A Non-Fickian Model of Packed-Bed Reactors

A model for packed-bed reactors with dispersion is derived rigorously via the volume averaging approach. Though it is quantitatively more consistent with experimental data, it requires less computational efforts than the prevalent Fickian model. The adverse effects of dispersion on conversion are demonstrated both numerically and analytically using the new model.

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SCOPE

The prevalent Fickian model for dispersion in packed-bed reactors has been found to be inadequate in many experimental investigations. The major inconsistency lies in its failure to predict the lack of back transport in the reactors. It thus becomes a useless model for design and control purposes when the effects of conditions upstream and downstream are relevant. In addition, analytical and numerical solutions of the Fickian model are often tedious and uninformative. The cross-flow model and the mixing cell model are the only two previous attempts to correct these inadequacies of the Fickian model. However, these models are not supported by experimental studies. In the present investigation, a more rigourous approach is adopted to yield a physically and quantitatively consistent model with experimental justification. The basis of dispersion is attributed to flow maldistributions caused by void fraction nonuniformity in packed beds. The relevant reduction in conversion due to this dispersion mechanism is then investigated numerically and analytically.

CONCLUSIONS AND SIGNIFICANCE

The present model is shown to be capable of explaining dispersion data from experimental studies. Its quantitative agreement with the Fickian model and the analytical simplicity of the model equations suggest that it can replace the ad-hoc Fickian model. More importantly, it offers an accurate description of the major physical mechanism that accounts for dispersion and thus becomes much more valuable for design and control purposes. The dependence of the dispersion phenomenon on system parameters is also available to allow a more systematic correlation of experimental data. The performance of the reactor is also shown to diminish due to the nonideal apportioning of residence time and catalyst.

This paper deals with the modelling of packed-bed reactors with dispersion. If a pulse of dye tracer is injected into a packed bed, the pulse spreads axially as it moves downstream from the point of infusion. This spreading, or dispersion, is expected to have an influence on the performance of the reactor. The prevalent pseudo-homogeneous model assumes a Fickian-like mechanism with an effective diffusivity that is greatly different from the actual diffusivity. The resulting governing equation is of second order with respect to the axial direction, and boundary conditions for both the inlet and exit of the bed must be specified. The appropriate set of boundary conditions is still undetermined. Danckwerts (1953), Choi and Perlmutter (1976), Wehner and Wilhelm (1956) have proposed inconsistent sets. Nevertheless, their boundary conditions are all based on the intuitive and unjustified assumption of a Fickian-like mechanism for dispersion. In spite of these inconsistencies, Burghardt and Zaleski (1968), Ray et al. (1972) have used this model to study the effects of dispersion on the conversion of a packed-bed reactor.

Recently, however, much experimental evidence has surfaced to refute the validity of the Fickian model. Experiments indicate that there is no upstream spreading as predicted by the model. More specifically, the Fickian model incorrectly predicts that any point in the reactor is influenced by the conditions downstream. In Deckwer and Mahlmann's experiments (1974), this lack of back transport is dramatically demonstrated in a reactor with three sections. Widely different reaction conditions in the last section are shown to have no effect on the concentration profiles of the upstream sections. This inconsistency is especially critical if the Fickian model is used for control purposes. The inaccurate back transport produces a feedback that can incorrectly destabilize the control system. Optimization of reactor performance can also be hampered if the effects of downstream conditions are of importance. A minor inconsistency is also pointed out by Hinduja et al. (1980), namely, that the Fickian model predicts the spreading of an injected pulse of tracer with a formally infinite velocity in all directions from the point of injection. Similarly, concentration discontinuities can also result from some of the proposed boundary conditions for the Fickian model (Choi and Perlmutter, 1976). There are even attempts to rationalize these concentration jumps (Standart, 1968). Quite recently Wicke (1975) specifically invalidated the Wehner and Wilhelm boundary conditions for a gas phase system. For a detailed discussion of the failures of the Fickian model, the readers are referred to the excellent analysis by Sundaresan, Amundson and Aris (1980).

Many workers realize that the fallacy lies in the assumption of the Fickian-like flux. While a second-order equation adequately describes the pulse response of a reactor, this does not establish the validity of the ad-hoc Fickian assumption and allow one to invoke them in specifying the boundary conditions. For example, some alternate models mentioned below are just as capable of simulating pulse responses of a packed-bed reactor. Consequently, the Danckwerts and Wehner and Wilhelm conditions have no physical or theoretical basis, and the lack of experimental support stipulates that they are inaccurate. Two models have been proposed to replace the Fickian model. In Hinduja et al.'s (1980) cross flow model, exchange of fluid between stagnant and flowing parts of the bed is used to model

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dispersion. In the mixing-cell model of Deans and Lapidus (1960) interstices between packing elements are idealized as perfectly stirred mixers which give rise to dispersion-type behavior.

In the past decade, the method of volume averaging as a rational approach to transport processes in two phase systems has been introduced by Gray (1975), Whitaker (1973) and Carbonell (1980). As indicated by the excellent review of Newman and Tiedemann (1975), the concept of volume averaging has also been used for many years in describing transport in porous electrodes. This approach rigorously and systematically derives the volume average equation from the basic point concentration equation, thus delineating the physical and theoretical basis of each term in the equation. In this paper, the model by Carbonnel (1980), which attributes dispersion to void fraction nonuniformity, is generalized to include reaction terms and finite length reactors. However, since the present model is required to be consistent with the previously mentioned physical phenomena, a different route is taken in the derivation of the final equations to retain these properties.

FORMULATION OF INTRINSIC-PHASE AVERAGE EQUATION

The microscopic (point) transport equation for the point concentration is

$$\frac{\partial c'}{\partial t} + \underset{\sim}{\nabla} \cdot (\underset{\sim}{v} c') = -\underset{\sim}{\nabla} \cdot J \qquad (1)$$

where J is the Fickian diffusive flux vector. The velocity vector $\underset{\sim}{v}$, is assumed to be uncoupled from Eq. 1 and can be obtained independently. Boundary conditions for Eq. 1, assuming that the catalytic reactions occur on the surface of the catalyst and the surface capacitance term is negligible to allow a pseudo-steady-state approximation, are

$$\underset{\sim}{J} \cdot \underset{\sim}{n} = F(c') \text{ on } A_{\alpha\beta} \text{ for } z > 0$$

$$\underset{\sim}{J} \cdot \underset{\sim}{n} = 0 \text{ on } A_{\alpha\beta} \text{ for } z \leqq 0 \qquad (2)$$

where $A_{\alpha\beta}$ is the catalyst surface area and F is a reaction expression involving the adsorption and surface reaction contributions. The catalyst section is arbitrarily chosen to start at $z = 0$ and the section before the catalyst section is filled with inert packing. The intrinsic phase average of a point property Ψ is defined as:

$$\langle \Psi \rangle^{\alpha} = \frac{1}{V_{\alpha}} V_{\alpha}\, \Psi \, dV \qquad (3)$$

where V_{α} is the fluid volume inside a control volume V of fixed dimension located at any point. The dimension of V in the z-direction spans from $z - \delta$ to $z + \delta$. From the average theorem (Gray, 1975),

$$\langle \underset{\sim}{\nabla} \Psi \rangle = \underset{\sim}{\nabla} \langle \Psi \rangle + \frac{1}{V} \mathrm{A}_{\alpha\beta} \Psi \underset{\sim}{n} dA \qquad (4)$$

where

$$\langle \Psi \rangle = \frac{1}{V} V_{\alpha} \Psi dV \qquad (5)$$

is the phase average. The void fraction ϵ is defined as the ratio of V_{α} to V and from Eqs. 3 and 5, it is clear that

$$\langle \Psi \rangle = \epsilon \langle \Psi \rangle^{\alpha} \qquad (6)$$

Taking the phase average of Eq. 1 and applying the boundary condition 2, one obtains

$$\frac{\partial \langle c \rangle}{\partial t} + \underset{\sim}{\nabla} \cdot \langle \underset{\sim}{v} c' \rangle + \frac{1}{V} \int_{A_{\alpha\beta}} (\underset{\sim}{v} c') \cdot \underset{\sim}{n} \, dA \qquad (7)$$

$$= - \underset{\sim}{\nabla} \cdot \langle \underset{\sim}{J} \rangle - \frac{1}{V} \int_{A_{\alpha\beta}} H(z) F(c') \, dA$$

where $H(z)$ is the Heavyside Function.

The intrinsic phase average property, like the point property, is a scalar or vector field and one can define the deviations of the two as

$$\hat{\underset{\sim}{v}} = \underset{\sim}{v} - \langle \underset{\sim}{v} \rangle^{\alpha} \qquad (8)$$

and

$$\hat{c} = c' - \langle c \rangle^{\alpha} \qquad (9)$$

Moreover, we will stipulate that the intrinsic phase averages are essentially constant in the control volume. Then it follows from Eqs. 8 and 9 that

$$\langle \hat{\underset{\sim}{v}} \rangle^{\alpha} = \langle \hat{c} \rangle^{\alpha} = \langle \hat{\underset{\sim}{v}} \rangle = \langle \hat{c} \rangle = 0 \qquad (10)$$

Furthermore, we will also assume that the control volume is small enough such that large gradients in the point concentrations inside the volume do not occur and thus

$$\frac{\hat{c}}{\langle c \rangle^{\alpha}} \ll 1 \qquad (11)$$

and

$$F(c') \approx \mathrm{F}(\langle c \rangle^{\alpha}) \qquad (12)$$

Finally, we will assume incompressible flow which stipulates that

$$\underset{\sim}{\nabla} \cdot \langle \underset{\sim}{v} \rangle = 0 \qquad (13)$$

and there is no flow into the catalyst

$$\int_{A_{\alpha\beta}} \underset{\sim}{v} \cdot \underset{\sim}{n} \, dA = 0 \qquad (14)$$

Invoking these properties, one can reduce Eq. 7 to

$$\frac{\partial \langle c \rangle^{\alpha}}{\partial t} + \langle \underset{\sim}{v} \rangle^{\alpha} \cdot \underset{\sim}{\nabla} \langle c \rangle^{\alpha} + \frac{1}{\epsilon} \underset{\sim}{\nabla} \cdot \langle \underset{\sim}{v} \hat{c} \rangle$$

$$= - \frac{1}{\epsilon} \underset{\sim}{\nabla} \cdot \langle \underset{\sim}{J} \rangle - \frac{1}{\epsilon} F\left(\langle c \rangle^{\alpha}\right) \frac{A_o}{V} \mathrm{G}(z) \qquad (15)$$

where

$$\frac{A_o}{V} \mathrm{G}(z) + \frac{1}{V} \int_{A_{\alpha\beta}} H(z) \, dA$$

$$= \frac{A_o}{V} \begin{Bmatrix} 0 \\ \dfrac{z + \delta}{2\delta} \\ 1 \end{Bmatrix} \quad \begin{matrix} z < -\delta \\ -\delta < z < \delta \\ z > \delta \end{matrix} \qquad (16)$$

and A_o is the catalyst surface area in a control volume.

We follow the approach of Whitaker (1973) andGray (1975) in defining a dispersion tensor $\underset{\approx}{D}$ by the following implicit definition

$$\underset{\approx}{D} \cdot \nabla \langle c \rangle^{\alpha} = \langle J \rangle - \langle \underset{\sim}{v} \hat{c} \rangle \qquad (17)$$

which reduces Eq. 15 to

$$\frac{\partial \langle c \rangle^{\alpha}}{\partial t} + \langle \underset{\sim}{v} \rangle^{\alpha} \cdot \nabla \langle c \rangle^{\alpha} = \frac{1}{\epsilon} \underset{\sim}{\nabla} \cdot (\underset{\approx}{D} \cdot \underset{\sim}{\nabla} \langle c \rangle^{\alpha})$$

$$- \mathrm{G}(z) \frac{A_o}{V_{\alpha}} F(\langle c \rangle^{\alpha}) \qquad (18)$$

By defining the dispersion tensor, we have actually lumped both the diffusive and convective contributions to dispersion into a Fickian-like mechanism. This seems to defeat our aforesaid objective of eliminating this particular description. However, the entire dispersion tensor will be shown to be negligible from experimental data and the introduction of Eq. 17 is actually to facilitate the introduction of empirical data for this justification.

It is determined experimentally that $\langle v_z \rangle^{\alpha} \gg \langle v_r \rangle^{\alpha}$ and that the dispersion tensor is approximately diagonal with

$$\frac{D_{rr}}{D_{zz}} = \alpha$$

a constant, regardless of position (Carbonell, 1980). Thus

$$\frac{\partial \langle c \rangle^{\alpha}}{\partial t} + \langle v_z \rangle^{\alpha} \frac{\partial \langle c \rangle^{\alpha}}{\partial z} = \frac{1}{\epsilon} \frac{\partial}{\partial z} D_{zz} \frac{\partial \langle c \rangle^{\alpha}}{\partial z} + \frac{\alpha}{\epsilon r} \frac{\partial}{\partial r} r D_{zz} \frac{\partial \langle c \rangle^{\alpha}}{\partial r} - G(z) \frac{A_o}{V_{\alpha}} F(\langle c \rangle^{\alpha}) \tag{19}$$

is the final form of our equation. Also, from the continuity equation, $\langle v_z \rangle^{\alpha}$ is a function of r only.

To estimate the relative contribution of each term, the following dimensionless variables are introduced

$$c = \frac{\langle c \rangle^{\alpha}}{c_o} \quad x = \frac{z}{l} \quad y = \frac{r}{R}$$

$$u = \frac{\langle v_z \rangle^{\alpha}}{u_o} \quad D^* = \frac{D_{zz}}{\mathcal{D}} \quad \theta = \frac{u_o t}{\ell} \tag{20}$$

where c_o is the feed concentration, ℓ the reactor length, R the reactor radius, $\mathcal{D}$ the diffusivity and u_o is defined as the area average interstitial velocity

$$u_o = \frac{2}{R^2} \int_o^R r \, \langle v_z \rangle^{\alpha} \, dr \tag{21}$$

In dimensionless form, Eq. 19 becomes

$$\frac{\partial c}{\partial \theta} + u(y) \frac{\partial c}{\partial x} = \frac{1}{\epsilon} \frac{1}{\text{Pe}} \frac{\partial}{\partial x} D^* \frac{\partial c}{\partial x} + \frac{\alpha}{\epsilon} \left(\frac{l}{R} \right)^2 \frac{1}{\text{Pe}} \frac{1}{y} \frac{\partial}{\partial y} y \, D^* \frac{\partial c}{\partial y} - G(x) \, \phi \, f(c) \tag{22}$$

where $\text{Pe} = u_o \ell / \mathcal{D}$ is the Peclet number based on molecular diffusivity.

$$\phi = \frac{A_o \ell k c_o^{\,n-1}}{V_{\alpha} u_o} \tag{23}$$

$$f(c) = \frac{F(c_o c)}{k c_o^{\,n}}$$

The rate constant k and the reaction order n are based on the general rate expression

$$F(c') = k c'^{n} \tag{24}$$

The following typical numbers are taken from Deckwer and Mählmann's (1974, 1976) experiment to study axial dispersion (numbers are evaluated for the glass sphere section):

$$d_p/\ell = 0.3125 \qquad \ell/R = 7.11$$
$$\phi = 1.0 \qquad \epsilon = 0.391 \tag{25}$$

The value for α is about 0.05 for liquid packed-bed reactors and the approximate value for D^* is (Carbonnel 1980)

$$D^* \approx 0.6 \qquad \text{Pe}_p < 1.0$$
$$D^* \approx \text{Pe}_p \qquad \text{Pe}_p > 1.0 \tag{26}$$

where

$$\text{Pe}_p = \frac{\epsilon u_o d_p}{\mathcal{D}} \tag{27}$$

For Deckwer and Mählmann's system, $\text{Pe}_p \gg 1.0$ and one obtains the following order of magnitude approximation:

$$\frac{D^*}{\epsilon \, \text{Pe}} \sim 0\,(10^{-2}) \qquad \frac{\alpha}{\epsilon} \left(\frac{\ell}{R} \right)^2 \frac{D^*}{\text{Pe}} \sim 0\,(10^{-2}) \tag{28}$$

Consequently, the axial and radial dispersion terms are essentially negligible. This is consistent with Kalthoff and Vortmeyer's (1980) conclusion for a different system. In addition, since the control volume is of the order of a catalyst pellet, $\delta/\ell \ll 1$, one can approximate the function $G(x)$ as unity. Thus,

$$\frac{\partial c}{\partial \theta} + u(y) \frac{\partial c}{\partial x} = \phi(y) \, f(c) \tag{29}$$

Similarly, the boundary condition for steady feed can be approximated as

$$c(x = 0) = 1 \tag{30}$$

If u is independent of y, Eq. 29 becomes the plug-flow equation and no dispersion is possible. Deckwer and Mählmann's study indicated that their data cannot be explained with a plug-flow model. Consequently, one expects the axial velocity to be dependent on the radial coordinate. We follow Carbonnell (1980) in proposing that the radial void fraction distribution is the cause of this axial flow nonuniformity. The large void fraction near the wall has already been utilized to explain large changes in Nusselt number (1978). In the next section, it will be shown that this small layer is sufficient to account for the large dispersion observed in Deckwer's and Mählmann's study. It is also interesting to note that Kalthoff and Vortmeyer (1980) have recently reported that their data can only be fitted with an equation including flow nonuniformity while the Fickian equation fails completely.

In previous volume averaging approaches (Carbonell, 1980), equations similar to Eq. 29 are area averaged and a definition analgous to the dispersion tensor for intrinsic phase average equation (Eq. 17) is introduced to yield a one-dimensional, second or higher order Fickian-type equation. While this allows easy comparison to pulse response data based on the latter equation, it introduces the physically inaccurate Fickian mechanism. In addition, the same transformation is possibly unjustifiable under reactive conditions. Consequently, to preserve the true mechanism for dispersion, Eq. 29 is designated the model equation. It is simple to verify that Eq. 29, a first-order equation, correctly accounts for the absence of back transport and since the flow rates are finite, tracers do not propagate at infinite velocities. Moreover, the solution of Eq. 29, whether analytical or numerical, is much simpler than the Fickian model which is infamous for its cumbersome results (Hinduja et al., 1980). In the next section, the pulse response prediction of Eq. 29 is favorably compared to Deckwer and Mählmann's (1974) data.

PULSE RESPONSE

The appropriate equation and initial condition for a pulse testing system are

$$\frac{\partial c}{\partial \theta} + u(y) \frac{\partial c}{\partial x} = 0$$
$$c(\theta = 0) = \delta(x) \tag{31}$$

The solution to Eq. 31 is:

$$c(x,y,\theta) = \delta(x - u(y)\theta) \tag{32}$$

Assuming that the pulse response data are collected by measuring the bulk-average concentration at the end of the reactor, the result is described by

$$\bar{c}_e(\theta) = 2 \int_o^1 y \, u(y) \, c(1,y,\theta) \, dy \tag{33}$$

The second moment about the mean of $\bar{c}$, σ^2, can be evaluated according to the following identity (Hinduja et al., 1980),

$$\sigma^2 = \mathcal{L}''(0) - [\mathcal{L}'(0)]^2 \tag{34}$$

where

$$\mathcal{L}(s) = \int_o^{\infty} e^{-s\theta} \, \bar{c}_e(\theta) \, d\theta \tag{35}$$

is the Laplace transform of $\bar{c}_e(\theta)$.

Applying Eqs. 32, 33 and 35 to Eq. 34, one obtains

$$\sigma^2 = 2 \int_o^1 \frac{y dy}{u(y)} - 1 \tag{36}$$

which indicates how the axial flow non-uniformity can be measured from pulse response data. The corresponding second moment from Fickian model is (Hinduja et al., 1980)

$$\sigma_F^2 = \frac{2}{\text{Pe}_e} \tag{37}$$

where

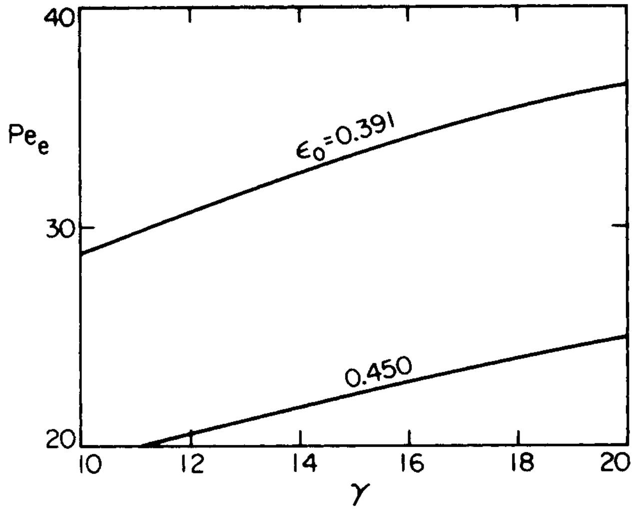

Figure 1. Dependence of effective Peclet number on γ and ϵ_o.

$$Pe_e = \frac{u_o \ell}{D_e}$$

is the effective Peclét number. Relating Eqs. 36 and 37, one obtains the following relationship between the effective Peclét number and the flow non-uniformity.

$$Pe_e = \frac{2}{2 \int_o^1 \frac{y dy}{u} - 1} \tag{38}$$

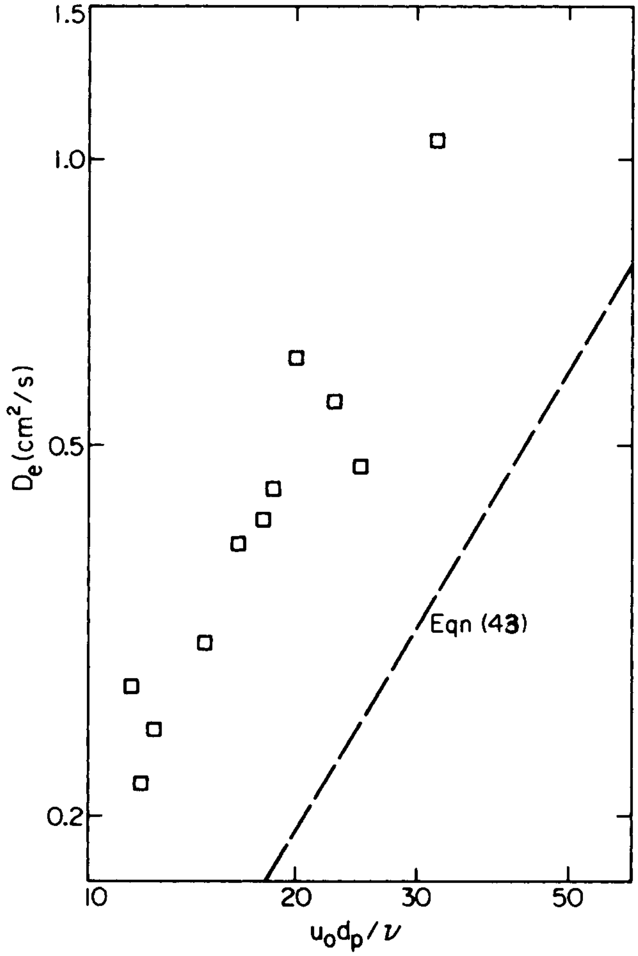

Figure 2. Comparison of Deckwer and Mählmann's data with theory.

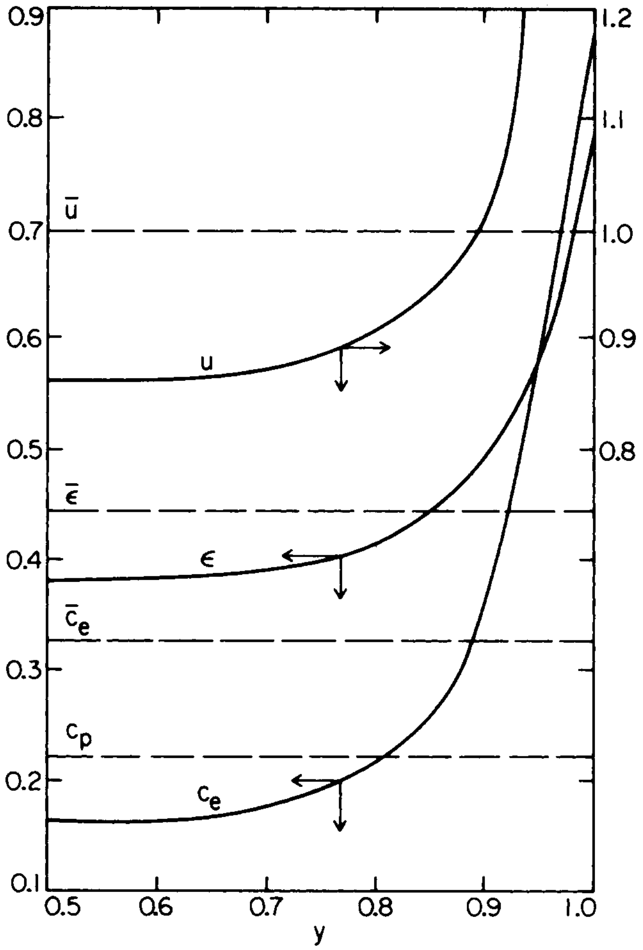

Figure 3. The axial velocity, void fraction and concentration profile for a first-order reaction as a function of radial position. The various area averaged values and the plug-flow concentration are also depicted ($\epsilon_o = 0.391$ $\gamma = 13.5$ $f(c) = c$ $\phi_o = 1$).

While it is commonly agreed that the interstitial velocity is largest where the void fraction is largest, the exact correlation between velocity and void fraction differs (Leron and Froment, 1977). It will be assumed here that the Ergun Equation describes this relationship adequately:

$$u(y) = \left(\frac{\epsilon}{1-\epsilon}\right)^{1/2} \Big/ 2 \int_o^1 \left(\frac{\epsilon}{1-\epsilon}\right)^{1/2} y\, dy \tag{39}$$

where the constraint from the definition of u,

$$2 \int_o^1 u(y)\, y\, dy = 1 \tag{40}$$

is accounted for.

The void fraction distribution can be approximated by the following empirical function by Kalthoff and Vortmeyer (1980),

$$\epsilon(y) = \epsilon_o \{1 + \exp[\gamma(y - 1)]\} \tag{41}$$

where

$$\gamma = \frac{3R}{d_p} \tag{42}$$

and ϵ_o is the void fraction in the center of the bed. The relationship between Pe_e and γ for $\epsilon_o = 0.391$ and 0.45 is depicted in Figure 1. The γ and ϵ_o values in Deckwer and Mählmann's study are 13.5 and 0.391, respectively, corresponding to an effective Peclét number of 31.83. Consequently,

$$\begin{aligned} D_e &= \frac{u_o \ell}{31.83} = \frac{\ell}{31.83} \frac{\nu}{d_p} \frac{u_o d_p}{\nu} \\ &\approx \frac{32}{31.83} \times \frac{0.011}{1} \times \frac{u_o d_p}{\nu} \\ &\approx 0.011 \frac{u_o d_p}{\nu} \end{aligned} \tag{43}$$

Equation 43 is plotted in Figure 2 with the data of Deckwer and Mählmann. The agreement is satisfactory considering that the model is deterministic from independent studies. Moreover, the mixing chamber preceding the reactor which is not considered here could account for the higher dispersion observed. Neglecting the convective contribution in Eq. 16 can also partially account for the discrepancy. Nevertheless, the linear dependence of D_e on $u_o d_p / \nu$ is well described. In Figure 3, the void fraction distribution and the velocity distribution along with their area average quantities are depicted. Note that the void fraction remains relatively constant until a small layer near the wall (~15%). This small layer of high void fraction is sufficient to cause the resulting large-scale dispersion.

STEADY-STATE CONVERSION

Under reactive conditions, ϕ is a function of y since the available catalyst surface area varies with ϵ. However, since the catalyst surface area per unit catalyst volume is a constant, the dependence of ϕ on ϵ can be found to be

$$\phi(y) = \phi_o \frac{1 - \epsilon}{\epsilon} \tag{44}$$

where

$$\phi = \frac{\ell k_o c_o{}^{n-1}}{u_o} a_v \tag{45}$$

is a constant and a_v is the catalyst surface area per unit volume catalyst.

Integrating Eq. 18 from zero to x at steady-state, one obtains

$$\int_1^c \frac{dc}{f(c)} = - \frac{\phi(y)}{u(y)} x \equiv \Omega(y)\, x \tag{46}$$

The bulk average concentration is then

$$\bar{c}(x) = 2 \int_o^1 c(x,y)\, u(y)\, y\, dy \tag{47}$$

With a flat void fraction distribution (plug-flow) the resulting equation is

$$\int_1^{c_p} \frac{dc}{f(c)} = - \phi_o \frac{1 - \bar{\epsilon}}{\bar{\epsilon}} x \tag{48}$$

where

$$\bar{\epsilon} = 2 \int_o^1 \epsilon\, y\, dy \tag{49}$$

is the area average void fraction. In Figure 3, c_e, c_p and $\bar{c}$ are depicted for an irreversible first-order reaction.

The differential equation describing the corresponding model as Fickian dispersion is

$$\frac{1}{\mathrm{Pe}_e} \frac{d^2 c_F}{dx^2} - \frac{dc_F}{dx} - \phi_o f(c_F) = 0 \tag{50}$$

If the Danckwerts set of boundary conditions are used for an irreversible first-order equation, the solution for Eq. 50 can be shown to be (Hinduja et al., 1980)

$$c(x) = \frac{(\lambda_2 - \lambda_1)}{\lambda_2 \left(1 - \frac{\lambda_1}{\mathrm{Pe}}\right) e^{-\lambda_1 x} - \lambda_1 \left(1 - \frac{\lambda_2}{\mathrm{Pe}}\right) e^{-\lambda_2 x}} \tag{51}$$

where

$$\lambda_{1,2} = \frac{\mathrm{Pe}_e}{2} \left[1 \pm \sqrt{1 + \frac{4\phi_o}{\mathrm{Pe}_e}}\right] \tag{52}$$

Table 1 compares the solutions of the first-order reaction for the different models. There is little difference between the numerical predictions of the Fickian model and the present one while the plug flow model yields considerable higher conversion. However, one must be reminded that analytical solutions for the Fickian model is often unavailable while the present model is more easily treated. Consequently, besides the physical insights, the present model offers a considerable advantage in computational efforts.

TABLE 1. NUMERICAL COMPARISON OF VARIOUS MODELS.
$\epsilon_o = 0.45 \quad \gamma = 20 \quad \mathrm{Pe}_e = 25 \quad \phi_o = 1 \quad f(c) = c$

x	c_p (Plug)	c_F (Fickian)	$\bar{c}$
0.1	0.8850	0.9070	0.8989
0.2	0.7831	0.8237	0.8099
0.3	0.6930	0.7481	0.7317
0.4	0.6133	0.6794	0.6628
0.5	0.5428	0.6170	0.6021
0.6	0.4803	0.5604	0.5486
0.7	0.4251	0.5089	0.5013
0.8	0.3762	0.4622	0.4595
0.9	0.3329	0.4198	0.4226
1.0	0.2946	0.3812	0.3898

CONVERSION REDUCTION DUE TO DISPERSION

The results of Table 1 indicate that dispersion reduces the conversion of a first-order irreversible reaction. This is due to the combined contributions of disapportioned residence time and nonuniform catalyst distribution. To quantify the difference in conversion, one defines

$$\Delta = \left(\frac{\bar{c}}{c_p}\right)_{x=1} \tag{53}$$

In Fig. 4, Δ is plotted against the plug-flow exit concentration, c_p, for different degrees of void fraction nonuniformity. Near com-

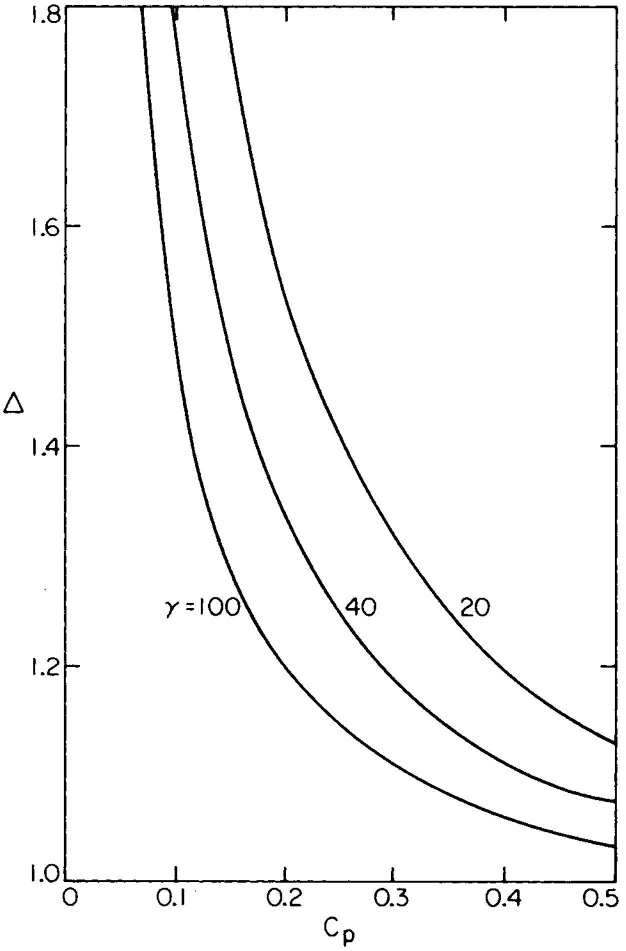

Figure 4. The amount of conversion reduction due to maldistribution for various plug-flow exit concentrations and degrees of nonuniformity (ϵ_o = 0.45).

pletion ($c_p = 0$), Δ approaches infinity and large deviations in conversion is seen for even the slightest void fraction nonuniformity. In this section, these numerical results are generalized analytically to other reaction mechanisms. Expanding c_e, the value of c at $x = 1$, in a Taylor series of ϵ about $\bar{\epsilon}$,

$$c_e(\epsilon) \sim c_p + \left(\frac{\partial c_e}{\partial \epsilon}\right)_{\bar{\epsilon}} (\epsilon - \bar{\epsilon}) \tag{54}$$

However, from the steady-state version of Eq. 29, one obtains

$$\frac{\partial c_e}{\partial \epsilon} \frac{1}{f(c_e)} = -\frac{d\Omega}{d\epsilon} \tag{55}$$

Substituting this into Eq. 54 and substituting the result into Eq. 54, one obtains

$$\Delta \sim 1 - \frac{f(c_p)}{c_p}\left(\frac{d\Omega}{d\epsilon}\right)_{\bar{\epsilon}} \left(2 \int_o^1 \epsilon u y dy - \bar{\epsilon}\right) \tag{56}$$

Applying Eqs. 39 and 44 one obtains

$$\frac{d\Omega}{d\epsilon} = -\phi \frac{3}{2}\left(\frac{1}{\epsilon} - 1\right)^{1/2} \Big/ 2\epsilon^2 \int_o^1 \left(\frac{\epsilon}{1-\epsilon}\right)^{1/2} y dy < 0 \tag{57}$$

Since ϵ is less than unity, the expression represented by Eq. 57 is negative definite. Expanding u in Taylor series in ϵ in a similar fashion, one obtains

$$u \sim 1 + \left(\frac{\partial u}{\partial \epsilon}\right)_{\bar{\epsilon}} (\epsilon - \bar{\epsilon}) \tag{58}$$

Consequently,

$$2 \int_o^1 \epsilon u y dy \sim \bar{\epsilon} + \left(\frac{\partial u}{\partial \epsilon}\right)_{\bar{\epsilon}} (\overline{\epsilon^2} - \bar{\epsilon}^2) \tag{59}$$

where

$$\overline{\epsilon^2} = 2 \int_o^1 \epsilon^2 y \, dy \tag{60}$$

From the Schwarz inequality,

$$\overline{\epsilon^2} > \bar{\epsilon}^2 \tag{61}$$

and applying this result with Eqs. 59 and 57 to Eq. 56, one concludes that

$$\Delta > 1 \text{ for } \epsilon \neq \bar{\epsilon} \tag{62}$$

Thus, void fraction nonuniformity-induced dispersion always reduces the conversion of a plug-flow model. This analytical result is consistent with the singular perturbation treatments of the Fickian model (Burghardt and Zaleski, 1958; Ray et al., 1972).

CONCLUSION

The origin of dispersion in a packed-bed reactor is rigorously investigated using the volume averaging technique. The resulting equations offer a more consistent physical picture than the Fickian model and the quantitative agreement with pulse response data is satisfactory. The computational efforts are also shown to be minimal while the results are agreeable with the Fickian model. Finally, dispersion, as simulated by the present model, is shown to reduce the conversion at ideal plug-flow considerably, especially at the high conversion regions.

NOTATION

a_v = surface area per unit catalyst volume
$A_{\alpha\beta}$ = interface area between fluid and catalyst
A_o = catalyst surface area in a control volume
c', c = concentration
c_e = exit concentration
$\bar{c}$ = bulk average concentration
c_p = plug flow concentration
c_F = Fickian model concentration
d_p = pellet diameter
$\underset{\sim}{D}$ = dispersion tensor
$\mathcal{D}$ = molecular diffusivity
D^* = dimensionless axial dispersion coefficient
D_e = effective dispersion coefficient from Fickian model
F, f = reaction expression
H = Heavyside step function
J = diffusive flux
l = length of reactor
$\underset{\sim}{n}$ = vector normal to surface
r = radial coordinate
R = radius of reactor
Pe, Pe_p, Pe_e = reactor, pellet and effective Peclêt number
t = time
u_o = interstitial velocity
V = volume of control volume
$\underset{\sim}{v}$ = velocity
x, y = dimensionless coordinates
z = axial coordinate

Greek Letters

α = fluid phase
β = catalyst phase
γ = dimensionless parameter representing uniformity of void fraction
δ = dimension of control volume in z direction, Dirac delta function
Δ = measure of effects of dispersion in conversion
ϵ = void fraction
σ^2 = variance of pulse response
θ = dimensionless time
ϕ = dimensionless reaction term
Ψ = physical property

Symbols, Subscripts and Superscripts

$\langle \ \rangle^\alpha$ = intrinsic phase average
$\underset{\sim}{\langle \ \rangle}$ = phase average
$\hat{}$ = deviation from intrinsic phase average
$\bar{}$ = area of bulk average
e = exit

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Photopolymerization in an Isothermal and Continuous Stirred Tank Reactor: Concentration Stability

An investigation of photopolymerization in an isothermal and continuous stirred tank reactor (CSTR) was made. The existence of multiple steady states induced by gel effects was demonstrated theoretically and experimentally. This multiple steady state problem is presented in relation to reactor stability and control. Also, the relative behavior of the batch and CSTR systems is discussed.

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SCOPE

Initiation of chemical reactions by absorption of radiation (ultraviolet or ionizing) is characterized by essentially complete lack of temperature dependence, and by physical separation of the source of the initiating agent from the reaction medium. Thus, in the case of radiation initiation, the rate of initiation may be changed very rapidly. This consequence may lead to greater reactor stability and greater ease of reactor control. This would result in less frequent instances of runaway reactions and explosive decompositions or elimination of these events altogether.

A number of studies of the design and analysis of photochemical reactors have appeared in the literature during the past ten years, with outstanding contributions in this area being made by J. M. Smith and J. S. Dranoff and their co-workers. But very little work has been done on the engineering aspect of photopolymerizations (Yemin and Hill, 1969; Jain et al., 1970; Chen and Hill, 1971; Sandru and Smith, 1973; Ibarra and Smith, 1974; Mendiratta et al., 1975; Chen and Steenrod, 1975), in part because of incomplete exploration of their characteristics and advantages.

Temperature stability of the polymerization reactor has been studied theoretically by Hoftyzer and Zwietering (1961), and Warden and Amundson (1962). Both studies were concerned with the mode of chemical initiation and concluded that, with certain modes of control, it was indeed feasible to control at certain of the metastable points. Knorr and O'Driscoll (1970) has mathematically demonstrated that there is a possibility of the existence of multiple steady states induced by viscosity effects in isothermal CSTR.

Recently, Chen and his co-workers (1980a and 1980b) have theoretically and experimentally examined the feasibility of operating a CSTR for the addition polymerization in the thermal metastable region. It has been shown that the use of ultraviolet light as a generator of free radicals offers a significant improvement in the control of polymerizations. Furthermore, the polymer formed at the metastable state has a higher number average chain length and narrower molecular weight distribution (low polydispersity) than that obtained at the low stable state. In addition, photochemical initiation has a positive temperature coefficient of the degree of polymerization, which is in contrast with the results found for the thermal chemical initiation. In this paper, the photopolymerization is an isothermal CSTR is experimentally and theoretically investigated. Emphasis is placed on steady-state multiplicity, stability, and controllability of the reaction system.

CONCLUSIONS AND SIGNIFICANCE

The photopolymerization of styrene in an isothermal and continuous stirred tank reactor was investigated. Conversion, molecular weight averages, and molecular weight distribution at the temperature of 338°K and up to 70% conversion were measured. Three steady states are found to exist if the gel effects become pronounced.

The reactor performance characteristics in terms of fractional conversion and number of average chain lengths are presented. There are three possible regions of operation: low stable (Region I), metastable (Region II) and high stable (Region III). Operation in Region III may be discounted for bulk polymerization because of very high viscosity. With regard to Regions I and II,

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