

Modeling of Transfer Phenomena on Heterogeneous Ziegler Catalysts. III. Modeling of Intraparticle Mass Transfer Resistance

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SYNOPSIS

The use of equations such as $D_{\text{pore}} = D_{\text{Bulk}} (\varepsilon/\tau)$ to predict pore diffusivities in the modeling of liquid phase polymerizations on heterogeneous Ziegler-type catalysts leads to highly unrealistic results when applied to situations with activities greater than 10,000 g/g/h or higher (polyethylene in suspension). A simple, isothermal model of mass transfer with reaction is presented and is used to examine the slurry polymerization of ethylene at activities higher than those previously studied in order to explore the major tendencies in the development of concentration gradients and average molecular weight of the polymer and to evaluate accepted estimates of monomer diffusivity in the catalyst pores. Experimental results are compared with the predictions of the classic reaction diffusion model, and it is shown that values of monomer diffusivity commonly used to model slurry polymerisations are not high enough in order to correctly simulate the activity levels obtained in this work. The modeling study shows that the effect of mass transfer resistance on the molecular weight is not all together negligible and that either estimates of the diffusion coefficient of ethylene in the catalyst pores need to be revised, or that more complete description of mass transfer is required than is provided by the classic reaction/diffusion equations. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

As discussed in part I,¹ earlier work on the modeling of mass and energy transport phenomena on Ziegler type catalysts has been presented, in particular by Chiovetta et al.^{2–7} and by the research group of Ray at the University of Wisconsin.^{8–16} These models were based on the well-known multigrain model of catalyst morphology and dealt with catalyst particle fragmentation (rupture of primary catalyst particles), the relationship between fragmentation and the development of concentration and temperature profiles in the growing polymer particle during the initial stages

of polymerization, intra- and extraparticle gradients and resistances, and their influence on the properties of the polymer being produced. Recent articles have discussed the merits of existing models.^{17,18}

It would seem that the multigrain model provides an adequate representation of particle morphology and simplifications, such as the possibility that neglecting microparticle concentration gradients are probably acceptable; hence, the use of isovolumetric shells in modeling single particle catalysts. It was also found that diffusion resistance could generally not explain the wide molecular weight distributions often observed in these systems. At the time these models were developed, peak activities for ethylene polymerization on the order of 10,000 grams of polymer per gram of catalyst per hour (g/g/h) and average activities on the order of 5000 g/g/h were considered to be

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high. Since then, activities of well over 25,000 g/g/h of catalyst per hour have come to be commonly observed in industrial practice for both the gas and slurry phase polymerization of ethylene. However, it was shown in part II of this series that there is no evidence of any mass transfer resistance in the pores of the growing polymer particles produced on such highly active catalysts, even under unfavorable conditions.¹⁹ Discrepancies have been encountered when trying to model these more active systems using the data and assumptions in the literature.^{1-16,19}

MASS TRANSFER AND MOLECULAR WEIGHT MODELS

In what follows, we deal exclusively with the problem of mass transfer in heterogeneous catalysts in suspension reactions. Also, because the solvent acts as a sort of thermal buffer, it can be assumed as an initial approximation that the growing catalyst/polymer particles are isothermal. This assumption is probably only approximate but allows us to decouple the heat and mass transfer problems. Mass transfer in the polymer particles is governed by the following equation:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot N_i - R_{pi} \quad (1)$$

where $N_i = D_i \nabla C_i - C_i u$, with the initial and boundary conditions of

$$\begin{aligned} t &= 0 \\ C_i &= C_i^o \\ r &= 0 \\ \frac{\partial C_i}{\partial r} &= 0 \\ r = RD_i \frac{\partial C_i}{\partial r} &= k_s (C_i|_{\text{bulk}} - C_i|_{\text{surface}}) \end{aligned}$$

Here, N_i is molar flux of species i , D_i is its diffusivity, C_i is its concentration, R_{pi} is the rate at which it is consumed per unit volume of growing particle, and u is a superficial convective velocity, implicitly assumed to be naught in some of the literature²⁻¹⁶ and most other works on this subject. k_s is a mass transfer coefficient, evaluated from Sherwood number calculations. In this study, it is estimated using the well-known Ranz–Marshall

correlation. R_p is, in reality, a complex function of catalyst composition, time, concentration, temperature, etc. However, due to the difficulty encountered in describing this value, an expression of the form

$$R_{pi} = kC_i \quad (2)$$

is generally used, where k is an empirical rate constant having units of inverse time, and C_i is the concentration of the polymerizing monomer per unit volume in the growing particle. It is not realistic to imagine that a general, nonempirical formula can be found to describe all types of kinetic behavior. We are thus obligated to use empirical expressions based on experimental observation; for example, $k = k_0 a(t) d(t)$ where k_0 is a constant, $a(t)$ is a time-dependent function describing the rate of activation of the catalyst (the time it takes to reach its peak intrinsic value), and $d(t)$ is an empirical function describing the rate of deactivation of the catalyst. Each of the parameters in eq. (2) can be adjusted to provide a rate curve fit to experimental results. Representations such as this are a double-edged sword. On the one hand, they are a convenient way of expressing reaction rates in the absence of a general model for catalyst kinetics; but, on the other hand, improper choices for the activation and deactivation portions of the rate constant expression can either create or mask potential transport limitations. In the following text, we provide a form for the rate expression that seems to fit the kinetic data commonly obtained in our laboratories but briefly explore the impact of removing the activating and deactivating portions of the constant in order to determine whether or not artificial transport limitations are created.

In the model used in this work, eq. (1) was solved numerically by dividing the growing particle into a series of isovolumetric shells at time 0. Each shell contains the same mass of catalyst for the entire reaction, and it is assumed that the concentration is identical everywhere inside a given shell but can vary from shell to shell. This solution technique, shown schematically in Figure 1, has been discussed by Spitz et al.²⁰ and is a simplified form of the model used by Hutchinson et al.¹⁶

The evaluation of the effect of mass transfer resistance on the molecular weight distribution is

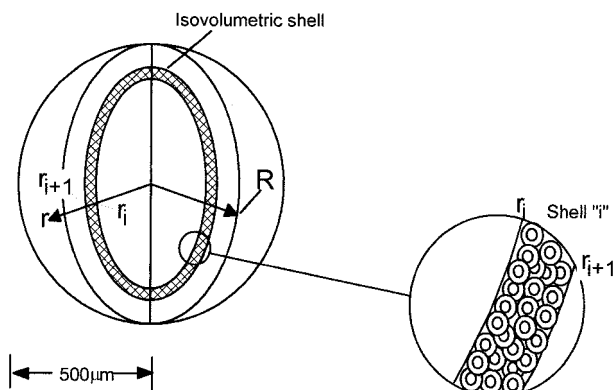


Figure 1 Schematic of MGM model of particle growth. The virgin catalyst particles are typically on the order of $10\ \mu\text{m}$ in radius. Monomer diffusing from the surrounding bulk phase penetrates the pores and is polymerized. Hydraulic forces caused by the formation of polymer caused the microparticles to rupture, but macromolecular entanglement holds the growing particles together. The final particle is on the order of $1\ \text{mm}$ in diameter. The arrangement of isovolumetric shells used in the numerical solution is also shown.

relatively straightforward and involves a number of simplifying assumptions. It is most likely that one can associate an intrinsic molecular weight distribution with a given catalyst in much the same way that one can define a theoretical intrinsic activity. This means that in the absence of any mass transfer resistance, the combination of active sites of the catalyst will produce a polymer with a fixed polydispersity q and a number average molecular weight M_n . The absolute values of q and M_n for a given polymer will depend on the chemical nature and distribution of the active sites in a given batch of catalyst but are proportional to the concentration of monomer at the sites. In the following study, it is assumed that intrinsic values of q and M_n can be assigned to the catalyst and that any deviations from these intrinsic values will be a reflection of mass transfer resistances. The simplified method of quantifying the effect of concentration gradients on the molecular weight distribution (MWD) is as follows.

1. A value for the polydispersity of the polymer produced at the active sites is specified; in the current work, we use a base case value of $q = 8$ (a value which represents something of an upper limit for this type of catalyst).
2. A value for the weight average molecular

weight that would be produced in the absence of any gradients (i.e., with the concentration in the growing particle equal to the concentration of monomer in the bulk phase, C_0) M_{w0} is specified. Dividing M_{w0} by q yields a value for M_{n0} .

3. It is assumed that M_n is proportional to the concentration C : $M_n = kC$. Using C_0 and M_{n0} from step 2, a value is calculated for k .
4. Using this value for k , M_n is calculated in each of the isovolumetric shells in the growing particle as a function of time and position. Weighted sums are then used to calculate overall values of M_n , M_w , and q . In doing so, it is assumed that q at the active sites is independent of time, concentration, and polymer molecular weight; i.e., in each shell, q remains unchanged. But since the molecular weight averages can vary from shell to shell, the overall polydispersity can be different from the intrinsic value. While this assumption of the invariability is probably not 100% accurate, such variations would have the effect of broadening our estimate of the MWD even further.

Note that the simplifications used in this type of calculation do not change the meaning of the results. This algorithm has the distinct advantage of being rapidly programmable on a personal computer without requiring the use of library subroutines to solve coupled partial differential equations, yet appears to yield results that are in good agreement with simulations performed using much more complex and time-consuming software routines. Soares and Hamielec¹⁷ used a similar approach for the calculation of molecular weight distributions *i*th success.

Equation (2) was solved, assuming that there was no convective flux inside the particles (i.e., the same equations were used here as in references).²⁻¹⁶ However, as was discussed in these same works, the results of the simulations are highly dependent on the choice of the value of the monomer diffusivity. The values used in the literature are summarized in Table I. Generally speaking, the diffusivity of ethylene and propylene monomers in a hydrocarbon diluent (hexane or heptane) is estimated to be on the order of $10^{-8}\ \text{m}^2/\text{s}$, with pore diffusivities being an order of magnitude smaller since they are estimated using the following well-known relation:

Table I Values of Olefin Diffusivities Used in Literature

Milieu	Diffusivity in m ² /s		
	Refs. 2–7	Refs. 8–16	Ref. 21 (for C ₃ H ₆)
Bulk phase	10 ⁻⁹ –10 ⁻⁸	8 × 10 ⁻⁹ –1.5 × 10 ⁻⁸ (40–80°C)	3.58 × 10 ⁻⁹
Particle pores	3.2 × 10 ⁻¹⁰ –1.9 × 10 ⁻⁹	10 ⁻¹⁰ –10 ⁻⁹	2.24 × 10 ¹⁰
Polymer	2.4 × 10 ⁻¹⁵ –2.4 × 10 ⁻¹⁶	10 ⁻¹² –10 ⁻¹⁰	10 ⁻¹¹

$$D_{\text{pore}} = D_{\text{Bulk}} \frac{\varepsilon}{\tau} \quad (3)$$

where ε is the porosity of the catalyst/growing polymer particles, and τ is their tortuosity.

SIMULATION RESULTS AND DISCUSSION

If we assume that a simple diffusion coefficient describes mass transport inside the particles, it is possible to solve eq. (1) using a combination of the parameters shown in Table I and an estimate of the pore diffusivity using eq. (3). In our simulations, it was assumed that the diffusivity did not vary as a function of position. An example calculation is shown in Figure 2 for the suspension polymerization of ethylene using the parameters in Table II, with the rate constant adjusted to give a productivity of approximately 1700 g of polyethylene per gram of catalyst in one hour. (Note that the second term in parentheses in the rate expression of Table II is a deactivation term, with deactivation becoming more important as the particles grow, i.e., as the productivity increases). The monomer concentration profiles for this polymerization are also shown in Figure 2. At one point, the center value is less than half the surface concentration, even at these low rates of reaction. Note that these curves are for ethylene; to find the equivalent propylene polymerization rates in g/g/h, it is necessary to multiply by 44/28. These results are in excellent agreement with the simulations presented in Hutchinson et al.¹⁶

Note that even though the concentration of monomer at the center of the particle drops significantly at short time, this effect disappears relatively rapidly at low levels of activity, and mass transfer resistances have only a very limited effect on the polydispersity of the polymer. It can

be seen in Figure 2 that after a relatively short lapse of time, the polydispersity is essentially equal to its (specified) intrinsic value of 8. When average activities reach 6000 g/g/h (not shown), the overall polydispersity is on the order of 13 at the end of one hour, and it falls to about 9.5 after three hours of polymerization for 25 μm particles. It is therefore not surprising that earlier workers who modeled this level of activity, concluded that mass transfer resistance does not influence the molecular weight distribution to a significant extent.

However, current levels of catalyst activity are commonly much higher than this, as shown by the curves in Figure 3. As shown in part II of this series, there is no evidence of mass transfer resistance in these experiments, even at activities on the order of 25,000–40,000 g/g/h with reduced monomer diffusivity.¹⁹ These experimental data, obtained on standard supported catalysts, show that activities much higher than 2000 g/g/h are easily obtainable and that it is possible to attain rates on the order of 40,000 g/g/h in less than three minutes without any mass transfer resistance.

Current models and parameter sets have difficulty in describing such highly active reactions, especially when the maximum activity is reached in less than two or three minutes. For example, the simulations shown in Figure 4, obtained using the diffusivities and particle sizes in Table II, predict that it is difficult to attain peak activities on the order of 25,000 g/g/h for particles of 25 μm in radius. It is predicted that the concentration gradient in the macroparticle was simply too high to permit the estimated activity levels to reach anywhere near the intrinsic level. [Note that intrinsic activity levels refer to the activity (and productivity) that would be observed in the absence of mass transfer resistance, i.e., if the con-

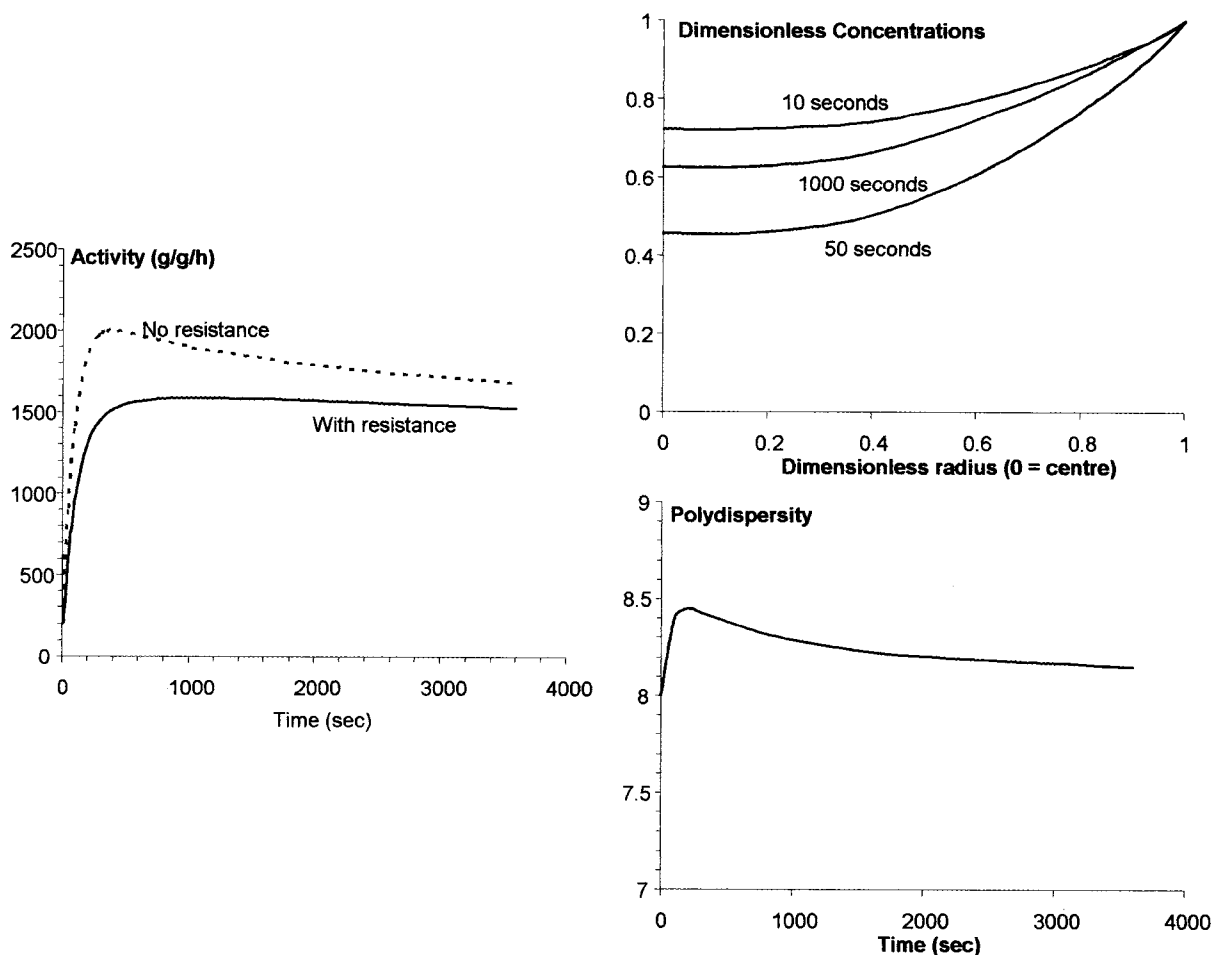


Figure 2 Suspension polymerization of ethylene at 80°C. Left: Activity profiles with resistance indicates a bulk diffusivity of 10^{-8} m²/s and a pore diffusivity of 6.67×10^{-10} m²/s. Top right: Dimensionless concentration profiles as a function of radial position and time. Bottom right: Polydispersity. At low activities, the polydispersity deviates only slightly from its intrinsic value of 8. The largest deviation occurs during the time during which the largest concentration gradients are observed across the growing particles.

Table II Parameters Used in Base Case Simulations

Bulk diffusivity	10^{-8} m ² /s
Pore diffusivity	6.7×10^{-10} m ² /s
Torosity	6
Porosity	0.4
Bulk conc. ethylene	450 mol/m ³
Original particle radius	25 microns
Intrinsic productivity	1700 g/g/h
Intrinsic M_{wo}	150,000
Intrinsic polydispersity	8
Temperature	80°C

Rate expression: $k = k_0 [1 - \exp(0.01t)] [\exp(-0.03R/R_0)]$

centration of monomer at the active sites equalled the concentration of monomer in the bulk phase of the reactor.] In fact, the concentration of ethylene at the centre hits zero after 10 s with the kinetic expression used here and stays there throughout the simulated period. As shown in Figure 4, almost half of the particle is void of monomer after a short period. The activity of the polymerization reaction at the end of one hour was found to be 6300 g/g/h for these particles. Also, the polydispersity obtained with these values is unrealistically high, even if we begin with a reasonable intrinsic value of $q = 8$. After four hours, the overall polydispersity is predicted to be 17.8. Such values are rarely seen experimentally,

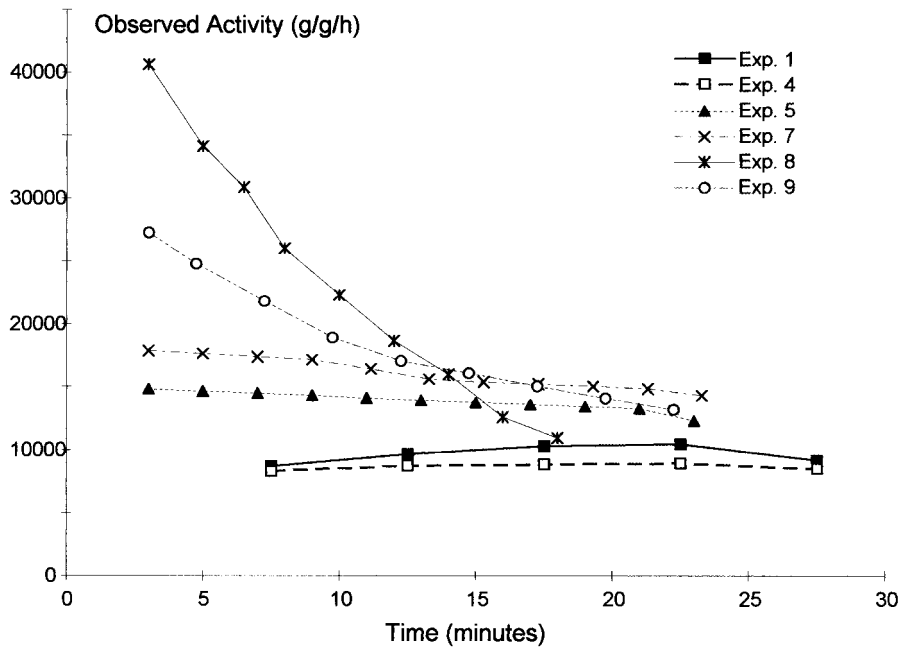


Figure 3 Experimentally observed rates for the slurry polymerization of ethylene. The same batch of catalyst was used for each reaction. Average particle diameter at $t = 0$ was $15 \mu\text{m}$.

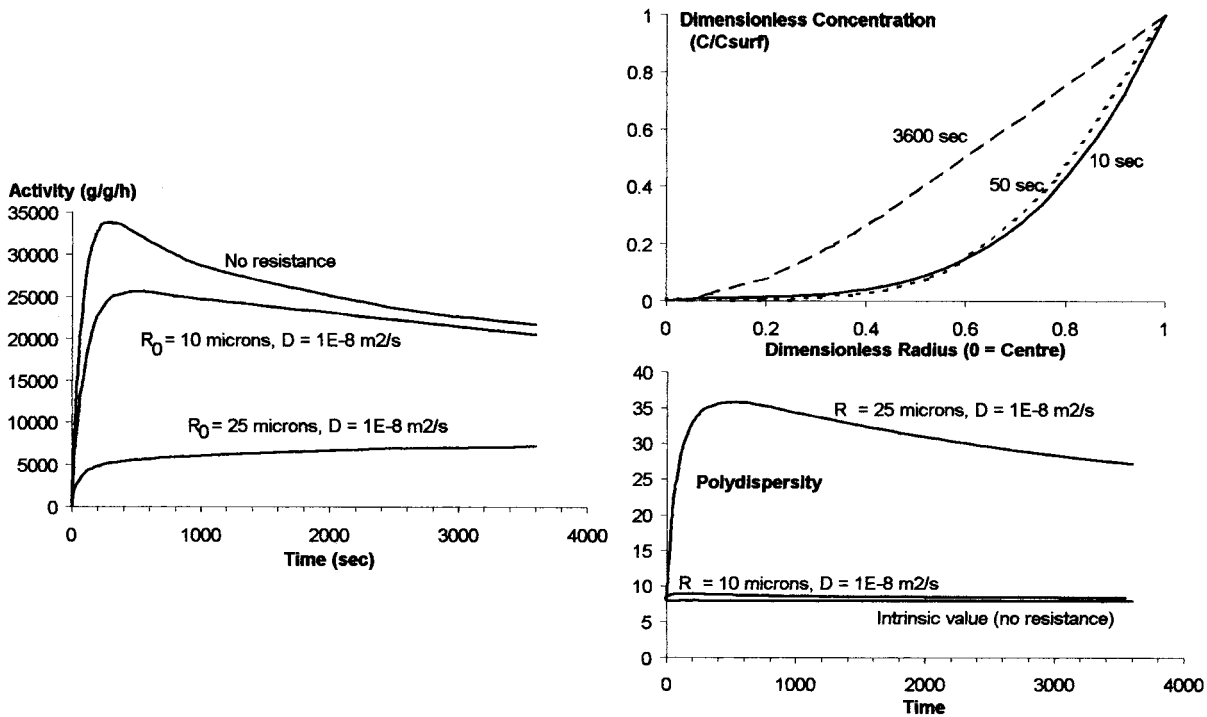


Figure 4 Suspension polymerization of ethylene at 80°C . Top: Activity profiles. Bottom left: Dimensionless concentration profiles as a function of radial position at 10, 50, and 1000 s for a particle of $25 \mu\text{m}$ radius. Bottom right: Evolution of global polydispersity.

and never with high activity catalysts. Additionally, if the concentration of monomer were really to fall to zero in a significant portion of the growing particles, polymerization in the exterior layers only would lead to the formation of hollow polymer particles, a result rarely, if ever, found.

Furthermore, increasing the specified value of the intrinsic activity of the catalyst in the simulations in order to obtain high observed rates that might be masked by mass transfer resistance does not help us to find experimentally observed results since the higher the intrinsic activity of the catalyst, the larger the part of the particle that sees no monomer. The observed activity of the particles of radius $25\ \mu\text{m}$ can be increased, but not much above $10,000\ \text{g/g/h}$; and even this requires that the intrinsic activity be increased by a factor of four (i.e., intrinsic productivities of almost $40,000\ \text{g/g}$). Doing so leads to dramatic increases in the predicted value of the polydispersity, again to levels that are never seen in reality.

However, it should be noted here that the particles considered in the simulation shown in Figures 2 and 4 are relatively large. A radius of $25\ \mu\text{m}$ was chosen to compare these results with those in Hutchinson et al.¹⁶ but radii on the order of $5\text{--}15\ \mu\text{m}$ are more common in slurry polymerizations. Nevertheless, even if the average radius is on the order of $5\text{--}15\ \mu\text{m}$, a significant portion of a batch of catalyst will be made of bigger particles that would undergo visible mass transfer resistance if the model presented above accurately described the physics of the polymerization. For example, the polymerizations shown in Figure 3 were performed on a batch of catalyst with an average particle diameter of $15\ \mu\text{m}$, but 30% of the particles were greater than $20\ \mu\text{m}$ in diameter, and approximately 15% were greater than $30\ \mu\text{m}$.

Secondly, the results, especially the concentration profiles, are sensitive to the slope of the activating portion of the activity curve. The faster the catalyst is activated, the faster the concentration gradients form, and the more important they are. The definition of this part of the activity curve depends to a large extent on the trade-off between chemical and mass transfer effects; it can also be seen in Figure 4 that cases of high mass transfer resistance can mask the intrinsic maximum activity. This has been discussed previously,^{2,6,8-10} and does not change from low to high activity ranges. On the other hand, the experimental polymerizations on the $\text{TiCl}_4/\text{MgCl}_2$ catalysts in Figure 3 reach their maximal activity levels in three min-

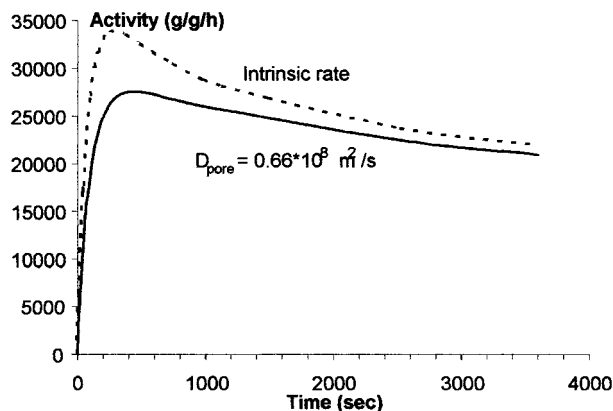


Figure 5 Curves of Figure 4 resimulated with a pore diffusivity ten times greater than that used above. The effect is to approach observed and intrinsic rates and to lower the polydispersity to a maximum of 8.26.

utes, much faster than the intrinsic rate curves in Figures 2 and 4.

In order to achieve polymerization rates on the order of tens of thousands of g/g/h in particles of $25\ \mu\text{m}$ in radius, it was necessary to increase the monomer diffusivity in the pores of the catalyst to values on the order of the diffusivity in the bulk phase. For example, it can be seen from the curves in Figure 5 that specifying a pore diffusion value ten times higher (i.e., almost equal to the bulk value) than the value used in the simulation shown in Figure 4 leads to a polymerization rate close to the intrinsic value. Also, the polydispersity never exceeds a value of 8.25 in this case and is 8.1 after one hour of polymerization. But while it may be reasonable to use values of pore diffusivities that approach bulk values at the end of the polymerization process, it is not reasonable to do so during the early stages of the reaction where the pores are extremely small. Hutchinson et al.¹⁶ allowed the diffusivity to evolve as the porosity and tortuosity of the particle changed; but although this approach does allow D_{pore} to increase as the polymerization progresses, it does not increase by enough, nor does it increase quickly enough to alter the above observations.

It is clear from the above discussion that, in order to describe highly active systems, the predicted flux in the mass transfer model must increase by approximately one order of magnitude (at least a factor of five to ten). If we examine eq. (1), such an increase can result from one of two sources: either the estimate of the bulk diffusivity is incorrect, which is possible since data are scarce

for this kind of system, and further experiments are needed to test this; or convection plays a role in the development of the flux of monomer inside the catalyst particles during the early stages of the polymerization.^{1,22} Results in McKenna and Schweich²² suggest that, for gas phase polymerizations, convective velocity profiles can be established in the particles. This will be the object of a forthcoming article.

CONCLUSIONS

The above discussion has focused on the need for a better description of mass transfer in the slurry polymerization of ethylene on heterogeneous catalysts. It turns out that the use of previously published models and data together lead to the prediction of polydispersities much higher than those actually observed and to the prediction of prohibitive mass transfer resistance in highly active systems.

In order to be able to model systems having peak activities over 10,000 g/g/h, it is necessary to increase the estimate of the internal particle mass transfer flux by a factor of approximately 5 to 10. This can be achieved by using a value of the pore diffusivity of ethylene that approaches its bulk phase value. This approximation can be justified in light of the fact that reliable data for this parameter is scarce. It can also be considered as an approximation that includes the eventual contribution of convection to the overall mass flux.

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