NOMENCLATURE

A^+ = coefficient in Van Driest mixing length formula ($A^+ = 26$ for zero drag reduction)
b_1, b_2 = geometric coefficients given by Eqs. 5 and 6
C_p = heat capacity at constant pressure, kcal/kg · °C
C_1, C_2, C_3 = constants defined by Eqs. 10-12
C_4 = constant taken to be 7
D_{AB} = molecular diffusivity, m^2/s
D_1, D_2, D_3 = constants defined by Eqs. 14-16
DR = drag reduction = $(f_o - f)/f_o$
DR_m = maximum value of DR
f = friction factor
f_o = friction factor for zero drag reduction
$G(y^+)$ = function defined by Eq. 4
h = heat transfer coefficient, kcal/m^2 · °C
k = constant in mixing length expression, Eq. 1
k_c = mass transfer coefficient, m/s
K_3, K_4, K_5 = coefficients in eddy diffusivity expression, Eq. 7
l = mixing length, m
l^+ = dimensionless mixing length = $\dfrac{lu^*}{\nu}$
M_4, M_5, M_6 = coefficients in eddy diffusivity expression, Eq. 8
$O(\ )$ = order symbol, $A = 0(\sigma^a) \rightarrow A \propto \sigma^a$, for $\sigma \rightarrow \infty$
Pr = Prandtl number = α/ν
R = tube radius, m
R^+ = dimensionless tube radius = $\dfrac{Ru^*}{\nu}$
Re = Reynolds number = $2\dfrac{Ru_b}{\nu}$
Sc = Schmidt number = $\dfrac{D_{AB}}{\nu}$
St = Stanton number = $\dfrac{k_c}{U_b}$, for mass transfer
Stanton number = $\dfrac{h}{pC_pU_b}$, for heat transfer
u = velocity, m/s
u_b = bulk velocity, m/s
u_c = centerline velocity, m/s
u^+ = dimensionless velocity = $\dfrac{u^+}{u^*}$
u^* = friction velocity = $u_b\sqrt{f/2}$, m/s
y = distance from the tube wall, m
y^+ = dimensionless distance from tube wall = yu^*/ν
z^+ = dummy variable for y^+
α = thermal diffusivity, m^2/s
ϵ = eddy diffusivity, m^2/s
ϵ^+ = dimensionless eddy diffusivity = ϵ/ν
ν = kinematic viscosity, m^2/s
σ = Prandtl or Schmidt number
ρ = density, kg/m^3

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Optimum Pore Size for the Catalytic Conversion of Large Molecules

E. RUCKENSTEIN and M. C. TSAI

State University of New York at Buffalo
Department of Chemical Engineering
Amherst, New York 14260

INTRODUCTION

The hydrodesulfurization of heavy petroleum residua and coal-derived liquids involves the intraparticle mass transport of large molecules inside a catalyst of cobalt-molybdate supported on alumina. The sizes of molecules in these heavy feedstocks (with molecular weight between 10^2 and 10^5) range between 25 and 150Å, the largest fraction being around 50Å (Tschamler and

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DeRuiter, 1963; Ohtsuka, 1977). The average pore size of typical catalysts used for hydrotreating residua also falls in this range (Schuit and Gates, 1973).

Since the diameter of the reactant molecules is comparable to the diameter of the catalyst pores, the ratio λ between the molecule diameter and the average pore diameter affects the partitioning of the molecules between the bulk liquid and the pellet at the interface of the pellet, as well as the diffusion of the molecules in the pores. Fewer molecules are partitioned in the pellet (when their adsorption on the surface of the pores is not too important) and their diffusion coefficient decreases with increasing λ. However, for constant free volume and constant amount of cobalt-molybdate per unit area of support, the reaction rate increases with decreasing pore diameter because the area of the reacting surface increases. The two opposing effects mentioned above result in the existence of an optimum pore size. The goal of this note is to provide some analysis and discussion regarding the occurrence of an optimum pore size in the hydrodesulfurization of petroleum feedstocks.

The available experimental data show that such an optimum pore size does indeed exist. Beuther and Schmid (1963) performed numerous tests with active desulfurization catalysts on various supports and obtained the following empirical expression for the initial desulfurization activity:

$$\text{Desulfurization (wt\%)} = K + 13.2V_p + 0.0589S_g + 0.006d_p \tag{1}$$

where K is a constant depending on reaction conditions, S_g is the internal surface area per gram of the supported catalyst (m^2/g), V_p is the pore volume (cm^3/g), and d_p is the average pore diameter (Å). Since $S_g = 4 \times 10^4\, V_p/d_p$, Eq. (1) becomes

$$\text{Desulfurization} = K + 13.2V_p + 2356V_p/d_p + 0.006d_p \tag{2}$$

One can observe that, at constant V_p, Eq. (2) provides an optimum pore size given by the expression

$$d_p = \left(\frac{2356V_p}{0.006}\right)^{1/2} \tag{3}$$

More recently, Inoguchi (1976) observed that catalysts with pore sizes around 100Å have higher activity for the hydrodesulfurization of heavy residua, and that Vanadium removal is maximized when the pore sizes range between 120 and 140Å. Eigenson et al. (1977) reported that a shift of the average pore diameter from 70Å to 150Å has increased the activity of MoO_3 supported on alumina in spite of a lower loading used for the larger pore diameter.

For coal liquefaction, Yen, Furlani and Weller (1976) reported that a cobalt-molybdate supported on alumina catalyst with pore diameter of 220Å performs better than a catalyst with pore diameter of 120Å, even though the former had a lower surface area. Brooks et al. (1976) also found that cobalt-molybdates on alumina with pore sizes between 100 and 200Å are the best catalysts for coal liquefaction.

FORMULATION OF THE EQUATIONS

Consider first an isothermal catalyst pellet in which the reaction occurs without external and internal diffusional limitations. A pseudo-homogeneous rate expression, written for a first order irreversible reaction has the form:

$$r = V_e\rho_p S_g k_s C_p \left(\frac{\text{moles}}{\text{sec}}\right) \tag{4}$$

where the concentration inside the pores equals the concentration, C_p, at the pore mouth. The concentration C_p can be related to the bulk concentration C_b outside the pellet by the equilibrium expression $K_p = C_p/C_b$, where K_p is the partition coefficient.

To account for the internal diffusion, the effectiveness factor η is introduced; hence the rate equation (4) becomes

$$r = V_e\rho_p S_g k_s (K_p C_b)\,\eta \tag{5}$$

The effectiveness factor η is a function of the Thiele modulus ϕ (Petersen, 1965). For a first order irreversible reaction, ϕ is defined as follows for both cylindrical and spherical pellets:

$$\phi = \frac{V_e}{A_e}\left(\frac{\rho_p S_g k_s}{D_{eff}}\right)^{1/2} \tag{6}$$

To simplify the analysis, the following approximate relations are employed for η:

(1) In the range, $\phi > 3$ or $\eta < 0.3$, the following relation is valid (Petersen, 1965):

$$\eta \simeq \phi^{-1} \tag{7}$$

(2) In the range, $\phi < 0.5$: $\eta \simeq 1$

(3) In the intermediate range, $0.5 < \phi < 3$ or $0.9 > \eta > 0.3$, η is approximated by

$$\eta \simeq 0.64\,\phi^{-0.59} \tag{8}$$

Table 1 compares the approximate values of η with the exact values calculated from the well known equations. The maximum error is about 10%, which is of the order of the usual experimental error.

Now consider the diffusion of large molecules through pores of comparable size. The effective diffusion coefficient D_{eff} depends upon the ratio λ between the diameter of the molecule, d_s, and the average diameter of the pore, d_p, as well as upon the equilibrium partition coefficient K_p, and is generally given by expressions of the form (Satterfield and Colton et al., 1973, 1975; Prasher and Ma, 1977, 1978):

$$D_{eff} = \frac{D_b}{\tau} f(\lambda, K_p) \tag{9}$$

The available empirical correlation has the form (Satterfield et al., 1973)

$$D_{eff} = \frac{D_b}{\tau}\,10^{-2\lambda} \quad \text{for } K_p = 1,\ \lambda \text{ from } 0.09 \text{ to } 0.51 \tag{10a}$$

$$D_{eff} = \frac{D_b}{\tau}\,\frac{10^{-2\lambda}}{1.7} \quad \text{for } K_p \sim 4,\ \lambda \text{ from } 0.20 \text{ to } 0.30 \tag{10b}$$

In addition, theoretical equations have also been suggested. For instance, Lane (1950) and Renkin (1953) derived the following equation

$$D_{eff} = \frac{D_b}{\tau}(1-\lambda)^2(1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5)$$

$$\text{with } K_p = (1-\lambda)^2 \tag{11}$$

When $K_p < 1$ (Eq. 11), the molecules of reactant encounter some exclusion at the pore mouth, while, when $K_p = 1$ (Eq. 10a), the molecules enter the pore mouth without any hindrance. Finally, the case $K_p > 1$ (Eq. 10b) implies adsorption of the molecules on the surface of the pores.

SOLUTION FOR OPTIMUM PORE SIZE

One can now compute an optimum pore size by choosing the appropriate expressions for the effectiveness factor η and the effective diffusion coefficient D_{eff}.

For the hydrodesulfurization of heavy petroleum residua, the reported effectiveness factors are between 0.3 and 0.9 (Adlington and Thompson, 1965; Van Deemter, 1965; Cecil et al., 1968); therefore, Eq. (8) is applicable to this case. Further, Eq. (10a) is chosen for D_{eff} and a first-order isothermal reaction is

TABLE 1. COMPARISON BETWEEN THE EXACT AND APPROXIMATE EQUATIONS FOR THE EFFECTIVENESS FACTOR

ϕ	Long Cylindrical Pellet $\eta = \frac{1}{\phi}\frac{I_1(2\phi)}{I_0(2\phi)}$	Spherical Pellet $\eta = \frac{1}{\phi}\left[\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right]$	Approximate Relations
0.4	0.93	0.92	1
0.5	0.89	0.88	0.96
0.6	0.86	0.83	0.87
0.7	0.82	0.79	0.79
0.8	0.77	0.75	0.73
0.9	0.74	0.71	0.68
1.0	0.70	0.67	0.64
1.5	0.54	0.52	0.50
2.0	0.43	0.42	0.43
2.5	0.36	0.35	0.37
3.0	0.30	0.30	0.33

assumed. For cylindrical pores, the specific surface area and pore volume are related by:

$$S_g = 4V_p/d_p, \text{ where } d_p \text{ is the pore diameter.}$$

Hence,

$$\rho_p S_g k_s = \frac{4V_p W k_s}{V_e d_s}\lambda \equiv \alpha\lambda \tag{12}$$

Substituting Eqs. (8), (10a), and (12) into Eq. (5), one obtains:

$$r = V_e\lambda\left(\frac{\lambda}{10^{-2\lambda}}\right)^{-\frac{0.59}{2}}(0.64\alpha C_b)\left(\frac{V_e}{A_e}\right)^{-0.59}\left(\frac{\tau\alpha}{D_b}\right)^{-\frac{0.59}{2}} \tag{13}$$

which is valid for both spherical and cylindrical pellets. Taking the derivative of Eq. (13) with respect to λ, one obtains for the optimum pore size the simple equation:

$$\lambda_{opt} = 0.52 \tag{14}$$

Similarly, by using Eq. (11) for D_{eff}, one obtains the result:

$$\lambda_{opt} = 0.18 \tag{15}$$

In the first case (Eq. (14)), the partition coefficient is equal to unity and the molecules have no difficulty to enter the pore mouth. Prasher and Ma (1977, 1978), measuring the partition coefficients and the pore diffusion coefficients in alumina for molecules frequently encountered in hydrodesulfurization, conclude that $K_p \approx 1$. In the latter case (Eq. (15)), the partition coefficient K_p is smaller than unity, the molecules enter the pore mouth with difficulty, and therefore the optimum pore size is larger than in the former case.

The molecules of the petroleum residua are about 50Å in diameter; hence the optimum pore diameter is of the order of 100Å, a value comparable to that found experimentally. More refined calculations which account for a distribution of pore diameters could also be carried out.

NOTATION

A_e = external surface area of a pellet
C_b = bulk concentration
C_p = concentration at the pore mouth
D_b = bulk diffusivity
D_{eff} = effective diffusion coefficient
d_p = average pore diameter
d_s = molecule diameter
f = function of λ and K_p in Eq. (9)
I_0, I_1 = modified Bessel functions of order 0 and 1
K_p = C_p/C_b, equilibrium partition coefficient
k_s = surface based reaction rate constant
R = radius of the spherical pellet
r = reaction rate per pellet volume
S_g = internal surface area per gram of catalyst pellet
V_p = pore volume per gram of catalyst pellet
V_e = volume of catalyst pellet
W = weight of catalyst pellet

Greek Letters

α = constant in Eq. (12)
η = effectiveness factor
λ = d_s/d_p
ρ_p = bulk density of pellet
τ = tortuosity factor
ϕ = Thiele modulus defined by Eq. (6)

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