

APPLICATION OF STOCHASTIC PROCESSES TO CHEMICAL REACTOR SYSTEMS

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT	i
CHAPTER 1: INTRODUCTION	1-1
CHAPTER 2: A STOCHASTIC DIFFUSION MODEL OF FLUIDIZED BED EXPANSION . . .	2-1
2.1 Introduction	2-1
2.2 Theory	2-2
2.3 Experimental Data	2-6
2.4 Results and Discussion	2-7
2.5 Conclusion	2-10
Nomenclature	2-11
References	2-12
CHAPTER 3: STOCHASTIC DIFFUSION MODEL OF A FLUID-SOLID REACTION	3-1
3.1 Introduction	3-1
3.2 Stochastic Diffusion Model	3-1
3.3 Numerical Method	3-5
3.4 Discussion and Conclusion	3-5
Nomenclature	3-8
References	3-10
CHAPTER 4: A STOCHASTIC MODEL OF THE UNSTEADY STATE AGE DISTRIBUTION IN A FLOW SYSTEM	4-1
4.1 Introduction	4-1
4.2 Pure Death Process	4-1
4.3 Model	4-4
4.4 CONCLUDING REMARKS	4-9
Nomenclature	4-9
References	4-10

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CHAPTER 1

INTRODUCTION

Modeling, simulation, optimization, and synthesis of chemical reactor systems are important to a number of chemical engineers who are involved in various areas including chemical, physical, biological and environmental processes. Frequently, fundamental equations for hydrodynamics, and heat and mass transport of a reactor system are not amenable to any available solution schemes. Therefore, it is highly desirable to have a proper model which takes into account significant features of the system operation. It should also be capable of assessing the combined effects of chemical rate processes and physical phenomena such as mass and heat transfer on the performance of the system. As a result of the evolution of a host of disciplines, such as transport phenomena, reaction engineering and unit operation, a great deal of work in this field has been successfully performed by chemical engineers during the past three decades (see e.g. Wen and Fan, 1975). However, great difficulties still exist in the treatment of processes with inherent random properties such as turbulent flow and flow involving more than one phase. This is due to the fact that the conventional chemical engineering approach, that is deterministic approach, is being used to approximate such processes. However, these complex systems could be more realistically described by employing a probabilistic approach.

The deterministic approach which was developed based on the continuum hypothesis is not valid for systems which are discontinuous. Such is the case when the elements of the discontinuous phase experience random activities such as collision and redispersion. A probabilistic model, or more specifically, the stochastic model should be introduced in place of the deterministic model in these situations.

The neglect of the stochastic elements of the problem can be attributed to the lack of a mathematical theory capable of providing satisfactory models for such systems. However, the situation has been changed significantly over the last twenty years. Following the pioneering work of Kolmogorov, Doob and Ito, an interesting and useful mathematical theory has emerged. This theory of stochastic differential equation is known as the "Ito equation", in honor of Ito's pioneering work.

The control system is an example in which the stochastic differential equation is employed to describe the system performances. This system is designed to provide good plant performance in the face of random disturbances and therefore needs a noisy feedback signal to do so. With comparatively few exceptions, the theory of feedback-control systems is based on deterministic methods, and very little consideration has been given to the stochastic nature. (King 1973).

The overall objective of this report is to demonstrate the applicability of the stochastic approach to the chemical reactor system involving random phenomenon. Three different chemical systems are utilized for this purpose. They are discussed separately in CHAPTER 2, 3, and 4. In CHAPTER 2, a stochastic diffusion model is used to portray the bed expansion in the gas-solid fluidized bed. In CHAPTER 3, the same model is used to describe the behavior of fluid-solid reactions. In CHAPTER 4, the concept of the pure death process is applied to describe the transient age distribution in a chemical reactor.

In conclusion, this report is by no means an exhaustive survey of the stochastic model in the field of chemical engineering. It is hoped that the coming years will see increased application of this principle to more challenging problems.

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A STOCHASTIC DIFFUSION MODEL OF FLUIDIZED BED EXPANSION

2.1 INTRODUCTION

The objective of this paper is to examine the validity of the so-called stochastic or Kolomogorov diffusion model for characterizing both the transient and steady state axial solid density distributions or, equivalently, axial porosity distributions in a gas-solid fluidized bed. The porosity distribution in the fluidized bed arises from the convective and diffusive transport of solids in the bed, which is often extremely complex or stochastic in nature. Knowledge and understanding of the porosity distribution are essential for rational design and operation of a fluidized bed reactor since the presence of solid particles and their vigorous motions are the key features of this reactor.

Investigations on the axial porosity distribution in a bubbling fluidized bed (see, e.g., Bakker and Hertjes, 1960; Fan et al., 1962; Urabe et al., 1965) indicate that the bed consists of three zones, namely, the lower entrance or jet zone of slightly increased porosity, the main zone of essentially constant porosity up to the point corresponding to the bed height at minimum fluidization, L_{mf} , and the upper lean phase zone of increasing porosity to the bubbling bed height, L_f . The differences in characteristics of the porosity distribution in the upper two zones have been explained in terms of the bubble hydrodynamics; the behavior of bubbles in one zone has been considered to be different from that in the other (see, e.g., Kunii and Levenspiel, 1969). The behavior of bubbles in the jet zone appears to be least understood (Wen, 1976).

It is known that the size and velocity of bubbles do not remain invariant during their transit through the bed (see, e.g., Kunii and Levenspiel, 1969). Since the rising bubbles are mainly responsible for the solids

motion in the bed, spatial variations of the bubble size and velocity induce a biased probability of particle motion toward a certain direction. Consequently, the mobility of particles is a function of the bed position and time, as confirmed experimentally by Jinescu et al. (1966). The stochastic diffusion model proposed in the present work can account for this observation. The experimental data reported by Bakker and Hertjes (1960) are employed to test the validity of the proposed model.

2.2 THEORY

Let us consider a fluidized bed at minimum fluidization as shown in Fig. 1. The solid volume fraction, C_{mf} , at this condition can be expressed as

$$C_{mf} = 1 - \epsilon_{mf} = \frac{M}{L_{mf} A_t \rho_s} \quad (1)$$

where

ϵ_{mf} = porosity at minimum fluidization

M = mass of the solid particles

L_{mf} = static bed height at minimum fluidization

A_t = cross-sectional area of the bed

ρ_s = density of the solid particles

When the gas flow exceeds that of the minimum fluidization velocity U_{mf} , the rising bubbles induce upward expansion of the bed, and simultaneously impart complex stochastic motions to particles in the bed. We can visualize this as solid particles diffusing into the void space, or alternatively, the void space diffusing into interstices of solids.

Suppose that a solid particle was initially observed at z_0 ($0 \leq z_0 \leq L_f$), and that after a certain period of fluidization the particle is found at z ($0 \leq z \leq L_f$). Let us assume that $\{Z(t), t \geq 0\}$ is a random variable which obeys the Markov process, and let us define a conditional probability function and its density such that

$$F(z_0, t_0; z, t) \equiv \Pr[Z(t) \leq z \mid Z(t_0) = z_0] \quad (2)$$

$$f(z_0, t_0; z, t) \equiv \frac{\partial F}{\partial z}$$

In the above expression, $F(z_0, t_0; z, t)$ is the conditional probability that a solid particle originally at z_0 migrates to z during the time period $\Delta t = t - t_0$.

From the assumption of the Markov property for the random variable, $Z(t)$, we have

$$f(z_0, t_0; z, t) = \int_0^{L_f} f(z_0, t_0; \xi, \eta) f(\xi, \eta; z, t) d\xi \quad (3)$$

where

$$0 \leq \xi \leq L_f$$

$$t_0 \leq \eta \leq t$$

Another assumption necessary for the derivation of the Kolmogorov diffusion equation is that the probability of particle motion during an infinitesimal time interval Δt is negligible compared to Δt , i.e.,

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\xi - z| \geq \delta} f(z, t; \xi, t + \Delta t) d\xi \quad (4)$$

$$= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\xi - z| \geq \delta} f(z, t - \Delta t; \xi, t) d\xi$$

$$= 0$$

where

$$\delta > 0 \quad \text{and} \quad 0 \leq \xi \leq L_f$$

Equations (3) and (4) give rise to the Kolmogorov diffusion equation of the following form:

$$\frac{\partial f}{\partial t} = \frac{\partial^2 (Df)}{\partial z^2} - \frac{\partial (Vf)}{\partial z} \quad (5)$$

where

$$f = f(z_0, t_0; z, t)$$

$$D(z, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\xi - z| < \delta} \frac{1}{2} (\xi - z)^2 f(z, t; \xi, t + \Delta t) d\xi$$

$$V(z, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\xi - z| < \delta} (\xi - z) f(z, t; \xi, t + \Delta t) d\xi$$

Equation (5) is equivalent to

$$\frac{\partial C(z, t)}{\partial t} = \frac{\partial^2 [D(z, t)C(z, t)]}{\partial z^2} - \frac{\partial [V(z, t)C(z, t)]}{\partial z} \quad (6)$$

where

t = time

z = upward distance from the gas distributor

D = axial diffusion coefficient of solid particles relative to the
"counter-diffusing" void space

C = axial volume fraction ($= 1 - \epsilon_f$, where ϵ_f is the porosity)

V = drift velocity of solid particles

We now assume that D is a function of z only but not of t , and that V is negligible. Then Eqn. (6) reduces to

$$\frac{\partial C(z,t)}{\partial t} = \frac{\partial^2 [D(z)C(z,t)]}{\partial z^2} \quad (7)$$

The appropriate initial condition for this equation is

$$C(z,0) = \begin{cases} C_{mf}(z) & , \quad 0 \leq z \leq L_{mf} \\ 0 & , \quad L_{mf} \leq z \leq L_f \end{cases} \quad (8)$$

If no particles elutriate from a batch fluidized bed, the particles are conserved. Thus the following boundary conditions are valid:

$$J = - \frac{\partial [D(z)C(z,t)]}{\partial z} \bigg|_{\substack{z=0 \\ z=L_{mf}}} = 0 \quad (9)$$

where J is the flux of solids

Equation (7) can be solved subject to Eqns. (8) and (9) to simulate the transient porosity distribution in the bed when the diffusion coefficient is given as a function of z . At the limit of $t \rightarrow \infty$, the solution of Eqn. (7) converges to the steady state porosity distribution.

At the steady state condition, solution of Eqn. (7) subject to (9) gives rise to

$$D(z) = \frac{k}{C_{\infty}(z)} \quad (10)$$

where

$C_{\infty}(z)$ = equilibrium solid particle distribution

k = positive constant.

Solving Eqn. (7) analytically, subject to Eqns. (8) and (9), is extremely difficult, if not impossible, when $D(z)$ is a complex function of z . In

general, we have to resort to a numerical solution. The computer package, PDESOL (Sincovec and Madsen, 1975), is available for the numerical solution of parabolic partial differential equations. It is based on the method of lines which converts, by means of a finite difference method, the original partial differential equation dependent on z and t into a set of ordinary differential equations dependent only on z . Let

$$D(z)C(z,t) = Y(z,t) \quad (11)$$

Then Eqn. (7) is transformed into

$$\frac{\partial Y}{\partial t} = D(z) \frac{\partial^2 Y}{\partial z^2} \quad (12)$$

and Eqns. (8) and (9) are transformed, respectively, into Eqns. (13) and (14), i.e.,

$$Y(z,0) = \begin{cases} C_{mf}/D(z) & , \quad 0 \leq z \leq L_{mf} \\ 0 & L_{mf} \leq z \leq L_f \end{cases} \quad (13)$$

and

$$J = - \left. \frac{\partial Y}{\partial z} \right|_{z=0}^{z=L_{mf}} = 0 \quad (14)$$

These three equations are more amenable to numerical solution by the finite difference scheme than the original ones because the set of transformed equations gives rise to smaller errors due to finite difference approximations of derivatives than the set of original equations.

2.3 EXPERIMENTAL DATA

The solid particle distribution at the center of the bed, as a function of the bed height, was experimentally determined by Bakker and Hertjes (1960) in a bed of 9 cm in diameter. The ranges of operating conditions

are summarized in Table 1. Two sets of experimental data are used in the present work. One set contains the data illustrating the variation of porosity with the gas velocity for a given bed mass, and the other set illustrating the variation of porosity with the bed mass for a given gas velocity.

2.4 RESULTS AND DISCUSSION

The normalized diffusion coefficient, $D(z)/k$, has been determined by fitting Eqn. (10) to equilibrium or steady state porosity data. A typical result is plotted in Fig. 2 for $U_0 = 40.7$ cm/s and $M = 1000$ g against the dimensionless bed height, z/L_f .

From Fig. 2 we can observe that, for given U_0 and M , the value of $D(z)/k$ is larger in the jet and lean phase zones than in the dense bubbling zone. It is essentially constant in the dense bubbling zone while it is a monotonically increasing function of z in the lean phase zone. $D(z)/k$ in the dense bubbling zone is slightly smaller than that in the jet zone, and much smaller than that in the lean phase zone. This is expected because the motion of a particle in the dense bubbling zone tends to be more restricted by the existence of the neighboring particles than the motions of particles in the other two zones, especially in the lean phase zone where the particle densities are relatively lower than that in the dense bubbling zone.

The constant, k , in Eqn. (10), which is generally a function of the system parameters, cannot be estimated from the equilibrium data alone. Additional data, such as the values of the diffusion coefficient or the transient porosity data, are needed in order to determine k .

The variation of $D(z)$ with the gas velocity can be estimated using the experimental data of Lewis et al. (1962) who measured the effective axial thermal conductivity of solids in which the bottom and top of fluidized bed acted, respectively, as the heat source and sink.

Lewis et al. assumed that the particles were the only media of heat transfer and thereby obtained the correlation of the effective thermal diffusion coefficient with respect to the gas velocity. It must be noted that the system of Lewis et al. is essentially identical to the system considered here, i.e., what they actually measured was the axial solids diffusion coefficient relative to the void space. Their experimental data yield the average solids diffusion coefficient, \bar{D} , over the entire bed. The operating conditions of their fluidized bed are shown in Table 2, which are similar to those of Bakker and Hertjes considered in this work (see Table 1). The results of Lewis et al. for glass beads are reproduced in Fig. 3.

Since the average diffusion coefficient over the entire bed, \bar{D} , can be represented by

$$\bar{D} = \frac{\int_0^{L_f} D(z) dz}{L_f}, \quad (15)$$

combining Eqns. (6) and (11) results in

$$k = \frac{L_f \bar{D}}{\int_0^{L_f} \frac{dz}{C_\infty(z)}} = \frac{\bar{D}}{\int_0^1 \frac{d(\frac{z}{L_f})}{C_\infty(\frac{z}{L_f})}} \quad (16)$$

Therefore, the value of k for different gas velocities can be estimated using Eqn. (16) and Fig. 3, and $D(z)$ can be obtained using Eqn. (10). Figure 4 shows $D(z)$ in terms of the normalized bed height with U_0 as a parameter.

According to Lewis et al. (1962), for a given gas velocity, the average diffusion coefficient, \bar{D} , is relatively independent of the

bed mass. Also the data of Bakker and Hertjes (1960) indicate that, except for a very shallow bed, the normalized equilibrium solids distribution, $C_{\infty}'(z/L_f)$ is essentially independent of the bed mass for a given gas velocity. Hence, using Eqn. (10), the effect of the bed mass on the normalized diffusion coefficient, $D(z/L_f)$, can be determined. In Fig. 5, $D(z)/k$ is plotted against the dimensionless bed height, z/L_f , with the bed mass, M , as a parameter. As can be seen except for a shallow bed in which the bed mass is 250 g and the ratio of L_{mf} to the bed diameter, d_t , is about 1/3, $D(z)/k$ is nearly independent of M . In this figure the normalized initial bed height corresponds to L_{mf}/L_f which is identical for all runs. Figure 5 shows that the rate of diffusion in the lower two zones in the shallower bed is higher than that in a deeper bed. This is probably due to the greater influence of the jet region in the shallower bed. The trend is reversed in the uppermost zone.

Figures 2 and 4 indicate that the diffusion coefficient can be approximated by

$$D(z) = \exp\left[\sum_{n=0}^m a_n z^n\right] \quad (17)$$

After substituting this expression into the transformed governing equation, Eqn. (12), it has been numerically solved subject to Eqns. (13) and (14).

Results are illustrated in Fig. 6 for $U = 40.7$ cm/s, $M = 1000$ g and $L_f = 20$ cm. This set of conditions yields $k = 9.3$. The parameter is the dimensionless time, τ , defined as

$$\tau = \frac{k}{L_f^2} t \quad (18)$$

The simulation also shows that the porosity profile virtually reaches the steady state at $\tau = 0.15$. The time needed to attain the steady state is approximately 6.5 seconds, indicating very fast solids movement.

The rate of bed expansion can be determined from the simulated porosity distribution. At any moment t , a position z where the solid concentration, $C(z,t)$, becomes less than an infinitesimally small prescribed constant is considered to be the top of the bed. Then, the extent of bed expansion at t is

$$\Delta z = z - L_{mf} \quad (19)$$

and the final bed expansion ΔL is

$$\Delta L = L_f - L_{mf} \quad (20)$$

Figure 7 plots the normalized or dimensionless bed expansion $\frac{\Delta z}{\Delta L}$ against the dimensionless time, τ , for various M and for $U_0 = 40.7$ cm/s. The dimensionless time constant τ_c at which $\frac{\Delta z}{\Delta L}$ attains 66.3% of the steady state value appears to be independent of the bed mass. In this case, since k is independent of M , Eqn. (18) shows that the time constant of bed expansion is proportional to L_f^2 . This feature of gas-solid fluidized bed expansion during the start-up is similar to that of a liquid-solid fluidized bed expansion in response to a relatively small perturbation in the liquid velocity (Fan et al., 1963).

2.5 CONCLUSION

A mechanistic model of transient porosity distribution or bed expansion of a fluidized bed has been derived. The model can portray the experimentally observed non-uniform equilibrium porosity distribution as well as the transient porosity distribution. The diffusion coefficient varies significantly along the bed height. Its average value increases with increasing gas velocities; however, it is only slightly dependent on the bed mass. The normalized time constant of bed expansion has been found to be nearly independent of the bed mass for a given gas velocity.

NOMENCLATURE

A_t	=	cross sectional area of the bed (cm^2)
C	=	volume fraction of solid (-)
C_∞	=	equilibrium volume fraction of solid (-)
C_{mf}	=	volume fraction of solid at minimum fluidization (-)
D	=	diffusion coefficient of solids (cm^2/s)
\bar{D}	=	diffusion coefficient of solids averaged over the entire bed (cm^2/s)
d_t	=	bed diameter (cm)
d_p	=	particle diameter (μ)
J	=	volume flux of solids (cm/s)
k	=	positive constant defined in Eqn. (6) (cm^2/s)
L_{mf}	=	static bed height at minimum fluidization (cm)
L_f	=	height of a bubbling fluidized bed (cm)
ΔL	=	bed expansion height at steady state (cm)
Δl	=	extent of bed expansion at t (cm)
M	=	mass of solids in the bed (g)
t	=	time (s)
U_{mf}	=	minimum fluidization velocity, superficial (cm/s)
U_0	=	gas velocity, superficial (cm/s)
V	=	drift velocity of solids (cm/s)
z	=	upward distance from the gas distributor (cm)
ϵ_{mf}	=	porosity at minimum fluidization (-)
ϵ_f	=	porosity (-)
ρ_s	=	density of solids (g/cm^3)
τ	=	dimensionless time defined in Eqn. (16) (-)
τ_c	=	dimensionless time constant of bed expansion (-)

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Table 1. Experimental Conditions of Bakker and Hertjes (1960).

$$d_t = 9 \text{ cm}$$

$$d_p = 175 \sim 210 \mu, \text{ glass beads}$$

$$\rho_s = 2.53 \text{ g/cm}^3$$

$$\epsilon_{mf} = 0.48$$

$$U_{mf} = 8.7 \text{ cm/s}$$

M, g	1000	$U_0, \text{ cm/s}$	22.7 ~ 98.4
		$L_f, \text{ cm}$	16 ~ 32
		$L_{mf}, \text{ cm}$	11

$U_0, \text{ cm/s}$	40.7	M, g	200 ~ 2000
		$L_f, \text{ cm}$	4 ~ 40
		$L_{mf}, \text{ cm}$	2.2 ~ 22

Table 2. Experimental conditions of Lewis et al. (1962).

d_t , cm	7.4
d_p , μ	155, glass beads
ρ_s , g/cm ³	2.53
U_{mf} , cm/s	2.33
U_0 , cm/s	12 ~ 64
ϵ_{mf}	0.44
L_f , cm	> 100

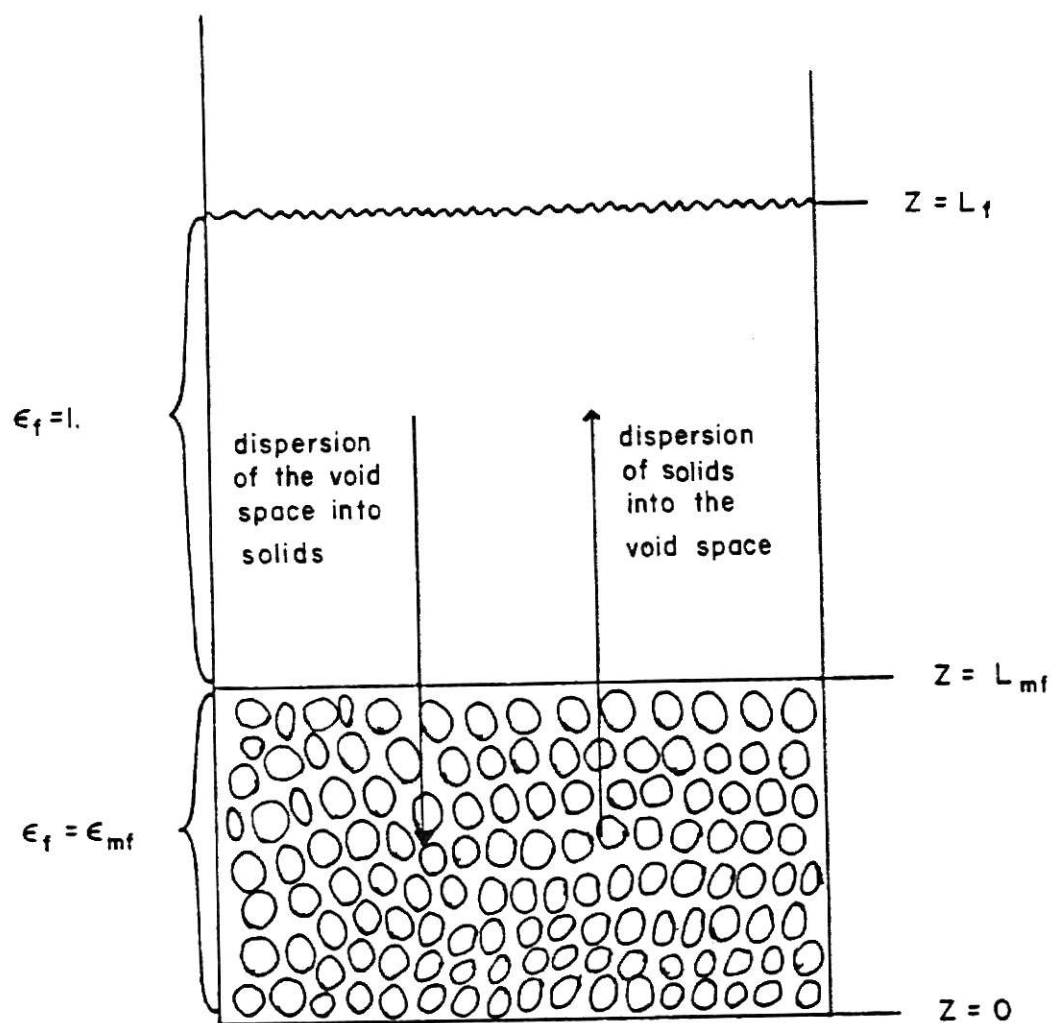


Fig. 1. Schematic representation of the stochastic diffusion model used in the present work.

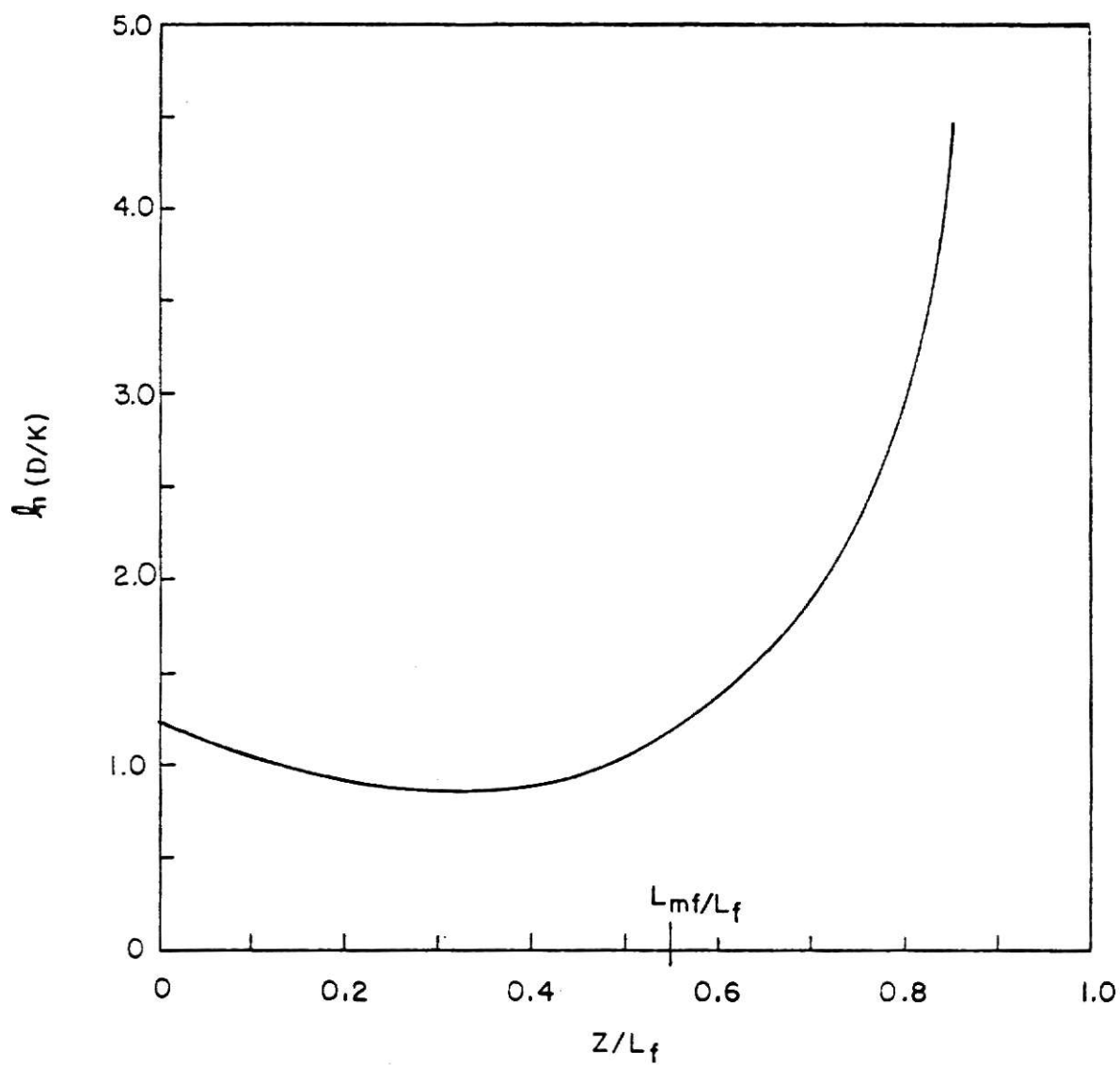


Fig. 2. Normalized diffusion coefficient of solids as a function of the bed height of a gas-fluidized bed.

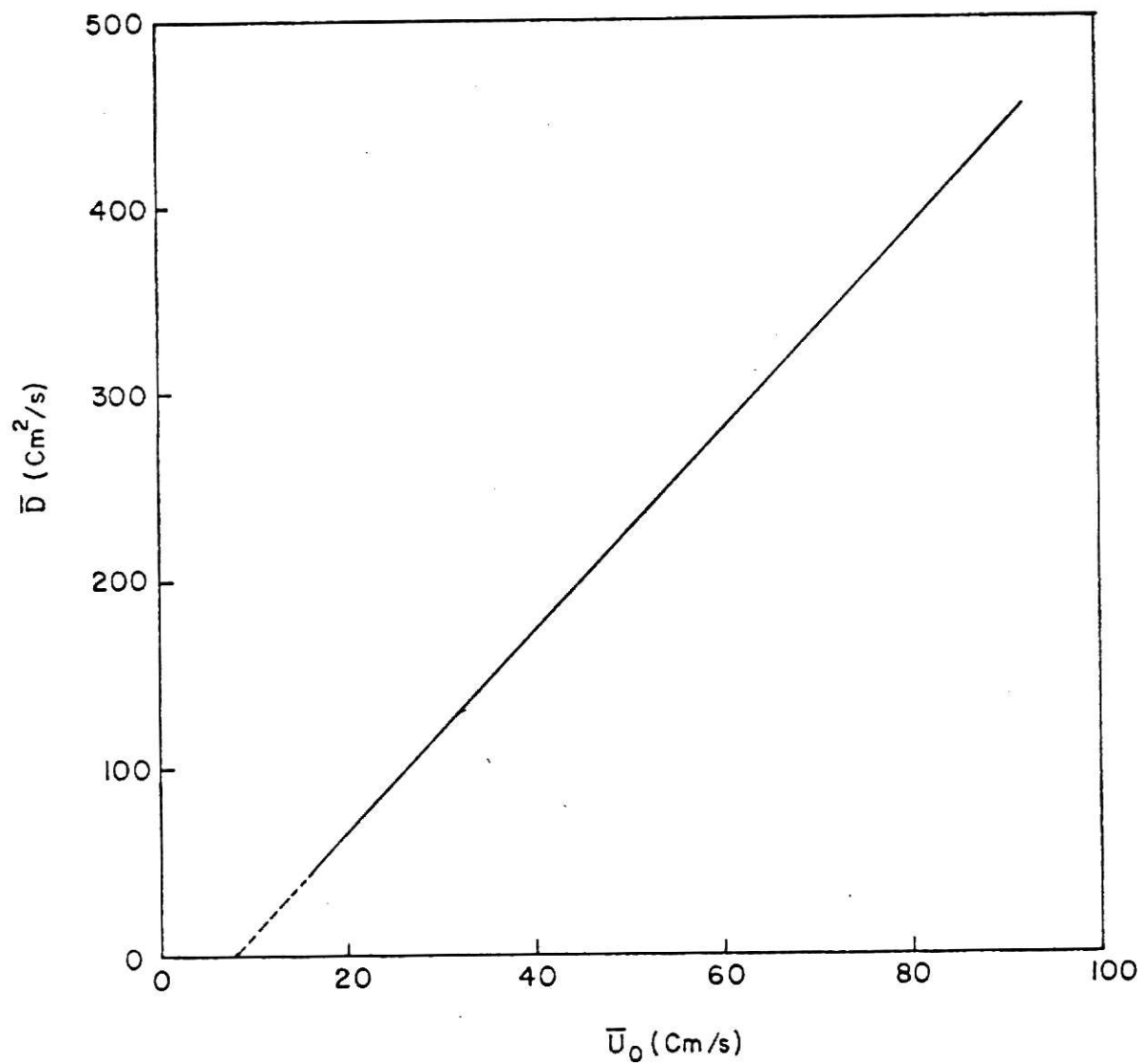


Fig. 3. Average diffusion coefficient of solids as a function of the gas velocity - experimental results of Lewis et al. (1962).

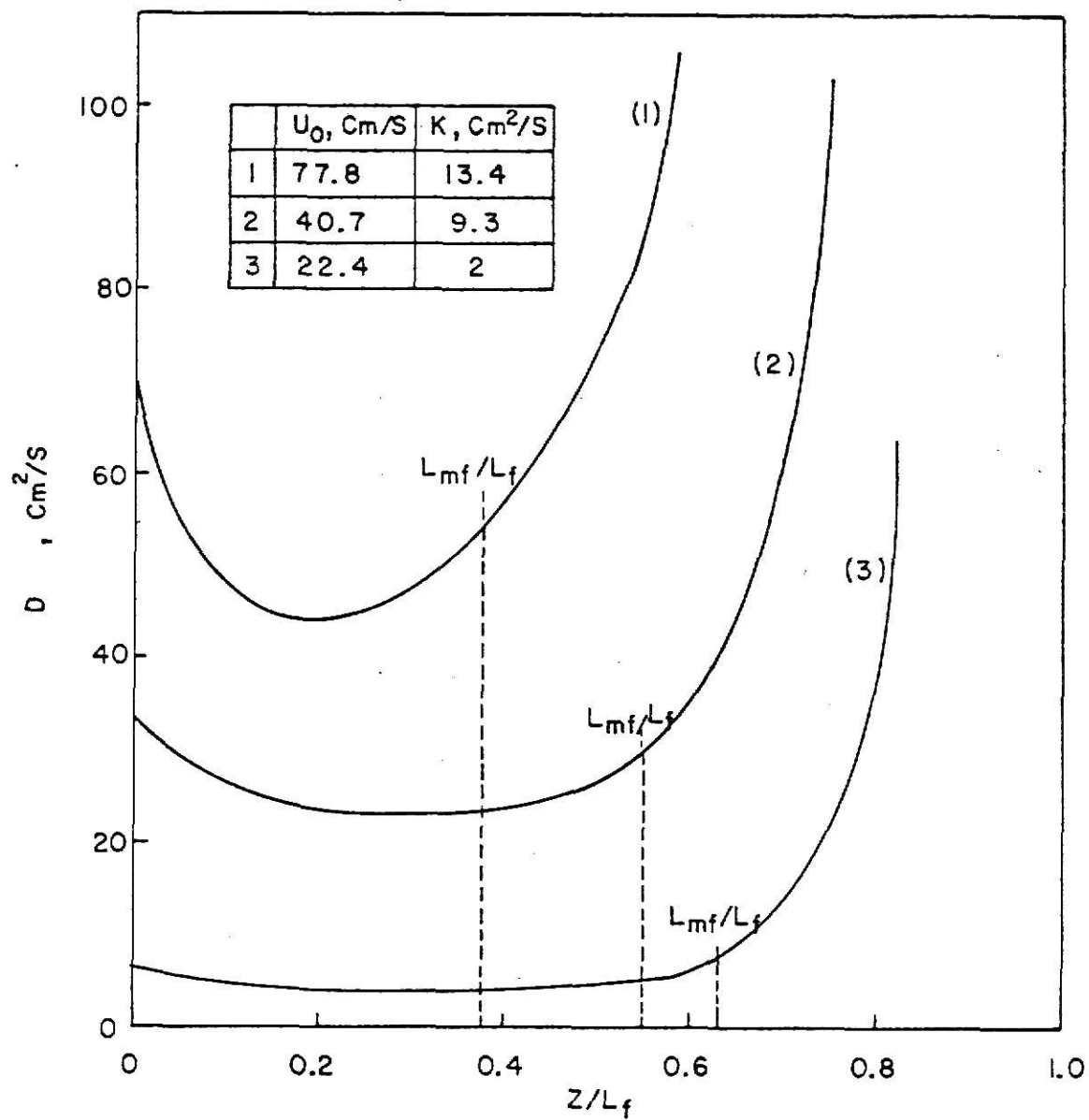


Fig. 4. Diffusion coefficient as a function of the bed height for a constant bed mass. The parameter is the gas velocity.

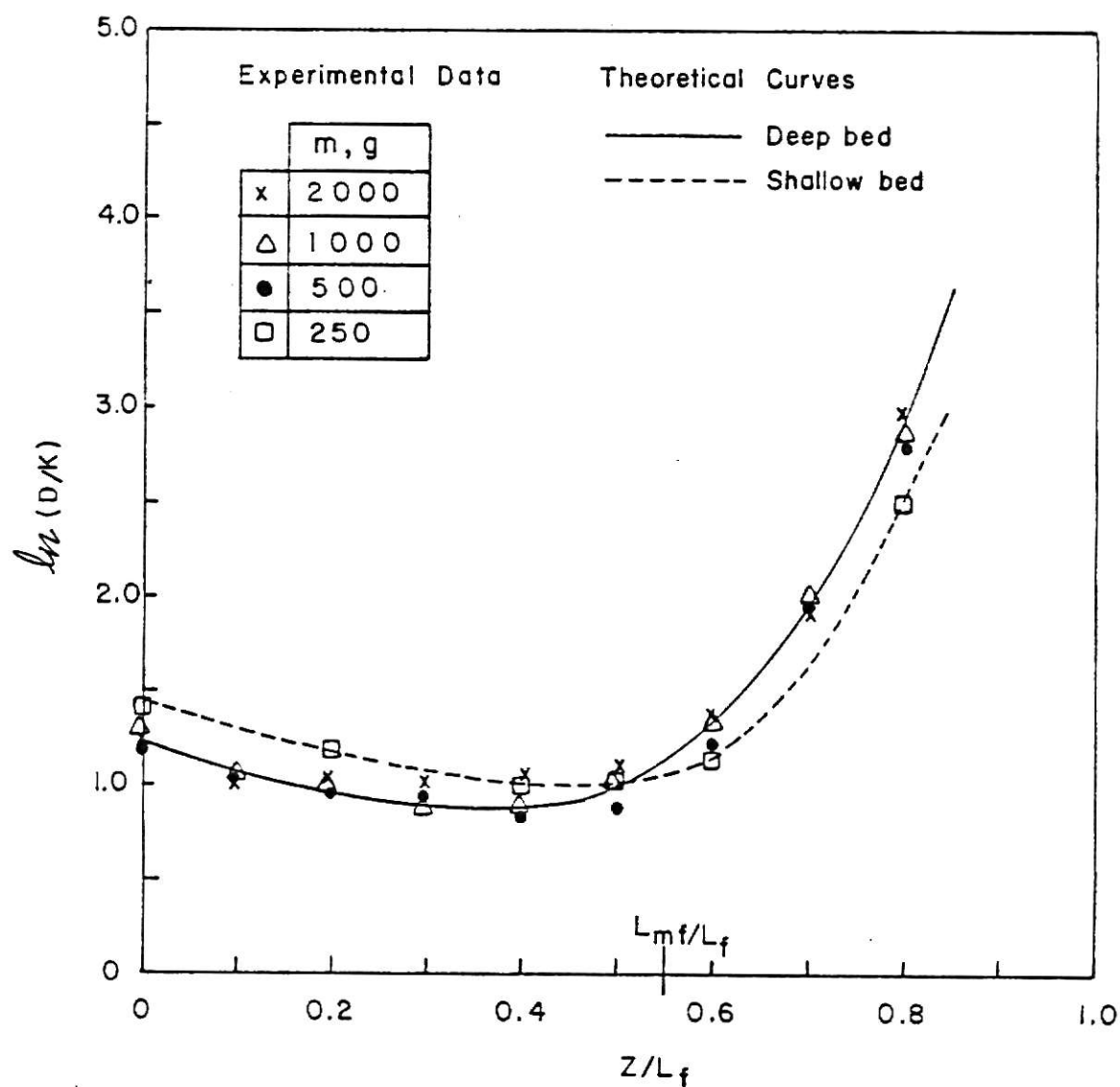


Fig. 5. Normalized diffusion coefficient as a function of the bed height for a constant gas velocity. $U_0 = 40.7$ cm/s.

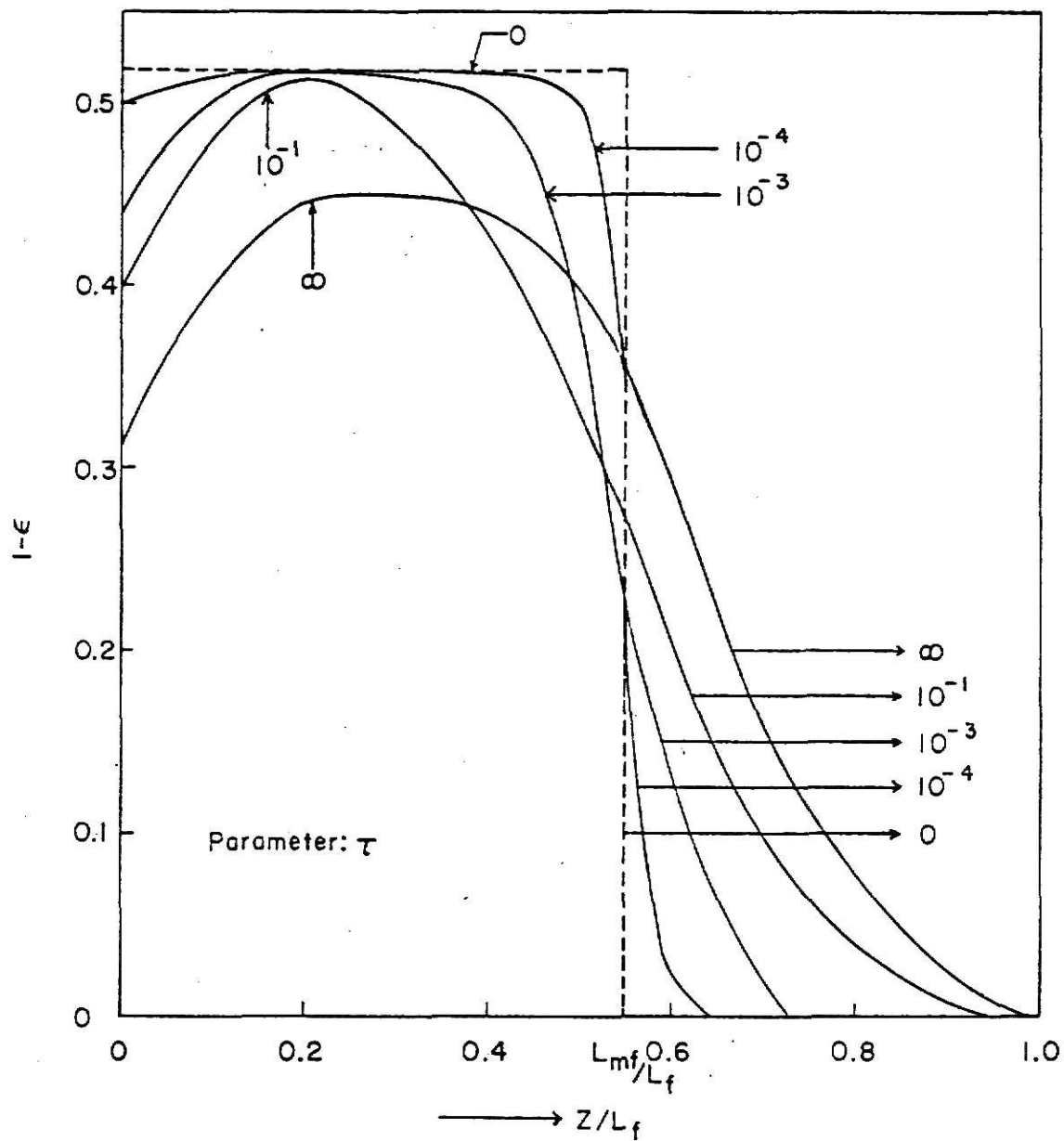


Fig. 6. Transient porosity distribution calculated from the theory. $U_0 = 40.7$ cm/s, $M = 100$ g, $L_f = 20$ cm.

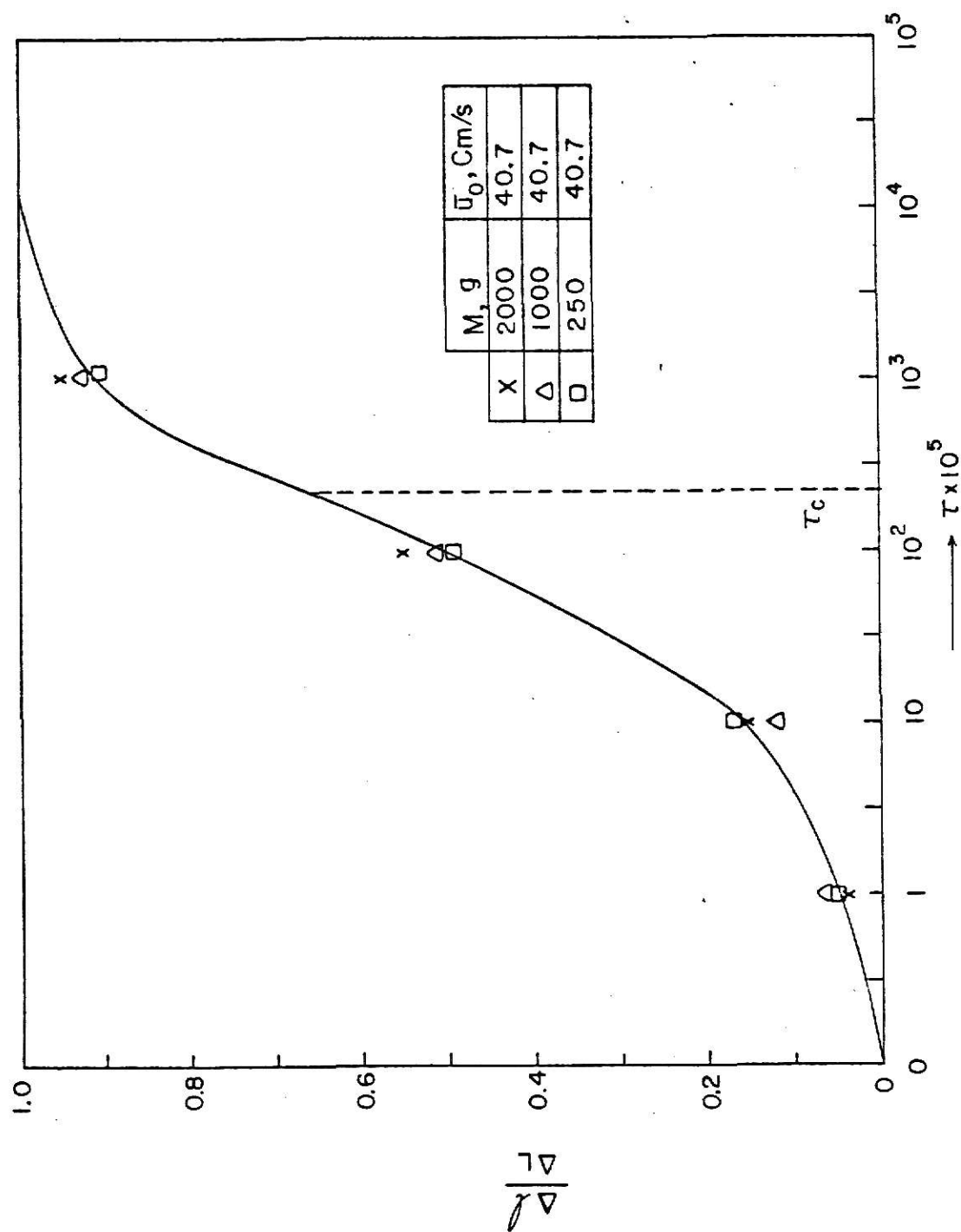


Fig. 7. Calculated transient bed expansion at a constant gas velocity for different bed masses.

3.1 INTRODUCTION

The objective of this paper is to propose an alternative model, namely, the stochastic or Kolmogorov diffusion model, for a heterogeneous reaction between fluid and solid reactants. More often than not, such a heterogeneous reaction under isothermal conditions has been modeled by a Fickian equation of the form (Wen, 1968; Borghi et al., 1976; Fan et al., 1977a, 1977b)

$$\frac{\partial(C_i \epsilon)}{\partial t} = \frac{1}{r^\lambda} \frac{\partial}{\partial r} (r^\lambda D_{fi} \frac{\partial C_i}{\partial r}) - a_i \tilde{\gamma}_S(C_1, C_2, \dots, C_M, C_S),$$

$$i=1, 2, 3, \dots, M$$
(1)

$$\frac{\partial C_S}{\partial t} = -\tilde{\gamma}_S(C_1, C_2, \dots, C_M, C_S)$$
(2)

The initial conditions for Eqns. (1) and (2) are, respectively,

$$\begin{aligned} t = 0 & \quad ; \quad C_i = 0, \quad i=1, 2, \dots, M \\ t = 0 & \quad ; \quad C_S = C_{S0}, \end{aligned}$$
(3)

and the boundary conditions for Eqn. (1) are

$$\begin{aligned} r = 0 & \quad ; \quad \frac{\partial C_i}{\partial r} = 0, \quad i=1, 2, \dots, M \\ r = R & \quad ; \quad D_{fi} \left(\frac{\partial C_i}{\partial r} \right) = k_{mi} (C_{i0} - C_i), \quad i=1, 2, \dots, M \end{aligned}$$
(4)

3.2 STOCHASTIC DIFFUSION MODEL

A heterogeneous reaction between fluid and solid reactants is frequently accompanied not only by molecular diffusion of the fluid reactant but also by complex and stochastic phenomena including interfacial turbulence, convective transport of the fluid reactant, pore formation, pore shape disconfiguration and others under the influence of a variety of internal and/or external factors such as gravitational force, pressure force,

frictional force, and temperature difference. Therefore, the Fickian diffusion model or any simple continuum model can hardly be considered as a theoretical model for such a reaction. It can only be considered semi-theoretical or mechanistic at best. Strictly speaking, the diffusivity, D_{fi} , is a proportionality coefficient relating the molecular diffusional mass flux of a component in a continuum to the concentration gradient (Hirschfelder et al., 1954; Bird et al., 1960).

It is proposed here that, because of the involvement of several complex stochastic phenomena, a stochastic diffusion equation of the Kolmogorov form (see, e.g., Bharucha-Reid, 1960; Seinfeld and Lapidus, 1974; Okubo, 1975),

$$\frac{\partial(C_i \epsilon)}{\partial t} = \frac{1}{r^\lambda} \frac{\partial}{\partial r} \left[r^\lambda \frac{\partial(D_{si} C)}{\partial r} \right] - a_i \tilde{\gamma}_S(C_1, C_2, \dots, C_M, C_S), \quad (5)$$

$$i=1, 2, \dots, M$$

coupled with Eqn. (2), is at least as valid a model for a heterogeneous reaction as a model resorting to the Fickian diffusion hypothesis, e.g., Eqn. (1). The two models, Eqns. (1) and (5), have an identical form only when both the Fickian diffusivity, D_{fi} , and the Kolmogorov or stochastic diffusivity, D_{si} , are constant. The Kolmogorov diffusivity, D_{si} , is a derived quantity (Bharucha-Reid, 1960; Seinfeld and Lapidus, 1974; Okubo, 1975) while the Fickian diffusivity, D_{fi} , is, as stated previously, a phenomenological or empirical parameter relating the diffusional mass flux to the concentration gradient in a continuum (Hirschfelder et al., 1954; Bird et al., 1960). The boundary conditions for the stochastic model, Eqn. (5), are

$$\left. \begin{aligned} r = 0 & \quad ; \quad \frac{\partial C_i}{\partial r} = 0 \quad , \quad i=1,2,\dots,M \\ r = R & \quad ; \quad \frac{\partial (D_{si} C_i)}{\partial r} = k_{mi} (C_{i0} - C_i) \quad , \quad i=1,2,\dots,M \end{aligned} \right\} \quad (6)$$

For a simple irreversible reaction involving one fluid reacting species,

$$\tilde{\gamma}_S = k_v C_1^q C_S^p \quad , \quad (7)$$

Eqns. (2) and (5) of the stochastic diffusion model, in dimensionless forms, become, respectively,

$$\frac{\partial S}{\partial \theta_v} = -C^q S^p \quad (8)$$

$$\frac{1}{a} \left(\frac{C_{10}}{C_{S0}} \right) \phi_v^2 \frac{\partial (C \epsilon)}{\partial \theta_v} = \frac{1}{\xi^\lambda} \frac{\partial}{\partial \xi} \left[\xi^\lambda \frac{\partial (D_S C)}{\partial \xi} \right] - \phi_v^2 C^q S^p \quad (9)$$

The corresponding initial conditions are

$$\begin{aligned} \theta_v = 0 & \quad ; \quad C = 0 \\ \theta_v = 0 & \quad ; \quad S = 1, \end{aligned} \quad (10)$$

and the corresponding boundary conditions are

$$\begin{aligned} \xi = 0 & \quad ; \quad \frac{\partial C}{\partial \xi} = 0 \\ \xi = 1 & \quad ; \quad \frac{\partial (D_S C)}{\partial \xi} = N_{shs} (1-C) \end{aligned} \quad (11)$$

In dimensionless form, Eqn. (1) of the Fickian diffusion model becomes

$$\frac{1}{a} \left(\frac{C_{10}}{C_{S0}} \right) \phi_v^2 \frac{\partial (C \epsilon)}{\partial \theta_v} = \frac{1}{\xi^\lambda} \frac{\partial}{\partial \xi} \left(\xi^\lambda D_f \frac{\partial C}{\partial \xi} \right) - \phi_v^2 C^q S^p \quad (12)$$

The corresponding boundary conditions are

$$\begin{aligned} \xi = 0 & \quad ; \quad \frac{\partial C}{\partial \xi} = 0 \\ \xi = 1 & \quad ; \quad D_f \frac{\partial C}{\partial \xi} = N_{shf} (1-C) \end{aligned} \quad (13)$$

The void fraction, ϵ , in Eqns. (9) and (12) can be related to the concentration of the solid reactant as (Wen, 1968; Fan et al., 1977a, 1977b)

$$\varepsilon = \varepsilon_0 + \gamma(1 - C_S/C_{S0}) \quad (14)$$

The stochastic diffusivity, D_s , is assumed to vary with respect to the spatial distance and concentration of the solid reactant according to (Fan et al., 1977a, 1977b)

$$D_s = \exp[\psi_1(1-S)] [\psi_2 \xi^2 + 1] \quad (15)$$

The same expression is also assumed for the Fickian diffusivity, D_f . The value of D_s or D_f is taken as unity at the center of the solid particle in the initial state of the reaction. The second derivative of D_s with respect to ξ , or $\frac{\partial^2 D_s}{\partial \xi^2}$, must exist at any ξ as required by the governing equation, Eqn. (9), in the stochastic diffusion model while only the first derivative of D_f with respect to ξ , or $\frac{\partial D_f}{\partial \xi}$, needs to exist at any ξ as required by the governing equation, Eqn. (12), in the Fickian diffusion model.

Note that the stochastic diffusion model proposed here is capable of producing a non-uniform steady fluid reactant concentration profile at the limit of $t \rightarrow \infty$ for a solid reacting with a single fluid reactant under isothermal conditions. In contrast, the Fickian diffusion model yields a flat concentration profile of the fluid reactant at the limit of $t \rightarrow \infty$ independent of the spatial and temporal dependence of the reactant diffusivity.

The conversion of the solid reactant is defined as

$$X = 1 - (\lambda+1) \int_0^1 S \xi^\lambda d\xi \quad (16)$$

and the effectiveness factor as

$$\begin{aligned} \eta &= \frac{\text{actual rate of the reaction}}{\text{reaction rate based on the fluid bulk concentration and the initial solid concentration}} \\ &= (\lambda+1) \int_0^1 C^q S^p \xi^\lambda d\xi \end{aligned} \quad (17)$$

3.3 NUMERICAL METHOD

Equations (8) and (12) of the Fickian diffusion model, subject to the initial conditions, Eqn. (10), and the boundary conditions, Eqn. (13), and Eqns. (8) and (9) of the stochastic diffusion model, subject to the initial conditions, Eqn. (10), and the boundary conditions, Eqn. (11) are solved numerically by the so-called "method of lines" (Liskovets, 1965; Madsen and Sincovec, 1974; Fan et al., 1977a, 1977b). The second-order, centered, finite difference formula is used to discretize the spatial coordinate of the parabolic partial differential equations. The resulting set of time-dependent ordinary differential equations are then solved by the method proposed by Gear (1971).

3.4 DISCUSSION AND CONCLUSION

The nominal values of the parameters in the models employed for the present numerical calculation are given in Table 1. Figure 1 shows the concentration profiles of the solid reactant at various reaction times computed from the stochastic diffusion model. The corresponding Fickian diffusion model yields the concentration profiles of the solid reactant shown in Fig. 2. Figure 1 indicates that the stochastic diffusion model is capable of yielding unexpected (or peculiar) concentration profiles of the solid reactant which increase outwardly in the radial direction. Such profiles imply that the rate of the solids conversion in the particle is greater in the interior than in the exterior. This may partially explain the coke deposition from the interior toward the exterior of a catalyst in a consecutive reaction of dehydrogenation of n-butyl alcohol (Murakami et al., 1968). This may also explain the terephthalate formation from the interior toward the exterior or in a wave band form in a potassium benzoate

particle during the thermal decomposition in the presence of carbon dioxide (Gokhale et al., 1975; Kulkarni and Doraiswamy, 1977). To model these peculiar observations by a classical model requires an assumption of complicated but ad hoc mechanism which often leads to a complex set of governing equations of the model. In contrast to the stochastic diffusion model, the Fickian diffusion model always yields the concentration profiles of the solid reactant which decrease outwardly in the radial direction at any given time and eventually become uniform as shown in Fig. 2. This implies that the rate of solids conversion in the particle is always smaller in the interior than in the exterior before the profiles become uniform.

The stochastic diffusivity, D_s , as given in Eqn. (9) is proportional to the mobility of the diffusing species, which may vary in a complex and stochastic fashion from position to position in the particle. Thus, the stochastic diffusion equation is capable of modeling reactive transport of a fluid diffusing against its own concentration gradient, e.g., active transport in a biological system (Lightfoot, 1974), mixing of cohesionless solid particles which differ in sizes and/or density in a drum mixer (Fan and Shin, 1977), and bacteria distribution in an ecological system (Keller and Segel, 1971).

Figure 3 shows the history of the solids conversion based on both the stochastic diffusion model and Fickian diffusion model. It can be seen that the stochastic diffusion model gives rise to a higher solids conversion than the Fickian diffusion model at any given time. Figure 4 shows the relationship between the effectiveness factor and the solids conversion based on both the stochastic diffusion model and the Fickian diffusion model. It can be seen that the stochastic diffusion model gives rise to a higher

effectiveness factor than the Fickian diffusion model at any given solids conversion. Thus, the rate of fluid-solid reaction can be enhanced significantly by the stochastic diffusion effect.

While the proposed model may be no more rigorous than classical models, it is at least as meaningful and useful as many of the classical models. However, the proposed model can sometimes be more versatile than the classical ones because it can mechanistically model several unusual phenomena. The proposed model can be extended to nonisothermal heterogeneous reactions and other reaction systems involving more than one phase, e.g., two liquid phases, and gas and liquid phases.

NOMENCLATURE

a_i	stoichiometric coefficient
C	C_1/C_{10} , (-)
C_i	molar concentration of the fluid reactant i within the solid particle, C_{i0} in the bulk phase, (mol/m ³)
C_s	molar concentration of the solid reactant; C_{s0} , for the initial concentration, (mol/m ³)
D_{fi}	Fickian diffusivity of fluid i ; D_{fi0} , for the initial Fickian diffusivity at the center of the particle, (m ² /s)
D_{si}	stochastic diffusivity of fluid i ; D_{si0} , for the initial stochastic diffusivity at the center of the particle, (m ² /s)
D_f	D_{f1}/D_{f10} , (-)
D_s	D_{s1}/D_{s10} , (-)
k_{mi}	mass transfer coefficient of the fluid reactant i across the fluid film, (m/s)
k_v	volumetric reaction rate constant, (m ^{3(p+q-1)} /mol ^(p+q-1) s)
M	total number of the fluid reactants, (-)
N_{shf}	modified Sherwood number based on the Fickian diffusivity, $k_{m1}R/D_{f10}$, (-)
N_{shs}	modified Sherwood number based on the stochastic diffusivity, $k_{m1}R/D_{s10}$, (-)
p, q	order of reaction for the solid reactant and that for the fluid reactant, respectively, (-)
r	distance from the center of the sphere, (m)
R	the radius of the solid sphere, (m)
S	C_s/C_{s0} , (-)
t	time, (s)
X	overall fractional conversion of the solid reactant, (-)

- ϵ void fraction of the particle, (-)
- ϵ_0 initial void fraction of the particle, (-)
- ξ r/R , (-)
- $\tilde{\gamma}_S$ local reaction rate based on the solid reactant, ($\text{mol}/\text{m}^3\text{s}$)
- γ constant defined by Eqn. (14), (-)
- ψ_1, ψ_2 constant defined by Eqn. (15), (-)
- ϕ_v $k_v C_{10}^q C_{S0}^{p-1} t$, (-)
- ϕ_v $R \sqrt{\frac{a k_v C_{10}^{q-1} C_{S0}^p}{D_{f10}}}$, (-)
- ϕ_v' $R \sqrt{\frac{a k_v C_{10}^{q-1} C_{S0}^p}{D_{s10}}}$, (-)
- λ index associated with the geometry of particle, $\lambda = 0$ for flat plate, $\lambda = 1$ for cylinder, $\lambda = 2$ for sphere
- η effectiveness factor defined by Eqn. (17), (-)

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Table 1. Nominal values of the parameters
employed in the present calculation.

$$\lambda = 2$$

$$C_{AO}/C_{SO} = 0.001$$

$$\phi_v = 1$$

$$\phi'_v = 1$$

$$a = 1$$

$$p = 1$$

$$q = 1$$

$$\epsilon_0 = 0.5$$

$$\gamma = 0.3$$

$$N_{shf} = 50,000$$

$$N_{shs} = 50,000$$

$$\psi_1 = 1.0$$

$$\psi_2 = 1.0$$

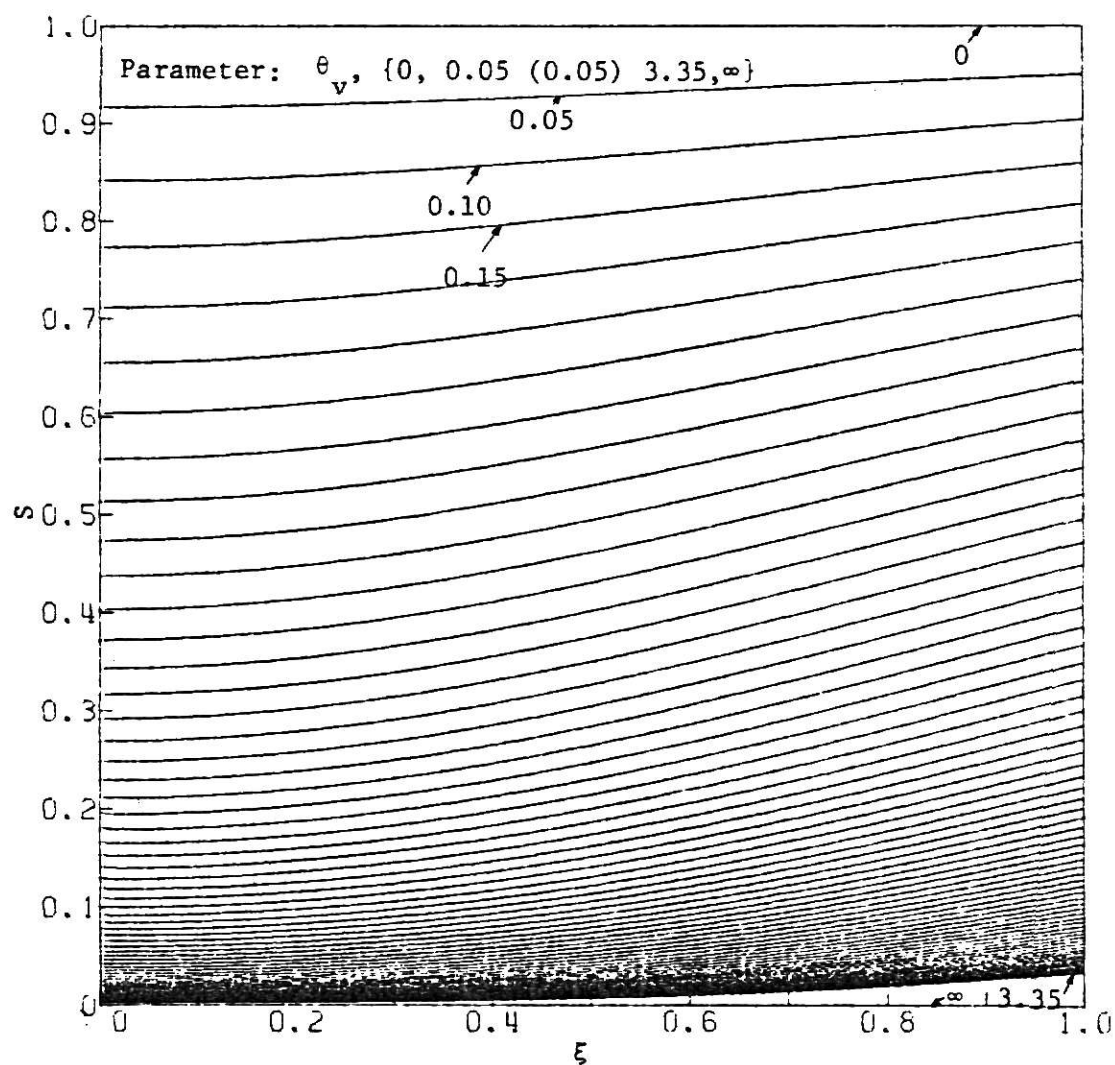


Fig. 1. Concentration profiles of the solid reactant as a function of time calculated from the stochastic diffusion model.

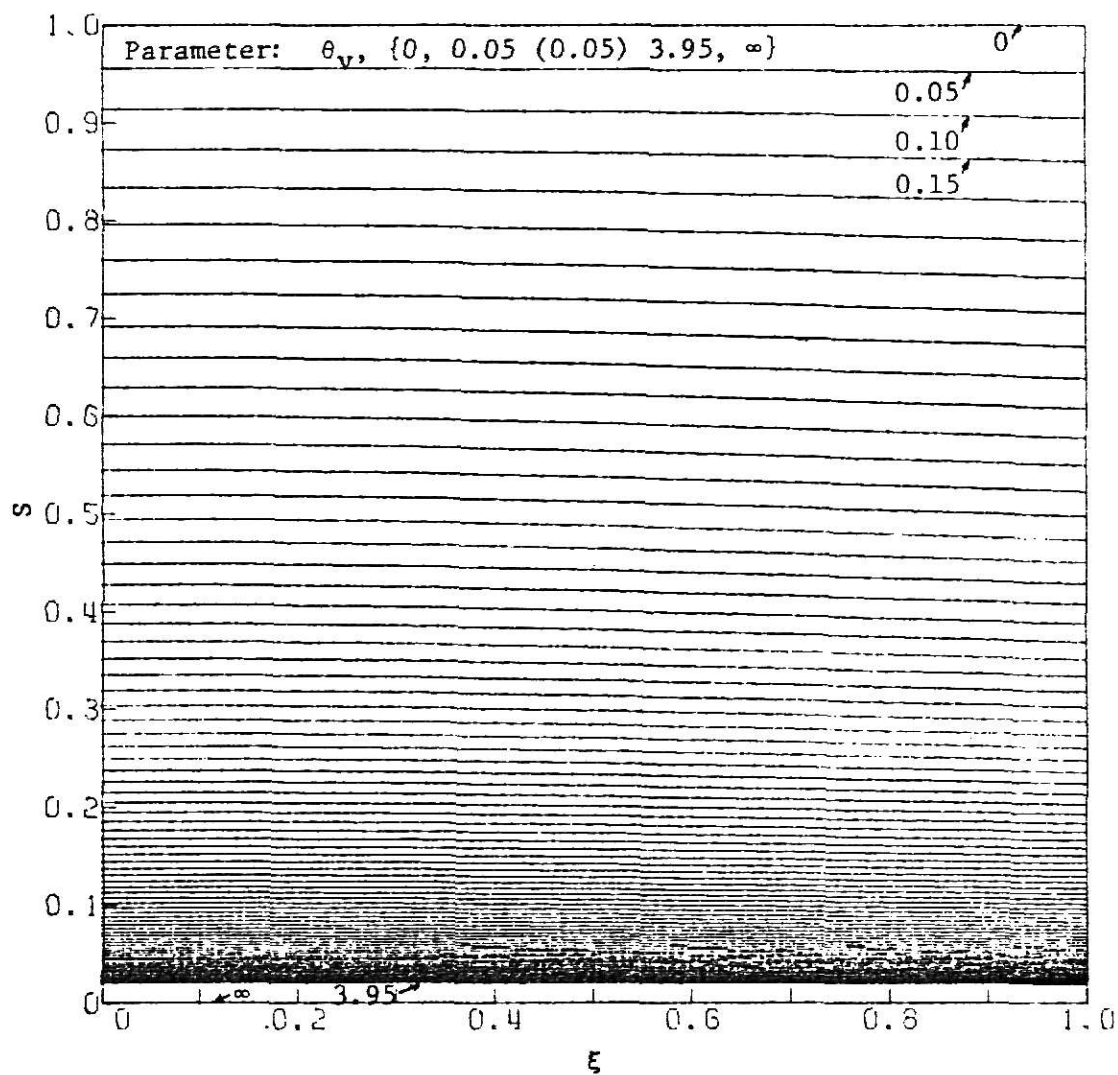


Fig. 2. Concentration profiles of the solid reactant as a function of time calculated from the Fickian diffusion model.

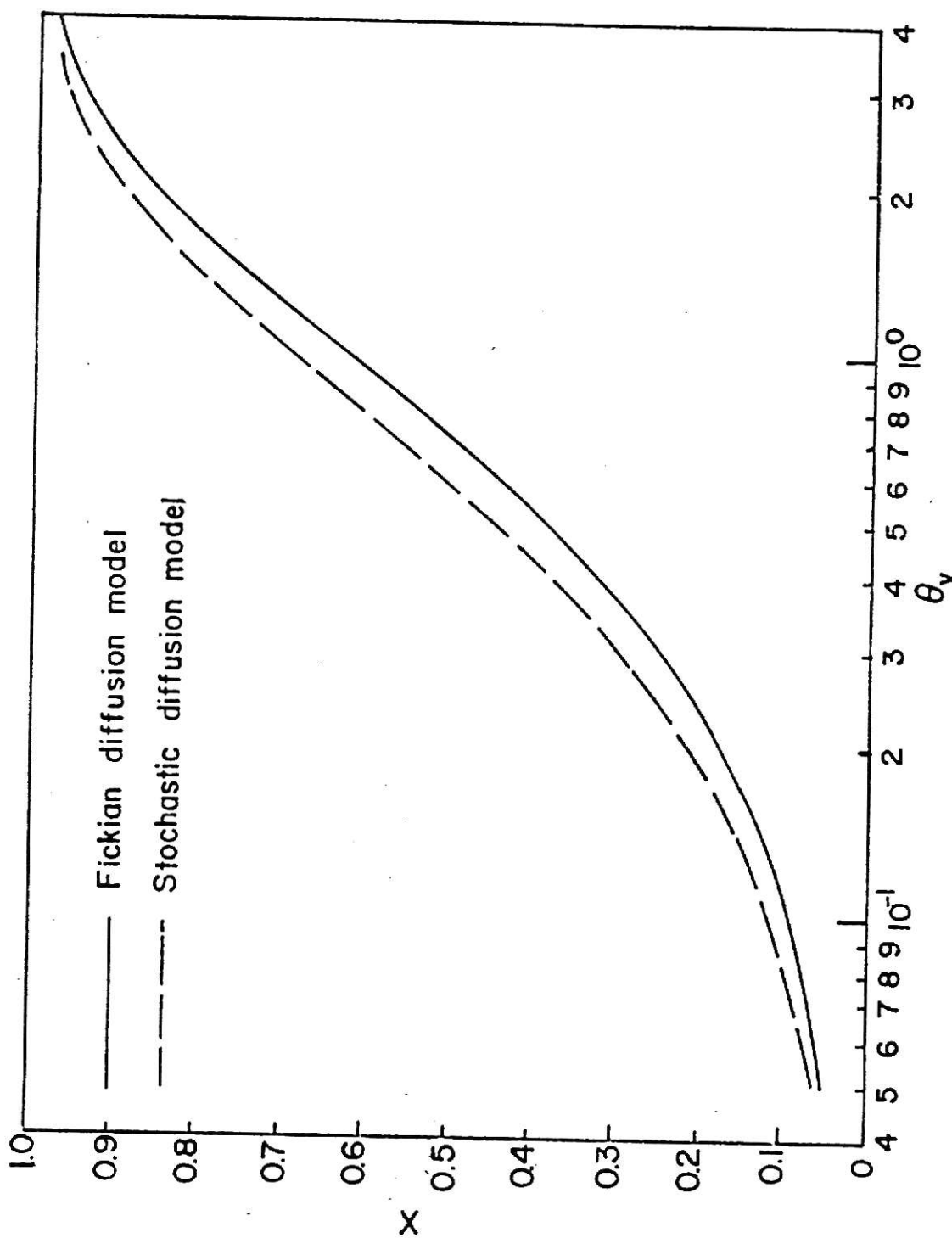


Fig. 3. Relationship between the solids conversion and the dimensionless time obtained from the Fickian diffusion model and the stochastic diffusion model.

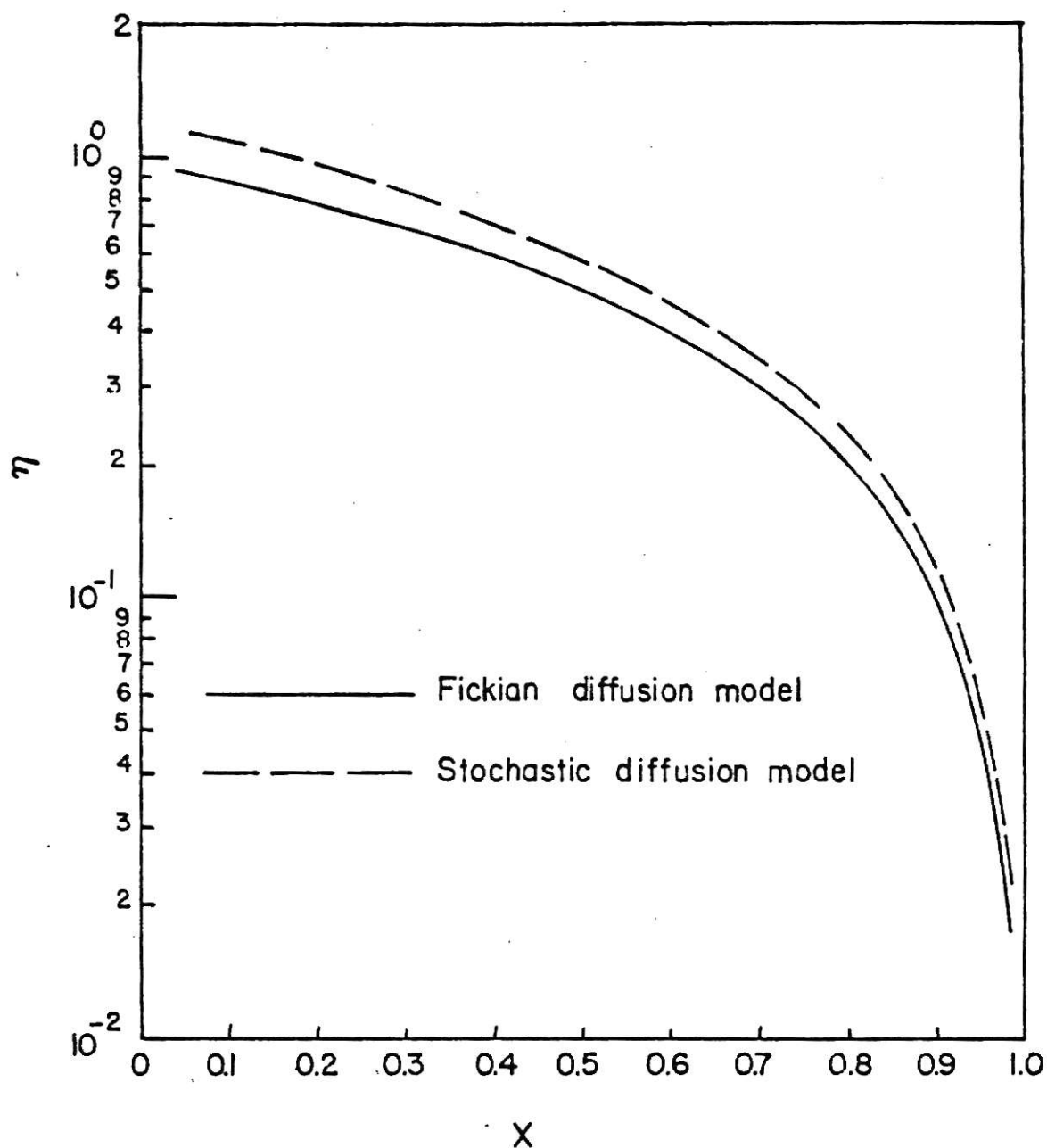


Fig. 4. Relationship between the effectiveness factor and the solids conversion obtained from the Fickian diffusion model and the stochastic diffusion model.

CHAPTER 4

A STOCHASTIC MODEL OF THE UNSTEADY STATE AGE DISTRIBUTION
IN A FLOW SYSTEM

4.1 INTRODUCTION

The knowledge of the age distribution in a flow system under the unsteady or transient state is important for a variety of reasons. The flow system operation is always in the transient condition during the start-up and shut-down periods; it is constantly exposed to external and environmental disturbances; the transient solution of a governing equation provides information on its dynamic characteristics, e.g., time constant and stability, which are essential for design of the control devices of the system; and the unsteady state operation may enhance or impede the performance of the system.

Published age distribution analyses of flow systems focus mainly on steady state systems (e.g., Himmelblau and Bischoff, 1968; Seinfeld and Lapidus, 1974). Cha and Fan (1963) considered the transient age distribution of the completely mixed tank with a pulsating feed. Nauman (1969) extended the Danckwerts-Zwietering treatment of micro-scale mixing, or micro-mixing in short, to the homogeneously stirred, unsteady state flow system. Chen (1971) used the population balance equation to describe the unsteady state micromixing in flow systems. All the approaches, however, are essentially deterministic. This work attempts to shed new light on the nature of unsteady state age distributions in a flow system.

4.2 PURE DEATH PROCESS

Let us consider a flow system containing incompressible fluid elements, and visualize a single fluid element as it traverses the system. This element enters the system at age 0, resides in it for a random length of

time, and leaves the system at age θ . If we identify the random exit of the fluid element from the system as death, the process is a pure death process (Chiang, 1968). The age of the fluid element coincides with the real time of the operation in this situation.

Let the continuous random variable, $\bar{\theta}$, be the age or life span in a pure death process (Chiang, 1968). The age distribution function can be expressed as

$$F_{\bar{\theta}}(\theta) = \Pr(\bar{\theta} \leq \theta)$$

where $F_{\bar{\theta}}(\theta)$ is the probability that the individual will die prior to (or at) age θ . Consider now the interval $(\theta, \theta + \Delta)$ and the corresponding distribution function, $F_{\bar{\theta}}(\theta + \Delta)$. For an individual to die prior to $\theta + \Delta$, he must die prior to θ or else he must survive to θ and die during the interval $(\theta, \theta + \Delta)$. Thus, the following relationship holds:

$$F_{\bar{\theta}}(\theta + \Delta) = F_{\bar{\theta}}(\theta) + [1 - F_{\bar{\theta}}(\theta)][\mu(\theta)\Delta + o(\Delta)] \quad (1)$$

where $\mu(\theta)$ is the force of mortality and $[\mu(\theta)\Delta + o(\Delta)]$ is the probability that an individual alive at age θ will die in the interval $(\theta, \theta + \Delta)$.

Rearranging Eqn. (1), we have

$$\frac{F_{\bar{\theta}}(\theta + \Delta) - F_{\bar{\theta}}(\theta)}{\Delta} = [1 - F_{\bar{\theta}}(\theta)]\mu(\theta) + \frac{o(\Delta)}{\Delta} \quad (2)$$

Taking the limits of both sides of Eqn. (2) as $\Delta \longrightarrow 0$ yields

$$\frac{dF_{\bar{\theta}}(\theta)}{d\theta} = [1 - F_{\bar{\theta}}(\theta)]\mu(\theta) \quad (3)$$

Solution of Eqn. (3) subject to the initial condition of

$$F_{\bar{\theta}}(0) = 0 \quad (4)$$

is

$$F_{\bar{\theta}}(\theta) = 1 - \exp \left\{ - \int_0^{\theta} \mu(\tau) d\tau \right\} \quad (5)$$

Equation (5) gives the probability that an individual will die prior to or at age θ . Thus, $\{1 - F_{\bar{\theta}}(\theta)\}$ or $\exp \left\{ - \int_0^{\theta} \mu(\tau) d\tau \right\}$ represents the probability that one individual alive at age 0 will survive to age θ . If k_0 fluid elements come into the system with age 0 or are originally alive at age 0, and if they survive independently, the number of survivors, $X(\theta)$, at age θ is then a binomial random variable with the probability of success (or being alive), $\{1 - F_{\bar{\theta}}(\theta)\}$, and that of failure (or being dead), $F_{\bar{\theta}}(\theta)$. Thus, $X(\theta)$ has the probability distribution of

$$\begin{aligned} & \Pr\{X(\theta) = k \mid X(0) = k_0\} \\ &= \binom{k_0}{k} [1 - F_{\bar{\theta}}(\theta)]^k [F_{\bar{\theta}}(\theta)]^{k_0 - k} \\ &= \binom{k_0}{k} \exp\left\{-k \int_0^{\theta} \mu(\tau) d\tau\right\} \cdot \left\{1 - \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right]\right\} \end{aligned} \quad (6)$$

This expression gives the expected number of elements that remain in the system or are alive with age θ , $E_a(k)$, as

$$E_a(k) = k_0 [1 - F_{\bar{\theta}}(\theta)] k_0 \exp\left\{-\int_0^{\theta} \mu(\tau) d\tau\right\} \quad (7)$$

The expected number of elements that exit from the system or die prior to age θ , $E_d(k)$, is

$$E_d(k) = k_0 : F_{\bar{\theta}}(\theta) = k_0 \left\{1 - \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right]\right\} \quad (8)$$

The variance of the number of elements alive with age θ or that die prior to age θ , $D^2(k)$, is

$$D^2(k) = k_0 \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] \left\{1 - \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right]\right\} \quad (9)$$

The probability density function of $\bar{\theta}$ is defined as

$$f_{\bar{\theta}}(\theta) = \frac{dF_{\bar{\theta}}(\theta)}{d\theta} = \mu(\theta) \exp\left\{-\int_0^{\theta} \mu(\tau) d\tau\right\}, \quad \theta \geq 0 \quad (10)$$

$$= 0, \quad \theta < 0$$

4.3 MODEL

Consider a flow system that contain an inventory of N fluid elements initially. At time 0^+ , new fluid elements flow into the system at a constant rate of n fluid elements per unit time. Meanwhile, n fluid elements, which consist of both new and inventory elements, flow out of the system. Note that while the rate of flow is constant, both the inventory and new fluid elements undergo temporal variations with respect to their composition.

It is assumed that the inventory-fluid elements and the new fluid elements that flow into the system at any time behave stochastically and independently. The force of mortality of the fluid elements, $\mu(\theta)$, varies with the age, θ , and the type of the fluid elements which include the inventory-fluid and new fluid elements. Furthermore, the stochastic behavior of the fluid elements that remain in the system (or are alive) or exit from the system (or die) obeys the pure death process (see, e.g., Parzen, 1962; Chiang, 1968). Thus, the expected number of inventory-fluid elements in the system at any time, t , is

$$N \exp\left\{-\int_0^t \mu(\tau) d\tau\right\} \quad (11)$$

and the expected number of new elements in the system at t is

$$n \int_0^t \exp\left\{-\int_0^{t'} \mu(\tau) d\tau\right\} dt'. \quad (12)$$

Therefore, the expected total number of fluid elements in the system at t becomes

$$E_{Nt}(k) = N \exp\left\{-\int_0^t \mu(\tau) d\tau\right\} + n \int_0^t \exp\left\{-\int_0^{t'} \mu(\tau) d\tau\right\} dt'. \quad (13a)$$

Since the fluid elements are assumed incompressible, the overall mass of fluid elements in the system remains invariant throughout the process. Thus, $E_{Nt}(k)$ is equal to N , and Eq. (13a) reduces to the equation of mass conservation in the system

$$\exp\left\{-\int_0^t \mu(\tau) d\tau\right\} + \frac{n}{N} \int_0^t \exp\left\{-\int_0^{t'} \mu(\tau) d\tau\right\} dt' = 1. \quad (13b)$$

At any time, t , the number of particles that are of age θ is $NI(t, \theta)$ where $I(t, \theta)$ is the internal age density function. This is equal to the sum of the number of inventory particles of age θ ,

$$N \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] \delta(t-\theta),$$

and the number of new particles of age θ ,

$$n \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] U(t-\theta).$$

In other words,

$$\begin{aligned} NI(t, \theta) = & N \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] \delta(t-\theta) \\ & + n \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] U(t-\theta) \end{aligned} \quad (14a)$$

Thus, we obtain from Eqn. (14a) the internal age distribution in the system at t as

$$I(t, \theta) = \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] \delta(t-\theta) + \frac{n}{N} \exp\left[-\int_0^\theta \mu(\tau) d\tau\right] U(t-\theta) \quad (14b)$$

where δ is the unit impulse function and U is the unit step function.

The expected number of inventory-fluid elements that leave the system (or die) in the time interval of $(t, t + \Delta t)$ is equal to the product of the number of fluid elements that are alive at t

$$N \exp\left[-\int_0^t \mu(\tau) d\tau\right]$$

and the probability of fluid elements to die in the time interval of $(t, t + \Delta t)$, $\mu(t)\Delta t$. The result is

$$N\mu(t) \exp\left\{-\int_0^t \mu(\tau)d\tau\right\}\Delta t \quad (15)$$

Similarly, the expected number of new elements that leave the system in the same time interval is

$$n(\Delta t) \int_0^t \{\mu(t') \exp\left[-\int_0^{t'} \mu(\tau)d\tau\right]\} dt' \quad (16)$$

and, therefore, the expected total number of fluid elements that leave the system in this time interval is

$$E_{nt}^*(k) = N\mu(t) \exp\left\{-\int_0^t \mu(\tau)d\tau\right\}\Delta t + n(\Delta t) \int_0^t \{\mu(t') \exp\left[-\int_0^{t'} \mu(\tau)d\tau\right]\} dt' \quad (17a)$$

The expected total number of fluid elements that leave the system per unit time, $E'_{nt}(t)$, becomes

$$E'_{nt}(k) = \frac{E_{nt}^*(k)}{\Delta t} \quad (17b)$$

As stated, the total number of fluid elements in the system remains unchanged during the process. Consequently, the total number of fluid elements in the exit stream also remains invariant during the process. Thus, $E'_{nt}(k)$ is equal to n , and Eqn. (17b) is simplified to the equation of mass conservation in the exit stream as

$$\frac{N}{n} \mu(t) \exp\left\{-\int_0^t \mu(\tau)d\tau\right\} + \int_0^t \{\mu(t') \exp\left[-\int_0^{t'} \mu(\tau)d\tau\right]\} dt' = 1 \quad (17c)$$

The age distribution function of fluid elements in the exit stream at t ,

$E(t, \theta)$, can be derived using the same argument as employed in deriving

Eqns. (14a) and (14b) by replacing N with n . Thus, we obtain the expression

$$E(t, \theta) = \frac{N}{n} \mu(\theta) \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] \delta(t-\theta) + \mu(\theta) \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] U(t-\theta), \quad (18)$$

and the cumulative age distribution function, $F(t, \theta)$, as

$$\begin{aligned} F(t, \theta) &= \int_0^{\theta} E(t, \theta) d\theta \\ &= \frac{N}{n} \mu(\theta) \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] \delta(t-\theta) \\ &\quad + \int_0^{\theta} \mu(\theta') \exp\left[-\int_0^{\theta'} \mu(\tau) d\tau\right] d\theta' U(t-\theta) \end{aligned} \quad (19)$$

Note that $\mu(\theta)$ needs to satisfy both Eqns. (13b) and (17c). When t approaches infinity, Eqns. (14b) and (18) reduce, respectively, to their steady state counterparts:

$$I(t, \theta) = (n/N) \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] \quad (20)$$

$$E(t, \theta) = \mu(\theta) \exp\left[-\int_0^{\theta} \mu(\tau) d\tau\right] \quad (21)$$

Two special cases are considered below:

(i) Spatially Uniform Flow System. For this system, $\mu(\theta)$ is independent of time and has a constant value of μ . Thus, Eqn. (10) becomes

$$\begin{aligned} f_{\theta}(\theta) &= \mu \exp(-\mu\theta), \quad \theta \geq 0 \\ &= 0, \quad \theta < 0 \end{aligned} \quad (22)$$

and Eqns. (13b) and (17c) are simplified, respectively, to

$$\exp\{-\mu t\} + \frac{n}{N} \frac{1}{\mu} [1 - \exp(-\mu t)] = 1 \quad (23a)$$

and

$$\frac{N}{n} \mu \exp(-\mu t) + [1 - \exp(-\mu t)] = 1 \quad (23b)$$

To satisfy both Eqns. (23a) and (23b), the following relationship must hold:

$$\mu = \frac{n}{N} \quad (24)$$

Since N/n is the mean residence time, α , of the new fluid elements passing through the system, we have

$$\alpha = \frac{1}{\mu} \quad (25)$$

From Eqns. (24) and (25), both $I(t, \theta)$, Eqn. (14b), and $E(t, \theta)$, Eqn. (18), are simplified to

$$I(t, \theta) = E(t, \theta) = \exp(-\mu\theta)\delta(t-\theta) + \mu \exp(-\mu\theta)U(t-\theta) \quad (26)$$

(ii) Piston Flow System. For this system,

$$\begin{aligned} \mu(\theta) &= 0, & \theta < \alpha \\ \mu(\theta) &= \infty, & \theta \geq \alpha \end{aligned} \quad (27)$$

for the new fluid elements, and

$$\begin{aligned} \mu(\theta) &= (\alpha - \theta)^{-1}, & \theta \leq \alpha \\ \mu(\theta) &= \infty, & \theta > \alpha \end{aligned} \quad (28)$$

for the inventory-fluid elements. Thus, Eqn. (5) gives rise to

$$\begin{aligned} F_{\bar{\theta}}(\theta) &= 0, & \theta < \alpha \\ F_{\bar{\theta}}(\theta) &= 1, & \theta \geq \alpha \end{aligned} \quad (29)$$

for the new fluid elements, and

$$\begin{aligned} F_{\bar{\theta}}(\theta) &= \theta/\alpha, & \theta \leq \alpha \\ F_{\bar{\theta}}(\theta) &= 1, & \theta > \alpha \end{aligned} \quad (30)$$

for the inventory-fluid elements. Note that $\mu(\theta)$'s given in Eqns. (27) and (28) satisfy the equations of mass conservation given in Eqns. (13b) and (17c).

Because of Eqns. (14b), (27), and (28), $I(\theta, t)$ can be expressed as

$$\begin{aligned} I(\theta, t) &= \delta(t-\theta)(1-\theta/\alpha) + (1/\alpha)U(t-\theta), & t \leq \alpha \\ I(\theta, t) &= (1/\alpha)U(\alpha-\theta)U(t-\theta), & t > \alpha \end{aligned} \quad (31)$$

From Eqns. (18), (25), and (26), $E(\theta, t)$ becomes

$$\begin{aligned} E(\theta, t) &= \delta(t-\theta), & t \leq \alpha \\ E(\theta, t) &= \delta(\alpha-\theta)U(t-\theta), & t > \alpha \end{aligned} \quad (32)$$

4.4 CONCLUDING REMARKS

The results given in Eqns. (26), (31) and (32) have been deterministically derived by Chen (1971). However, they are the special cases of the generalization expressed by Eqns. (14b) and (18) which have been derived from the probabilistic point of view. Variation of $\mu(\theta)$ generates the age distributions in a variety of flow systems.

NOMENCLATURE

k_0	number of fluid elements alive at age 0 in the pure death process.
n	number of fluid elements in the exit stream in the continuous flow system.
N	number of fluid elements in the reactor in the continuous flow system.
t	real time.
$\mu(\theta)$	force of mortality, intensity of risk of dying or failure rate at age θ .
Δ	small time (or age) increment in the pure death process.
θ	age.
$\bar{\theta}$	continuous random variable for age that varies between 0 and θ .
α	mean residence time, $\frac{N}{n}$.

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APPLICATION OF STOCHASTIC PROCESSES TO CHEMICAL REACTOR SYSTEMS

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This report describes the application of the stochastic processes to the chemical reaction and reactor systems which possess inherent random properties. Three examples, each corresponding to a particular chemical system, are used to demonstrate its applicability. These examples are, solid movement in a fluidized bed expansion, fluid diffusion in a fluid-solid reaction, and life expectancy of fluid elements in a chemical reactor.

Expansion of a fluidized bed may be visualized as upward stochastic diffusion of fluidized solid particles or, equivalently, downward stochastic diffusion of "void" in the bed. Such a visualization of the fluidized bed gives rise to the so-called stochastic or Kolmogorov diffusion model when the stochastic motion is assumed to be Markovian, which is markedly different from the Fickian diffusion model. In the limit of $t \rightarrow \infty$, the stochastic diffusion model proposed here is capable of reproducing the non-uniform steady state axial solid concentration or void distribution in the fluidized bed. Available experimental data have been employed to test the applicability of the proposed model. The model can explain the transient porosity distribution as well as the transient bed expansion.

The stochastic or Kolmogorov diffusion model is proposed as an alternative model for a heterogeneous reaction between fluid and solid reactants. The model is capable of mechanistically modeling several unusual phenomena.

Finally, a discrete state continuous time stochastic process, or more specifically, a pure death process, is used to portray the performance of the fluid elements in the reactor. The internal age distribution, external age distribution, and external cumulative age distribution are derived for the general case where the parameter, i.e. the force of mortality, varies with respect to time.