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Modelling of heat and mass transfer during the polymerisation of olefins on heterogeneous Ziegler catalysts

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Abstract

The modelling of heat and mass transfer during the gas and slurry phase polymerisation of olefins is examined. It is demonstrated that it might not be necessary in many cases to calculate concentration gradients in the growing catalyst/polymer complex, and that the currently used representation of heat transfer from small, highly active particles using standard chemical engineering correlations might not be accurate.

Close examination of the morphology of catalyst particles shows that it is unlikely that the particles should be treated as a pseudo-homogeneous medium, and in fact the critical length scale for mass transfer is not the particle radius, but is much smaller. Furthermore, computational fluid dynamic simulations of single and interacting particles shows that convection is not the dominant heat transfer mechanism during the critical stages of the reaction.

Keywords: Computational fluid dynamics; Polyolefins; Heat transfer; Mass transfer

1. Introduction and current models

Polyolefins (i.e. polyethylene, polypropylene, and their copolymers with other α-olefins) are typically produced using heterogeneous catalysis. The most common types of catalysts are organo-metallic compounds on highly porous, solid supports such as magnesium chloride or silica. These catalysts can be used in either gas phase fluidised bed reactors (FBR), liquid–solid slurry, or in the three-phase liquid pool process (only polypropylene).

The reactants diffuse from the continuous phase, through the boundary layer surrounding the particles, through the pores of the catalyst to the active sites where they polymerise to form a solid polymer. The heat produced by the reaction is evacuated in the opposite direction. Immediately after the reaction starts the original particle support fragments due to the hydraulic forces created by the formation of the polymer, but nevertheless retains its original form due to the adhesive forces of the polymer molecules. As shown in Fig. 1, the particles thus their intitial internal cohesion throughout the reaction, and one generally observes that the particle size distribution at the beginning and end of the reaction are of the same width. As such, the reaction begins with small particles (10–50 μm in diameter), and finishes 1–2 h later with the same number of particles with a diameter on the order of 500–1000 μm in diameter.

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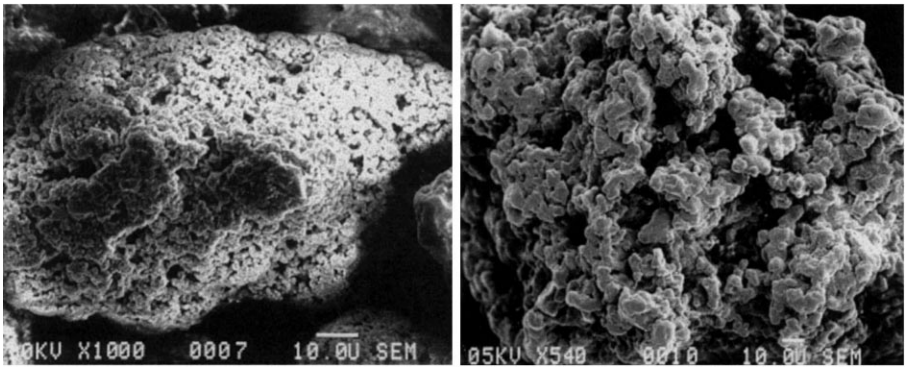

Fig. 1. Electron micrographs of a virgin catalyst particle (left), and a polymer particle (right) taken from the reactor after 5 min of polymerisation. It can be seen that the original particle, which is in fact an agglomeration of smaller micrograins, grows, but retains its original shape throughout the reaction. Note that the catalyst particle is much larger than those normally used in typical industrial reactions.

Typical reaction rates for modern catalysts are on the order of 10 000–50 000 of polymer per gram of catalyst per hour (g/g/h). It is thus reasonable to suppose that one could encounter mass transfer resistance, especially in slurry and liquid pool reactions (but probably not in the gas phase). Furthermore, since the polymerisation is highly exothermic, with ΔH_p (heat of polymerisation) being on the order of 100 kJ/mol, it is very important to understand and optimise heat transfer in order to avoid meltdown and reactor runaway. Obviously, mechanistic models of these phenomena are indispensable if we are to understand and control industrial scale reactions.

The original work in the area of modelling of mass and energy transport phenomena on Ziegler type catalysts was developed in particular by Chiovetta et al. [1,2], and by the research group of Ray at the University of Wisconsin [3,4]. These models were based on what is now called the MultiGrain Model (MGM). In this, and similar models (e.g. polymer flow), a growing particle is assumed to be a pseudo-homogeneous medium where mass transport in the entire polymer/catalyst particles is characterised by a single diffusivity, and the characteristic length scale for diffusion is the particle radius.

If we accept these assumptions, then the concentration profiles of species i in the macroparticles can be estimated with the following general equation:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot N_i - R_{p_i}, \tag{1}$$

where

$$N_i = D_i \nabla C_i - C_i u$$

with initial and boundary conditions:

$$t = 0, \quad C_i = C_i^0, \tag{1a}$$

$$r = 0, \quad \frac{\partial C_i}{\partial r} = 0, \tag{1b}$$

$$r = R, \quad D_i \frac{\partial C_i}{\partial r} = k_s (C_i|_{\text{bulk}} - C_i|_{\text{surface}}). \tag{1c}$$

Here D_i is the effective diffusivity in the pseudo-homogeneous medium, k_s the boundary layer mass transfer coefficient, and u is the convective velocity (function of r, t) in the macropores. It is generally accepted that there is very little mass transfer resistance across the particle boundary layer, and boundary condition (1c) is usually replaced by $(C_i\text{bulk} = C_i\text{surface})$.

The temperature profile can be calculated from the energy balance

$$\frac{\partial T}{\partial t} = \nabla \cdot (k_e \nabla T - \rho c_p u T) + \sum \Delta H_{p_i} R_{p_i} \tag{2}$$

with initial and boundary conditions:

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

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

$$r = R, \quad -\frac{\partial T}{\partial r} = \frac{h}{\rho C_p} (T|_{\text{bulk}} - T_{\text{surface}}), \tag{2c}$$

where h is the convective heat transfer coefficient.

The convective velocity u, which is generally neglected in the previously cited works, can be estimated using the continuity equation when necessary.

2. Results and discussion

Eqs. (1) and (2) were used to attempt to simulate real laboratory experiments for both slurry and gas phase experiments under industrial conditions. Generally speaking, the agreement was unsatisfactory. We will begin by looking at problems related to modelling mass transfer in Section 2.1, and go on to treat heat transfer in the following section.

2.1. *Mass transfer: example, the slurry polymerisation of ethylene*

A review of the literature reveals that a wide range of values of the effective diffusivity are proposed in the literature. For example, in [1,2], a range of 8×10^{-9}–1.5×10^{-8} m^2/s is proposed for the bulk phase diffusivity of ethylene in liquid heptane over a range 40–80°C, and values on the order 10^{-10}–10^{-9} m^2/s are proposed for the effective diffusivity. In [3,4], the bulk diffusivities range from 10^{-9} to 10^{-8}, and pore diffusivities are on the order 3.2×10^{-10}–1.9×10^{-9} m^2/s. This variation demonstrates that certain "adjustments" must be made in order to fit the models to the available data. Since no precise values are available, we use a compromise value of 10^{-8} m^2/s for the bulk diffusivity, and 10^{-9} m^2/s for the effective diffusivity.

Using these values in Eq. (1) lead to the simulation results shown in Fig. 2. Note that the symbols in Fig. 2 correspond to experimental results obtained in our laboratories. The "no resistance" curve corresponds to a theoretical catalyst having an intrinsic activity similar to the experimental results (note that in the presence of mass transfer resistance during the course of the experiment, the intrinsic activity would be higher than the observed value). It can be seen that even for these reasonable values of diffusivities, and relatively small particles (10 μm – the particle size distribution of the catalyst used in these experiments is shown in Fig. 3) there is still a significant loss of activity. Further as the particle size increases, the model predicts a significant loss of activity (a decrease

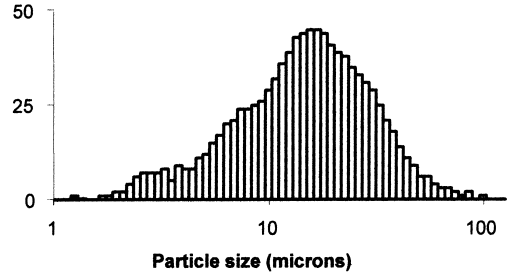

Fig. 3. Particle size distribution for the catalyst used in the experiment shown in Fig. 2.

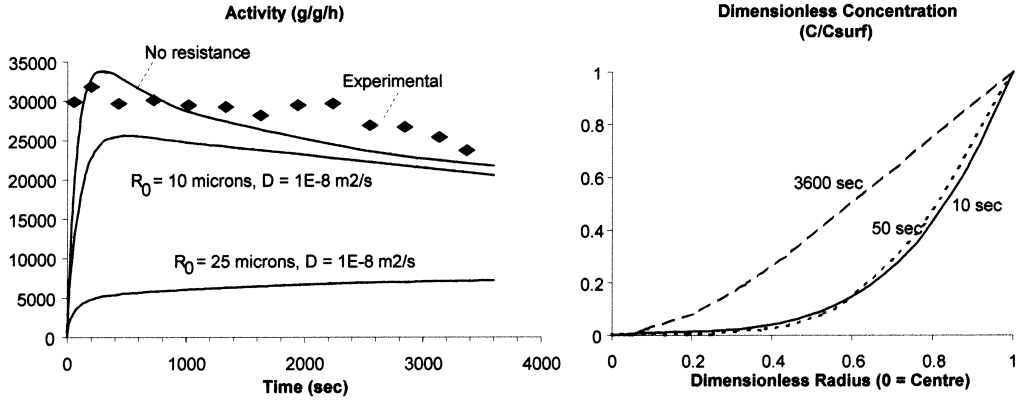

Fig. 2. Simulated "observed" activities (left) and concentration profiles (right) for 25 μm particles as a function of time for the intrinsic catalytic activity.

of 60%), and concentration profiles that rapidly tend toward zero at the centre of the particle, and then stay there for quite some time. This would lead to the production of hollow catalyst particles, and extremely large molecular weight distributions (polydispersities on the order of 5–10 times higher than those observed): phenomena which are most certainly not observed in our experiments. Note also that if the intrinsic activity of the catalyst were higher, and the observed rate of around 30 000 g/g/h were the result of a compromise between mass transfer resistance and high reaction rates, the concentration profiles would tend toward zero even more quickly and the predicted effect on molecular weight would be even greater.

In fact, it would be interesting to identify the critical length scales involved in these systems in order to determine why the currently accepted models breakdown, and how we should correct them. To do so, we will look at a simplified model of the reaction/diffusion problem defined in Eq. (1). In this representation, the growing particle is likened to a semi-infinite slab of thickness $2L$, where unidirectional diffusion takes place.

Eq. (1) can be written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC \tag{3}$$

in linear co-ordinates if we suppose that the rate of reaction is linearly proportional to the local concentration. If we use the following boundary conditions:

$$\frac{\partial C}{\partial x} = 0, \quad \text{for } x = 0, \tag{3a}$$

$$C = C_{\text{surf}} \quad \text{for } x = L, \tag{3b}$$

then the analytical solution to Eq. (3) is

$$\hat{C} = \frac{e^{\Phi y} + e^{-\Phi y}}{e^{\Phi} - e^{-\Phi}}, \tag{4}$$

where, $\hat{C} = C/C^0$, $y{=}x/L$, and $\Phi^2 = kL^2/D$.

The solution given by Eq. (4) is shown in Fig. 4 for different length scales, and a value of k that corresponds to an initial activity of 35 000 g/g/h. The ratio of the concentration in the centre of the particle to that in the bulk phase gives an indication of the importance of the concentration gradients that arise at different length scales. As mentioned above, an estimate of 10^{-10} m^2/s is probably a bit conservative, but nevertheless, it can be seen that significant concentration gradients are predicted in the semi-infinite slab for values of L on the order of 1–5 μm, depending on the value that one chooses for the diffusivity. It has been shown in [5] that the shape of the medium in question has little impact on the predicted levels of mass transfer resistance, so we can probably assume that the value of the critical length scale for diffusion in "pseudo-homogeneous" particles characteristic of those used in Ziegler-catalysed olefin polymerisations

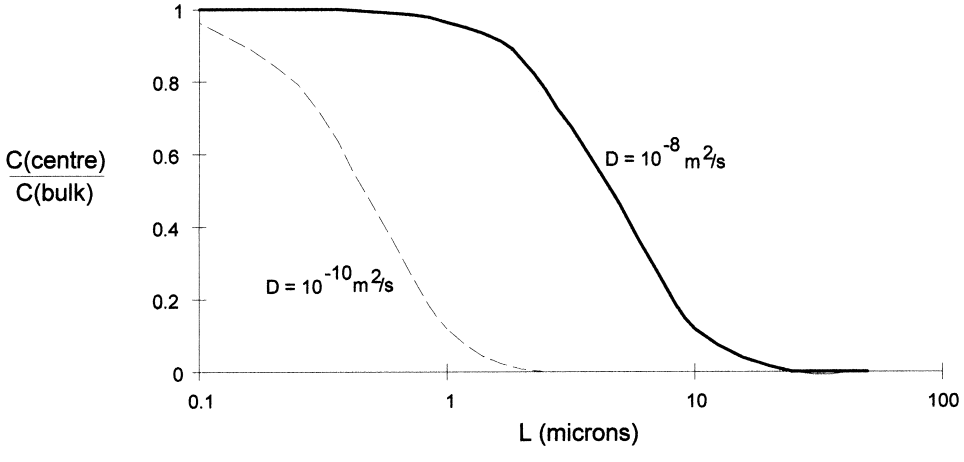

Fig. 4. Dimensionless concentration gradients arising for different diffusivities as a function of slab thickness in a semi-infinite medium with no external transfer resistance. It appears that the critical length scale is on the order of 1–5 μm. Above this, concentration gradients become unrealistically high.

is also of the order of 1–5 μm. It is important to note two things about this result.

1. This value is smaller than the typical radius of virgin catalyst particles. Reaction seems to be dominant only over a shorter length scale than that used in MGM calculations.
2. The value of the rate constant k was chosen in order to yield an effective ''observed'' activity of 35 000 g/g/h at the beginning of the reaction. The value of this rate constant implicitly includes the particle volume and will effectively decrease rapidly as the particle grows. Therefore, any mass transfer resistance detected by the calculation in Fig. 4 will decrease at speeds that will depend on reaction rates, catalyst deactivation, etc. The length scale L at which significant concentration gradients are observed thus increases as the reaction progresses.

Since there is no experimental evidence of mass transfer resistance in this type of reaction, there must be a problem with the representation (i.e. model) of the physical system. In fact, the important question is to know whether or not the critical length scales identified in Fig. 4 are overtly related to the morphology of the polymerising particles. If we consider the electron micrographs in Fig. 5, we can see that, at least for the $TiCl_4/MgCl_2$ catalyst system employed here, it is unreasonable to assume that these particles are pseudo-homogeneous media. It can be seen from both the prepolymer and polymer particles that the particles contain empty zones, linked to the bulk phase by very large pores that are on the order of several microns in diameter. Close inspection of the micrographs in Fig. 1 also reveals the presence of relatively large openings on the surface of the catalyst particles as well. Almost every one of the several dozens of polymer particles examined in this manner contained these large, empty zones connected by relatively wide pores to the external environment.

The implications of this are obvious: neither the catalyst particles, nor the growing polymer particles are pseudo-homogenous media, and it is not reasonable to model them using a characteristic length scale for diffusion equal to the radius of the particle. It is probably more realistic to suppose that the zones that appear to be empty on the micrographs act as reservoirs of monomer during the reaction since they are connected to the continuous phase by large openings through which low viscosity liquids should have no trouble passing. The particle is thus composed of relatively small ''pseudo-homogeneous'' zones, the length scale of which is significantly less than the radius of the particle, all of which are surrounded by areas of concentration equal to that of the bulk phase. Furthermore, it would appear that those zones that might realistically be called ''pseudo-homogeneous'' are of a length scale where no significant mass transfer occurs, even at relatively high reaction rates. For example, in the prepolymer sample seen in Fig. 5, the longest diffusional path is on the order of about 5 μm. This suggests that it is quite reasonable to

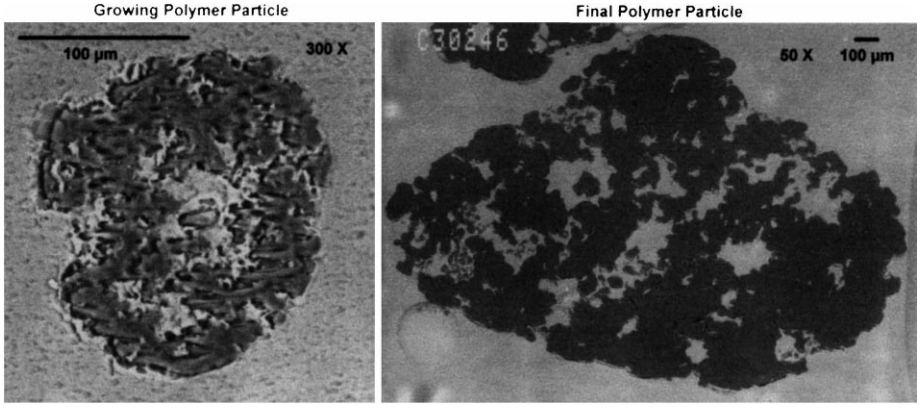

Fig. 5. Electron micrographs of a polymer particle during the early stages of growth (left) and a final particle. The non-homogeneous nature of particle morphology is clearly visible. Both particles produced on $TiCl_4/MgCl_2$ catalysts.

suppose that concentration gradients are never established in this type of catalyst particle, and that it would not be particularly realistic, nor useful to attempt to calculate concentration gradients on the scale of the macroparticle.

2.2. Heat transfer mechanism

Much as mass transfer resistance is dominant only in slurry phase reactions, heat transfer resistance is much more important in gas phase reactors. We will therefore consider only gas phase reactors in the rest of this section. ''Classic'' chemical engineering models used to calculate temperature profiles in growing particles are based on an energy balance (usually supposing that the particles are relatively spherical) that is a simplified form of Eq. (2):

$$\frac{\partial T}{\partial t} = \nabla \cdot (k_e \nabla T) + \sum \Delta H_{p_i} R_{p_i} \tag{5}$$

with the same initial and boundary conditions.

By writing boundary condition (2c), one generally assumes that the heat transfer between the particle and the bulk phase of the reactor is dominated by convection, and is controlled by the film-side convective heat transfer coefficient h. As in other applications, Nusselt number (Nu) correlations are used to estimate h as a function of system parameters. However, it has been shown [6] that the use of this type of correlation and the assumptions mentioned above in the modelling of modern catalyst systems (note that since 1983 catalyst activities have increased by a factor of 10–50) leads to physically unrealistic predictions of high internal temperature gradients in the particles – results that are contradicted by experimental and industrial results since if the centre was the hottest spot in the particle, melt down would begin there, and not at the surface. In this case, the pores of the particles would fill with molten polymer, thereby creating mass transfer resistance and shutting down the reaction [6]. This would imply that the reaction is ''self-regulating'' in terms of heat transfer, and that we should never see melt-down in gas phase reactors – an event which is encountered all to often in reality.

In a previous study [6], it was suggested that a Peclet number analysis (Pe) would help to determine whether or not heat transfer occurs via a mixed conductive–convective mechanism, or, as originally thought, via convection only. However, this conclusion needed to be evaluated more rigorously. We therefore used FLUENT/UNS [7], a computation fluid dynamics CFD code, to calculate Pe in the boundary layer of different sized particles and for different relative velocities:

$$Pe = \frac{L_c \rho u_c}{\mu} = \frac{\text{convection}}{\text{diffusion}}, \tag{6}$$

where μ is the molecular viscosity, and L_c and u_c are the local length scales and convective velocities, respectively. When $Pe \gg 1$, convection is the dominant means of momentum transfer (i.e. flow in the system), and for $Pe \ll 1$ molecular diffusion dominates. When convection is the dominant means of momentum transport (i.e. fluid movement), it is reasonable to suppose that convective heat transfer will be important, and vice versa for diffusion.

FLUENT/UNS was used to calculate streamlines, temperature fields, Nu, skin friction coefficients and Pe around single and pairs of particles. For the sake of brevity, only those results dealing with the evolution of Pe will be presented here since they are the most pertinent in terms of understanding the mechanism underlying heat transfer around these highly active catalyst particles.

The results for the Pe calculations are shown in Fig. 6 for single particles of different size immobilised in a gas stream with a velocity of 0.02 m/s (which corresponds to flow in a gas phase, stirred bed reactor). Pe is calculated along a radius perpendicular to the direction of bulk fluid flow. Here r/d is the dimensionless radial position, where $r/d=0$ is the centre of the particle, $r/d=0.5$ is the particle surface, and $r/d=1$ is a point 1 particle radius away from the centre. It can be seen that $Pe \gg 1$ very rapidly for large particles ($d_p > 250\,\mu m$) very near the particle surface. This means that it is justified to assume that heat transfer takes place by convection for large particles, and that if there is a boundary layer effect, it is only important for small particles.

For the 20 μm particles, it can be seen that the particle is surrounded by a momentum boundary layer almost as thick as the radius of the particle. This means that conductive heat transfer is very important at length scales of 10–50 μm under typical reaction conditions, and that the model in Eq. (5) needs to be adjusted to take this into account. This is an

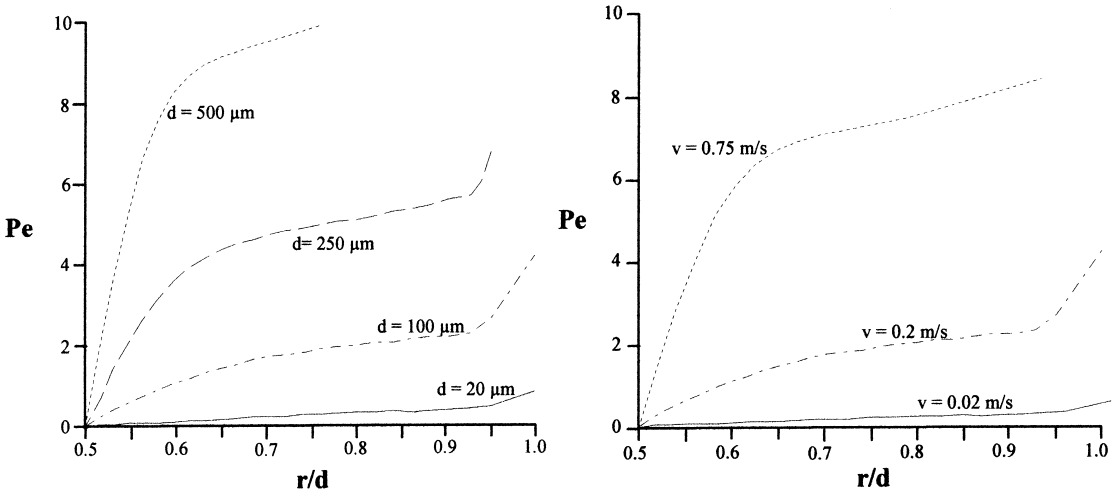

Fig. 6. Variations of *Pe* as a function of particle diameter (single sphere) for a relative gas–particle velocity of 0.02 m/s (left), and for different flow rates for a 20 µm particle (right).

important result because all of the available correlations for *Nu* were developed for large particles – i.e. those greater than 400 or 500 µm in diameter. As we have just seen, the assumption that all heat is evacuated via convection is valid for particles of this size. However, if we consider particles having a size characteristic of that of the initial stages of olefin polymerisation it is clear that this assumption is no longer valid.

The relative gas–particle velocity will obviously have an effect on this result, but the calculations for a 20 µm particle at different gas flow rates shown in Fig. 6(b) show that the *Pe* is still rather small near the particle surface at 0.20 m/s (steady state FBR conditions). Therefore, even at relatively high flow rates conduction can be important. These results give credibility to the mechanism proposed by McKenna et al. [5,6] that might explain two important phenomena: heat evacuation rates that are higher than predicted; and melt down beginning on the particle surface.

If we consider the results in Fig. 6, we might be able to say that small particles are surrounded by a "conductive" boundary layer that is of the same size as the particle, as is illustrated schematically in Fig. 7. If this were the case, it would be reasonable to say that this layer (of thickness *L*) would be at a temperature similar to that of the particle surface, and that convection heat transfer would then take place at a distance *R*+*L* above the particle surface, but with a heat exchange area four times as large as that of the particle.

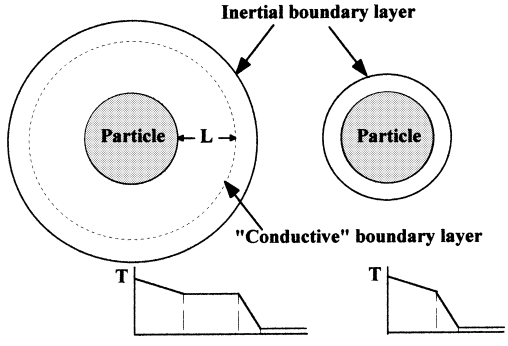

Fig. 7. Schema of "conductive" boundary layer representation.

Secondly, if heat transfer took place across this "conductive boundary layer", it is possible that a reduction in the effective heat transfer surface area of a particle coming into prolonged contact with another object (particle, wall, etc.) would lead to localised melting at the hot spot thus formed.

3. Conclusions

The recent advances in terms of activity and productivity of Ziegler–Natta (and possibly metallocene) catalysts for the production of polyolefins have brought to light several difficulties in applying tradi-

tional chemical engineering models in these multiphase systems. For example, heat transfer from these systems, characterised by extremely fast exothermic reactions on small particles cannot be modelled using *Nu* correlations developed for much larger particles. Ignoring conductive heat transfer through particle boundary layers is acceptable for particles with diameters much larger than the boundary layer thickness, but not when the particles and boundary layers have the same characteristic length scale. A qualitative physical model explaining this has been presented, and used to explain one of the possible origins of particle melt down during gas phase reaction. Nevertheless, it should not be forgotten that other mechanisms such as large–small particle interaction might also play an important role in the evacuation of energy from small, highly active (and therefore very hot) particles.

Additionally, it has been shown that poor assumptions about particle morphology result in unrealistic model predictions under highly reactive conditions. It turns out that, for certain types of catalyst support, the particles are highly porous and have a very open structure. As a result, the characteristic length scale for diffusion is not the particle radius as assumed in the pseudo-homogeneous models, but is in fact much smaller: probably on the order of 1–5 μm at the beginning of the reaction. This means that there is most likely no concentration gradient in the macroparticle during the reaction. This result needs to be verified for other types of catalyst support that exhibits different fragmentation behaviour.

While the current example is of an olefin polymerisation process, the underlying philosophy can be applied to a wide range of applications. The reconsideration of basic chemical engineering models and assumptions is becoming more and more necessary in a large number of hetero-phase processes involving porous catalysts due to ever-increasing reaction rates and active site efficiencies.

Acknowledgements

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