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A Study of Particle-Surface Interactions During Olefin Polymerisation in Gas Phase Reactors

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Summary: This work focuses on the heat exchange between a polymer particle and the reactor wall, especially for cases with low gas velocity. The role of different wall materials (or heat transfer conditions) is investigated with an eye to understanding how this influences the likelihood of particle melting, and, indirectly, wall sheeting. The main focus of this work was to simulate the temperature profiles inside growing polymer particles in the vicinity of the reactor wall when it is clean (steel) or covered with a layer of non reactive polymer. As a comparison, we have also simulated the reactor wall as being glass to represent bench scale polymerization equipment. The results from this work can help to understand how for instance wall sheeting can be accelerated if the reactor walls are not clean and how we can compare results from bench scale experiments to industrial scale units.

Keywords: gas phase reactions; heat transfer; olefin polymerization; supported catalyst; sheet formation

Introduction

In the future, plant capacity and therefore reactor yields will have to continually increase for commodity gas phase processes to remain competitive. Such improvements obviously require a better understanding of how the catalyst particles interact with their environment since the rate of reaction, the quality of the polymer created at the active sites, the local temperature and reactor behaviour are all intimately linked.[1] Given the highly exothermic nature of the polymerisation reaction and the high rates of polymerisation characteristic of industrial processes, it is clear that heat transfer is going to pose a problem for reaction operation if we need to increase space time yields in the reactor. In gas phase reactions this problem is doubly important as the heat transfer characteristics of gas phase reactors are typically even less favourable than in slurry or supercritical processes.

Because of the nature of the reactor contents, the hydrodynamics inside a fluidised bed reactor, or stirred powder bed reactors (the major types of PO reactors used in commercial processes) can be very complex,[2] most attempts at modelling olefin polymerisation reactors (gas or slurry phase) have used a residence time distribution approach with averaged properties for heat and mass transfer.[3–7] Since correlations by nature impose an averaged or pseudo-homogeneous view on the entire reactor, it is not easy to use such an approach for modelling hot spot formation, the effect of particle-particle interaction and similarly important issues.

Since developing a full hydrodynamic model of a gas phase polymerisation reactor seems to be fraught with uncertainty (as well as being costly in terms of time), we have chosen to use CFD as a tool to learn about the mechanisms that control heat transfer in specific, idealised situations thought to be representative of different parts of a polymerisation reactor. For

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instance, previous papers from this group showed that local hydrodynamic conditions can be important[8] that conduction played a role in heat transfer even in a turbulent fluidised bed. In current paper we focus on interactions between individual polymer particles and a larger solid surface, for instance the reactor wall. Unlike in the previous papers we will consider not only two bodies in contact, but will also study interactions at short separation distances. Two and three dimensional simulations were used to study several different factors.

Model Set-up and Parameters

The models used in this work were non-axisymmeteric two- and three-dimensional (2D, 3D) simulations. Model equations were solved using Fluent® (version 6.0.12). The momentum and energy balances are solved in finite control volumes (cells). The velocities, temperatures and pressures are stored in the centre of each finite control volume. The model is based on the two dimensional form of the general conservation (transport) equations: The momentum equation for the gas Equation (1) and the energy balances for the gas Equation (2) and the solid particle Equation (3):

$$\frac{\partial}{\partial t}(\rho \cdot u_i) + \frac{\partial}{\partial x_j}(\rho \cdot u_j \cdot u_i) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\right] \tag{1}$$

$$\frac{\partial}{\partial t}(\rho \cdot c_{p,g} \cdot T_g) + \frac{\partial}{\partial x_j}(\rho \cdot u_j \cdot c_{p,g} \cdot T_g) = \frac{\partial}{\partial x_j}\left[k_{e,g}\left(\frac{\partial T_g}{\partial x_j}\right)\right] \tag{2}$$

$$\frac{\partial}{\partial t}(\rho \cdot c_{p,s} \cdot T_s) = \frac{\partial}{\partial x_i}\left[k_{e,s}\left(\frac{\partial T_s}{\partial x_i}\right)\right] + \hat{Q}_{vol} \tag{3}$$

When studying the heat transfer effects we are especially interested in the last term in Equation (3), the volumetric heat flux. This term is calculated using Equation (4):

$$\hat{Q}_{vol} = \frac{R_p \cdot \rho_{eff} \cdot R_0^3}{R_1^3} \cdot \Delta H_p \cdot \exp\left(-\frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right) \tag{4}$$

The rate expression used for the polymer growth rate is shown in Equation (5). The reaction rate is calculated using the following values:

- Maximum reaction rate constant ($k_{p,0}$) = 20 kg/g/h
- Activation constant (τ) = 30 s (i.e. maximum activity after 189 s)
- Deactivation constant ($k_d = 0.00005\ \mathrm{s}^{-1}$

$$R_p(t) = k_{p,0} \cdot \left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \cdot \exp(-k_d \cdot t) \cdot \left(\frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right) \tag{5}$$

As the computational time is highly dependent on the level of detail in the mesh, and that the use of a 3D instead of a 2D mesh increases the number of cells by at least ten times (keeping the same level of detail), 2D meshes have been used whenever possible. For a two dimensional simulation, the typical number of used cells lies around 12 000 to 20 000, where about 10% of the cells are used for each solid particle and the rest for the particle environment. In the case of a three dimensional simulation, the typical number of cells increase to about 80 000 to 100 000, where about 5% of the cells are used for each solid particle. The parameters used in all simulations are shown in Table 1. The reference gas temperature is set to 350 K.

In order to investigate the effect of being near a solid wall on the growing polymer particle, two different wall materials were examined: steel and polyethylene. The material properties of the different solids are presented in Table 2.

Table 1.
Simulation Parameters.

$C_{p,g}$	specific heat capacity ethylene	2230	J/kg/K
$k_{e,g}$	thermal conductivity ethylene	0.0242	W/m/K
$T_{gas,in}$	inlet gas temperature	350	K
T_{ref}	reference temperature	350	K
ΔH_p	heat of polymerisation	100000	J/mol
η	viscosity ethylene	0.000011	kg/m/s
$\rho_{ethylene}$	ethylene density	40	kg/m^3

Table 2.
Material properties of the different wall materials and the growing particles.

Material	Specific Heat (J/kg K)	Conductivity (W/m K)	Density (kg/m^3)
Polymer	2150	0.117	900
Silica	740	1.38	2200
Steel	460	13.8	8010

Results and Discussions

Polymer Particle – Wall, Contact Single Point In an initial step, we studied the interaction between a growing polymer particle and a solid wall, assuming that the two are in contact at a single point. The temperature in the growing polymer particle was calculated for different wall materials: steel and polyethylene as different wall materials. In the initial simulations, two different cases of growing particles were studied: (i) the growing polymer particle is considered to be essentially 100% polymer; (ii) the growing particle is assumed to initially consist of 100% silica and as the particle grows it becomes ‘‘diluted’’ with polymer as the polymerisation progresses. The thermal properties of the hybrid material are assumed to be directly proportional to the weight fraction of each material in the particles, as expressed in Equation (6).

$$property = x_a \cdot property_a + (1 - x_a) \cdot property_b \tag{6}$$

The initial simulations were carried out assuming a stagnant gas flow. As expected, the different wall materials have different impacts on the temperature in the growing particle.

The results of the different wall materials and growing particle properties are reported in Figure 1. If the wall in contact with the growing particle has the thermal properties of steel (e.g. a clean reactor wall), it can be seen that there is a very efficient heat evacuation and that the maximum temperature inside the particle increases by only about 2 K compared to the bulk gas temperature, even under stagnant fluid conditions. The maximum temperature is observed after 25 s of reaction, and decreases slightly after this point in time as expected. Furthermore, taking into account a variation in the conductivity of a growing particle leads to only a small difference in maximum temperature as compared to the results found when the growing particle is assumed to consist of pure polymer. As the particle grows, the difference between the two cases becomes less significant, until after about 60 s, identical particle temperatures are observed (expected as the difference in material properties becomes negligible. Thus we will neglect this aspect in subsequent simulations). A wall with the thermal properties of polyethylene shows a quite different scenario. As the conductivity of the wall is identical to that of the particle, a higher particle temperature was observed than for the other cases (steel and glass as wall material) due to the higher heat transfer resistance. In other words, on a fouled reactor wall, the heat transfer will be significantly less favourable than on a clean wall.

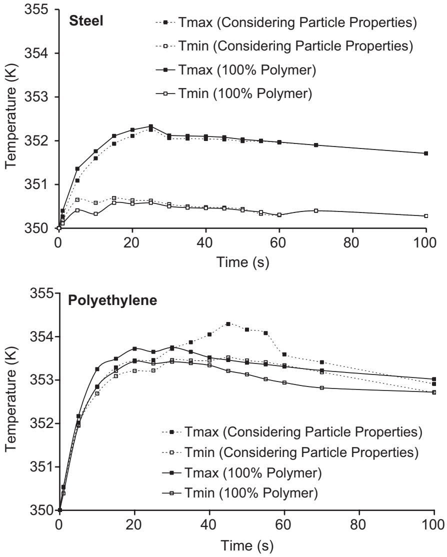

Figure 1.

Maximum and minimum temperature of growing particles assuming different wall materials, stagnant gas. "Considering Particles Properties" indicates that the thermal properties of the particles are a weighted sum of silica and polymer.

A shorter activation time will be used in subsequent simulations in order to simulate catalyst where we reach a maximum activity at shorter times. Thus, instead of assuming an activation constant of 30 s (i.e. maximum activity after 189 s) we used an activation constant of 5 s which is equivalent reaching the maximum activity after 41 s. The reaction rate profile and the particle size are shown using this faster activation rates are shown in Figure 2.

As shown in Figure 3, as expected, the particle temperature increases faster with the shorter activation times than in the cases presented in Figure 1. With the faster activation, the particle in contact with the steel plate reaches its maximum temperature after about 5 seconds. These results thus show a difference between the maximum and minimum temperatures calculated inside the particle. Simulations for the case of a polyethylene covered wall are not shown as the particles appeared to overheat immediately (N.B. Here thermal runaway is defined as observing a particle with a temperature above 385 K, which near the softening point of LLDPE. This is admittedly an arbitrary value, but in most cases presented here running the simulations for a longer time than this cut off does indeed lead to a situation where the extra heat generated by the reaction cannot be evacuated and we do indeed simulate a situation where all of the heat generated in the particle cannot be removed.)

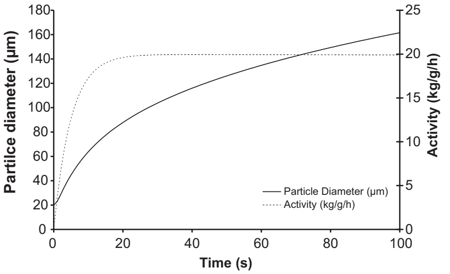

Figure 2.

Reaction rate profile and particle size as a function of time assuming a faster activation.

Polymer Particle – Wall Separated by a Gap

As demonstrated above, the temperature inside a growing particle touching a wall (contact in a single point) depends on the thermal characteristics of the wall surface. However, it is useful to understand whether or not the particles need to be touching a solid surface in order to observe any modification of the evolution of the temperature inside them. In order to answer that question, we studied evolution of the maximum and minimum temperatures in a particle as a function of the distance

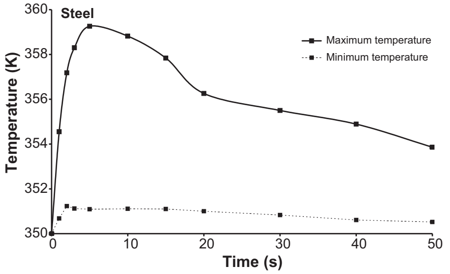

Figure 3.

Maximum and minimum temperature of growing particles assuming steel and glass as wall materials at a faster particle activation, stagnant gas flow.

between the wall and the growing particle using three different initial particle sizes for a stagnant and a moving gas phase.

The simulations in this section will look at particles with initial particle diameters of 20 and 30 microns simulated after 2.5 s of reaction. At this reaction time, the particles have started to react and we can observe the differences between the different materials. Both stagnant gas and a bulk gas velocity of 0.2 m/s have been applied.

As these simulations are not truly axisymmetric, they should normally be carried out in a 3D mode. Since this is very time demanding, we compared a 2D and 3D case in order to evaluate the difference. These results showed that in a 3D case, the maximum particle temperature was slightly lower but on the other hand the difference was less than 2 K. From this we can conclude that the 2D simulations presented here show temperatures that are slightly higher than a 3D case, but on the other hand the difference is marginal thus allowing us (in this case) to study the wall effects using a 2D case. In addition, given the approximate nature of the calculations, temperature differences of 2 K or less will not change the general conclusions.

In the case of a stagnant gas (Figure 4) we can see that the heat transfer is highly dependent on the distance between the wall and the polymer particle. It can be seen that there is a stronger interaction between the particle and the surface in terms of heat transfer for a steel reactor wall, undoubtedly due to the relatively high thermal conductivity of steel. As the separation distance between the wall and the particle increases in the case of glass and steel surfaces, there is an observable increase in the temperature of the particle, whereas for the polyethylene the particle temperature starts from a higher value, but varies much less. In other words the polyethylene covered surface interacts less with the particle than do the other two materials. Note also that as expected, once the particle is sufficiently far from the surface one observes essentially the same temperatures – temperature that concord with the isolated particle simulations presented by Eriksson and McKenna.[8] It should be noted here that a particle in a stagnant flow field suspended above the reactor wall is of course a purely theoretical case for comparison. These simulations can be thought of as addressing an idealised case of low velocity and thus negligible heat transfer due to convection, and are shown to underline the role that the surface might have even if the particles are not in touch with it.

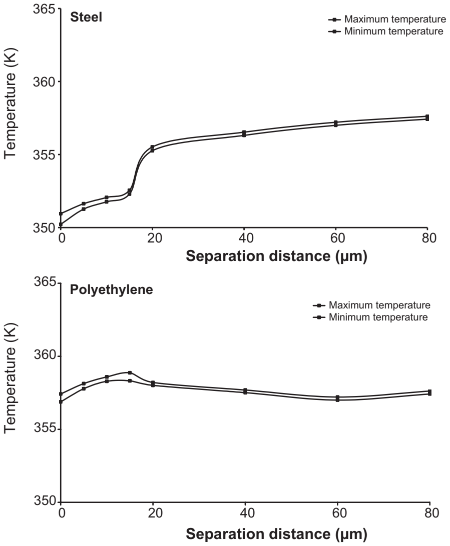

Figure 4.

Case 1: Particle temperature as a function of wall material and separation distance between the particle and the wall. (Bulk gas flow stagnant.)

The same particle set-up as was used in Figure 5, but this time with the inlet bulk gas velocity set to 0.2 m/s. The temperature difference can be seen to be less significant for the different wall materials as the convective contribution of the gas flow becomes important and enhances the evacuation of heat at the surface of the growing particles. Note that for the steel wall, the particle is coolest when in contact with the wall, whereas for polyethylene the opposite is found. In other words, for this last case, an improvement in heat transfer is obtained as the isolated particle moves and begins to be enveloped by a fully developed

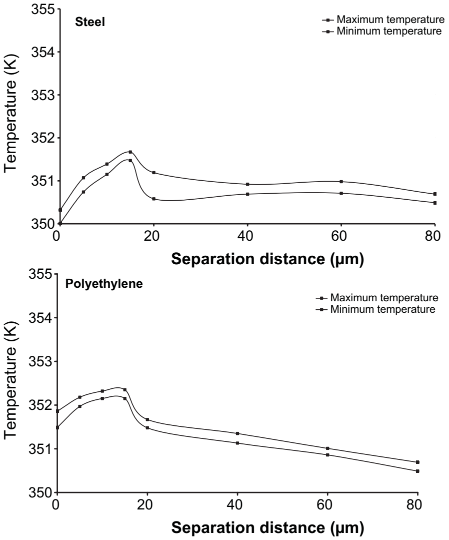

Figure 5.
Case 1: Particle temperature as a function of wall material and separation distance between the particle and the wall. (Bulk gas flow 0.2 m/s.)

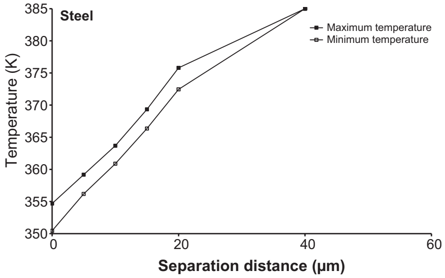

Figure 6.
Case 3: Particle temperature as a function of wall material and separation distance between the particle and the wall. Bulk gas flow stagnant.

flow. A shift in the shape of the curve is seen at a separation distance of about 15 µm (roughly equivalent to the particle diameter), where convection becomes more important and the shape of the curve becomes similar to the profile in Figure 4. At a smaller distance than 15 µm, the velocity between the particle and the wall will be low, and the convective contribution to heat transfer will be less significant than in the fully developed flow field. Once the particles are far enough away form the wall (roughly the diameter of the particles) the influence of the wall essentially disappears.

An increase in the initial particle size has an even greater impact on the particle temperature, as can be seen in Figures 6 and 7. In the case of a stagnant gas (Figure 6), the additional heat flux per unit surface is enough to guarantee that the particle near the polyethylene covered wall overheats (i.e. never achieves a steady state temperature less than 385 K), which is why one does not see the curves for this simulation in Figure 6.

As was seen for the smaller particles above, the particle temperature increase was limited in the case of steel as wall material when the wall and the particle are in contact in a single point. Here, we observe that the particle temperature (in a stagnant gas flow as well as a bulk gas flow of 0.2 m/s) increases about 5 K. In the case of polyethylene as wall material, the stagnant gas is not presented here because the particle overheats for all simulated separation distances. In the case of a bulk gas flow of 0.2 m/s (Figure 7) the particle overheats at a certain distance from the

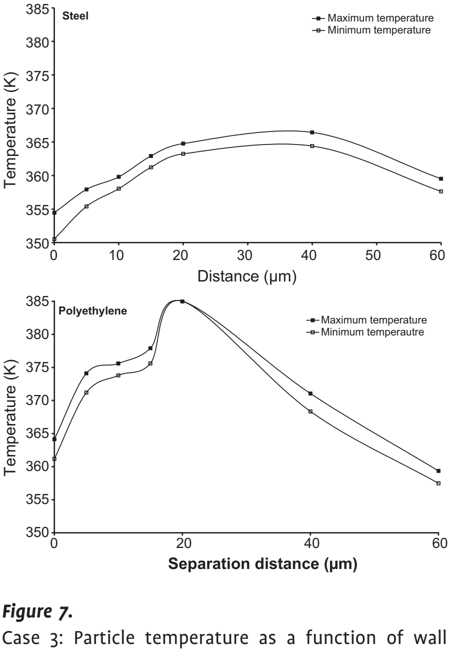

Figure 7.
Case 3: Particle temperature as a function of wall material and separation distance between the particle and the wall. Bulk gas flow 0.2 m/s.

wall, but as it moves away from further the wall the heat is removed by the passing gas thus decreasing the particle temperature. In this case, we can see that for both stagnant flow and a bulk gas flow of 0.2 m/s, at a separation distance of less than 60 μm the particle temperature becomes identical regardless of the wall material.

Conclusion

In summary it can be seen that the particle temperature depends to a large extent on the capacity of the wall to evacuate the produced heat over distances as large as 20 μm (admittedly this is not a lot on the scale of a FBR, but once the interior walls start to foul, this will only continue to get worse). In all three cases, using steel as a wall material the particle temperature increase (in contact with the wall) never exceeds 5 K, regardless of the gas flow and the particle size (of course this is only true for the cases studied here – higher activities and catalysts that activate more quickly will overheat more, and more rapidly). On the other hand, using glass as a wall material, a particle in contact with the wall does not overheat. Finally, for a wall consisting of polyethylene deposits, the particle temperature rise becomes so large that in certain cases the particle overheats. This obviously has implications in terms of the condition of the reactor wall, and demonstrates that a fouled wall can lead to local overheating even if the particles in the reactor do not come into contact with it.

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