A Probabilistic Time Delay Description of Flow in Packed Beds

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A simple model for describing residence time distributions (RTD) in packed beds is derived and applied to a trickle flow system. It is based on the concept of fluid elements being randomly delayed in time on their passage through the bed and leads to a simple and flexible mathematical description.

In this paper, we take a fresh look at factors governing the distribution of residence times of material flowing continuously through packed bed systems. The picture presented is simple and physically plausible with obvious application in a wide variety of continuous processes. It is based on the abstraction that material would flow uniformly (in plug flow) through the system were it not that elements have a chance of being detained at all points of their passage; an element so detained eventually rejoins the main stream after a period of time, the time delay, has elapsed. The cumulative effect of the individual time delays is to distribute the total residence times in some manner.

For the most simple case in which delayed elements are all delayed for the same time t_D, a mass balance on a differential element of bed length (Figure 1) yields

$$A \frac{\partial c}{\partial t}(x,t) = -F \frac{\partial c}{\partial x}(x,t) + f\,c(x,t-t_D) - f\,c(x,t) \quad (1)$$

This description leads to a family of models mutually differentiated by their delay time distributions. For any particular distribution, the model parameters will depend solely on the probability of a delay occurring and the average time for which elements are delayed. The mechanism is analogous to that of surface renewal in the penetration theories of mass transfer, in which fluid elements that find their way to the surface are detained and then returned to the bulk fluid. In the time-delay model, this effect is distributed through the system; bulk material flows at a uniform rate, while the delayed elements have negligible velocity in the direction of the main flow.

This way of looking at the problem has certain very clear advantages over the usual models based on analogies with diffusion theory. These are discussed later, and it will be shown that time-delay models retain their mathematical simplicity when elaborated to suit particular physical situations. This is not so with diffusion models. The mathematically delicate (although often physically irrelevant) problems concerning choice of boundary conditions for diffusion models do not arise in the time-delay treatment. Also, the physical mechanisms resulting in the spread of residence times are often more accurately described by time delays then by diffusion.

The trickle bed is a good example to illustrate the concepts involved. Consider a packed bed down which liquid flows in the form of a highly distorted film partly covering the packing; there are stagnant regions at points of contact in the packing, between the packing and the walls, and on horizontal surfaces. Downward flow takes place mainly in the film; the effect of the slow flow in the almost stagnant regions is to remove some of the liquid from the film and return it some time later.

Different tracer elements will be delayed more or fewer times, depending on the path they take; some will pass through faster than all the others, there being an absolute minimum transit time through the bed. With respect to this minimum, delay occurs because not all of the main stream moves at the same speed, not all the paths are of the same length, and so on. Stream splitting causes lateral mixing, so that if entry into a lateral pore is relatively rare, after effects will be relatively unimportant. This is idealized by assuming perfect lateral mixing of the main stream. At any axial position, the behavior of particles that have been delayed is indistinguishable from those that have not. It is assumed that all hydrodynamic mechanisms can be accounted for in this way by suitably choosing the distribution of delay times. Clearly, the process of diffusion into pores can be described in a simliar way by introducing extra microscale lateral flows superimposed on the hydrodynamic lateral flows. The role of lateral diffusion in the main stream is to put the assumption of perfect lateral mixing on a sounder basis, while it is assumed that the effects of axial diffusion can be lumped into the general delay process.

PROBABILISTIC TREATMENT

If the input to the system is a unit impulse, the output is identical with the residence time distribution, a concept which is meaningful without any probabilistic interpretation. However, one can imagine a tracer experiment being carried out with a single tracer molecule, in which case the result of the experiment would be random. A tracer impulse test can be regarded as the simultaneous performance of an extremely large number of single-molecule experiments, so that the measured impulse response may be regarded as a frequency diagram for many individual-molecule experiments.

The probabilistic treatment of the time-delay model falls into two independent parts: establishing the distribution of the number of times a particle stops, and then assessing the effect of the random nature of the delay

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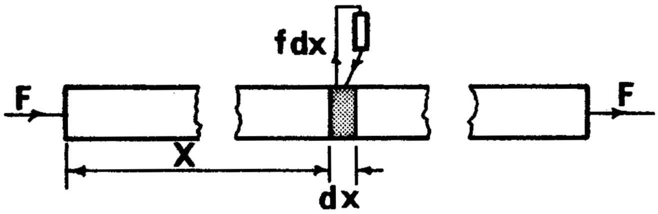

Fig. 1. Time-delay model.

process itself. Generally, there will be several ways in which a tracer particle can pass through the bed in a given time; the probabilities of these ways must finally be combined.

The Stopping Process

With reference to Figure 1, the proportion of tracer particles arriving at x that enters lateral pores in the bed zone $(x, x + dx)$ is $f\,dx/F$. This may be restated in terms of probability by saying that the probability of a particle which has arrived at x entering a lateral pore in $(x, x + dx)$ is $f\,dx/F$. As there is no need to interpret the original model too literally, suppose merely that the stopping probability is αdx, where α is a constant to be identified empirically, or perhaps related to other concepts in a separate theoretical exercise.

Stopping is a random process, and the number of stops n can only take nonnegative integral values. Discrete random processes of this type are the basis of many branches of applied probability theory, for example, queueing theory. The random events considered are usually sequential in time rather than in space, but this makes no difference to the mathematical analysis. When the conditional probability of an event occurring in an increment dx of the independent variable x is αdx, the probability of the number of events occurring in $(0, x)$ being n is given by

$$p_n(x) = \frac{(\alpha x)^n}{n!} e^{-\alpha x}. \qquad (2)$$

that is to say n is distributed in a Poisson distribution with parameter αx. This result is presented in any text on stochastic processes and very clearly by Cramer and Leadbetter (*1*).

The Delay Process and Residence Time Distributions

In statistical treatments of processes in which a prototype process is repeated many times, the final result is not very sensitive to the detailed description of the prototype. In order to predict residence time distributions as simply as possible, the pore residence time distributions should be simple and easily combined. In view of the analogy between the time-delay model and the surface renewal models of steady state mass transfer and the success of those models, suitable choices for the pore residence time distribution include the impulse distribution (Higbie's model) and the exponential distribution proposed by Danckwerts (*2*). Physically, these distributions correspond to the pores or pockets being regions of either plug flow or perfect mixing. This is not to say that these conditions exist physically, but merely that the observed behavior can be described in this way. For instance, a situation in which perfect mixing obtains in the pores is indistinguishable from plug flow in pores where the residence times are exponentially distributed owing to differences in lateral flow rates and pore sizes.

Fixed Time Delays. For those tracer elements which make n stops in their journey through the bed, the total delay time is the sum of n independent observations from the pore residence time distribution. For the case of plug flow pores, the sum of n independent observations is nt_D, and those tracer elements that are delayed n times emerge from the bed after a residence time $t_0 + nt_D$. Therefore, the probability of an element emerging after time t is given by

$$p(t) = \frac{(\alpha x)^n}{n!} e^{-\alpha x}$$

where

$$n = \frac{t - t_0}{t_D}$$

It follows that the residence time distribution $\phi\,(t)$ may be written as

$$\phi\,(t) = e^{-\alpha x} \sum_{n=0}^{\infty} \frac{(\alpha x)^n}{n!} \delta\,(t - t_0 - nt_D) \qquad (3)$$

where $\delta\,(\ )$ is the Dirac delta function.

Exponentially distributed time delays. The sum of n independent observations θ from an exponential distribution with mean t_D has the probability density function

$$g_n(\theta) = \frac{t_D^{-n}\,\theta^{n-1}}{(n-1)!} e^{-\theta/t_D} \qquad (4)$$

as may be easily established by an n fold convolution of exponentials, or by considering the physical analogue of n stirred tanks.

The total delay-time distribution is obtained by weighting the $g_n(\theta)$ by the $p_n(x)$ and by summing over all values of n. The justification for this procedure is that the probability of both being delayed n times and being delayed for a total time in the interval $(\theta, \theta + d\theta)$ is $p_n\,(x)\,g_n\,(\theta)\,d\theta$ by the multiplication rule for conditional probabilities; since the ways of being delayed for this time in different numbers of stops are mutually exclusive, the probability regardless of n is obtained by summing over all possible values of n. The residence time distribution is obtained by displacing the total delay-time by t_0, with the result

$$\phi\,(t) = 0\,, t < t_0$$

$$= \frac{e^{-(\alpha x + t^*/t_D)}}{t^*} \sum_{n=0}^{\infty} \frac{(\alpha x t^*/t_D)^n}{n!\,(n-1)!}\,, t \geqq t_0 \qquad (5)$$

where $t^* = t - t_0$. The first term in the series is an impulse which is usually negligible in practice, so that Equation (5) could be expressed in terms of a Bessel function.

Normalization. It is often convenient, especially when dealing with experimental data, to express RTD's in normalized form by converting the time scale to units of the mean time. To preserve the unit area property of the RTD, the frequency density is multiplied by the mean time. The mean or expectation is defined by

$$\bar{t} = E(t) = \int_0^{\infty} t\,\phi\,(t)\,dt$$

The expectation of a sum is the sum of the expectations of the components of the sum so, that

$$E(t) = t_0 + E(t^*)$$

Because the distribution of t^* is made up of infinitely many distributions with weighting factors $(\alpha x)^n\,e^{-\alpha x}/n!$ and expectations nt_D

$$E(t^*) = \sum_{n=1}^{\infty} \frac{(\alpha x)^n}{n!} e^{-\alpha x}\,nt_D \qquad (6)$$

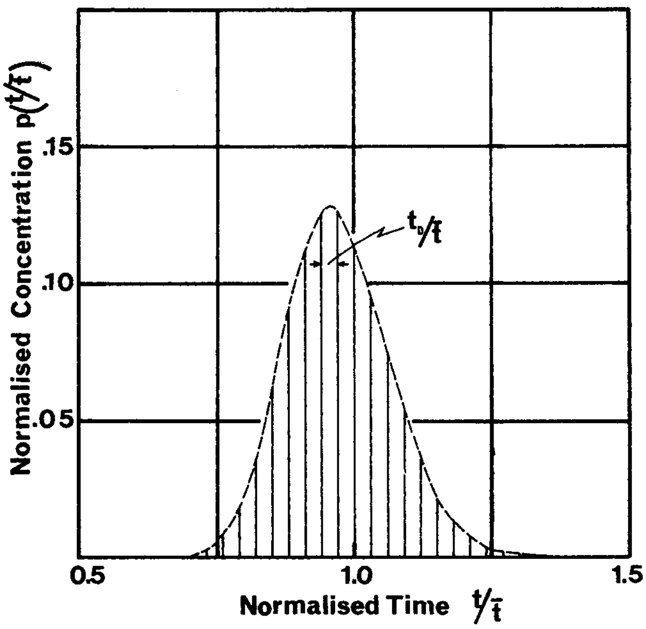

Fig. 2. Time-delay model: fixed time delays for $\alpha x = 10$; $t_0/\bar{t} = 0.7$.

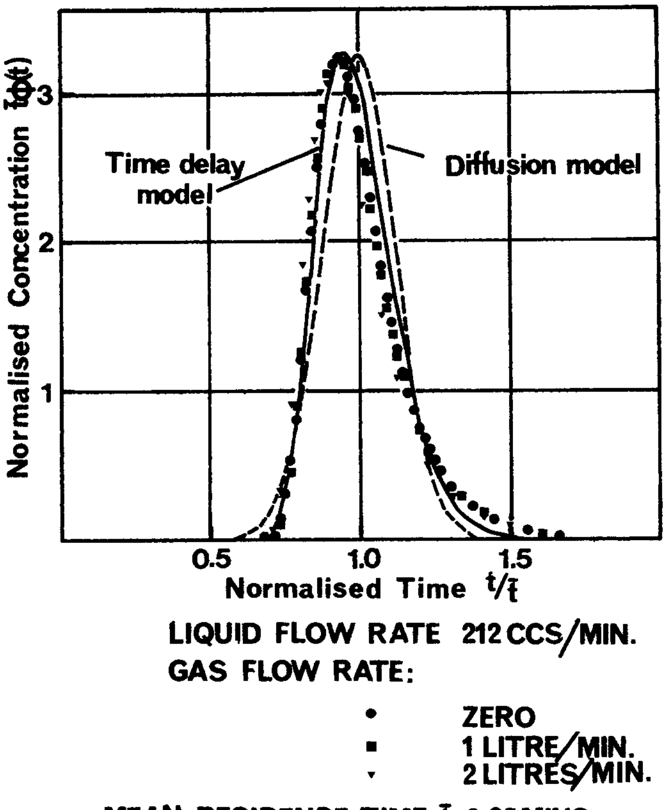

Fig. 4. Comparison of normalized response curves with time-delay model (exponentially distributed delay times) and diffusion model.

a result that is independent of the delay time distribution. Hence

$$\bar{t} = t_0 + \alpha x\, t_D \tag{7}$$

Often the mean time may be measured independently of the RTD; it is equal to the ratio of the total volume through which flow takes place to volumetric flow rate. If this condition is to be met, there are only two adjustable parameters which may be chosen arbitrarily from $t_0/\bar{t}$, $t_D/\bar{t}$, and αx.

As the number of stops a fluid element makes while traveling a distance x is a random variable with the Poisson distribution, Equation (2), the expected number of stops is equal to the Poisson parameter:

$$E(n) = \alpha x \tag{8}$$

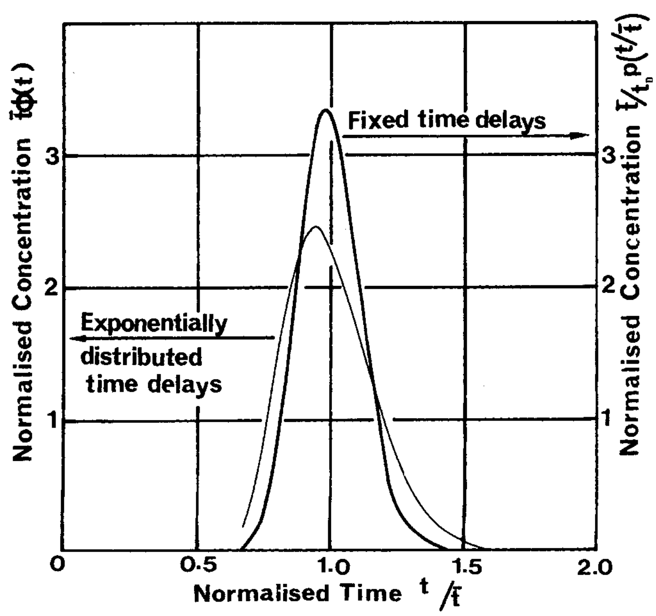

Fig. 3. Time-delay models: normalized solutions $\alpha x = 10$; $t_0/\bar{t} = 0.62$.

Figure 2 shows a model response for fixed time delays. It consists of a series of impulses of strength $p(t/\bar{t})$ separated by $t_D/\bar{t}$. Figure 3 compares the fixed time-delay solution with that for exponentially distributed delays under otherwise identical conditions; for purposes of comparison, the fixed time-delay case has been plotted as a continuous curve in such a way as to maintain the unit area property.

APPARATUS AND EXPERIMENTAL PROCEDURE

The column consisted of 1½-in. diameter glass tubing packed with ⅛-in. ceramic Raschig rings. Metered air and water were supplied to distributors at the bottom and top of the column, respectively.

Residence time distributions were obtained by a simple dye injection technique. The tracer concentration in the liquid effluent, following an injection of nigrosene dye in the inlet water stream, was measured by means of a photocell detector whose output was logged on punched paper tape at ½-sec. intervals. This was processed on a digital computer to produce the normalized response curves. Runs were carried out at various liquid and gas flow rates for two column lengths.

The injection time was of the order of 1 sec. and so regarded as a true impulse. The mean residence time in the detector was also found to be negligible, about 1% of the total.

EXPERIMENTAL RESULTS

To observe the effect of liquid and gas rates on the liquid side RTD, normalized response curves were plotted. As was expected, the spread decreased with increasing liquid flow rate. The effect of gas rate was found to be negligible, Figures 4 and 5, which confirms the reported results of Sater (3).

The solution of the diffusion model having the same

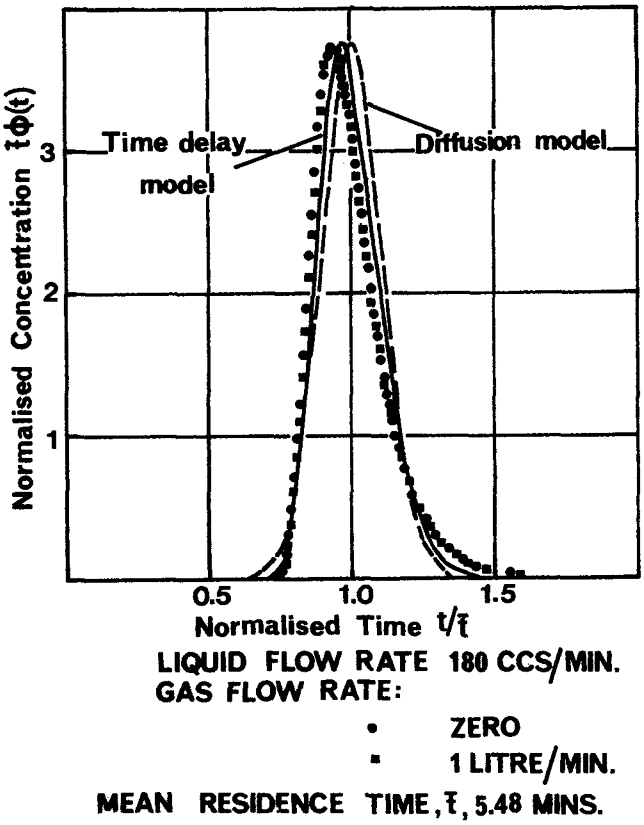

Fig. 5. Comparison of normalized response curves with time-delay model (exponentially distributed delay times) and diffusion model.

peak response and the time-delay model with exponentially distributed delay times indicated that the latter model represents a considerable improvement in describing the responses.

Figures 4 and 5 are typical. The initial sharp rise is well fitted, and the slowly decaying long time response of the model solution comes close to that which is obtained in practice, particularly at high liquid flow rates.

Table 1 summarizes the results of eleven runs under widely varying conditions. It is interesting to note that the parameter α which measures the ratio of the lateral flow rate per unit length to the axial flow rate remains remarkably constant; the average value of α was found to be 1.32, with a standard deviation of less than 0.04. The corresponding term in the diffusion model D shows considerable scatter, no clear trend being discernable.

EVALUATION OF MODEL PARAMETERS FROM EXPERIMENTAL RESPONSE CURVES

To evaluate the response of the model, precise values of the normalized dead line $t_0/\bar{t}$ and the parameter αx are required. While in principle the dead time and peak height can be used to determine these values, in practice the true dead time is unobservable owing to the insensitivity of the detector at very low tracer concentrations.

To overcome this difficulty, an apparent dead time $t_0'/\bar{t}$ has been defined. It is taken to be the time at which the normalized concentration reaches 0.05; to relate this to the true dead time, two sets of curves have been prepared. Figure 6 relates the peak height to the apparent dead time $t_0'/\bar{t}$ and Figure 7 the true dead time $t_0/\bar{t}$ to the apparent dead time, both for different values of αx.

So, to obtain the model parameters $t_0/\bar{t}$ and αx, the apparent dead time $t_0'/\bar{t}$ and the peak height are obtained from the normalized response curve. Figure 6 is then used to obtain a value for αx.

This value of αx may be used to find the true dead time $t_0/\bar{t}$ from Figure 7.

COMPARISON WITH OTHER MODELS

In this section we examine how the time-delay ap-

TABLE 1.

Run No.	Bed length, x, ft.	Liquid flow rate, cc./min.	Gas flow rate, liters/min.	Mean residence time, $\bar{t}$, min.	Dispersion No., D/UL	Apparent dead time, $t'_0/\bar{t}$	True dead time, $t_0/\bar{t}$	αx	α
1.1			0						
1.2	10.5	46	1	11.10	0.0140	0.619	0.5560	14.0	1.33
2.1			0						
2.2	10.5	51	1	7.55	0.0128	0.613	0.5650	13.0	1.24
3.1			0						
3.2	10.5	99	1	5.40	0.0090	0.683	0.6250	14.7	1.40
4.1			0						
4.2	10.5	128	2	4.15	0.0078	0.689	0.6400	14.0	1.33
5.1			0						
5.2	10.5	212	1	3.25	0.0076	0.710	0.6665	14.0	1.33
5.3			2						
6.1			0						
6.2	10.5	364	2	2.20	0.0065	0.730	0.6895	14.0	1.33
7.1			0						
7.2	15.5	120	1	7.40	0.0068	0.7150	0.6360	20.5	1.32
8.1			0						
8.2	15.5	180	1	5.48	0.0056	0.735	0.6500	20.5	1.32
9.1	15.5	240	0	4.46	0.0050	0.748	0.6680	21.0	1.35
10.1	15.5	300	0	3.85	0.0046	0.757	0.6795	21.0	1.35
11.1	15.5	360	0	3.42	0.0041	0.774	0.7080	20.0	1.29

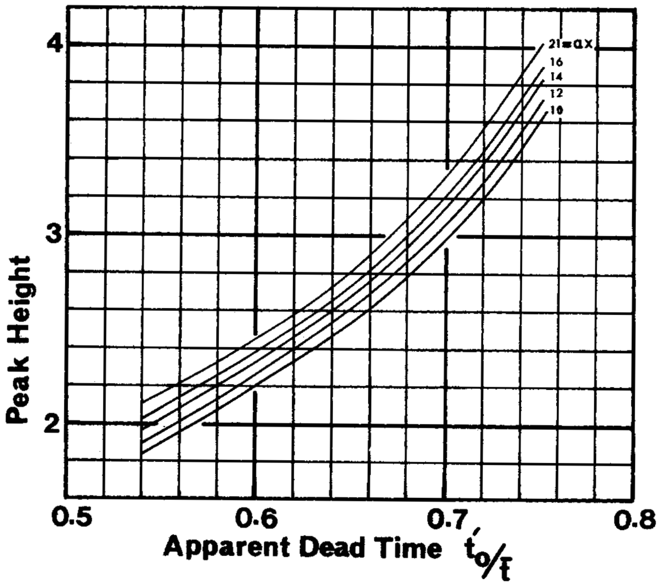

Fig. 6. Determination of αx from experimental response curve.

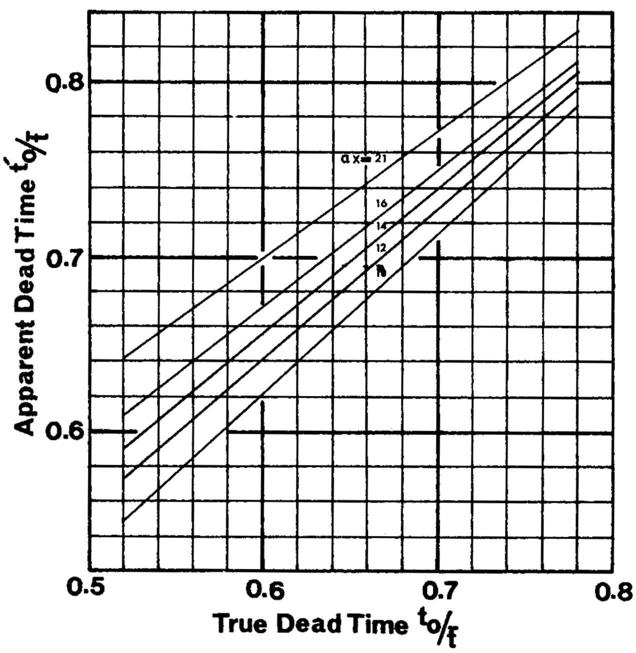

Fig. 7. Determination of true dead time $t_0/\bar{t}$ from experimental response curve.

proach is related to previous models of similar intent. The principal distinguishing features of the time-delay model are that is is one dimensional spatially, uncomplicated by boundary conditions, and based on a mechanism that is nonspecific in terms of physical properties. The object in formulating a model with these characteristics is to enable a wide variety of processes to be treated in the same way by suitably choosing the parameters. The ultimate aim is to make a priori predictions of the parameters in particular cases.

The diffusion model of Levenspiel and Smith (*4*) has as its underlying mechanism shuffling of flow elements backwards and forwards relative to the main flow. Negative flow element velocities are not precluded. In contrast, the time-delay approach assigns a constant velocity or zero velocity to a particle at any instant. The effect is that although a flow element is moving either slower or faster than the average velocity, the conceptional difficulties of the diffusion model do not arise. These problems are of identification; it is not possible to establish the magniture of the flux from the concentration, because an instrument sensing concentration cannot distinguish the direction in which flow elements are traveling. Even if both the concentration and its gradient are measured, the resulting net flux estimate includes the effects of flow elements moving in both directions. The result is that the boundary conditions cause grave difficulty, and the impulse response and RTD are not the same. Except, that is, in the special case, where the diffusion mechanism does not operate across the boundary, the so-called *closed-closed case*. Mathematically, the particular time-delay derivations presented above are less complex than solutions of moving diffusion equations. A further advantage is that a second parameter is introduced in a natural way which enables the skewness of the RTD to be adjusted for a fixed variance. Klinkenberg's (*5*) method of adding variances can be used to introduce a second parameter into the one-dimensional diffusion model to achieve a similar result. A dead time is combined with diffusive mixing, so that to obtain the same value of the relative variance, a higher dispersion number, and consequently more skewness, is required. Physically, the interpretation is that the diffusive mixing process operates for a time equal to the elapsed time less the dead time. An alternative procedure is to consider that the mixing process only operates for a proportion of the elapsed time. This idea may be incorporated into the mathematics merely by multiplying time in the diffusion equation by a constant, but the boundary condition problems remain. Which method to adopt should be dictated by the process considered. The time-delay approach is more natural for trickle flow.

The earliest work on column dynamics was the investigation of heat transfer between a flowing medium and the packing. The classical model considers plug flow of the fluid and heat exchange between the solid and fluid at a rate proportional to the difference of their temperatures, each of which is uniform at a particular axial position. The solution of this problem was due to Anzelius (*6*) and now appears in most texts on heat transfer. This model becomes a fluid mixing model on replacing enthalpy by concentration and on considering the two phases to be identical. The model so obtained is identical with the time-delay model with exponentially distributed delays, the reason being that as they are characterized only by their concentrations, the phases are tacitly assumed to be locally well mixed, precisely the assumptions of the exponential time-delay model. Giddings (*7*) coupling theory of chromatography leads to the same Bessel function solution and is closer in spirit to the time-delay approach.

A third model that is worthy of mention is the Deans cell model (*8*). This is a modification of the well-known tanks-in-series model in which the effects of stagnant regions are taken into account by attaching to each cell a second well-mixed cell through which fluid recycles. It is of particular interest in the present context because it can be reduced to either the Gaussian or Bessel function form by suitably choosing the limiting process. If the number of stages is increased with the volume and the flows are kept constant, the stages become progressively more like well-stirred tanks and the response more Gaussian and finally plug flow. Alternatively, the number of stages may be increased, keeping the volume and the interstage flows constant and reducing the recycle flows proportionately to the inverse of the number of stages.

When this is done, the time constant for the delays in the stagnant regions is constant, and in the limit the exponential time-delay (or Anzelius) model results.

The ability of the various models to represent observed RTD's depends primarily on the number of parameters, but usually one will seem more appropriate in the light of qualitative background information about the process. Even when a model is found to be compatible with observed RTD's, this does not prove the existence of the postulated mechanism. More subtle experiments, such as the carrying out of reactions with nonlinear kinetics, are required.

DISCUSSION

It is clear that a considerable improvement over the one-dimensional dispersion model has been achieved; the constancy of α over the widely varying conditions is particularly striking and suggests the form of the model to constitute an even more reliable description than the direct comparison of responses would indicate.

The two parameters of the time-delay model are easy to identify with the aid of Figures 6 and 7; although the moments of the model response can be easily obtained, the parameter matching method described above is preferable to moments matching which places undue weight on the tail of the curves.

The model, although semiempirical in application, results from a reasonable interpretation of flow behavior in packed bed systems. The mixing mechanism can be variously ascribed to lateral bulk flow, as would appear to predominate in the physical system here considered, lateral diffusion, and even to physical adsorption at the solid/fluid interface. The form of the model remains identical, the total effect of these different mechanisms being lumped together in the parameter αx and the distribution of delay times.

If the postulated random stopping process really exists, the effect of the distribution of delay times could be considerable, as indicated by Figure 3. The average number of stops, Equation (8), for both cases illustrated is ten, but the curves are significantly different. However, if it is not required that αx be the same for both cases, very similar responses can be obtained by suitably adjusting this parameter. The variants of the model are thus difficult, if not impossible, to identify solely on the basis of RTD's. This is analogous to the situation encountered in surface renewal processes where, as here, the mechanism can be usefully applied regardless of the distribution of life times of surface elements (2).

Although the model has been used purely for describing experimental response curves, it may be often possible to make predictions concerning the axial mixing on the transport processes; this requires some knowledge of the location of the most probable delay zones in relation to the transport interface. Elements delayed close to this interface are likely to be of primary significance, while for systems where the delays occur in isolation from the transfer surface, the steady state behavior may be virtually unaffected by the delay process. There is some evidence to suggest that this latter situation occurs in packed distillation columns. Kropholler et al. (9) measured liquid side distributions and tried to incorporate their effect by means of a dispersion term in the equations for a packed batch distillation column. It was found, however, that the dispersion model poorly represented their results, and as subsequent steady state experiments showed the mass transfer to be well represented by a plug flow model, the authors chose to ignore the axial mixing effect on the column dynamics. The time-delay model resolves this apparent anomaly. Addition of a mass transfer term to Equation (1) represents the liquid side situation; it will be seen that in the steady state (left-hand side = 0), the axial mixing does not affect the mass transfer, although the effect on the dynamics could be considerable. This applies not only to the simple impulse distribution of Equation (1) but to any distribution of delay times.

CONCLUSIONS

A plausible abstraction of flow behavior in a packed bed leads to a simple probabilistic model for describing RTD's.

Although applied solely to liquid side distributions in a countercurrent gas/liquid packed bed system, where reasonable fits were easily obtained, the model lends itself to a wide variety of physical situations.

Its flexibility and mathematical simplicity make it an attractive alternative to the one-dimensional dispersion model which does not account for the skewed distributions that occur in practice and which, on elaboration, leads to unwieldy analysis.

NOTATION

A = cross-sectional area through which forward liquid flow takes place
c = liquid concentration
f = lateral liquid flow rate per unit bed length
F = forward liquid flow rate
$g_n(\theta)$ = probability density function for θ
n = number of stops
$p_n(x)$ = probability of stopping n times while traveling a distance x
$p(t/\bar{t})$ = probability of leaving system at time $t/\bar{t}$
t = residence time in a section of bed of length x
t_D = average delay time
t_o = minimum residence time in a section of bed of length x
t_o' = apparent dead time
t^* = $t - t_o$
$\bar{t}$ = mean residence time
αdx = probability of stopping while traveling a distance dx
θ = sum of n independent observations from an exponential distribution with mean t_D
$\phi(t)$ = residence time distribution density function

Dimensionless Groups

D/UL = dispersion number

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