A Stochastic Model of Packed-Bed Mixing and Mass Transfer

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A new model of packed-bed behavior based on a second-order stochastic process is developed and examined. The model takes as the basic process the transitions of fluid "packets" among allowed velocity states. The observable phenomenon, that is, the spatial distribution of packets, is a projection of the velocity state process.

Results from the model compare well with results from experiments for mixing in packed beds. Model parameters are consistent, and correlate with the physical parameters of the systems. Present results under mass transfer conditions are inconclusive but encouraging.

Packed beds are common devices in the chemical industries. The transient behavior of such reactors is of interest for startup, control, and other considerations. The amount of mixing that will occur in a packed bed is of fundamental importance in design considerations. Such mixing will affect productivity, raise recycle requirements, or, perhaps, make a particular process inherently impossible. Both the feasibility of deliberate cycling of a reactor to increase yields of an equilibrium-limited reaction by *in situ* separation of reactants and products, and that of separating chemical components by chemical parametric pumping (*21*), are strongly dependent on the degree of mixing.

Many different models of packed-bed behavior have been proposed but most have been variations of the mixers-in series and dispersion models. The former assumes that a characteristic bed length equivalent to a perfectly mixed tank can be determined, while the latter treats the mixing as though it were a diffusion process.

Serious objections to both these models may be raised on fundamental grounds (*8, 13, 15, 16*). Moreover, as illustrated by Figure 1 (after Miller & King), existing theory seems not entirely adequate for the correlation of experimental data.

A number of problems exist in present packed-bed technology. There is, first, need for a knowledge of the dependence of the gross velocity profile on the various pertinent physical parameters, and, second, a better understanding of the internal mixing and mass transfer process. The interaction of these constitutes a third problem. Others, of course, exist.

Recent experimental evidence (*13*) indicates that the differing relative velocities of fluid volumes may actually be the major source of mixing (in the absence of strong velocity profile effects). The object of the present study was to develop and examine a model which more closely corresponds to the mixing process and which better describes observed behavior.

A STOCHASTIC MODEL

Introduction

A stochastic model of packed-bed behavior is one approach which may better represent the actual behavior of such beds while avoiding the mathematical intractability of a complete description via the classical partial differential equations written for all physical elements of the system with the appropriate boundary conditions.

A number of model types and levels of sophistication are available. Here the mixing process will be modeled as a walk in velocity states. This is a second-order stochastic process and more accurately reflects the physical process than would a first-order stochastic process such as a walk in a position space. A similar process has been used by others (*5, 7, 9, 12*) in modeling turbulent diffusion. Note that the following is certainly not the only stochastic model which might be employed. Other formulations could be made, perhaps with equal or better results, and such further exploration of stochastic models for packed beds seems clearly indicated to the desirable by the results from this first effort.

Statement of the Model

Consider three velocity states, $\pm V$, 0, and a characteristic length L. A characteristic time interval τ can be defined as the time required to travel one characteristic length. Each packet of fluid takes on one of the three possible velocity states in each time interval. Each packet is allowed some probability of changing its velocity state at the end of each time interval. This probability will be taken as dependent only on the present velocity state. The position space is taken as the one-dimensional space of integers and represented as the line through, 0, $\pm$ 1, $\pm$ 2, . . . $\pm \nu$. A large number of packets will enter the system at position $\nu = 0$ at time $t = 0$, none being present prior to $t = 0$. An initial distribution of the packets among the three velocity states will be assumed.

It is desirable to attach some physical significance to the various constructs employed. By a packet of fluid we shall

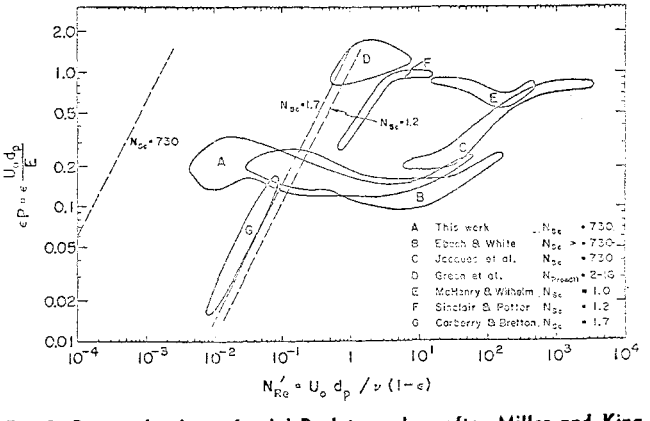

Fig. 1. Reported values of axial Peclet number, after Miller and King (*14*).

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mean a volume element large with respect to the molecular mean free path but small with respect to the volume of a bed interstice. The characteristic length L can readily be associated with the characteristic size of the packing d_p. The postulation of three velocity states is clearly a strong deviation from physical reality. In fact, three velocity states appear to be the minimum number which can simultaneously account for mass exchange between the fixed and fluid phases and imperfect correlation of velocity states in the fluid phase.

The postulation that the transition probabilities are dependent only on the present velocity implies that they are stationary, that is, that they do not vary in time or space. This in turn implies that the bed is spatially uniform and that the flow is not time varying.

The postulation that the packets enter the system at $\nu = 0$ and $t = 0$ is largely a matter of convenience. No loss of generality is encountered as a linear transformation of coordinates can bring any desired ν and t into a $\nu' = 0$, $t' = 0$. The choice of a Dirac delta type input is clearly an idealization. The introduction of a tracer into any real system must occupy both space and time.

The extension of the model to more general spatial and temporal distributions of the input function is indicated elsewhere (*15*).

Two additional hypotheses or restrictions on the system will be made: (1) The packets have a large propensity to move toward the right. (2) The propensity to become and remain stationary is small.

The first of these restrictions is quite natural in a flow system, the "right" being in the direction of the mean flow, and the choice of direction is clearly arbitrary and unimportant. It creates no significant restriction on the model.

The existence of such a state (of zero velocity) for a packet may be interpreted physically in two ways. The packet may be thought to just sit still in the fluid phase for a time interval or it may be thought to represent material adsorbed by the packing. There appears to be no basis for precluding the first of these while allowing a state, $-V$. It is profitable, however, to consider that virtually all of the packets in velocity state zero represent adsorbed material.

The second of the restrictions carries implications which may limit the model. It implies that the bed is not strongly adsorbing and that the fluxes between the fluid and solid phases are in some sense "small." The degree of restrictiveness of this second hypothesis remains to be explored.

As a consequence of hypothesis 1 (bulk flow to right), the probability of a packet entering or remaining in velocity state $-V$ must be small. In such a system the question of the possibility of such behavior, that is, "swimming upstream," may be raised. No direct experimental test of this is known to exist. A swim upstream the order of d_p appears unlikely in a system under viscous flow, while the situation is not clear if turbulence exists. In not precluding such an event we invoke a result from statistical mechanics, that is, that the apparent absence of an event in a macroscopic measurement does not preclude its occurrence on a microscopic scale.

The long-time behavior of the model is also of interest. The model should predict long-term behavior compatible with known long-term behavior, that is, Fickian.

Mathematical Statement of the Model

Proceeding more formally, the changing of velocity states by the packets can be characterized by a set of transition probabilities. The transitions will comprise a first-order Markov chain, that is, there will be a distinct correlation between the velocity in the n^{th} and the $n + 1^{st}$ time steps expressed by the transition probabilities.

The conditional probabilities (velocity transition probabilities) expressing this are

$p = P(\nu, \nu + 1/\nu + 2)$	probability that a packet traveling to the right will continue to the right in the next interval
$q = P(\nu, \nu + 1/\nu)$	probability that a packet traveling to the right will reverse itself and travel left in the next interval
$r = P(\nu, \nu + 1/\nu + 1)$	probability that a packet traveling to the right will remain stationary in the next interval

Six additional transition probabilities of similar definition are required:

$$p' = P(\nu, \nu - 1/\nu - 2) \qquad p'' = P(\nu, \nu/\nu)$$
$$q' = P(\nu, \nu - 1/\nu) \qquad q'' = P(\nu, \nu/\nu + 1)$$
$$r' = P(\nu, \nu - 1/\nu - 1) \qquad r'' = P(\nu, \nu/\nu - 1)$$

As the model allows only three velocity states and each packet must be in one of those states in each time interval

$$\begin{aligned} p + q + r &= 1 \\ p' + q' + r' &= 1 \\ p'' + q'' + r'' &= 1 \end{aligned} \tag{1}$$

The (Markovian) matrix of transition probabilities can be written as

	+V	O	−V
+V	p	r	q
O	q''	p''	r''
−V	q'	r'	p'

or, alternatively

$$\begin{vmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{vmatrix}$$

where $p_{11} = p$, $p_{12} = r$, etc.

Two statements may immediately be made about this matrix:

1. All the elements p_{ij} are real and $0 \leq p_{ij} \leq 1$
2. The row sums are unity, that is, $\sum_{j=1}^{3} p_{ij} = 1$, $i = 1, 2, 3$

The first of these statements is a consequence of using "normal" notions of probability on the set of real numbers. The second is a restatement of Equation (1).

In general, we will be interested in the case where there are no absorbing or reflecting states, that is, $0 < p_{ij} < 1$ all i, j. The case in which one or more velocity states is absorbing may be approached arbitrarily closely by applying continuity arguments to the nonabsorbing case. Reflecting velocity states may be treated similarly.

The following are defined:

$\gamma(n, \nu)$ = fraction of packets (or probability of a given packet) at point ν after n time intervals
$\alpha(n, \nu)$ = fraction at ν after n time intervals arriving from left
$\beta(n, \nu)$ = fraction at ν after n time intervals arriving from right
$\zeta(n, \nu)$ = fraction at ν after n time intervals arriving from ν

Then

$$\gamma(n, \nu) = \alpha(n, \nu) + \beta(n, \nu) + \zeta(n, \nu) \quad (2)$$

Expressions for the fraction arriving at a given point from the various directions are

$$\alpha(n, \nu) = p_{11}\,\alpha(n-1, \nu-1) + p_{31}\,\beta(n-1, \nu-1) + p_{21}\,\zeta(n-1, \nu-1) \quad (3)$$

$$\beta(n, \nu) = p_{13}\,\alpha(n-1, \nu+1) + p_{33}\,\beta(n-1, \nu+1) + p_{23}\,\zeta(n-1, \nu+1) \quad (4)$$

$$\zeta(n, \nu) = p_{12}\,\alpha(n-1, \nu) + p_{32}\,\beta(n-1, \nu) + p_{22}\,\zeta(n-1, \nu) \quad (5)$$

The function $\gamma(n, \nu)$ is a density of packets at a given position and time. γ or a direct function of γ will be the normally observable experimental variable. It is then desirable to have a recurrence relation for γ in which the directional quantities α, β, ζ do not appear. It has been shown elsewhere (*15*) that no exact one- or two-step recurrence relation in γ exists and that a very large number of possible expressions exist for a three-step relation. An approximate two-step relation in γ was developed and shown to be useful only under certain very restrictive conditions on the transition probabilities.

An exact, one-step recurrence relation for γ containing the α, β, ζ can be obtained from Equations (2) to (5). It is

$$\gamma(n+1, \nu) = p_{11}\,\alpha(n, \nu-1) + p_{31}\,\beta(n, \nu-1) + p_{21}\,\zeta(n, \nu-1) + p_{12}\,\alpha(n, \nu) + p_{32}\,\beta(n, \nu) + p_{22}\,\zeta(n, \nu) + p_{13}\,\alpha(n, \nu+1) + p_{33}\,\beta(n, \nu+1) + p_{23}\,\zeta(n, \nu+1) \quad (6)$$

This relation can be used to calculate the distribution of packets in the bed for all subsequent times.

Long-Term Behavior of the Model

We shall indicate how one may show that the distribution of packets among velocity states will converge to an equilibrium distribution, and that after it has converged the spatial position process may be treated as a pseudo-Markov process. This will provide computational advantages over the direct recurrence relation [Equation (6)].

The three allowed velocity states comprise a closed, finite irreducible set. Each of the three velocity states can be reached from any of the three velocity states but no other state can be reached. Under these conditions, it follows from the theory of Markov processes (*6*) that

1. An equilibrium distribution exists
2. It is unique and independent of the initial distribution
3. It may be calculated from

$$U = P^T\,\mathbf{U} \quad (7)$$

where

$$\mathbf{U} = \begin{bmatrix} U_1 \\ U_2 \\ U_3 \end{bmatrix} \qquad \mathbf{P} = \begin{bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{bmatrix}$$

and $\mathbf{U}$ is a characteristic vector of $\mathbf{P}$ associated with the characteristic root one. $\mathbf{U}$ can be found by standard matrix procedures. Details of this are available elsewhere (*6, 15*).

A direct, one-step recurrence relation containing only the γ's can be written for all times after the convergence of the distribution among velocity states:

$$\gamma(n+1, \nu) = U_1\,\gamma(n, \nu-1) + U_2\,\gamma(n, \nu) + U_3\,\gamma(n, \nu+1) \quad (8)$$

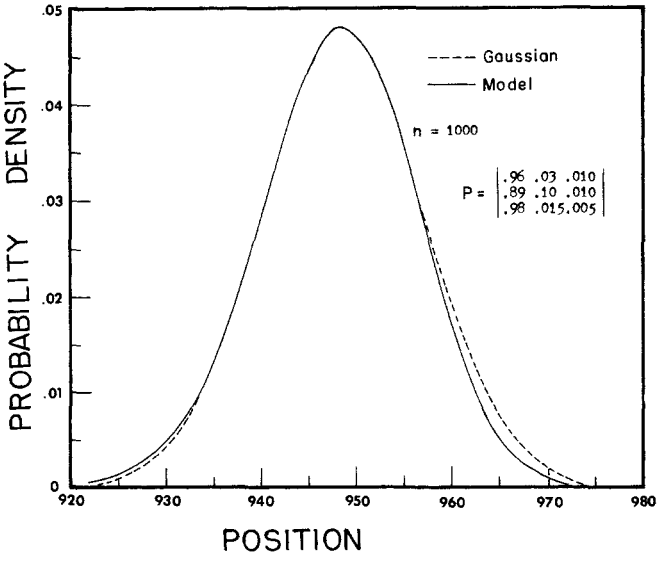

Fig. 2. Long-term spatial distribution.

If the system is observed after a stationary distribution of velocities has been achieved, it will appear to be Markovian in position states. It should be pointed out that while the long-time process appears to be Markovian, it is not (*15*). Furthermore, it may be possible to show theoretically that the spatial distribution will converge to a distribution *observably indistinguishable* from that of a Gaussian Markov process. Stratanovich (*19*) has demonstrated such a result for quite general processes having continuous distribution functions, and has indicated (*20*) that an extension to discrete processes is feasible. Figure 2 indicates the degree of convergence obtained after 1,000 steps for a typical set of transition probabilities.

NUMERICAL RESULTS AND ANALYSIS

Certain facets of the theoretical development and results are best explored numerically. Both the stationary velocity distribution and the rate of convergence to that distribution have significance only when values of the initial conditions and transition probabilities are specified. Similarly, the effect of the initial conditions will depend on the transition probabilities.

Equally important is a comparison of the model with existing experimental results. This will test the ability of the model to concur with extant results and provide some insight into the values of the transition probabilities and their physical interpretation.

Convergence of the Velocity Distribution

The rapidity of the convergence and the actual stationary distribution of packets among the velocity states must be explored numerically. An iterative approach to the stationary distribution which provides actual velocity distribution in each step can be taken directly from Equation (7):

$$\mathbf{U}^{(r+1)} = \mathbf{P}^t\,\mathbf{U}^{(r)} \quad (9)$$

where r is the number of the time step and $\mathbf{P}$ and $\mathbf{U}$ are those of Equation (7).

Alternatively, U_{sta} can be computed using standard procedures for finding the eigenvalues and eigenvectors of matrices.

Some transition matrices, their associated stationary distributions, and the number of time steps required for a given degree of convergence are shown in Table 1.

The convergence of the velocity distribution usually is rapid. Three-digit convergence is generally obtained in

TABLE 1. CONVERGENCE OF VELOCITY DISTRIBUTION

P			U_{sta}	N_3	N_6	Comments
0.98	0.01	0.01	0.979487			
0.95	0.025	0.025	0.010256	2–4	3–5	Variation in number of time steps for a given convergence caused by differing initial conditions.
0.96	0.02	0.02	0.010256			
0.95	0.04	0.01	0.922253			
0.50	0.4	0.1	0.062008	6–8	13–16	
0.96	0.02	0.02	0.015738			
0.98	0.01	0.01	0.969772			
0.95	0.025	0.025	0.015121	6–9	13–14	
0.333	0.334	0.333	0.015106			
0.98	0.01	0.01	0.976470			
0.7	0.15	0.15	0.011765	4	7–8	
0.96	0.02	0.02	0.011765			
0.6	0.2	0.2	0.558441			
0.4	0.5	0.1	0.285714	3–7	9–14	
0.7	0.2	0.1	0.155844			
0.98	0.01	0.01	0.0			
0.0	1.0	0.0	1.0	>50		
0.9	0.025	0.025	0.0			Irreversible adsorption

N_3, N_6 are the number of time steps for three-digit and six-digit convergence, respectively.

two to nine time steps, while six-digit convergence is generally complete in less than 18 time steps.

Two convergence criteria have been illustrated because differing circumstances may require more or less stringent convergence. For example, if the spatial distribution is to be calculated 200 or 300 steps from the origin, the precision of the computations must be greater than for a short bed if the same accuracy is to be preserved.

Sensitivity to Initial Conditions

The model requires the specification of both the initial spatial and velocity distributions. The impact of these initial conditions will depend on the distance from the inlet and on the velocity transition probabilities.

To explore this, a typical set of velocity transition probabilities was chosen and several initial conditions were examined. They were a Dirac delta at $\nu = 0$ and a square pulse of width five units. Velocity distributions were chosen as an equipartition among the velocity states and as a distribution near the stationary distribution.

Figures 3 and 4 illustrate the effect of the initial conditions. The first is the case when the initial velocity distribution is near the stationary distribution; the second is the case when the initial distribution differs sharply from the stationary distribution. Several observations can be made:

1. The Dirac pulse is affected much more strongly than the square pulse.
2. The spatial distribution in the early time steps is strongly affected by both the initial spatial and velocity conditions.
3. Substantial differences in the spatial distribution, resulting from the differing initial spatial distributions, persist as many as 50 d_p down the bed.
4. Differences in the spatial distribution, resulting from differing initial velocity distribution, have essentially disappeared at 50 d_p down the bed.

Other numerical observations can be made with respect to the accuracy of approximate recurrence relations, the effect of the transition probabilities on the long-term velocity distribution, and, as illustrated earlier, the behavior of the long-term spatial distribution.

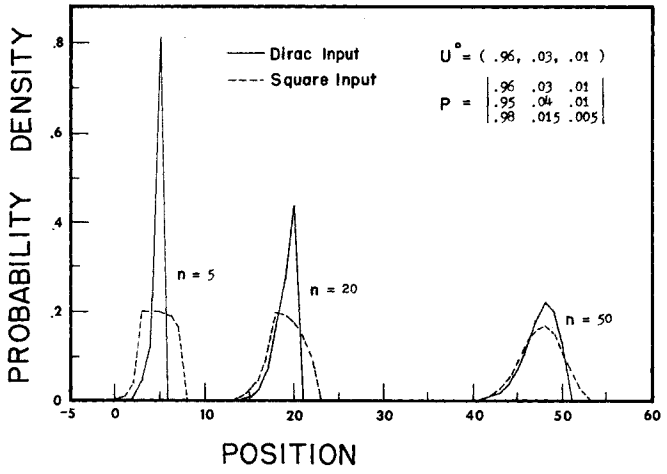

Fig. 3. Effect of initial conditions. Initial velocity distribution near stationary.

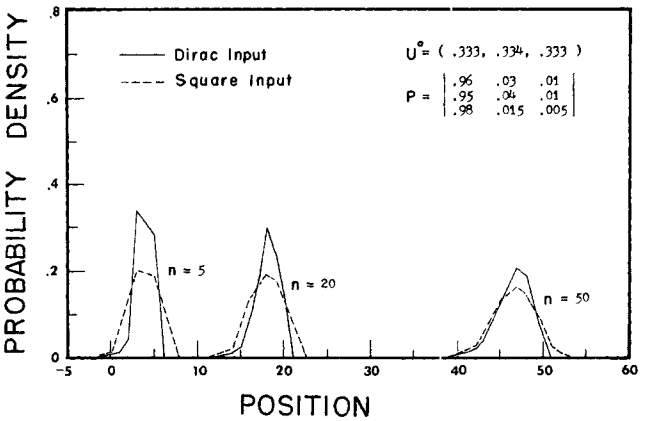

Fig. 4. Effect of initial conditions. Initial velocity distribution far from stationary.

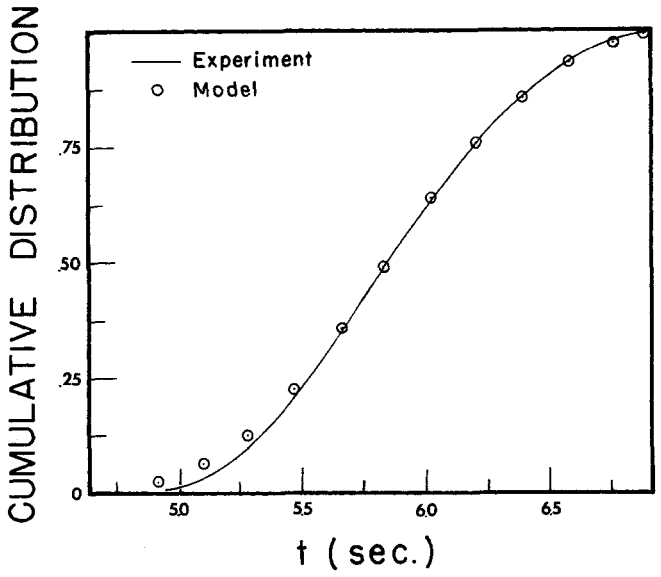

Fig. 5. Comparison of model with data of Cairns and Prausnitz.

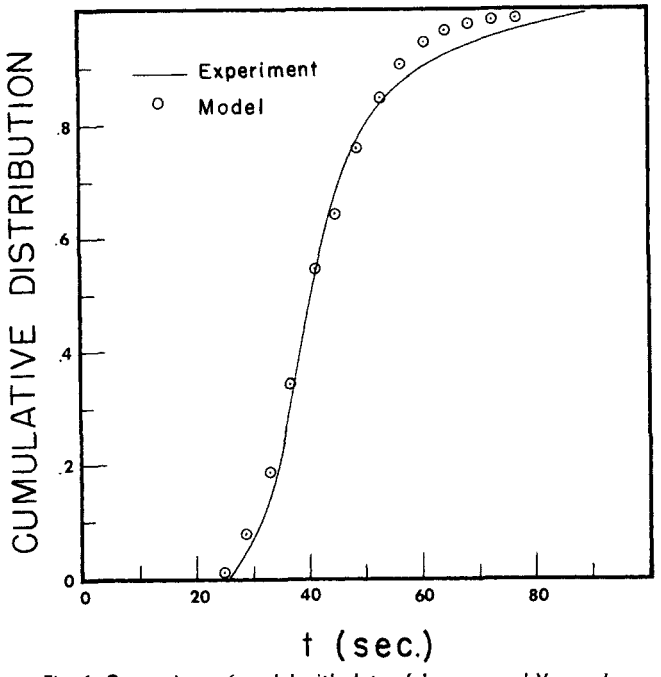

Fig. 6. Comparison of model with data of Jacques and Vermeulen.

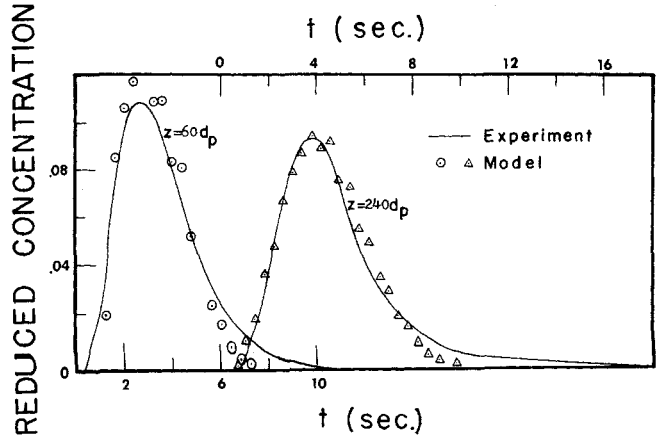

Fig. 7. Comparison of model with data of Carberry and Bretton.

Comparison of Model with Experimental Results

Results from the stochastic model were tested against data reported from experimental studies of packed beds. This was done to explore the model's ability to concur with experimental results and to examine the relation of the model parameters to the physical parameters of packed beds.

The choice of experimental results for comparison was based on the desire to explore a wide range of experimental conditions and on the availability of data. Model parameter determination was performed by successive trials, much as the dispersion coefficient is normally fitted.

The theoretical development is in terms of spatial distribution as a function of time while virtually all experimental results have been reported as temporal distribution at fixed positions. Comparisons will be made in terms of temporal distributions at the fixed positions of the experiments.

Liquid-Solid Systems

Three liquid-solid systems were examined. Two of the systems involved response to step changes in input (breakthrough curves), while the third was system response to a square pulse type input. The well-known relation between cumulative distribution and the local probability density was used in treating the breakthrough data.

Figures 5, 6, and 7 show the experimental curves and the corresponding results of the model for three liquid-solid systems, and Table 2 summarizes the experimental and model parameters for both the liquid-solid and gas-solid systems.

The data of Cairns and Prausnitz (*1*) were fit using an inlet spatial distribution equivalent to their assumed initial condition (step function) and an initial velocity distribution equal to the stationary distribution (tracer entering at mean flow velocity). The detector was located 191 d_p from the point of injection, hence, the curve should not be strongly influenced by the initial conditions.

The results of Jacques and Vermeulen (*10*) were measured in a much shorter bed at higher N_{Re} and considerably lower D_t/d_p. This result should be, and was, much more sensitive to the initial conditions. It was not possible to fit the data using spike input spatial distribution (equivalent to their assumed step input). The data were taken 32 d_p from the point of injection, a distance at which the influence of the initial conditions remains important. Both the data and the fit show a distinct tailing. This may be the result of the initial conditions or the velocity profile since the D_t/d_p ratio is quite low. These possibilities cannot be clearly separated from data at a single detector.

The data of Carberry and Bretton (*2*) were taken at lower N_{Re} and longer bed lengths than either of the two just discussed. Their data have the advantage of having been taken at two points some 102 d_p apart in the bed. Their tracer injection was accomplished by rotating a thin wafer of dye solution into the flow stream. This initial dispersion is reflected in the initial spatial distribution chosen.

The result of the model and that of the experiment are in good agreement at the first detector, while at the second detector there is some divergence of the latter halves of the peaks. This may imply a nonoptimum choice of model parameters but also could be caused by the relatively large void detectors and the resulting bed reentrance effects (*17*).

Gas-Solid Systems

Gas-solid system data are quite sparse. McHenry and Wilhelm (*11*) used a sinusoidal input function not amenable to comparison with the model, while the data of

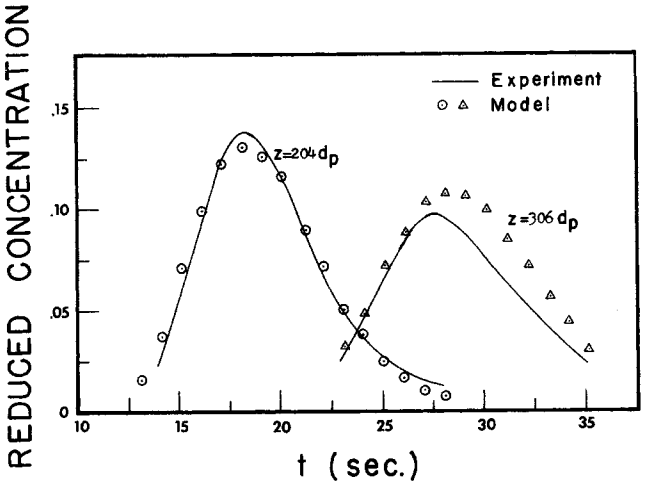

Fig. 8. Comparison of model with data of Chao and Hoelscher. No mass transfer.

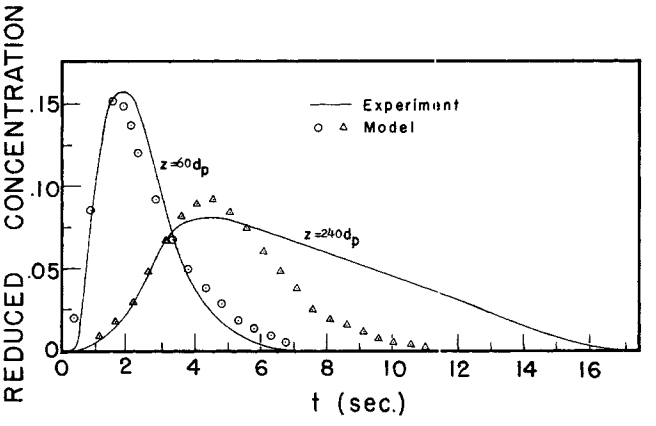

Fig. 9. Comparison of model with data of Chao and Hoelscher. Mass transfer allowed.

Schneider and Smith (*18*) were not reported in sufficient detail for this purpose. Two sets of measurements by Chao and Hoelscher (*3, 4*) were suitable. One of these is a mixing experiment (inert packing); the other involves mass transfer (activated charcoal packing). Their measurements were made at a much lower N_{Re} than any of the liquid-solid systems.

Figures 8 and 9 show the experimental curves and the corresponding results of the model, while Table 2 again summarizes the experimental and model parameters.

The initial spatial distribution was taken as slightly dispersed and tailed. This appears reasonable in terms of the size of the injector, the method of injection, and the high diffusivities in the gas phase. Since initial velocity distributions could not be obtained from the data, a reasonable initial distribution was selected.

The results of the model and that of the experiment (for mixing conditions) agree only moderately well at the first detector. Differences exist both at the peak and at the tail. The results conform much more closely at the second detector (240 d_p). The experimentally determined peak remains more tailed than that from the model.

No set of model parameters was found that would make the result of the model conform to the experimental result found when the packing was activated charcoal. Nor was any set found which could produce a curve like the experimental curve at 240 d_p and maintain reasonable initial conditions. The exact cause of this is uncertain but (*15*) is believed due to a nonlinear adsorption isotherm for the hydrogen on the charcoal. This is reinforced by the qualitative agreement of the results of Schneider and Smith with those of the model. Schneider and Smith used butane and propane as adsorbable gases (silica gel packing) with helium as the carrier. The injection concentrations of butane and propane were kept below 1 mole %. In the work of Chao and Hoelscher the carrier was butane or propane and the injected pulse was pure hydrogen. The assumption of a linear adsorption isotherm made by both Chao and Hoelscher and Schneider and Smith is much more viable at the concentrations employed by Schneider and Smith.

Model Parameters

Several observation can be made about the model parameters, particularly the velocity transition probabilities. Some of these may be apparent from Table 2 and the associated figures, while others were observed while fitting the experimental data.

From the table and figures (for no mass transfer)

1. The correlation of sequential positive velocity states ($C = p_{11} - p_{13}$) differs in the laminar ($N_{Re} < 100$) and turbulent ($N_{Re} > 200$) flow regimes.
2. The relative stability ($K = p_{11} - p_{33}$) of the two

Table 2. Experimental and Model Parameters

Investigators	Length (d_p)	D_t/d_p	N_{Re}	P			γ°	U°	U_{sta}
Cairns & Prausnitz (5-3-13)	191	17	330	0.9	0	0.1		0.9	0.9
				0	0	0	$\delta(0)$	0	0
				0.9	0	0.1		0.1	0.1
Jacques & Vermeulen (217-1)	32	7.5	480	0.9	0	0.1		0.8	0.897
				0.9	0	0.1	(0.1, 0.4, 0.4, 0.1)	0.1	0
				0.87	0	0.13		0.1	0.103
Carberry & Bretton (13-A-3)	204,306	8.5	100	0.99	0	0.01		0.8	0.990
				0.9	0	0.1	(0.15, 0.35, 0.35,	0.1	0
				0.965	0	0.035	0.15)	0.1	0.010
Chao & Hoelscher (18BN)	60,240	10	2.5	0.99	0	0.01	(0.02, 0.6, 0.06, 0.08,	0.8	0.988
				0.9	0	0.1	0.08, 0.125, 0.125,	0.1	0
				0.85	0	0.15	0.2, 0.2, 0.05)	0.1	0.012
Chao & Hoelscher (EA1)	60,240	10	in range 0.5–5	0.975	0.0225	0.0025	(0.1, 0.02, 0.04, 0.08,	0.9	0.893
				0.18	0.80	0.02	0.15, 0.3, 0.3,	0.01	0.102
				0.85	0.075	0.075	0.07, 0.03)	0.09	0.005

velocity states decreases with increasing N_{Re} for the liquid systems.

3. The tendency to develop a tail is related to p_{31}.

Also observed were

1. The slope of the leading edge of the peaks and tendency of the peak to become more disperse are sensitive to the value of p_{11}; for example, values of p_{11} of 0.985 and 0.980 other things equal, produce noticeably different peaks.

2. The slope of the trailing edge of the peak and the size of the tail are sensitive to p_{31} though less so than the leading edge to p_{11};

3. The peaks were relatively insensitive to moderate choices of initial velocity distribution in the cases examined here.

Nothing further can be said at this time about the sensitivity of results to the various model parameters. This is obviously an important question and one that deserves further study.

Little can be inferred from the one comparison of the model and experimental measurement of a bed under mass transfer conditions.

SUMMARY AND CONCLUSIONS

A new model of packed-bed behavior, based on a second-order stochastic process has been presented. The model takes the basic process to be the transitions of fluid packets among the allowed velocity states on a time and size scale of the flow time past a packing particle and the size of a packing particle respectively. The observable phenomenon, that is, the spatial distribution of packets, is a projection of the velocity state process.

This model, while still a decidedly naive representation of the complex processes in a packed bed, represents an advance over present models and avoids the total mathematical intractability of a completely rigorous approach. The analogy between the transitions of the packets among the velocity states, and the relative shifting of various fluid elements, believed to be a major source of dispersion, is direct.

The stochastic model satisfies the obvious tests, that is, the dispersion of the spatial distribution grows with time (*15*), the spatial distribution becomes Gaussian at large distances from the point of injection, and the distribution of packets among velocity states becomes stationary, an internal requirement of the model.

A comparison of the model with a number of experimental studies under mixing conditions, while not extensive, is encouraging. The model showed good ability to fit the experimental results, and, moreover, the values of the model parameters were consistent and were correlated with the physical parameters of the systems. Additionally, the model predicts that the effect of the initial conditions extends considerably farther into the bed ($\sim 50\ d_p$) than that predicted from the dispersion model ($\sim 10\ d_p$). This is in agreement with experimental observations.

Present results, under mass transfer conditions, are inconclusive. The data examined showed strong evidence of nonlinearity and the model seemed incapable of fitting them. Qualitative agreement between the model and other apparently linear mass transfer data was found.

The stochastic model proposed here cannot be considered predictive at this point. It does seem to contribute a new element to the understanding of dispersion in fixed beds and will hopefully stimulate others to examine this (and other) processes in this light. A wide range of data must be examined to determine the existence and nature of relationships (if any) between the model parameters and the physical parameters of packed beds.

NOTATION

d_p = diameter of packing particles
D_L = overall axial dispersion coefficient
D_t = diameter of packed bed
D = molecular diffusivity
E = dispersion coefficient, Figure 1
n = time step index
N_{pe} = Peclet number = $d_p\,U/D_L$
N_{Re} = Reynolds number = $d_p\,U/\nu$
N_{Sc} = Schmidt number = ν/D
p, q, r / p', q', r' / p'', q'', r'' = velocity transition probabilities defined in text
p_{ij} = velocity transition probability
$\mathbf{P}$ = matrix of velocity transition probabilities defined in text
t = time
u = mean interstitial velocity
U_1, U_2, U_3 = fraction of packets in velocity states, 1, 2, and 3, respectively
U_0 = superficial velocity
$\mathbf{U}$ = vector of distribution of packets among velocity states
V = characteristic packet velocity
$\alpha, \beta, \gamma, \zeta$ = probabilities defined in text
ϵ = void fraction
μ = viscosity
ν = spatial index, also kinematic viscosity
τ = characteristic time, L/V
(n) = time step n
$^\circ$ = initial condition

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