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Effectiveness Factors of Ink-Bottle Type Catalyst Pores

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The effectiveness factors of two types of ink-bottle type catalyst pores have been studied with a two-dimensional model assuming a heterogeneous chemical reaction. For the Type 1 ink bottle, which is a sphere with a small aperture, the effectiveness factor is greater than that of a cylindrical pore with the same internal surface. For the Type 2 ink bottle, which is a cylinder with a small aperture, the effectiveness factor is smaller than that of an ordinary cylindrical pore without a narrow neck. In both cases the effectiveness factor decreases appreciably as the aperture size is reduced.

The occurrence of ink-bottle type pores in porous systems was first suggested by Kraemer (*4*). These pores are so named because they consist of wide bodies fitted with narrow necks. According to Broekhoff and De Boer (*1*), there are in general two types of ink-bottle type pores. One type is essentially spheroidal and another essentially cylindrical. Since these pores are different from the pores ordinarily visualized to exist in catalyst pellets, it is of interest to know how mass transfer interacts with chemical reaction kinetics in cases where catalyst pellets contain ink-bottle type pores. This work therefore studies the effectiveness factors of the two known types of ink bottles.

The effectiveness factor of single catalyst pores was studied by Thiele (*5*). The pores considered by him are open at both ends and are uniform in cross section. In that case, when the longitudinal dimension of the pore is much longer than the transverse dimension, it is permissible to employ a one-dimensional model assuming a pseudo-homogeneous chemical reaction. In the case of ink-bottle type pores such an approach is inadequate. A two-dimensional model is, therefore, used in this work and a heterogeneous chemical reaction is assumed. Since the main purpose of this work is to study the effect of the geometrical shape of the pore on the effectiveness factor, simplifying assumptions are employed in many other aspects. These assumptions are:

1. First-order irreversible reaction takes place at the inner surface of the pore.
2. Ordinary diffusion rather than Knudsen diffusion prevails. In other words, the lowest dimension of the pore is greater than the mean free path of the molecules.
3. No forced flow.
4. No volume change during the reaction.
5. Constant temperature.

TYPE 1 INK BOTTLE, SPHERICAL

Consider a sphere of radius R which has a circular aperture with polar angle $\theta \leq \theta_1$. The equation of continuity for component A in a reactive gas mixture is

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_A}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin \quad \frac{\partial C_A}{\partial\theta}\right) = 0. \quad (1)$$

The boundary conditions are

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$$\begin{array}{llll} \text{B.C. 1} & \text{At } r = 0 & C_A = \text{finite}, & \\ \text{B.C. 2} & \text{At } r = R & 0 \leq \theta \leq \theta_1 & C_A = C_{A_0}, \\ & & \theta_1 < \theta \leq \pi & -D\dfrac{\partial C_A}{\partial r} = kC_A. \end{array} \tag{2}$$

If we let $\rho = (r/R)$, $\gamma = \dfrac{C_A}{C_{A_0}}$ and $q = (kR/D)$, the above equation and boundary conditions become

$$\frac{\partial}{\partial \rho}\left(\rho^2 \frac{\partial \gamma}{\partial \rho}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \gamma}{\partial \theta}\right) = 0. \tag{3}$$

$$\begin{array}{llll} \text{B.C. 1} & \text{At } \rho = 0 & \gamma = \text{finite}, & \\ \text{B.C. 2} & \text{At } \rho = 1 & 0 \leq \theta \leq \theta_1 & \gamma = 1, \\ & & \theta_1 < \theta \leq \pi & \dfrac{\partial \gamma}{\partial \rho} = -q\gamma. \end{array} \tag{4}$$

Solving Eq. (3) by the method of separation of variables and using B.C. 1, we obtain

$$\gamma = \sum_{n=0}^{\infty} A_n \rho^n P_n(\mu), \tag{5}$$

where $\mu = \cos\theta$, $P_n(\mu)$ = Legendre function of μ and A_n = coefficients to be evaluated presently.

B.C. 2 can be rewritten as

$$\begin{array}{lll} \text{B.C. 2} & 1 \geq \mu \geq \cos\theta_1 & \gamma|_{\rho=1} = 1, \\ & \cos\theta_1 > \mu \geq -1 & \gamma|_{\rho=1} = -\dfrac{1}{q}\dfrac{\partial \gamma}{\partial \rho}\Big|_{\rho=1}. \end{array} \tag{6}$$

Multiplying $\gamma|_{\rho=1}$ by $P_m(\mu)$ and integrating the product between 1 and -1 give

$$\int_1^{-1} \gamma\Big|_{\rho=1} P_m(\mu)\, d\mu = \int_1^{\cos\theta_1} P_m(\mu)\, d\mu - \frac{1}{q}\int_{\cos\theta_1}^{-1} \frac{\partial \gamma}{\partial \rho}\Big|_{\rho=1} P_m(\mu)\, d\mu.$$

Since

$$\gamma|_{\rho=1} = \sum_{n=0}^{\infty} A_n P_n(\mu),$$

$$\frac{\partial \gamma}{\partial \rho}\Big|_{\rho=1} = \sum_{n=0}^{\infty} A_n n P_n(\mu),$$

and, by Carslaw and Jaeger (*2* b),

$$\int_1^{-1} P_n(\mu) P_m(\mu)\, d\mu = -\frac{2}{2m+1}\delta_{mn},$$

we obtain a set of simultaneous equations from which A_n, $n = 0, 1, \ldots \infty$, can be determined:

$$\sum_{n=0}^{\infty} A_n \left(n \int_{\cos\theta_1}^{-1} P_n(\mu) P_m(\mu)\, d\mu - \frac{2q}{2m+1}\delta_{mn}\right) = q\int_1^{\cos\theta_1} P_m(\mu)\, d\tau,$$
$$m = 0, 1, \ldots \infty \tag{7}$$

The effectiveness factor, η, is defined as

$$\eta = \frac{r_1}{r_2}$$

where r_1 = the actual rate of reaction and r_2 = the rate of reaction if the interior surface of the pore were equally available for the reaction. Thus,

$$r_1 = 2\pi R^2 \int_0^{\theta_1} \left(-D\frac{\partial C_A}{\partial r}\right)\Big|_{r=R} \sin\theta\, d\theta$$
$$= -2\pi RDC_{A_0} \sum_{n=1}^{\infty} A_n n \int_1^{\cos\theta_1} P_n(\mu)\, d\mu,$$

and

$$r_2 = kC_{A_0}\left(4\pi R^2 - 2\pi R^2 \int_0^{\theta_1} \sin\theta\, d\theta\right)$$
$$= 2\pi R^2 k C_{A_0}(1 + \cos\theta_1)$$

Hence,

$$\eta = \frac{1}{q(1+\cos\theta_1)} \sum_{n=1}^{\infty} nA_n \int_{\cos\theta_1}^{1} P_n(\mu)\, d\mu. \tag{8}$$

The computation of the effectiveness factors was done on an IBM 360/75 computer. In the determination of the coefficients A_n, integration was done by a 24-point Gaussian quadrature and the set of Eqs. (7) was solved by the Gaussian elimination method, both procedures being in double precision. As shown above, Eqs. (7) involve $n \times m$ matrix where both n and m approach infinity. In actual computation, a 2×2 matrix is first employed and, after determination of A_n, $n = 1$ to 2, the effectiveness factor is computed. The matrix size is then expanded to 3×3 and another effectiveness factor is computed. If these two consecutive values of effectiveness factors agree within 0.001 of their values, the last computed value is taken as the effectiveness factor being sought. Otherwise, the matrix size is expanded to 4×4 and so on until the last pair of consecutive effectiveness factors match within the preassigned tolerance stated above. The matrix size necessary to obtain a final answer was found to increase as the aperture size decreased. For example, when $q = 0.005$, a 35×35 matrix was needed when $\theta_1 = 5°$ whereas a 48×48 matrix was necessary when $\theta_1 = 1°$.

The effect of aperture size (represented by the polar angle θ_1) on the effectiveness factor is plotted in Fig. 1 at three levels of q. The effectiveness factor decreases sharply as the aperture size decreases. The reduction of the effectiveness factor is more remarkable when q is high (that is, when the radius R of the sphere is large, the reaction velocity constant k is high or the diffusivity D is low).

In an attempt to compare these results with the effectiveness factor of the ordinary pore, we define an area-equivalent cylindrical pore. The area-equivalent cylindrical pore has an open-end base area equal to the aperture area of the spherical ink bottle and the remaining surface area (the lateral surface plus the closed-end base area) equal to the wall surface of the spherical ink bottle. The radius of this equivalent cylinder is

$$R' = R[2(1 - \cos\theta_1)]^{1/2}$$

and its length is

$$L = \frac{2R\cos\theta_1}{[2(1 - \cos\theta_1)]^{1/2}}$$

Hence the Thiele modulus of this equivalent cylinder is

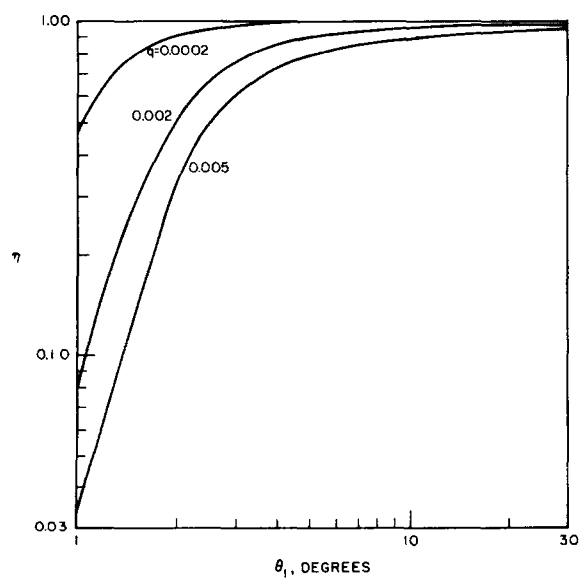

FIG. 1. Effect of aperture size (polar angle θ_1) on effectiveness factor η; Type 1 ink bottle.

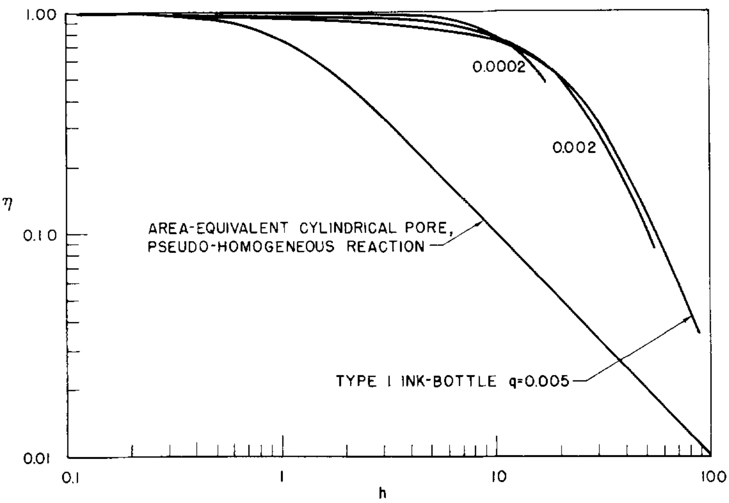

FIG. 2. Comparison between Type 1 ink bottle and its area-equivalent cylindrical pore.

$$h = \frac{2\cos\theta_1}{[2(1-\cos\theta_1)]^{(3/4)}}(2q)^{1/2}.$$

The effectiveness factor of the Type 1 ink bottle is plotted against this h in Fig. 2. For comparison, the effectiveness factor for an ordinary cylindrical pore with a pseudohomogeneous reaction is also plotted. This latter curve is, as we well know, describable by the equation [Thiele (*5*)]

$$\eta = \frac{1}{h}\tanh h.$$

Reduced to the area-equivalent basis, the effectiveness factor of the Type 1 ink bottle is much greater than that of a cylinder without a narrow neck.

TYPE 2 INK BOTTLE CYLINDRICAL

Consider a cylinder of length L and radius R which has a circular aperture with radius $r \leq \rho_1 R$ at one end where $\rho_1 \leq 1$. The equation of continuity for component A is

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{\partial^2 C_A}{\partial Z^2} = 0. \qquad (9)$$

The boundary conditions are

$$\begin{array}{llll}
\text{B.C. 1} & \text{At } Z = 0 & 0 \leq r \leq \rho_1 R & C_A = C_{A_0}, \\
 & & \rho_1 R < r \leq R & D\dfrac{\partial C_A}{\partial Z} = kC_A, \\
\text{B.C. 2} & \text{At } Z = L & & -D\dfrac{\partial C_A}{\partial Z} = kC_A, \\
\text{B.C. 3} & \text{At } r = 0 & & C_A = \text{finite}, \\
\text{B.C. 4} & \text{At } r = R & & -D\dfrac{\partial C_A}{\partial r} = kC_A. \qquad (10)
\end{array}$$

If we let $\zeta = (Z/L)$ and use the same definitions for ρ, γ, and q as before, the above equation and boundary conditions become

$$\left(\frac{L}{R}\right)^2\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\gamma}{\partial\rho}\right) + \frac{\partial^2\gamma}{\partial\zeta^2} = 0. \qquad (11)$$

$$\begin{array}{llll}
\text{B.C. 1} & \text{At } \zeta = 0 & 0 \leq \rho \leq \rho_1 & \gamma = 1, \\
 & & \rho_1 < \rho \leq 1 & \gamma = \dfrac{R}{Lq}\dfrac{\partial\gamma}{\partial\zeta}, \\
\text{B.C. 2} & \text{At } \zeta = 1 & & \dfrac{\partial\gamma}{\partial\zeta} = -\dfrac{L}{R}q\gamma, \\
\text{B.C. 3} & \text{At } \rho = 0 & & \gamma = \text{finite}, \\
\text{B.C. 4} & \text{At } \rho = 1 & & \dfrac{\partial\gamma}{\partial\rho} = -\dfrac{L}{R}q\gamma. \qquad (12)
\end{array}$$

Solving Eq. (9) by the method of separation of variables and using B.C. 2 and 3, we obtain

$$\gamma = \sum_{n=1}^{\infty} A_n J_0(\lambda_n \rho) \frac{\lambda_n \cosh\left[\frac{L}{R}\lambda_n(1-\zeta)\right] + q \sinh\left[\frac{L}{R}\lambda_n(1-\zeta)\right]}{\lambda_n \cosh \frac{L}{R}\lambda_n + q \sinh \frac{L}{R}\lambda_n}, \tag{13}$$

where A_n = the coefficients to be evaluated and λ_n = the eigenvalues obtainable by solving the equation

$$\lambda J_1(\lambda) - qJ_0(\lambda) = 0, \tag{14}$$

which is derived from B.C. 4. In Eqs. (13) and (14), $J_0(x)$ and $J_1(x)$ are Bessel functions of the first kind of zeroth and first order, respectively.

To determine the coefficients A_n in Eq. (13), we make use of B.C. 1. Multiplying $\gamma|_{\zeta=0}$ by $\rho J_0(\lambda_m \rho)$ and integrating between 0 and 1 we obtain

$$\int_0^1 \gamma\Big|_{\zeta=0} \rho J_0(\lambda_m\rho)\, d\rho = \int_0^{\rho_1} \rho J_0(\lambda_m\rho)\, d\rho + \frac{R}{Lq}\int_{\rho_1}^1 \frac{\partial\gamma}{\partial\zeta}\Big|_{\zeta=0} \rho J_0(\lambda_m\rho)\, d\rho.$$

Here,

$$\gamma\Big|_{\zeta=0} = \sum_{n=1} A_n J_0(\lambda_n\rho)$$

and

$$\frac{\partial\gamma}{\partial\zeta}\Big|_{\zeta=0} = -\frac{L}{R}\sum_{n=1}^{\infty} A_n\lambda_n J_0(\lambda_n\rho) Q_n,$$

where

$$Q_n = \frac{\lambda_n \sinh\frac{L}{R}\lambda_n + q\cosh\frac{L}{R}\lambda_n}{\lambda_n\cosh\frac{L}{R}\lambda_n + q\sinh\frac{L}{R}\lambda_n}.$$

From Carslaw and Jaeger (*2*a), for λ_n satisfying Eq. (14),

$$\int_0^1 \rho J_0(\lambda_n\rho) J_0(\lambda_m\rho)\, d\rho = \frac{1}{2\lambda_m^2}(q^2 + \lambda_m^2) J_0^2(\lambda_m)\delta_{mn},$$

and, from Dwight (*3*),

$$\int_0^{\rho_1} \rho J_0(\lambda_m\rho)\, d\rho = \frac{\rho_1 J_1(\rho_1\lambda_m)}{\lambda_m}.$$

We thus obtain a set of simultaneous equations from which A_n can be evaluated

$$\sum_{n=1}^{\infty} A_n\left[\lambda_n Q_n \int_{\rho_1}^1 \rho J_0(\lambda_n\rho)J_0(\lambda_m\rho)\, d\rho + \frac{q}{2\lambda_m^2}(q^2+\lambda_m^2)J_0^2(\lambda_m)\delta_{mn}\right] = \frac{\rho_1 q}{\lambda_m} J_1(\rho_1\lambda_m)$$

$$m = 1, 2, \ldots \infty. \tag{15}$$

The actual reaction rate is

$$r_1 = 2\pi\int_0^{\rho_1 R}\left(-D\frac{\partial C_A}{\partial Z}\Big|_{z=0}\right) r dr$$

$$= 2\pi\ RDC_{A_0}\rho_1 \sum_{n=1}^{\infty} A_n Q_n J_1(\rho_1\lambda_n).$$

The reaction rate if the interior surface were entirely available for reaction is

$$r_2 = [2\pi RL + 2\pi R^2 - \pi(\rho_1 R)^2]kC_{A_0}$$

Hence the effectiveness factor is

$$\eta = \frac{\rho_1}{q\left(1 + \frac{L}{R} - \frac{1}{2}\rho_1^2\right)}\sum_{n=1}^{\infty} A_n Q_n J_1(\rho_1\lambda_n). \tag{16}$$

Here again, the 24-point Gaussian quadrature and the Gaussian elimination procedure, both in double precision, were used in the evaluation of A_n. The size of the matrix in Eq. (15) was increased until the agreement between the last pair of consecutive effectiveness factors fell within 0.001 of their values.

The effectiveness factor as a function of the aperture size (represented by the dimensionless radius ρ_1) is plotted in Fig. 3 at two levels of q. The effectiveness factor decreases as the aperture size is reduced. This reduction is more remarkable when q is higher.

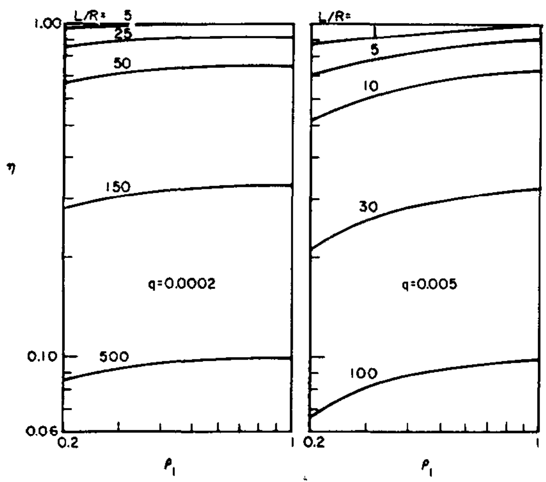

FIG. 3. Effect of aperture size (dimensionless radius ρ_1) on effectiveness factor η; Type 2 ink bottle.

To compare the effectiveness factor of the Type 2 ink bottle with that of the ordinary cylindrical pore without a narrow neck, the effectiveness factor is plotted in Fig. 4 against the Thiele modulus h which is defined as

$$h = \frac{L}{R}(2q)^{1/2}.$$

The effectiveness factor of Type 2 ink bottle is smaller than that of the ordinary pore. This reduction is more pronounced when q is increased.

Comparisons were made between a Type 2 ink bottle and two area-equivalent cylinders without narrow necks. One of these equivalent cylinders has a radius equal to that of the cylindrical part of the ink

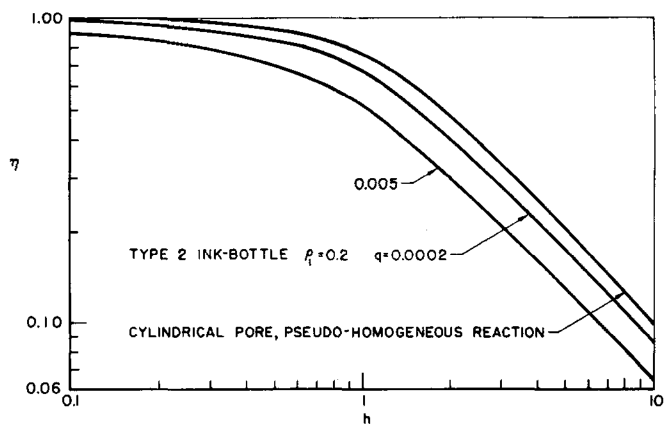

FIG. 4. Comparison between Type 2 ink bottle and cylindrical pore without a narrow neck.

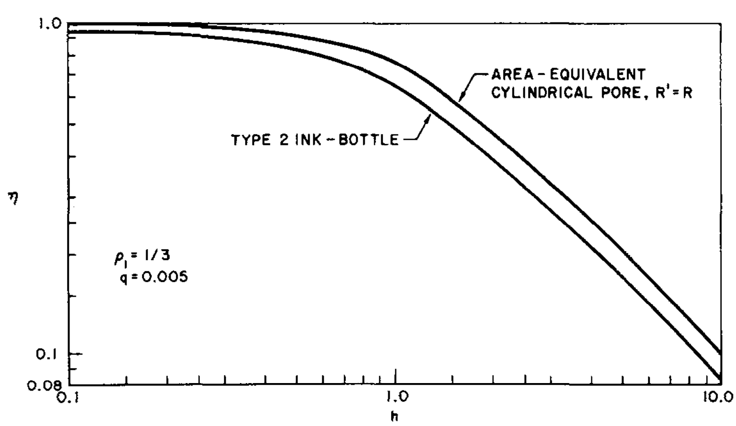

FIG. 5. Comparison between Type 2 ink bottle and its area-equivalent cylindrical pore with $R' = R$.

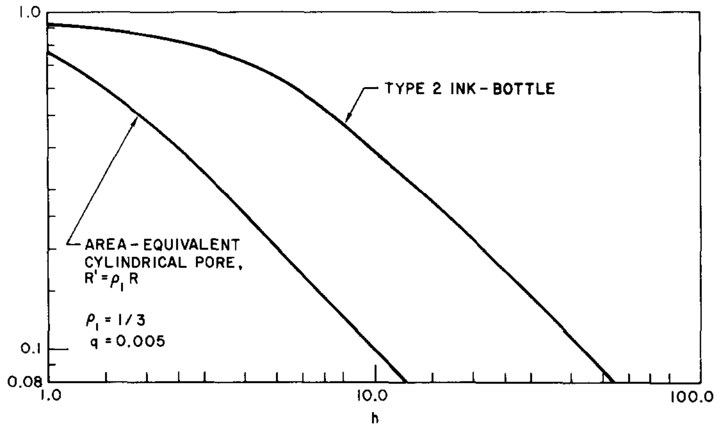

FIG. 6. Comparison between Type 2 ink bottle and its area-equivalent cylindrical pore with $R' = \rho_1 R$.

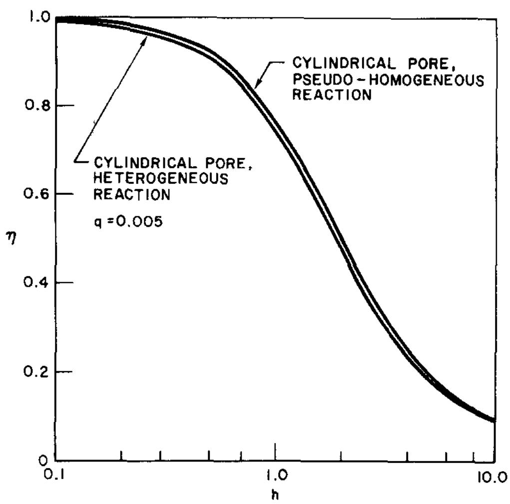

FIG. 7. Comparison between cylindrical pore with heterogeneous reaction and that with pseudo-homogeneous reaction.

bottle ($R' = R$) whereas another has a radius equal to that of the aperture ($R' = \rho_1 R$). When $R' = R$, the Thiele modulus of the equivalent cylinder is

$$h = \left[\frac{L}{R} + \frac{1}{2}(1 - \rho_1^2)\right](2q)^{1/2}.$$

When $R' = \rho_1 R$,

$$h = \frac{1}{\rho_1^{3/2}}\left(\frac{L}{R} + 1 - \rho_1^2\right)(2q)^{1/2}.$$

The results are shown in Figs. 5 and 6, respectively. The effectiveness factor of a Type 2 ink bottle is lower than that of an area-equivalent cylinder with $R' = R$ and a great deal higher than that of an area-equivalent cylinder with $R' = \rho_1 R$.

For the special case of $\rho_1 = 1$, the Type 2 ink bottle becomes an ordinary cylindrical

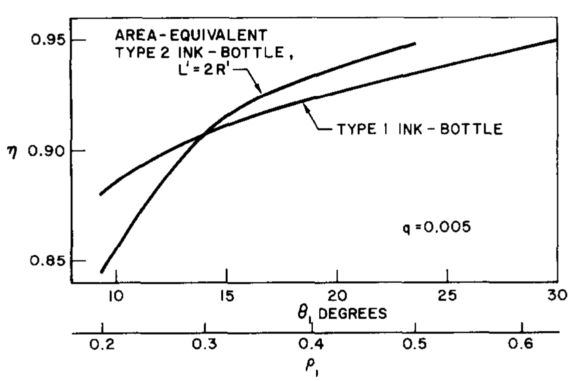

FIG. 8. Comparison between Type 1 ink bottle and its area-equivalent Type 2 ink bottle with $L' = 2R'$.

pore without a narrow neck. The difference between the present work and Thiele's analysis is the fact that we considered a heterogeneous reaction on the cylindrical surface, including the surface at the closed end, while Thiele used a pseudohomogeneous reaction model with no concentration gradient at the closed end. The effectiveness factors with heterogeneous and pseudohomogeneous reaction models are compared in Fig. 7. Since the difference is rather small, we reconfirm that the pseudohomogeneous reaction model is a good one for a cylindrical pore without a narrow neck.

To compare with a Type 1 ink bottle, we consider an area-equivalent Type 2 ink bottle with $L' = 2R'$; i.e., as in a sphere, with equal dimensions in three principal directions. For this area equivalency, the relation between θ_1 and ρ_1 characterizing the aperture sizes is given by

$$\rho_1 = [3(1 - \cos\theta_1)]^{1/2}.$$

The comparison is shown in Fig. 8. For a fairly large aperture, the Type 1 ink bottle has a lower effectiveness factor than that of its area-equivalent Type 2 ink bottle with $L' = 2R'$. The reverse is true, however, as the aperture size is reduced.

Acknowledgments

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