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Heat Transfer in Gas Phase Olefin Polymerisation

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Summary: A fixed bed microreactor has been used to study heat transfer during the initial transient state of gas phase olefin polymerization on a supported catalyst. It has been shown that heat transfer during this stage of the polymerisation is critical, and under conditions found commercially problems can arise with hot spots and polymer melting. It is proven how the thermal properties of the gas mixture flowing on the catalytic bed exert great influence on heat dissipation reducing the sudden increase in temperature by as much as a factor of 5. Flow rate and especially the process gas composition are the key factors in controlling the bed temperature.

Keywords: fixed bed; heat transfer; nascent polymerization; olefin polymerization; supported catalyst

Introduction

Since the discovery of the catalytic reaction for the polymerization of ethylene by Ziegler[1], polyolefins have become rapidly the most widely used class of commodity polymers in the world, and the market demand shows no signs of decline. In addition it is now well-accepted that it is possible to produce polyolefin-based materials with a wide range of properties by correctly modifying the catalysts used for the polymerization.[2] As a consequence of this ever-growing demand, manufacturers are obliged to continually increase the quantity and the quality of their production. This implies investing consistent effort to increase catalyst activity (e.g. faster reactions with higher yields), develop new catalysts for new material properties, and improve process design. Gas phase processes (i.e. processes using a solid catalyst and gaseous monomers) are an attractive means of producing a wide range of polymers for their simplicity of operation, and relatively low environmental impact (no solvent). However the thermal properties of the continuous gas phase are very poor, and one of the major challenges is to achieve faster reactions and higher yields in these processes is over-coming heat transfer limitations. Given the highly exothermic nature of the reaction, poor heat transfer could lead to particle overheating, sintering, catalyst deactivation or loss of control over polymer properties including particle morphology

It appears that the morphology of polymer particles is fixed during the first instants of the polymerization. It has been observed that the reactions proceed very fast during first few fractions of a second, and, in the case of Ziegler-Natta catalysts supported on $MgCl_2$, the catalyst fragments almost totally at this point under conditions approaching those used in commercial production.[3,4] This is accompanied by a high heat generation and monomer consumption so that heat and mass transfer rate can become critical, especially in gas phase. However, despite the importance of understanding this phase of the reaction, there is little literature published on heat and mass transfer and particle morphology

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during the nascent phase of polymerization. The first systematic studies on the nascent polymerization of olefins were performed by Keii and Terano[5] with the help of a quenched flow reactor capable of stopping the reaction after 0.2 s. The group of Terano and other groups[6–11] immediately understood the potentiality of the quench flow technique and used it in different works, focusing essentially on determining kinetic parameters, active site type and polymerization mechanisms.

Di Martino et al.[3,12,13] used a similar approach, but altered the reactor design to study the reaction kinetics and the morphology of nascent polyolefin particles in slurry. The particularity of their work is to be capable to work under industrial conditions of temperature and pressure. Previous works on morphology of nascent polyolefin powders have been done but either at idealized conditions [14–18] or on ideal flat supports.[19]

In parallel, Silva et al. [4] developed an approach for morphological and kinetic studies and for following the evolution of polymer properties for gas phase systems using a fixed bed reactor capable of working over a wide range of temperatures and pressures. This original design was improved upon by Ollala et al.,[20] allowing for better control of the flow field in the reactor. They used this reactor configuration to show how the heat transfer rate depends on the gas flow rate and affects the productivity of the catalyst. They also showed how in the first instants of the reaction the kinetics seems to be controlled partially by fragmentation of the support.

In the current paper we present our results showing how the thermal properties of the flowing gas mixture (especially thermal conductivity) influence strongly the heat transfer between the solid bed and the gas and as a consequence influence the catalyst activity and the overall reaction kinetics. The major objective of this work is to understand: (1) how the thermal characteristics of the gas influence the heat transfer and temperature rise in the reactor; (2) to understand how best to get a measurement of the surface temperature of the reacting particles in the bed.

Experimental Part

NaCl (Laurylab, France) with particle size between 250 and 500 μm was used as seedbed. It was dried under high vacuum for 4 h at 120 °C before use in order to eliminate all the traces of water.

The zirconocene complex ($EtInd_2ZrCl_2$) was used as received and supported over silica treated with methylaluminoxane (MAO). Silica particles were obtained from Grace Davidson (Sylopol 952) and dehydroxylated at 200 °C for 4 h before use. MAO was obtained from Aldrich (Germany) and impregnated on the pre-dried silica. The preparation of the catalyst is largely discussed on the literature and we followed the synthesis developed by Welborn[21] and Takahashi[22] adapted to the $EtInd_2ZrCl_2$ complex.

Ethylene with minimum purity of 99.5% was purchased from Air Liquide (France) and is passed over zeolite and active carbon filled purifying columns before use. Argon from Air Liquide (France) with minimum purity of 99.5% was used to keep the reaction environment free of oxygen. Helium and Nitrogen purchased from Air Liquide (France) were used as received.

The reactor consists of an internal circular metal chamber with a diameter of 22 mm and a depth of 7 mm closed with a frittered metal cartridge (c.f. reference [20] for more details). The chamber is filled with a mixture of seedbed and catalyst (1–6% catalyst w/w) in a glove box to avoid contamination of the contents, inserted into the external chamber and then closed with the frittered metal lid. Gas enters through the hole in the bottom of the external chamber and leaves through a similar hole at the back of the metal lid. Filters are present at the inlet and at the outlet of the gas to assure the bed stability under the flow of gas. A metering valve is present on the outlet stream allowing regulating the gas flow rate inside the

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reactor. The entire assembly is then plunged into a water bath to ensure constant inlet gas and jacket wall temperatures. Thermocouples at the inlet and outlet of the reactor allow us to record the temperature rise of the gas phase as it flows through the bed.

Productivities are measured by weighing the reactor before and after the polymerization step in a glove box (after a drying period to ensure that there is no residual water on the reactor assembly of course). The polymer is recovered from the support bed after 3 washing steps: one with demineralised water followed by one with a solution of 10% w/w of HCl in demineralised water and finally one with pure demineralised water again. The polymer recovered is then dried under vacuum at 100 °C for 1 hour to eliminate the last traces of water.

Results and Discussion

The typical reaction conditions are 80 °C and 6 bars of ethylene. With this situation using the Ergun equation we can calculate a pressure drop in the bed of 3×10^{-4} bar, which is absolutely negligible. In the previous work with this reactor [20] it has been determined that increasing the flow rate of the gas flowing on the fixed bed will lead to an increase in heat transfer from the solid to the gas.

Table 1.
ΔT_{max} and productivity in ethylene polymerisation at 80 °C, 6 bar.

Run	ΔT (°C)	Y (gPe/gcat)
1	27	5.05
2	29	4.72
3	25	5.22

Since poor heat transfer can lead to overheating of the fixed bed with a risk of melting the polymer particle and loose a lot of precious information about nascent morphology we have therefore decided to work with a relatively high volumetric gas flow (measured at the outlet of the system, at room temperature and pressure) of 20 cm^3/s.

Repeatability Study

In an initial step we conducted a series of experiments in order to test the reproducibility of the system. With 50 mg of supported catalyst and for 75 s of reaction we obtained acceptably reproducible results in terms of productivity (Table 1) and of evolution of the outlet gas temperature increase (Figure 1). While the experiments are not perfectly reproducible, dT_{out}/dt shows very similar behavior for the three reactions. It is interesting to note that the temperature (and perhaps the reaction rate) reaches a maximum approximately 50 seconds after the slope of the

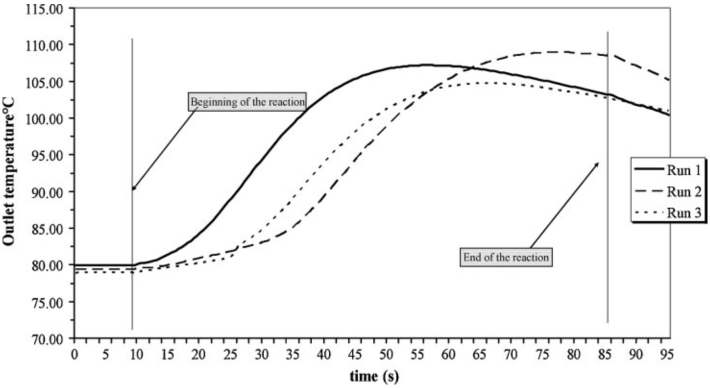

Figure 1.
Outlet gas temperature profiles for reactions of Table 1.

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temperature vs. time curve starts to increase.

What is not worthy and surprising at the same time is that the outlet gas temperature increases by approximately 25 °C. With a reaction temperature of 80 °C it is highly possible that hot spots present in the bed can reach the softening temperature of the polymer. This is probably happening because after the reaction the polymer and NaCl grains form a quite compact and not free flowing mass with visible lumps.

Influence of Helium on Heat Transfer

Increasing the heat transfer from the solid to the gas will result in a better heat removal with gas temperature closer to particle temperature and elimination of hot spots. The heat transfer coefficient h between a solid and a fluid can be calculated from the Nusselt number:

$$Nu = \frac{hL}{k_f}$$

where L is a characteristic dimension for heat transfer (here it can be the mean diameter of the catalysts or growing polymer particles) and k_f is the thermal conductivity of the fluid.

The correlations used to calculate Nusselt number in a packed bed imply a linear dependence of $Re^{0.5}$ and $Pr^{0.33}$. The Prandtl and Reynolds numbers are defined as

$$\mathrm{Pr} = \frac{C_p \mu}{k_f}, \mathrm{Re} = \frac{\rho V_\infty L}{\mu}$$

where μ is the fluid viscosity, C_p its heat capacity, ρ the density and V_∞ the bulk fluid velocity. Finally h is proportional to $k_f^{0.67}$, $V_\infty^{0.5}$, and $C_p^{0.33}$. In other words, choosing a fluid with a high thermal conductivity and/or heat capacity can then lead to an improvement in heat transfer. This can be easily done by adding helium to the reacting mixture. The thermal conductivity of helium is 0.172 W/m/K at 300 K and 1 bar, while that of ethylene equals 0.0236 at the same conditions.[23] Another advantage of using Helium is that it is an inert gas, so it will not affect the kinetics for any reason other than because of its thermal properties.

Table 2.
ΔTmax and productivity in ethylene polymerisation at 80 °C, 6 bar in presence of helium.

Run	P_{C2} (bar)	P_{He} (bar)	ΔT (°C)	Y (g_{PE}/g_{cat})
4	6	0	21.2	4.7
5	6	3	3.0	1.5
6	6	6	4.0	2.06
7	6	12	3.7	1.91

A series of reactions conducted with 30 mg of supported catalyst at 80 °C, 6 bars of ethylene partial pressure and variable He partial pressure shows that addition of as little as 33% of He to the process gas without changing the flow rate increases leads to much lower outlet gas temperatures than previously showed. The increase in outlet gas temperature drops from 21 °C to 3–4 °C (c.f. Table 2). The disappearance of the hot spots inside the bed is confirmed by recovering a perfect free flowing powder after the reaction with He.

When helium is added to the reacting mixture the measured productivity (and the catalyst activity as a consequence) also decreases (Table 2). There are two possible reasons for this phenomenon. The increased capacity of the system to transfer the heat generated during the reaction from the solid to the gas results in a much lower average reactor temperature as manifested by the lower outlet gas temperature. Thus the exothermic polymerization reaction is inherently slower than when the local temperature increases. Note that there is no visible deactivation in the curves with He (Figure 2), whereas there is in absence of He (Figure 1). It is also true that diluting the reacting gas with an inert could lower the ethylene concentration at the active site (nevertheless, the partial pressure of ethylene remains constant). Strong convection effects are possible especially at the beginning of the reaction if the monomer consumption is very high and for big and/or active catalytic particles. In this case the monomer concentration will not be constant in the particle pores along the radial dimension with accumulation of inerts at

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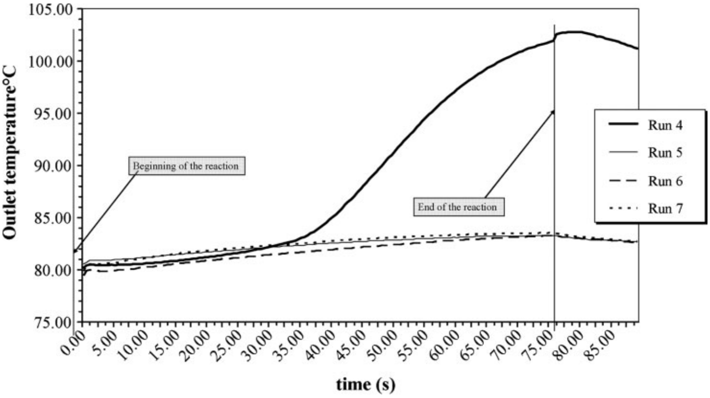

Figure 2.
Outlet gas temperature profiles in presence of Helium.

the active site.[24] This seems not to be the case because the measured productivity does not change greatly increasing the helium partial pressure. This will be verified experimentally in the following section.

Influence of Nitrogen on Heat Transfer

Replacing helium with nitrogen has the advantages of retaining the inert characteristic of the diluent and, at the same time, deleting the positive effect of the increased heat transfer coefficient (the thermal conductivity of nitrogen is 0.026 W/m/K at 300 K and 1 bar; comparable to the one of ethylene).

A series of experiences similar to that realized with helium has been carried out using nitrogen. As can be seen in Figure 3, in this case the ΔT_{max} decrease from 14 °C if no nitrogen is present (run 8) to 10 °C if 6 bars of nitrogen are added (run 10). The productivity drops respectively from $6.7\,g_{PE}/g_{cat}$ to $5.8\,g_{PE}/g_{cat}$ (c.f. Figure 4). Recall that in the case of He, the productivities dropped from 4.7 g/g with no He, to 1.8 ± 0.3 g/g with He.

This shows very clearly that dilution by inerts does not play a significant role in the decrease of the measured productivity, but the thermal characteristics of the inerts (He vs N_2) are important in determining the maximum outlet temperature from the fixed bed. Figure 4 shows that while the yield decreases a little with the

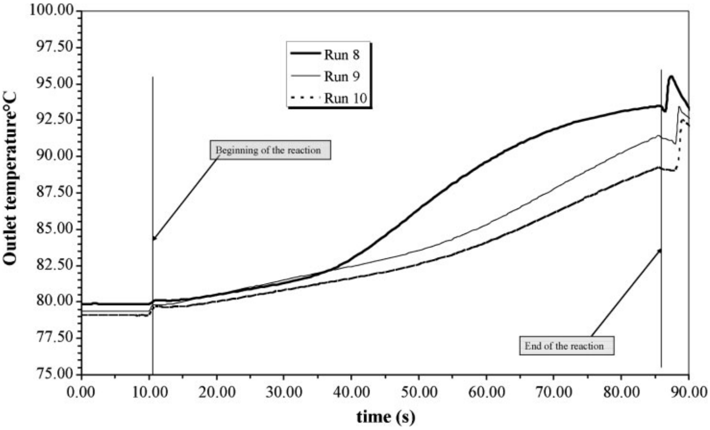

Figure 3.
Outlet gas temperature profiles in polymerisation of ethylene in presence of Nitrogen.

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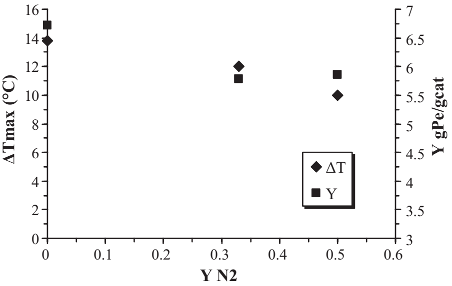

Figure 4.
ΔTmax and productivity at 80 °C, 6 bar in presence of nitrogen.

increase in N_2 pressure, this is possibly due to the fact that the particles are not as hot (therefore reacting more slowly) rather than to any dilution of the monomers

Conclusions

We have begun to look at the role played by the process gas in terms of the observable temperature rise in the fixed bed of our stopped flow gas phase reactor for olefin polymerization. Adding helium to the reacting mixture does not influence on the observed reaction kinetics, helps to avoid hot spots in the bed, and has a strong impact on the outlet temperature of the bed. This implies that if we want to perform kinetic studies to look at intrinsic reaction kinetics, or to keep the condition of the reactor isothermal, it is far more useful to use a certain amount of He in the process gases rather then N_2.

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