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Diagnostic Criteria for Heat Transport Limitations in Fixed Bed Reactors

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Dimensionless criteria are derived for evaluating the significance of interphase and interparticle temperature gradients in fixed bed catalytic reactors. Comparison of the criteria reveals that the magnitudes of the heat transport resistances are generally in the order: interparticle > interphase > intraparticle. The criteria show the critical importance of decreasing the diameters of the reactor and the catalyst particles to minimize transport limitations. Dilution of the bed with inert solids is shown to be advantageous only at Reynolds numbers sufficiently low that the effective thermal conductivity of the bed is insensitive to the flow rate.

INTRODUCTION

Rate data for heterogeneous catalytic reactions are frequently impaired by the occurrence of temperature gradients which seriously disguise the intrinsic kinetics or selectivities. In experimental fixed bed reactors with heat exchange at the wall, these gradients can occur in three domains: (i) intraparticle *within* a porous catalyst particle; (ii) interphase *between* the external surface of the particle and the fluid adjacent to it; and (iii) interparticle *between* the local fluid regions and the wall. The intrusion of gradients can cause severe deviations from the ideal isothermal performance upon which simple kinetic interpretations are based. Consequently, the experimenter requires criteria to determine whether heat transport limitations in any domain are significantly altering his results.

Anderson (*1*) derived such a criterion for the absence of significant temperature gradients within a catalyst particle. If the deviation of the observed rate $\mathcal{R}$ (per unit particle volume) from the isothermal rate is to be less than 5%, his criterion requires:

$$\frac{q\mathcal{R}(r_p)^2}{\lambda T_0} < 0.75\,\frac{RT_0}{E}, \qquad (1)$$

where q is the absolute value of the heat of reaction, λ is the thermal conductivity of the particle, r_p is its radius, E is the true activation energy, R is the gas constant, and T_0 is the absolute temperature. The object of this paper is to derive analogous criteria for the interphase and interparticle domains.

NOMENCLATURE

A	pre-exponential factor in Arrhenius expression (sec^{-1} for first-order reaction)
b	dilution ratio (ml inert/ml catalyst)
B	parameter, $= \delta(\exp\lvert\theta_{\max}\rvert)/8$
$(\text{Biot})_i$	thermal Biot number $= hd_p/\lambda$
$(\text{Biot})_w$	thermal Biot number at the wall $= h_w d_p/k_e$
d_p	diameter of catalyst particle (cm)
E	activation energy for catalytic reaction (g-cal/g-mole)
$f(c)$	function of concentration
G	mass velocity (g/sec cm^2 of total or superficial bed cross-section)
h	gas–solid heat transfer coefficient (g-cal/sec cm^2 °C)
h_w	heat transfer coefficient at the wall (g-cal/sec cm^2 °C)
ΔH	heat of chemical reaction (g-cal/g-mole)
k	intrinsic rate constant per unit

	volume of particle ($\sec^{-1}$ for first-order reaction)
k_e	effective thermal conductivity across bed (g-cal/sec cm °C)
q	absolute value of heat of reaction (g-cal/g-mole)
r	radial coordinate in tubular reactor (cm)
r_p	particle radius (cm)
R	gas constant (g-cal/g-mole °K)
Re	Reynolds number, $= Gd_p/\mu$
R_0	radius of tubular reactor (cm)
$\mathcal{R}$	reaction rate per unit particle volume (g-mole/sec cm^3)
$\mathcal{R}'$	reaction rate per unit bed volume (g-mole/sec cm^3), $= \mathcal{R}(1 - \epsilon)/(1 - b)$
T	absolute temperature (°K)
T_0	temperature of bulk fluid adjacent to a particle (°K)
T_w	temperature of wall (°K)
u	dimensionless radius of reactor, $= r/R_0$
δ	dimensionless parameter defined by Eq. (11b)
ϵ	void fraction in reactor bed
λ	effective thermal conductivity of particle (g-cal/sec cm °C)
μ	viscosity (g/sec cm)
θ	dimensionless temperature, $= (T - T_w)E/RT_w^2$

Discussion

Interphase Transport

For the gas–solid catalyst system, Fulton and Crosser (*7*) experimentally demonstrated that the heat transfer resistance of the boundary layers or "film" adjacent to the particle can be much larger than the resistance within the particle. Consequently, the catalyst particle can often be treated as isothermal at a temperature dictated by heat transfer in the boundary layers (*2, 3*). In the case of a highly exothermic reaction, the particle temperature may then be considerably greater than that of the bulk stream. In contrast, the principal mass transfer resistance occurs within the catalyst particle, so that the external concentration gradient is usually negligible.

A criterion for detecting the onset of an interphase heat transport limitation will now be derived by the perturbation approach (*1*). Assume that the rate of reaction depends on temperature in the Arrhenius fashion:

$$\mathcal{R} = Ae^{-E/RT}f(c), \tag{2}$$

where A is a pre-exponential or frequency factor and $f(c)$ is a function of concentration. Then the rate at any temperature T close to T_0, the temperature of the adjacent bulk fluid, is given by a Taylor expansion of Eq. (2) about T_0 with terms higher than the first neglected:

$$\mathcal{R} = \mathcal{R}_0\left[1 + \frac{T - T_0}{T_0}\cdot\frac{E}{RT_0}\right]. \tag{3}$$

where $\mathcal{R}_0$ is the rate which would prevail if the particle temperature were at T_0.

An energy balance for a spherical catalyst particle gives:

$$q\mathcal{R}\frac{4\pi}{3}(r_p)^3 = h(T - T_0)4\pi(r_p)^2, \tag{4}$$

where h is the heat transfer coefficient from fluid to catalyst particle. Heat conduction to adjacent touching particles is assumed negligible. Simplifying and combining Eq. (4) with Eq. (3) yields:

$$\frac{\mathcal{R}}{\mathcal{R}_0} = 1 + \frac{q\mathcal{R}r_pE}{3hT_0^2R}. \tag{5}$$

In order for the rate $\mathcal{R}$ not to deviate from $\mathcal{R}_0$ by more than an acceptable amount, say 5%, the second term on the right must be less than 0.05. The resulting dimensionless criterion,

$$\frac{q\mathcal{R}r_p}{hT_0} < 0.15\frac{RT_0}{E}, \tag{6}$$

is valid whether diffusional limitations exist in the particle or not.

Note that the criterion is similar in form to Eq. (1), with h replacing λ/r_p. Comparison shows that the interphase heat transfer resistance becomes limiting before the intraparticle heat transfer resistance providing:

$$(\mathrm{Biot})_i = \frac{hd_p}{\lambda} < 10, \tag{7}$$

a condition which is usually met in laboratory reactors. Thus, interphase heat transport limitations can be expected for fast reactions with high heats of reaction at low Reynolds numbers (low h).

As an example, consider a study of the vapor-phase dehydrogenation of cyclohexane at 700°K and 30 atm over a platinum–alumina catalyst of 0.2-cm diameter. For these conditions, reaction rates of the order of 1×10^{-4} g-mole/sec ml catalyst are typical. The endothermic heat of reaction is 52 kcal/mole and a slightly higher activation energy of 60 kcal/mole is assumed. For a gas mixture with 6 moles of hydrogen/mole of cyclohexane, the heat capacity is about 1.07 cal/g °C and the Prandtl number about 0.33. For a Reynolds number of 25 and mass velocity of 81 g/hr cm^2 (166 lb/hr ft^2), the correlation of De Acetis and Thodos (*5*) gives a heat transfer coefficient of 0.025 cal/sec cm^2 °C. A value of 0.03 results for the term on the left of the criterion, which considerably exceeds the value of 0.0034 for the term on the right. Consequently, the heat transfer resistance of the film is significantly influencing the experimental results.

Interparticle Transport

When a fixed bed is operated as an integral reactor, radial and axial temperature gradients often cause severe deviations from the desired isothermal, plug-flow operation. A complete mathematical description of the problem involves coupled partial differential equations. Numerical solutions (*3*, *6*) yield radial temperature profiles which are approximately parabolic. The fluid temperature along the axis rises to a maximum at the "hot spot" before gradually returning to T_w, the wall temperature. Carberry and White's study (*3*) showed that the yields obtained are quite sensitive to radial heat transport, but virtually insensitive to radial mass transport.

An approximate criterion for determining the existence of a radial interparticle heat transport limitation will now be derived. For beds with length-to-pellet diameter ratios sufficiently great that plug flow occurs, axial conduction can be neglected (*3*). At the hot spot, the sensible heat term can also be omitted from the conservation equation for energy, which simplifies to:

$$k_e\left(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr}\right) = (-\Delta\mathrm{H})\,\frac{(1-\epsilon)}{(1+b)}\,\mathcal{R} = (-\Delta\mathrm{H})\mathcal{R}' \qquad (8)$$

in which k_e is the effective thermal conductivity of the bed given in correlations (*9*, *10*), ϵ is the void fraction, and b is the dilution ratio (inert/catalyst). The latter two quantities are introduced to convert the reaction rate per pellet to $\mathcal{R}'$, the local rate per unit bed volume. It will also be assumed, subject to checking, that intraphase and interphase transport limitations are negligible at the onset of the interparticle limitation.

Chambre and Grossman (*4*) derived an analytic solution to Eq. (8) for the radial temperature profiles:

$$\theta - \theta_{\max} = -2\ln(Bu^2 + 1) \qquad (9)$$

where the dimensionless temperature and radius are defined:

$$\theta = \frac{E(T - T_w)}{RT_w^{\,2}} \qquad (10a)$$

$$u = \frac{r}{R_0} \qquad (10b)$$

and R_0 is the radius of the reactor. The parameters of the solution are given by:

$$B = \frac{\delta}{8}\exp|\theta_{\max}|, \qquad (11a)$$

$$\delta = \frac{(-\Delta H)\mathcal{R}'_w R_0^{\,2} E}{k_e T_w^{\,2} R}, \qquad (11b)$$

where $\theta_{\max}$ is the maximum dimensionless temperature at the hot spot (cold spot if endothermic) and $\mathcal{R}'_w$ is the local reaction rate evaluated at the wall temperature. By utilizing an assumed boundary condition at the wall:

$$u = 1 : \theta = 0, \qquad (12)$$

they obtained a relation between $\theta_{\max}$ and δ:

$$\delta = 8[\exp(-\,0.5|\theta_{\max}|) - \exp(-\,|\theta_{\max}|)]. \qquad (13)$$

For the case of interest here, δ, and hence B, are small when the radial temperature gradient is just starting to become significant. Consequently, the natural log term of Eq. (9) can be expanded so that the equation reduces to a parabola:

$$\theta - \theta_{\max} = -2B\,u^2. \tag{14}$$

Adopting boundary condition (12) and expanding the exponential, an expression for $\theta_{\max}$ is obtained:

$$\theta_{\max} = \frac{\delta/4}{1 - \delta/4} \approx \delta/4. \tag{15}$$

As expected, Eq. (13) also reduces to $\delta/4$ for small δ.

In small laboratory reactors, the heat transfer resistance at the wall usually cannot be neglected. The appropriate boundary condition to replace Eq. (12) is:

$$k_e \left.\frac{dT}{dr}\right|_{r=R_0} = h_w(T - T_w)|_{r=R_0}, \tag{16}$$

in which h_w is the heat transfer coefficient at the wall given by correlation (9). In dimensionless terms Eq. (16) becomes:

$$\left.\frac{d\theta}{du}\right|_{u=1} = \frac{h_w R_0}{k_e} \cdot \theta_{u=1} = \frac{(\mathrm{Biot})_w}{2} \cdot \frac{R_0}{r_p} \cdot \theta_{u=1}, \tag{17}$$

where the Biot number at the wall:

$$(\mathrm{Biot})_w = \frac{h_w d_p}{k_e}. \tag{18}$$

expresses the ratio of thermal transport at the reactor wall to that in the core of the bed. Using condition (17), one obtains:

$$\begin{aligned}\theta_{\max} &= \frac{\delta}{4}\left[1 + \frac{4k_e}{R_0 h_w}\right] \\ &= \frac{\delta}{4}\left[1 + \frac{8}{(\mathrm{Biot})_w} \cdot \frac{r_p}{R_0}\right]\end{aligned} \tag{19}$$

which reduces to $\delta/4$ when the wall heat transfer resistance is small ($r_p/R_0 \ll 1$). For endothermic reactions, $\theta_{\max}$ is negative because δ is negative, but Eq. (14) still applies.

The effect of the radial temperature gradient on the reaction rate can now be determined by substituting Eqs. (10a) and (14) into (3) and integrating across the cross-section:

$$\pi(1)^2\bar{\mathcal{R}}' = \mathcal{R}_w \int_0^1 (1 + \theta_{\max} - 2Bu^2)2\pi\, u\,du. \tag{20}$$

There results:

$$\frac{\bar{\mathcal{R}}'}{\mathcal{R}'_w} = 1 + \theta_{\max} - B, \tag{21}$$

where $\bar{\mathcal{R}}'$ is the average reaction rate at the cross-section of the hot spot. For quasi-isothermal behavior across the bed, $\bar{\mathcal{R}}'$ must not deviate from $\mathcal{R}'_w$ by more than an acceptable 5%. Hence:

$$[\theta_{\max} - B] < 0.05. \tag{22}$$

When the heat transfer resistance at the wall is negligible (i.e., $R_0/r_p > 100$), substitution of Eqs. (11a) and (15) into (22) yields the dimensionless criterion:

$$\frac{q\bar{\mathcal{R}}' R_0^2}{k_e T_w} < 0.4\,\frac{RT_w}{E}. \tag{23}$$

Note that the functional form is similar to Eq. (1), with the reactor radius replacing the particle radius, and the effective thermal conductivity of the bed replacing that of the particle. Since $R_0 \gg r_p$ and k_e approaches the order of magnitude of λ at low Reynolds numbers, the interparticle transport problem is usually much more severe than the intraparticle one.

Comparison with the interphase criterion shows that the interparticle resistance becomes limiting first unless:

$$\frac{(1 - \epsilon)}{(1 + b)}\left(\frac{hd_p}{k_e}\right)\left(\frac{R_0}{r_p}\right) < 5.3. \tag{24}$$

This condition is achieved only for low values of (R_0/r_p) or high dilution ratio b. Once the interparticle criterion is violated, the interphase heat transfer resistance will eventually become limiting also.

When the heat transfer resistance at the wall is significant, the interparticle criterion becomes:

$$\frac{q\bar{\mathcal{R}}' R_0^2}{k_e T_w} < \frac{0.4RT_w/E}{[1 + 8r_p/R_0(\mathrm{Biot})_w]}. \tag{25}$$

The data of Yagi and Kunii (*9*) yield wall

Biot numbers of 0.8 to 2 for Re < 100 and $0.05 < r_p/R_0 < 0.2$, so the denominator becomes of the order of 2. Thus heat transfer resistance at the wall aggravates the interparticle transport problem in small laboratory reactors.

Consider the previous example of cyclohexane dehydrogenation, now performed in a 1-cm i.d. reactor with an undiluted bed of 0.4 void fraction. The thermal conductivity of the gas mixture is estimated to be 5×10^{-4} cal/sec cm °C. The correlations of Yagi and Kunii (*9*) yield an effective bed conductivity of 5×10^{-3} cal/sec cm °C and a wall Biot number of 2. A value of 0.2 results for the left side of the criterion, considerably exceeding the value of 0.005 for the right. Hence, significant radial interparticle heat transport limitations are indicated for this case.

CONCLUSIONS

Simple criteria provide a means for evaluating the significance of interparticle, interphase, and intraparticle heat transport limitations, and for assessing the best ways to minimize them. Reducing the reactor radius is particularly important because the interparticle criterion depends explicitly on R_0^2 and because the mass velocity is inversely proportional to R_0^2 at constant mass flow. While h and k_e depend only weakly on mass velocity at low Reynolds numbers, they become proportional to about the 0.6 and 1.0 powers, respectively, of the mass velocity at Re > 100. Consequently, the interparticle criterion becomes effectively proportional to the fourth power of R_0 and the interphase criterion to the 1.2 power at higher Reynolds numbers. Decreasing the reactor radius is therefore a critical step in minimizing both transport resistances.

Dilution of the bed with inert particles, reducing the rate per unit volume, is often used to minimize the interparticle transport problem. However, in diluting the bed, the mass velocity is reduced proportionately. The interparticle criterion shows that dilution will be advantageous in minimizing radial gradients only if the reactor is operating at Reynolds numbers sufficiently low that k_e is relatively insensitive to the mass velocity (i.e., Re < 100). It should also be noted that bypassing and residence time effects can intervene if a dilution criterion is exceeded (*8*).

Finally, changing to smaller particles reduces both the interphase and intraparticle heat transport resistances, as well as the corresponding mass transfer resistances. Should these steps prove inadequate, the reaction rate can be lowered by changing process conditions or by operating the reactor differentially.

REFERENCES

1. ANDERSON, J. B., *Chem. Eng. Sci.* **18**, 147 (1963).

2. CARBERRY, J. J., *Ind. Eng. Chem.* **58**(10), 40 (1966).

3. CARBERRY, J. J., AND WHITE, D., *Ind. Eng. Chem.* **61**(7), 27 (1969).

4. CHAMBRE, P. L., AND GROSSMAN, L. M., *Appl. Sci. Res. Sect. A* **5**, 245 (1955).

5. DE ACETIS, J., AND THODOS, G., *Ind. Eng. Chem.* **52**(12), 1003 (1960).

6. FROMENT, G. F., *Ind. Eng. Chem.* **59**(2), 19 (1967).

7. FULTON, J. W., AND CROSSER, O. K., *AIChE J.* **11**, 513 (1965).

8. VAN DEN BLECK, C. M., VAN DEN WIELE, K., AND VAN DEN BERG, P., *Chem. Eng. Sci.* **24**, 681 (1969).

9. YAGI, S., AND KUNII, D., *AIChE J.* **6**, 97 (1960).

10. YAGI, S., AND WAKAO, N., *AIChE J.* **5**, 79 (1959).