A Physical Model for Mixed Phase Flow Through Beds of Porous Particles

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In recent years there has been considerable interest in liquid and gas dispersion in fixed bed reactors. Perhaps the most complex case of this type is one where both liquid and gas are flowing through a bed of porous catalyst particles, the so-called *mixed-phase* flow reactor. The classical design approach to such a reactor is to assume a uniform velocity across the bed, with piston-flow throughout the length of the bed; that is, there is no radial or axial dispersion of the fluid. However residence time distribution measurements have shown that this is far from being an accurate description of the flow (*2, 3, 5, 6, 9, 10, 11*).

The most common approach to describing fluid dispersion is the assumption of a single eddy diffusion mechanism in the bed. While this may not be physically correct (*8*), the mathematical description of fluid dispersion with a single or average eddy diffusion coefficient assumed for the bed often succeeds in correlating the data for single-phase flow. Dispersion data are generally obtained from various types of tracer experiments. Deisler and Wilhelm (*6*) studied diffusion in beds of porous solids with a frequency response technique and related the dispersion diffusivity to amplitude and frequency changes of a sinusoidal input. McHenry and Wilhelm (*10*) used the same technique for gas mixture in a bed of spherical particles. Cairns and Prausnitz (*3*) measured change in conductivity of a salt tracer and correlated their data with the Einstein model. The latter paper also collects much of the previously reported data in a general correlation. Schiesser and Lapidus (*11*) separated the hydrodynamic and diffusional flow contributions to residence time distribution curves (from a downflow trickle bed reactor) obtained from measurements of salt tracer conductivity or colorimetric changes in a dye reactor.

There are two factors which strongly suggest that the assumption of a single eddy diffusivity for flow in packed beds is not physically correct. First Carberry (*4*) has obtained data showing that the eddy diffusivity varies with bed length. Second the assumption of a single or average eddy diffusivity for the entire bed does not satisfactorily describe the measured output tracer concentration—time (residence time) distributions for these beds. In flow over porous packing the single eddy diffusion model does not account for capacitance effects in the bed such as fluid diffusion into the pores which produces a long tail on the residence time curves (Figure 1).

The present work explores in a preliminary manner the conclusions that can be drawn by postulating a mechanism that probes further into the bed dynamics than the simple eddy diffusion or mixing cell models. It is based primarily on the simplified models of Turner (*12*) and Aris (*1*) for a single-phase flow.

PHYSICAL STRUCTURE OF THE PACKED BED

The present model for mixed-phase flow through a bed of porous particles is depicted in Figure 2. The figure represents a section cut through a bed of cylindrical packing, although the model to be proposed is applicable to all packing geometries. The bed is assumed to consist of two basic structures which play key roles in determining the fluid dispersion:

1. Void channels. These are channels external to the packing. Dead-ended pockets that can hold stagnant pools of liquid are associated with these channels. The size and distribution of these channels are a function of the packing material, sizes, packing methods, etc.

2. Pore channels and pockets. These are continuous and dead-ended pores in the particles. They represent the part of the total bed voids inside the particles.

To help define this picture beds whose flow lines had been emphasized with dye were frozen in wax and sections cut out. These experiments showed a distribution of void channels through the bed which are similar to those considered in the proposed model.

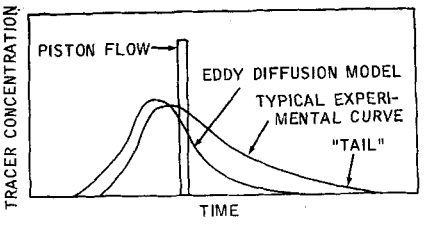

Fig. 1. Single eddy diffusion mechanisms fail to account for bed capacitance effects.

MIXED-PHASE FLOW CHARACTERISTICS

The need to consider two phases flowing over the beds adds much complexity to the above picture. Some of the flow characteristics which are postulated for the two-phase flow are:

1. Both liquid and gas can flow in the external channels.
2. Pores can hold liquid or gas.
3. Flow into the porous particles is by molecular diffusion only.
4. Flow in the void channels can be characterized by suitable diffusion or mixing mechanisms with either a laminar or turbulent flow regime.

A similar flow mechanism was proposed by Frankel (*7*) for gas-liquid flow in petroleum recovery from porous media.

To describe such a system requires the definition and evaluation of a number of parameters:

1. The number of the channels and pockets of a given size and shape and their locations in the bed.
2. The fractions of the pockets containing gas.
3. The distribution of the gas and liquid in the channels and the regime of flow (whether laminar or turbulent). Only laminar (Poiseuille) flow will be considered here.
4. The liquid diffusion coefficients in the pockets and channels.

THEORETICAL DEVELOPMENT

The approach for describing the above system in terms of its parameters will be to consider disturbing the flow with an impulse input at the top of the bed. The diffusion equations for the various channels and their associated pockets are then solved and combined to give the concentration-time relation for the bed output. A mathematical treatment for such systems has been given by Aris (*1*), and his nomenclature will be adopted.

Consider a void channel characterized by a shape s, length l, and radius r, the latter being the radius of a circle with the same cross-sectional area as

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the channel. A fraction of these channels is flowing liquid, the rest gas. Fluid flows through the void channels at a velocity $U_s(r, l)$, and the tracer concentration in the channel at any depth at any time is $c(z, t)$. Associated with the void channels are pores of depth and volume, which contain dead ended pockets. A fraction of these pores contain liquid, the remainder gas. The relative volume of a pore associated with a void channel is $\beta(\lambda) = \frac{\alpha}{\pi r^2}$. The concentration of tracer at any depth in the pore at any time is $\gamma(y, t)$, while the average tracer concentration in a single pore is $q(\lambda)$.

Basic equations can be written to describe tracer diffusion in the pores and diffusion and flow in the void channels.

Tracer Diffusion in the Pores

$$D\frac{\partial^2\gamma}{\partial y^2} = \frac{\partial\gamma}{\partial t} \qquad (1)$$

The boundary conditions state that

1. There is no tracer in the pore initially:

$$\gamma = 0 \text{ at } t = 0$$

2. The tracer concentration at the entrance of the pore is equal to that in the void channel at any time:

$$\gamma = c(t, z) \text{ at } y = 0$$

3. There is no flow from the end of the pore:

$$\frac{\partial\gamma}{\partial y} = 0 \text{ at } y = \lambda$$

Taking the Laplace Transform of Equation (1) and denoting this by a bar, that is

$$\bar{c}(y, p) = \int_0^\infty e^{-pt}\, c(y, t)\, dt$$

one can show (*1*) that the Laplace Transform of average tracer concentration in a given pore is

$$\bar{q}_\lambda = \frac{\bar{c}\tanh\omega}{\omega}, \quad \omega = \lambda\sqrt{p/D} \qquad (2)$$

The mean concentration transform for all pockets associated with the channel is

$$\bar{q}(p) = \frac{\bar{c}}{\beta\phi}\int_0^\infty \beta(\lambda)\frac{\tanh\omega}{\omega}\, d\lambda = \frac{\bar{c}\,\Omega(p)}{\beta\phi} \qquad (3)$$

Tracer Diffusion and Flow in Channel

The continuity equation for flow in the void channel can now be written:

$$D_c\frac{\partial^2 c}{\partial z^2} - U_s\frac{\partial c}{\partial z} = \frac{\partial c}{\partial t} + \beta\phi\frac{\partial q}{\partial t} \qquad (4)$$

The boundary conditions state that

1. There is no tracer in the channel initially:

$$c = 0 \text{ at } t = 0$$

2. There is no diffusion from the end of the channel:

$$\frac{\partial c}{\partial z} = 0 \text{ at } z = l$$

3. The input to the channel is a mathematic pulse and can be described by the Dirac delta function:

$$D_c\frac{\partial c}{\partial z} - U_s c = U_s\delta(t) \text{ at } z = 0$$

Transforming Equation (4) and substituting for $\bar{q}$ from Equation (3) one obtains the solution in terms of the transformed concentration:

$$\bar{c}(z, p) = \exp\frac{U_s z}{2D_c}\left\{1 - \left[1 + \frac{4D_c}{U_s}\frac{p}{2}(1 + \Omega(p))\right]^{1/2}\right\} \qquad (5)$$

The remaining problem is to find the inverse transform of $\bar{c}$, evaluate it at $z = l$, and combine for all channels. However the problem can be considerably simplified if just the moments of the concentration—time distribution, rather than the distribution itself, are used. In this case the moments of the concentration—time distribution in a channel can be expressed (*1, 13*) as

$$\mu_1 = \operatorname*{Lim}_{p\to o}\left(\frac{d\bar{c}}{dp}\right) = \int_0^\infty ct\,dt = \theta \qquad (6)$$

$$\mu_2 + \mu_1^2 = \operatorname*{Lim}_{p\to o}\left(\frac{d^2\bar{c}}{dp^2}\right) = \int_0^\infty ct^2\,dt + \mu_1^2 \qquad (7)$$

The first moment is related to the mean residence time, and the second moment is related to the variance of residence times.

Differentiating Equation (5) and substituting into Equation (6) and (7) one gets for a channel

$$\mu_1 = \frac{l}{U_s}(1 + \beta\phi) \qquad (8)$$

$$\mu_2 + \mu_1^2 = (1 + \beta\phi)^2\left[\left(\frac{l}{U_s}\right)^2 + \frac{2D_c l}{U_s^3} + \frac{2l\phi}{3DU_s}\bar{\beta}^2\right] \qquad (9)$$

where $\bar{\beta}^2$ is the mean square depth of pores which governs the diffusion rate in the pores.

Equations (8) and (9) are the moments of the output distribution for a given channel and its associated pockets. To obtain the output for the entire bed the output from each channel is weighted according to the relative volumetric flow in the channel,

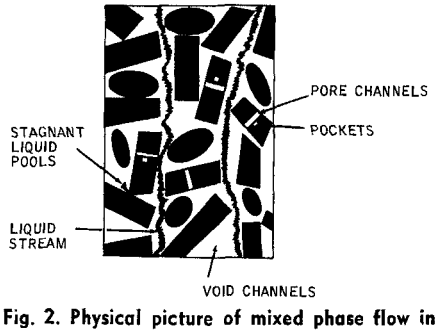

Fig. 2. Physical picture of mixed phase flow in a bed of porous particles.

and the result is summed over all the channels. In addition it is assumed that the channel diffusion coefficient can be expressed as a Taylor diffusivity for the laminar flow case. Thus one finds

$$D_c = \frac{k_s U_s^2(r, l)\, r^2}{D} \qquad (10)$$

where k_s is a shape factor for the channel (48 for circular channels) and $U_s(r, l)$ is governed by Poiseiulles law

$$U_s(r, l) = \frac{r^2 P}{\xi_s l\mu} \qquad (11)$$

ξ_s is a channel shape factor (32 for circular channels).

Thus for the entire bed the first moment is

$$[\mu_1]_{\text{Bed}} = \sum\int_0^\infty dl\int_0^\infty \frac{l}{U_s(r, l)}(1 + \beta\phi)\frac{Q_s(r, l)}{Q}\, dr \qquad (12)$$

where $Q_s(r, l) = f\eta v(r, l)\, U_s(r, l)\,\pi r^2$. Similar expressions can be written for the second moment.

Integration of these expressions gives the results for the first and second moment. It has also been shown (*1*) that for single-phase flow the Peclet number for the bed is related to the first and second moments of the residence time distribution through

$$[\mu_1]_{\text{Bed}} = \frac{L}{U} \qquad (13)$$

$$[\mu_2]_{\text{Bed}} = \frac{2D_c L}{U^3} \qquad (14)$$

$$\left[\frac{\mu_2}{\mu_1^2}\right]_{\text{Bed}} = \frac{2D_c L}{U^3}\left(\frac{U}{L}\right)^2 = \frac{2D_c}{LU} = \frac{2}{P_e} \qquad (15)$$

Thus for the present mixed-phase treatment

$$[\mu_1]_{\text{Bed}} = \theta = \frac{L}{U}\eta v(1 + \beta\phi) \qquad (16)$$

$$\left[\frac{\mu_2}{\mu_1^2}\right]_{\text{Bed}} = \frac{2}{P_e} = S_B + \frac{2U}{LD\eta_v}(S_v + \phi S_p) \qquad (17)$$

S_B, S_v, and S_p are shape factors which are constant for a given bed and are functions of the bed packing alone. They are obtained by combining properties of the bed packing such as channel and pore distributions.

DISCUSSION

The above analysis has given an expression for the axial dispersion in the bed in terms of three bed parameters, rather than a single-eddy diffusion coefficient. The physical significance of these factors is

1. S_B gives the liquid dispersion due to mixing of streams from various channels of different residence times.

2. S_v gives the dispersion from axial diffusion in the void channels.

3. S_p gives the dispersion from diffusion into the pores.

The model represented by Equations (16) and (17) shows first that when all the channels are in laminar flow the mean residence time increases with increasing bed height and liquid holdup and with decreasing liquid velocity. The mean residence time will also depend on the fraction of pores containing liquid, and this is a function of both the fluid and catalyst properties. Second the dimensionless dispersion parameter $2/Pe$ should be directly proportional to superficial liquid velocity while decreasing with bed length and liquid holdup. The dispersion parameter is also a function of the three shape factors.

EXPERIMENTAL VERIFICATION OF MODEL

To check out the model some residence time distribution data have been obtained for 1-in. diameter wax desulfurizing pilot unit operations in which the liquid space velocity is so low that the condition of laminar flow is met. Bed height and liquid holdup were maintained constant at 47 in. and 50 vol. %, respectively. Packing consisted of 10 to 14-mesh particles.

$2/Pe$ does increase with liquid velocity as expected (Figure 3). In spite of the good fit of the data in Figure 3 more complete data are needed to establish the exact relationship involved. Unfortunately most of the reported literature data are for single-phase flow well into the transition and turbulent regions (particle $N_{Re} > 10$ based on liquid flow). Preliminary results for turbulent region flow indicate a slight decrease of $2/N_{Pe}$ with increasing liquid velocity or particle Reynolds number. Therefore a broad region where a reciprocal Peclet number dispersion parameter is relatively insensitive to flow rate might be expected. This would occur because a significant fraction of the channels would be in laminar flow, while an equally significant fraction would be in turbulent flow. Most of the available data (3) have shown a relatively insensitive Pe vs. Re relationship for moderate flows.

The data of Figure 3 have not been extrapolated to zero particle Reynolds number because the present model may not be valid at extremely low liquid velocities. One would expect the channel dispersion to approach zero as liquid velocity approaches zero because the Taylor diffusion coefficient approaches zero. However as liquid velocity approaches zero, molecular diffusion would become controlling, and this has been ignored in the present derivation. Therefore the present model is not applicable at velocities where molecular diffusion would be comparable to the Taylor diffusion. This region is unlikely to be of interest for real beds.

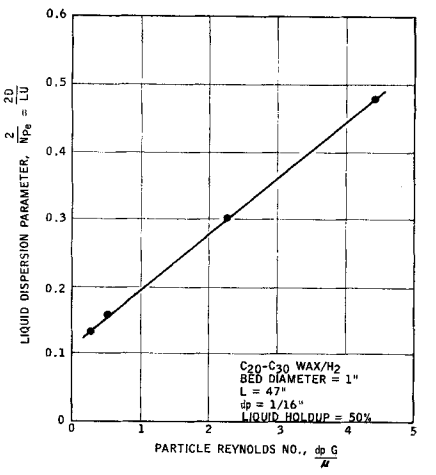

Fig. 3. Liquid dispersion increases with flow rate in laminar region.

EVALUATION OF SHAPE FACTORS

Since the shape factors are complex function of the distributions of channels and pore sizes, shapes, and lengths, they will vary with both packing material and method of packing. Such distributions are so complex that they could be evaluated mathematically only for very simple models of synthetic beds as proposed by Turner (12) and Aris (1). For real beds they must be investigated experimentally.

In accordance with Equation (17) the intercept of the line of Figure 3 directly yields the shape factor S_B, while $(S_v + \phi S_p)$ can be obtained from the slope. For the bed studied $S_B = 0.11$ and $(S_v + \phi S_p) = 0.082$. The contribution to liquid dispersion caused by mixing of streams from various channels of different residence times appears to play a larger role than the combined dispersion from axial diffusion in the void channels and diffusion into the pores. Further breakdown of S_v, ϕ, and S_p is not possible without additional experiments.

A simple technique for evaluating the shape factors would make use of a flooded bed, that is one with $\phi = 1$, $\eta_v = 1$, or a single-phase system. If such a bed is considered, packed with either porous (P) or nonporous (NP) particles of the same size and shape, then from Equations (16) and (17)

$$\beta = 1 - \frac{\theta_P}{\theta_{NP}} \tag{18}$$

$$\frac{2}{Pe_{NP}} = S_B + \frac{2S_v}{\theta_{NP}D} \tag{19}$$

$$\frac{2}{Pe_p} = S_B + \frac{2(S_v + S_p)}{\theta_{NP}D} \tag{20}$$

Thus the plot of the inverse of Peclet number vs. average residence time gives the three shape factors, while the ratio of residence times for the two beds yields β.

SUMMARY

A model for the liquid-phase dispersion in mixed-phase flow through porous beds has been developed. This model is not restricted to describing the flow in terms of a single or average bed eddy diffusivity but provides three bed parameters for describing liquid dispersion. These parameters are functions of the bed packing alone. The present treatment applies only to laminar flow in the channels, that is very low particle Reynolds numbers, but it could be extended to turbulent flow if desired. Data for a low space velocity wax desulfurization reactor verifies the general trend predicted by the model. However more complete data are needed to establish the exact relationship involved.

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NOTATION

$c(z,t)$ = tracer concentration in channel, mass/vol. liquid
D = molecular diffusivity of tracer, sq. ft./sec.
D_e = Taylor diffusion coefficient in channel, sq. ft./sec.
D_e = axial diffusivity of the entire bed
d_p = particle diameter in packed bed, ft.
f = fraction of channels in flowing liquid, dimensionless
G = superficial mass velocity, lb./hr.-sq. ft.
k_e = shape factor (12), dimensionless
l = length of void channel external to packing, ft.
L = length of packed bed, ft.
P = pressure drop, lb./sq. ft.
p = Laplace transform variable
P_e = length Peclet number for packed bed (LU/D), dimensionless
$q(\lambda)$ = average tracer concentration in pore, mass/vol. liquid
Q = total liquid volumetric flow, cu. ft./hr.
$Q_s(r,l)$ = volumetric liquid flow in a given channel, cu. ft./hr.
r = radius of void channel, ft.
Re = particle Reynolds number, d_pG/μ, dimensionless
S_B, S_v, S_p = derived shape factors for packed bed, dimensionless

s = suffix denoting shape of channel
t = time, hr.
U = average liquid velocity in bed, ft./sec.
$U_s(r,l)$ = average liquid velocity in channel, ft./sec.
y = distance variable down pore, ft.
z = distance variable down channel, ft.

Greek Letters

α = volume of pore of depth λ, cu. ft.
β = fraction volume of pores participating in dispersion, dimensionless
$\beta(\lambda)$ = relative volume of pore of depth λ to associated void channel, dimensionless
$\overline{\beta^2}$ = mean square depth of pores, $\frac{1}{1+\beta^2}\int_0^\infty \beta(\lambda)\lambda^2 d\lambda$
$\gamma(y,t)$ = tracer concentration in pore, mass/vol. liquid
δ = Dirac delta function
η_v = liquid holdup in channels, dimensionless
θ = mean residence time in bed, hr.
λ = depth of pore, ft.
μ = viscosity, lb./ft.-hr.
μ_1 = first moment of concentration-time distribution, time
μ_2 = second moment of concentration-time distribution, time^2
ξ_s = shape factor (13)
ϕ = fraction of pores filled with liquid, dimensionless
$\Omega(p) = \int_0^\infty \beta(\lambda)\frac{\tanh\omega}{\omega}d\lambda$
$\omega = \lambda\sqrt{p/D}$

Shape Factor

$S_B = \frac{I_1 I_2}{\epsilon_v} - 1$
$S_v = \Sigma k_s d_s$
$S_p = \frac{s}{3}\beta^{-2}$
$I_1 = \Sigma_s \xi_s \int_0^\infty dl \int_0^\infty \epsilon_s \frac{l^2}{r^2} dr$
$I_2 = \Sigma_s \frac{1}{\xi_s}\int_0^\infty dl \int_0^\infty \epsilon_s \frac{r^2}{l^2} dr$
$d_s = \int_0^\infty r^2 dr \int_0^\infty \epsilon_s dl$, mean square radius for channels of shape s
ϵ_v = fraction voids in channels, dimensionless
ϵ_s = voidage due to species of channels, dimensionless

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Perturbation Velocities in Gas-Liquid Partition Chromatographic Columns

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The characteristic velocities in binary and particular ternary cases allow straightforward calculation of equilibrium partition coefficients for components present in both flowing and fixed phases. It is shown in the case of a general N-component flowing phase that N-1 characteristic velocities arise. In theory N-1 equilibrium partition coefficients can be obtained from measurements of these velocities. It is also shown that radioactive tagging of one component provides a distinct characteristic velocity, which can be used either to obtain the N^{th} equilibrium coefficient or to eliminate a parameter which is especially subject to experimental error.

The analytically determined characteristic velocities are compared with pulse velocities obtained from numerical solution of the original balance equations. The agreement over a range of solute concentrations is excellent.

Gas-liquid partition chromatography (GLPC) has been shown experimentally to be a valid and convenient tool for measuring equilibrium information for gas-liquid systems. The normal experimental procedure involves the determination of the residence time in a packed column of a small sample of gaseous material. The latter is soluble in a nonvolatile liquid which is fixed on the porous solid packing. The sample is swept through the bed by an elution gas which is normally relatively insoluble in the fixed liquid phase.

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Stalkup and Kobayashi (3) have extended the experimental investigations to cover the case of an elution gas which is appreciably soluble in the fixed liquid phase. They have also reviewed the literature on both the experimental and theoretical aspects of GLPC.

It is the purpose of this paper to extend the theoretical analysis of the motion of multicomponent gas mixtures through beds packed with porous material supporting a fixed liquid phase. In particular equations applicable to the systems studied by Stalkup and Kobayashi are derived.

BALANCE AND EQUILIBRIUM EQUATIONS

Under the experimental conditions normally encountered in GLPC the following assumptions are more or less valid: constant temperature and pressure, both fixed and flowing phases are effectively one-dimensional, and total molar concentration is constant.

The continuity equation for component k in the flowing phase under these conditions is

$$\frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x}[c_k (V_k)_x] + R_k \qquad k = 1, 2, \ldots, N \quad (1)$$

Total continuity is assured by

$$\frac{\partial}{\partial x}(W_x) = \sum_{k=1}^{N}\frac{R_k}{c} \quad (2)$$

where $c\,W_x = \sum_k c_k (V_k)_x$

If the motion of component k relative to the center of moles can be expressed as

$$c_k[(V_k)_x - W_x] = -c\mathcal{D}\frac{\partial y_k}{\partial x} \quad (3)$$