Approximation of Rate Expressions Involving Pore Size Distributions

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According to the mean value theorem for definite integrals (Korn and Korn, 1961) there exists a value ξ of r in the interval a to b such that

$$\int_a^b y(r)g(r)dr = y(\xi) \int_a^b g(r)dr \tag{1}$$

provided there is no change in sign of $y(r)$. This theorem offers a technique for simplifying rate integrals arising in models for fluid-solid or catalytic reactions in porous solids when pore size is represented by a distribution function rather than by a mean values. The theorem apparently has not been applied to this problem before. Our purpose is to illustrate its use and thereby demonstrate its utility.

If one allows for a distribution of pore sizes, diffusion controlled gasification within the micropores of a solid gives rise to an expression (Hashimoto and Silveston, 1973)

$$g_n = k \int_0^\infty \frac{\tanh\phi}{\phi} r^{n-1} f(r)dr \tag{2}$$

where $\phi = h_0 r_0/r$, r is the radius at time t assuming cylindrical pores, r_0 is the most probable pore radius for the pore size density distribution function $f(r)$ at time $t = 0$, and h_0 is the Thiele modulus based on r_0. Knudsen diffusion and gasification kinetics independent of the apparent density of the solid but first order in oxidant concentration have been assumed. k is a constant containing the gasification rate constant, molecular weight of the solid and its true density (Hashimoto and Silveston, 1973). The integral in Equation (2) must be replaced by a moment expression to obtain a practical model of the gasification process.

Letting $y(r) = \tanh\phi$ in Equation (1), Equation (2) may be replaced by

$$g_n = \frac{k}{h_0 r_0} \tanh\left[\frac{h_0 r_0}{\xi}\right] M_n \tag{3}$$

provided $0 < \xi < \infty$. M_n is the nth moment of $f(r)$. In this case the function ξ cannot be found. However, an approximation ξ^* may be used to approximate g_n. This may be found by requiring that the asymptotes of the approximation g_n^* approach those of g_n. From Equation (2) $g_n \to \dfrac{k}{h_0 r_0} M_n$ when $h_0 \to \infty$, and $k\,M_{n-1}$ when $h_0 \to 0$. Equation (3) holds for g_n^* and may be written

$$g_n^* = k \frac{\tanh \dfrac{h_0 r_0}{\xi^*}}{\psi} M_{n-1} \tag{4}$$

where $\psi = h_0 r_0\, M_{n-1}/M_n$.

To satisfy the asymptote conditions,

$$\xi^* = \frac{M_n}{M_{n-1}} \tag{5}$$

The approximation then is

$$g_n^* = k\, M_{n-1}\, e_n \tag{6}$$

where

$$e_n = \frac{\tanh\psi}{\psi} \tag{7}$$

When $n = 2$, Equation (7) is the effectiveness factor for a first-order irreversible reaction occurring in a porous catalyst (Hashimoto and Silveston, 1971).

The approximation, Equation (5), has been tested assuming Maxwellian and Gaussian functions: $f^M(r) = \alpha_M\, r/r_0 \exp\,[r/r_0]$, $f^G(r) = \alpha_G \exp\,[-\beta^2\,(r/r_0 - 1)^2]$ with $\beta = 2$ and 5. According to Mingle and Smith (1961), these functions bound the distributions normally encountered for porous catalysts. Figure 1 plots the absolute error of the approximations g_1^* and g_2^* versus the Thiele modulus, h_0. For $f^M(r)$, representing broad distributions, the error is notable only for $0.6 < h_0 < 6$. Whereas, for $f^G(r)$ with $\beta = 2$ which represents narrow distributions such as found in the micropore range of bidispersed catalysts, the worst error is only about 5%.

Other choices of $y(r)$ are possible but are not always satisfactory. Although $y(r) = r \tanh\phi$ leads to Equations (5) to (7), $y(r) = r^n \tanh\phi$ is not satisfactory because ξ^* must be $(M_n/M_0)^{1/n}$ at $h_0 \to \infty$, but $(M_{n-1}/M_0)^{\frac{1}{n-1}}$ at $h_0 \to 0$.

If bulk rather than Knudsen diffusion controls gasifica-

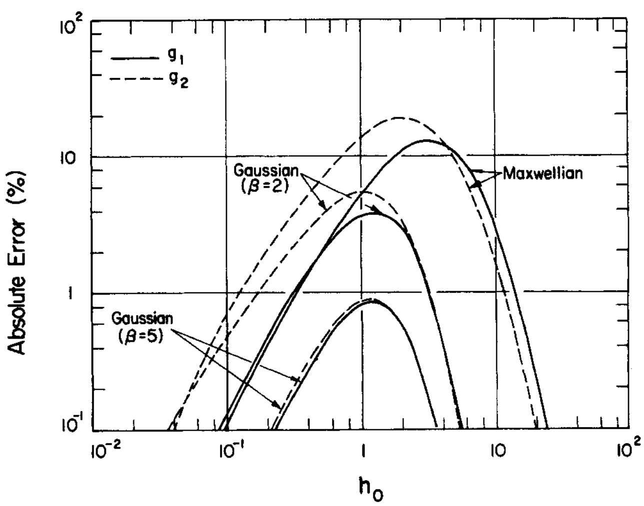

Fig. 1. Absolute error of the approximation as a function of the Thiele modulus.

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tion, $\phi = h_0 \sqrt{\frac{r_0}{r}}$, and either $y(r) = \tanh \phi$ or $\sqrt{r} \tanh \phi$ will generate Equations (6) and (7) but with

$$\psi = h_0 \sqrt{r_0}\, M_{n-1}/M_{n-1/2}.$$

ACKNOWLEDGMENTS

This study was made possible by support from the Canadian Federal Department of Energy, Mines and Resources, Faculty of Engineering, University of Waterloo, and the Japanese Ministry of Education.

NOTATION

$f(r)$ = pore size density distribution function
g_n = rate of gasification function
$y(r)$ = function occurring in Equation (1)
h_0 = Thiele modulus for a first-order reaction based on the most probable pore radius at $t = 0$ in a transient system
M_n = nth moment of $f(r)$
r, r_0 = pore radius, most probable radius for $f(r)$ at time $t = 0$
β = coefficient in Gaussian distribution
e_n = pseudo effectiveness factor
ξ = value of r satisfying Equation (1)
$*$ = (superscript) approximation

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Manuscript received April 2, 1971; revision received August 29, 1972; note accepted October 13, 1972.

Behavior of Gas Bubbles in Fluidized Beds

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In a recent paper, Rieke and Pigford (1971) described experiments on injected bubbles in a two-dimensional gas-fluidized bed which were interpreted as contradicting commonly held theories of fluidization. In particular, they surmised that the flow of gas inside bubbles rising in fluidized beds is downwards, whereas fluid mechanical theories suggest that the gas flow inside a bubble is upwards and of order U_{mf} (the minimum fluidization velocity) with respect to a frame of reference moving with the bubble (Davidson, 1961; Davidson and Harrison, 1963; Jackson, 1963; Murray, 1965). Moreover, Rieke and Pigford interpreted their photographs as showing that there is a large wake of gas which moves with a bubble and grows with time. By contrast, theory predicts that for a bubble in steady motion, even when there is a particle wake, the size of the gas cloud enveloping the bubble and its particle wake is constant (Clift et al., 1972; Collins, 1965). Finally, Rieke and Pigford concluded that there is a substantial flow of particles through a bubble falling from the roof to the floor, whereas the theoretical studies either assume or deduce that the particle motion relative to a bubble is approximately as in an incompressible irrotational flow.

In this note, we show that it is possible to interpret the photographs of Rieke and Pigford as being consistent with all essential conclusions of fluid mechanical theories of fluidization. We also present direct experimental evidence that the velocity of gas inside a rising bubble is upwards and of order of magnitude U_{mf}, in agreement with theory.

EXPERIMENTAL DETAILS

In observing coal particles of very wide size distribution fluidized in a two-dimensional column, one of the present authors noted that the resulting bubbles appeared grey, apparently because fines were being entrained in the rising bubble. This suggested that small particles could be used as tracers to provide a rough measure of throughflow velocities in fluidized beds. In the present work, a simple experiment was devised in which small glass beads were used as tracer particles in a bed of larger glass beads.

The experiments were performed in a transparent acrylic column of inside dimensions 1.5 cm × 51 cm × 120 cm deep having a sintered bronze distributor. The column was filled to a depth of 90 cm with glass beads having a size range of 420 to 600 μm and a minimum fluidization velocity (with air) of 24 cm/s. The tracer particles were glass beads which had been sieved to four narrow size ranges having surface mean diameters of 20, 23, 27, 35, and 44 μm, respectively. These particles were dyed red to allow them to be distinguished clearly from the larger particles which formed the bulk of the bed.