$$1.6(H/D)^2 \leq Fr \leq 5.1(H/D)^2 \qquad (8)$$

The Harleman theoretical equation proposed by Simpson (1968) as a design equation for minimum liquid height for gas-liquid separators is not satisfactory for that use. Instead, it is recommended that the following relationships be used for conservative design in critical applications:

$$Fr \leq 1.6(H/D)^2 \qquad (9)$$

$$Q \leq 1.26(g'D)^{1/2}H^2 \qquad (10)$$

The equivalent head H_e represented in Figure 3 is effectively the total static and pressure head required to maintain full liquid flow at steady state. The curve for weir flow, where the static head of liquid height H is the total driving force, is shown for comparison. Maximum steady state vacuum is attained in sucking flow just at the transition from weir flow to full flow. At this point, flow pressure drop (H_e) is only about 0.1 cm of the total available head represented by the length of the downcomer (1.27 cm) plus H (about 0.25 cm). Liquid Euler numbers decrease from a maximum of about 0.9 in the H/D range of 0.5 to 1.0 to about 0.6 at H/D values near 1.5. Thus, true orifice entrance control is realized only at the higher flow velocities. Inferences normally given for use of standard orifice equations with decreasing discharge coefficients at lower velocities for efflux of liquid from a vessel are thus incorrect for values of H/D between 0.4 and 1.5. For the weir flow regime, superficial Euler numbers decrease to zero with H/D, since from Equation (1)

$$Eu = \frac{2.36}{\sqrt{2}}(H/D) \qquad (11)$$

This experimental study has been directed to gas-liquid systems; the experimental equation of Harleman et al. (1959) should still be used for design related to selective removal of stratified liquid or liquid from lower phases of decanters, etc. Converted for volumetric flow, this equation is

$$Q = 1.61\sqrt{g'}\,H^{2.5} \qquad (12)$$

It is interesting to note that the diameter of the drain does not appear in this equation. The only geometric factor is the lower phase height. This is a consequence of the assumption of a point sink.

NOTATION

C = dimensionless discharge coefficient
D = inside diameter of drain, cm
Eu = Euler number $= V/\sqrt{2g'H_e}$
Fr = Froude number $= V/\sqrt{g'D}$
g = acceleration of gravity, cm/s^2
g' = $g(\rho_1 - \rho_2)/\rho_1$
H = height of lower liquid phase above bottom of vessel, cm
H_e = equivalent head across drain $= H + P + L$ for full pipe flow or $= H$ for weir flow, cm H_2O
L = length of drain, cm
P = static pressure head above lower liquid phase, cm H_2O
Q = liquid volumetric flow rate, cm^3/s
V = liquid superficial velocity in drain, cm/s
ρ = density, g/cm^3

Subscripts

1, 2 = designation of phase or stratified layer number from bottom of vessel

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The Characterization of Fixed Beds of Porous Solids from Pulse Response

The response of a fixed bed of porous particles through which fluid flows to a pulse of tracer gas has been analyzed by a number of methods. It is found that analysis of the Fourier transformed and the Laplace transformed response curves for small values of the parameters of the integrals provides accurate estimates of intraparticle diffusivity and Peclet group for axial dispersion when additional information provided by the experiments is used to resolve interaction between the process coefficients in the dynamic response.

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SCOPE

The response of a fixed bed of porous particles through which a gas flows to an injected pulse of tracer gas may be used in theory to provide estimates of the process coefficients, the coefficient of axial dispersion, the intraparticle diffusivity, the particle to fluid mass transfer coefficient, and the interstitial fluid velocity. The response

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may be analyzed in the time domain, in the frequency domain, or in the Laplace transform domain so that a broad agreement between the experimental and theoretical response curves may be sought by varying the parameters of the theoretical curve until the best measure of agreement is obtained. The values of the parameters that reconcile the theoretical and experimental response curves are the best estimates provided by that experiment, but in practice the presence of experimental errors can make the comparison uncertain.

An alternative procedure is to examine particular mathematical features of the response curves and to estimate the parameters as the values that give the best correlation between the functional forms of the theoretical and experimental curves. Two methods of this type are described, both based upon integrals of the response curves. The first method relates to properties of the Fourier transform of the response curves for small values of w, the parameter of the integral; values of the intraparticle diffusivity and the coefficient of axial dispersion may be calculated from the intercept and gradient of a linear graph. The second is an analogous method related to properties of the Laplace transform of the response curves for small values of the transform parameter. Values of the process coefficients have been calculated by the two methods for two grades of porous particle throughout a range of particle Reynolds number from 5 to 200. As the resistance due to intraparticle diffusion dominated mass transfer resistance at the surface of the particles, the response curves were not sensitive to the particle to fluid mass transfer coefficient, and therefore no reliable estimates of this coefficient could be made.

The calculation of the process coefficients obtained by the two methods of the latter class is compared with estimation from minimum variance in the frequency and Laplace transform domain, and by the method of moments.

CONCLUSIONS AND SIGNIFICANCE

Consistent estimates of intraparticle diffusivity and Peclet group were obtained by the methods based upon the analytical properties of the Fourier and Laplace transforms of the response for small values of the parameters of the integrals. The estimates of intraparticle diffusivity agreed with earlier estimates for the same particles found by the method of frequency response. The values of Peclet group agreed with established measurements for dispersion in single phase flow throughout the range of Reynolds group under investigation.

A knowledge of the range of integral parameters for which a particular analytical approximation is valid was found to be useful because the effect of isolated experimental errors could sometimes be identified. An example is given of such an application.

Good estimates of diffusivity and Peclet group could not be obtained from minimum variance searches in the Laplace transform or frequency domain when a wide range of the parameter of the transform integrals was considered; the process coefficients became insensitive to the integral error because of the growth of random error. In all cases, the range of the transform parameter had to be arbitrarily curtailed to give consistent estimates of diffusivity and Peclet group, but even then, the estimates depended upon the range of integration. This dependence was due, in part, to interaction between the parameters of the response. Methods based upon the analytical properties of the transforms were successful because additional information was introduced to remove the interaction.

The amount of computation required for a minimum variance search was much greater than that required either for the first two methods or for the method of moments.

As several sizes of particle were not available, the method of moments required accurate estimates of the second and third moments of the responses. But the accuracy found for the third moment was variable; the values were even variable in sign. This had the effect of giving negative or complex numbers for dispersion coefficients in a high proportion of cases.

It is concluded that methods for the estimation of intraparticle diffusivity and dispersion coefficients in fixed beds of porous solids based upon simple analytical properties of the integrals of the response curve are superior both to estimation from minimum variance in the Laplace transform and the frequency domain, and to the method of moments. The analytical methods gave accurate estimates of intraparticle diffusivity and the amount of computation required was small, although larger than that required by the method of moments.

The dynamic response of a bed packed with porous particles is influenced by dispersion in the bed, by mass exchange between particles and fluid, and by intraparticle diffusion. In principle, the measurement of the response of the bed to a known stimulus may be used to provide estimates of the coefficients for each process, although in particular experiments the response may be sensitive to some of the processes and insensitive to others.

The generation of a pulse of heat or mass tracer and the measurement of the response of the bed are convenient when compared with, say, the generation of a sinusoidal stimulus and measurement of the frequency response, so that the method of pulse response may be chosen because of experimental simplicity. A variety of theoretical methods may be used in the analysis of the pulse.

In one class of method, the variance of the experimental measurements about a theoretical curve is calculated, and the values of the coefficients are changed so that the variance is reduced until the minimum is found. The values of coefficients associated with the minimum variance are taken to be the best values given by that experiment. The variance may be calculated in the time domain by numerical integration of the partial differential equation, in the frequency domain, or in the transform (Laplace) domain. The methods are subject to inaccuracy in the presence of isolated rather than uniformly distributed errors.

A second class of method utilizes analytical relations between the process coefficients and certain integrals of the response; the best known is the method of moments. These methods are subject to inaccuracy in the presence

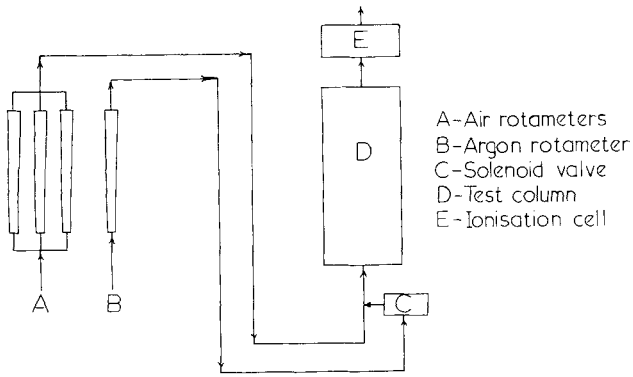

Fig. 1. Flow diagram of the experimental arrangement.

of isolated and of distributed errors but are simple to apply compared with the first class.

The third class of method also uses analytical relations between the process coefficients and certain integrals of the response, but the functional dependence of the coefficients upon a parameter of the integral is also examined. For example, the magnitude of the Fourier integral of the pulse response is linearly related to w^2 when w is small, where w is the parameter of the integral. This simple functional dependence may be used to determine the process coefficients, and since isolated errors may be identified under some circumstances and the effect of distributed errors may be minimized, this class of method often gives an accuracy of estimate that is greater than that provided by the other two classes.

In this paper we consider the use of two methods of the third class in the estimation of the process coefficients from the pulse response of a fixed bed of porous particles through which fluid flows at a constant velocity. The two methods of parameter estimation are compared with established methods from the first and second classes.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Figure 1 is a flow diagram of the experimental arrangement.

Compressed air from the laboratory supply was reduced in pressure and passed through a bank of rotameters to the fixed bed. A cylinder of compressed argon was connected to a solenoid valve, the outlet of which formed one leg of a tee junction with the main air line near the base of the fixed bed. The solenoid valve was controlled by an electrical timer that provided electrical pulses from 0.1 to 10 s controllable in increments of 0.1 s.

Gas entered the fixed bed through a distributor and after passing through the bed left through a narrow constriction that contained the composition detector. The composition detector consisted of two copper plates, each 3 by 1 cm held at a spacing of 1 mm. A film of titanium holding tritium in interstitial solution coated the face of one of the plates. The sensing circuit consisted of the plates in series with a 500 MΩ resistor. When 1 400 V was applied to this circuit, a standing current was generated that was linearly proportional to the argon concentration of the air stream, so that after amplification of the current, an output voltage suitable for a conventional recorder was produced that was directly proportional to the concentration of argon in the gas stream. Further details of the equipment are given elsewhere (Gunn and Pryce, 1969).

The experiments were performed with two different lengths of bed, each filled with porous catalyst spheres 5 mm in diameter. After the flow rate was set to the bed, a pulse of argon was injected into the main air stream, and a record of the detector signal was made on a strip chart recorder. The bed was replaced by a second of greater length, a similar injection of argon gas was made, and the detector signal was again recorded. This first record corresponded to the inlet pulse and the second corresponded to the outlet pulse from a bed equal in length to the difference between the two. This arrangement corrected for the influence of the gas distributor and the sampling cell so that end effects were fully accounted for (Gunn and Pryce, 1969).

The experiments were repeated for a range of flow rates. Two different types of porous particle were investigated. Both types of particle were silica-alumina catalyst supports supplied by the Norton Company.

THEORETICAL TREATMENT

The partial differential equation that describes convection and dispersion within the bed has been given previously (Gunn, 1970):

$$D_L \frac{\partial^2 c}{\partial z^2} - K_f V \frac{\partial c}{\partial z} - N \frac{(1-\eta)}{\eta} \phi - K_f \frac{\partial c}{\partial t} = 0 \tag{1}$$

where the rate of diffusion N into a single particle is given by

$$N = \int_o^t c(\lambda) \frac{\partial}{\partial t} G(t-\lambda)\, d\lambda \tag{2}$$

and $G(t)$ is the rate of diffusion into the particle following a unit step change at the surface at $t = 0$. The initial condition is one of zero concentration within the bed and particles. The boundary conditions are

$$c = c_o(t) \quad \text{at} \quad z = 0, \quad \text{the inlet face} \tag{3}$$

$$c \to 0 \quad \text{as} \quad z \to \infty$$

If we take the Fourier transform of Equation (1), where the Fourier transform is defined as

$$F(w) = \hat{c} = \int_{-\infty}^{\infty} e^{-iwt} c(t)\, dt \tag{4}$$

the equation after transformation becomes

$$\frac{d^2\hat{c}}{dz^2} - \frac{K_f V}{D_L} \frac{d\hat{c}}{dz} - \left[\phi \frac{(1-\eta)}{\eta} \hat{B} + \frac{iwK_f}{D_L} \right] \hat{c} = 0 \tag{5}$$

In this equation $B(t)$ is the rate of diffusion into the particle following a unit impulse at the surface at $t = 0$, and $\hat{B}$ is the Fourier transform of B. The properties of the transform of the convolution integral (2) have been used. The solution to Equation (5) has been given in terms of frequency response. In terms of the transform, the solution is

$$\hat{c} = \hat{c}_o e^{([K_f V/2D_L) - \theta\sigma]z} e^{-i\theta z} \tag{6}$$

where

$$\theta = \sqrt{\left(\frac{K_f^2 V^2}{8 D_L^2} + \frac{p}{2D_L} \right)} \sqrt{[\sqrt{(1+\gamma^2)} - 1]} \tag{7}$$

$$\sigma = \sqrt{\left[\frac{\sqrt{(1+\gamma^2)} + 1}{\sqrt{(1+\gamma^2)} - 1} \right]} \tag{8}$$

$$\gamma = \frac{4D_L(q + wK_f)}{K_f^2 V^2 + 4pD_L} \tag{9}$$

The variables p and q are defined by the shapes and boundary conditions for the particle. Expressions defining p and q have been given for a variety of particles (Gunn, 1970).

The first method of pulse analysis is concerned with the behavior of the magnitude of the right-hand side of Equation (6) when w is small. For this condition, p and q may be defined by simple expressions. For spherical particles

$$p = \frac{w^2 K_s^2 (1-\eta)}{\eta}\left(\frac{R}{3HD} + \frac{R^2}{15D}\right) \tag{10}$$

$$q = \frac{wK_s(1-\eta)}{\eta} \tag{11}$$

The logarithm of the ratio of transform $\hat{c}/\hat{c}_o$ may now be represented by a McMaurin series in w. When the magnitude of the ratio of the transform is considered

$$\ln\left|\frac{\hat{c}}{\hat{c}_o}\right| = -zw^2 I + 0(w^4) \tag{12}$$

where

$$I = \frac{K_s^2}{K_f V}\left(\frac{1-\eta}{\eta}\right)\left(\frac{R}{3HD} + \frac{R^2}{15D}\right) + D_L \frac{\left[K_s\frac{(1-\eta)}{\eta} + K_f\right]^2}{K_f^3 V^3} \tag{13}$$

To the degree of accuracy specified by Equation (12), I for a given experiment may be found by plotting $\ln(\hat{c}/\hat{c}_o)$ against w^2. If the definition of the Peclet group $Pe = Vd/D_L$ is inserted into Equation (13), this equation may be arranged to give

$$IV = \frac{K_s^2}{K_f}\left(\frac{1-\eta}{\eta}\right)\left(\frac{R}{3HD} + \frac{R^2}{15D}\right) + \frac{d\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]^2}{K_f^3 VPe} \tag{14}$$

For particle Reynolds numbers greater than about 10, the group Pe is substantially constant; thus a graph of IV against $1/V$ should be linear because for mass transfer, the film resistance to diffusion at the surface of the particle is small compared to the intraparticle resistance. The value of the intraparticle diffusivity may now be determined from the intercept of such a graph, and the values of Peclet group may be determined once the intraparticle diffusivity has been found.

The second method of pulse analysis is concerned with properties of the solution to the equation obtained after we take the Laplace transform of Equation (1). The solution is

$$\bar{c} = \bar{c}_o \exp\left[\frac{VK_f z}{2D_L}\left\{1 - \sqrt{\left(1 + \frac{4D_L s}{V^2 K_f^2}\left(\phi\left(\frac{1-\eta}{\eta}\right)\bar{G} + K_f\right)\right)}\right\}\right] \tag{15}$$

where $\bar{c}$ is the transform of the input pulse, and $\bar{G}$ is the transform of G. On taking logarithms of this equation and dividing by the Laplace transform parameter s, we get

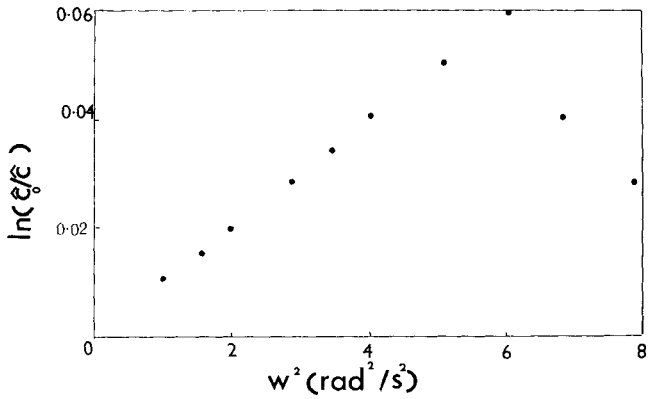

Fig. 2. Random variation of $\ln|\hat{c}/\hat{c}_0|$ with w^2 when w is large.

$$\frac{1}{s}\ln\frac{\int_o^\infty e^{-st}cdt}{\int_o^\infty e^{-st}c_o dt} = \frac{VK_f z}{2D_L s}\left[1 - \sqrt{\left\{1 + \frac{4D_L s}{V^2 K_f^2}\left(\phi\left(\frac{1-\eta}{\eta}\right)\bar{G} + K_f\right)\right\}}\right] \tag{16}$$

The dependence of the left-hand side upon s when s is small may be found by expanding the right-hand side by means of the binomial theorem. In the vicinity of $s = 0$, a linear dependence upon s is found with a limiting intercept and gradient of

$$\text{Intercept} = \frac{-z}{VK_f}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right] \tag{17}$$

$$\text{gradient } I = \frac{-z}{VK_f}\phi\left(\frac{1-\eta}{\eta}\right)\left(\frac{d\bar{G}}{ds}\right)_{s\to 0} + \frac{D_L z}{V^3 K_f^3}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]^2 \tag{18}$$

Substituting for $(d\bar{G}/ds)_{s\to 0}$ (Gunn, 1970) and rearranging Equation (18) in the same manner as Equation (13), we get

$$IV = \frac{zK_s^2}{K_f}\left(\frac{1-\eta}{\eta}\right)\left(\frac{R}{3HD} + \frac{R^2}{15D}\right) + \frac{zd}{K_f^3 VPe}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]^2 \tag{19}$$

If we take into account the relative constancy of the Peclet group for Reynolds numbers greater than 10, a graph of IV against 1/V should be linear, the value of the intraparticle diffusivity may be determined from the intercept, and the individual values of Peclet group may be determined once the intraparticle diffusivity has been found.

A COMPARISON OF THE METHODS OF PARAMETER ESTIMATION

The formal definition of variance in the frequency domain when applied to the impulse response, is

$$\sigma_f^2 = \int_{-\infty}^{\infty} |F(w) - F_e(w)|^2 dw \tag{20}$$

where $F(w)$ corresponds to the ratio of the two transforms in Equation (6), and $F_e(w)$ is the exponential ex-

Table 1. Influence of the Range of Integration of Variance in the Fourier Transform Domain upon Estimates of the Process Coefficients

Reynolds number	Maximum value of $\|w\|$ (s^{-1})	Peclet group Pe	D/D_m	hd/D_m
199	0.2	0.93	2.2×10^{-4}	99
	2.0	0.94	8.8×10^{-3}	41
	12.0	0.088	3.3×10^{-4}	35
50	0.2	0.90	6.3×10^{-4}	90
	2.0	1.02	9.1×10^{-5}	72
	12.0	0.063	4.9×10^{-4}	66

Table 2. Influence of the Range of Integration of Variance in the Fourier Transform Domain upon Estimates of the Process Coefficients

Reynolds number	Maximum value of $s(s^{-1})$	Peclet group	D/D_m	hd/D_m
143	1×10^{-3}	8.4	0.24	148
	5×10^{-3}	10.7	0.39	167
	5×10^{-2}	16.9	0.55	176

pression on the right of the same equation. It is a consequence of the Plancherel Identity (Feller, 1967) that the variance of the untransformed variable in the time domain is equal to the variance of Equation (20), so that, at least formally, parameter estimation from minimum variance in the frequency domain is equivalent to estimation from minimum variance in the time domain.

When the ratio of the Fourier transforms of the experimental pulses was calculated, it was found that oscillations were present in both the modulus and the argument of the ratio at high values of w, with the oscillations persisting to lower values of w in the argument. The oscillations were not present in the modulus and argument of the analytical equivalent of the ratio, the exponential terms on the right of Equation (6).

Figure 2 is a graph of the experimental dependence of $\ln |\hat{c}_o/\hat{c}|$ upon w^2 for SA 201 particles at a Reynolds number of 15. Beyond a certain frequency, large and random variations were found as shown in the figure, and the same behavior was always found when large values of w were considered. In theory, as Equation (6) shows, $\ln |\hat{c}_o/\hat{c}|$ always increases monotonically with w, and the random variations are due to the dominance of experimental error when the experimental results are transformed to the frequency domain and the frequency is high.

Because of the random variations, it was necessary to curtail the range of integration; therefore we investigated the effect of restricting the range of the integral parameter w upon the values of the process coefficients found for minimum variance. Table 1 shows the effect of range upon the parameter estimates for two experiments and three different ranges of w.

Numerical tests showed that the variance was sensitive to changes in the groups Pe and D/D_m but not to hd/D_m. The values of Peclet group found for the first two ranges of w are consistent for both experiments, but the values of Peclet group for the higher range of w differ by an order of magnitude. The values of the group D/D_m are low and variable.

For small values of w, there is a high degree of interaction between the effective process variables Pe and D/D_m. A change in one of the variables will perturb the agreement between experiment and theory, but experiment and theory may be brought into agreement again by making a compensating change in the other process variable. The interaction is shown by Equations (12) and (13) for the modulus. It is apparent that when the range of w is low, the separate influence of the process variables can only be found by changing the velocity.

For wide ranges of w, the significance of agreement between experiment and theory is uncertain because of the random variations found in integrals of the experimental responses when w is large. The difficulties of parameter estimation by this method, illustrated by Table 1, are probably due to the combination of interaction between the parameters at small w and random variations arising from experiment found for large w.

The formal definition of variance in the Laplace transform domain is (Seinfeld and Lapidus, 1974)

$$\sigma_L^2 = \int_o^\infty \left[\frac{\bar{c}}{\bar{c}_o} - g(s) \right]^2 ds \qquad (21)$$

where $g(s)$ is the exponential expression on the right-hand side of Equation (15), and $\bar{c}/\bar{c}_o$ is the ratio of Laplace transform of the output pulse to the transform of the input pulse (the transfer function). Since

$$\frac{\bar{c}}{\bar{c}_o}(s) = \frac{\int_o^\infty e^{-st} c(t)\, dt}{\int_o^\infty e^{-st} c_o(t)\, dt} \qquad (22)$$

it is clear that for large values of s, the ratio (22) depends only upon the forms of the two pulses at earlier times. At small enough times, the accuracy of the measurement of the pulse is low, because the pulse is small in amplitude and therefore the contribution of the part of the integral defined for high values of s is not accurate.

When the range of s is small, there is a high degree of interaction between the process variables as found for the Fourier transform. The interaction is shown by Equations (17) and (18). Table 2 shows the influence of the range of s upon estimates of the process variables found from minimum variance for one experiment. The variance was sensitive to changes in the groups D/D_m and Pe, but not to hd/D_m. The values of axial Peclet group and D/D_m are high compared to values reported in Table 1 and sensitive to range as for estimates in the frequency domain, even though the maximum value of s in each range of integration was not large.

Because of the variability of the estimates illustrated in Tables 1 and 2, satisfactory estimates of the process variables could not be obtained from the minimum variance methods of parameter estimation either in the Laplace transform domain or in the frequency domain.

The method of moments may also be used to estimate values of the process coefficients. When particles of different size are available, the coefficient of dispersion and the intraparticle diffusivity may be calculated from second moments of the response. Schneider and Smith (1968) have analyzed the response of beds containing particles of silica gel using second moments. The response experiments were repeated for several beds, each containing particles of different size ranges. When particles of different size are not available, third moments as well as second are necessary for the calculation of the process coefficients. The relationships between the moments and

the coefficients have been given previously (Gunn, 1970):

$$\frac{\int_o^\infty t(c_o - c)\,dt}{\int_o^\infty c_o dt} = \frac{-z}{VK_f}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right] \tag{23}$$

$$\frac{\int_o^\infty t^2(c - c_o)dt}{\int_o^\infty c_o dt} + \frac{\left(\int_o^\infty tc_o dt\right)^2 - \left(\int_o^\infty tc dt\right)^2}{\left(\int_o^\infty c_o dt\right)^2}$$

$$= \frac{-2z}{VK_f}\phi\left(\frac{1-\eta}{\eta}\right)\left(\frac{d\bar{G}}{ds}\right)_{s\to 0} + \frac{2D_L z}{V^3 K_f^3}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]^2 \tag{24}$$

$$\frac{\int_o^\infty t^3(c_o - c)dt}{\int_o^\infty c_o dt}$$

$$+ 3\frac{\int_o^\infty tcdt \int_o^\infty t^2 cdt - \int_o^\infty tc_o dt \int_o^\infty t^2 c_o dt}{\left(\int_o^\infty c_o dt\right)^2}$$

$$+ 2\frac{\left(\int_o^\infty tc_o dt\right)^3 - \left(\int_o^\infty tcdt\right)^3}{\left(\int_o^\infty c_o dt\right)^3}$$

$$= \frac{-3z}{VK_f}\phi\left(\frac{1-\eta}{\eta}\right)\left(\frac{d^2\bar{G}}{ds^2}\right)_{s\to 0} + \frac{12D_L z}{V^3 K_f^3}\phi\left(\frac{1-\eta}{\eta}\right)$$

$$\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]\left(\frac{d\bar{G}}{ds}\right)_{s\to 0}$$

$$- \frac{12D_L{}^2 z}{V^5 K_f^5}\left[K_s\left(\frac{1-\eta}{\eta}\right) + K_f\right]^3 \tag{25}$$

where

$$\text{Lt. } \phi\left(\frac{d\bar{G}}{ds}\right)_{s\to 0} = \frac{-K_s{}^2 R^2 (RH + 5)}{15DRH} \tag{26}$$

$$\text{Lt. } \phi\left(\frac{d^2\bar{G}}{ds^2}\right)_{s\to 0} = \frac{2K_s{}^3 R^4}{315D^2(RH)^2}\left[2(RH)^2 + 14RH + 35\right] \tag{27}$$

When (26) and (27) are substituted into Equations (24) and (25), it may be seen that the right-hand side of (24) is always positive and the right-hand side of (25) is always negative. Values of the left-hand side of Equations (24) and (25) were calculated by numerical integration of the experimental pulses. The values calculated in four experiments are shown in Table 3.

In two of the experiments, the value of the integrals on the left of Equation (25) is positive, giving rise to a complex value for the Peclet group. In the last two experiments, the value of the Peclet group calculated for each is negative. The experimental measurements were not sufficiently accurate for a successful application of the method of moments.

TABLE 3. NUMERICAL VALUES OF THE LEFT-HAND SIDES OF EQUATIONS (24) AND (25)

Reynolds number	L.H. Equation (24) (s^2)	L.H. Equation (25) (s^{-3})	Peclet group
6.9	12.72	267.1	Complex number
54.7	0.295	0.545	Complex number
102.3	0.010	−0.0171	negative
199.2	0.0061	−0.0817	negative

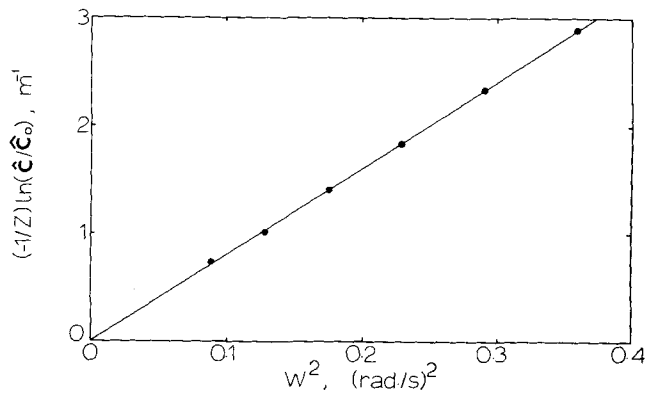

Fig. 3. A particular dependence of ln $|\hat{c}/\hat{c}_0|$ upon w^2 for small w.

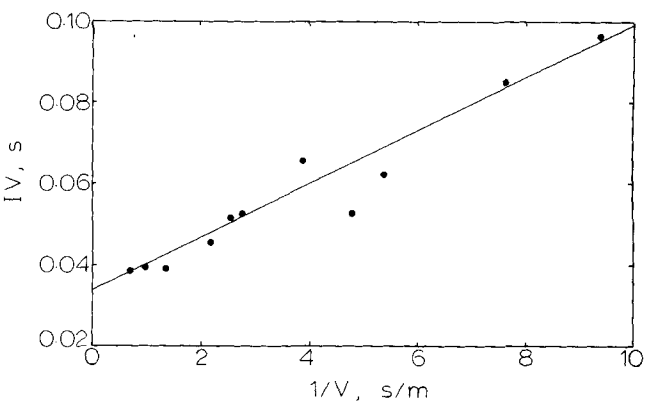

Fig. 4. Graphical determination of intraparticle diffusivity for particles SA201 from the Fourier transform.

Figure 3 is a typical graph illustrating the dependence of ln $|\hat{c}/\hat{c}_0|$ upon w^2 for small values of w. The dependence is linear, and the graph passes through the origin to accord with Equation (12). The gradients of a number of such graphs were measured for experiments characterized by a particle Reynolds group greater than 20. From the measured gradients I, values of IV were calculated and plotted against $1/V$. Figure 4 is the graph obtained for particles of the SA201 grade, and Figure 5 is the graph obtained for particles of the LA622 grade. For experiments in this range of Reynolds number, values of the Peclet group should be substantially constant, and as $R/(3HD)$ is small compared to $R^2/(15D)$, the intercepts of each graph on the IV axis will give the value of intraparticle diffusivity. The linear dependence of IV upon $1/V$ is confirmed by both Figures 4 and 5, so that the values of Peclet group are substantially constant for the range of Reynolds number. The average value of Peclet group may be calculated from the slope of the

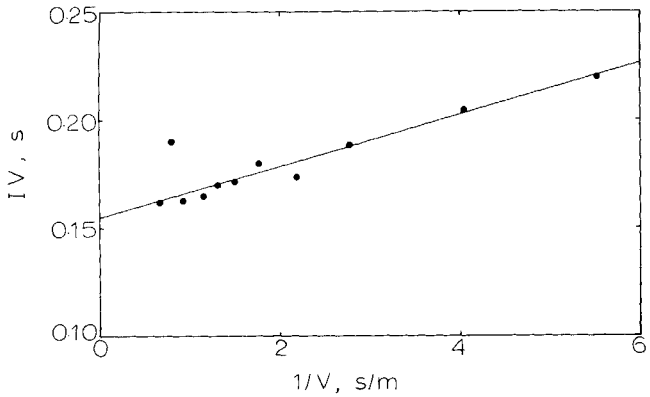

Fig. 5. Graphical determination of intraparticle diffusivity for particles LA622 from the Fourier transform.

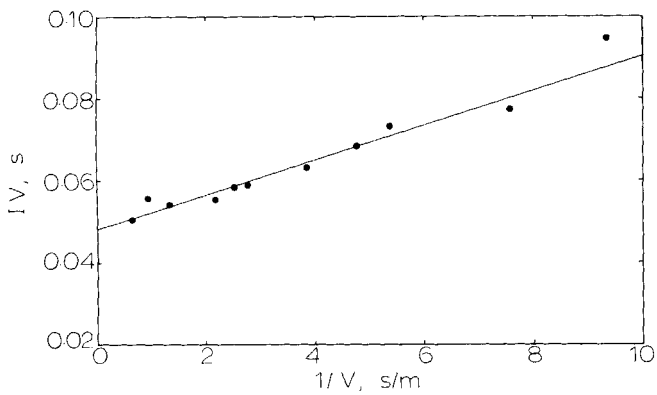

Fig. 7. Graphical determination of intraparticle diffusivity for particles SA201 from the Laplace transform.

graph, and individual values may be calculated from Equation (14) once the intraparticle diffusivity has been found.

The method of analysis of the Laplace transform of the experimental response is similar. In some cases the effect of an intrusive experimental error may be found and corrected. Figure 6 is a graph that shows the dependence of $1/s \ln (\bar{c}/\bar{c}_o)$ upon s when s is small, measured for SA201 particles at a Reynolds number of 6.9. A linear dependence should be found provided that $4D_L s/V^2K_f^2 [K_s(1 - \eta)/\eta + K_f]$ is < 0.1 when expansion of the square root within brackets on the right-hand side of Equation (16) should be accurate to quadratic terms and the right-hand side will show a linear dependence upon s. For this experiment, the linear dependence upon s should hold up to values of s at least as great as 0.3. Figure 6 shows that there is a departure from linearity for values of s much smaller than 0.3, although the linear relationship is evident for values of s greater than 0.05. Values of the gradient taken at low values of s were not consistent with values taken from experiments that did not show such a deviation, while values of the gradient measured when s ranged from 0.05 to 0.30 were consistent. For this particular example, we have concluded that the deviation at low s is the result of experimental error, and it is a feature of merit that the error could be identified and corrected. A similar deviation was found for the Fourier transform on occasions.

Figure 7 shows the dependence of IV upon $1/V$ for beds of SA201 particles, while the dependence for LA622 particles is shown on Figure 8, both calculated from the Laplace transform analysis. The value of intraparticle

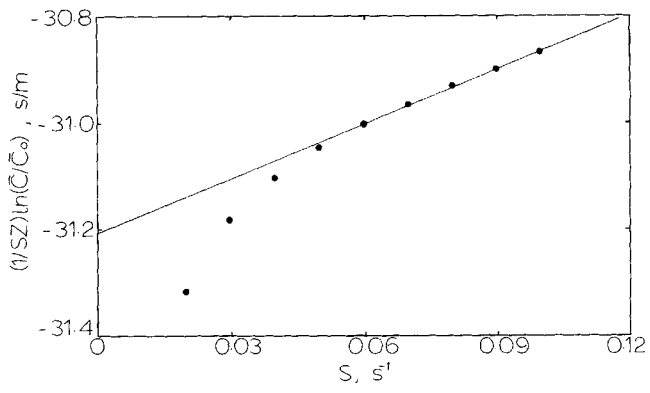

Fig. 6. A particular dependence of $[1/s \ln (\bar{c}/\bar{c}_0)]$ upon s for small s.

Table 4. Estimates of Intraparticle Diffusivity for Particles SA201 and LA622

Particles	Laplace transform D/D_m Equation (19)	Fourier transform D/D_m Equation (14)	Reported values Gunn and England (1971) D/D_m
SA201	0.073	0.109	0.083
LA622	0.087	0.0823	0.087

diffusivity was found from the intercept, and, once calculated, the individual values of Peclet group for each experiment could be found.

The ratio of intraparticle diffusivity to molecular diffusivity found by each of the methods is shown in Table 4.

The reported values were obtained by a similar method from the experimental frequency response. Catalyst particles used in both experiments were taken from the same batches of SA201 and LA 622, so that the comparison of Table 2 should reflect differences between the experiments and methods and not differences between particles of the same type.

Once the values of intraparticle diffusivity have been obtained, since the particle to fluid mass transfer coefficient has little influence upon the experimental response, values of Peclet group may be obtained from Equation (13) for the Fourier transform analysis and Equation (18) for the Laplace transform analysis. Values of Peclet group as a function of Reynolds number for particles of type SA201 are shown in Figure 9, in which we have distinguished between values calculated from the different transform methods. The values shown in Figure 9 are similar for the two methods and also agree fairly well with values reported from experimental frequency response (Gunn and England, 1971).

Values of Peclet group as a function of Reynolds number for particles of type LA622 are shown in Figure 10. Again, the values obtained from the two transform methods are similar but lie above the Peclet group-Reynolds number relationship obtained from the experimental frequency response. In the experiments of Gunn and England the particles of LA622 were soft, powdery and irregular in shape. In the present experiments, the same particles were carefully sieved and de-dusted so that the quality of packing was improved, and therefore Peclet groups were generally increased.

It is of interest to compare parameter estimation from the pulse response of fixed beds with estimation from experimental frequency response. The findings of this

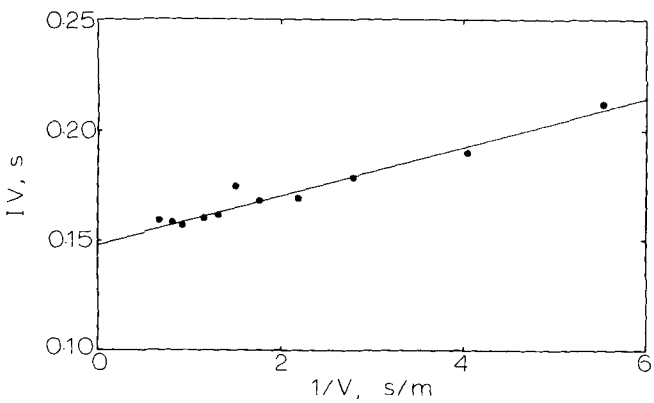

Fig. 8. Graphical determination of intraparticle diffusivity for particles LA622 from the Laplace transform.

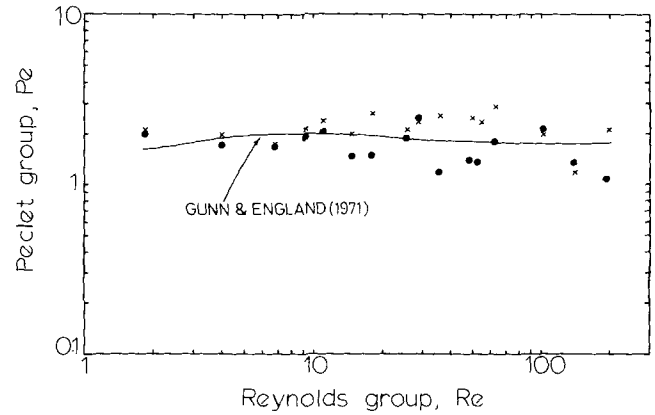

Fig. 9. Dependence of Peclet group upon Reynolds number for particles SA201: ● calculated from the Fourier transform, × calculated from the Laplace transform.

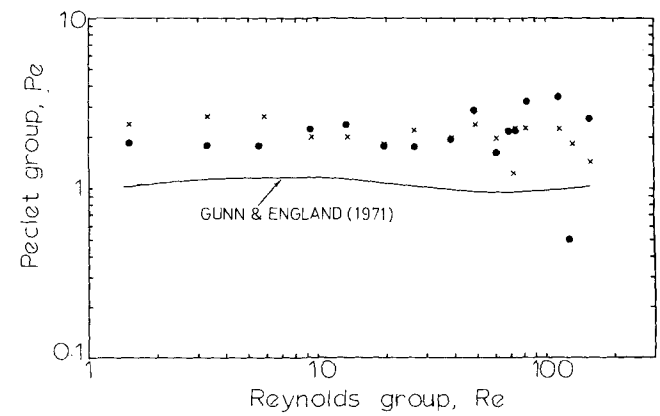

Fig. 10. Dependence of Peclet group upon Reynolds number for particles LA622: ● calculated from the Fourier transform, × calculated from the Laplace transform.

investigation may be directly compared with the findings from the study of experimental response of Gunn and England. In addition, experimental frequency response has been used in the study of heat transfer in packed beds (Gunn and de Souza, 1974) and in the study of dispersion in fixed beds of impermeable particles. Both studies may be compared with investigations of the pulse response of similar systems.

In our experience, estimation of parameters from pulse response is inferior to estimation from experimental frequency response. The principal reasons for the difference may be found in the treatment of the experimental results and in the design and operation of the equipment.

If equipment can be designed and constructed so that the variation of temperature or concentration at the entry to the fixed bed is sinusoidal, the only measurements that are necessary are the amplitude and phase change of the peak of the wave at the bed outlet. The measurements may be repeated for several waves in the normal course of operation so that good averages can be obtained. In studies of pulse response, on the other hand, the full response curve has to be measured, a more critical requirement.

The design of equipment for experimental frequency response is more difficult than for pulse response, but as the experimental measurements for frequency response are simple, the effect of changes in the arrangement of equipment can be seen directly. In particular, the response of the system to different frequencies may be tested in a direct manner. The pulse response of a fixed bed cannot be analyzed in experiment as simply, and the reproducibility of equipment for pulse response cannot be checked as easily.

Although it is convenient to distinguish between methods of the first class and of the third, it should be stressed that there is no fundamental difference of principle between the two classes. Because of the influence of experimental error, it is always necessary to restrict the range of the integral error criterion in minimum variance methods. If the integration is carried out over a range that is too wide, there is such a large growth in random error that the response of the integral to the parameters of the system becomes insensitive. However, if the range of integration is curtailed too much, interaction between the parameters of the response curve may be so severe that the influence of one parameter cannot be distinguished from another. An example of such a situation is shown in Figure 2, where there is an abrupt transition between a linear dependence of z ln $(\hat{c}/\hat{c}_o)$ upon w^2 to a region dominated by noise when $w^2 > 6$. It is then necessary to turn to methods of the third class in which agreement within a well-defined range is sought between experiment and theory according to the principles of minimum variance, but in which additional knowledge of the dependence of the process parameters upon the variables of the system is introduced.

It is clear from the examples given in this paper that methods of the third class when applied to pulse response can provide estimates of parameters to a good accuracy. It is a further merit of methods of the third class that the analysis is based entirely upon integrals of the experimental response, and the calculations may be performed upon a machine of relatively low computing power, even upon some types of desk calculator.

NOTATION

B = rate of diffusion into single particle following a unit impulse at the surface
c = concentration
$\bar{c}$ = Laplace transformed concentration
$\hat{c}$ = Fourier transformed concentration
D = particle effective diffusivity
D_L = dispersion coefficient
D_m = molecular diffusivity
d = diameter of particle
G = rate of diffusion into single particle following a unit step change at surface
h = mass (heat) transfer coefficient

H = ratio of transfer coefficient to diffusivity
K_f = mass (heat) capacity of fluid (volumetric)
K_s = mass (heat) capacity of solid (volumetric)
N = rate of diffusion into single particle
Pe = Peclet group Vd/D_L
p, q = real quantities that correspond to the Fourier transform of the rate of diffusion into unit volume of solid following a surface impulse
R = radius of particle
Re = Reynolds Group, $dU\rho/\mu$
s = Laplace transform parameter
t = time
U = superficial velocity
V = interstitial velocity
w = Fourier transform parameter
z = coordinate
γ = defined by Equation (9)

Greek Letters

η = bed porosity
θ = defined by Equation (7)
μ = viscosity of fluid
ρ = density of fluid
σ = defined by Equation (8)
ϕ = number of particles per unit volume of solid phase

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Stirred-Tank Mechanical Power Requirement and Gas Holdup in Aerated Aqueous Phases

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Gas holdup and the ratio of the turbulent regime mechanical power consumed in aerated compared to that in nonaerated aqueous phases were measured in two laboratory sized tanks. Standard six-blade turbine ($D/T = 1/3$), six-blade paddle ($D/T = 1/3$), and four-blade paddle ($D/T = 2/3$) impellers were used over a wide range of impeller rotational speed and gas sparging rate. For all systems, the power ratio results were found to fit a semitheoretical correlation (derived from dimensional analysis) involving the impeller Weber number, the aeration number, and the ratio of dispersion and liquid densities. Empirical correlations for gas holdup in water, aqueous solutions of nonelectrolytes, and an aqueous electrolyte solution are given. The overall results lead to the conclusion that power ratio and gas holdup correlations are highly specific to a particular impeller type and are also dependent on the tank size and the liquid phase physicochemical properties.

SCOPE

Gas-to-liquid mass transfer often can be the rate limiting step in stirred-tank gas absorbers, chemical reactors in which one of the reactants is a dissolved gas, and in aerobic fermentation systems. Chemical and biochemical engineers, therefore, are frequently interested in predicting the rate of absorption of a gaseous species in a stirred-tank, gas-liquid dispersion, such predictions usually being based on correlations of the overall volumetric mass transfer coefficient (K_La) with mechanical agitation power per unit volume (P_g/V) and gas sparging rate expressed as the superficial velocity. Although no universally applicable correlation is yet available, if P_g/V is known the mass transfer characteristics of gaseous dispersions in water, organic liquids, or nonelectrolytic solutions (Calderbank, 1958, 1959; Calderbank and Moo-Young, 1961), or aqueous solutions of inorganic electrolytes (Lee and Meyrick, 1970; Robinson and Wilke, 1973) can at least be estimated.

The mechanical agitation power requirement of an ungassed Newtonian liquid (P_o) can be predicted for a number of impeller types from semitheoretical correlations of power number (N_P) with impeller Reynolds number (N_{Re}) as given, for example, by Rushton et al. (1950) and Bates et al. (1962). When a stirred liquid is sparged with a gas, the impeller power input to the gas-liquid dispersion decreases compared to that of the gas free

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