titative study of subtle changes in the diffusion coefficient it is better to eliminate the effects of external mass transfer in improved experimental equipment than to account for external mass transfer in more complicated mathematical descriptions of adsorption uptake.

NOTATION

a = specific surface area for mass transfer, cm^2/cm^3
c = concentration of solute in aqueous soln., mmol/L
c_0 = concentration of solute in aqueous soln. at start of run, mmol/L
c_∞ = concentration of solute in aqueous soln. at end of run, mmol/L
$c_{\infty,p}$ = concentration of solute in aqueous soln. at end of previous run, mmol/L
K = adsorption equilibrium constant for linear isotherm
k_f = external mass transfer coefficient, cm/s
n = number of measurements
q_0 = concentration of adsorbed solute at start of run, mmol/g
q_∞ = concentration of adsorbed solute at end of run, mmol/g
q_{equ} = equilibrium concentration of adsorbed solute, mmol/g
t = time, s
V_{fl} = volume of particle-free liquid in adsorber, cm^3
V_s = total volume of wet particles in adsorber, cm^3

Greek Letters

γ = adsorption uptake, Eq. 1
ϵ_p = porosity of wet particles
ϕ = defined by Eq. 5
ρ = apparent adsorbent density, g/L

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The Hopping Model for Residence Time Distributions of Systems with Splitting and Merging Streams

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The residence time distribution for fluid flow through packed beds has been analyzed by considering a main path through which all the fluid flows and along which are distributed relatively stagnant zones into which some fluid elements enter and are delayed for some time (the delay time) in their passage through the system (Buffham et al., 1970; Buffham and Gibilaro, 1970). This notion leads to a family of simple models for the overall residence time distribution of flow material in terms of parameters that are

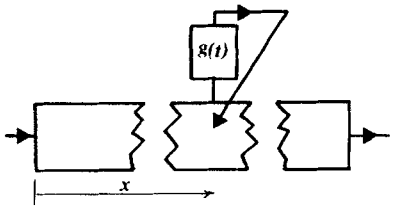

Figure 1. Time delay models.

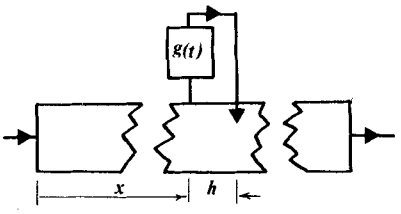

Figure 2. Hopping models.

amenable, to a greater or lesser extent, to mechanistic interpretation; in this respect they differ from the purely descriptive models (dispersion, tanks-in-series, tanks-in-series-with-dead-time, etc.) in which the parameters provide flexibility in matching experimental data without relating in any way to the mechanisms responsible for producing them.

A shortcoming of the time delay models in their ability to incorporate known features of the mixing processes occurring in packed beds concerns the return of delayed material to the main flow stream. Previously, the assumption has been that this takes place at the same axial position in the bed where the delay occurs (Figure 1); a more satisfactory representation would be for material to rejoin the main pathway at a point some distance downstream from the delay point (Figure 2), thereby incorporating stream splitting and merging effects (Porter, 1968) into the overall pattern of behavior. The purpose of this note is to show that such a modification incorporates easily into the time delay concept, thereby increasing its descriptive capability.

TIME DELAY MODELS

These may be treated probabilistically: if the probability of a fluid element entering a lateral delay zone from an elemental segment (length dx) of the main flow path is αdx, it has been shown (Buffham et al., 1970) that the probability of n such events occurring in a journey of axial distance x is given by

$$p_n(x) = \frac{(\alpha x)^n}{n!} e^{-\alpha x} \tag{1}$$

If the distribution of delay times in a lateral zone is $g(t)$, then the residence time distribution $f(t)$ for a system of total length x will be

$$f(t) = u(t - t_0) \sum_{n=0}^{\infty} p_n(x) \cdot g_n(t - t_0) \tag{2}$$

where $g_n(t)$ is the n-fold convolution of the prototype delay distribution $g(t)$, and t_0 is the transit time of all fluid elements in the main flow path. Fixed and exponentially distributed delays have been considered (Buffham et al., 1970), as well as the more general gamma distribution for $g(t)$ (Buffham and Gibilaro, 1970).

HOPPING MODELS

If we now stipulate that delayed material rejoins the main flow path at an axial distance h downstream from the point where the delay occurred (Figure 2), the effect on the overall behavior of the system will be twofold. In the first place there will now be a finite maximum number of possible delays, given by

$$N = \text{integer}\left(\frac{x}{h}\right) \tag{3}$$

and, second, the transit time of fluid elements in the main flow path will no longer be the same for all elements but will depend on the total number of delays, or "hops," an element experiences in its journey through the system. The maximum transit time t_0 will be taken by elements that do not hop at all and corresponds exactly to the main path transit time taken by all elements in the unmodified time delay description; material that hops n times will have a reduced main path transit time t_{0n}, given by

$$t_{0n} = t_0(1 - nh/x) \tag{4}$$

It remains to determine the probability $p_n(x)$ of element hopping n times in traversing an axial distance x; this differs from the simple delay case, Eq. 1, because hopping can occur only from the main flow path, which is effectively shortened by an amount h for each hop performed. Thus the counterpart of Eq. 1 becomes

$$p_n(x) = \frac{\alpha^n(x - nh)^n}{n!} e^{-\alpha(x-nh)} \tag{5}$$

a result that is formally derived eleswhere (Rathor, 1969).

The response of the hopping model is thus seen to be

$$f^*(t) = \sum_{n=0}^{N} u(t - t_{0n}) p_n(x) g_n(t - t_{0n}) \tag{6}$$

where t_{0n} and $p_n(x)$ are given by Eqs. 4 and 5, respectively.

One small problem remains: Eq. 5 describes the probability that a fluid element arrives at axial distance x on the main flow path after having executed n hops; however, elements that start a hop less than distance h from the system exit will not be counted on this basis, and as a consequence the probabilities $p_n(x)$ for n from 0 to N do not sum to unity, and Eq. 6 does not represent a residence time distribution.

The problem is easily resolved by including in the count of material that leaves the system after n hops those elements that commence an additional hop in this last section of the main flow path. This is effectively achieved by dividing Eq. 6 by P

$$P = \sum_{n=0}^{N} p_n(x) \tag{7}$$

yielding for the residence time distribution

$$f(t) = f^*(t)/P \tag{8}$$

Additionally, it can be shown that for parameter values relating sensibly to the physical systems envisaged in this development (that is, excluding very large hops and/or very large hopping probabilities) the series of Eq. 7 sums to $1/(1 + \alpha h)$; incorporating this and relation 3 into Eq. 8 yields the final result for the unnormalized residence time distribution of the general hopping model in terms of parameters αh, N, and t_0;

$$f(t) = (1 + \alpha h) \sum_{n=0}^{N} u\left(t - t_0\left(1 - \frac{n}{N}\right)\right) (\alpha h)^n \times \frac{(N - n)^n}{n!} e^{-\alpha h(N-n)} g_n\left(t - t_0\left(1 - \frac{n}{N}\right)\right) \tag{9}$$

It is often convenient, especially when dealing with experimental data, to express residence time distributions in normalized form by converting the time scale to units of the mean time:

$$\theta = t/\bar{t} \tag{10}$$

The unit area property of the residence time distribution is then preserved by multiplying the unnormalized frequency by the mean time:

$$\phi(\theta) = \bar{t} f(t) \tag{11}$$

The normalization is readily achieved for the hopping model by noting that

$$\bar{t} = t_0\left(1 - \frac{\bar{n}}{N}\right) + \bar{n} t_D \tag{12}$$

where t_D is the mean of the prototype delay distribution $g(t)$

$$t_D = \int_0^\infty tg(t)dt \tag{13}$$

and $\bar{n}$ is the average number of hops executed by fluid elements:

$$\bar{n} = (1 + \alpha h) \sum_{n=0}^{N} n(\alpha h)^n \frac{(N-n)^n}{n!} e^{-\alpha h(N-n)} \tag{14}$$

Other methods of dealing with the end conditions are possible once specific assumptions have been made concerning the way in which fluid elements leave (and enter) the test section; that given here is simple and suitable for many practical purposes.

A considerable attraction of the time delay concept in residence time distribution modeling lies in the ease with which the postulated underlying mechanisms can be modified to suit individual circumstances without in any way destroying the extreme simplicity of the analysis; in this respect at least it compares very favorably with other commonly used abstractions of the flow-mixing process. This inherent flexibility is highlighted once again in the above derivation of the general hopping model; just as for the original time delay description, Eq. 9 respresents a family of models individually defined by their delay distribution $g(t)$. It has been used (Rathor, 1969) with the exponential delay distribution

$$g(t) = \frac{1}{t_D} e^{-t/t_D} \tag{15}$$

$$g_n(t) = \frac{t^{n-1} e^{-t/t_D}}{t_D^n (n-1)!} \tag{16}$$

to describe flow in trickle beds, where it is shown that, with hopping distances of the same order as observed liquid rivulets (h = 3 to 5 cm), significant improvements over the corresponding time delay model response can be obtained.

NOTATION

$f(t)$ = residence time distribution, s^{-1}
$f^*(t)$ = defined by Eq. 6, s^{-1}
$g(t)$ = prototype delay distribution, s^{-1}
$g_n(t)$ = n-fold convolution of $g(t)$, s^{-1}
h = hopping distance, m
n = index, number of delays or hops
$\bar{n}$ = average number of hops
N = maximum possible number of hops
$p_n(x)$ = probability of n delays, or hops, occurring in distance x
P = probability, defined by Eq. 7
t = time, s
t_0 = maximum main path transit time, s
t_{0n} = main path transit time for elements that make n hops, s
$\bar{t}$ = mean residence time, s
t_D = mean delay time, s
$u(t)$ = unit step function: $t < 0, u = 0; t \geq 0, u = 1$
x = distance, m

Greek Letters

α = defined in discussion above Eq. 1, m^{-1}
θ = normalized time
$\phi(\theta)$ = normalized residence time distribution

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The Behavior of a Hybrid Fixed-Point Method in a Chemical Process Design Environment

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INTRODUCTION

In a recent paper, Lucia and Macchietto (1983) suggested the use of a hybrid fixed-point method for solving equation-oriented process design problems. This hybrid method, which makes combined use of Newton's method and the Schubert (1970) update, was subsequently applied to condenser design problems modeled by simultaneous heat and mass transfer by Taylor et al. (1983), to flash and distillation calculations by Westman et al: (1984), and to multistage, multicomponent separation problems by Lucia and Westman (1984). All of the numerical evidence gathered so far indicates that the hybrid method is both computationally efficient and robust. That is, it has displayed the robustness of Newton's method while, at the same time, has generally used significantly fewer rigorous physical physical properties calculations. Moreover, the hybrid method has been shown to be both more robust and

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