On the Particle Size Distribution Function and the Attrition of Cracking Catalysts

J. E. GWYN
Shell Oil Company, Deer Park, Texas

The rate of attrition of a catalyst sample, of a single particle size, can be expressed by a simple function of initial diameter and time. The initial rate is a function of initial diameter, whereas the decrease in attrition rate of a catalyst of a given size as it ages depends only on time.

The attrition equation for a single size of particles is introduced into the particle size distribution function and, through mathematical analyses, yields a relationship for the attrition of a full size-range catalyst. The form of this relationship, which includes terms for attritability and severity of attrition conditions, is verified by laboratory and commercial attrition data on two full-range catalysts. The size distribution of an attrited sample is not expressible in simple analytical form, but is readily obtained by numerical analysis.

Dispersions, consisting of particles of a full range of sizes, introduce complexities in the analyses of even simple chemical and physical processes. In the simplest case, where the size distribution does not change and the process is a simple function of diameter, some average diameter can be derived which represents the whole dispersion. However, when the size distribution is altered by the process, the size which is representative of the process varies with time in some complex fashion. An example of this complexity has been observed in the evaporation of sprays. Here, small drops disappear very rapidly, and the mass median diameter of the remaining spray can actually increase as vaporization proceeds. In the spray drying of materials such as coffee, the dried particle size varies with drying conditions and can be larger than the liquid drop from which it came. Indeed, the relationship between initial and final properties of a dispersion process frequently appears confused by the influence of a distribution of sizes of particles.

It appears necessary to investigate these dispersion processes by including the whole population of particle sizes in the analyses. In more complex processes, numerical machine solutions will probably be required. In the problem considered here, the attrition of cracking catalyst under laboratory conditions, the equations of attrition of a full size range of catalyst are solved analytically. It is the purpose of this presentation to demonstrate the value of incorporating the size distribution function into the process equations in order to obtain the proper influence of particle size variables on the process.

EXPERIMENTAL

The attrition apparatus is based on that of Forsythe and Hertwig (*1*). The apparatus is represented in Figure 1. Attrition occurs primarily in the vicinity of the inlet orifice where high local velocities and turbulence exist. In the upper section, the cross section was enlarged and the eluting velocities reduced. For the tests made, the apparatus was operated at an air rate such that the elutriation diameter was 37 μ.

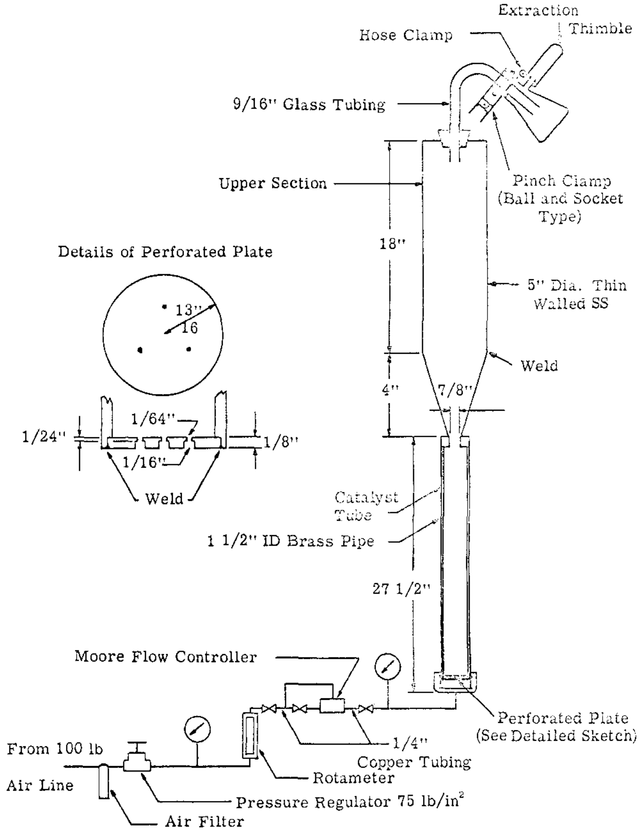

Fig. 1. Apparatus for determination of attrition.

ATTRITION OF SINGLE-SIZE PARTICLES

Screened cuts of a silica-alumina cracking catalyst were attrited in the laboratory apparatus (*1*). The cumulative size distributions of the screened cuts and the distributions of their attrited fines are shown in Figure 2. The fines from all cuts had nearly equivalent size distributions and there was little intermediate-sized catalyst. It was concluded that fines of a given narrow range of sizes are produced directly from the surfaces of the large particles (designated as being primary attrition) rather than by fracture of the particles into intermediate-sized fragments and their subsequent breakdown to fines.

The attrition changed systematically with time for each size of catalyst (Figure 3). The attrition may be represented as a simple function of time as given by:

$$W = K_p\ t^m \tag{1}$$

where W = weight fraction attrited; t = time, hr.; m = exponent, approximately constant for all catalyst particle sizes; K_p = constant, a function of initial particle size. The rate of attrition is given by the derivative:

$$\frac{dW}{dt} = K_p\ m\ t^{m-1} \tag{2}$$

Since all of the attrited particles are essentially of the

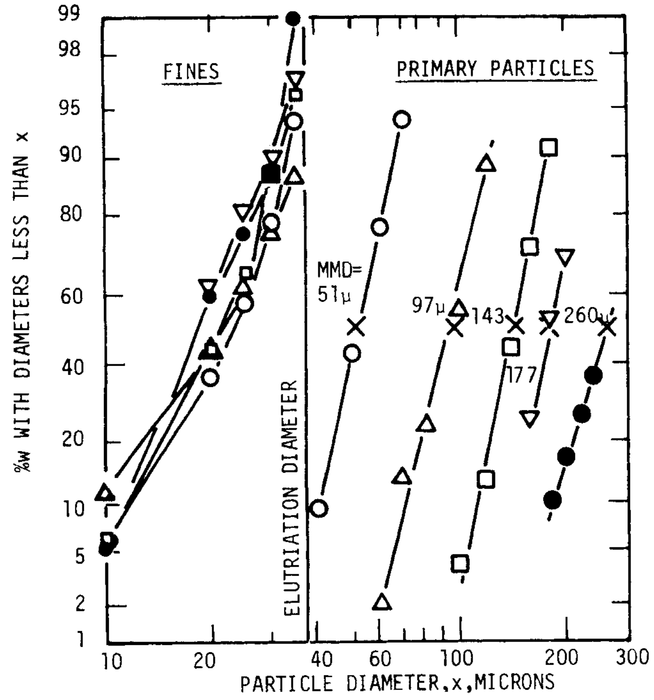

Fig. 2. Sizes in attrition of screened cuts of cracking catalyst.

same size [22μ mass median diameter (MMD) from Figure 2], the number of attrited particles is proportional to the weight attrited. That is,

$$N = K_n t^m \tag{3}$$

and

$$\frac{dN}{dt} = K_n \, m \, t^{m-1} \tag{4}$$

From Figure 3 the exponent is $m = 0.46$, and the proportionality constants, K_p, K_n, as evaluated are listed in Table I.

It is apparent that the attrition rate coefficients change in a regular fashion with the diameter of the primary catalyst (Figure 4). Accordingly, the mass rate coefficient, K_p, decreased with increasing primary diameter as given by:

$$K_p = \alpha \, x^{-2/3} \tag{5}$$

where α is a constant and $x = x_{\text{primary}}$.
Since the number of attrited fines per primary particle is related to the weight attrited by:

$$N = \frac{W x^3}{x_f^3} \quad (x_f = x_{\text{fines}}) \tag{6}$$

it follows that the number rate constant, K_n, is given by:

$$K_n = \frac{\alpha \, x^{2.33}}{x_f^3} \tag{7}$$

The number of fines per particle was, for the specific case:

$$N = 7.05 \; (10^{-5}) \; x^{2.33} t^{0.46} = a t^m \; x^c \tag{8}$$

The diameter, x_t, of a particle after attriting for time, t, is given by:

$$x_t = (x^3 - N x_f^3)^{1/3} \tag{9}$$

or

$$x_t = (x^3 - B_t x^c)^{1/3} \tag{10}$$

where:

$$B_t = a \; t^m x_f^3$$

ATTRITION OF FULL SIZE-RANGE CATALYSTS

In considering the full size-range catalysts, it is necessary to work with the number size distribution function. This follows since the number of primary particles remains constant (to the point of attrition to extinction) while the diameters, area, and volume change continually during attrition.

The particle sizes of the initial catalyst are satisfactorily represented by the log-normal size distribution function (Figure 5). The log-normal function is convenient in mathematical form and is extensively used in small particle statistics. The size distribution is:

$$F_n(x) = \int_{-\infty}^{\ln x} \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left[-\frac{1}{2\sigma^2} (\ln x - \mu)^2 \right] d \ln x \tag{11}$$

TABLE 1. ATTRITION OF CATALYST PARTICLES

$t = 23$ hr.

Primary diameter, MMD, x, in microns	51	97	143	177	260
Ratio of diameters, $\frac{x_{\text{primary}}}{x_{\text{fines}}}$	2.32	4.41	6.50	8.04	11.82
Mass ratio, $R = \left(\frac{x_{\text{primary}}}{x_{\text{fines}}}\right)^3$	12.5	85.5	274	520	1650
Mass fraction attrited in 23 hr., F	0.205	0.145	0.118	0.0967	0.0683
Number of attritions/particle $= R \times F$	2.56	12.4	32.2	50.2	112.5
Mass rate constant, $K_p = \frac{W}{4.23}$	0.0485	0.0343	0.0279	0.0229	0.0161
Number rate constant, $K_n = \frac{N}{4.23}$	0.605	2.93	7.64	11.87	26.6

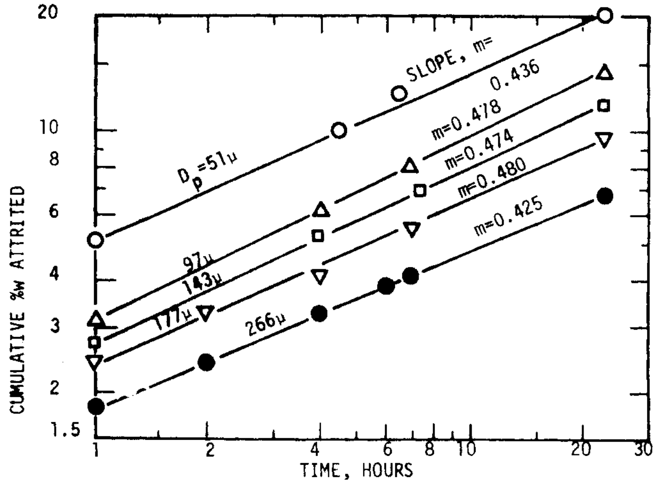

Fig. 3. Effect of particle size on attrition.

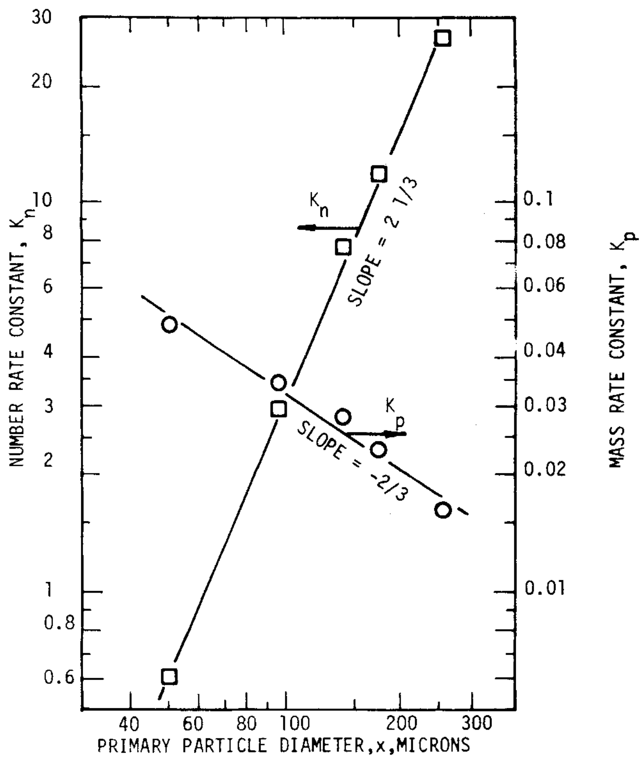

Fig. 4. Effect of particle size on attrition rates.

$$= \int_{-\infty}^{\ln x} f_n(x)\ d \ln x \qquad (11a)$$

where: $F_n(x)$ is the fraction by number of particles whose diameters are x or less.

$$\mu = \int_{-\infty}^{\infty} \ln x\, f_n\,(x)\ d \ln x = \ln x_{50}$$

$$\sigma^2 = \int_{-\infty}^{\infty} [\ln x - \mu]^2 f_n\,(x)\ d \ln x$$

$$\sigma = \ln x_{84.13} - \ln x_{50}$$

The mass (assuming constant particle density) is represented by multiplying each particle by x^3 to give:

$$M_x = \int_{-\infty}^{\ln x} x^3 f_n\,(x)\ d\ln x \qquad (12)$$

The total mass is represented by integration over the limits

$$M = \int_{-\infty}^{\infty} x^3 f_n\,(x)\ d\ln x \qquad (13)$$

If x^3 is expressed in the exponential form, $x^3 = \exp[3 \ln x]$, for the log-normal case,
Equation (13) yields

$$M = \exp\,[3\mu + (9/2)\sigma^2] \qquad (14)$$

The mass after attrition for time, t, is

$$M_t = \int_{-\infty}^{\infty} x_t^3 f_n\,(x)\ d\ln x \qquad (15)$$

or

$$M_t = \int_{-\infty}^{\infty} (x^3 - B_t x^c)\ f_n\,(x)\ d\ln x \qquad (16)$$

which gives:

$$M_t = \exp\,[3\mu\ (+\ 9/2)\sigma^2] - B_t \exp\,[c\mu + (c^2/2)\ \sigma^2] \qquad (17)$$

The mass attrited is

$$M_a = M - M_t = B_t \exp\,[c\mu + (c^2/2)\ \sigma^2] \qquad (18)$$

The mass fraction attrited is

$$W = M_a/M = B_t \exp\,[(c-3)\ \mu + (c^2/2 - 9/2)\sigma^2] \qquad (19)$$

or

$$-\ln W = (3-c)\ \mu + (9/2 - c^2/2)\sigma^2 - \ln B_t \qquad (20)$$

or in terms of mass median diameter, $\mu_{y3} = \ln$ (MMD)

$$-\ln W = (3-c)\ \mu_{y3} - 1/2\ (3-c)^2\, \sigma^2 - \ln B_t \qquad (21)$$

Since $B_t = at^m x_f^3$, it follows that

$$-\ln W = (3-c)\ \mu_{y3} - 1/2\ (3-c)^2 \sigma^2 - \ln a - 3 \ln x_f - m \ln t \qquad (22)$$

$$-\ln W = (2/3)\ \mu_{y3} + 2/9\, \sigma^2 - \ln a - 3 \ln x_f - m \ln t \qquad (22a)$$

or

$$-\ln W = \gamma - m \ln t \qquad (23)$$

Thus, for attrition by the direct production of fines from the surface of primary particles, the log-log plot of weight attrition vs. time is expected to be a straight line for a distribution of particles in the same fashion as it was for uniformly sized particles.

APPLICATION TO DATA ON FULL-SIZE RANGE CATALYSTS

The form of Equation (23) is verified by laboratory and commercial attrition data (Figures 6 and 7, respectively). The laboratory data are for two full size-range (> 75μ) fresh catalysts under fairly severe attrition conditions. The same catalysts were used for the commercial tests. The commercial tests cover the period after the catalyst has been in the unit for one day and has lost about 75% of its surface area and 50% of its pore volume. An additional

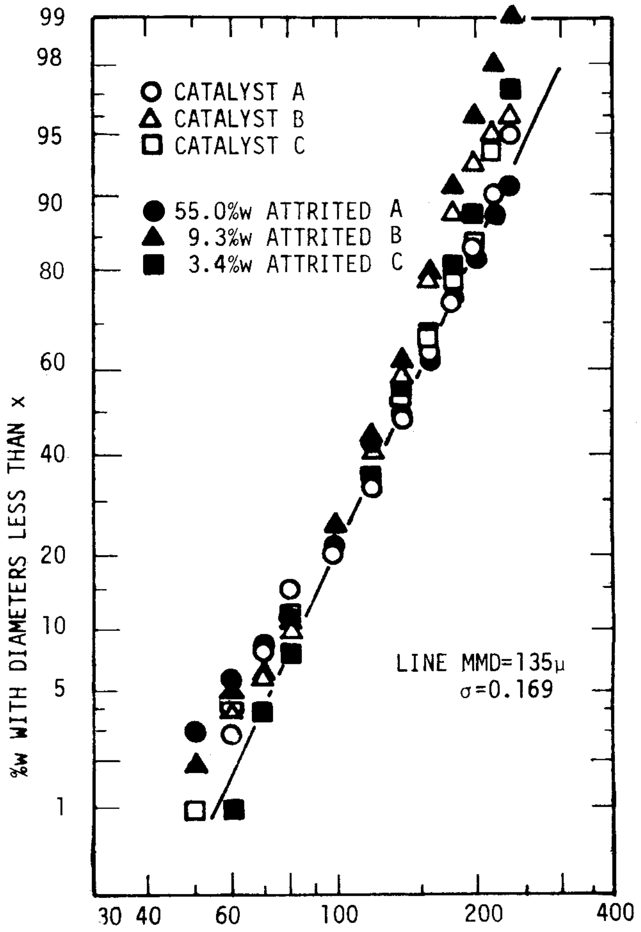

Fig. 5. Particle size distribution of three similar cracking catalysts.

difference between the laboratory and commercial tests is the milder attrition conditions in the commercial unit. Although the laboratory data do not predict the commercial results under the greatly different conditions, all of the data conform to Equation (23).

Change in Size Distribution Function

The size distribution at any given time, t, does not enter into attrition calculations since attrition rate is related to initial particle diameter only. This is indeed fortunate since the form of the size distribution function does not remain a simple analytical function during attrition.

The size distribution function can be evaluated numerically as follows. The cumulative mass fraction in terms of initial diameter x, is given by Equations (16) and (17).

$$F_m(x) = \frac{\int_{-\infty}^{\ln x} x^3 f_n(x)\, d\ln x - \int_{-\infty}^{\ln x} B_t x^c f_n(x)\, d\ln x}{\exp\,[3\mu + (9/2)\sigma^2] - B_t \exp\,[c\mu + (c^2/2)\sigma^2]} \qquad (24)$$

The initial diameter of a particle and its diameter at time, t, are related through Equation (10).

$$x_t = (x^3 - B_t x^c)^{1/3} \qquad (10)$$

Thus the size distribution as a function of time, t, is obtainable through numerical analyses of Equations (10) and (24).

It should be noted that attrition must occur to a considerable extent before a size distribution differs considerably from its initial distribution as evaluations of Equations (10) and (24) have indicated. Figure 5 indicates experimental evidence of this conclusion. Thus, changes in particle size distribution were not good tests of the attrition equations.

CONCLUSIONS

Equation (22) enumerates the important factors for primary attrition as investigated in laboratory equipment. These are:

1. Both the average particle size and the spread in sizes of the initial particle size distribution affect attrition rate. When the initial distribution can be represented by a log-normal distribution, the mass median diameter (antilog of μ_{y3}) and geometric standard deviation (antilog of σ) can be used to describe these effects.

2. The average of the attrited fine diameter, x_f, is presumably a function of the agglomerate structure of a catalyst and is directly measurable. If the elutriation diameter had been less than the diameter of the primary fines then consideration of secondary attrition would have been necessary.

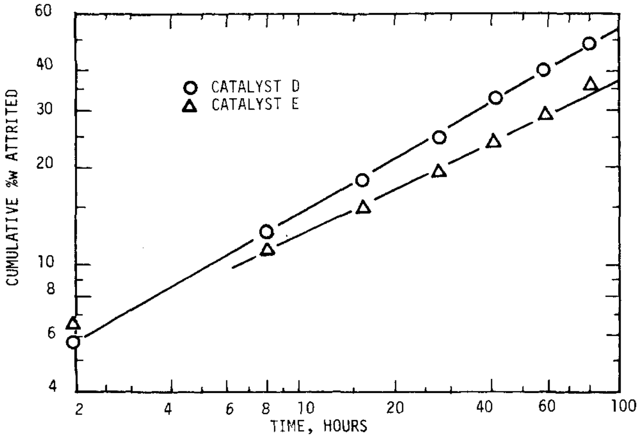

Fig. 6. Laboratory attrition of tagged catalyst.

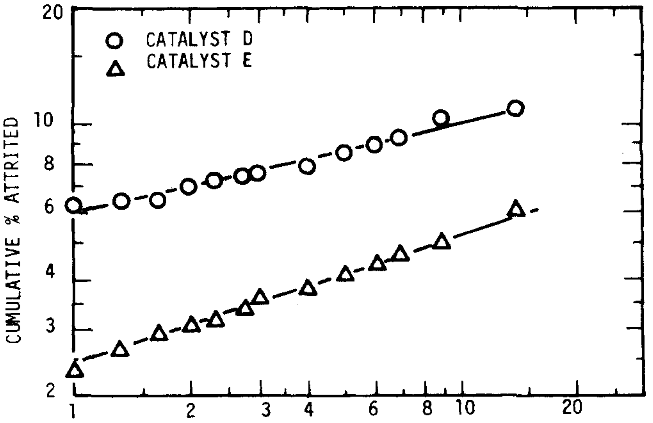

Fig. 7. Attrition of tagged catalysts in a commercial catalytic cracking unit.

3. The constant, a, in Equation (22) appears to include the severity of attrition conditions and the initial attritability of the catalyst. The constant, m, appears to be a measure of the decrease in the attritability of the catalyst with age. Thus, these two constants are related to both the physical qualifications of the catalysts and the amount of abrasive activity in the unit in which attrition occurs.

Equation (22) serves as a basis for comparison of catalysts and indicates the importance of the size distribution function in attrition.

ACKNOWLEDGMENT

The author wishes to thank the Shell Oil Company for permission to publish these results.

NOTATION

a = dimensional constant = α/x_f^3
α = proportionality constant
B_t = $at^m x_f^3$, multiplier, function of time, t
c = exponent of diameter effect on attrition
d = derivative operator
$F_n(x)$ = cumulative number distribution; fraction of total number of particles with diameters $\leqq x$
$F_m(x)$ = cumulative mass distribution
$f_n(x)$ = frequency number distribution, $f_n(x) = \dfrac{dF_n(x)}{d\ln x}$
fines = subscript for small diameter particles attriting from primary particles
K_n = dimensional constant, units t^{-m}, in number rate equation
K_p = dimensional constant, units t^{-m}, in mass rate equation
ln = $\log_e$
m = exponent for time dependence of attrition
M = total mass of particles
M_a = mass attrited at time, t
M_t = mass remaining at time, t
M_x = mass of particles with diameters $\leqq x$
MMD = mass median diameter
μ = ln mean diameter basis number distribution $\equiv$ ln x when $F_n(x) = 0.5$
μ_{y3} = ln mean diameter basis mass distribution = ln(MMD)
N = number of small particles attrited from a single larger particle
primary = subscript for particle from which fines are attriting
R = mass ratio

σ = standard deviation of size distribution in ln units
t = time
W = weight fraction attrited
x = particle diameter in microns
x_f = diameter of fine particles
x_t = diameter of primary particle after attriting for time t
84.13, 50 = subscripts, percentage levels of cumulative size distribution

LITERATURE CITED

1. Forsythe, W. L., Jr., and W. R. Hertwig, *Ind. Eng. Chem.*, 41, 1200 (1949).

Manuscript received May 10, 1967; revision received December 8, 1967; paper accepted January 10, 1968.

An Approximate Solution for Countercurrent Heat Exchangers

CHI TIEN and SESHADRI SRINIVASAN

Syracuse University, Syracuse, New York

An approximate solution is presented for the countercurrent parallel plate exchanger with laminar flow. With the use of the integral method, the problem is reduced to one of solving a pair of first-order differential equations in a straightforward manner. Comparisons between the results of this work and those obtained from a more elaborate orthogonal expansion technique are found to be excellent.

Counterflow heat exchangers are extensively used for a variety of applications. Nevertheless, detailed analytical studies of this type of operation have been absent until very recent years. A finite-difference solution on countercurrent mass transfer was first given by King (*3*). Nunge and Gill (*7, 8, 9*), and Stein (*10, 11*) independently obtained an analytical solution for laminar counterflow heat exchangers (parallel plate as well as double pipe). These authors succeeded in generalizing the classical Graetz solution for single stream to the case of two streams in counterflow. The analysis requires the use of denumerable sets of both positive and negative eigenvalues. This approach has been considered to be mathematically correct by Blanco (*1*) who based his argument on the earlier work of Mason (*5, 6*). A check of the references indicate that the problem considered by Mason (*6*) and the counterflow problem are similar but not identical, except for the special case of negligible interphase resistance, that is, $K_w = 0$. Consequently, one cannot accept the validity on the use of this orthogonal expansion technique with absolute certainty to cases where interphase resistance is significant.

In terms of computation, the Nunge-Gill approach requires the solution of an infinite matrix for the evaluation of expansion coefficients. Their suggested method, however, was found unsatisfactory by Stein (*12*) who attempted the solution of the plug flow case by using the Nunge-Gill procedure. Instead, Stein offers an alternative method (named *Argonne Procedure*) for the calculation of expansion coefficients. In a recent note, Blanco, Gill, and Nunge (*2*) pointed out that the difficulty involved in the evaluation of expansion coefficient using the so-called "Nunge-Gill procedure," is only limited to the case of plug flow. For the general case of laminar flow, both procedures yield essentially the same results. Although it is entirely likely that one particular procedure may be more suitable for certain cases, no theoretical argument has been advanced by these authors, which enables the selection of a proper procedure for a given application.

In addition to the proper choice of a numerical procedure for the computation of expansion coefficients, there also exist some other limitations on the use of this orthogonal expansion technique for the detailed study of countercurrent heat exchangers as pointed out elsewhere (*1*). First, like the Graetz problem, the series expansions are slow in convergence for small longitudinal distances and require more terms than can be accurately calculated. Also, as the longitudinal distance increases, due to the rapid increases in values of the exponential function associated with the negative eigenvalues, increasingly fewer terms can be included in the equations from which the expansion coefficient can be calculated. On the other hand, because of the large number of physical parameters involved in the counterflow problem, it is impractical to make calculations for all cases of interest and obtain a so-called "master plot". Instead, calculation has to be made for each specific application. Because of these considerations, it seems desirable to consider an alternative approach to this problem in spite of the theoretical elegance of the Nunge-Gill method.

The object of our work is to present an alternative method to the solution of countercurrent heat exchangers, although the result can be readily adapted to mass transfer apparatus such as hemodialyzer. The approach consists of the use of the integral approximation which reduces the energy equations into a pair of first-order differential equations. The use of the integral approximation eliminates one independent variable (the transverse direction across the conduit) by direct consideration. Furthermore, if one treats the length of the exchanger as a dependent variable and considers the problem as one in which the size of the exchanger is to be determined for a given heat transfer requirement, then the two first-order equations can be numerically integrated in a straightforward manner, thus circumventing the difficulty of matching the inlet condition for both streams at the opposite ends of the exchanger, as required by the previous investigators. The integral approach has been found satisfactory in the solution of cocurent hemodialyzer (*13*). Apparently, some of the earlier investigators had considered the possibility of employing an integral method for the solution of counterflow exchangers (*4, 5*); however, for some unspecified reason, this approach was not fully explored.

Seshadri Srinivasan is at the University of Dayton, Dayton, Ohio.