



Advance Chemical Reaction Engineering

Heterogeneous Catalysis: Non-isothermal Kinetic in Porous Catalyst Particles

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Giving up is the ultimate tragedy

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Introduction

- When the heat of reaction is large, intrapellet temperature gradients may have a larger effect on the rate per pellet than concentration gradient.
- Even when ΔH is low the center and surface temperatures may differ appreciably, because catalyst pellets have low thermal conductivities.
- The combined effect of mass and heat transfer on *rate of reaction* can still be represented by the general definition of the effectiveness factor.

$$\eta = \frac{\text{actual rate for the whole pellet}}{\text{rate evaluated at outer surface conditions}} = \frac{4\pi R^2 D_e \left(\frac{dC}{dr}\right)_R}{\frac{4}{3}\pi R^3 k_1 C_s}$$

is not limited to isothermal conditions

$$-r_A'' := \eta (-r_A''_s) = \eta f(C_s, T_s)$$

Where η is the nonisothermal effectiveness factor

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Balance on Spherical Particle

- For irreversible first-order reaction $A \rightarrow B$
- If the effective diffusivity is independent of the concentration of reactant and temperature
- The differential mass balance and boundary conditions

$$\left(-4\pi r^2 D_e \frac{dC}{dr}\right)_r - \left(-4\pi r^2 D_e \frac{dC}{dr}\right)_{r+\Delta r} = 4\pi r^2 \Delta r \rho_P k_1 C$$

take the limit as $\Delta r \rightarrow 0$

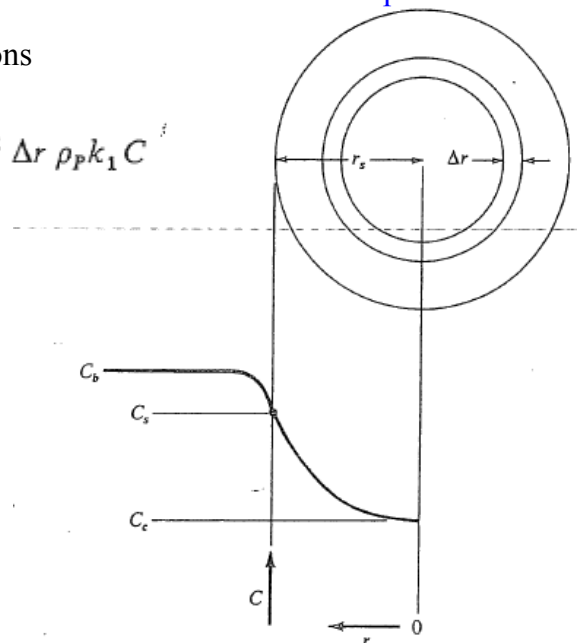
$$\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dC}{dr} - \frac{k_1 \rho_P}{D_e} C = 0$$

At the center of the pellet symmetry requires

$$\frac{dC}{dr} = 0 \quad \text{at } r = 0$$

and at the outer surface

$$C = C_s \quad \text{at } r = r_s$$



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Balance on Spherical Particle

- The energy balance over the spherical shell of thickness,

$$\left(-4\pi r^2 k_e \frac{dT}{dr}\right)_r - \left(-4\pi r^2 k_e \frac{dT}{dr}\right)_{r+\Delta r} = 4\pi r^2 \Delta r \rho_P k_1 C \Delta H$$

$$k_1 = A e^{-E_i/R_g T}$$

Taking the limit as $\Delta r \rightarrow 0$ and assuming that k_e is independent of temperature, we find

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{k_1 \rho_P C}{k_e} \Delta H = 0$$

with boundary conditions

$$\frac{dT}{dr} = 0 \quad \text{at } r = 0$$

$$T = T_s \quad \text{at } r = r_s$$

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Balance on Spherical Particle

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{k_1 \rho_P C}{k_e} \Delta H = 0$$

$$\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dC}{dr} - \frac{k_1 \rho_P}{D_e} C = 0$$

Numerical solution is necessary

- Nevertheless, the similarity of the nonreaction terms in the two differential equations does permit an analytical relation between concentration of reactant and temperature at any point in the pellet

eliminating $k_1 \rho_P C$

$$D_e \left(\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dC}{dr} \right) = \frac{k_e}{\Delta H} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right)$$

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Balance on Spherical Particle

or

$$D_e \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = \frac{k_e}{\Delta H} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right)$$

integrate this equation once, using

$$\frac{dT}{dr} = 0 \quad \text{at } r = 0 \quad \frac{dC}{dr} = 0 \quad \text{at } r = 0$$

then integrate a second time, using

$$T = T_s \quad \text{at } r = r_s \quad C = C_s \quad \text{at } r = r_s$$

$$\rightarrow T - T_s = \frac{\Delta H D_e}{k_e} (C - C_s)$$



Balance on Spherical Particle

- The maximum temperature rise in a pellet would occur when the reactant has been consumed by the time it diffuses to the center.

for $C = 0$

$$\rightarrow (T_c - T_s)_{\max} = -\frac{\Delta H D_e}{k_e} C_s$$

- The maximum temperature rise depends on the heat of reaction., transport properties of the pellet, and the surface concentration of reactant.

$$\eta = \frac{4\pi R^2 D_e \left(\frac{dC}{dr} \right)_R}{\frac{4}{3}\pi R^3 k_1 C_s}$$

k_1 is evaluated at the surface temperature.



Nonisothermal Effectiveness Factors

η is a function of

1. The Thiele-type modulus,

$$3(\Phi_s)_s = r_s \sqrt{\frac{(k_1)_s \rho_P}{D_e}}$$

Φ_s is evaluated at the surface temperature;

$(k_1)_s$ is the rate constant at T_s .

2. The Arrhenius number,

$$\gamma = \frac{E}{R_g T_s}$$

3. A heat-of-reaction parameter,

$$\beta = \frac{(-\Delta H) D_e C_s}{k_e T_s}$$

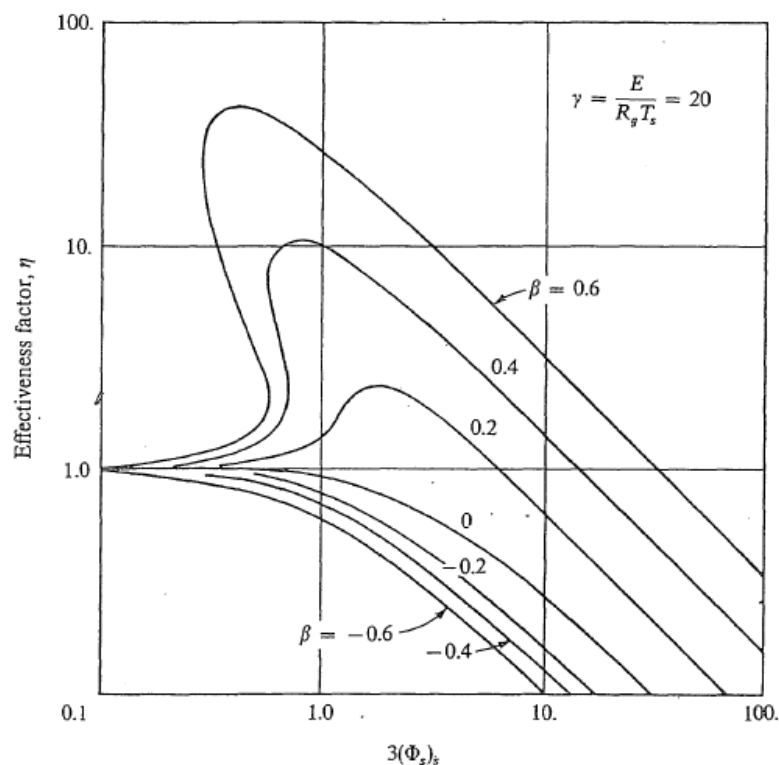
$\beta = 0$ corresponds to isothermal operation

($\Delta H = 0$)

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Nonisothermal Effectiveness Factors



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Nonisothermal Effectiveness Factors

For an exothermic reaction (positive β) η values are greater than unity.

- The temperature rises going into the pellet.
- The increase in rate of reaction accompanying the temperature rise can more than offset the decrease in rate due to drop in reactant concentration
- The reaction rate depends on the temperature, but also on the concentrations.
- These two dependencies cause **opposite responses** in the catalyst pellet
- The effect of k rising - due to a rise of the temperature in the pellet - exceeds by far the effect of the drop of c on the rate (- at least in the **initial range** of ϕ).
- As a consequence, the **average reaction rate** in the pellet is **higher** than for the conditions at the surface.



Nonisothermal Effectiveness Factors

With large η

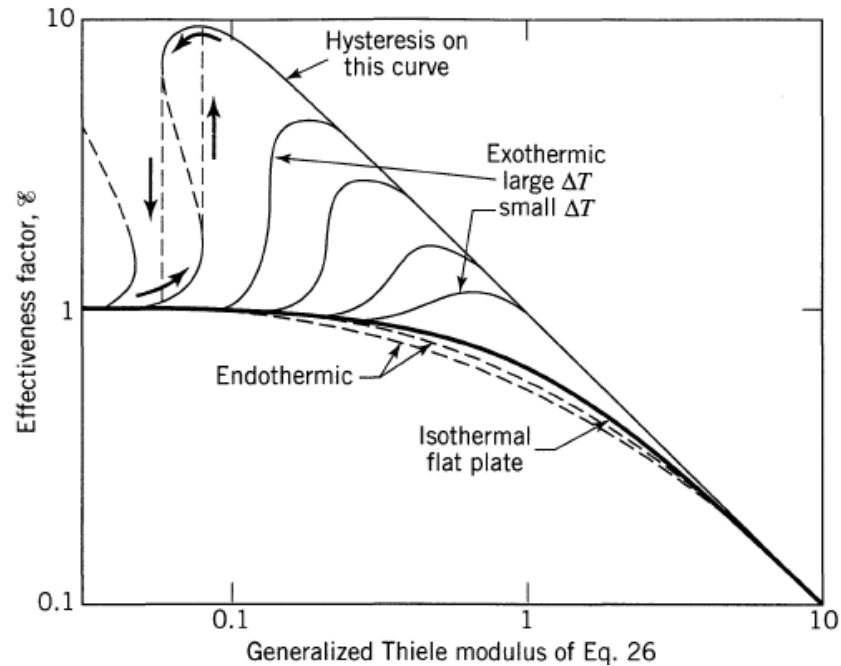
- There will be a large increase in temperature toward the center of the pellet, resulting in sintering and catalyst deactivation.

For an endothermic reaction η is always less than unity.

- There is a decrease in temperature and rate into the pellet.
 - In this case the effect of k and c on the rate act in the same direction.
 - i.e. η **decreases only** as compared with the isothermal case.
- Since the rate decreases with drop in temperature, the effect of heat-transfer resistance is diminished



Nonisothermal Effectiveness Factors



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Nonisothermal Effectiveness Factors

for a first-order irreversible reaction

$$\eta = \frac{1}{(\Phi_s)_s} e^{\beta\gamma/5} \quad \text{for } (\Phi_s)_s > 2.5$$

where

$$\beta\gamma = \frac{(-\Delta H)D_e C_s}{k_e T_s} \frac{E}{R_g T_s}$$

when **external** mass and heat transport has to be considered

As in the isothermal case with film diffusion

- the equations inside **the pellet** stay the same
- only the boundary conditions change

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Nonisothermal Effectiveness Factors

mass:

$$\frac{d\bar{c}}{d\bar{r}} = B(1 - \bar{c}) \quad \bar{r} = 3$$

$$\frac{d\bar{c}}{d\bar{r}} = 0 \quad \bar{r} = 0$$

energy:

$$h_f(T - T_b) = -\lambda_e \left(\frac{dT}{dx'} \right)_{x'=R}$$

$$Bi_h(\theta - 1) = \left(\frac{d\theta}{dx} \right)_{x=1}; \quad Bi_h = \frac{h_f \cdot R}{\lambda_e}$$

On the basis of this extension the following plots as a function of 5 parameters result

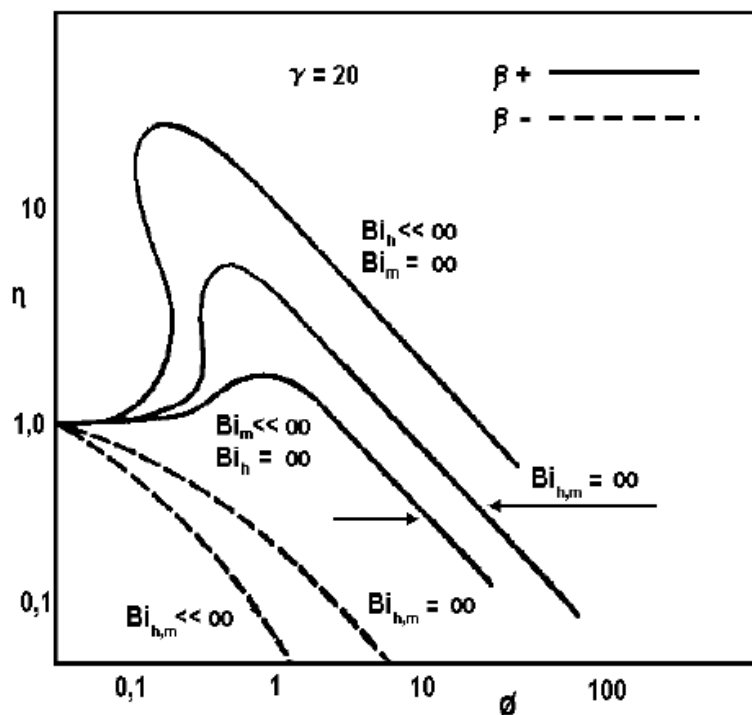
$$\eta = f(\phi, \gamma, \beta, Bi_m, Bi_h)$$

Biot is the ratio of porediffusion \cong internal resistance.

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Nonisothermal Effectiveness Factors



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Nonisothermal Effectiveness Factors

Exothermal case:

- Bi_h small - **normal case**
↪ η becomes **larger**, as T_{Pellet} is even larger
- Bi_m small - **rarely**
↪ η becomes **smaller**, as not enough educt can be fed.

Endothermal case

η becomes **smaller** for smaller Bi_h , Bi_m , i.e. therefore stronger drop of temperature and concentration. Both effects go in the same direction.

Both Bi -numbers show large values, the cases without external transport influences, already known.

For very large values of Bi , but small values for γ and β , we come back to the simple case of pore diffusion in the isothermal pellet.

