} \, A_1 \, Z} \exp\left[-\frac{N_A}{\theta \, k_{p1} \, X_{1p} \, A_1 \, Z}(V - V_0) \right] \qquad (51a)$$

Table 4. Total particle size distribution and average particle volume for a model including two types of active sites with active site reduction mechanism

$$f(V) = \frac{q_{cf}}{V_R \, \rho_{cf} \, V_0 \, r_{v_0} \, N_A} \left(\frac{\sqrt{V_0} + \frac{1}{P_1}}{\sqrt{V} + \frac{1}{P_1}} \right)^{1 - \frac{2P_2}{P_1}} \exp[- 2 P_2(\sqrt{V} - \sqrt{V_0})]$$

$$F = f(V) = \frac{q_{cf}}{V_R \, \rho_{cf} \, V_0 \, r_{v_0} \, N_A} \left(\frac{\sqrt{V_0} + \frac{1}{P_1}}{\sqrt{V} + \frac{1}{P_1}} \right)^{1 - \frac{2P_2}{P_1}}$$

$$\exp[- 2 P_2(\sqrt{V} - \sqrt{V_0})]$$

$$CUM = \pi_1 V_0 \int_1^{\bar{V}} \frac{\bar{V}}{(\sqrt{\bar{V}} + \alpha)^\beta} \, \exp[-\pi_2(\sqrt{\bar{V}} - 1)] \, d\bar{V}$$

$$<V> = V_0 = \frac{\int_1^{\infty} \frac{\bar{V}}{(\sqrt{\bar{V}} + \alpha)^\beta} \, \exp[-\pi_2(\sqrt{\bar{V}} - 1)] \, d\bar{V}}{\int_1^{\infty} \frac{1}{(\sqrt{\bar{V}} + \alpha)^\beta} \, \exp[-\pi_2(\sqrt{\bar{V}} - 1)] \, d\bar{V}}$$

where $\quad G = \sqrt{\frac{k_{I1} \, [CO]_p \, N_A^2 \, [N^*]_1^0 \, V_0}{2 \, k_t C \, 1 + k_{I1} \, [CO]_p \, \theta}}, \quad P_1 = \frac{BG}{D} \frac{\alpha_{v_1}}{\alpha_{v_2}}$

$$P_2 = \frac{1}{\alpha_{v_1} \, G \, \theta}, \quad \alpha = \frac{1}{P_1 \sqrt{V_0}}, \quad \beta = 1 - \frac{2 P_1}{P_2},$$

$$r_{v_0} = r_v \, (V = V_0), \quad \pi_1 = \frac{q_{cf}}{V_R \, \rho_{cf} \, \alpha_{v_1} \, GV_0 \, N_A} \, (1 + \alpha)^{\beta - 1},$$
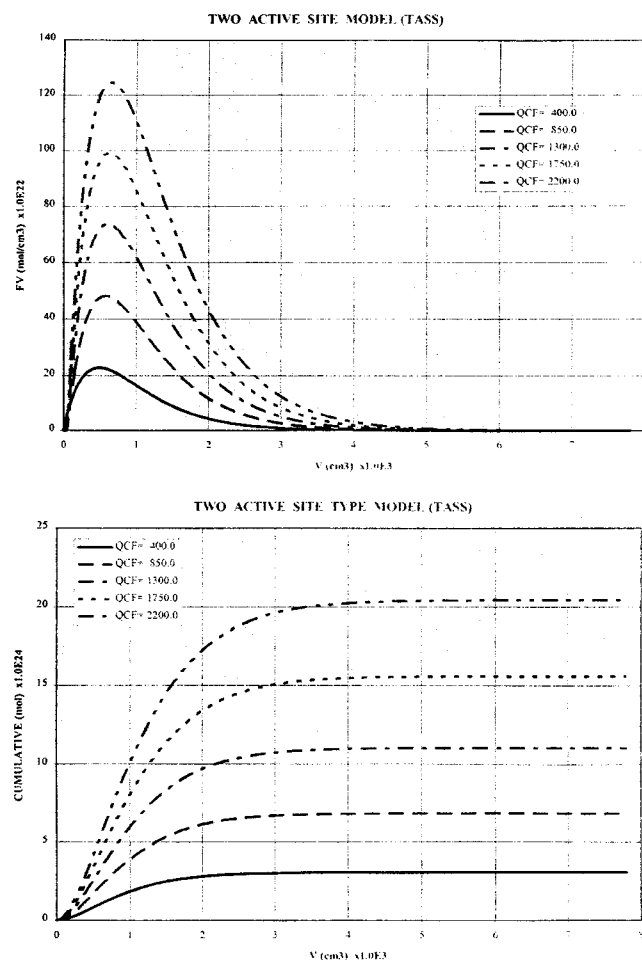
$$\pi_2 = 2 \, P_2 \sqrt{V_0}$$

Fig. 4. Particle size distribution curves for a simple reaction mechanism with two types of active sites.

$$F = fV = \frac{q_{cf} V}{V_R \, \rho_{cf} \, V_0 \, k_{p1} \, X_{1p} \, A_1 \, Z}$$

$$\exp\left[-\frac{N_A}{\theta \, k_{p1} \, X_{1p} \, A_1 \, Z}(V - V_0) \right] \qquad (51b)$$

$$CUM = \frac{\pi_1 V_0^2}{\pi_2} \left\{ \left(1 + \frac{1}{\pi_2} \right) - \left(\bar{V} + \frac{1}{\pi_2} \right) \exp[-\pi_2(\bar{V} - 1)] \right\} \qquad (51c)$$

$$<V> = V_0 \left(1 + \frac{1}{\pi_2} \right) \qquad (51d)$$

where $\pi_1 = \dfrac{q_{cf}}{V_R \, \rho_{cf} \, V_0 \, k_{p1} \, X_{1p} \, A_1 \, Z}, \quad \pi_2 = \dfrac{N_A \, V_0}{\theta \, k_{p1} \, X_{1p} \, A_1 \, Z}$

Fig. 4 shows that mean particle volume and the total PSD change slightly. This follows from the assumption that the order of magnitude of kinetic constants of the second is one order lower. Since it is generally known in olefin polymerization using Ziegler-Natta type catalysts that the second type active site concentration is much smaller, it may be concluded that total PSD does not change significantly with the addi-

tion of another type of active site.

CONCLUSION

The work presented here sought to determine the particle size distribution (PSD) of polymer produced in a reactor. This may be an important contributing factor affecting the polymer properties and reactor dynamics. We derived the PSD using population balances. Using the data published literature on Ziegler-Natta catalysts, we developed three reasonable mechanisms for propylene polymerization, i.e., a simple reaction mechanism, active site reduction mechanism, and two-active-sites model. We observed that:

1. PSD for Ziegler-Natta catalysts derived using three reasonable reaction mechanisms depends not only on reactor residence time, but also the reaction mechanism.

2. PSD depends slightly on the multiple types of active sites in the catalyst.

3. The initial catalyst volume does not change the shape of the PSD.

4. The cumulative PSD derived using a simple reaction mechanism agrees well with experimental data.

NOMENCLATURE

A : deactivation reaction term defined in Eq. (15)
B : deactivation reaction term of active sites for type-2 defined in Eq. (45c)
C : initiation reaction term defined in Eq. (15)
C_i : concentration of species i
CO : cocatalyst concentration
C_{pi} : heat capacity of species i
C_{pMl} : heat capacity of liquid propylene
CUM : cumulative particle size distribution function in a volume V to V+dV at time t
D : initiation reaction term of active sites for type-2 defined in Eq. (45c)
<D> : number average diameter
F : total particle size distribution [mol/cm^3]
F_i : molar flow rate of species i
f (V, t) dV : total particle size distribution function in a volume V to V+dV at time t
f_i (V, t) dV : number distribution function of particles containing i active site centers in a volume V to V+dV at time t
$f_{r, i-r}$ dV : number of particles with r active sites (type-1) and i-r active sites (type-2) in a volume V to V+dV at time t
g_n (i, V, t) : number of active sites of chain length n in a particle of size V
H_2 : hydrogen concentration
h : parameter defined in Eq. (31a)
I_α : modified Bessel function of order α
$\bar{i}$: average number of active sites
$\overline{i-r}$: average number of active sites defined in Eq. (46c)
M : monomer concentration
N : potential sites
N_A : Avogadro's number
N_d : dead sites

N_0 : active sites
q_{cf}, QCF : catalyst injection rate
Q_n : dead polymer of chain length n
$\bar{r}$: average number of active sites defined in Eq. (46b)
r_M : rate of monomer consumption
r_p : polymer mass growth rate
r_{trH} : rate of hydrogen chain transfer
r_v : rate of particle growth [cm^3/hr]
t : time
TR : residence time
V : particle volume
<V> : number average volume
V_R : reactor volume for olefin polymerization

Greek Letters

α_{vi} : variables defined in Eq. (49)
$\delta(V - V_0)$: delta function
ε : ratio of gas withdrawal rate to product withdrawal rate
ρ_{par} : particle density
λ_k : eigenvalues defined in Eq. (44)
μ_i : moment of the ith order for dead polymer
$\psi(\xi, t)$: generating function defined in Eq. (12)
$\psi(\zeta, \xi, t)$: bivariate generating function defined in Eq. (42)

Subscripts

c : catalyst
f : feed
H : hydrogen
M, m : monomer
o : initial
p : particle

Superscript

* : initial condition

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