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Progress in Describing Particle Growth for Polyolefins: A Look at Particle Morphology

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SUMMARY: Discussion focuses on the strengths and weaknesses of current methods of modelling particle growth, and heat and mass transfer during the polymerisation of olefins on supported Ziegler-Natta Catalysts. It is demonstrated that improvements need to be made in the area of mass transfer models in the form of a mechanistic description of particle morphology. Scanning electron microscopy (SEM) is used to examine particle morphology. Simplified models of particle growth demonstrate the need to include convection in gas phase processes and a better description of particle morphology.

Introduction

As work continues in the field of the reaction engineering of polyolefins, it is clear that we have made much progress in the field of modelling heat and mass transfer over the course of the past 15 years - and that even more progress needs to be made over the course of the next few years. The well-known MGM and PFM (multigrain and polymer flow models respectively) proved to be interesting concepts[1,2,3,4,5,6)]. They told us a great deal about how transport phenomena occurred at the level of the single particle, where the most significant resistances are localised, etc. Nevertheless it is apparent that these representations of growing particles are not sufficient if we are to improve our physical and mathematical descriptions of particle growth, if we hope to clearly distinguish between chemical effects (e.g. intrinsic catalyst activity or chemical deactivation of catalysts) and physical effects in the catalyst, and if we are to ultimately understand (and use) the relationship between reactor conditions and the material properties of the final particles[7,8)]. This paper will describe some of the issues that need to be better addressed if we are to improve our ability to accurately model particle grow.

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Mass transfer modelling and morphology

Consider what happens to a particle once it is injected into the reactor. Immediately upon injection, monomer starts to flow into the pores of the catalyst particle, and polymer forms on the surface of the active sites. Monomer continues to flow into the pores if they do not fill up, then through the layer of polymer (of course, diffusion through the polymer will occur whether or not the pores fill up, it will just be excessively slow if they do). As shown schematically in the top part of Figure 1, once enough polymer forms, the support fragments and the micrograins move apart, but the original particle maintains its integrity due to the polymer already formed. From a chemical engineering point of view, fragmentation is absolutely necessary. It was shown in the literature that if fragmentation does not occur, the build-up of polymer slows down the diffusion process so much that the reaction shuts down for want of monomer$^{9)}$.

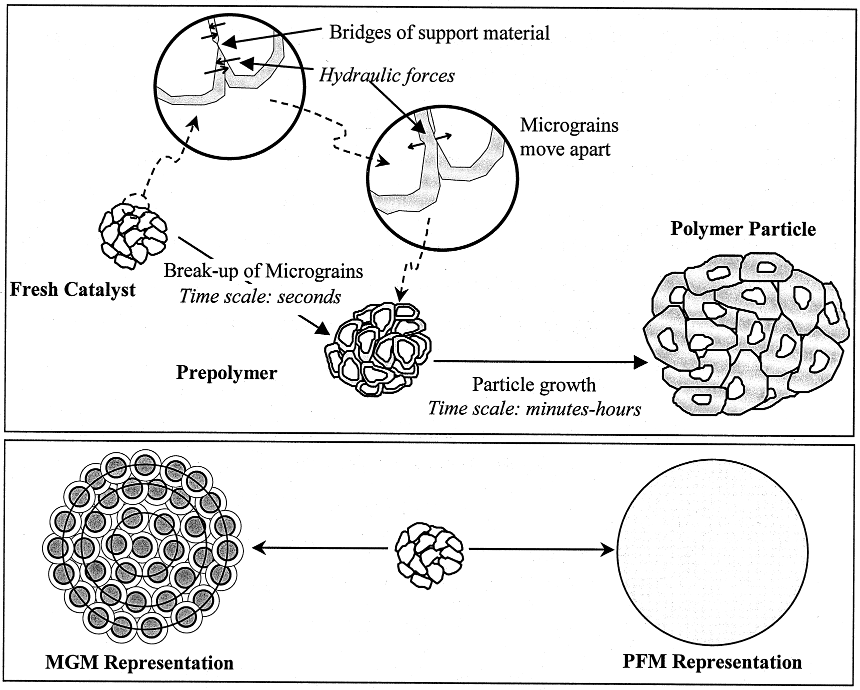


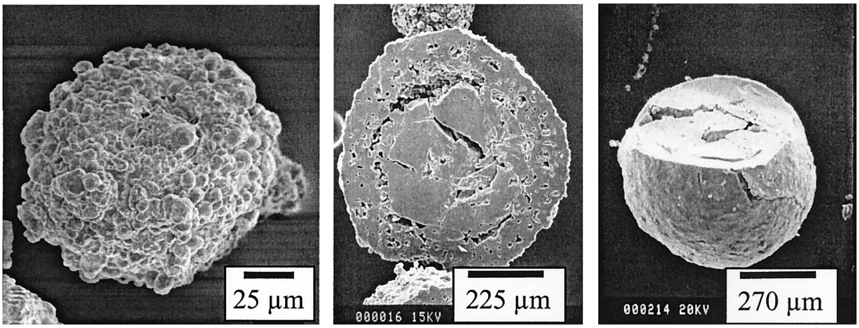
Fig. 1: (top) A schema of the process of fragmentation of a supported catalyst particle. (bottom) 2 mathematical representations of particle morphology used to model particle growth. MGM = Multigrain model, PFM = polymer flow model.

Clearly, **one** of the key issues here is particle morphology, (size, shape, porosity and pore size distribution). Morphology will govern the rate of diffusion in the particle. The rate of diffusion, reflected by the characteristic diffusion time, τ_d, varies as a function of time and morphology according to the very simple law:

$$\tau_d \propto \frac{L^2}{D_{eff}} \tag{1}$$

where L^2 is the characteristic length scale for diffusion and D_{eff} is the effective diffusivity in the particle. Let us consider a gas phase reaction. Under typical reaction conditions, D_{eff} will be on the order of 10^{-12}-10^{-10} m²/s for the diffusion of an olefin monomer through a polyolefin, and on the order of 10^{-7}-10^{-6} for the monomers in the pores of the growing particle5). This means that, for the same value of L^2, the characteristic time for diffusion in the growing particles will be thousands of times faster in the pores than in the polymer. The total mass transfer time inside the particles will therefore depend on the absolute length scales for diffusion in the pores and in the polymer. If this transfer time is long enough (i.e. longer than the characteristic time of the reaction), the reaction can become diffusion limited.

Clearly, we will need an accurate description of the morphology of the growing particles if we are to hope to model them correctly. In the case of the MultiGrain Model (MGM) where the particle is considered to be an arrangement of concentric spherical layers of micrograins, it is usually assumed that we get total particle replication, and the individual micrograins "survive" throughout the entire reaction. This leads to the conclusion that the polymer layers are very thin (10^3 times smaller than the radius of the particle), so the characteristic time for diffusion in the polymer is very short compared to the characteristic time for reaction, despite the difference in diffusivities6). Modern versions of the MGM therefore neglect the presence of micrograins and model the particle as if it were a pseudo-homogeneous body, where mass transfer occurs by diffusion only with an effective diffusion coefficient approximately one tenth of that for the monomer in the continuous phase of the reactor6,10) (for example 10^{-7}-10^{-6} m^2/s in gas phase). This simplified model is very similar to the polymer flow model (PFM), the difference being that in the PFM the particle is considered to be made up of a continuous polymer matrix, in which the active sites are uniformly dispersed. So, according to the PFM, the monomer must diffuse through the polymer matrix to the active sites (with a diffusivity about 10^{-10} m²/s for the diffusion of an olefin monomer through a polyolefin). This means that since the characteristic length scale for diffusion in the polymer is seven orders of magnitude larger than that of the MGM (i.e. the effective diffusivities are not the same), this model predicts significant diffusion resistance with respect to the MGM.



Prepolymer **impact PP** **PP Homopolymer**

Fig. 2: Different experimentally obtained particle morphologies for polypropylenes. All polymers produced on $MgCl_2$-supported Ziegler-Natta catalysts.

The justification for the MGM model was the examination of particle morphology using SEM. We can see from the image of the prepolymer SEM micrograph in Figure 2 that the concept of the growing particle as a collection of individual micrograins is justified in certain cases. However the other 2 micrographs in this Figure show that we can end up with particles having highly different morphologies with respect to the MGM. The impact polypropylene, which contains approximately 50% EPR, has a very different morphology from the prepolymer, with a shell-like structure surrounding a number of "large" (with respect to micrograins) agglomerates. Finally the PP homopolymer has an almost solid structure. Mercury porosimetry measurements indicate a void fraction of 0.14 for the impact PP, and less than 0.05 for the PP, further indication of the differences in their structures. Clearly mass transfer resistances risk being very different in these different polymers.

Consider the MGM mass balance around the macroparticle (assuming mass transfer is by Fickian diffusion only):

$$\frac{\partial C_i}{\partial t} = \nabla\cdot(D_{eff}\nabla C_i) - R_{p_i} \tag{2}$$

with initial and boundary conditions:

$$t=0 \quad C_i=C_i^0 \tag{2a}$$

$$r=0 \quad \frac{\partial C_i}{\partial r}=0 \tag{2b}$$

$$r=R(t) \; D_i\frac{\partial C_i}{\partial r}=k_s\left(C_i\big|_{bulk}-C_i\big|_{surface}\right) \tag{2c}$$

Here, C_i is the concentration of monomer at a point in the macrograin, r the radial coordinate, R(t) the radius of the particle at a given instant, R_{pi}, the volumetric rate of polymerisation of species i at a point in the particle, D_{eff} is the effective diffusivity in the pseudo-homogeneous medium, and k_S the boundary layer mass transfer coefficient. It is generally accepted that there is very little mass transfer resistance across the particle boundary layer, and boundary condition (2c) is usually replaced by $\left(C_i\big|_{bulk}=C_i\big|_{surface}\right)$. The very definition of the boundary conditions here shows us that we are assuming that the critical length scale for diffusion is is the particle radius. We will use this mass balance, along with the data in Table 1 to simulate the slurry polymerisation of ethylene in heptane on an $MgCl_2$-supported ZN catalyst for the two highly idealised cases shown in Figure 3.

Table 1. Data for simulation in Figure 3.

Porosity	0.3		D_{eff}	2.10^{-10} m^2/s
Pressure	6 bars		R_0	10 μm
Temperature	343 K		$R_{p,max}$	25,000 g/g/h

In the first case, we will use a pseudo-homogeneous particle as described by the MGM, and in the second case we will approximate the morphology shown for the impact PP polymer (which we have also observed for PE and PP homopolymers) with a spherical particle that contains a 1 μm "pore" that goes around the particle in a spherical shell. This pore is connected to the bulk phase, and therefore has the same concentration of monomer. Of course this is admittedly an overly simplistic way of describing the real morphology, but it should give us an idea of how large influxes of monomer could alter the mass transfer scenario. First of all, we see once again that significant concentration gradients are predicted for the standard MGM model. However, if we have one or more large "pores" in the particle, the significance of the mass transfer resistance is attenuated. This is reflected in the values of the productivity, defined as:

$$P=\iint R_{pv}\partial V\partial t$$

The higher productivities predicted for the pores with an open structure clearly show that the lack of significant diffusion resistance can increase the observed kinetics of the process. This is further confirmed by the persistent reduction in the reaction rate observed for the "non porous" particle. Although not shown here for the sake of brevity, the simulations show that even after several hours the rate curves for the "solid" particle remains well below that simulated for the "porous" particles. The fact that the simulations predict mass transfer resistance in the form of persistent concentration gradients and "observed" rates much lower than intrinsic ones is not in itself a problem. The problem arises from the fact that a number of authors have shown that mass transfer resistance should be negligible under these conditions[7,11,12,13,14)]. There is clearly a discrepancy between the model and experimental results for catalytic systems as active as those used in industry today.

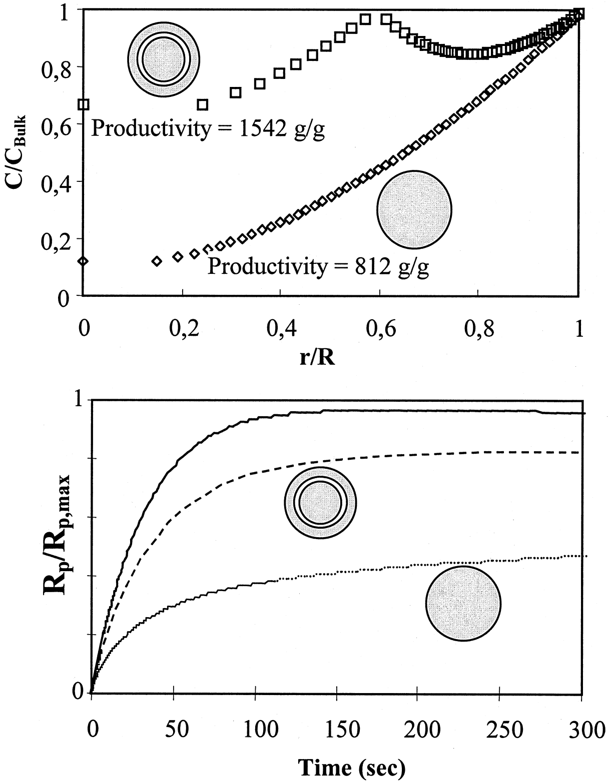


Fig. 3: Idealised simulations to demonstrate the effect of particle morphology on mass transfer resistance. Data in table 3. Profiles and productivity given after 300 seconds of polymerisation. The upper curve in the bottom graph represents the intrinsic activity (i.e. the activity that would be obtained if we encountered no diffusion resistance).

It is in fact interesting to attempt to understand the "real" value of the critical length scale for diffusion in a growing particle. To do so, let us use a simplified version of equation (2). We will assume that the quasi-steady state assumption is valid since we are interested only in very short times. Furthermore, we will assume the local volumetric rate of monomer consumption in equation (2) is given by:

$$R_{pv}(r)=k(t)C_i(r,t) \tag{3}$$

In equation (3), the pseudo-rate constant k(t) takes into account the volumetric dilution of active sites due to particle growth, and the sorption of the monomer in the polymer (i.e. the rate constant also includes the sorption constant, and it is assumed that the equilibrium between the pore phase and the polymer phase is established instantaneously). Furthermore, we can define the following dimensionless variables: $\overline{C}=\frac{C_i}{C_{i,bulk}}$, $x=\frac{r}{R}$, $-\Phi^2=\frac{kR^2}{D}$. With these simplifications, the steady state solution to equation (1) becomes:

$$\overline{C}(x)=\frac{\sinh(\Phi x)}{x\sinh(\Phi)} \tag{4}$$

We can use the solution of equation (4) to plot a graph of the concentration gradient in the growing particle as a function of the critical length scale for monomer transport (R) and of the intrinsic rate of polymerisation, reflected by the value of k. If we consider an activity of 50000 g/g/h, an average concentration inside the particle of 0,6 mol/l for a slurry polymerisation, and an effective density for the particle (including the porosity) of 1 g/cm^3, k is found to be equal to 1200 s^{-1}. Note that result is valid only when there is no concentration gradient inside the particle and no particle growth, and the value of k declines as the catalyst is "diluted" since it is proportional to 1/R^3. So we will look at values of k ranging from 30 to 1200 s^{-1}, and assume that this tells us about the impact of dilution of active sites and particle growth as well.

The results of this simulation for the case of an ethylene slurry polymerisation are shown in Figure 4, where we see graphs of the value of the concentration gradient (expressed as the concentration at the centre of the particle divided by the concentration in the bulk phase) as a function of the value of R, k, and D_{eff}. If we arbitrarily define a concentration gradient of 20% as not being particularly significant (i.e. mass transfer resistance will have little to no influence on observed rate and polymer properties if the concentration at the centre of the particles is 80% of the concentration in the reactor), then we can easily see that characteristic mass transfer lengths are less than one micron for relatively active particles early in the polymerisation (e.g., k = 600 corresponds to an activity of 25,000 g/g/h for a particle of radius 10μm). In fact, we can clearly see from this figure that we need to polymerise under fairly mild conditions ($k = 30\ s^{-1}$) in order to avoid significant concentration gradients in the particle for length scales approaching the nominal particle size.

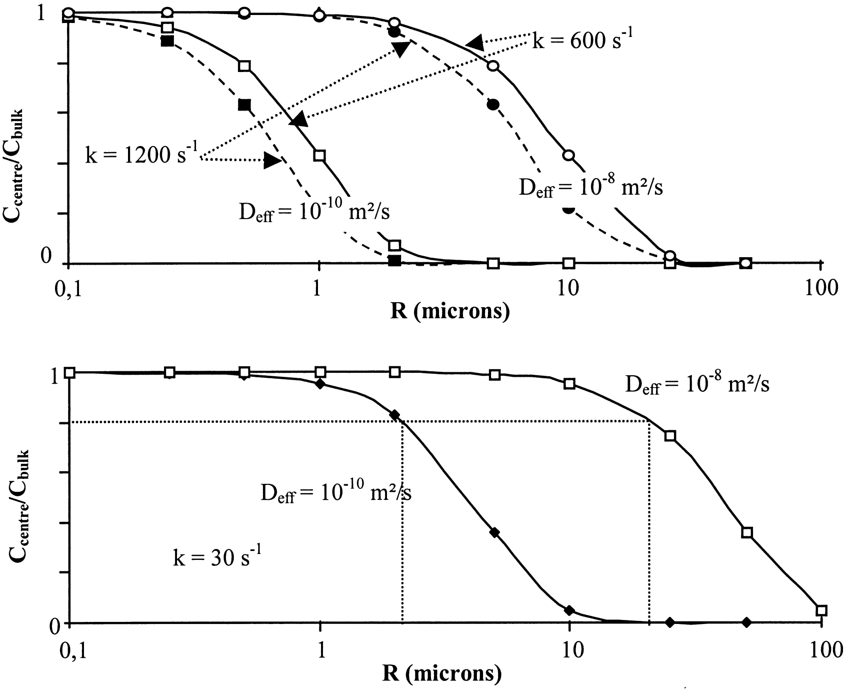


Fig. 4: Graphs of the concentration gradient as a function of particle size for different intrinsic rates (reflected by k) and diffusivities. The diffusivities are representative of the values cited in the literature as being typical of those found in slurry polymerisations[4,5].

These results, combined with those presented in Figure 3 push us to ask whether or not we have an accurate representation of particle morphology with the MGM/PFM, or not. If we look again at Figure 2, it is clear that we have a multiplicity of physical structures that are obtained during olefin polymerisation. Claiming that particle morphology is a complex issue is, to say the least, an understatement. However, it seems that a number of factors must act to change particle morphology during the reaction. It is not possible to begin and end a highly active polymerisation with a particle having the morphology of the PP homopolymer in Figure 2, and clearly, although we can get the MGM agglomeration of micrograins in certain cases (and clearly, this is an accurate representation of the morphology of $MgCl_2$ catalysts15,16,17)), we do not always end up with such structures. Nevertheless, it should be clear from the above discussion that a powerful single particle model, especially one needed for the description of multi-layered (e.g. impact PP) products must include the effect of changing morphologies.

A pertinent question to ask is whether or not reaction rate influences the morphology (as it certainly seems that the corollary is true). An interesting summary of the impact of changing something as basic as the reaction rate has been previously presented in the literature18,19). These experiments dealt with influence of temperature (and thus polymerisation rate) on the morphology of PP produced in liquid monomer for ZN catalysts supported on $MgCl_2$. At low temperatures (40°C), the particles they obtained were compact agglomerations of 10-15 spherical structures, which passes through several intermediate stages where the spherical globes get smaller and smaller, until they get a sponge-like morphology at 80°C that looks a bit like MGM-type structures. They also noted that as the morphology changes, the bulk density of the particles also decreases from low to high temperature. These results were obtained without prepolymerisation. Prepolymerisation eliminates the dependence of morphology on temperature and/or reaction rate. Finally, although none are suggested in their article, they also conclude that two-phase 'real morphology' models are needed in order to better described the polymerisation process.

If we limit our conclusions to magnesium-chloride supported system, it is possible that the schema presented in Figure 5 explains how the morphology of the particles evolves. In this proposed schema, catalyst and prepolymer particles (i.e. particles with "low" degree of polymerisation) retain an MGM-type morphology where the particle is an assembly of micrograins that expand during the early stages of polymerisation. As the reaction advances, neighbouring micrograins "meld" into larger agglomerates under the pressure created by isotonic polymer grow in the particle. Whereas the MGM considers that a micrograin contains one (or at most a small number of) catalyst fragments, these agglomerates would contain several fragments. The existence of such structures has been proposed for the specific case of impact polypropylene20,21), but the evidence presented here suggests that such structures can occur in a wide number of polyolefins systems. The determination of the rate at which this agglomeration of micrograins would occur (if indeed it does happen), the transition from MGM-type morphology to more complex structures will require a significant amount of work. The exact evolution will of course depend on a number of factors including temperature, polymer composition, phases present in the reactor, rate of production of polymer, and the type of support. It is important to mention that this schema is based on data collected for $MgCl_2$ supports, so one should not generalise the results reported herein for other systems (e.g. silica supports).

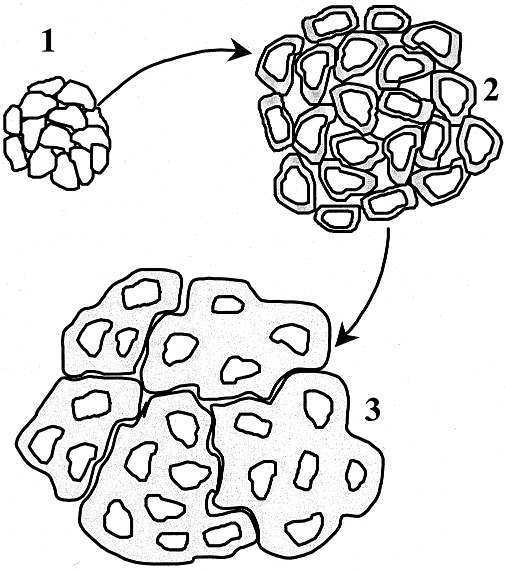


Fig. 5: Schema of proposed particle growth model where catalyst (1) and prepolymer particle (2) retain "MGM-style" morphology, and polymer particle (3) assumes a more or less agglomerated structure as the reaction proceeds.

Mass transfer modelling and convection

Note that the model presented in equation (2) is based on "standard" chemical engineering techniques. In other words, it uses the well-known *diffusion with chemical reaction* equation to describe mass transfer inside the growing particles. Now this is probably realistic. However, as mentioned in an earlier paper, convection inside growing polymer particles and its influence on the concentration of monomer at the active sites in gas phase copolymerisations, and in particular, in the production of linear low density polyethylene (LLDPE) or ethylene-propylene copolymers, might turn out to be important[11,22)]. These last two products differ from high density PE (HDPE) in that a second α-olefin comonomer is added to the reaction during polymerisation. It is well known that comonomers such as propylene, butene, hexene, or even octene have at least two major effects on the polymerising system: first of all they reduce the real density of the PE by introducing imperfections into the polymer chains, and secondly they significantly enhance the rate of ethylene polymerisation in the system (for Ziegler-Natta catalysts) even though they polymerise at intrinsic rates 5-40 times more slowly than the latter. It is this combination of influence on polymer properties and relatively low reaction rate (w.r.t. the ethylene) that makes it useful to have a more physically realistic description of mass transfer inside the growing particles.

If we consider gas phase mass transfer in the presence of chemical reaction in a spherical particle, the concentration profile of reactive species "i" inside the growing particles can be estimated from equation (2). However equation (2) is a simplified form of the more general expression

$$\frac{\partial C_i}{\partial t}=\nabla\cdot N_i-R_{p_i} \tag{5}$$

In traditional modelling efforts the flux term in equation (5) is replaced by a diffusive term, usually Fick's law, to yield equation (2). However, it has been pointed out that in the case of a gas phase copolymerisation in particular, this model does not allow for constant molar density inside the porous particles. In this case, the correct expression for the molar flux inside the growing particles should include both a diffusive and convective term. We will define the flux (J_i*) of species i with respect to the molar average velocity, v*,using the notation of [22] as $J_i^* = c_i(v_i - v^*)$. Since this flux is also equal to the diffusive flux, it is a simple step to arrive at the net molar flux of species i in equation (5):

$$N_i=\frac{-cD_i\nabla x_i+x_i\sum_{j\neq i}N_j}{1-x_i} \tag{6}$$

where x_i is the mole fraction of species i and c is the total molar concentration.

Using equation (6) to express the molar flux leads to a different set of concentration gradients than one would calculate from the simpler diffusion-only model. The impact of this change is shown in Figure 6 for the case of the gas phase polymerisation of ethylene and butene.

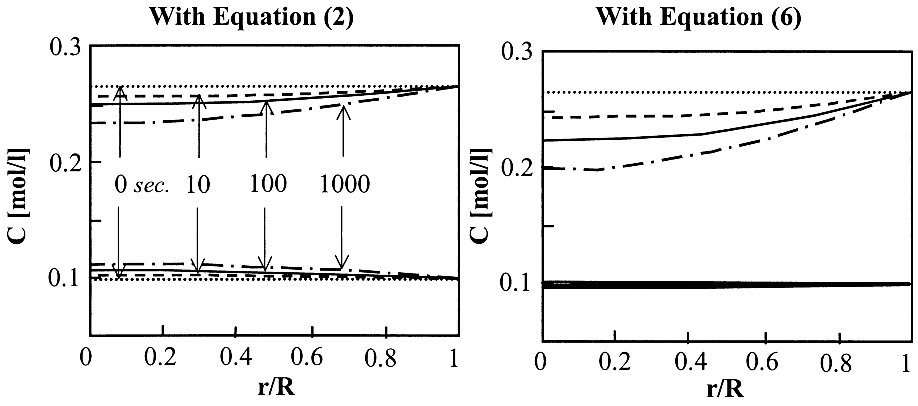


Fig. 6: Comparison of LLDPE reactions with convective plus diffusive fluxes (left) and diffusive fluxes only (right) for 4 different times. Times in seconds, with same legend on right hand graph. Simulation conditions: gas phase polymerisation of ethylene with butene (24 bars C_2 + 6 bars C_4, $k_{p,C2} = 50k_{pC4}$, $D_{eff} = 10^{-6}$ m^2/s, $R_{p,max}$ = 25,000 g/g/h).

It can be seen from Figure 6 that in the event that the correct expression for the diffusive flux is used, there is in fact a net accumulation of butene in the particles which of course has an influence on how polymer properties, but also on other phenomena that will be discussed in more detail such as capillary condensation inside the particles. This simulation was for the gas phase polymerisation of ethylene with butene. It was assumed that the intrinsic rate of polymerisation of ethylene rose from zero to a maximum of 25,000 g/g/h in one minute, and that the rate constant for the polymerisation of butene was one fiftieth of the value of that of ethylene. While this is somewhat simplified, it shows the impact of the "aspiration" of a less reactive gas by the more reactive ethylene. A more detailed discussion of the role of convection, and its sensitivity to process parameters like particle size, diffusivity and kinetics will presented in a forthcoming paper from this group$^{23)}$.
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Conclusions

A quantitative description of the growth of supported particles during olefin polymerisation is a *sine qua non* for improved process operation and material properties. From the traditional stand point of process engineering, models that describe heat and mass transfer, coupled with a reliable kinetic model help us to predict reactor behaviour (safety, monitoring, stability) and the evolution of certain quantities related to polymer quality such as the molecular weight or polymer composition distributions. Such models are also important from the point of catalyst and product design, helping us to learn how "fast" we can really go - in other words to clearly differentiate between chemical and physical effects. In certain circumstances, we might want to increase production levels as high as possible without overheating. In other cases, we might want to create mass transfer gradients inside particles in order to build complex sequential copolymers (là, c'est un peu compliqué !!). However, regardless of our motivation, it is clear that single particle models are both very useful... and very difficult to build. Our discussion focused on the importance of describing the evolution of the morphology of the growing particles. Improved models will need to take into consideration:

- the possibility of convection inside growing particles,
- the need to relate particle growth to material properties (esp. crystallinity),
- the possibility of modelling stress fracturing inside rapidly growing particles,
- the implications of deviations from MGM/PFM pseudo-homogeneous particle morphology,

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