

February 28, 2013

PERTINENT NOTES ON TUBULAR REACTORS

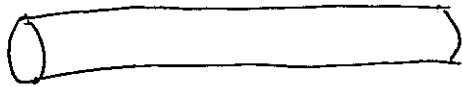
This is scan of handwritten notes taken by S. Nayak my past student, after my type-written notes taken by some students to proofread them mysteriously disappeared. Unfortunately, the electronic version got lost too due to a corrupt disk. The notes contain the following material:

1. Brief discussion of the laminar flow reactor in empty tubes and possible approaches. Comparison of Axial dispersion model (ADM) and segregated flow model. Issues of scale up.
2. Modeling of packed beds (inert packing). ADM and cross flow model. Development of cross flow model equations and their use.
3. Development of the wave model for tubular reactors and packed beds. Westerterp's papers for use of the wave model.
4. Distinction between convection and diffusion dominated systems. Scale up issues.

PERTINENT NOTES ON TUBULAR REACTION, PACKED BEDS, CROSS-FLOW S. NAYAK

04/01/04

Laminar Flow



Segregated Flow model works for set Pe_1, Pe_2
Axial dispersion

$$\frac{dC}{dt} = D_{app} \frac{\partial^2 C}{\partial z^2} - \bar{u} \frac{dC}{dz} - R$$

$$Pe_{app} = \frac{\bar{u}^2 R^2}{4gD}$$

$$\frac{1}{Pe_{app}} \frac{\partial^2 C}{\partial \xi^2} - \frac{\partial C}{\partial \xi} - Pe_{ax} C^n = \frac{\partial C}{\partial \theta}$$

$$\theta = \frac{t}{\bar{\tau}} \quad \bar{\tau} = \frac{L}{\bar{u}} \quad \xi = \frac{z}{L}$$

$$Da = k C_{in}^{n-1} \bar{\tau}$$

$$C = \frac{C_{in}}{C_{in0}}$$

$$\xi = 0 \quad C|_0 - \frac{1}{Pe_{app}} \frac{dC}{d\xi} \Big|_0 = C_0(\theta) \quad (\stackrel{\text{steady}}{=} 1)$$

$$\xi = 1 \quad \frac{dC}{d\xi} = 0$$

$$Pe_{app} = \frac{\bar{u}L}{D_{app}} = \frac{\bar{u}dt}{D_{app}} \left(\frac{L}{dt} \right)$$

Laminar flow

$$P_{app} = P_T = \frac{\bar{u}^2 R^2}{48D} + 0$$

Turbulent flow
 $E_z \propto dt \bar{u}^x$

$$u^x = \sqrt{\frac{f}{2}} \bar{u}$$

$$E_z = K \bar{u} dt \sqrt{f} \quad f = 0.0791 Re^{-0.25}$$

$$K = 3.57 \quad (\text{Taylor})$$

Correlation

$$\frac{E_z}{\bar{u} dt} = \frac{3 \times 10^7}{Re^{2.1}} + \frac{1.35}{Re^{1.8}}$$

* Use Axial dispersion model for $Pe_{app} > 5$
 For $Pe_{app} < 1$ don't use axial dispersion models

Generalization of Tank in series

$$E_0(\theta) = \frac{N^N \theta^{N-1} e^{-N\theta}}{(N-1)!} \quad \sigma_D^2 = \frac{1}{N}$$

* Dispersion as Dominant in spreading material

$$E \approx \frac{1}{2 \sqrt{\pi} \frac{DL}{\bar{u}^3}} e^{-\frac{(t-\bar{t})^2}{4 \frac{DL}{\bar{u}^3}}} \quad \left. \begin{array}{l} \sigma^2 \propto L \\ \sigma \propto \sqrt{L} \end{array} \right\}$$

$$\sigma^2 = \frac{2 P_{app}}{\bar{u} L} \times \left(\frac{L}{\bar{u}}\right)^2 = 2 \frac{P_{app} L}{\bar{u}^3}$$

But at sufficiently large Re

$$\frac{E_2}{\bar{u} d_t} = \text{constant} \quad b=0$$

$$\frac{d_{tLS}}{d_{tPP}} = S^{1/3} = \frac{L_{LS}}{L_{PP}} \Rightarrow \text{geometric similarity holds} \parallel$$

$$\Delta P_{LS} = S^{1/2} \Delta P_{PP}$$

Laminar Flow

$$\Delta P = 32 (\rho \bar{u}^2) \left(\frac{L}{d_t} \right) Re^{-1}$$

Eqs (1) and (2) must hold $E_2 = Dax$

$$\frac{\bar{u} L}{Dax} = \left(\frac{L}{d_t} \right) \left(\frac{192 D}{\bar{u} d_t} \right) \Rightarrow \text{scale up } d_{tLS} = d_{tPP}$$
$$Re_{LS} = S Re_{PP}$$

$$| \Delta P_{LS} = S^2 \Delta P_{PP} |$$

Packed beds \rightarrow Plug flow with superimposed dispersion

(A.D.M) Axial Dispersion model most frequently used

A D M
 $\left(\frac{u d_p}{E_z}\right)$ from σ_D^2

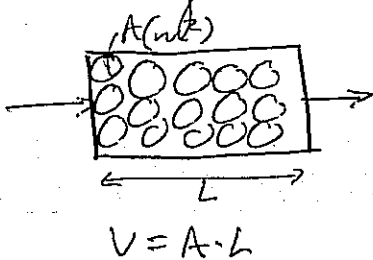
- Several problem
- 1] No trace present in upstream of injection point - contrary to model
 - 2] Does not scale right with L
 - 3] Speed of propagation from not infinite as predicted by model.

Instead people suggested

- \rightarrow Tank in series
- Cell model
- Cross flow model

|| Krishna, Jackson and Sundareshan ||
 AICHE (1980) Vol 26, 274.

Cross flow model



- 1] Fluid that actively flow through
- 2] Fluid trapped behind particles forming wakes, recirculating cells, stagnant zones and exchange betⁿ two fluid

	x	$x + \Delta x$
$E_A A \rightarrow$ flowing fluid	$\uparrow q$	
$E_B A \rightarrow$ Stagnant fluid	$\downarrow q_2$	
Packed bed		

$(E_A + E_B) A = EA$
 \uparrow
 Voidage

* Solid is non porous non catalytic

$$\bar{u} = \frac{Q}{A}$$

$$\bar{u}_a = \frac{Q}{E_a A}$$

$$\bar{F} = \frac{E A L}{Q} = \frac{E V}{Q} = \frac{E L}{E_a \bar{u}_a} = E \frac{L}{\bar{u}}$$

* Balance for flowing zone

$$u_a E_a A C_1 \Big|_x - u_a E_a A C_1 \Big|_{x+\Delta x} - \int A \Delta x (C_1 - K C_2) + R_1 E_a A \Delta x = E_a A \Delta x \frac{dC_1}{dt} \quad \text{--- (1)}$$

$\int \left(\frac{m^3}{m^3 \cdot s} \right) =$ exchange flow rate between flowing and stagnant liquid per unit volume of bed

* Balance for stagnant zone

$$\int A \Delta x (C_1 - K C_2) + R_2 E_b A \Delta x = E_b A \Delta x \frac{dC_2}{dt} \quad \text{--- (2)}$$

$R_2 \frac{\text{mol}}{m^3 \cdot \text{sec}}$ = rate of formation of our species in zone per unit vol fluid

$$K = \left(\frac{C_2}{C_1} \right)_{\text{eq}} \equiv 1$$

For eq (1)

$$-u_a \epsilon_a \frac{dC_1}{dx} - f(C_1 - C_2) + R \frac{\epsilon_a}{\epsilon} = \epsilon_a \frac{dC_1}{dt} \quad \text{--- (3)}$$

For eq (2)

$$f(C_1 - C_2) + R \frac{\epsilon_b}{\epsilon} = \epsilon_b \frac{dC_2}{dt} \quad \text{--- (4)}$$

$$t=0 \quad C_1 = C_2 = 0 \\ x=0 \quad C_1 = C_0$$

Define

$$Y_1 = \frac{C_1}{C_0} \quad Y_2 = \frac{C_2}{C_0} \quad \tau = \frac{\bar{u} t}{d_p \epsilon} \quad s = \frac{\epsilon_b}{\epsilon}$$

$$y = \frac{x}{d_p} \quad \bar{R} = \frac{d_p R}{\epsilon C_0} \quad F = \frac{f d_p}{\bar{u}}$$

So eq (3)

$$-\frac{\partial Y_1}{\partial y} - F(Y_1 - Y_2) + (1-s)\bar{R} = (1-s) \frac{\partial Y_1}{\partial \tau} \quad \text{--- (5)}$$

So eq (4)

$$F(Y_1 - Y_2) + s\bar{R} = s \frac{\partial Y_2}{\partial \tau} \quad \text{--- (6)}$$

$$\tau=0 \quad Y_1 = Y_2 = 0 \quad y=0$$

$$Y_{10} = Y_{10}(\tau)$$

$$Y_1 \left(\tau, \frac{y}{d_p} \right)$$

Ergebn Equation

$$-\frac{dP}{dz} = \underbrace{150 \mu (1-\epsilon)^2 \bar{u}}_{\text{Drag}} + \underbrace{1.75 \left(\frac{1-\epsilon}{\epsilon^3}\right) \rho \bar{u}^2}_{\text{Turbulence}} \frac{d\eta}{d\eta}$$

Hypothesis

$$-\epsilon a \left(\frac{dP}{dz}\right)' = \int \rho \frac{\bar{u}^2}{\epsilon a}$$

$$\left(\frac{dP}{dz}\right)' = \int \frac{\rho \bar{u}^2}{\epsilon a^2} = 1.75 \left(\frac{1-\epsilon}{\epsilon^3}\right) \frac{\rho \bar{u}^2}{d\eta}$$

$$F = \int \frac{d\eta}{\bar{u}} = 1.75 \left(\frac{1-\epsilon}{\epsilon}\right) (1-s)^2 \quad (*)$$

$$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 1-s = \frac{\epsilon a}{E}$$

$$\bar{Y}_1 = \mathcal{L}\{Y_1\} \quad \bar{Y}_2 = \mathcal{L}\{Y_2\}$$

$$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \mathcal{L}\left(\frac{\partial Y_1}{\partial z}\right) = -s \bar{Y}_1 - \frac{\bar{Y}_1(z=0)}{z=0}$$

$$\frac{d\bar{Y}_1}{dy} = -F(\bar{Y}_1 - \bar{Y}_2) - (1-s)s\bar{Y}_1 \quad (7)$$

$$F(\bar{Y}_1 - \bar{Y}_2) = s s \bar{Y}_2 \quad (8)$$

Solve for \bar{Y}_2

$$\frac{d\bar{Y}_1}{dy} = - \left[\frac{F s s}{F + s s} + (1-s)s \right] \bar{Y}_1; \quad y=0 \quad \bar{Y}_1 = 1$$

$$\bar{Y}_1 = e^{-\left[\frac{FSs}{F+Ss} + (1-s)s \right] y}$$

$$\bar{Y}_{1 \text{ exit}} = \bar{Y}_1 \left(s, y = \frac{L}{dp} \right) = e^{-\frac{L}{dp} \left[\frac{FSs}{F+Ss} + (1-s)s \right]} \quad (*)$$

$$\bar{Y}_{1 \text{ exit}} = e^{-\frac{L}{dp} \left[F - \frac{F}{1 + \frac{S}{F}s} + (1-s)s \right]}$$

by binomial

$$= e^{-\frac{L}{dp} \left[s - \frac{S^2}{F}s + \frac{S^3}{F^2} - \dots \right]}$$

$$= 1 - \frac{L}{dp} s + \left[\frac{S^2}{F} \frac{L}{dp} + \frac{1}{2} \left(\frac{L}{dp} \right)^2 \right] s^2 - O(s^3)$$

compare with

$$\bar{Y}_{1 \text{ exit}} = \mu_0 - \mu_1 s + \frac{\mu_2}{2} s^2 - \frac{\mu_3}{6} s^3$$

$$\mu_0 = 1$$

$$\mu_1 = \frac{L}{dp}$$

$$\mu_2 = 2 \left[\frac{S^2}{F} \frac{L}{dp} + \frac{1}{2} \left(\frac{L}{dp} \right)^2 \right]$$

$$\frac{s^2}{F} \frac{dp}{L} = \frac{1}{B_0} \frac{dp}{L}$$

$$\frac{s^2}{F} = \frac{1}{B_0} \quad \text{--- (**)}$$

$$F = \int \frac{dp}{u} = 1.75 \left(\frac{1-\epsilon}{\epsilon} \right) (1-s)^2 \quad (***)$$

From (**) (***)

$$s = \frac{\sqrt{\frac{1.75}{B_0} \left(\frac{1-\epsilon}{\epsilon} \right)}}{1 + \sqrt{\frac{1.75}{B_0} \left(\frac{1-\epsilon}{\epsilon} \right)}}$$

$$F = \frac{1.75 \left(\frac{1-\epsilon}{\epsilon} \right)}{\left[1 + \sqrt{\frac{1.75}{B_0} \left(\frac{1-\epsilon}{\epsilon} \right)} \right]^2}$$

Steady State reactor model ^{1st order}
 Rate of formation

$$\frac{dY_1}{dy} = -F(Y_1 - Y_2) + (1-s) \bar{R}_{Y_1} \quad (1)$$

$$F(Y_1 - Y_2) + s \bar{R}_{Y_2} = 0 \quad (2)$$

↑ Rate of formation

$$y = 0 \quad Y = 1$$

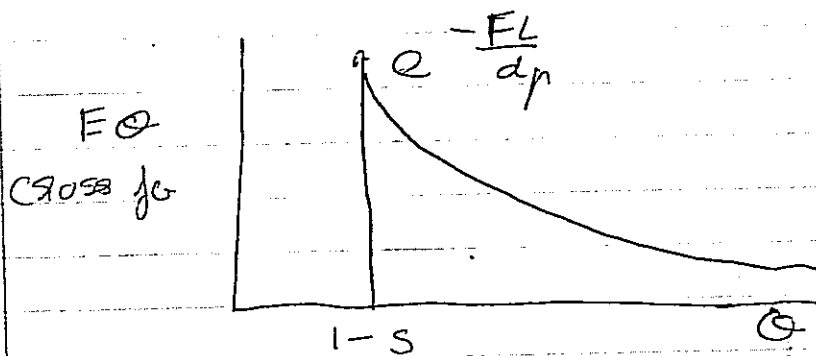
$$R = Da Y^n$$

$$E_{\theta}(\theta) = \left(\frac{L}{d_p} \right) Y_{1, \text{exit}}(\tau)$$

$$\theta = \frac{\bar{u}}{EL} t = \left(\frac{d_p}{L} \right) \tau$$

$$E_{\theta}(\theta) = e^{-L F / d_p} e^{-F H / d_p s (\theta - (1-s))} \left\{ \frac{L}{d_p} s (\theta - (1-s)) \right\}$$

$$+ \frac{F L / d_p}{\sqrt{s / \theta - (1-s)}} I_1 \left(2 \frac{F L}{d_p} \sqrt{\frac{\theta - (1-s)}{s}} \right) H(\theta - (1-s))$$



Packed bed model must match t and variance. Always match various physical meaning

$$\frac{dc}{dz} = -Da f(c) \quad \text{PFR}$$

$$z=0 \quad c=1$$

ADM

Cells in series

Recycle model

Cross flow mode

$$\sigma_D^2 = \frac{2}{Peax} - \frac{2}{Peax} (1 - e^{-Peax})$$

y_N

$R/(1+R)$

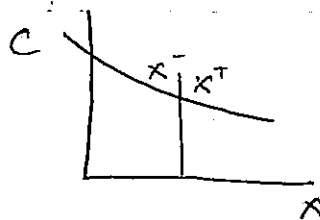
$$\frac{2}{F}$$

Micro flow Howard Benner

Macro Transport processes. Finans book

Fickes 1st Law

$$J_x = -D \frac{dc}{dx}$$



$$J_x(x, t+\tau) = -D \frac{dc}{dx}(x, t)$$

$$J_x(x, t+\tau) = J_x(x, t) + \frac{dJ}{dt}(x, t)(\tau - t)$$

$$j + \tau \frac{dj}{dt} = -D \frac{dc}{dx}$$

$$\tau = \frac{L}{U}$$

$$D \propto LU$$

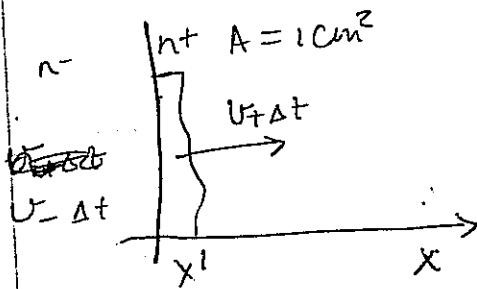
$$\frac{SDa}{20}$$

Ref: ^{Richard} Robert P. Feynman, Robert B Leighton,
^{Matthew} Sands

The Feynman lectures of Physics I and II
 Addison - Wesley, Cal Tech, 1963

02/10/05

Random walk \rightarrow diffusion



$$j_x = \frac{n_- v_{-Δt} - n_+ v_{+Δt}}{Δt} = (n_- - n_+) v \quad (1)$$

$$n_+ - n_- = \frac{dc}{dx} = \alpha l \frac{dc}{dx} \quad (2)$$

$$j_x = -\alpha l v \frac{dc}{dx} = -D \frac{dc}{dx} \quad (3)$$

$$D = \frac{1}{3} v l \quad (4a)$$

$$l = \tau v \quad (5)$$

mean free path = $\left(\begin{array}{l} \text{mean} \\ \text{time} \\ \text{bet}^n \\ \text{collision} \end{array} \right) \times \left(\begin{array}{l} \text{mean} \\ \text{molecular} \\ \text{velocity} \end{array} \right)$

O₂ at 25°C, 1 atm

$$v = \left(\frac{8RT}{\pi M} \right)^{1/2} = 444 \text{ m/sec}$$

$$l = \frac{l}{\sqrt{2} \pi \left(\frac{N}{V} \right) d^2} = 2.28 \times 10^{-7} \text{ m}$$

$$\tau = \frac{l}{v} = 5 \times 10^{-10} \text{ (s)} \quad \text{Mean free path } l = \lambda$$

$$J_x(t + \tau) = -D \frac{\partial C(t)}{\partial x} \quad (9)$$

$$J_x(t + \tau) = J_x(t) + \tau \frac{\partial J_x}{\partial t} = -D \frac{\partial C}{\partial x} \quad (10)$$

If we make an unsteady state balance
if we use eq (3)

$$\frac{\partial C}{\partial t} = D \nabla^2 C \rightarrow \text{or in 1D} \quad \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Count particles that reach position x at time t which has their last collision at time $(t - \eta)$ at the point $(x - \eta v_t)$ ($\eta > 0$) and obtained velocity v_t in the positive x direction moved during time η without further collision and without disappearing by reaction.

The total number of collision at point $x - \eta v_+$ and at time $t - \eta$, in terms of continuous function $C(x, t)$ is equal to

$$\frac{C(x - \eta v_+, t - \eta)}{\tau} \quad \text{where, } \tau \text{ is mean time bet}^h \text{ collision}$$

The flux of particle at x, t from left to right.

$$J_+(x, t) = \frac{p_+ v_+}{\tau} \int_0^{\infty} G(\eta) H(\eta) C(x - \eta v_+, t - \eta) d\eta \quad \text{--- (11)}$$

$G(\eta) =$ Probability that particle survives time η without colliding

$H(\eta) =$ Probability without reacting

$$H(\eta) = e^{-k\eta} \quad \text{--- (14)}$$

$$G(\eta) = e^{-\eta/\tau} \quad \text{--- (13)}$$

$$J_-(x, t) = \frac{p_- v_-}{\tau} \int_0^{\infty} G(\eta) H(\eta) C(x + \eta v_-, t - \eta) d\eta \quad \text{--- (12)}$$

$$P_+ v_+ = P_- v_- \quad (13a)$$

Concentration Definition

$$c = \frac{j_+}{v_+} + \frac{j_-}{v_-} \quad (13b)$$

Net Flux

$$j = j_+ - j_- \quad (13c)$$

Probability

$$P_+ + P_- = 1 \quad (13d)$$

For j_+
Consider eq (11) drop subscript for now.

$$j = \frac{P_+ v_+}{2} \int_0^{\infty} e^{-a\eta} c(x - \eta v_+, t - \eta) d\eta \quad (16)$$

where

$$a = \left(k + \frac{1}{\tau} \right)$$

Integrate by parts

$$u = c(x - \eta v_+, t - \eta) \quad du = -v_+ \frac{dc}{dx}$$

$$du = \frac{dc}{dw} + \frac{dw}{d\eta} + \frac{\partial c}{\partial \theta} \cdot \frac{\partial \theta}{\partial \eta} = -v_+ \frac{dc}{dx} - \frac{dc}{dt}$$

$$dv = e^{-a\eta} d\eta \quad v = -\frac{1}{a} e^{-a\eta}$$

$$j = \frac{\rho v}{\epsilon} \left\{ \left[-\frac{1}{a} e^{-a\eta} c(x-\eta v, t-\eta) \right]_0^{\infty} - \frac{1}{a} \int_0^{\infty} e^{-a\eta} \left(v \frac{dc}{dx} + \frac{dc}{dt} \right) d\eta \right\}$$

$$a j^{\circ} = \frac{\rho v}{\epsilon} c(x, t) - \frac{\rho v}{\epsilon} v \int_0^{\infty} e^{-a\eta} \frac{dc}{dx} (x-\eta v, t-\eta) d\eta - \frac{\rho v}{\epsilon} \int_0^{\infty} e^{-a\eta} \frac{dc}{dt} d\eta$$

But

$$\frac{dj^{\circ}}{dc} = \frac{\rho v}{\epsilon} \int_0^{\infty} e^{-a\eta} \frac{dc}{dx} d\eta$$

$$\frac{dj^{\circ}}{dt} = \frac{\rho v}{\epsilon} \int_0^{\infty} e^{-a\eta} \frac{dc}{dt} d\eta$$

Put $j = j^+$

$$a j^{\circ}_+ = \frac{\rho v}{\epsilon} c - v_+ \frac{dj^{\circ}_+}{dx} - \frac{dj^{\circ}_+}{dt} \quad (17a)$$

For $j = j^-$

$$a j^{\circ}_- = \frac{\rho - v_-}{\epsilon} c + v_- \frac{dj^{\circ}_-}{dx} - \frac{dj^{\circ}_-}{dt} \quad (17b)$$

$$\left(k + \frac{1}{z}\right) j_+ = \frac{p_+ u_+}{z} C - u_+ \frac{dj_+}{dx} - \frac{dj_+}{dt} \quad (18a)$$

$$\left(k + \frac{1}{z}\right) j_- = \frac{p_- u_-}{z} C + u_- \frac{dj_-}{dx} - \frac{dj_-}{dt} \quad (18b)$$

Divide 18a by u_+ and 18b by u_-
and adding 18a and 18b

$$\begin{aligned} \left(k + \frac{1}{z}\right) \left(\frac{j_+}{u_+} + \frac{j_-}{u_-}\right) &= \left(\frac{p_+}{z} + \frac{p_-}{z}\right) C - \left[\frac{1}{u_+} \frac{dj_+}{dt} + \frac{1}{u_-} \frac{dj_-}{dt}\right] \\ \text{Sub to (15d)} \quad \underbrace{\quad}_{(15d) \text{ } \frac{dC}{dt}} &- \underbrace{\left(\frac{dj_+}{dx} - \frac{dj_-}{dx}\right)}_{(15c) \frac{dj}{dx}} \end{aligned}$$

$$\frac{dC}{dt} + \frac{dj}{dx} + kC = 0 \quad (19a)$$

Subtract 18b from 18a

$$\begin{aligned} \left(k + \frac{1}{z}\right) (j_+ - j_-) &= \left(\frac{p_+ u_+}{z} - \frac{p_- u_-}{z}\right) C - \frac{d}{dt} (j_+ - j_-) \\ &- u_+ \frac{dj_+}{dx} - u_- \frac{dj_-}{dx} \end{aligned}$$

$$\left(k + \frac{1}{z}\right) j = - \frac{dj}{dt} - u_+ \frac{dj_+}{dx} - u_- \frac{dj_-}{dx} \quad (*)$$

Adding and subtracting eq X

$$\left(k + \frac{1}{\tau}\right) j^{\circ} = -\frac{dj^{\circ}}{dt} \left(-u_+ \frac{dj^{\circ}}{dx} \right) - \left[u_- \frac{dj^{\circ}}{dx} \right] \\ + u_+ \frac{dj^{\circ}}{dx} - u_- \frac{dj^{\circ}}{dx} - \left[+u_+ \frac{dj^{\circ}}{dx} \right] - u_- \frac{dj^{\circ}}{dx}$$

$$\left(k + \frac{1}{\tau}\right) j^{\circ} = -\frac{dj^{\circ}}{dt} - u_+ \frac{dj^{\circ}}{dx} + u_- \frac{dj^{\circ}}{dx} - u_- \frac{dj^{\circ}}{dx} \\ - u_+ \frac{dj^{\circ}}{dx} \\ \text{From (13 b)} \\ -u_+ u_- \frac{dc}{dx}$$

$$\left(k\tau + 1\right) j^{\circ} + \tau \frac{dj^{\circ}}{dt} + (u_+ - u_-) \tau \frac{dj^{\circ}}{dx} + u_+ u_- \tau \frac{dc}{dx} = 0$$

Hyperbolic equation with finite speed of propagation define the "diffusion Phenomena" (19a) and (19b) (19b)

Solved for C and j^o subject to I.C and B.C
No 1st order reaction k=0

Ref: Westerberg, K.R., Delman V.V., Kronberg, A.E

Wave model for longitudinal dispersion: I Development of the model.

AIChE J. 41 (9), 2013 - 2029 (1995)

Part II : Analysis and Application
 AIChE J 4(9), 2029-2039 (1995)

ADM replaced by

$$\frac{d\bar{C}}{dt} + \bar{u} \frac{d\bar{C}}{dx} + \frac{d_j}{dx} = 0$$

$$j + \frac{1}{15} \frac{a^2}{D} \left(\frac{d_j}{dt} + \frac{5\bar{u}}{4} \frac{d_j}{dx} \right) = -De \frac{d\bar{C}}{dx} \quad \therefore De = \frac{a^2 \bar{u}^2}{48D}$$

Handbook

61, 62, 63, 64, 66, 68

1 H.W 2

2) Axial Dispersion model

a) Perturbation technique. Plug flow than the accurate

c) Assume Segregated flow & generalise tank of series model.

Cross flow model

$$-\frac{dy_1}{dz} - F(y_1 - y_2) - (1-s) Da_1 y_1^2 = 0$$

$$F(y_1 - y_2) - s Da_1 y_2^2 = 0$$

$$(\xi, \tau) \rightarrow (y, \theta)$$

$$\frac{\partial}{\partial \xi} = \frac{\partial}{\partial y} \frac{\partial y}{\partial \theta} + \frac{\partial}{\partial \theta} \frac{\partial \theta}{\partial \xi}$$

Convection Dominates

$$E \approx \frac{L}{\sqrt{2\pi}\sigma^2} e^{-\frac{(t-\bar{t})^2}{2\sigma^2}}$$

$$\bar{t} = \text{constant}$$

$$\sigma^2 \propto \left(\frac{L}{\bar{v}}\right)^2$$

$$\sigma \propto L$$

Ref: Levenspiel and Fitzgerald

"A Warning on the Miss use of the Dispersion Model" CES 38 # 3, 489-491, 1982
Chem Engg Sci

Scale up of Tubular Reactors with Premixed Feed

$$\text{Scale up ratio} = S = \frac{Q_{\text{Full Scale}}}{Q_{\text{Pilot Plant}}} = \frac{Q_{FS}}{Q_{PP}}$$

Scale up by multiplication use S tubes of same d_t , L and Q_{PP} as used in single tube in the pilot

$$P.P : L, \bar{u}, d_t \rightarrow R_{pp} X_A$$

$$Q_{pp} = \frac{d_{tpp}^2}{4} \pi \bar{u}$$

$$V_{pp} = \frac{d_{tpp}^2}{4} \pi L$$

$$\bar{t} = \frac{L}{\bar{u}}$$

For scale up

1] Mean must be constant

2] Variance must be constant.

02/03/05

Scaleup of Tubular Reactors

- By multiplication

$$S = \frac{Q_{LS}}{Q_{PP}}$$

and satisfactory performance was obtained in PP in a tube of d_t , L use S much larger in plant

Empty Tubes

Turbulent \odot

$$Re > 2,100$$

$$\bar{t} = \text{constant} = \left(\frac{L}{\bar{u}}\right)_{PP} = \left(\frac{L}{\bar{u}}\right)_{LS}$$

$$\sigma_D^2 = \text{const} = \left(\frac{\bar{u}L}{E_z}\right)_{PP} = \left(\frac{\bar{u}L}{E_z}\right)_{LS}$$

$$\frac{E_z}{\bar{u} d_t} = a Re^{-b} \quad Re = \frac{\bar{u} d_t}{\nu}$$

$$E_z = a \nu^b d_t^{1-b} \bar{u}^{1-b}$$

$$\frac{d_{tLS}}{d_{tPP}} = S^{\frac{1+b}{3+b}} (*) \quad \frac{L_{LS}}{L_{PP}} = \frac{\bar{u}_{LS}}{\bar{u}_{PP}} = S \quad (1-b)/3+b \quad (**)$$

$$\Delta P_{LS} = S^{\frac{3-8b}{2(3+b)}} \Delta P_{PP}$$

Typically $b = \frac{1}{8}$

Wave Model for Longitudinal Dispersion: Analysis and Applications

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An analysis and applications of the wave model for longitudinal dispersion are presented. Asymptotic forms of the wave model are considered and analytical solutions of typical linear stationary and nonstationary problems of chemical reactor engineering interest are obtained and compared to those for the Fickian dispersion model. The wave model leads to efficient analytical solutions for linear problems, which in principle differ from the solutions of the Fickian dispersion model; only for slowly varying concentration fields do the solutions of both models approach each other. Spatial and time moments of the concentration distribution are obtained for pulse-dispersion problems; the first three spatial moments of the mean, variance, and skewness have exact, large-time asymptotic forms in the case of Taylor dispersion. Old experiments that could not be explained with the standard dispersion model are reconsidered and explained: the change with time of the variance of a concentration pulse when the flow direction is reversed and the difference in values of the apparent axial dispersion coefficient and the back-mixing coefficient in a rotating disk contactor. The experimental determination of model parameters is discussed.

Introduction

Many processes of interest in chemical engineering are analyzed in terms of transport equations for concentrations that are in some way averaged or in terms of what are referred to as dispersion equations. For mass- or heat-dispersion fluxes simple gradient laws like Fick's law for diffusion are commonly used. The most widespread model is the one-dimensional dispersed-plug-flow model or standard dispersion model (SDM) for a concentration averaged over the cross section to the flow. The shortcomings of this model are well known (see Westerterp et al., 1995). In the cited article the mathematical description of the way in which substances are dispersed along a channel, through which fluid flows in steady motion, has been reconsidered. As an alternative to the Fickian-type dispersion model and on the basis of two different approaches, a hyperbolic system of two first-order equations for the average concentration c and the dispersion flux j was obtained:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + \frac{\partial j}{\partial x} + q(c, x, t) = 0 \quad (1)$$

$$[1 + \tau q'(c, x, t)]j + \tau \frac{\partial j}{\partial t} + \tau(u + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial c}{\partial x} \quad (2)$$

where D_e , τ , and u_a are the parameters of the wave model (see Westerterp et al., 1995). For a first-order chemical reaction with a position-independent rate constant, Eqs. 1 and 2 become one second-order hyperbolic equation

$$\begin{aligned} \frac{\partial^2 c}{\partial t^2} + (2u + u_a) \frac{\partial^2 c}{\partial x \partial t} + (u^2 + uu_a - D_e/\tau) \frac{\partial^2 c}{\partial x^2} \\ + (\tau^{-1} + 2k) \frac{\partial c}{\partial t} + [u/\tau + k(2u + u_a)] \frac{\partial c}{\partial x} \\ + k(\tau^{-1} + k)c = 0. \quad (3) \end{aligned}$$

The wave model of Eqs. 1 and 2 does not contain the conceptual deficiencies of the SDM. It also leads to a better under-

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standing of the mechanisms responsible for the characteristics of longitudinal dispersion phenomena.

The question arises: What does the application of the wave model give from a practical point of view and how does it interrelate to the SDM? There have been a number of papers setting up similar, mostly heuristic, models that are rarely compared with experiments. Therefore the general properties of the wave model and its potential benefits are treated here. The wave model will also be applied to several problems of interest to the chemical reactor or process engineering in order to demonstrate the essential advantages of the wave model over the SDM.

The asymptotic forms of the wave model and the conditions under which plug flow and ideal mixing are attained are considered. The analytical solutions of the linear stationary problem and the solutions of two nonstationary problems with an initial concentration pulse specified at some moment of time and at some point are obtained and compared with those of the Fickian dispersion model. For the linear problem the analytical solutions of the equations are as simple as for the Fickian dispersion model. The solutions differ fundamentally; only in slowly varying concentration fields are both models close to each other. Spatial and time moments of the concentration distribution are obtained; the first three spatial moments—mean, variance, and skewness—have exact long-term asymptotic forms in the case of Taylor dispersion. Two experimental studies are considered that cannot be explained with the SDM: the change over time of the variance of a concentration pulse, when the flow direction is reversed, and the difference in values of the apparent axial dispersion coefficient and the backmixing coefficient in a rotating disk reactor.

Asymptotic Forms of the Wave Model

For an analysis of the asymptotic forms of the wave model it is expedient to rewrite Eqs. 1 and 2 in dimensionless form:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial X} + \frac{\partial J}{\partial X} + Q(C, \theta, X) = 0 \quad (4)$$

$$(P + Q')J + \frac{\partial J}{\partial \theta} + (1 + u_a^*) \frac{\partial J}{\partial X} = -D_e^* \frac{\partial C}{\partial X} \quad (5)$$

where

$$C = \frac{c}{c_{ch}}; \quad J = \frac{j}{uc_{ch}}; \quad \theta = \frac{t}{t_{ch}}; \quad X = \frac{x}{ut_{ch}}; \quad P = \frac{t_{ch}}{\tau}$$

$$u_a^* = \frac{u_a}{u}; \quad D_e^* = \frac{D_e}{u^2\tau}; \quad Q = \frac{qt_{ch}}{c_{ch}}$$

and prime denotes derivative to the dimensionless concentration $Q' = dQ/dC$ and c_{ch} is the characteristic concentration. To be able to evaluate the relative contribution of each term in Eqs. 4 and 5, the characteristic time of the process t_{ch} must characterize the time of concentration changes. It depends, of course, on the problem under consideration. For example, for the stationary process in a chemical reactor it is the characteristic time of the chemical reaction; for a nonsta-

tionary tracer propagation it is the average residence time; and for steady periodic processes it is the cycle period.

From Eqs. 4 and 5 it follows that the dispersion flux can be neglected when the characteristic time t_{ch} is much larger than the relaxation time τ or $P \gg 1$: the wave model transforms into the plug-flow model:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial X} + Q(C, X, \theta) = 0.$$

In the opposite case of $P \rightarrow 0$ we will restrict ourselves to the linear problem, assuming first-order kinetics with $q = kc$ where k is constant. We do so to avoid the difficulties in representing the consumption rate q through the average concentration c . In this limiting case Eqs. 4 and 5 transform into

$$\frac{\partial^2 C}{\partial \theta^2} + (2 + u_a^*) \frac{\partial^2 C}{\partial X \partial \theta} + (1 + u_a^* - D_e^*) \frac{\partial^2 C}{\partial X^2} + 2Da \frac{\partial C}{\partial \theta} + Da(2 + u_a^*) \frac{\partial C}{\partial X} + Da^2 C = 0$$

where $Da = kt_{ch}$ is the Damköhler number. This equation can be reduced to

$$\frac{\partial^2 V}{\partial \theta^2} + (2 + u_a^*) \frac{\partial^2 V}{\partial X \partial \theta} + (1 + u_a^* - D_e^*) \frac{\partial^2 V}{\partial X^2} = 0$$

by substituting $C = V \exp(-Da\theta)$. Introducing new variables $\omega_1 = X - u_1^*\theta$ and $\omega_2 = X - u_2^*\theta$, we arrive at the normal form of the hyperbolic equation

$$\frac{\partial^2 V}{\partial \omega_1 \partial \omega_2} = 0$$

where $u_{1,2}^* = 1 + (u_a^*/2)(1 \pm \sqrt{1 + 4D_e^*/u_a^{*2}})$ are the dimensionless wave velocities. From this equation it follows that the most general solution of the problem under consideration is in the form of the sum of two waves that are damped by the chemical reaction:

$$C = f_1(\omega_1)e^{-Da\theta} + f_2(\omega_2)e^{-Da\theta}$$

where f_1 and f_2 can be any functions of ω_1 and ω_2 , respectively. The obtained equation and its solution show that in the limiting case $t_{ch} \ll \tau$ the wave model corresponds to a linear combination of two plug-flow models with velocities equal to the wave velocities.

The wave model also transforms into the plug-flow model for sufficiently small values of the parameter of velocity asymmetry u_a^* and the dispersion coefficient D_e^* at fixed values of P . Actually from the definition of these parameters (see Westerterp et al., 1995) it follows that $D_e^* \rightarrow 0$ and $u_a^* \rightarrow 0$ when, as expected, the dispersion velocities of the longitudinal mixing process, or the wave velocities in a coordinate system moving with the average velocity, approach zero. This means the longitudinal velocity distribution approaches a

uniform velocity profile. In this case the initial and boundary values of the dispersion flux are equal to zero, and the dispersion flux is always equal to zero due to Eq. 5. In the opposite case of large values of D_e^* and fixed values of u_a^* we may expect ideal mixing conditions. Note that in the general case the parameters of the wave model can have arbitrary values. But such a situation is impossible for Taylor dispersion in a unidirectional flow system, because longitudinal and transverse mixing are interrelated and the longitudinal dispersion coefficient D_e^* cannot exceed the value of $1 + u_a^*$ in this case (Westerterp et al., 1995). The more general problem of independent longitudinal and transverse mixing—similar to the generalization of Taylor's theory made by Aris (1956)—must be considered if we desire to obtain the ideal mixing model as a limit in this case.

Relaxation of the Dispersion Flux

To study the properties of the wave model let us assume that the local concentration in a vessel does not depend on the longitudinal coordinate x , but does depend on the transverse coordinate. If we are interested in the phenomena in the central part of a sufficiently long reactor where the effect of the boundaries is insignificant, it is possible to consider the problem for an infinite region with initial conditions only. For this case the initial conditions are

$$t = 0 \quad c = c_{in}, \quad j = j_{in},$$

and these initial values of the concentration and the dispersion flux are independent of the longitudinal coordinate x . The solution of Eqs. 1 and 2 for the case of no reaction is

$$c = c_{in}, \quad j = j_{in} e^{-t/\tau}.$$

This simple example shows that in contrast to SDM the dispersion flux is a variable independent of the concentration and that the relaxation time τ characterizes how quickly the system approaches the steady state.

Apparatus with Dispersion and Reaction in the Steady State

A good understanding of many of the issues involved can be developed from the study of linear problems. Accordingly, we start with a first-order irreversible chemical reaction and unidirectional flow. For that case, solutions for different initial and boundary conditions can be obtained analytically. The equation for the average concentration in the stationary state can conveniently be written in dimensionless form as

$$\alpha(1 + u_a^* - D_e^*) \frac{d^2 C}{dX^2} + (1 + 2\alpha + \alpha u_a^*) \frac{dC}{dX} + (1 + \alpha)C = 0 \quad (6)$$

with the boundary conditions:

$$X = 0, \quad C = \beta, \quad \frac{dC}{dX} = - \frac{(1 + u_a^*)\beta - (1 - \beta)(1 + \alpha^{-1})}{1 + u_a^* - D_e^*} = -\Lambda \quad (7)$$

where $X = x/(ut_{ch}) = kx/u$, $\alpha = k\tau$, $\beta = c_0/c_{b0}$, and c_{b0} is the bulk average concentration in the inlet stream; the characteristic time in this case is $t_{ch} = 1/k$. The dimensionless dispersion flux at the reactor inlet is equal to $J = j_0/(uc_{b0}) = 1 - \beta$, so the value of β characterizes the nonuniformity of the transverse concentration distribution at the reactor inlet. For a uniform concentration distribution at the inlet $\beta = 1$.

The bulk average concentration $c_b = (cu + j)/u$, in dimensionless form $C_b = c_b/c_{b0}$, also obeys Eq. 6, but with different boundary conditions:

$$X = 0, \quad C_b = 1; \quad \frac{dC_b}{dX} = -\beta. \quad (8)$$

The SDM in the chosen variables has the form:

$$-\alpha D_e^* \frac{d^2 C_s}{dX^2} + \frac{dC_s}{dX} + C_s = 0 \quad (9)$$

$$X = 0, \quad C_s - \alpha D_e^* \frac{dC_s}{dX} = 1, \quad X = X_L, \quad \frac{dC_s}{dX} = 0. \quad (10)$$

The essential difference between the wave model and SDM is obvious. In the case of unidirectional flow the coefficients of the first and second derivatives in Eq. 6 are of the same sign, and both boundary conditions for this equation are set up at the inlet of the reactor, whereas in Eq. 9 the signs of these coefficients are opposed to each other. Moreover, the wave model does not contain the length of the reactor, the SDM does so in X_L . This fundamental difference is important from the physical point of view, and from the mathematical point of view it becomes very important for nonlinear problems as well as for multivariable linear problems, where a numerical solution is necessary.

It is interesting to compare the solutions of the wave model and the SDM for the problem considered. The solution of Eq. 6 with boundary conditions, Eq. 7, is

$$C = \frac{\Lambda + \beta\gamma_2}{\gamma_2 - \gamma_1} e^{\gamma_1 X} - \frac{\Lambda + \beta\gamma_1}{\gamma_2 - \gamma_1} e^{\gamma_2 X} \quad (11)$$

where γ_1 and γ_2 are the roots of the equation

$$\alpha(1 + u_a^* - D_e^*)\gamma^2 + (1 + 2\alpha + \alpha u_a^*)\gamma + 1 + \alpha = 0.$$

The distribution of the bulk average concentration along the reactor has the same form:

$$C_b = \frac{\beta + \gamma_2}{\gamma_2 - \gamma_1} e^{\gamma_1 X} - \frac{\beta + \gamma_1}{\gamma_2 - \gamma_1} e^{\gamma_2 X}. \quad (12)$$

The solution of Eq. 9 with the boundary conditions, Eq. 10, is

$$C_s = \frac{\delta_1 e^{\delta_2(X-X_L)} - \delta_2 e^{\delta_1(X-X_L)}}{\delta_1(1 - \alpha D_e^* \delta_2) e^{-\delta_2 X_L} - \delta_2(1 - \alpha D_e^* \delta_1) e^{-\delta_1 X_L}} \quad (13)$$

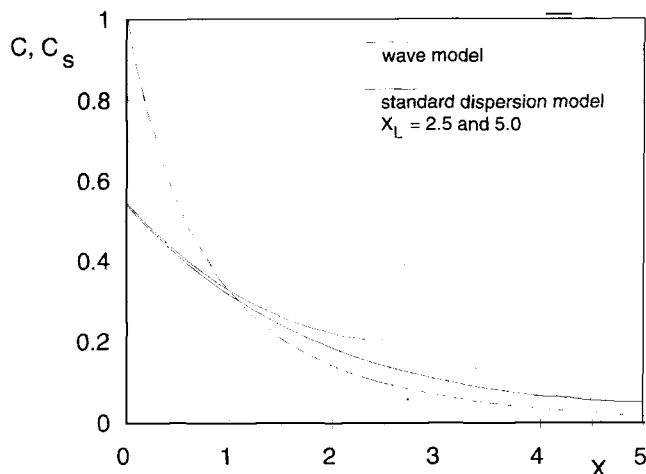


Figure 1. Concentration profiles for a first-order reaction calculated with the wave model and the standard dispersion model.

Model parameters: $D_e^* = 5/16$, $u_a^* = 1/4$, $\alpha = 5$.

where

$$\delta_{1,2} = \frac{1 \pm (1 + 4\alpha D_e^*)^{1/2}}{2\alpha D_e^*}.$$

The bulk average concentration for the SDM is expressed through the area average concentration by the equation

$$C_{sb} = C_s - \alpha D_e^* \frac{dC_s}{dX}. \quad (14)$$

The qualitative difference of the concentration distributions given by the wave model and the SDM for reactors of two different lengths is shown in Figure 1. The values of the parameters chosen for the calculations of $D_e^* = 5/16$ and $u_a^* = 1/4$ correspond to the well-developed laminar flow in a straight round tube.

The solutions of the wave model and the SDM are considered below for limiting values of the dimensionless chemical reaction rate α . For practical purposes the values of interest of X do not exceed 6 to 8, and therefore all asymptotic solutions below are given for the case when X is bounded. For a low reaction rate ($\alpha \rightarrow 0$) and fixed finite values of the model parameters it is easy to show that for a uniform concentration at the reactor inlet ($\beta = 1$) both models give the same results as the plug-flow model:

$$C = C_b = C_s = C_{bs} = e^{-X}.$$

For a nonuniform inlet concentration distribution, the solutions of the two models also coincide except for a narrow region close to the inlet.

For fast reaction rates ($\alpha \rightarrow \infty$) the solutions are determined by Eqs. 11 to 14 with $\gamma_1 = -1/u_2^*$, $\gamma_2 = -1/u_1^*$, $\Lambda = [(u_1^* + u_2^*)\beta - 1]/(u_1^* u_2^*)$, and $\delta_{1,2} = \pm(\alpha D_e^*)^{-1/2}$. In this limiting case the SDM gives the following results, showing an incredible concentration dependence on the reactor length X_L :

$$C_s = \frac{1}{1 + X_L}, \quad C_{bs} = 1 - \frac{X}{1 + X_L}.$$

Note that for a reactor of semiinfinite length where $X_L \rightarrow \infty$ we have $c_s \rightarrow 0$ and $c_{bs} \rightarrow 1$. The corresponding solutions of the wave model for an inlet concentration distribution that is uniform over the cross section ($\beta = 1$) are

$$C = \frac{u_1^* - 1}{u_1^* - u_2^*} e^{-X/u_2^*} + \frac{1 - u_2^*}{u_1^* - u_2^*} e^{-X/u_1^*} \quad (15)$$

$$C_b = \frac{u_2^*(u_1^* - 1)}{u_1^* - u_2^*} e^{-X/u_2^*} + \frac{u_1^*(1 - u_2^*)}{u_1^* - u_2^*} e^{-X/u_1^*}. \quad (16)$$

Equations 15 and 16 show that for high reaction rates the wave-model limit corresponds to a combination of two plug-flow models with velocities equal to the wave velocities. These solutions differ noticeably from the ones for the SDM.

Analytical Solutions of the Wave Model for a Pulse Injection

For linear problems, analytical solutions of Eqs. 1 and 2, can be obtained for various initial and boundary conditions by standard methods, using, for instance, integral forms of solution (see Tikhonov and Samarskii, 1963) or Laplace transforms (see Aris and Amundson, 1973). Two of the typical pulse-response problems are presented below. For the sake of simplicity the component consumption rate q is assumed to be equal to zero, although for a first-order chemical reaction this does not influence the complexity of the solution. This can be seen after substituting $v \exp(-kt)$ for c in Eq. 3 and in the initial and boundary conditions, which reduces Eq. 3 to an equation for v without the reaction term.

Initial spatial distribution

First consider the solution for an amount M of material, released at time $t = 0$ and in the narrow x -axis region in the neighborhood of the point $x = 0$ uniformly over the cross section to the flow. The initial conditions for Eqs. 1 and 2 are

$$t = 0, \quad c = \frac{M}{A} \delta(x), \quad j = 0$$

where $\delta(x)$ is a Dirac delta function. The corresponding initial conditions for Eq. 3 are

$$t = 0, \quad c = \frac{M}{A} \delta(x), \quad \frac{\partial c}{\partial t} = -\frac{Mu}{A} \delta'(x)$$

where the prime denotes the derivative. The solution of Eq. 3 for an infinitely long domain is not equal to zero for $u_2 t \leq x \leq u_1 t$, and can be written as

$$c = \frac{M}{A u \tau} e^{-\beta_1 \eta_2 - \beta_2 \eta_1} \left\{ \frac{u_1 - u}{u_1 - u_2} \delta(\eta_2) + \frac{u - u_2}{u_1 - u_2} \delta(\eta_1) + p I_0(Y) + p(\beta_1 \eta_1 + \beta_2 \eta_2) \frac{I_1(Y)}{Y} \right\} \quad (17)$$

where I_0 and I_1 are modified Bessel functions of zero and first order, and

$$\eta_1 = \frac{u_1 t - x}{u\tau}, \quad \eta_2 = \frac{x - u_2 t}{u\tau}, \quad \beta_1 = \frac{(u_1 - u)u}{(u_1 - u_2)^2},$$

$$\beta_2 = \frac{(u - u_2)u}{(u_1 - u_2)^2}, \quad Y = 2(\beta_1 \beta_2 \eta_1 \eta_2)^{1/2},$$

$$p = \frac{2(u_1 - u)(u - u_2)u}{(u_1 - u_2)^3} = 2\beta_1 \beta_2 \frac{u_1 - u_2}{u}. \quad (18)$$

The obtained solution has two abrupt fronts at $x = u_1 t$ and $x = u_2 t$, where the concentration suddenly falls to zero. Using the asymptotic form for the modified Bessel functions for a sufficiently large time:

$$\frac{t}{\tau} \gg \frac{(u_1 - u_2)^2}{(u_1 - u)(u - u_2)} = 4 + \frac{u_1^2 \tau}{D_e}$$

and provided $|x - ut| \ll \min[(u_1 - u)t, (u - u_2)t]$, Eq. 17 develops into a Gaussian distribution of the concentration as a function of x with the mean ut and a variance $2D_e t$:

$$c = \frac{M}{A} \frac{1}{2\sqrt{\pi D_e t}} e^{-(x-ut)^2/4D_e t} \quad (19)$$

as is also given by the SDM for the initial condition $c = (M/A)\delta(x)$ at $t = 0$ and for the infinite region, where the effect of the boundaries is not significant. Thus the solution of the wave model coincides with the normal distribution only in the central part of the tracer cloud and only after a sufficiently long time.

Input concentration specified as a function of time

The next problem we wish to solve is the one where the concentration is specified as a function of time at some fixed point $x = 0$. Suppose that at the initial moment $t = 0$ the concentration is zero everywhere along the x -axis and that solute of an amount M is introduced at point $x = 0$ during a sufficiently short period of time and uniformly over the cross section to the flow. The initial and boundary conditions in this case for Eqs. 1 and 2 are

$$t = 0, \quad c = 0, \quad j = 0; \quad x = 0, \quad c = \frac{M}{Au} \delta(t), \quad j = 0.$$

The corresponding initial and boundary conditions for Eq. 3 are

$$t = 0, \quad c = 0, \quad \frac{\partial c}{\partial t} = 0; \quad x = 0, \quad c = \frac{M}{Au} \delta(t),$$

$$\frac{\partial c}{\partial x} = -\frac{M}{Au} \frac{u_1 + u_2 - u}{u_1 u_2} \delta'(t).$$

The solution of Eq. 3 for the problem is

$$c = \frac{M}{Au\tau} e^{-\beta_1 \eta_2 - \beta_2 \eta_1} \left\{ \frac{(u_1 - u)u_2}{(u_1 - u_2)u} \delta(\eta_2) + \frac{(u - u_2)u_1}{(u_1 - u_2)u} \delta(\eta_1) \right.$$

$$\left. + p \frac{u_1 + u_2}{2u} I_0(Y) + p \left(\beta_1 \eta_1 \frac{u_2}{u} + \beta_2 \eta_2 \frac{u_1}{u} \right) \frac{I_1(Y)}{Y} \right\}. \quad (20)$$

Equation 20, like Eq. 17, has the Gaussian asymptotic of Eq. 19 at the central part of the concentration distribution at the same conditions as for Eq. 17.

Equations 17 and 20 give similar concentration distributions. The characteristic features of these distributions are two concentration spikes in the front of the cloud of material, which are remnants of the initial and boundary conditions, respectively. Spikes in the form of δ -functions are unrealistic, but one should realize that they are the direct consequence of the two-velocity character of the simplest version of the wave model being considered. The positions of the spike and the quantities of substance in them correspond qualitatively to the double-peaked structure of known experimental results and numerical solutions for a short time (see Smith, 1981; Wang and Stewart, 1983, 1989; Korenaga et al., 1989; Takahashi et al., 1990). These concentration spikes were observed only at an early stage compared to the relaxation time of the dispersion. At a later stage in the dispersion process the amount of substance in the spikes becomes relatively small.

The obtained solutions give the residence time distributions of tracer for two different inputs that coincide after a sufficiently long time, but differ for short periods. The considered tracer inputs differ in the distribution of the amount of the substance introduced over the cross section or over the longitudinal velocity. In the first case, the distribution of a tracer over the cross section of the flow is uniform. In the second case, the tracer is injected in such a way that the amount introduced at some position is proportional to the velocity in this point, so the residence time distribution of tracer, Eq. 20, corresponds to the residence time distribution of the fluid elements. It is easy to prove that Eq. 20 predicts the conversion in a reactor with a first-order chemical reaction in a steady-state operation: the solution of Eq. 6 for a uniform input—Eq. 11 at $\beta = 1$ —in dimensional form is equal to

$$c(x) = c_0 \int_0^\infty e^{-kt} E(x, t) dt$$

where $E(x, t)$ is the function determined by Eq. 20 at the coordinate $x = L$, that is, it is related to the residence time distribution of the fluid elements via a Laplace transform. The preceding result shows that the relation between the residence time distribution and conversion, which is well known for the SDM (see Westerterp et al., 1987), is also valid for the wave model, although with additional restrictions on material inputs.

Consideration of pulse-propagation problems on the basis of the wave model avoids the conceptual difficulties associated with material flow through "open" boundaries as we observe for the SDM (see Nauman, 1981 and Westerterp et al.,

1987). The treatment of problems with initial and boundary conditions on the basis of the wave model differs only slightly from the treatment of limiting problems without boundary conditions, whereas consideration of the boundary conditions for a Fickian dispersion model makes the solution of the equations very difficult (see Novy et al., 1990).

Spatial and Temporal Moments

After the pioneering work of Aris (1956) the description of the distribution of a solute in terms of the moments of the concentration distribution has been widely used for the mathematical description of dispersion processes, since the moments of a cloud of solute are easier to calculate than the concentration distribution itself. Also knowledge of the first two or three moments of the concentration distribution gives much information about the concentration distribution itself (see Brenner, 1980, 1982; Brenner and Edwards, 1993). Models often are also compared by means of calculating the spatial—at a fixed moment of time—and the temporal—at a fixed coordinate location—moments of the concentration of an injected solute.

The spatial and temporal moments can easily be calculated by means of the proposed wave model by standard methods when the distribution of the concentration c at time $t = 0$ or at longitudinal position $x = 0$ is known. As an example, spatial moments of concentration around the mean are introduced:

$$\mu_n = \frac{\int_{-\infty}^{\infty} (x - \bar{x})^n c dx}{m}; \quad n = 2, 3, \dots \quad (21)$$

where

$$\bar{x} = \frac{\int_{-\infty}^{\infty} xc dx}{m}; \quad m = \frac{M}{A} = \int_{-\infty}^{\infty} c dx. \quad (22)$$

The expressions for the first three moments are given below for the case of an arbitrary concentration distribution at $t = 0$ and a finite mass of solute:

$$\bar{x} = ut + \lambda_0 \tau (1 - e^{-\xi}) \quad (23)$$

$$\mu_2 = \mu_{2,\text{in}} + 2\tau(\lambda_1 + \tau u_a \lambda_0 - D_e)(1 - e^{-\xi}) + 2\tau\xi(D_e - \tau u_a \lambda_0 e^{-\xi}) \quad (24)$$

$$\begin{aligned} \mu_3 = & \mu_{3,\text{in}} + 3\tau(\lambda_2 - \mu_{2,\text{in}}\lambda_0)(1 - e^{-\xi}) + 2\lambda_0^3\tau^3(1 - e^{-\xi})^3 \\ & - \lambda_0\lambda_1\tau^2(1 - e^{-\xi})^2 + 6u_a\lambda_0^2\tau^3(1 - e^{-\xi})(\xi e^{-\xi} - 1 + e^{-\xi}) \\ & + 6D_e\lambda_0\tau^2(2\xi e^{-\xi} - 1 + e^{-2\xi}) \\ & + 6u_a\tau^2[(\lambda_1 + u_a\tau\lambda_0)(1 - \xi e^{-\xi} - e^{-\xi}) \\ & + D_e(\xi + \xi e^{-\xi} + 2e^{-\xi} - 2) - u_a\tau\lambda_0(\xi^2/2)e^{-\xi}] \quad (25) \end{aligned}$$

where $\xi = t/\tau$ and $\mu_{n,\text{in}}$ and λ_n are the initial values of the concentration and dispersion flux moments in a coordinate system chosen such that $\bar{x} = 0$ at $t = 0$:

$$\mu_{n,\text{in}} = \frac{\int_{-\infty}^{\infty} x^n c_{\text{in}}(x) dx}{m} \quad \lambda_n = \frac{\int_{-\infty}^{\infty} x^n j_{\text{in}}(x) dx}{m}, \quad n = 0, 1, 2, \dots \quad (26)$$

After a small time t just after injection or $\xi \ll 1$, the moments are

$$\bar{x} = (1 + \lambda_0)ut \quad (27)$$

$$\mu_2 = \mu_{2,\text{in}} + 2\lambda_1 t + (u_a \tau \lambda_0 - \lambda_1 + D_e)t^2/\tau \quad (28)$$

$$\begin{aligned} \mu_3 = & \mu_{3,\text{in}} + (\lambda_2 - \mu_{2,\text{in}}\lambda_0)t/\tau + 3\lambda_1(u_a - 2\lambda_0)t^2 \\ & + (2\lambda_0 - 3u_a\lambda_0^2 - 2D_e\lambda_0/\tau + u_a D_e/\tau - 2\lambda_1 u_a/\tau + \lambda_0 u_a^2)t^3 \quad (29) \end{aligned}$$

and asymptotic values of moments after a very large time or $\xi \gg 1$ are

$$\bar{x} = ut; \quad \mu_2 = 2D_e t; \quad \mu_3 = 6D_e u_a \tau t. \quad (30)$$

The mean and variance in Eq. 30 do not depend on the relaxation time, the parameter of velocity asymmetry, and the initial value of the dispersion flux; they are the same as predicted by the SDM. When the injected solute is initially uniform over the cross section to the flow, then $j_{\text{in}}(x) = 0$, $\lambda_n = 0$ for $n = 0, 1, 2, \dots$ and the expressions for the moments are essentially simplified:

$$\bar{x} = ut; \quad \mu_2 = \mu_{2,\text{in}} + 2\tau D_e (\xi - 1 + e^{-\xi}) \quad (31)$$

$$\mu_3 = \mu_{3,\text{in}} + 6D_e u_a \tau^2 (\xi + \xi e^{-\xi} + 2e^{-\xi} - 2).$$

The equations for the moments with respect to the coordinate x were first formulated by Aris (1956), who also found the asymptotic behavior of the second moment around the mean. After Aris this problem was investigated by Chatwin (1970). The most general results were obtained by Barton (1983), who derived the second and third moments for arbitrary values of time. The calculations of Barton for the third moment are restricted to the case where solute is injected initially uniformly over the cross section. Equation 25 gives the approximate value of the third moment for an arbitrary initial concentration. Using the expressions for D_e , τ , and u_a obtained in the previous paper (see Westerterp et al., 1995), it can be easily shown that Eqs. 30 coincide with the asymptotic expressions of the first three moments obtained by Barton (1983). At small and moderate values of time, Eqs. 23, 24, and 25 have the same qualitative structure as the exact equations. Note that application of the SDM for calculating spatial moments gives $\mu_2 = 2D_e t$ and $\mu_3 = 0$ for all moments of time.

It is interesting to note that Taylor (1921), in a classic paper on turbulent diffusion, written long before his 1953 papers on axial dispersion, found the law of dispersion of the form of Eq. 31 for μ_2 .

The temporal or time moments of concentration at some point x also can be calculated easily from the wave model for different initial and boundary conditions. As an example the

mean residence time and the variance at point x for a tracer input uniform over cross section are

$$\bar{t} = \frac{x}{u} + \frac{D_e(1 - e^{-\lambda\zeta})}{u^2} \quad (32)$$

$$\begin{aligned} \sigma_t^2 = \sigma_{t,0}^2 + 2\left(\frac{x}{u}\right)^2 \frac{D_e}{xu} \left[\lambda(1 + D_e^*) \right. \\ \left. + \left(\lambda(u_a^* - 2D_e^*) + \frac{3D_e^* - 1 - 2u_a^*}{\zeta} \right) (1 - e^{-\lambda\zeta}) \right. \\ \left. - \frac{D_e^*}{2\zeta} (1 - e^{-2\lambda\zeta}) \right] \quad (33) \end{aligned}$$

where $\sigma_{t,0}^2$ is the value of the variance at point $x = 0$; further, $\zeta = x/(u\tau)$ and $\lambda = (1 + u_a^* - D_e^*)^{-1}$. The mean residence time and variance in Eqs. 32 and 33 are determined by standard equations:

$$\bar{t} = \frac{\int_0^\infty tc \, dt}{m}; \quad \sigma_t^2 = \frac{\int_0^\infty (t - \bar{t})^2 c \, dt}{m}; \quad m = \frac{M}{A} = \int_0^\infty c \, dt, \quad (34)$$

and the origin on the x -axis is chosen such that $\bar{t} = 0$ at $x = 0$. At a sufficiently long distance from the point $x = 0$ or $\zeta \gg 1$ the mean residence time and variance approach those for the SDM:

$$\begin{aligned} \bar{t} = \frac{x}{u} + \frac{D_e}{u^2} \\ \sigma_t^2 = \sigma_{t,0}^2 + 2\left(\frac{x}{u}\right)^2 \frac{D_e}{xu} \left[1 + \frac{5}{2} \frac{D_e}{ux} - \frac{u\tau}{x} \left(1 + \frac{u_a}{u} \right) \right]. \end{aligned}$$

In the opposite limiting case of $\zeta \ll 1$, we have

$$\begin{aligned} \bar{t} = \frac{x}{u} \left(1 + \frac{D_e}{u(u + u_a)\tau - D_e} \right) \\ \sigma_t^2 = \sigma_{t,0}^2 + \left(\frac{x}{u}\right)^2 \left(1 + \frac{D_e u^2 \tau}{(u(u + u_a)\tau - D_e)^2} \right). \end{aligned}$$

The values obtained here differ essentially from those of the standard dispersion model.

Axial Mixing in a Rotating Disk Contactor

More than thirty years ago Westerterp and Landsman (1962) and Westerterp and Meyberg (1962) investigated the axial mixing in a rotating disk contactor for homogeneous liquid-phase operation. The rotating disk contactor (see Figure 2) is a column that is divided by equally spaced stator rings into a number of compartments. Half-way in the stator rings a number of disk rotors are mounted on a shaft, the diameter of the rotors being smaller than the inner diameter of the stator rings. Experimental results have been interpreted by

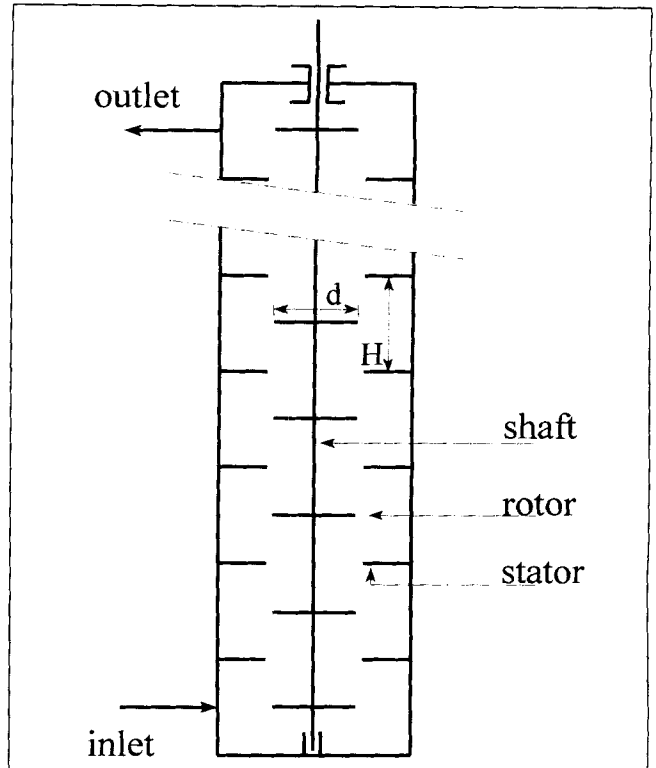


Figure 2. Rotating disk contactor.

means of a diffusion model. The axial dispersion coefficient was found from the response at the outlet of the column to a stepwise change in the inlet concentration of a tracer; this axial dispersion coefficient was called the apparent axial diffusivity D_a (see Westerterp and Landsman, 1962). The apparent axial diffusivity could be considered to be the sum of a flow contribution and a rotational contribution:

$$D_a = \frac{1}{2} Hu + 13 \cdot 10^{-3} \frac{1}{2} Hnd, \quad \text{m}^2/\text{s} \quad (35)$$

where H is the height of a compartment in m, u is the average liquid velocity in m/s, n is the rotational speed in s^{-1} , and d the diameter of rotor in m. Also the true backmixing was measured under steady-state conditions, and the corresponding axial dispersion coefficient was called the backmixing coefficient, D_b (see Westerterp and Meyberg, 1962). The backmixing coefficient appeared to be equal to that part of the apparent axial diffusivity in Eq. 35 that is caused by the stirring, being $D_b = \text{const} \times Hnd$. The results of these two investigations cannot be reconciled by the SDM, since the axial dispersion coefficient depends on the experimental method. The same problem is known for dispersion in estuaries, where the apparent dispersion coefficient is a few times higher than the backmixing coefficient (see Fischer et al., 1979). Therefore we will interpret these experiments again by means of the wave model.

First let us consider the steady-state backmixing experiments. We are interested in the mixing in the central part of the column, where over a compartment averaged velocity re-

mains constant along the column; therefore we can apply Eq. 3 for the steady state and with $q = 0$:

$$(\tau u^2 + \tau u u_a - D_e) \frac{d^2 c}{dx^2} + u \frac{dc}{dx} = 0. \quad (36)$$

If the tracer is injected at the plane $x = 0$ in the upper part of the column into the upward flowing fluid stream under steady-state conditions, some tracer will be found in the fluid upstream of the injection point at the locations with $x < 0$. This transport against the main flow of the fluid is caused by the fluid backflow caused by the stirring. The existence of a backflow in terms of the wave model means that the velocity of one of the waves, as well as the value of $\tau u^2 + \tau u u_a - D_e$, is negative in contrast to the case of unidirectional flow. This means that the boundary conditions for the central part of the column should be specified at both ends. For a sufficiently long column, as was used by Westerterp and Meyberg (1962), the boundary conditions are:

$$x = 0, \quad c = c_0; \quad x \rightarrow -\infty, \quad c \rightarrow 0.$$

The solution of Eq. 36 using these boundary conditions is

$$\frac{c}{c_0} = \exp\left(\frac{ux}{D_e - \tau u^2 - \tau u u_a}\right), \quad (37)$$

whereas the solution of the SDM, used by Westerterp and Meyberg is

$$\frac{c}{c_0} = \exp\left(\frac{ux}{D_b}\right). \quad (38)$$

Equations 37 and 38 show that the backmixing coefficient D_b measured by Westerterp and Meyberg is equal to $D_e - \tau u^2 - \tau u u_a$.

Let us now suppose that the relaxation time τ is much smaller than the mean residence time in the column. In that case the apparent axial diffusivity D_a , measured by Westerterp and Landsman (1962), is the axial dispersion coefficient of the wave model, D_e . Thus for the difference of the apparent diffusivity D_e and the backmixing coefficient D_b we can write

$$D_e - D_b = D_a - D_b = \tau u(u + u_a) = \frac{1}{2} Hu. \quad (39)$$

In the case of no net flow through the column, the rotating elements create an approximately symmetrical velocity distribution with respect to the cross section of the column. We can also expect that for low average velocities u used in experiments—relative to the velocities created by rotating disks—the violation of the symmetry of the tracer propagation in both the upflow and downflow directions is insignificant. In that case, $u_a \ll u$ and Eq. 39 gives the physically reasonable estimate of the relaxation time $\tau \approx (1/2)H/u$. The number of compartments in the column was $N = 24$. Therefore the relaxation time obtained is much lower than the mean residence time $t = NH/u$ —as was supposed earlier—and the ap-

parent diffusivity measured by Westerterp and Landsman (1962) is actually the axial dispersion coefficient of the wave model.

Flow reversal

An interesting effect was observed when the flow direction was reversed during a dispersion experiment. Such an investigation in a two-dimensional model of a packing of spheres was made by Hiby (1963); measurements in naturally occurring porous media have also been reported by Jasti and Fogler (1992). The spread in the spatial distribution narrows initially during a certain period of time after the flow direction has been reversed (see Figure 1 of Jasti and Fogler, 1992). The standard deviation of the tracer signal decreases upon flow reversal, whereas the local concentration of the tracer increases. The tracer again undergoes the typical dilution process after this initial period has passed. This example can be used to demonstrate the essential differences between the SDM and the wave model; it also helps to explain the essential properties of the wave model.

The equation describing the tracer distribution before the reversal of the flow direction is

$$\begin{aligned} \frac{\partial^2 c_1}{\partial t^2} + (2u + u_a) \frac{\partial^2 c_1}{\partial x \partial t} + (u^2 + u u_a - D_e/\tau) \frac{\partial^2 c_1}{\partial x^2} \\ + \frac{1}{\tau} \left(\frac{\partial c_1}{\partial t} + u \frac{\partial c_1}{\partial x} \right) = 0, \quad 0 \leq t \leq t_R. \quad (40) \end{aligned}$$

For simplicity we assume that initially the tracer was uniformly distributed over the cross section of the flow and is concentrated in a narrow region of the x -axis. In this case, $j = 0$ at $t = 0$, and the initial conditions for Eq. 40 are

$$t = 0, \quad c = c_0 \delta(x), \quad \frac{\partial c}{\partial t} = -c_0 \delta'(x). \quad (41)$$

At the moment, t_R , the flow direction is reversed, the signs of u and u_a change, and the governing equation transforms into:

$$\begin{aligned} \frac{\partial^2 c_2}{\partial t^2} - (2u + u_a) \frac{\partial^2 c_2}{\partial x \partial t} + (u^2 + u u_a - D_e/\tau) \frac{\partial^2 c_2}{\partial x^2} \\ + \frac{1}{\tau} \left(\frac{\partial c_2}{\partial t} - u \frac{\partial c_2}{\partial x} \right) = 0, \quad t \geq t_R. \quad (42) \end{aligned}$$

To specify the initial conditions for Eq. 42, we can use the assumption—justified in particular for liquids—that the concentration field does not change appreciably during the reversing of the flow. This means that at $t = t_R$ the average concentration is a continuous function of time, that is, $c_2 = c_1$, whereas the dispersion flux changes in sign, $j_2 = -j_1$. The mass conservation equations for $t \leq t_R$ and for $t \geq t_R$ are

$$\frac{\partial c_1}{\partial t} + u \frac{\partial c_1}{\partial x} + \frac{\partial j_1}{\partial x} = 0, \quad 0 \leq t \leq t_R$$

$$\frac{\partial c_2}{\partial t} - u \frac{\partial c_2}{\partial x} + \frac{\partial j_2}{\partial x} = 0, \quad t \geq t_R.$$

From these equations and the conditions just mentioned at $t = t_R$, we find the initial conditions for Eq. 42:

$$t = t_R, \quad c_2 = c_1, \quad \frac{\partial c_2}{\partial t} = -\frac{\partial c_1}{\partial t}. \quad (43)$$

The determination of the spatial moments of the concentration distribution from Eqs. 40 and 42 with the initial conditions Eqs. 41 and 43 is straightforward. Before the flow reversal, the moments of the spatial distribution are determined by Eq. 31. After the reversal, the mean and variance are

$$\bar{x} = u(2t_R - t) \quad (44)$$

$$\sigma_x^2 = 2D_e\tau \left[\frac{t}{\tau} - 3 + 2e^{-t/\tau} + (2e^{t/\tau} - 1)e^{-t/\tau} \right]. \quad (45)$$

Dependence on the time of the variance of the spatial distribution of the tracer is shown in Figure 3 for different reversing times t_R . The calculated results coincide qualitatively with those obtained experimentally by Jasti and Fogler (1992). A quantitative agreement between theory and the experiments of Jasti and Fogler can be obtained by the choice of parameters D_e and τ . Note that according to the SDM $\sigma_x^2 = 2D_e t$, so the flow reversal does not influence the dependence of the variance on time.

The phenomenon considered is referred to as “unmixing” (see Jasti and Fogler, 1992). The physical reason for this phenomenon is known and easy to understand (see Hiby, 1963). After reversal, the concentration profile has to change, but a time of approximately τ is required before the concentration profile can completely adapt itself to the new velocity profile; immediately after reversing, the tracer molecules seem to retrace their flow paths and, as a consequence, the tracer pulse undergoes a concentrating process. The wave model is capable of describing this phenomenon, whereas the SDM is not.

From Eq. 45 we find that the spatial distribution narrows after reversing the flow during a period of time Δt :

$$\Delta t = \ln(2e^{t_R/\tau} - 1) - t_R \quad (46)$$

and that the maximum decrease of the variance is

$$\begin{aligned} \Delta\sigma_{x,\max}^2 &= \sigma_x^2(t_R) - \sigma_x^2(t_R + \Delta t) \\ &= 2D_e\tau \left[\frac{t_R}{\tau} + 1 - e^{-t_R/\tau} - \ln(2e^{t_R/\tau} - 1) \right]. \end{aligned} \quad (47)$$

If flow reversal occurs at moments of time much smaller than the relaxation time or $t_R \ll \tau$, we find

$$\Delta t = t_R, \quad \Delta\sigma_{\max}^2 = D_e \frac{t_R^2}{\tau}. \quad (48)$$

In the opposite case of $t_R \gg \tau$, then

$$\Delta t = \tau \ln 2, \quad \Delta\sigma_{x,\max}^2 = 2(1 - \ln 2)D_e\tau. \quad (49)$$

The results for $t_R \ll \tau$ show that a purely convective, completely reversible contraction of the concentration cloud occurs after flow reversal during a period of time of the order of t_R (see Hiby, 1962).

Discussion

The use of hyperbolic-type equations for the description of different heat and mass dispersion phenomena was suggested a long time ago (see Stewart, 1965; Thacker, 1976; Maron, 1978; Smith, 1981). Such models did not receive much attention, however, probably because we are not accustomed to hyperbolic-type equations for dispersion processes. But physical considerations require that there should be finite velocity limits that are not exceeded by any fluid element, provided molecular diffusion is neglected. For this reason, from the physical point of view relaxation-type equations for dispersion fluxes should be preferred over Fickian-type dispersion

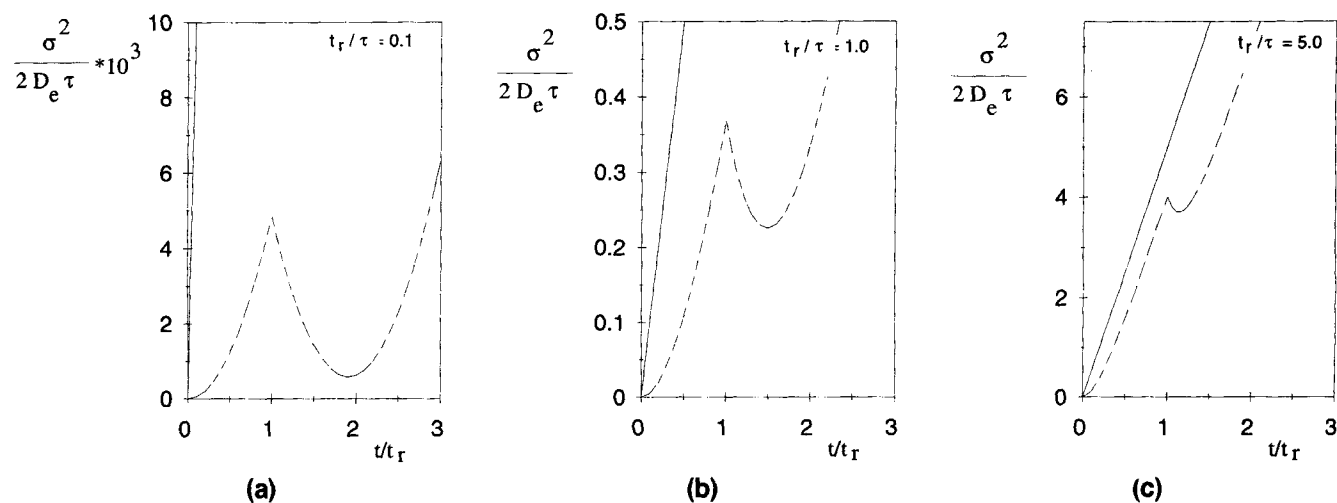


Figure 3. Effect of flow reversal on the variance of the tracer spatial distribution as calculated with the wave model (---) and the standard dispersion model (—).

(a) $t_r/\tau = 0.1$; (b) $t_r/\tau = 1.0$; (c) $t_r/\tau = 5.0$.

equations. Moreover, almost all fields of science or engineering involve some questions of wave motion. Wave equations are used in acoustics, elasticity, and electromagnetism, and their basic properties and solutions were first studied in these areas of classical physics (see Whitham, 1974). Therefore applying the wave model to longitudinal dispersion does not create unresolved mathematical problems or unknown physics.

The main practical advantages of the wave model

Being physically more realistic than the SDM, the wave model is open to solutions for arbitrary linear problems. In contrast to the SDM, the mathematical complexity of the wave model does not depend essentially on the boundary and initial conditions for Eqs. 1 and 2. An important aspect of Eqs. 1 and 2 is that the boundary conditions—in contrast to those of the Fickian-type dispersion model—for unidirectional flow are set at the inlet only. This also gives rise to a considerable mathematical simplification of nonlinear problems as well as multicomponent and multivariable linear problems, where a numerical solution is necessary. Consequently, since it offers a more consistent physical picture than the Fickian dispersion model, the present model has a considerable advantage in computational efforts. The mathematical solutions of the wave model are simpler or as simple as for the SDM.

Physical contradictions in the SDM give rise to the problem of boundary conditions. As a consequence, a multiplicity of different boundary conditions, such as different combinations of “open” and “closed” boundary conditions for reactor inlets and exits or for semiinfinite or infinite regions, and corresponding solutions occupy much of the literature over the past forty years (see Nauman, 1981 and Kreft and Zuber, 1978). For some relatively simple problems the analytical solutions have not even been available until now (see Kreft and Zuber, 1978). Application of the wave model permits us to avoid the uncertainties in the boundary conditions and thereby essentially to reduce the number of possible variants of solutions.

The wave model also has a wider region of validity. It is able to describe phenomena that cannot be explained in terms of the SDM. Dispersion during flow reversal and the difference between apparent diffusivity for pulse propagation and backmixing under stationary conditions are examples of these phenomena. In addition, the wave model gives a qualitatively correct concentration distribution for arbitrary time moments for pulse propagations through a system; it also gives exact long-time asymptotic values of the first three spatial moments of concentration for the case of Taylor dispersion and qualitatively correct steady-state concentration distributions for arbitrary chemical reaction rates.

Physical meaning and experimental determination of the model parameters

Model parameters have a clear physical sense. The dispersion coefficient D_e has the same sense as in the SDM: it characterizes the dispersion flux or the increase of the variance when the concentration distribution is close to equilibrium. The relaxation time τ can be considered to be a characteristic time, corresponding to the time of the mean free path of the diffusion process. After Taylor (1953) for Taylor

dispersion phenomena, the relaxation time is also known as the “time of decay” during which transverse variations of concentration are reduced to a fraction of their initial value through the action of transverse dispersion. For laminar flow through a tube of a radius a , the relaxation time is $\tau = a^2/(15 D)$, and the estimate of this time constant as $a^2/(3.8^2 D)$ by Taylor (1953) is very close to the one obtained in this work. The relaxation time characterizes the inertia of the dispersion process or the rate of approaching equilibrium. The asymmetry parameter u_a characterizes the asymmetry of the dispersion process (see Eq. 30); it is determined by the differences in the positive and negative convective velocity profiles in a coordinate system moving with average velocity, and it is equal to the difference in the absolute values of the wave velocities in such a coordinate system. The importance of the model parameters for a quantitative treatment of chemical reactor problems will be considered in a subsequent article.

The wave model permits simple analytical solutions for various linear problems. Some of them are presented in this work. The solutions can be used for determination of the parameters of the model. The model parameters can be obtained by the standard experimental methods, which are used for the determination of longitudinal dispersion coefficients, in particular by the method of moments or the frequency response technique. The parameters of the model can be calculated by comparing the time moments of responses measured at two or more points along an apparatus or two or more spatial moments. Equations 23 to 25, 32, and 33 and their asymptotic forms obtained show that the model parameters can be obtained through knowledge of the long-term and short-term behavior of the first and second axial or time moments of the solute concentration fields. Two experimental studies—the change with time of the variance of a concentration pulse when the flow direction is reversed, and the difference in values of the apparent axial dispersion coefficient and the backmixing coefficient in a system with real backmixing—show how conveniently this new method of the wave model gives new possibilities for determining model parameters (see, e.g., Eqs. 46 to 49).

Additional remarks on the wave model

The preceding analysis shows that for slowly varying concentration fields the wave model can be approximated by the SDM. The use of the wave model instead of the Fickian dispersion model, however, is justified in all circumstances including slow processes, even if the parameters τ and u_a of the wave model are unknown. If somebody has some difficulties with the calculation or experimental determination of these parameters, he may put $u_a = 0$ and τ equal to the characteristic time scale that determines the applicability of the SDM. This recommendation permits the avoidance of physical contradictions, the resolution of the problem of boundary conditions of the SDM, the acquisition of correct results for slow processes where the SDM is applicable, and the acquisition of an approximate description of fast processes where the Fickian model gives absolutely incorrect results.

Conclusion

The preceding results provide support for the theory developed by the authors and demonstrate the importance of ac-

counting for relaxation effects in longitudinal mixing in chemical reactors and contactors. Evidently, the wave model is physically more realistic than the conventional Fickian-type model. It has a much wider region of validity, and in most cases, is also more preferable from the mathematical point of view.

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Notation

- A = cross-sectional area of the flow
 C = dimensionless area-averaged concentration, c/c_{ch}
 J = dimensionless dispersion flux, $j/(uc_{ch})$
 L = reactor length
 $m = M/A$
 $p = 2(u_1 - u)(u - u_2)u/(u_1 - u_2)^3$
 P = dimensionless parameter, t_{ch}/τ
 q' = derivative of the consumption rate over concentration, $\partial q/\partial c$
 Q = dimensionless consumption rate of component per unit of reactor volume, qt_{ch}/c_{ch}
 \bar{t} = mean residence time, Eq. 32
 $u_{1,2}$ = characteristic or wave velocities in Eqs. 1 and 2, $u + (u_a/2)[1 \pm \sqrt{1 + 4D_c/(\tau u_a^2)}]$
 u_a = parameter of velocity asymmetry
 u_a^* = dimensionless parameter of velocity asymmetry, u_a/u
 X = dimensionless longitudinal coordinate, $x/(uc_{ch})$
 $Y = 2(\beta_1 \beta_2 \eta_1 \eta_2)^{1/2}$

Greek letters

- β_i = parameter ($i = 1, 2$), Eq. 18
 η_i = dimensionless variable ($i = 1, 2$), Eq. 18
 θ = dimensionless time, t/t_{ch}
 Λ = dimensionless value of the inlet concentration gradient, Eq. 7
 μ_n = central spatial moment ($n = 2, 3, \dots$), Eq. 21

Subscripts

- 1, 2 = before and after reversal of the flow
 0 = inlet at $x = 0$ in the entering stream

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Wave Model for Longitudinal Dispersion: Application to the Laminar-Flow Tubular Reactor

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The wave model for longitudinal dispersion, published elsewhere as an alternative to the commonly used dispersed plug-flow model, is applied to the classic case of the laminar-flow tubular reactor. The results are compared in a wide range of situations to predictions by the dispersed plug-flow model as well as to exact numerical calculations with the 2-D model of the reactor and to other available methods. In many practical cases, the solutions of the wave model agree closely with the exact data. The wave model has a much wider region of validity than the dispersed plug-flow model, has a distinct physical background, and is easier to use for reactor calculations. This provides additional support to the theory developed elsewhere. The properties and the applicability of the wave model to situations with rapidly changing concentration fields are discussed. Constraints to be satisfied are established to use the new theory with confidence for arbitrary initial and boundary conditions.

Introduction

In a recent article by Westerterp et al. (1995a) a new one-dimensional model for the residence time distribution in flowthrough contactors and chemical reactors has been developed as an alternative to the commonly used dispersed plug-flow model, also called the standard dispersion model (SDM). A qualitative analysis of the proposed wave model has been made in a second article (Westerterp et al., 1995b). The wave model differs fundamentally from the SDM and is not afflicted with the physical contradictions of the SDM. In contrast to the SDM, which works only with an average concentration, the wave model contains a second independent state variable, the dispersion flux, characterizing the deviation from plug-flow conditions. The equation relating the dispersion flux to the area mean concentration has the same form as Maxwell's constitutive law for viscoelastic fluids. From a mathematical point of view the wave model appeared to be simpler than the SDM for many practical purposes. The wave model gives the same results as the SDM for slow processes, although not for all of them. For rapidly varying concentration fields, where the SDM definitely produces wrong results, the wave model gives a qualitatively correct description of the phenomena. The wave model correctly predicts the reversibility of longitudinal dispersion with respect to a change

in the flow direction and distinguishes between apparent and real backmixing. The essential advantage of the wave model—if compared to other known alternatives to the SDM—is that it does not depend on the type of equipment under consideration. These features of the new model and its simplicity are an essential advantage for a wide class of problems, if compared to the Fickian dispersion models. However, the quantitative accuracy of the wave model for rapid processes has not been checked in the papers just mentioned, nor has its ability to represent adequately actual multidimensional phenomena occurring in the case of rapidly varying concentration fields, as in reactors with rapid chemical reactions. Therefore, in the present article we will test quantitatively the applicability of the wave model over a wide range of conditions. This can be done, of course, by comparing experimental reactor data with the model predictions. Eventually, this is probably the best approach, but because of the many experimental problems in obtaining accurate kinetics, in many cases it is difficult to achieve a high precision. In other words, it is often difficult to decide whether discrepancies are because of the model or the data. As an alternative a mathematical comparison between the wave model, the SDM, and more precise multidimensional calculations presents itself.

The laminar-flow tubular reactor is considered in this article in order to test certain concepts regarding the wave model.

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This application has the great virtues of mathematical tractability and practical experimental execution. The predictions of the theory can be compared with numerical solutions of the exact multidimensional equation and with numerous results obtained by other methods. It is the most investigated reactor problem and is often used as a test example for simplifying approaches to reactor modeling. The problem is also of practical interest, particularly for high-viscosity fluids. Moreover, this relatively simple problem is also of interest because it contains many of the essential features of dispersion in various flowing systems and provides a considerable insight into the effect of velocity shear on axial dispersion.

After the initial work by Taylor (1953), Aris (1956), and Cleland and Wilhelm (1956), diffusion with or without a chemical reaction when there is a fully developed laminar flow in a straight tube has been the subject of a large number of theoretical investigations. Numerical steady-state solutions for the case of a homogeneous first-order chemical reaction have been reported, among others, by Cleland and Wilhelm (1956), Vignes and Trambouze (1962), and Bailey and Gogarty (1962). Exact series solutions of the same problem have been presented by Hsu (1965), Dang and Steinberg (1977), and Dang (1978).

Different analytical approaches to the residence time distribution during laminar flow in a tube have been reported by Farrel and Leonard (1963), Philip (1963), Gill (1967), Chatwin (1970), Gill and Sankarasubramanian (1970, 1971, 1972), Whitaker (1971), Tseng and Besant (1970, 1972), Fife and Nicholes (1975), DeGance and Johns (1980), Smith (1981, 1987a,b), Barton (1983), Yamanaka (1983), Shankar and Lenhoff (1989), and Stokes and Barton (1990). Short-time asymptotic solutions to the pulse-input problem have been proposed by Lighthill (1966), Chatwin (1977) and Vrentas and Vrentas (1988). Numerical solutions of the same problem have been utilized by Ananthkrishnan et al. (1965), Gill and Ananthkrishnan (1967), Mayock et al. (1980), Yu (1981), Wang and Stewart (1983, 1989) and Takahashi et al. (1990). Dynamic behavior of a tubular reactor with a first-order reaction has been analyzed by Subramanian et al. (1974) and Nigam and Vasudeva (1976). The laminar-flow tubular reactor with a first-order homogeneous reaction was used as an example to examine the applicability of the SDM to the otherwise two-dimensional situation by a number of investigators (Bischoff, 1968; Wissler, 1969; Mashelkar, 1973; Kulkarni and Vasudeva, 1976; Carbonell and McCoy, 1978).

Experimental results have been presented by Cleland and Wilhelm (1956), Vignes and Trambouze (1962), Nigam and Vasudeva (1976), and Korenaga et al. (1989).

Publications with respect to the investigation of the nonlinear systems are quite scarce. Houghton (1962) and Wan and Ziegler (1970) investigated the conditions under which Taylor diffusion can be applied with steady systems in the presence of a reaction with a power-law rate equation. An analysis of the propagation of an injected pulse through a system in which a second-order chemical reaction takes place, has been made by Barton (1986) and Smith (1989). A diffusional type of equation for the area averaged concentration with an effective flow velocity, which depends on the concentration, for systems involving weak nonlinear reactions was recently derived by Yamanaka and Inui (1994) on the basis of the projection operator technique.

In this article the accuracy of the wave model is examined over the whole range of reaction rates for the steady-state behavior of a laminar flow reactor, in which a homogeneous reaction with first- or second-order irreversible kinetics takes place. The transient behavior of the reactor is investigated only for a first-order irreversible reaction. The first three spatial moments of the concentration—mean, variance, and skewness, as well as the mean and the variance of the residence time distribution—for uniform and nonuniform pulse injections are calculated for arbitrary moments of time. The theoretical predictions are compared to numerical, exact, and experimental results and to the predictions with the SDM and plug flow model. Many different theoretical approaches can be used to explore the laminar flow reactor (see the papers just cited). We engage in the comparison of two of them: the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1972) and the orthogonal collocation method as frequently used for the analysis of various convective diffusion problems. It will be shown for a rather wide variety of problems that the wave model provides a good approximation to the more exact, but also more complicated two-dimensional equations. For instance, the maximum error in the calculated bulk concentrations for arbitrary values of the reaction constants and a conversion of 99% as determined with the exact solution does not exceed 8.7% in the case of a steady-state reactor with a first-order chemical reaction and 16.7% for a second-order reaction.

The examples considered also demonstrate that the wave model, having a clear physical significance and being more general, is simpler from the mathematical point of view and has a much wider region of validity for reactor calculations than a Fickian-type dispersed plug-flow model.

For the application considered an explanation is given for why the wave model with parameters as obtained in Westertep et al. (1995a) for asymptotic conditions is also applicable to rapid processes.

It was found that the wave model gives results close to those of the collocation method when used to handle the radial gradients in a reactor. The model corresponds to the two-point collocation that, as shown by Wang and Stewart (1983, 1989), in many cases closely approximates the fine-grid computations. This well-known procedure may serve as an additional justification of the wave model. It also provides a useful approach to obtain a one-dimensional equation.

The wave model fails when the radial concentration distribution at the reactor inlet or at the initial moment of time is essentially nonuniform. Restrictions to the value of the dispersion flux are derived in order that this theory can be used with confidence for arbitrary initial and boundary conditions.

Different Approaches for the Investigation of the Laminar-Flow Reactor

Exact description—the problem chosen for comparison

We assume that the concentration variation in the laminar-flow tubular reactor can be described by the two-dimensional convective diffusion equation:

$$\frac{\partial c}{\partial t} + 2\bar{u}\left(1 - \frac{r^2}{a^2}\right)\frac{\partial c}{\partial x} + q(c) = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \quad (1)$$

along with the following initial

$$t = 0, \quad c = \zeta_{\text{init}}(x, r) \quad (2)$$

and boundary conditions

$$x = 0, \quad c = \zeta_0(r, t); \quad r = 0 \quad \text{and} \quad a, \quad \frac{\partial c}{\partial r} = 0. \quad (3)$$

The molecular diffusion coefficient D in Eq. 1 is considered to be independent of the solute concentration. We have neglected the molecular diffusion in the axial direction on the assumption that the longitudinal mixing is completely dominated by the combined effects of the nonuniform convection and transverse diffusion.

Standard dispersion model

The commonly encountered one-dimensional model for chemical reactors is the longitudinally dispersed plug-flow model. We also call it the standard dispersion model (SDM). The model equation is usually written as:

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + q(\bar{c}) = D_e \frac{\partial^2 \bar{c}}{\partial x^2} \quad (4)$$

with the boundary conditions known from Danckwerts (1953):

$$x = 0, \quad \bar{u} \bar{\zeta}_0 = \bar{u} \bar{c} - D_e \frac{\partial \bar{c}}{\partial x}; \quad x = L, \quad \frac{\partial \bar{c}}{\partial x} = 0. \quad (5)$$

Here and throughout this article an overbar on a quantity denotes its cross-sectionally averaged value as defined for an axisymmetrical problem in a tube by

$$\overline{(\dots)} = \frac{2}{a^2} \int_0^a (\dots) r dr.$$

The value of the dispersion coefficient for laminar flow in a circular tube is well known from Taylor (1953) as being $D_e = a^2 \bar{u}^2 / 48D$. The peculiarity of this model is the presence of an additional parameter—the reactor length L —that is absent in the multidimensional model of Eqs. 1–3. The appearance of this parameter is due to the description of the hydrodynamical axial dispersion by an equation of the parabolic type. Thus, the application of the SDM is burdened with the uncertainty of choosing the reactor length L . Different recommendations are known at this point. To be concrete we will assume the reactor is infinitely long as often recommended—see, for example, Wissler (1969) and Subramanian et al. (1974)—so $L \rightarrow \infty$.

Convective dispersion theory of Gill and Sankarasubramanian

This theory, later called the G-S theory, is frequently used for the analysis of different convective diffusion equations. It gives the solution of multidimensional convective diffusion equations—in our case Eq. 1 with $q = 0$ —in terms of an area-averaged concentration $\bar{c}_I(x, t)$, when the concentration

is specified at the initial moment of time $t = 0$ in the form of $\zeta_{\text{init}}(x, r) = \psi(x)Y(r)$, see Gill and Sankarasubramanian (1970, 1971). For practical reasons the shortened two-term approximation of this theory is used, and the previously mentioned solution is found from the equation:

$$\frac{\partial \bar{c}_I}{\partial t} = K_1(t) \frac{\partial \bar{c}_I}{\partial x} + K_2(t) \frac{\partial^2 \bar{c}_I}{\partial x^2}, \quad (6)$$

where $K_1(t)$ and $K_2(t)$ are known functions of time that also depend on the initial transverse concentration distribution $Y(r)$.

For the solution of linear problems with other initial and boundary conditions different variants of the superposition technique have been developed using the solution of the basic equation Eq. 6 (Gill and Sankarasubramanian, 1972; Subramanian et al., 1974).

Wave model

This model has been proposed as an alternative to the SDM. A quasi-linear hyperbolic system of two first-order equations for the average concentration \bar{c} and the dispersion flux j was obtained (Westerterp et al., 1995a):

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}) = 0 \quad (7)$$

$$[1 + \tau q'(\bar{c})]j + \tau \frac{\partial j}{\partial t} + \tau(\bar{u} + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x} \quad (8)$$

with the following initial and boundary conditions:

$$t = 0, \quad \bar{c} = c_{\text{init}}(x) = \bar{\zeta}_{\text{init}}(x), \quad j = j_{\text{init}}(x) = \overline{(u - \bar{u}) \zeta_{\text{init}}} \quad (9)$$

$$x = 0, \quad \bar{c} = c_0(t) = \bar{\zeta}_0(t), \quad j = j_0(t) = \overline{(u - \bar{u}) \zeta_0}. \quad (10)$$

Here the prime indicates the derivative with respect to c , so $q' = \partial q / \partial c$. The dispersion flux—the second unknown variable—is defined as

$$j = \overline{(u - \bar{u})c}. \quad (11)$$

The wave model contains three parameters—the longitudinal dispersion coefficient D_e ; the relaxation time τ ; and the parameter of velocity asymmetry u_a . In Eqs. 7 and 8 the dispersion coefficient D_e is the Taylor dispersion coefficient, the same as in the SDM. For laminar flow in a tube the parameters of the wave model were calculated in an earlier article by Westerterp et al. (1995a), and are

$$D_e = \frac{a^2 \bar{u}^2}{48D}; \quad \tau = \frac{a^2}{15D}; \quad u_a = \frac{\bar{u}}{4}. \quad (12)$$

For nonlinear chemical reaction rates more refined equations may be used instead of Eqs. 7 and 8 (Westerterp et al., 1995a):

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}) + \frac{1}{2} q''(\bar{c}) \frac{\tau}{D_e} j^2 = 0 \quad (13)$$

$$\left(1 + \tau q'(\bar{c}) + \frac{1}{2} j \frac{\tau}{v} q''(\bar{c})\right) j + \tau \frac{\partial j}{\partial t} + \tau(\bar{u} + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x} \quad (14)$$

This system compared to Eqs. 7 and 8 contains an additional parameter v , which is equal to $7\bar{u}/1,558$ for laminar flow in a round tube. For a linear reaction rate $q''(c) = 0$, and Eqs. 13 and 14 coincide with Eqs. 7 and 8. Equations 13 and 14 contain a more exact representation of the averaged reaction rate, or take into account that $\bar{q}(c) \neq q(\bar{c})$ for nonlinear chemical reactions.

Orthogonal collocation technique

The well-known orthogonal collocation technique with two interior radial nodes will also be involved in the comparison, according to the variant given by Wang and Stewart (1983).

Application of the Different Approaches to the Laminar Flow Reactor

In this section we consider some typical examples showing the capabilities of the different approaches.

Steady-state reactor performance

We restrict ourselves to a simple but practical problem, namely, the reactor with a constant and uniform inlet concentration. In this case the boundary condition at the reactor inlet for Eq. 1 is

$$x = 0 \quad c = \zeta_0 = c_0 = \text{constant} \quad (15)$$

We present the results in the form of the area average concentration \bar{c} and bulk concentration c_b that is defined as

$$c_b = \frac{4}{\bar{u}a^2} \int_0^a \bar{u} \left(1 - \frac{r^2}{a^2}\right) cr \, dr = \bar{c} + \frac{j}{\bar{u}}$$

The solution of the SDM is well known. The dispersion flux is related to the concentration by $j = -D_e \partial \bar{c} / \partial x$. The G-S theory is applicable only for a first-order reaction with $q = k_1 c$ and is described by Subramanian et al. (1974). In this case the two coefficients $K_1(t)$ and $K_2(t)$ of Eq. 6 should be found for the initial transverse concentration distribution $Y(r) = 1 - r^2/a^2$ and the solution of Eq. 6 should be obtained for the initial condition $t = 0$, $\bar{c}_I = c_0 \bar{u} \delta(x)$, where $\delta(x)$ is a Dirac delta function. The bulk average concentration is calculated as (Gill, 1975)

$$c_b(x) = -\frac{1}{\bar{u}} \int_0^\infty \left(K_1(t') \bar{c}_I(x, t') + K_2(t') \frac{\partial \bar{c}_I(x, t')}{\partial x} \right) e^{-k_1 t'} dt'$$

This is a rather tedious procedure especially at small distances from the reactor inlet and for high reaction rates, be-

cause of singular behavior of $\bar{c}_I(x, t)$ at $x = 0$ and the slow convergence of the series for $K_1(t)$ and $K_2(t)$.

The equations of the wave model for the problem considered are

$$\bar{u} \frac{d\bar{c}}{dx} + \frac{dj}{dx} + q(\bar{c}) = 0 \quad (16)$$

$$[1 + \tau q'(\bar{c})] j + \tau(\bar{u} + u_a) \frac{dj}{dx} = -D_e \frac{d\bar{c}}{dx} \quad (17)$$

with the following boundary conditions:

$$x = 0, \quad \bar{c} = \bar{\zeta}_0 = c_0, \quad j = \overline{(u - \bar{u}) \zeta_0} = 0 \quad (18)$$

For a first-order chemical reaction with $q = k_1 c$ and a position-independent rate constant k_1 , Eqs. 16 and 17 can be combined to one equation of the second order for the average concentration

$$\left(\tau \bar{u}^2 + \tau \bar{u} u_a - D_e\right) \frac{d^2 \bar{c}}{dx^2} + (\bar{u} + k_1 \tau (2\bar{u} + u_a)) \frac{d\bar{c}}{dx} + k_1 (1 + k_1 \tau) \bar{c} = 0 \quad (19)$$

with boundary conditions:

$$x = 0, \quad \bar{c} = c_0, \quad \frac{d\bar{c}}{dx} = -\frac{\tau(\bar{u} + u_a) k_1 c_0}{\tau \bar{u}(\bar{u} + u_a) - D_e} \quad (20)$$

which follows from Eqs. 16–18. The bulk concentration in this case also obeys Eq. 19 but with different boundary conditions:

$$x = 0, \quad c_b = c_0, \quad \frac{dc_b}{dx} = -k_1 c_0 \quad (21)$$

For a first-order chemical reaction the analytical solutions of the SDM and the wave model are straightforward. The general properties of these solutions have been considered in a previous article (Westerterp et al., 1995b). Both these solutions are much simpler than the G-S solution. In the case of a nonlinear chemical reaction rate the numerical solution of the wave model can easily be obtained by “marching” numerically through the reactor from the inlet to the end, as for the simple plug-flow model, whereas in this case the SDM needs iterative calculations.

The dimensionless area-mean concentration \bar{c}/c_0 for a first-order reaction as a function of the dimensionless axial distance $X_1 = k_1 x / \bar{u}$ is presented in Figure 1. The ratio of the bulk concentration calculated by different approximate methods to the numerical solution of the steady-state form of Eq. 1 with the inlet boundary condition of Eq. 15 is given in Figures 2 and 3 for the values $\alpha_1 = k_1 a^2 / D = 100$ and $\alpha_2 = k_2 c_0 a^2 / D = 100$. For a second-order reaction with $q = k_2 c^2$ the results calculated with Eqs. 13 and 14 are also given in Figure 3.

It is seen that the agreement between the wave model and the two-dimensional equation Eq. 1 is far better than ob-

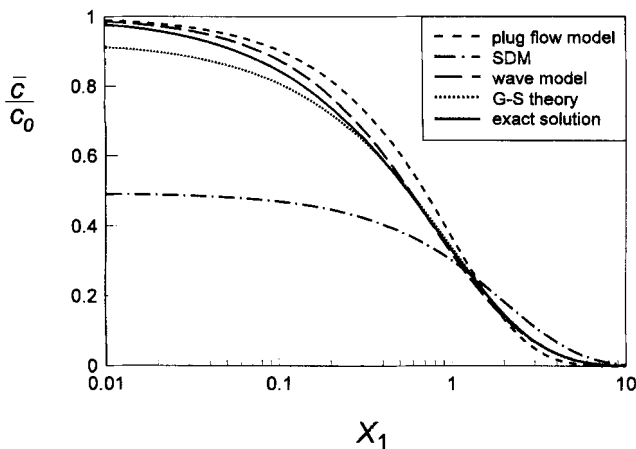


Figure 1. Steady-state area-mean concentrations for a first-order reaction as a function of $X_1 = k_1 x / \bar{u}$ and for $k_1 a^2 / D = 100$.

tained with conventional models. In spite of the wide variation of yield values, the magnitude of the ratio $c_b / c_{b, \text{exact}}$ remains within narrow limits along the reactor. It is noteworthy that the wave model also gives satisfactory results in the case of no diffusion in the radial direction or of infinitely fast chemical reactions with $\alpha_{1,2} \rightarrow \infty$, that is for purely convective mass transfer. The maximum absolute error in c_b for the wave model does not exceed 16.7%, when the concentration changes from 1 to 0.01—over a hundredfold concentration change—and for arbitrary reaction rates. The SDM gives adequate results only if $\alpha_{1,2} \leq 15$, as is well known. On the contrary, we would like to point out that for high reaction rates the SDM becomes even less accurate than the plug-flow model, which is a simplest variant of the wave model. Despite the large error the plug-flow model, in contrast to the Fick-

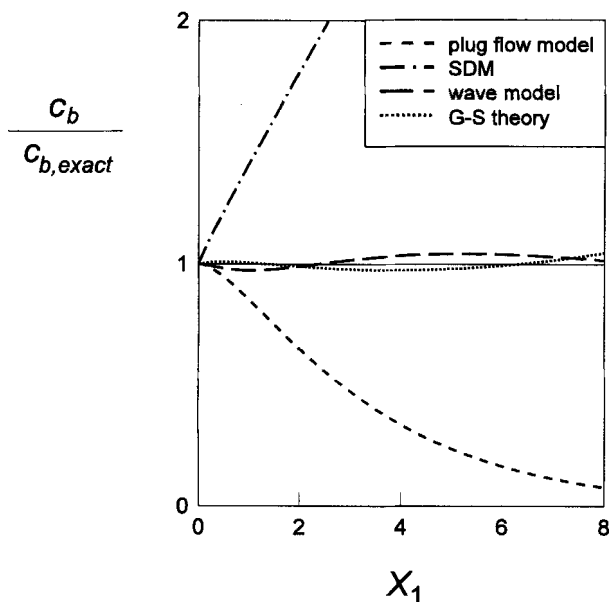


Figure 2. Values of $c_b / c_{b, \text{exact}}$ for a first-order reaction as a function of $X_1 = k_1 x / \bar{u}$ and for $k_1 a^2 / D = 100$.

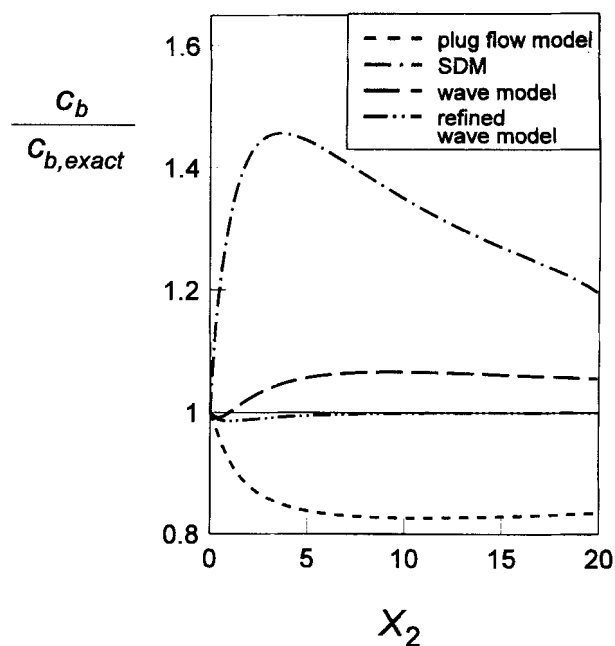


Figure 3. Values of $c_b / c_{b, \text{exact}}$ for a second-order reaction as a function of $X_2 = k_2 c_0 x / \bar{u}$ and for $k_2 c_0 a^2 / D = 100$.

ian dispersion model, remains qualitatively correct, whereas the SDM completely fails in the limiting cases of $\alpha_{1,2} \rightarrow \infty$ and fixed values of $X_{1,2}$. This also shows an inherent weakness of the SDM for reactor calculations. Agreement between the one-dimensional Fickian-type equation and the exact two-dimensional model can be reached only with an empirical reaction-dependent dispersion coefficient (Kulkarni and Vasudeva, 1976) or through empirical manipulation with the boundary conditions.

Spatial moments

The spatial moments of the concentration distribution of a solute injected into a stream can directly be calculated by means of the wave model for arbitrary methods of the solute injections. Examples of the application of the wave model for the calculations of the moments are presented in Westerterp et al. (1995b). The analytical calculation of the moments using the SDM is only possible for infinite and semi-infinite media. Besides that the analytical solutions are not available for all initial and boundary conditions (Kreft and Zuber, 1978).

For convenience we define the following dimensionless quantities:

$$C = \frac{c}{c_r}, \quad J = \frac{j}{\bar{u}c_r}, \quad \theta = \frac{tD}{a^2}, \quad X = \frac{xD}{\bar{u}a^2}, \quad \rho = \frac{r}{a},$$

where c_r is a reference concentration; its value is not important.

In order to test the accuracy of the wave model for the calculation of the first spatial moments we will consider two initial distributions of tracer material:

Table 1. Second Spatial Moments $1,000m_2$ for the Initial Condition $G = \delta(X)$ at Different Moments of Time θ

θ	Exact	Wave Model	Collocation	SDM
0.01	0.03121	0.02974	0.03162	0.4166
0.05	0.6296	0.6177	0.6493	2.083
0.10	2.024	2.009	2.088	4.167
0.20	5.702	5.694	5.835	8.333
0.40	13.90	13.90	14.07	16.67
1.00	38.89	38.89	39.06	41.67

$$\theta = 0 \quad C = G(X, \rho) = \begin{cases} \delta(X) & \text{case A} \\ 2\rho^2\delta(X) & \text{case B.} \end{cases}$$

These particular initial distributions have been used as examples by Chatwin (1977) and Wang and Stewart (1983) and represent situations where the initial distribution is uniform in case A or increasing monotonically from the axis to the wall in case B. The expressions of the first three spatial moments of the mean, variance, and skewness for the wave model are presented in Westerterp et al. (1995b).

The simple and accurate calculations of the moments for developed laminar flow of a Newtonian fluid can be made by means of the orthogonal collocation method with as few as two radial collocation points, as shown by Wang and Stewart (1983). These computations as well as the predictions of the SDM and G-S procedure are also included in the comparison.

We present the spatial moments around the mean as defined by

$$m_0 = \int_{-\infty}^{\infty} \bar{C} dX, \quad m_1 = \frac{\int_{-\infty}^{\infty} X\bar{C} dX}{m_0},$$

$$m_n = \frac{\int_{-\infty}^{\infty} (X - m_1)^n \bar{C} dX}{m_0}, \quad n = 2, 3.$$

In the important case A the second and third central spatial moments m_2 and m_3 are compared to the exact solutions derived by Aris (1956), Chatwin (1977), and Barton (1983). The first moment m_1 in this case is equal to 1 according to all approaches. Table 1 and Figure 4 show the spatial variance and skewness as a function of dimensionless time θ .

In case B the calculation of the first moment is also of interest. Table 2 shows the calculated mean and variance for the nonuniform initial solute distribution in comparison to

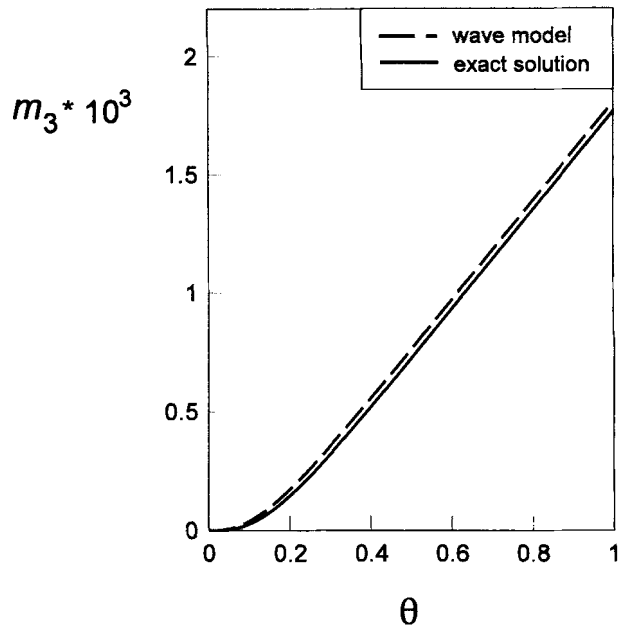


Figure 4. $m_3(\theta)$: predicted by the wave model vs. the exact solution by Barton (1983).

the exact results given by Chatwin (1977) and Barton (1983). The moments by the collocation method differ from the ones of Wang and Stewart (1983) who presented the exact value of the second moment in a coordinate system moving with the mean fluid velocity and not relative to the center of gravity of the pulse. Moreover, we use the mean velocity as the reference velocity, whereas Wang and Stewart used the maximum velocity.

The SDM cannot handle any initial radial concentration distribution— $m_1 = \theta$ and $m_2 = \theta/24$ for arbitrary initial transverse concentration distributions—and is not valid for the initial period before the equalization of the concentration over the cross section has been attained. The SDM, of course, gives $m_3 = 0$ whatever θ is. The truncated two-term dispersion equation, Eq. 6, has the remarkable property that two of the spatial moments are exact. However, it predicts a symmetric distribution around the center of gravity of the tracer and the third central moment is zero. Thus there is a need to retain higher-order terms in the application of the generalized dispersion theory, in order to predict the results observed. The orthogonal collocation method used by Wang and Stewart (1983) gives $m_3 = 0$ independent of the initial concentration distribution. To our knowledge no results for the

Table 2. Spatial First Moments $100(m_1 - \theta)$ and Second Moments $1,000m_2$, Respectively, for the Initial Condition $G = 2\rho^2\delta(X)$ at Different Moments of Time θ

θ	$100(m_1 - \theta)$			$1,000m_2$		
	Exact	Wave Model	Collocation	Exact	Wave Model	Collocation
0.01	-0.3022	-0.3095	-0.3080	0.02035	0.02220	0.4167
0.05	-1.1082	-1.1725	-1.1472	0.4328	0.4893	2.083
0.10	-1.6172	-1.7264	-1.6627	1.517	1.681	4.167
0.20	-1.9760	-2.1116	-1.9984	4.794	5.101	8.333
0.40	-2.0776	-2.2167	-2.0799	12.79	13.17	16.67
1.00	-2.0834	-2.2222	-2.0833	37.76	38.15	41.67

skewness for the case of a nonuniform pulse have been presented in the literature, with which we can make a comparison. As pointed out by Barton (1983) "the calculation of the m_3 in the general case is very laborious and the resulting expression is too long and complicated to reproduce."

It is notable that the large-time asymptotic values of the first three moments given by the wave model are exact (Westerterp et al., 1995b). The model does not correctly predict the time dependence of the third moment at $\theta \rightarrow 0$: according to the wave model $m_3 \sim \theta^3$ in this limit, whereas from the exact expression of m_3 as obtained by Barton (1983) $d^3 m_3 / d\theta^3 = 0$ should hold at $\theta = 0$. However, such a small difference hardly can be detected in an experiment. Note that at $\theta \rightarrow 0$ or if dispersion is caused by convection alone, we find $m_3 \sim \theta^3 (u - \bar{u})^3$, but for the parabolic velocity profile we have $(u - \bar{u})^3 = 0$.

Temporal moments

The most common approach in experimental work is based on measuring the distribution of residence times as a function of the axial distance, that is, on the measurement of the concentration variations as a function of time at fixed locations. Therefore, as a further test of the wave model, we will calculate the temporal moments of the residence time distribution. Such calculations can also be made directly by the wave model for arbitrary tracer injections (Westerterp et al., 1995b). The results available for comparison are given by Houseworth (1984). This author has analyzed the residence time distribution in laminar flow in a tube with a Monte Carlo method, based on an analytical solution of the diffusion equation over the tube cross section.

We consider, as Houseworth did, the case of an instantaneous injection of a small amount of tracer arbitrarily distributed over the cross section of the tube at the point $X = 0$, whereas at the initial moment $\theta = 0$ the concentration is zero all over the tube. The initial and boundary conditions for the two-dimensional equation, Eq. 1, in our case can be written in dimensionless form as

$$\theta = 0, \quad C = 0; \quad X = 0, \quad C = F(\rho) \delta(\theta),$$

where the function $F(\rho)$, describing the concentration distribution over the inlet cross section, has been normalized such that $\bar{F} = 1$. These boundary conditions describe the problem of tracer injection proportional to the fluid flux along a given streamline rather than introducing the material uniformly over the cross section, as we did for the calculation of the spatial moments. The corresponding initial and boundary conditions for the wave model of Eqs. 7 and 8 with no reaction or $q = 0$ in dimensionless form are

$$\theta = 0, \quad \bar{C} = 0, \quad J = 0; \quad X = 0, \quad \bar{C} = \delta(\theta), \\ J = w \delta(\theta),$$

where $w = \overline{(u - \bar{u})F} / \bar{u}$. Let:

$$\mu_n = \int_0^\infty \theta^n \bar{C}(X, \theta) d\theta, \quad n = 0, 1, 2$$

be the temporal moments of the residence time distribution of the solute in the tube. The calculation of the first moments with the wave model gives the following results:

$$\mu_0 = 1 + w(1 - e^{-\gamma}) \\ \mu_1 = \gamma \alpha^{-1} [(1 + w)y + w\beta(1 - e^{-\gamma} - \gamma e^{-\gamma}) \\ + (\beta - \alpha - w(1 + \alpha))(1 - e^{-\gamma})] \\ \mu_2 = \gamma^2 \alpha^{-2} \{ (1 + w)y^2 - w\beta^2 y^2 e^{-\gamma} \\ + 4[\beta - \alpha + w(\beta - \alpha - 1/2)](y - 1 + e^{-\gamma}) \\ + 2[\beta(\beta - \alpha) + w(\alpha + \beta(\beta - \alpha - 2))](1 - e^{-\gamma} - \gamma e^{-\gamma}) \},$$

where

$$\alpha = \frac{\bar{u}^2 \tau}{(\bar{u} + u_a)\bar{u}\tau - D_e}, \quad \beta = \frac{\bar{u}^2 \tau + D_e}{(\bar{u} + u_a)\bar{u}\tau - D_e} \\ \gamma = \frac{\tau D}{a^2} \quad \text{and} \quad y = \frac{X \alpha a^2}{D \tau}.$$

Using these expressions we can calculate the mean ν_1 and the variance σ_t^2 of the residence time distribution, which are

$$\nu_1 = \frac{\mu_1}{\mu_0}, \quad \sigma_t^2 = \frac{\int_0^\infty (\theta - \nu_1)^2 \bar{C}(X, \theta) d\theta}{\mu_0} = \frac{\mu_2}{\mu_0} - \nu_1^2.$$

For a tracer input uniform over the cross section $w = (u - \bar{u})F / \bar{u} = 0$ and the variance can be represented in the form:

$$\sigma_t^2 = 2\gamma^2 \alpha^{-2} (\beta - \alpha) \{ (2 - \beta)y \\ + [(\beta - 1)y - (2 - \beta)](1 - e^{-\gamma}) - (1/2)(\beta - \alpha)(1 - e^{-\gamma})^2 \}.$$

Note that there are some errors in the same formula in the earlier article by Westerterp et al. (1995b). In order to illustrate the theory we consider two special forms for $F(\rho)$, the distribution of the tracer over the inlet cross section: the first one where the inlet distribution is uniform or $F(\rho) = 1$, and the second where the tracer is supplied through a point source situated in the tube axis or $F(\rho) = \delta(\rho) / (2\rho)$. Tables 3 and 4 show the mean ν_1 and variance σ_t^2 of the residence time distribution for the two inlet conditions obtained by Houseworth (1984), the wave model and the SDM. For the SDM the following boundary conditions were used:

$$X = 0, \quad \bar{C} - \frac{1}{48} \frac{\partial \bar{C}}{\partial X} = \delta(\theta); \quad X \rightarrow \infty, \quad \bar{C} \rightarrow 0.$$

From Table 3 we see that the wave-model solution is accurate in the case of a uniform radial distribution and not too close to the inlet. The predictions of the SDM are independent of the inlet concentration distribution and therefore they are not shown in Table 4. A point source is an extreme case of a nonuniform inlet concentration and it is evident

Table 3. Mean $100\nu_1$ and Variance $1,000\sigma_t^2$ of the Residence Time Distribution as a Function of $X = xD/a^2\bar{u}$ for the Inlet Condition $F(\rho) = 1$

X	100ν ₁			1,000σ _t ²		
	Monte Carlo	Wave Model	SDM	Monte Carlo	Wave Model	SDM
0.01	0.9813	1.308	3.083	0.04706	0.03413	1.687
0.05	4.920	6.147	7.083	0.6995	0.7169	3.225
0.10	9.978	11.66	12.08	2.117	2.307	5.148
0.20	19.96	21.99	22.08	5.534	6.299	8.994
0.30	29.97	32.07	32.08	9.631	10.48	12.84
0.50	50.06	52.08	52.08	18.35	18.84	20.53

that a one-dimensional reactor model cannot be a suitable tool for the investigation of such a problem. This case is included in Table 4 to explore the region of applicability of the wave model. The unrealistic negative values of the variance for small distances as predicted by the wave model is explained later.

Transient behavior of the reactor

Consider the problem of a tubular reactor where the reacting component enters at the inlet of the tube with a constant uniform concentration c_0 . Initially, the tube contains no reactant. If the reaction is of the first order with a rate constant k_1 , the concentration of reactant satisfies the equation:

$$\tau \frac{\partial^2 \bar{c}}{\partial t^2} + \tau(2\bar{u} + u_a) \frac{\partial^2 \bar{c}}{\partial x \partial t} + (\tau\bar{u}^2 + \tau\bar{u}u_a - D_e) \frac{\partial^2 \bar{c}}{\partial x^2} + (1 + 2k_1\tau) \frac{\partial \bar{c}}{\partial t} + (\bar{u} + k_1\tau(2\bar{u} + u_a)) \frac{\partial \bar{c}}{\partial x} + k_1(1 + k_1\tau)\bar{c} = 0. \quad (22)$$

The initial and boundary conditions to be applied are

$$t = 0 \quad \bar{c} = 0, \quad \frac{\partial \bar{c}}{\partial t} = 0; \quad x = 0 \quad \bar{c} = c_0 H(t), \quad \frac{\partial \bar{c}}{\partial x} = - \frac{\tau(\bar{u} + u_a)(\delta(t) + k_1 H(t))}{\tau\bar{u}(\bar{u} + u_a) - D_e} c_0, \quad (23)$$

where $H(t)$ is the Heaviside unit step function. These conditions are the direct consequence of the Eqs. 7 and 8 and their initial and boundary conditions:

$$t = 0 \quad c = 0, \quad j = 0; \quad x = 0 \quad c = c_0 H(t), \quad j = 0.$$

The solution of Eq. 22 can be written as

$$\bar{c} = c_0 e^{-k_1 x/\bar{u}} \int_0^t E(x, t') dt',$$

where $E(t)$ is the solution of Eq. 22 for an instantaneous source of unit strength injected at time zero at the reactor inlet, that is for the initial and boundary conditions:

$$t = 0 \quad E = 0, \quad \frac{\partial E}{\partial t} = 0; \quad x = 0 \quad E = \delta(t), \quad \frac{\partial E}{\partial x} = - \frac{\tau(\bar{u} + u_a)}{\tau\bar{u}(\bar{u} + u_a) - D_e} \delta'(t).$$

This solution was presented in Westerterp et al. (1995b). It is not equal to zero for $u_2 t \leq x \leq u_1 t$, where u_1 and u_2 are the characteristic velocities of the hyperbolic system of Eqs. 7 and 8, which for laminar flow in a tube are

$$u_{1,2} = \bar{u} + \frac{u_a}{2} \pm \sqrt{\frac{u_a^2}{4} + \frac{D_e}{\tau}} = \bar{u} \left(1 \pm \frac{1 + \sqrt{2I}}{8} \right). \quad (24)$$

Figure 5 shows the bulk concentration as a function of the axial position as calculated by the different methods and for the parameter values used in the experiments of Nigam and Vasudeva (1976). The analytical solution of the unsteady-state SDM with a first-order reaction term probably has not yet been presented. Therefore the simplified boundary conditions of the form

$$x = 0 \quad \bar{c} = c_0, \quad x \rightarrow \infty \quad \bar{c} \rightarrow 0$$

have been used, as in the articles of Subramanian et al. (1974) and Nigam and Vasudeva (1976).

Breakthrough curve for a pulse input specified at the initial moment of time

The problem of dispersion in laminar flow through a straight tube for a pulse input specified at the initial moment has been the subject of a large number of theoretical investigations. Because the exact analytical solution of the partial differential equation is difficult to obtain, a number of inter-

Table 4. Mean $100\nu_1$ and Variance $1,000\sigma_t^2$ of the Residence Time Distribution as a Function of $X = xD/a^2\bar{u}$ for the Inlet Condition $F(\rho) = \delta(\rho)/(2\rho)$

X	100ν ₁		1,000σ _t ²	
	Monte Carlo	Wave Model	Monte Carlo	Wave Model
0.01	0.5052	0.4347	0.0000017	-0.02530
0.05	2.661	3.681	0.005200	0.09790
0.10	5.919	8.626	0.2061	0.9911
0.20	14.37	18.81	2.274	4.141
0.30	24.01	28.91	5.764	8.038
0.50	43.75	48.96	14.01	16.30

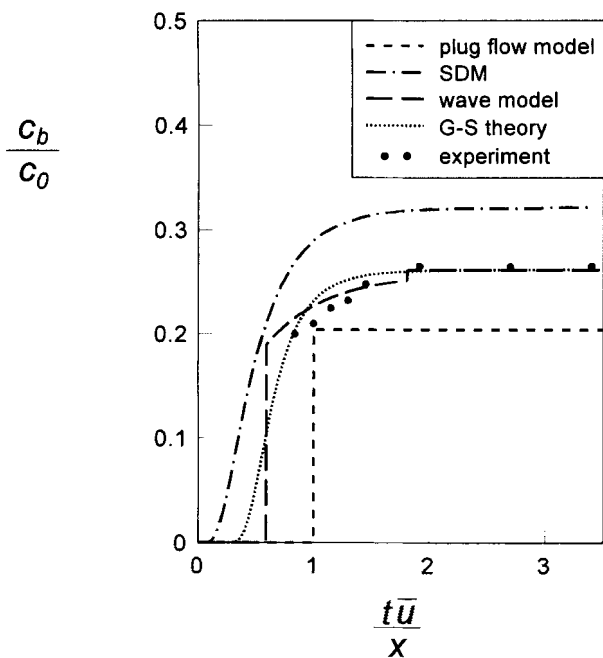


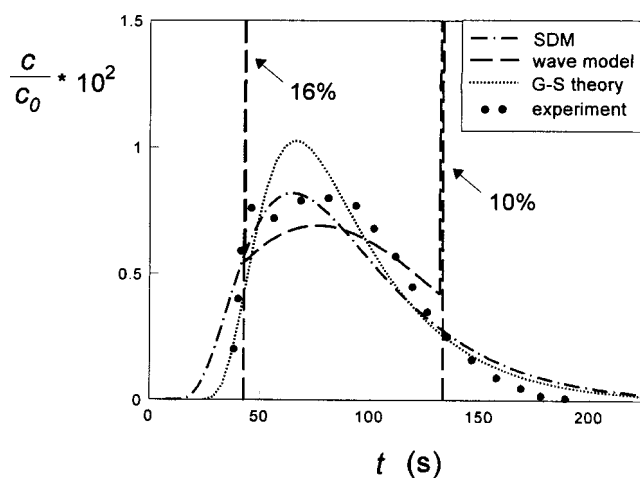
Figure 5. Breakthrough for a step change of the inlet concentration in a laminar flow reactor for $D/(k_1 a^2) = 0.037$ and $k_1 x/\bar{u} = 1.59$ calculated by different methods vs. experimental data of Nigam and Vasudeva (1976).

tigators have attempted to develop approximate analytical or numerical solutions. Comprehensive numerical calculations have been made by Yu (1981), Shankar and Lenhoff (1989) and by Takahashi et al. (1990). These numerical solutions agree very well with the experimental results by Korenaga et al. (1989) for a finite slug of a dye solution dispersed in water. The analytical solution of the wave model for the initial condition of the two-dimensional equation, Eq. 1, in the form:

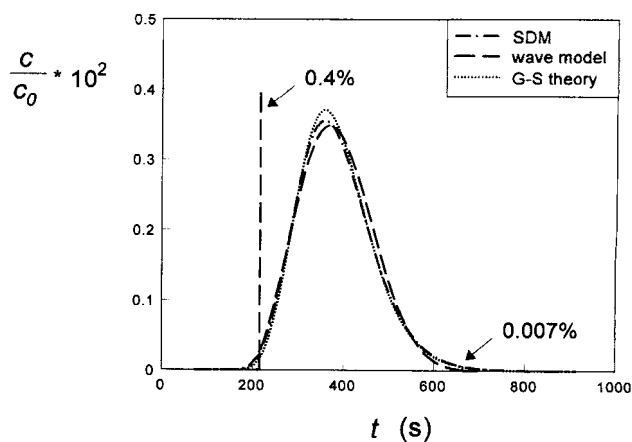
$$t = 0, \quad c = \frac{M}{\pi a^2} \delta(x)$$

is given in Westerterp et al. (1995b), where M is the amount of material injected. This solution can be used to handle problems with any radially uniform initial conditions through the conventional superposition integral similar to those as in the previous example. An example of the calculated breakthrough curve at a small distance from the inlet in the case of a rectangular, radially uniform initial concentration profile is presented in Figure 6a and compared to the experimental data of Korenaga et al. (1989) and to the predictions of the G-S theory and the SDM. For the small initial slug length used in the experiments of Korenaga et al. (1989) the solutions are very close to those with initial conditions approximated by the delta function.

The wave model predicts unrealistic concentration peaks that, however, correspond to the double-peaked behavior of the experimental breakthrough curves. These concentration spikes were observed only at an early stage of the dispersion for delta Dirac type or other sharp initial distributions. At a later stage in the dispersion process the area under the spikes



(a)



(b)

Figure 6. Breakthrough for an initial rectangular pulse calculated by different methods.

(a) $x = 40$ cm, the calculated curves are compared to experimental data of Korenaga et al. (1989); (b) $x = 200$ cm. Other parameters are $a = 0.403$ mm; $\bar{u} = 0.545$ cm/s; $D = 3.78 \cdot 10^{-6}$ cm²/s; the initial slug length is 0.39 cm. The numbers near the spikes indicate the fractions of the amount of tracer under the spikes.

becomes relatively small and the solution of the wave model closely corresponds to the exact solution. The breakthrough curves at a long distance from the inlet calculated by the wave model, G-S theory, and by the SDM are presented in Figure 6b. All solutions are close to each other in the central part of the concentration cloud, but differ near the front and the end. In contrast to the other approximate solutions the solution of the wave model is permanently zero outside the region $x/u_1 \leq t \leq x/u_2$. For a smoother initial distribution, as in experimental work, the results of the hyperbolic model are not unrealistic anymore at any stage of dispersion. The solution of the wave model after a short period of time or at small distances is easily understood and has been explained in an earlier article by Westerterp et al. (1995b). One should realize that the prediction of the concentration profile of a solute initially injected into a stream over a short time is a very difficult problem. Although a number of special analyti-

cal and numerical approximations have been developed, there are only a few solutions that are valid for arbitrary moments of time, as was shown by Yu (1981).

Limitations of the Wave Model

In most practical systems molecular diffusion in the axial direction can be neglected and axial mass transport occurs due to convection. This results in restrictions to the value of the dispersion flux:

$$(u_{\min} - \bar{u})\bar{c} \leq j \leq (u_{\max} - \bar{u})\bar{c}, \quad (25)$$

where u_{\min} and u_{\max} are minimum and maximum values of the axial velocities. According to the SDM the dispersion flux is proportional to concentration gradient $-\partial\bar{c}/\partial x$ and can have arbitrary values, including $\pm\infty$. A signal can never travel faster than the velocity of the "fastest streamline" if molecular diffusion in the axial direction is negligible. This physical contradiction also exposes the shortcomings of the SDM and narrows the limits of its applicability. According to the wave model axial mass transport occurs by two convective flows with the velocities u_1 and u_2 of Eq. 24. Therefore the dispersion flux in the wave model can be represented as

$$j = u_1 c_1 + u_2 c_2 - \bar{u}\bar{c} = (u_1 - \bar{u})c_1 + (u_2 - \bar{u})c_2, \quad (26)$$

where c_1 and c_2 are the concentrations in the first and second wave and $c_1 + c_2 = \bar{c}$. Taking into consideration the inequalities $0 \leq c_1 \leq \bar{c}$ and $0 \leq c_2 \leq \bar{c}$, we conclude that the dispersion flux of the wave model must obey the constraints:

$$(u_2 - \bar{u})\bar{c} \leq j \leq (u_1 - \bar{u})\bar{c}. \quad (27)$$

So the wave model predicts confined values of the dispersion flux for any concentration gradient: this is as it should be. However, the restrictions of the wave model to the value of the dispersion flux as given in Eq. 27 are only approximations and narrower than the exact restrictions of Eq. 25; this leads to some limitations of the model. For laminar flow in a round tube $u_{\min} = 0$, $u_{\max} = 2\bar{u}$, and from Eq. 24 we have $u_1 = 1.698\bar{u}$ and $u_2 = 0.552\bar{u}$. So for the wave model:

$$-0.448\bar{u}\bar{c} \leq j \leq 0.698\bar{u}\bar{c}, \quad (28)$$

whereas allowed values of j are

$$-\bar{u}\bar{c} \leq j \leq \bar{u}\bar{c}. \quad (29)$$

The discrepancies of the constraints of Eqs. 28 and 29 may lead to physically unrealistic results: if j is higher than $0.698\bar{u}\bar{c}$ or lower than $-0.448\bar{u}\bar{c}$, the concentration in one of the waves will be negative, as follows from Eq. 26. Fortunately, such contradictions occur only in extreme situations with essentially nonuniform radial concentration profiles, where the application of a one-dimensional model obviously does not make sense. Such situations arise for example in the case of a point injection of solute in the center of the tube, where the initial or inlet value of the dispersion flux is equal to $\bar{u}\bar{c}$. This explains the negative values of the variance of the residence

time distribution for a point injection in the tube axis at short distances from the injection point with $X \ll 1$ or $x \ll \bar{u}\tau$; see Table 4. In the case of spatial moments such contradictions have not been observed even for point injections.

Unrealistic negative values of the variance of the residence time distribution are found due to an inconsistency of the approximate Eqs. 7 and 8 and the exact boundary condition for essentially nonuniform, inlet radial concentration profiles. The dispersion flux in the equations is approximate, whereas its boundary value is exact and can exceed the approximate constraints. A simple way to exclude this contradiction, whenever the exact values exceed the permissible limits, is to bring the boundary values of the dispersion flux in line with the model equations, that is to use the limiting values of the dispersion flux instead of its exact values.

The second reason for the decrease in the accuracy of Eqs. 7 and 8 is the approximate representation of the nonlinear consumption rate averaged over cross-section, through the mean concentration. The approximation used—where the consumption rate is represented through the first term only of a Taylor expansion about the mean concentration (Westertorp et al., 1995a)—may be insufficient for nonlinear rapid chemical reactions with characteristic times lower than the relaxation time. In this case the transverse concentration profiles are very steep and a more refined cross-sectional averaging of the source term becomes necessary. This can be seen from Figure 2, which shows that for the second-order reaction, Eqs. 13 and 14 are considerably more accurate than Eqs. 7 and 8. Regrettably Eqs. 13 and 14 are not suitable to describe the reactor because of the additional parameter ν .

Discussion

We have tested the accuracy of the wave model by comparing it to known solutions of only certain standard problems for laminar flow in a circular tube. The results of the comparison show that the wave model gives a fair approximation to the exact solutions in a wide range of situations and is definitely preferable to the SDM. Similar results were obtained for many other problems of mass transfer in laminar flows of Newtonian and non-Newtonian fluids and for turbulent flows in tubes, between parallel plates, in Couette flow and in open channels.

The main parameters of the wave model—the dispersion coefficient D_e and relaxation time τ , which make it different from the SDM—must also be known for the application of the SDM. D_e is a parameter of the basic equation, Eq. 4, and τ is a measure for the applicability of the SDM. The SDM is only applicable if τ is much smaller than other characteristic times of the system, like the average residence time and the chemical reaction time constant. Therefore the beauty of the wave model is that it can be used on the basis of the same information as needed for the SDM. More precise determinations of τ and of the velocity asymmetry u_a are desirable but not absolutely necessary. In particular, many results presented in this article could be obtained, although with some loss of accuracy, using only the findings of Taylor (1953), who determined D_e and in fact introduced and estimated the relaxation time, called by him the "time of decay" being $a^2/[3.8)^2 D]$, and further the value of u_a in his case would have been set to zero.

It is important from the mathematical point of view that the more general wave model is simpler than the SDM for reactor calculations for all situations where the boundary conditions are important. For linear steady-state and unsteady-state problems the analytical solutions of the wave model can be obtained by standard methods and for arbitrary initial and boundary conditions. For nonlinear systems the solutions of the wave model can be obtained by "marching" through the reactor from the inlet to the outlet, whereas the SDM needs iterative calculations.

The parameters of the wave model in Eq. 12 were obtained on the basis of a modification of Taylor's (1953) analysis of the asymptotic behavior, where the concentration is approximately uniform over the cross section and varies only slowly with respect to both time and the axial coordinate. Therefore the wave model as well as Taylor's model is also asymptotic, only with different properties and it is not surprising that the hyperbolic model gives excellent quantitative results for slow processes and, for instance, gives the exact asymptotic values of the first three spatial moments. Moreover, the results presented here demonstrate that the model also gives reasonably accurate descriptions under conditions of rapidly changing concentrations. The moments of the concentration distribution, the predictions of the steady-state reactor behavior at high reaction rates or $k_1 a^2/D$, $k_2 c_0 a^2/D \rightarrow \infty$, and the description of the transient behavior of the reactor are examples of these. This is not obvious. Some considerations why the wave model with the asymptotic parameters gives good results over a wide range of situations are given below.

The procedure used in a previous article by Westerterp et al. (1995a) to obtain Eqs. 7 and 8 with the parameters of Eq. 12 is the same closure procedure as that based on Taylor's (1953) original ideas: to find the expression relating the dispersion flux to the average concentration, some appropriate radial concentration distribution should be used. Instead of the radial concentration distribution used by Taylor, we have taken a more universal form of this distribution, namely:

$$c = \bar{c} - \frac{g_1}{D_e} j, \quad (30)$$

where

$$g_1 = -\frac{\bar{u}a^2}{4D} \left(\frac{1}{3} - \rho^2 + \frac{1}{2}\rho^4 \right), \quad \rho = \frac{r}{a}.$$

Such a simple modification of Taylor's procedure allows us to introduce the second state variable—the dispersion flux—and it leads to an essential change in the final result. It is obvious that Eq. 30 cannot be universally adequate, and sometimes a more refined approximation is necessary. To this end the concentration, as a continuous function, can be approximated uniformly by a polynomial:

$$c(x, r, t) = \sum_0^{\infty} a_n(x, t) \rho^{2n}, \quad (31)$$

where $\rho = r/a$ and $a_n(x, t)$, $n = 0, 1, 2, \dots$, are unknown functions of the axial position and time. This approximation satisfies the boundary condition in Eq. 3 at the reactor axis.

Also taking the boundary condition Eq. 3 at the reactor wall into account and introducing the concentration averaged over the cross section, Eq. 31 can be rewritten as

$$c(x, r, t) = \bar{c}(x, t) + 6\bar{u} \sum_{n=2}^{\infty} \frac{(n+1)(n+2)}{(n+1)(n+2)-6} \times \left(\frac{1}{2} - \frac{1}{n(n+1)} - \rho^2 + \frac{1}{n}\rho^{2n} \right) j_n(x, t), \quad (32)$$

where the unknown functions $j_n(x, t)$, with $n = 2, 3, \dots$, are normalized such that

$$j = \sum_{n=2}^{\infty} j_n, \quad (33)$$

and can be considered as the corresponding components of the dispersion flux in the series of Eq. 32 for the radial concentration distribution. If only the first term in the series in Eq. 32 is used we exactly have Eq. 30 again. The use of the exact representation of the concentration profile of Eq. 32 instead of Eq. 30 in the procedure described in Westerterp et al. (1995b) leads to a new equation instead of Eq. 8:

$$\sum_{n=2}^{\infty} (1 + \tau_n q'(\bar{c})) j_n + \sum_{n=2}^{\infty} \tau_n \frac{\partial j_n}{\partial t} + \sum_{n=2}^{\infty} \tau_n (\bar{u} + u_{an}) \frac{\partial j_n}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x}, \quad (34)$$

where D_e is the Taylor dispersion coefficient and parameters τ_n and u_{an} with $n = 2, 3, \dots$ are easily calculated through known formulas. It is remarkable that for laminar flow in a tube the values of τ_n change only from $a^2/15D$ to $a^2/16D$ and the values of u_{an} from $\bar{u}/4$ to $\bar{u}/8$ when n varies from 2 to ∞ . The same trends are also observed for other velocity profiles. Equation 33 and a weak dependence of the parameters of Eq. 34 on n may serve, at least on an intuitive basis, as a justification to use Eq. 8 instead of the exact Eq. 34 for processes with concentration fields rapidly changing with respect to time and coordinates: that is for those with a characteristic time of an order of magnitude of τ or lower. In addition, it easily can be checked that the use of any values of τ_n and u_{an} , $n = 2, 3, \dots$, instead of τ and u_a , does not influence essentially the steady-state concentration profiles calculated by Eqs. 16 and 17.

The comparisons presented earlier as well as other examples show that in many cases the results given by the wave model are in close agreement with those of the collocation method. This agreement can be easily explained.

In the case of two interior collocation points the application of the collocation procedure of Wang and Stewart (1983, 1989) to Eq. 1 with boundary conditions Eq. 3 gives rise to equations that can be rewritten as

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} = 0$$

$$j + \frac{a^2}{16D} \left(\frac{\partial j}{\partial t} + \bar{u} \frac{\partial j}{\partial x} \right) = -\frac{a^2 \bar{u}^2}{48D} \frac{\partial \bar{c}}{\partial x}.$$

These equations are Eqs. 7 and 8 of the wave models, but with different parameter values:

$$D_e = \frac{a^2 \bar{u}^2}{48D}; \quad \tau = \frac{a^2}{16D}; \quad u_a = 0. \quad (35)$$

The relation $u_a = 0$ is a reason why the collocation method m_2 does not depend on the initial concentration distribution; see Tables 1 and 2, as well as $m_3 = 0$. These disadvantages can be avoided by using other collocation points than the zeros of the shifted Legendre polynomial. The collocation method does not tell us how to choose the "best" collocation points in the first approximations. However, this powerful method, as well as other variants of the method of weighted residuals (Finlayson, 1972), are very useful in obtaining the structure of one-dimensional equations that should be used for the description of longitudinal dispersion; see, as an example, Dil'man and Kronberg (1983). Thus, all these well-known procedures may serve as additional mathematical justifications of the wave model. For many calculations the difference between the parameters in Eqs. 12 and 35 is not very important.

Here we remark on a terminological contradiction in the work of Wang and Stewart (1983, 1989). It is generally assumed that the area averaging of multidimensional convective-diffusion equations gives rise to a diffusional-type one-dimensional equation. These authors oppose radial averaging and favor the collocation method; they stated that radially averaged equations have only a limited predictive power. But orthogonal collocation is also a way of averaging radially, which results in equations essentially different from the commonly used diffusional equations, and has a high predictive power.

We have neglected molecular diffusion in the axial direction in Eq. 1 because for most practical problems, including the laminar-flow reactor, the transport in the axial direction is dominated by shear dispersion and by other hydrodynamical mechanisms. For more complex problems than dispersion in laminar flow, we also have to consider the combined action of different hydrodynamical mechanisms through the application of the wave approach to each individual mechanism. The axial molecular diffusion, if necessary, can be incorporated into the wave model. This incorporation changes the type of governing equations and leads to mathematical complications. It should be noted that, as was shown by Wang and Stewart (1983), the solution of linear dispersion problems with axial molecular diffusion incorporated, and in an infinitely long tube with the concentration specified at the initial moment, can be obtained as a convolution of the concentration profile for the case where the axial molecular diffusion is neglected.

One should realize that the total variety of multidimensional situations cannot be represented only in terms of a few averaged characteristics, like the average concentration and the dispersion flux. Therefore there is no reason to expect that the wave model will predict arbitrary multidimensional distributions well. The wave model fails in the detailed description of processes with essentially nonuniform transverse concentration distributions. More complex models are needed to describe such complex situations. A more detailed repre-

sentation needs more one-dimensional equations—an infinite number of coupled equations for the exact representation—but such refinements can hardly be justified in reactor engineering practice because of the mathematical complexities and the many additional parameters, which cannot be evaluated in sufficient detail from experimental data in a way useful for design or scale-up purposes.

It should be stressed that the wave model should not be confused with a mathematical tool for the approximate solution of the partial differential equations, as it may seem from this article. First of all it should be considered as a simple alternative to the conventionally used dispersed plug-flow model or SDM and as a basic method for reactors with a complex flow behavior. This is an important difference of the wave approach in comparison to other known dispersion theories.

Conclusions

The validity of the wave model has been tested through a comparison with available solutions for the laminar-flow reactor. The results obtained provide additional support for the theory described in previous papers by Westerterp et al. (1995a,b) and clearly demonstrate the advantages of the wave model over the conventionally used standard dispersion model. The solutions of the wave model in a wide range of situations are in very reasonable agreement to the exact data. Hyperbolic-type equations are definitely preferable to parabolic ones for the description of hydrodynamical dispersion. If the necessary restrictions to the values of the dispersion flux are imposed the model can be used for almost all situations.

Notation

- a = tube radius
- k_2 = constant of second-order chemical reaction
- q = consumption rate of component per unit of reactor volume
- r = radial coordinate
- u = axial velocity
- x = axial coordinate
- X_2 = dimensionless axial coordinate, $k_2 c_0 x / \bar{u}$
- ζ = inlet or initial concentration

Subscript

- 0 = inlet, at $x = 0$

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