ratio of bubble to oil in the two-phase droplet (β_i) and the volume equivalent sphere diameter (d) are expressed by Eq.(3) and Eq.(4).

$$\beta = \beta_i \frac{P}{P - \rho_w \gamma (g/g_c)} \quad (3)$$

$$d = d_i \left(\frac{1 + \beta}{1 + \beta_i} \right)^{1/3} \quad (4)$$

Figures 3, 4 and 5 are shown to determine the constants A , k_1 , k_2 and k_3 .

As the result, the final correlation for H.T.U. based on dispersed phase (H_d) is shown in Fig. 5, and is expressed by the equation

$$\left(\frac{H_d}{d} \right) \cdot N_{Ca} = 3.80 \times 10^{-5} \cdot N_{Pe}^{1/2} \quad (5)$$

The equation agrees satisfactorily with previous experimental data^{1,3)}.

Nomenclature

A	= constant in Eq.(2)	[—]
C	= solute concentration of oil	[mol/l]
C_i	= solute concentration of oil initially	[mol/l]
$\mathcal{D}$	= diffusion coefficient	[cm ² /sec]
d	= volume equivalent sphere diameter of droplet	[cm]
$d_{b,i}$	= volume equivalent sphere diameter of bubble in two-phase droplet at tip of nozzle	[cm]
d_i	= volume equivalent sphere diameter of droplet at tip of nozzle	[cm]
d_{NI}	= inside diameter of nozzle	[mm]
H_d	= height per transfer unit based on dispersed phase for mass transfer	[cm]
k_1	= exponent in Eq.(2)	[—]

k_2	= exponent in Eq.(2)	[—]
k_3	= exponent in Eq.(2)	[—]
N_{Ca}	= Capillary number, $= \mu_w u_{dt} / \sigma$	[—]
N_{Pe}	= Peclet number, $= u_{dt} \gamma / \mathcal{D}$	[—]
P	= pressure at tip of nozzle	[force-g/cm ²]
Q_o	= volumetric flow rate of oil	[cm ³ /sec]
u_{dt}	= rise velocity of droplet	[cm/sec]
γ	= column height	[cm]

β	= volume ratio of air bubble to oil in the two-phase droplet	[—]
β_i	= volume ratio of air bubble to oil in the two-phase droplet at tip of nozzle	[—]
$\varepsilon_{d,i}$	= hold-up of dispersed phase at tip of nozzle	[—]
μ_w	= viscosity of water	[g/cm-sec]
ρ_w	= density of water	[g/cm ³]
σ	= interfacial tension	[dynes/cm]

<Subscripts>

d	= dispersed phase (= liquid droplet or two-phase droplet)
i	= initial
o	= oil
w	= water

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CHROMATOGRAPHIC MOMENTS FOR PACKED BED REACTORS AND BOUNDARY CONDITION AT BED EXIT*

NORIAKI WAKAO, KENJI TANAKA AND D. S. SCOTT**

Department of Chemical Engineering, Yokohama National University, Yokohama, Japan

In estimating kinetic and transport parameters in the packed bed reactor the chromatographic technique, which requires exact solution for tracer output in Laplace domain, is becoming popular.

When the tracer is injected deep in a bed free from bed-inlet effect, there are the following two cases regarding the location of measurement of output signal:

Case 1: Output signal is measured at bed exit.

Case 2: Output signal is measured in bed and the bed extends sufficiently far downstream beyond the measurement point.

Kubin¹⁾ and Kucera²⁾ have obtained Eq.(11). The purpose of this note is to obtain the moments for Case

1, considering Danckwerts' exit-boundary condition. The particles are assumed to be porous and of uniform size.

(A) Homogeneous Reaction Model

This is the model for catalyst particles. It is assumed that the reaction in the particles is of isothermal first order with regard to the imposed reactant.

The system is expressed as

$$\frac{\partial C}{\partial \tau} = \beta \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} - \frac{3\eta}{\kappa} \left(\frac{\partial c_i}{\partial \rho} \right)_{\rho=1} \quad (1)$$

$$\kappa \frac{\partial c_i}{\partial \tau} = \frac{\partial^2 c_i}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial c_i}{\partial \rho} - \phi^2 c_i \quad (2)$$

$$C(x, 0) = 0 \quad (3)$$

$$c_i(\rho, x, 0) = 0 \quad (4)$$

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** Dept. of Chem. Eng., University of Waterloo, Waterloo, Ontario, Canada

〒233 横浜市南区大岡2-31-1

横浜国立大学工学部化学工学科 若尾法昭

Table 1 Comparison of moments for homogeneous reaction model

Moment	Case 1		Case 2
	General expression	When β is sufficiently small	
m_0	$\frac{e^{1/2\beta}}{\cosh \frac{H}{2\beta} + \frac{1}{H} \sinh \frac{H}{2\beta}}$	$\frac{2}{1 + \frac{1}{H}} e^{(1-H)/2\beta}$	$e^{(1-H)/2\beta}$
$\frac{m_1}{m_0}$	$\frac{\left(1 - \frac{2\beta}{H^2}\right) \sinh \frac{H}{2\beta} + \frac{1}{H} \cosh \frac{H}{2\beta}}{\cosh \frac{H}{2\beta} + \frac{1}{H} \sinh \frac{H}{2\beta}} A$	A	A
when no reaction takes place; $k_v=0$			
m_0	$\frac{1}{(1-\beta + \beta e^{-1/\beta})(1+\eta)}$	$\frac{1}{1+\eta}$	$\frac{1}{1+\eta}$
m_1/m_0			
$H = \sqrt{1 + \frac{24(1-\varepsilon_b)N_{Sh}}{N_{Pe}N_{Sc}N_{Re}}} \left[1 - \frac{1}{1-\gamma + \gamma\phi \coth\phi} \right], \quad A = \frac{1}{H} - \frac{3\eta}{2H} \frac{1 - \frac{1}{2\phi} \sinh 2\phi}{[(1-\gamma)\sinh\phi + \gamma\phi \cosh\phi]^2}, \quad n\text{-th moment, } m_n = (-1)^n \left(\frac{d^n \bar{C}_e}{ds^n} \right)_{s=0}$			

Table 2 Comparison of moments for shell reaction model

Moment	Case 1		Case 2
	General expression	When β is sufficiently small	
m_0	$\frac{e^{1/2\beta}}{\cosh \frac{T}{2\beta} + \frac{1}{T} \sinh \frac{T}{2\beta}}$	$\frac{2}{1 + \frac{1}{T}} e^{(1-T)/2\beta}$	$e^{(1-T)/2\beta}$
$\frac{m_1}{m_0}$	$\frac{\left(1 - \frac{2\beta}{T^2}\right) \sinh \frac{T}{2\beta} + \frac{1}{T} \cosh \frac{T}{2\beta}}{\cosh \frac{T}{2\beta} + \frac{1}{T} \sinh \frac{T}{2\beta}} \Omega$	Ω	Ω
$T = \sqrt{1 - \frac{48(1-\varepsilon_b)}{N_{Pe}N_{Sc}N_{Re}} \frac{D_e}{D_v} \frac{1}{1-\gamma - \frac{1}{\rho_c} \left(1 + \frac{1}{\lambda\rho_c}\right)}}, \quad \Omega = \frac{1}{T} + \frac{\eta}{T} \frac{1 - \frac{3\lambda\rho_c^2}{1+\lambda\rho_c} + \frac{3\lambda^2\rho_c - \lambda^2\rho_c^2 + \lambda\rho_c - 1}{(1+\lambda\rho_c)^2} \rho_c^3}{\left[1 - (1-\gamma) \frac{\lambda\rho_c^2}{1+\lambda\rho_c}\right]^2}$			

$$\gamma \left(\frac{\partial c_i}{\partial \rho} \right)_{\rho=1} = C - (c_i)_{\rho=1} \quad (5)$$

$$C(0, \tau) = \delta(\tau=0) \quad (6)$$

$$\left(\frac{\partial C}{\partial x} \right)_{x=1} = 0 \quad (7)$$

The Laplace transform of the output is obtained as

$$\bar{C}_e = \frac{2\psi e^{1/2\beta}}{\left(\frac{1}{2\beta} + \psi\right) e^\psi - \left(\frac{1}{2\beta} - \psi\right) e^{-\psi}} \quad (8)$$

where

$$\psi = \frac{1}{2\beta} \left[1 + 4\beta \left\{ s + \frac{3\eta}{\kappa\gamma} \right. \right. \\ \left. \left. \times \left(1 - \frac{1}{1-\gamma + \gamma\sqrt{\kappa s + \phi^2} \coth\sqrt{\kappa s + \phi^2}} \right) \right\} \right]^{1/2} \quad (9)$$

For Case 2, instead of Eq.(7) the following boundary condition is to be used.

$$C=0, \text{ at } x=\infty \quad (10)$$

The solution in the Laplace domain is

$$\bar{C}_{e,inf} = e^{(1/2\beta) - \psi} \quad (11)$$

As shown in **Table 1**, the moments for Case 1 are never identical with those for Case 2.

When β is sufficiently small, however, there are no differences in absolute moments between these two cases.

The solution in the time domain is obtained³⁾ by the change of variables in the system of Eqs.(1) to (7),

$$W = C e^{-x/2\beta}, \quad w = c_i e^{-x/2\beta} \quad (12)$$

followed by the Fourier transform

$$G_n = \int_0^1 W \sin \alpha_n x dx$$

$$\text{inverse transform, } W = 2 \sum_{n=1}^{\infty} \frac{\sin \alpha_n x}{1 - \frac{\sin 2\alpha_n}{2\alpha_n}} G_n$$

with similar expression for w , and finally by Laplace transform with regard to τ .

The output is

$$C_e = 2\beta \sum_{n=1}^{\infty} \sum_{j=1}^{\infty} \frac{\alpha_n \sin \alpha_n}{1 - \frac{\sin 2\alpha_n}{2\alpha_n}} \\ \times \frac{(1-\gamma) \sin z_j + \gamma z_j \cos z_j}{A_{n,j} \sin z_j + B_{n,j} \cos z_j} e^{-\{2\beta(z_j^2 + \phi^2)\tau - \kappa\}/2\kappa\beta} \quad (13)$$

$$\text{where } A_{n,j} = 1 - \gamma + \frac{3\eta}{2} + \frac{\kappa\gamma}{2} \left(\frac{1}{4\beta} + \beta\alpha_n^2 - \frac{z_j^2 + \phi^2}{\kappa} \right) \quad (14)$$

$$B_{n,j} = \gamma z_j - \frac{\kappa}{2z_j} \left(\frac{1}{4\beta} + \beta\alpha_n^2 - \frac{z_j^2 + \phi^2}{\kappa} \right) \quad (15)$$

α_n is a root of

$$\tan\alpha_n = -2\beta\alpha_n \quad (16)$$

and z_j is a root of

$$\tan z_j = -z_j \frac{\gamma \left(\frac{1}{4\beta} + \beta\alpha_n^2 - \frac{z_j^2 + \phi^2}{\kappa} \right) + \frac{3\eta}{\kappa}}{(1-\gamma) \left(\frac{1}{4\beta} + \beta\alpha_n^2 - \frac{z_j^2 + \phi^2}{\kappa} \right) - \frac{3\eta}{\kappa}} \quad (17)$$

(B) Shell Reaction Model

This model has been applied to many non-catalyzed solid-gas reactions. Let us consider a bed packed with particles consisting of non-porous unreacted core of radius ρ_c (in non-dimension) and porous ash layer outside the core. Because the amount of injected gas reactant is small, the core radius will be kept unchanged. If the reaction at the core surface is of iso-thermal first order with regard to the gas reactant, the system is expressed as Eq.(1) and

$$\kappa \frac{\partial c_i}{\partial \tau} = \frac{\partial^2 c_i}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial c_i}{\partial \rho}, \quad \text{for } \rho_c < \rho < 1 \quad (18)$$

with Eqs.(3) to (7) and

$$\left(\frac{\partial c_i}{\partial \rho} \right)_{\rho_c} = \lambda(c_i)_{\rho_c} \quad (19)$$

The Laplace transform of the output is

$$\bar{C}_e = 2\Gamma e^{1/2\beta} / \left\{ \left(\frac{1}{2\beta} + \Gamma \right) e^\Gamma - \left(\frac{1}{2\beta} - \Gamma \right) e^{-\Gamma} \right\} \quad (20)$$

where

$$\Gamma = \frac{1}{2\beta} \sqrt{1 + 4\beta \left[s + \frac{3\eta}{\kappa\gamma} (1-b) \right]} \quad (21)$$

$$b = \frac{a + \tanh\sqrt{\kappa s}}{\gamma\sqrt{\kappa s} + a(1-\gamma) + (1-\gamma + a\gamma\sqrt{\kappa s}) \tanh\sqrt{\kappa s}} \quad (22)$$

$$a = \frac{\rho_c\sqrt{\kappa s} - (1 + \lambda\rho_c) \tanh\rho_c\sqrt{\kappa s}}{1 + \lambda\rho_c - \rho_c\sqrt{\kappa s} \tanh\rho_c\sqrt{\kappa s}} \quad (23)$$

For Case 2 the solution in the Laplace domain is

$$\bar{C}_{e,inf} = e^{(1/2\beta) - \Gamma} \quad (24)$$

Similarly to (A), as compared in **Table 2**, there are differences in moments between Case 1 and Case 2.

The solution in the time domain is obtained by the same procedures as before.

$$C_e = 2\beta \sum_{n=1}^{\infty} \sum_{j=1}^{\infty} \frac{\alpha_n \sin\alpha_n}{1 - \frac{\sin 2\alpha_n}{2\alpha_n}} \frac{P_j \sin z_j + Q_j \cos z_j}{U_{n,j} \sin z_j + V_{n,j} \cos z_j} e^{-(2\beta z_j^2 \tau - \kappa)/2\kappa\beta} \quad (25)$$

$$\text{where } P_j = 1 - \gamma - \gamma F_j z_j \quad (26)$$

$$Q_j = \gamma z_j + F_j (1 - \gamma) \quad (27)$$

$$U_{n,j} = P_j + a_{n,j} \left(\frac{\kappa F_j}{2z_j} + \frac{\kappa\gamma}{2} - \gamma q_j z_j \right) + 3\eta \left(\frac{1}{2} - \frac{q_j z_j}{\kappa} \right) \quad (28)$$

$$V_{n,j} = Q_j + a_{n,j} \left[q_j (1 - \gamma) + \frac{\kappa\gamma F_j}{2} - \frac{\kappa}{2z_j} \right] - 3\eta \left(\frac{q_j}{\kappa} - \frac{F_j}{2} \right) \quad (29)$$

$$a_{n,j} = \frac{1}{4\beta} + \beta\alpha_n^2 - \frac{z_j^2}{\kappa} \quad (30)$$

$$F_j = \frac{\rho_c z_j - (1 + \rho_c \lambda) \tan \rho_c z_j}{1 + \rho_c \lambda + \rho_c z_j \tan \rho_c z_j} \quad (31)$$

$$q_j = \frac{\kappa \rho_c}{2z_j} \left[1 - \frac{1 - F_j (\rho_c z_j - \rho_c \lambda \tan \rho_c z_j)}{1 + \rho_c \lambda + \rho_c z_j \tan \rho_c z_j} \right] \quad (32)$$

α_n is a root of Eq.(16), and z_j is a root of

$$\tan z_j = - \frac{a_{n,j} Q_j + \frac{3\eta}{\kappa} (z_j - F_j)}{a_{n,j} P_j - \frac{3\eta}{\kappa} (1 + F_j z_j)} \quad (33)$$

Nomenclature

C	= dimensionless tracer concentration in bulk stream; (concentration)/(amount of tracer input/extraparticle void volume of bed) [—]
C_e	= C at reactor exit [—]
$\bar{C}_e$	= Laplace transform of C_e [—]
c_i	= dimensionless tracer concentration in particle; (concentration)/(amount of tracer input/extraparticle void volume of bed) [—]
D_{ax}	= axial fluid mixing coefficient based on extraparticle void area [cm ² /sec]
D_e	= effective diffusivity in porous solid [cm ² /sec]
D_p	= particle diameter [cm]
D_v	= molecular diffusivity [cm ² /sec]
k_f	= particle-fluid mass transfer coefficient [cm/sec]
k_s	= reaction rate constant for shell reaction model [cm/sec]
k_v	= reaction rate constant for homogeneous reaction model [1/sec]
L	= packed bed height [cm]
m_n	= n -th moment [—]
N_{Pe}	= $D_p U / D_{ax}$ [—]
N_{Re}	= $D_p \epsilon_b U / \nu$ [—]
N_{Sc}	= ν / D_v [—]
N_{Sh}	= $k_f D_p / D_v$ [—]
R	= particle radius [cm]
r	= radial distance variable [cm]
r_c	= radius of unreacted core [cm]
t	= time [sec]
U	= interstitial fluid velocity [cm/sec]
X	= axial distance variable [cm]
x	= X/L [—]
z_j	= root of Eq.(17) or (33) [—]
α_n	= root of Eq.(16) [—]
β	= $1 / N_{Pe} \left(\frac{L}{D_p} \right)$ [—]
γ	= $2 \left(\frac{D_e}{D_v} \right) / N_{Sh}$ [—]
δ	= Kronecker's delta function [—]
ϵ_b	= extraparticle void fraction [—]
ϵ_p	= void fraction in particle for homogeneous reaction [—]

	model or void fraction in ash layer for shell reaction model	[—]	τ	$= Ut/L$	[—]
η	$= \varepsilon_p \frac{1-\varepsilon_b}{\varepsilon_b}$	[—]	ϕ	$= R\sqrt{k_v/D_e}$	[—]
κ	$= \frac{N_{Re}N_{Sc}\left(\frac{\varepsilon_p}{\varepsilon_b}\right)}{4\left(\frac{D_e}{D_v}\right)\left(\frac{L}{D_p}\right)}$	[—]	Literature Cited		
λ	$= k_s R/D_e$	[—]	1) Kubin, M.: <i>Collection Czechoslov. Chem. Commun.</i> , 30 , 1104 (1965); 2900 (1965)		
ν	= kinematic viscosity	[cm ² /sec]	2) Kucera, E.: <i>J. Chromatography</i> , 19 , 237 (1965)		
ρ_s, ρ_c	= r/R , r_c/R , respectively	[—]	3) Wakao, N. and Tanaka, K.: <i>J. Chem. Eng. Japan</i> , 6 , 338 (1973)		