Percolation in Catalytic Porous Media with Application to Polymerization

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Heterogeneous Ziegler-Natta catalysts, which are used primarily in the production of polyolefins, create a complex reaction medium in which diffusion and reaction are accompanied by continuous structural transformation of the pore space in the catalyst-polymer matrix. With the aid of percolation theory, a mathematical model has been developed that accounts for the effect of particle morphology on the polymerization reaction by monitoring the way it influences the transport phenomenon, and thus traces its effects on the properties of the final product (Rafi, 1986). In this note, a brief description of the model and its results are presented.

The relevant reactions of the polymerization system are the following, with hydrogen being the chain terminating agent.

Initiation: $P_0 + M \xrightarrow{K_p} P_1$

Propagation: $P_n + M \xrightarrow{K_p} P_{n+1} \quad n \geq 1$

Termination: $P_n + H_2 \xrightarrow{K_t} M_n + P_0 \quad n \geq 1$

Monomer (M) and hydrogen (H_2) are the only gaseous components; the rest of the molecules are either growing chains that are attached to the active sites (P_n, $n \geq 1$), or dead chains which, due to their large size, are practically immobile (M_n, $n \geq 1$).

The issue of transport phenomenon in porous catalysts was studied by Jackson (1977), among others, who developed the dusty gas model in which the solid portion of the porous medium is assumed to consist of giant and stationary molecules around which the small molecules travel, thus transforming the problem into that of binary diffusion. Based on this assumption, the model was further developed to encompass the cases of multicomponent gaseous systems and porous media of different structures. The molar flux equation for the components of a binary gaseous system flowing into a porous medium, in the most general case where the pore sizes range from the limit of Knudsen diffusion to that of bulk diffusion, is a combination of diffusive and viscous fluxes as shown in Eq. 1 (Jackson, 1977).

$$\underline{N}_i = -\frac{P}{R_g T} U_D \underline{\nabla} X_i - \frac{X_i}{R_g T} U_p \underline{\nabla} P$$

$$P = P_i + P_j; \quad i, j = 1, 2 \quad i \neq j \tag{1}$$

$$U_{Di} = \frac{\dfrac{1}{D_j}}{\dfrac{1}{D_i D_j} + \dfrac{1}{D_{ij}}\left(\dfrac{X_i}{D_i} + \dfrac{X_j}{D_j}\right)} \tag{2}$$

$$U_{Pi} = \frac{\dfrac{1}{D_j} + \dfrac{1}{D_{ij}}}{\dfrac{1}{D_i D_j} + \dfrac{1}{D_{ij}}\left(\dfrac{X_i}{D_i} + \dfrac{X_j}{D_j}\right)} + \frac{B_0 P}{\mu} \tag{3}$$

$$D_\alpha^K = \frac{2}{3} r \sqrt{\frac{8 R_g T}{\pi M_\alpha}} \tag{4}$$

$$D_{\alpha\beta} = \frac{2.2646 \cdot 10^{-5}}{C} \frac{\sqrt{T\left(\dfrac{1}{M_\alpha} + \dfrac{1}{M_\beta}\right)}}{\sigma_{\alpha\beta}^2 \Omega_{\alpha\beta}}$$

(Chapman-Enskog theory) (5)

Percolation theory, invented by Broadbent and Hammersley (1957), has served as a useful tool for quantitatively characterizing the randomly disordered media through statistical means, and thus describing their morphology and transport properties. The approach involves representing the chaotic medium via a geometrical lattice and evaluating certain properties of the medium by calculating the corresponding properties of the lattice, Figure 1. Ziman (1968) pointed out the connection between percolation theory and the conductivity or transport

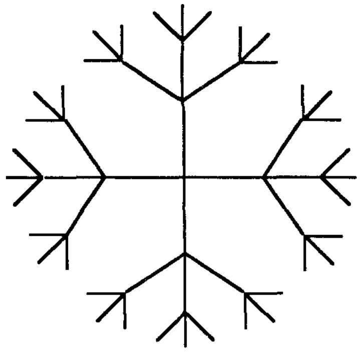

Figure 1. Bethe lattice with coordination number $Z = 4$.

properties of the disordered systems, an idea that was later supported by experiments (Kirkpatrick, 1971). Stinchcombe (1974) calculated the conductivity for distributed bond conductances in the case of a Bethe lattice, an endlessly branching structure with no reconnections which due to its simple topology has allowed for exact calculation of several of its other percolation properties (Fisher and Essam, 1961). In addition to the field of solid state physics, in which the idea originated and evolved, the concept has also proven useful in treating some chemical engineering topics, such as explaining various aspects of multiphase flow in porous media (Heiba et al., 1982), or estimating transport coefficients through coal particles in coal gasification (Reyes and Jensen, 1985).

Table 1. Dimensionless Variables

$$M = \frac{C_M}{C_{MB}}$$

$$\mathrm{H}_2 = \frac{C_{\mathrm{H}_2}}{C_{\mathrm{H}_2B}}$$

$$\pi = \frac{P(r;t)}{P_B} = \frac{MC_{MB} + H_2 C_{\mathrm{H}_2B}}{C_{MB} + C_{\mathrm{H}_2B}}$$

$$L_{MD} = \frac{U_{MD}(r;t;C)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}$$

$$L_{MP} = \frac{U_{MP}(r;t;C)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}$$

$$L_{HD} = \frac{U_{HD}(r;t;C)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}$$

$$L_{HP} = \frac{U_{HP}(r;t;C)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}$$

$$\xi = \frac{r}{R(t)}$$

$$\epsilon = \frac{R(t)}{R(t=0)}$$

$$\Psi_k^l = \frac{\mu_k^l}{P_0^*(t=0)}$$

$$\Psi_k^D = \frac{\mu_k^D}{P_0^*(t=0)}$$

$$P_0 = \frac{P_0^*(t)}{P_0^*(t=0)}$$

$$\tau = \frac{D_{M\mathrm{H}_2}(1\mathrm{atm})}{R^2(t=0)}\, t$$

$$x_{MB} = \frac{C_{MB}\, R_g T}{P_B}$$

$$x_{\mathrm{H}_2B} = \frac{C_{\mathrm{H}_2B}\, R_g T}{P_B}$$

$$H_p = \frac{k_p P_0^*(t=0)\; R^2(t=0)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}$$

$$H_t = \frac{k_t P_0^*(t=0)\; R^2(t=0)}{D_{M\mathrm{H}_2}(1\mathrm{atm})\; \sqrt{C_{\mathrm{H}_2B}}}$$

$$\alpha = \frac{C_{\mathrm{H}_2B}}{P_0^*(t=0)}$$

$$\beta = \frac{C_{MB}}{P_0^*(t=0)}$$

$$\mathrm{u} = \frac{R(t=0)}{D_{M\mathrm{H}_2}(1\mathrm{atm})}\, v$$

$$\gamma = \frac{M_{mon} C_{MB}}{(1-\phi)\, \rho_p}$$

The average transport coefficient of the porous medium is (Stinchombe, 1974):

$$L = -ZC'(0) \tag{6}$$

L is the dimensionless transport coefficient ($L = U/D_{\alpha\beta}$) through which the molecular properties of the percolating components are entered into the computation, taking into account the morphological properties of the medium. $C'(0)$ in Eq. 6 is the solution to the following nonlinear equation (which can be approximated by a series solution using Laplace transform):

$$\int_0^\infty e^{-tx} C(x)\, dx = \int dL\, g(L) \cdot \left\{ \frac{-1}{t+L} + \frac{L^2}{(t+L)^2} \int_0^\infty \exp\left(-\frac{Lt}{t+L} x \right) [C(x)]^{Z-1}\, dx \right\} \tag{7}$$

and the boundary condition:

$$C'(0) = 1$$

$$g[L(r)] = (1-\phi)\delta[L(r)] + \phi F[L(r)] \tag{8}$$

$$F[L(r)]\, dL(r) = f(r)\, dr \tag{9}$$

The average transport coefficients obtained in this manner are later substituted in the flux equations for monomer and hydrogen, which are combined with the balance equations of the polymerization model, that is, live and dead moments and the particle size, Eqs. 10–22. (See Table 1 for definitions of dimensionless variables.)

$$\frac{\partial M}{\partial \tau} = \frac{1}{x_{MB}\epsilon^2} \left[\frac{\partial x_M}{\partial \xi} \left(\frac{\partial(\pi L_{MD})}{\partial \xi} + \frac{2\pi L_{MD}}{\xi} \right) + \pi L_{MD} \frac{\partial^2 x_M}{\partial \xi^2} + \frac{\partial \pi}{\partial \xi} \left(\frac{\partial(x_M L_{MP})}{\partial \xi} + \frac{2 x_M L_{MP}}{\xi} \right) + x_M L_{MP} \frac{\partial^2 \pi}{\partial \xi^2} \right] - \mathrm{H}_p M(\psi_0^l + P_0) \tag{10}$$

$$\frac{\partial \mathrm{H}_2}{\partial \tau} = \frac{1}{x_{\mathrm{H}_2B}\epsilon^2} \left[\frac{\partial x_{\mathrm{H}_2}}{\partial \xi} \left(\frac{\partial(\pi L_{\mathrm{H}D})}{\partial \xi} + \frac{2\pi L_{\mathrm{H}D}}{\xi} \right) + \pi L_{\mathrm{H}D} \frac{\partial^2 x_{\mathrm{H}_2}}{\partial \xi^2} + \frac{\partial \pi}{\partial \xi} \left(\frac{\partial(x_{\mathrm{H}_2} L_{\mathrm{H}P})}{\partial \xi} + \frac{2 x_{\mathrm{H}_2} L_{\mathrm{H}P}}{\xi} \right) + x_{\mathrm{H}_2} L_{\mathrm{H}P} \frac{\partial^2 \pi}{\partial \xi^2} \right] - \mathrm{H}_t \psi_0^l \sqrt{\mathrm{H}_2} \tag{11}$$

$$\frac{\partial \psi_0^l}{\partial \tau} = \beta \mathrm{H}_p M P_0 - \alpha \mathrm{H}_t \psi_0^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial(u\xi^2 \psi_0^l)}{\partial \xi} \tag{12}$$

$$\frac{\partial \psi_1^l}{\partial \tau} = \beta \mathrm{H}_p M (\psi_0^l + P_0) - \alpha \mathrm{H}_t \psi_1^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial(u\xi^2 \psi_1^l)}{\partial \xi} \tag{13}$$

$$\frac{\partial \psi_2^l}{\partial \tau} = \beta \mathrm{H}_p M (\psi_0^l + P_0 + 2\psi_1^l) - \alpha \mathrm{H}_t \psi_2^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial(u\xi^2 \psi_2^l)}{\partial \xi} \tag{14}$$

$$\frac{\partial \psi_0^D}{\partial \tau} = \alpha \mathrm{H}_t \psi_0^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial(u\xi^2 \psi_0^D)}{\partial \xi} \tag{15}$$

$$\frac{\partial \psi_1^D}{\partial \tau} = \alpha \mathrm{H}_t \psi_1^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial (u \xi^2 \psi_1^D)}{\partial \xi} \tag{16}$$

$$\frac{\partial \psi_2^D}{\partial \tau} = \alpha \mathrm{H}_t \psi_2^l \sqrt{\mathrm{H}_2} - \frac{1}{\epsilon \xi^2} \frac{\partial (u \xi^2 \psi_2^D)}{\partial \xi} \tag{17}$$

$$\frac{\partial P_0}{\partial \tau} = \alpha \mathrm{H}_t \psi_0^l \sqrt{\mathrm{H}_2} - \beta \mathrm{H}_p M P_0 - \frac{1}{\epsilon \xi^2} \frac{\partial (u \xi^2 P_0)}{\partial \xi} \tag{18}$$

$$\frac{\partial \epsilon}{\partial \tau} = u(\xi = 1) = \mathrm{H}_p \gamma \epsilon \int_0^1 M \psi_0^l \xi^2 \, d\xi \tag{19}$$

Initial Conditions:

$$\begin{aligned} \text{at } \tau = 0 \quad & M = \mathrm{H}_2 = 0 \\ & \psi_0^l = \psi_1^l = \psi_2^l \\ & \psi_0^D = \psi_1^D = \psi_2^D = 0 \\ & P_0 = 1 \\ & \epsilon = 1 \end{aligned} \tag{20}$$

Boundary Conditions:

$\forall \tau > 0$

$$\begin{aligned} \text{at } \xi = 0 \quad & \frac{\partial M}{\partial \xi} = \frac{\partial \mathrm{H}_2}{\partial \xi} = 0 \\ & \frac{\partial \psi_0^l}{\partial \xi} = \frac{\partial \psi_1^l}{\partial \xi} = \frac{\partial \psi_2^l}{\partial \xi} = 0 \\ & \frac{\partial \psi_0^D}{\partial \xi} = \frac{\partial \psi_1^D}{\partial \xi} = \frac{\partial \psi_2^D}{\partial \xi} = 0 \\ & \frac{\partial P_0}{\partial \xi} = 0 \end{aligned} \tag{21}$$

$$\text{at } \xi = 1 \quad M = \mathrm{H}_2 = 1 \tag{22}$$

The resulting initial boundary value problem is solved numerically using orthogonal collocation for spatial discretization (Villadsen and Michelsen, 1978), and the backward difference method for time integration (Hindmarsh, 1981). The pore size distribution of the medium, $f(r)$, Figure 2, and the connectivity of the porous medium (symbolized by the coordination number Z) are two morphological characteristics of the particle which enter the calculation of transport coefficients. According to the results obtained, any change in the former parameters that alters the value of transport coefficients noticeably also affects the molecular weight distribution of the polymer product and this is detected by observing the value of polydispersity. Figures 3 and 4 demonstrate the sensitivity of polydispersity to both the pore size distribution and the coordination number. In Figure 3, an increase in coordination number indicates a more concentrated network of channels and thus more efficient transport, which in turn amounts to a more homogeneous concentration of monomer inside the particle, and a polymer product with lower polydispersity. The same explanation holds for Figure 4, in which the pore size distribution that contains a higher concen-

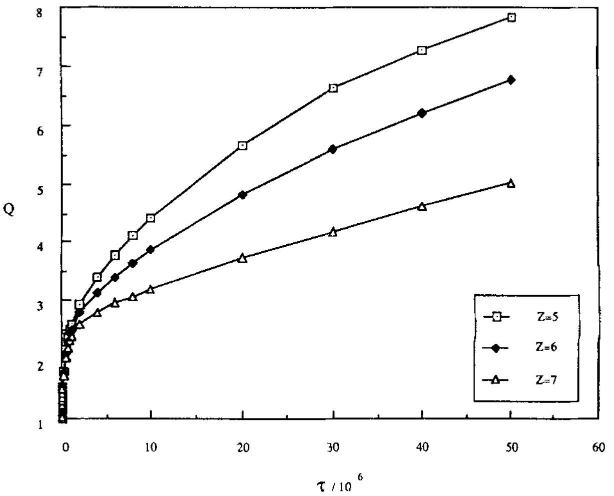

Figure 3. Polydispersity vs. time.
Three different coordination numbers Z (connectivity of the medium) with one pore size distribution (PPSD)

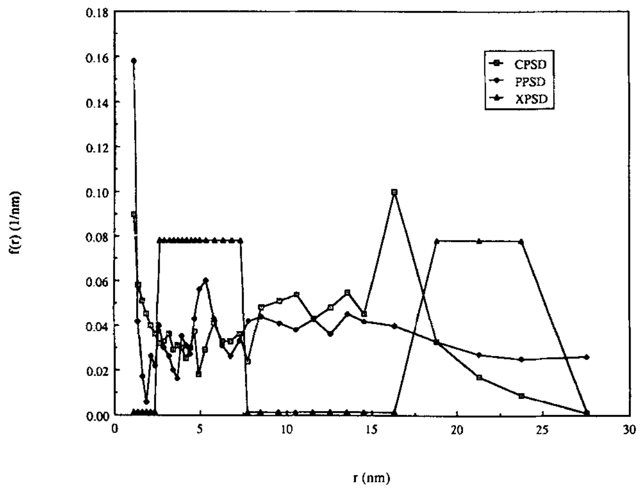

Figure 2. Pore size distribution vs. pore radius.
Three different cases of catalyst (C), polymer (P), and arbitrary (X) pore size distributions (PSD)

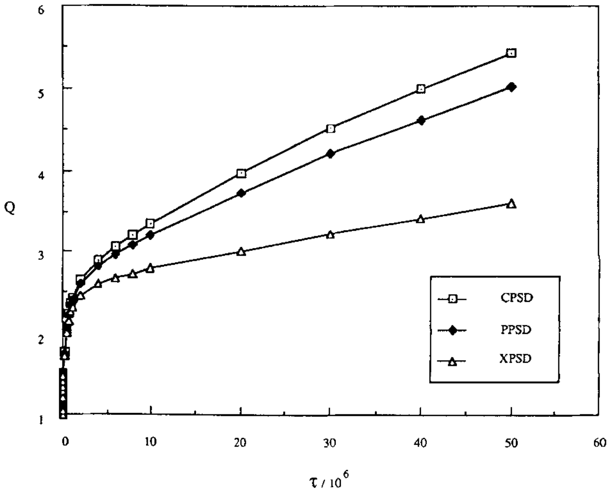

Figure 4. Polydispersity vs. time.
Three different pore size distributions for the same degree of connectivity, $Z = 7$.

tration of large pores provides easier transport and thus lower polydispersity. The three different cases of the pore size distribution are those of the catalyst particle before the reaction (CPSD), the polymeric product pellet after the reaction (PPSD), both of which are based on experimental data, and an arbitrary but plausible bimodal distribution in order to study its effect (XPSD).

The results of this work vividly demonstrate the importance of physical effects (morphology, mass transport) in contributing to the broadness of molecular weight distribution, although one is well aware of the fact that chemical effects, namely the existence of more than one type of catalytic active site, are also responsible for this phenomenon (Goodall, 1981). We emphasize the fact that we have not adjusted the values of transport coefficients, but rather only the geometry of the medium in an attempt to closely examine its effect. The completely random structure of the pores is able to impose a steep monomer concentration profile along the radius of the particle, and thus favor some loci with respect to the availability of monomer molecules; this consequently produces longer chains in regions that are richer in monomer. It is clear that any additional knowledge regarding the behavior of the catalyst particle, as provided by this model, can be utilized in tailoring certain types of catalysts designed to perform specific tasks.

Acknowledgment

The experimental data for the catalyst and polymer pore size distributions were provided by the Mobil Chemical Company. A major portion of this work was supported by the Minnesota Supercomputer Institute.

Notation

B_0 = permeability of medium
C = concentration
CPSD = catalyst pore size distribution
D = Knudsen diffusion coefficient
D = binary diffusion coefficient
$f(r)$ = pore size distribution
F = probability distribution
g = probability distribution
H_2 = dimensionless hydrogen concentration
K_p = propagation rate constant
K_t = termination rate constant
L = dimensionless transport coefficient
M = dimensionless monomer concentration
M_α = molecular weight of species α
M_n = concentration of dead polymer chain of length n
N = mass flux
P = pressure
P_n = concentration of live polymer chain of length n
P_0^* = concentration of unreacted active sites
P_0 = dimensionless concentration of unreacted active site
PPSD = polymer pore size distribution
Q = polydispersity
r = pore radius
r = radial position
R = radius of particle
R_g = gas constant
t = time
T = temperature
u = dimensionless local expansion velocity
U = transport coefficient
V = local expansion velocity inside pellet
X_i = mole fraction of component i
XPSD = an arbitrary bimodal pore size distribution
Z = coordination number

Greek letters

δ = Dirac delta function
ϵ = dimensionless radius of particle
ϕ = pore volume fraction
μ = viscosity
μ_i^l = ith live moment
μ_i^D = ith dead moment
π = dimensionless pressure
ρ = density
$\sigma_{\alpha\beta}$ = collision diameter for species α and β (Chapman-Enskog theory)
τ = dimensionless time
Ω = collision integral (Chapman-Enskog theory)
ξ = dimensionless radial position
ψ_i^l = dimensionless ith live moment
ψ_i^D = dimensionless ith dead moment

Subscripts

α = species
β = species
b = bulk
D = diffusion
i = component i
j = component j
n = chain length
P = polymer
P = pressure

Superscripts

D = dead
l = live
K = Knudsen

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Manuscript received June 29, 1987, and revision received Nov. 2, 1987.