

Polymerization of Olefins through Heterogeneous Catalysis— the Effect of Condensation Cooling on Particle Ignition

In catalyzed olefin polymerization, a critical design problem for gas phase reactors is removal of the heat of polymerization. Even with good macroscopic reactor heat removal, hotspots and polymer buildup on internal reactor surface can still occur.¹⁻³ An analysis of the mass and energy balances across the external boundary layer of the growing polymer particle shows that temperature gradients across the boundary layer are often significant enough to cause particle overheating⁴; the possibility of multiple steady states for the polymer particle is also demonstrated. Recently it has been shown that the injection of liquid into a gas phase reactor is a feasible means of heat removal for fluidized bed reactor systems.^{3,5,6} The cooling from condensate evaporation increases the heat removal capacity of the reactor and thus increases the production capacity. It has been speculated that the evaporative cooling from condensate coated particles could also help prevent the overheating and multiple steady states possible for these particles.⁴ Unfortunately, as we shall show in this note, condensation cooling has little or no effect on particle overheating.

To analyze the issue, we make use of the same assumptions and notation as in Ref. 4. Figure 1 shows a

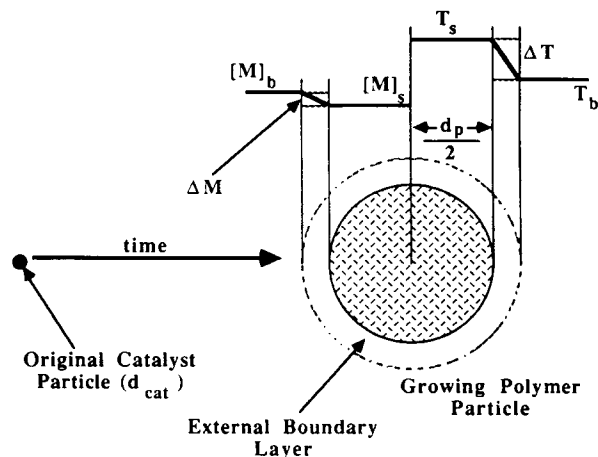


Figure 1 Boundary layer analysis: schematic of the growing polymer particle.

polymer particle of diameter d_p and surface area A_p that has grown from a catalyst particle of original diameter d_{cat} and volume V_{cat} . Gradients may exist for the monomer concentration and temperature from the bulk phase ($[M]_b$, T_b) through the boundary layer to the surface of the growing particle ($[M]_s$, T_s). For this analysis, internal temperature or concentration gradients within the particle are neglected. Furthermore, we assume:

- Physical properties of the fluid are constant across the particle boundary layer;
- The rate of polymerization is first order with respect to monomer concentration and follows the Arrhenius law;
- The quasi-steady state assumption is valid; i.e., the accumulation terms of the energy and mass balance equations are negligible.

The justification of these assumptions are more fully discussed in Ref. 4.

Visual observation has shown that, with condensation cooling, the liquid droplets wet the surface of the polymer particles.³ Thus it can be assumed that the condensate entering the reactor is evenly distributed among the particles in the reactor on a surface area basis. The rate of condensate evaporation, q ($\text{g}/\text{cm}^2 \text{ s}$), is represented by

$$q = \frac{Q}{P} (1 - \epsilon) \rho_{pol} \frac{(d_p)_{avg}}{6} \quad (1)$$

where Q = mass flow rate of condensate into reactor (g/s), P = mass of polymer particles in reactor (g), $(1 - \epsilon) \rho_{pol}$ = particle density (g/cm^3), ϵ = particle void fraction, and $(d_p)_{avg}$ = average particle diameter (cm).

The steady state energy balance for a polymer particle is

$$(-\Delta H_p) V_{cat} R_p = A_p h (T_s - T_b) + q A_p (-\Delta H_c) \quad (2)$$

where R_p is the rate of polymerization ($\text{mol}/\text{cm}^3 \text{ cat s}$), h is the heat transfer coefficient, and ΔH_p (cal/mol) is the heat of polymerization. The rate of condensate vaporization per particle surface area, q ($\text{g}/\text{cm}^2 \text{ s}$), is estimated by eq. (1); ΔH_c (cal/g) is the heat of condensate vaporization. The corresponding mass balance is given by

$$V_{cat} R_p = A_p k_s ([M]_b - [M]_s) \quad (3)$$

where k_s is the mass transfer coefficient across the growing boundary layer. Simultaneous solution of eqs. (2) and (3) gives the monomer concentration at the particle surface:

$$\frac{[M]_s}{[M]_b} = 1.0 - \frac{y_s - (1 - \zeta)}{\beta} \quad (4)$$

where the dimensionless parameters are defined as follows:

$$y_s = \frac{T_s}{T_b}, \quad \beta = \frac{(-\Delta H_p) k_s [M]_b}{h T_b}, \quad \zeta = \frac{q(-\Delta H_c)}{h T_b} \quad (5)$$

The rate of polymerization is related to the rate of reaction under bulk reactor conditions $(R_p)_b$ according to

$$R_p = (R_p)_b \frac{[M]_s}{[M]_b} \exp\left[\gamma\left(1 - \frac{1}{y_s}\right)\right], \quad \gamma = \frac{E}{RT_b} \quad (6)$$

Using the above expressions, the energy balance [Eq. (2)] becomes

$$F(y_s) = \frac{\theta}{\alpha} = \frac{(1 - \zeta) + \beta - y_s}{y_s - (1 - \zeta)} \exp\left[\gamma\left(1 - \frac{1}{y_s}\right)\right] \quad (7)$$

where

$$\theta = h A_p T_b, \quad \alpha = \frac{(R_p)_b V_{\text{cat}} h T_b}{k_s [M]_b} \quad (8)$$

In eq. (7), the fraction of heat removed by evaporation, f_e can be expressed as

$$f_e = \frac{\zeta}{(y_s - 1) + \zeta} \quad (9)$$

This parameter gives a measure of the relative importance between convective and evaporative heat removal from the particle.

Using the methodology of Luss,⁷ a necessary condition for multiple steady states in systems described by eq. (7) is

$$\gamma\beta > 4(1 - \zeta)[(1 - \zeta) + \beta] \quad (10)$$

If the inequality described by eq. (10) is satisfied, then multiple steady states will exist if and only if

$$F(y_{\min}) \leq \frac{\theta}{\alpha} \leq F(y_{\max}),$$

$$y_{\max, \min} = (\gamma(2(1 - \zeta) + \beta)$$

$$\pm \{\gamma\beta[\gamma\beta - 4(1 - \zeta)((1 - \zeta) + \beta)]\}^{1/2} / 2(\gamma + \beta) \quad (11)$$

For reactor systems with no condensation cooling, the parameter ζ is set to zero, and the analysis collapses to that described in Ref. 4.

It is necessary to obtain estimates for heat and mass transfer coefficients in order to proceed. This analysis uses the Ranz-Marshall correlation⁸ for a single sphere moving with relative velocity u :

$$\text{Sh} = 2.0 + 0.6(\text{Sc})^{1/3}(\text{Re})^{1/2} \quad (12a)$$

$$\text{Nu} = 2.0 + 0.6(\text{Pr})^{1/3}(\text{Re})^{1/2} \quad (12b)$$

The dimensionless numbers are defined as usual:

$$\begin{aligned} \text{Sh} &= \frac{k_s d_p}{D_b}, & \text{Nu} &= \frac{h d_p}{k_f}, \\ \text{Sc} &= \frac{\eta}{\rho D_b}, & \text{Pr} &= \frac{\eta C_p}{k_f}, & \text{Re} &= \frac{\rho u d_p}{\eta} \end{aligned} \quad (13)$$

The Ranz-Marshall correlation assumes an infinite boundary layer around the particle, leading to the theoretical single-sphere asymptote of 2. Physical properties of the fluid are estimated as a function of reactor temperature, pressure and composition using the correlations summarized in Ref. 9.

EXAMPLE

As an example of the effect of condensation cooling, consider the LLDPE fluidized bed system. The rate of condensate evaporation in the reactor can be estimated from patents issued to Union Carbide.^{5,6} The amount of liquid condensed in the recycle stream can be as high as 20% by weight, but generally is kept between 2 and 12%. Further details can be obtained from an examination of the examples described in the patents. A typical reactor with a polymer bed of 34,000 kg has a recycle rate of 500,000 kg/h. If the recycle stream contains 12% liquid, condensate enters the reactor at a rate of 17 kg/s. Equation (1) can then be used to calculate the rate of condensate evaporation on a surface area basis. The operating conditions summarized below are taken from Ref. 6:

Reactor temperature:	90°C
Reactor pressure:	20 atm
Reactor composition (mole fractions):	
Ethylene	0.5
Butene	0.1
Hydrogen	0.1
Nitrogen	0.3
R_{ob} (production rate at reactor T, P):	5000 g/g-cat h

Activation energy: 7 kcal/mol
 Catalyst diameter: 60 μm
 Relative particle-fluid velocity: 50 cm/s
 Heat of condensate vaporization: 100 cal/g
 Average particle diameter: 1000 μm
 Mass of polymer bed: 34,000 kg

The production rate at reactor conditions is related to $(R_p)_b$ according to

$$R_{ob} = \frac{3600(R_p)_b(MW)_{mon}}{\rho_{cat}} \quad (13)$$

Three simulations have been run with the above conditions. The first (Case I) is for a reactor with no condensate cooling, the second (Case II) is for a reactor with the rate of condensate cooling set to double (24%) the suggested maximum level, and the third (Case III) assumes complete condensation of the recycle stream. Note that Case III is similar to propylene stirred bed gas phase reactors; these systems have employed complete recycle condensation for cooling purposes for many years (e.g., Ref. 10).

Simulation results are shown in Figure 2, a plot of ΔT , the boundary layer temperature gradient, vs. particle diameter. These solutions are quasisteady states which result because particle growth occurs over a period of hours while particle dynamics are on the order of seconds. Thus the particle temperature rise constantly changes in a quasisteady fashion throughout the polymerization as the polymer particle grows. Also shown in the figure are results

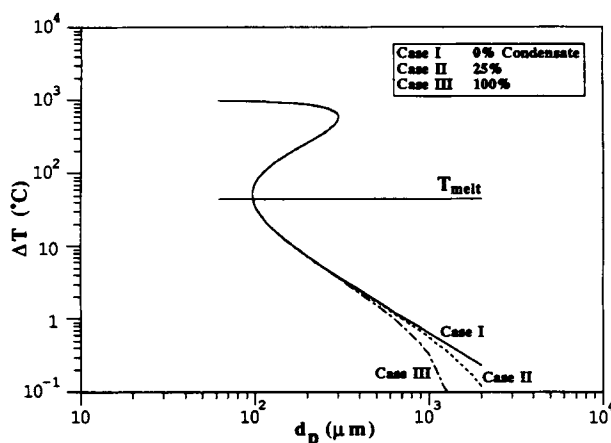


Figure 2 Effect of condensation cooling on particle temperature rise: LLDPE production at 90°C and 20 atm.

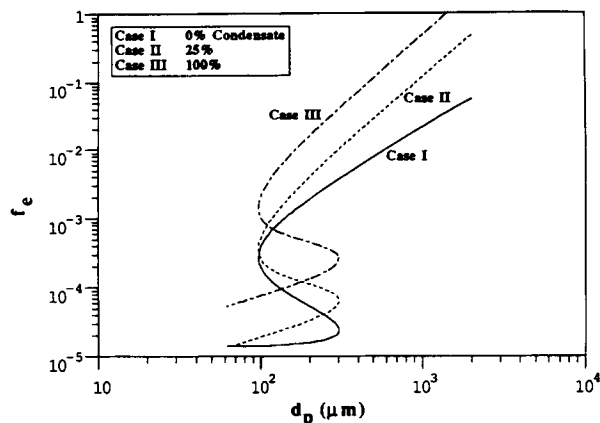


Figure 3 Fraction of heat removed by condensation cooling (f_c) vs. particle diameter: LLDPE production at 90°C and 20 atm.

for particle growth under identical conditions, but without condensation cooling.

For all curves in Figure 2, there are two stable steady state branches—the upper one at a ΔT at 1000°C, and the lower one which starts at a ΔT of $\approx 40^\circ\text{C}$ and decreases with increasing particle size. The upper steady state can never be reached, as particle melting and agglomeration would occur at the melting point of the polymer. Notice, however, that the lower branch does not start until the particle has grown to a diameter of 100 μm , a growth factor of 1.6 over the original catalyst particle size. Before this diameter is reached, only the upper steady state exists. At small growth factors, there is insufficient surface area to remove the heat generated by polymerization; polymer melting will occur. This result has interesting implications. At the start of a gas phase polymerization under the simulation conditions, the only steady state solution which exists results in particle melting.

Figure 2 also clearly shows the condensation cooling has no effect on the phenomenon of particle overheating. The critical diameter at which the lower steady state branch begins (100 μm) is not affected by the additional heat removal mechanism. The greatest predicted effect of the evaporative heat transfer is for the larger polymer particles, which have little chance of overheating even without condensation cooling. Figure 3 plots f_c , the fraction of heat removed by condensation cooling [Eq. (9)], as a function of particle diameter. Even for the most extreme case—100% condensation of a fluidized bed recycle stream—the heat removal by evaporation is negligible for the small particles most prone to overheating.

This analysis demonstrates that, although condensation cooling may be an effective macroscale means of heat removal, it has little or no effect on polymer particle overheating. Thus, the trends and conclusions summarized in the previous paper⁴ hold true for all gas phase reactor systems, with or without condensation cooling.

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