Detection of Flow Maldistribution in Packed-Beds via Tracers

Peter J. Hanratty
Milorad P. Duduković
Chemical Reaction Engineering Laboratory
Washington University
St. Louis, MO 63130

Scaled-up packed-bed reactors (both single- and two-phase flow) sometimes achieve lower than expected yields. The cause usually is either changes in the catalyst activity or gross flow maldistribution. It is important to differentiate between the two so tools for diagnosing flow maldistribution are needed. The most commonly used methods for detecting flow maldistribution utilize tracers (usually responses to impulses of tracers). An impulse tracer study is conducted by injecting a slug of tracer (a detectable fluid which has similar properties to the flowing fluid) into the reactor entrance stream and then measuring the tracer concentration in the reactor effluent vs. time. From the data obtained the residence time density function (E-curve) is obtained, commonly but erroneously called in the chemical engineering literature the residence time distribution (RTD) curve.

The RTD curve for the fluid in a packed-bed reactor reflects the combined history of the fluid flowing external to the porous particles in the reactor bed and the fluid which enters the catalyst pore structure. However, only the response curve of the fluid flowing external to the particles is wanted to determine flow distribution. Particle-tracer interactions usually broaden (seen as an increased variance of the response curve) and shift to longer times the peak of the response curve (chromatography effect). These effects can mask the maldistribution of the flowing liquid, if present, in the observed tracer response curve. The currently used methods for identifying flow maldistribution from tracer data [the intensity function (Naor and Shinnar, 1963), the dimensionless variance of the impulse response curve (Schneider and Smith, 1968), and the cumulative internal RTD function (Robinson and Tester, 1986)] should only be applied to the response curve of the fluid flowing external to the particles. Application of these methods to the overall response curve (the combined effects of the flowing fluid and transport in the porous particles) can and has been shown to lead to faulty and unreliable results (Hanratty, 1988). Therefore, a method is needed to separate the particle effect from the overall response curve of the packed bed in order to establish the response curve of the flowing fluid external to the particles which is needed for accurate assessment of flow maldistribution.

Our objective is to find a reliable method for the identification of the flow pattern of the fluid external to the particles. While ultimately such a method must be confirmed experimentally, only the approach that is robust in presence of experimental error can be expected to work. The goal of this work was to demonstrate that the response of the fluid external to particles can be decoupled from the overall response (i.e., flow plus transport to and in particles) and that the procedure leads to reliable conclusions regarding maldistribution in the presence of simulated errors.

Method for Decoupling External Flow and Transport in Particles

A procedure is presented here for decoupling the particle effects from the external flow effects for an impulse tracer response curve in order to determine the response curve for the fluid external to the particles. From the external $E(t)$ curve, $E_{Ext}(t)$, maldistribution can be readily assessed by applying to it any of the before-mentioned procedures. Since the decoupling procedure is effectively performed using the Laplace transform for briefness we will call it the Laplace Transform method (LT method).

To decouple the particle and flowing fluid effects we view the bulk flowing fluid and the particle phase as two regions which communicate with each other through mass transfer or an exchange coefficient. Assuming a pulse tracer study with a non-volatile (for two-phase flow), reversibly and linearly adsorbing tracer, a mass balance over the tracer in the flowing region gives the following equation:

$$\pounds(C_{TL}) = \epsilon_L \frac{\partial C_{TL}}{\partial t} + k_{ex}(C_{TL} - C_P) \qquad (1)$$

where C_{TL} and C_P are the tracer concentration in the flowing region and the particle region, respectively, ϵ_L is the liquid hold-up, k_{ex} is the exchange coefficient between the two regions, t is the time elapsed since the tracer was injected and $\pounds(C_{TL})$ is a linear differential or algebraic operator modeling the flowing fluid. For example, if the flowing fluid was modeled by the axial dispersion model, $\pounds(C_{TL})$ would take the form:

$$\pounds(C_{TL}) = D_a \frac{\partial^2}{\partial x^2}(C_{TL}) - u_L \frac{\partial}{\partial x}(C_{TL}) \qquad (2)$$

where D_a is the axial dispersion coefficient, u_L is the liquid superficial velocity, and x is the axial distance.

For a pulse tracer study the initial tracer concentration in the reactor is zero and the initial condition for Eq. 1 is:

$$\text{at } t = 0; \quad C_{TL} = C_P = 0 \qquad (3)$$

Equation 1 needs to be supplemented with equations which model the transport of the tracer within the particle region. The exact equations and boundary conditions will depend upon the assumptions used to model the particle. For now, a general particle transfer function, $H(s)$, is defined to simplify the development of the LT method:

$$H(s) = \frac{\overline{C}_{TL} - \overline{C}_P}{\overline{C}_{TL}} \qquad (4)$$

where s is a Laplace domain variable. For example, it has been shown (Ramachandran and Smith, 1983) that for a completely internally- and externally-wetted sphere, the particle transfer function has the form given below:

$$H(s) = \left[1 + \frac{Bi}{\Phi_t}\left(\frac{1}{\coth(3\Phi_T) - 1/(3\Phi_T)}\right)\right]^{-1} \qquad (5)$$

with

$$Bi = \frac{k_{LS}V_P}{D_{\text{eff}}S_x} \qquad (6)$$

$$\Phi_T = \frac{V_P}{S_x}\left[\frac{\epsilon_P s}{D_{\text{eff}}}\left(1 + K\rho_P/\epsilon_P\right)\right]^{1/2} \qquad (7)$$

where S_x and V_P are the external surface area and volume of the particle, respectively, ϵ_P is the particle porosity, ρ_P is the particle density, k_{LS} is the liquid-solid mass transfer coefficient which is equal to $k_{ex}V_P/[S_x(1 - \epsilon)]$, D_{eff} is the effective diffusivity, and K is the adsorption equilibrium constant. Different particle transfer functions, useful for trickle-bed studies, are given by Beaudry (1986).

Taking the Laplace transform of Eq. 1 and eliminating $\overline{C}_P$ by using Eq. 4 gives:

$$\pounds(\overline{C}_{TL}) = \epsilon_L s \overline{C}_{TL} + k_{ex}H(s)\overline{C}_{TL}$$

$$= \epsilon_L(s + k_{ex}H(s)/\epsilon_L)\overline{C}_{TL} \qquad (8)$$

where s is the Laplace domain variable. We will consider this as general case (case 1) for any tracer.

Now consider the case of an injected pulse of tracer that does not interact with the particle region ($k_{ex} = 0$). Assume that the tracer cannot penetrate into the particle. This, although hard to realize in practice, represents a useful limiting case 2. This tracer would trace only the fluid region external to the particles. A mass balance over the tracer in the flowing fluid region gives

$$\pounds(C_{TL}) = \epsilon_L \frac{\partial C_{TL}}{\partial t} \qquad (9)$$

In the Laplace domain that becomes

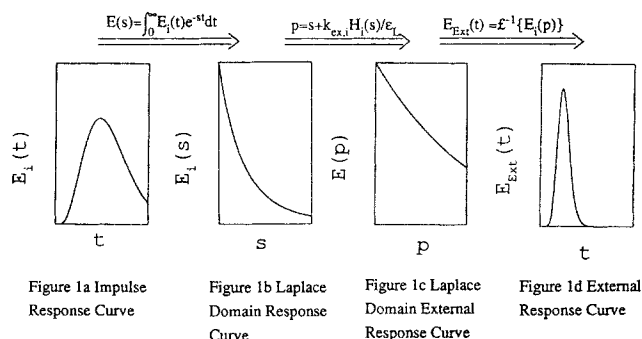$$\pounds(\overline{C}_{TL}) = \epsilon_L p \overline{C}_{TL} \qquad (10)$$

where p is the new Laplace domain variable. Since the same linear operator, $\pounds(\overline{C}_{TL})$, is applied to the tracer concentration in both Eqs. 8 and 10 (cases 1 and 2), p can be related to s by:

$$p = s + k_{ex}H(s)/\epsilon_L \qquad (11)$$

Therefore, Eq. 10 can be obtained from Eq. 8, provided Eq. 11 is satisfied. This means that, in order to get the transfer function (i.e., Laplace domain impulse response) of the flowing fluid region external to the particles, when using tracers which adsorb and penetrate the particle (case 1), $E(p)$ must be obtained as a function of p. In other words, s must be transformed to p by Eq. 11. One should note that $H(s)$ and k_{ex} depend on the tracer used.

Figure 1 demonstrates how the external response curve can be determined from the overall response curve using the LT method. First, an impulse tracer study is conducted to get the $E_i(t)$ curve, Figure 1a, for the ith tracer. Second, the $E_i(t)$ curve is transformed to the Laplace domain to get $E_i(s)$, Figure 1b. Third, the coordinate system is transformed (s-axis to the p-axis) by Eq. 11, Figure 1c. Finally, the $E(p)$ curve is inverted back to the time domain to give the $E_{\text{Ext}}(t)$ curve, Figure 1d. It should be noted that the method works for all tracers $i = 1, 2 \ldots N$. For each tracer, the same $E_{\text{Ext}}(t)$, and therefore $E(p)$ is obtained. However, each tracer may have a different $k_{ex,i}$ and $H_i(s)$ to be used in Eq. 11.

One limitation to this method is that it assumes that the tracer enters and exits the particle at the same point in the reactor. The requirement for Eq. 11 to hold is that the covariance of the joint

$$E(s) = \int_0^\infty E_i(t)e^{-st}dt \qquad p = s + k_{ex,i}H_i(s)/\epsilon_L \qquad E_{\text{Ext}}(t) = \pounds^{-1}\{E_i(p)\}$$

Figure 1a Impulse Response Curve

Figure 1b Laplace Domain Response Curve

Figure 1c Laplace Domain External Response Curve

Figure 1d External Response Curve

Figure 1. Procedure for the decoupling of the external fluid age distribution from the overall response by the LT method.

probability density function for the sojourn in the particle and external flow region is zero (Aris, 1982). This means that the tracer cannot enter a particle at one point then exit the particle either upstream or downstream of that point. This assumption should be a very good approximation if the ratio of the reactor length to the particle diameter is large. This is the case in almost all (if not all) packed-bed reactors.

The idea behind the procedure outlined above is not new. The mathematics of RTD curves in heterogeneous (multiregion) systems has been thoroughly discussed by Aris (1982), Villermaux (1981), and Duduković (1986). The methodology which was fully developed and presented here was suggested by Shinnar and Rumschitzki (1984) and Ramachandran et al. (1986) among others. It is worth noting that early on Shinnar et al. (1972) developed a more general approach of which the above procedure, leading to Eq. 11, may be seen as a subcase. However, there is an important difference between this work and their study. Shinnar et al. (1972) concentrated on biomedical applications where the impulse response of substances confined to blood [equivalent to our $E_{\text{Ext}}(t)$] can be obtained directly by experiment as well as responses of tracers that spread into extravascular space leading to $E_i(t)$, $i = 1, \ldots N$. Shinnar et al. (1972) then developed the procedures for investigating transport parameters from the measured $E_i(t)$ and $E_{\text{Ext}}(t)$. Here we address the problem of getting $E_{\text{Ext}}(t)$ in systems where it cannot be measured directly but $E_i(t)$ for different tracers can be obtained and transport parameters can be estimated. We are thus solving the difficult inverse problem of getting $E_{\text{Ext}}(t)$ given $E_i(t)$. Regarding this problem, Shinnar et al. (1972) wrote "these transforms might be useful in studying specific models of the system, but since we know them only for real s, we would be faced with a rather delicate numerical job if we wanted simply to invert them to find the appropriate functions of t." We show here how this can be done. Full implementation of the procedure outlined here and presented below has not been demonstrated, to our knowledge, in the open literature.

Generation of the $E_{\text{Ext}}(t)$ Curves

The first logical step in the testing of the LT method is to apply it to computer-generated tracer response curves with significant added simulated experimental error. Therefore, it is necessary to generate overall response curves that have a known external flow response curve. To generate the overall response curves, the LT method was reversed. To mimic actual response curves, random and/or periodic error were added to the generated $E_i(t)$ curves.

First, a known flow model was chosen to describe the external flow. Two different flow models were utilized to mimic a near-ideal flow and a maldistributed reactor. To generate near-ideal flow reactor conditions, 15 CSTR's in series were used to model the external response curve:

$$E_{\text{Ext}}(t) = \frac{t^{14}}{14! \tau^{15}} \exp\left(-t/\tau\right) \quad (12)$$

In the Laplace domain this becomes

$$E(p) = \frac{1}{(\tau p + 1)^{15}} \quad (13)$$

where p is the Laplace transform variable and τ is the space time of a single CSTR.

To generate the maldistributed reactor response curves, ten CSTR's (20% of the overall flow) in parallel to five CSTR's (80% of the overall flow) were used to model the external response curve. In the Laplace domain the external response curve is

$$E(p) = \frac{0.8}{(\tau_1 p + 1)^5} + \frac{0.2}{(\tau_2 p + 1)^{10}} \quad (14)$$

where τ_1 and τ_2 are the space times for a single CSTR in each branch. The ratio of τ_1/τ_2 is kept constant at 2.5.

The overall transfer function, $E_i(s)$, for each assumed tracer is calculated as follows. A value for s is assumed, from which a corresponding value for p is determined by Eq. 11. Then $E(p)$ is calculated by Eq. 13 or 14. Equation 5 was used for the particle transfer function. To simulate different tracers, the values of $0.0, 4 \cdot 10^{-4}, 1 \cdot 10^{-3}$ (m³ liquid/kg particle) were used for the adsorption equilibrium constant. For this study the effective diffusivity was kept constant. The physical properties used for the particle model are shown in Table 1 and were taken from actual data (Beaudry, 1986).

The $E(s)$ curve was inverted to the time domain to give the overall $E_i(t)$ curve. The IMSL subroutine DINLAP was used. To introduce simulated experimental error, random and/or periodic error of maximum magnitude δ_c [a value between 0–4% of the maximum $E(t)$ value] were added to the overall response curve. The random error added can be described by:

$$\text{error} = \delta_c R_N \quad (15)$$

where R_N is a random number distributed evenly between -1 and 1, generated by the IMSL subroutine DRNUN. Note that this represents the worst scenario for random error. The added periodic error is:

$$\text{error} = \delta_c \sin\left(\omega t\right) \quad (16)$$

where ω is the period of the added error. Figures 2 and 3 illustrate the computer-generated overall $E_i(t)$ curves for the three tracers with superimposed error for both the near-ideal and the maldistributed reactor flow configurations, respectively.

The tail of the generated response curve becomes unknown because the added error becomes larger than the magnitude of the values for the response curve. Therefore, an assumption is required for the shape of the tail of the response curve. An exponentially decaying tail has been suggested to produce the best results (Robinson and Tester, 1986). When the tail of the $E_i(t)$ curve reaches a value less than δ_c (maximum magnitude of the added error), the response curve is truncated and approximated

Table 1. Physical Parameters for Computer Simulation

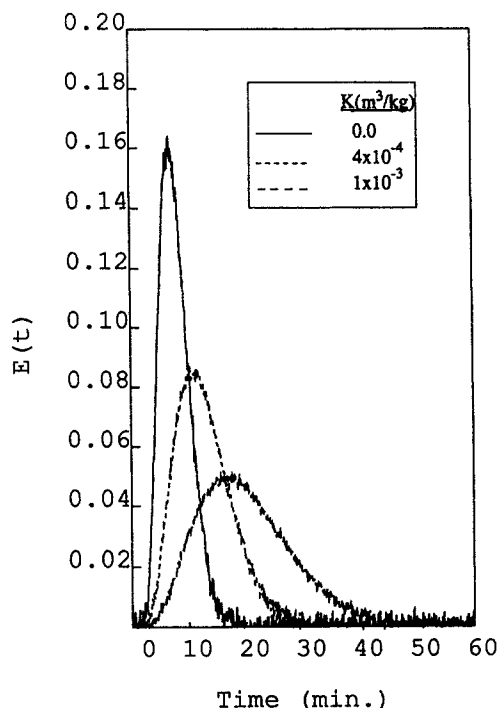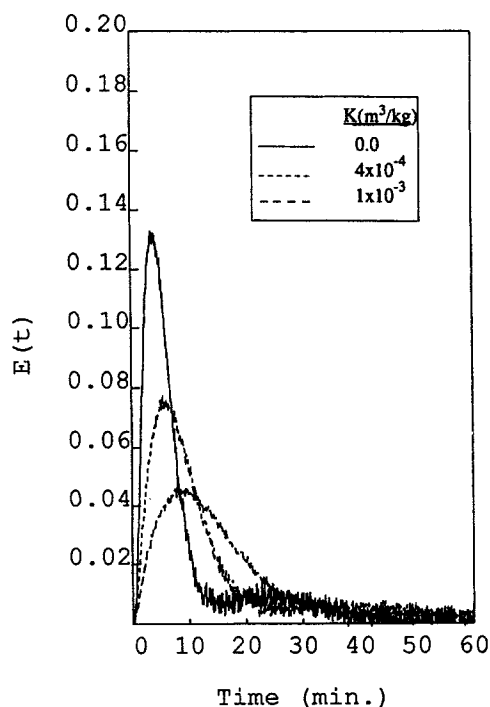| Catalyst Diameter (m)	$1.6 \cdot 10^{-3}$
Catalyst Density (kg/m³), ρ_P	1,250
Catalyst Porosity, ϵ_P	0.408
Bed Porosity, ϵ	0.54
Liquid Holdup, ϵ_L	0.174
Liquid-Solid Mass Trans. Coeff., k_{LS} (m/s)	$2.5 \cdot 10^{-5}$
Effective Diffusivity, D_{eff} (m²/s)	$1.06 \cdot 10^{-9}$

Figure. 2. Overall impulse tracer responses with superimposed simulated error for near-ideal reactor.

by an exponentially decaying tail. The equation for the tail is:

$$E(t) = E(t_f) \, exp\left[\frac{-E(t_f)}{\gamma} (t - t_f)\right] \qquad (17)$$

where $E(t_f)$ and t_f are the value of $E(t)$ and the time at which the tail is exponentially extrapolated, and γ is defined by the requirement that the mass balance for the tracer be satisfied:

$$\gamma = 1 - \int_0^{t_f} E(t)dt \qquad (18)$$

Results and Discussion

For the near-ideal flow reactor, the LT method was tested for the overall response curves with 4% imposed error, for each of the three K values. It was assumed that the correct particle transfer function and parameter values were known. Figure 4 demonstrates that in the presence of experimental error the LT method predicts the correct $E_{Ext}(t)$. Figure 4 also illustrates that the LT method will predict the correct $E_{Ext}(t)$ for all K values, i.e., all tracers.

For the maldistributed reactor response curves with 4% imposed error, the LT method again was shown to closely approximate the correct $E_{Ext}(t)$ for all tracers (all K values), as illustrated in Figure 5. From Figure 5, it easily can be seen that the reactor is maldistributed.

The intensity function and the cumulative internal RTD curve method when applied to $E_{Ext}(t)$ predict that the reactor of Figure 4 is a well distributed and the reactor of Figure 5 is not.

Figure 3. Overall impulse tracer responses with superimposed simulated error for the maldistributed reactor.
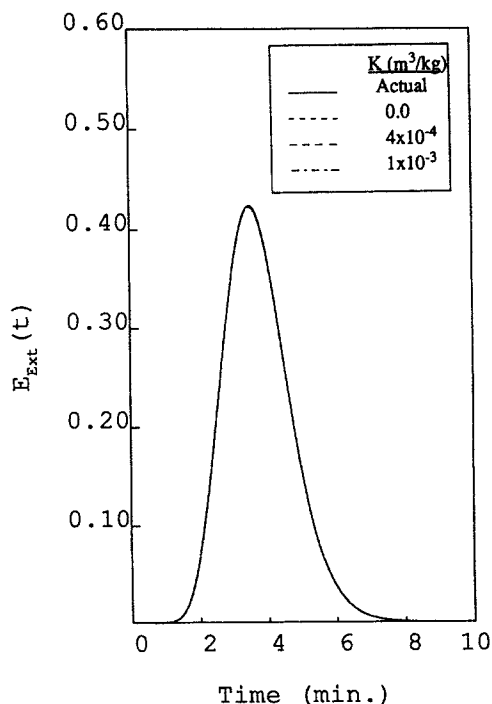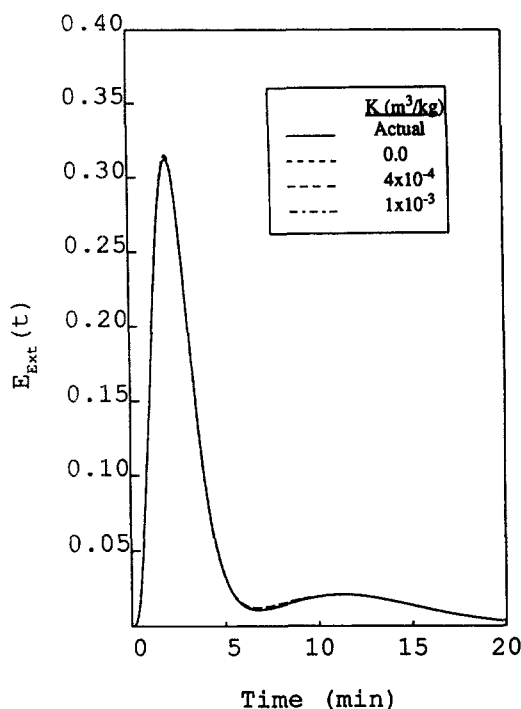

Figure 4. Actual external fluid age distribution for the near-ideal reactor and model predictions obtained by the LT method from the overall impulse responses vs. simulated error for three tracers of different adsorbtivity.

Figure 5. Actual external fluid age distribution for the maldistributed reactor and model predictions obtained by the LT method from the overall impulse tracer responses vs. simulated error for three tracers of different adsorbtivity.

Thus it can be claimed that the LT method predicts the correct $E_{Ext}(t)$ curve in the presence of experimental error if the correct particle model and parameter values are known. The major disadvantage of the LT method is that the particle model and parameter values (k_{LS}, D_{eff}, K) need to be determined experimentally. The correct particle model can be determined for a particular catalyst particle by the following procedure. Tracer studies with tracers with different adsorption equilibrium constants should be conducted and the LT method applied. If the same $E_{Ext}(t)$ curve is produced for each of the tracers, then the correct particle model has been determined. The particle parameter values also can be determined experimentally for each particle-tracer pair since their values are particle-tracer-dependent. Therefore, the LT method offers a procedure which will give the entire $E_{Ext}(t)$ curve for wide range of reactor conditions at the cost of additional experimental work.

Acknowledgment

Notation

Bi = modified Biot number defined by Eq. 6
C_P = concentration of tracer at the particle-flowing fluid interface, mol/m^3
C_{TL} = concentration of the tracer in the flowing fluid, mol/m^3
D_a = axial dispersion coefficient, m^2/s
D_{eff} = effective diffusivity, m^2/s
$E(t)$ = residence time distribution curve (density function), s^{-1}
$E(t_f)$ = value of the response curve at which its tail is extrapolated, s^{-1}

$E_{ext}(t)$ = external residence time distribution curve (density function), s^{-1}
$H(s)$ = particle transfer function
K = adsorption equilibrium constant, m^3/kg
k_{ex} = mass exchange coefficient, s^{-1}
k_{LS} = solid-liquid mass transfer coefficient, m/s
p = Laplace transform variable, s^{-1}
R_N = random number evenly distributed between -1 and 1
s = Laplace transform variable, s^{-1}
S_x = external particle surface area, m^2
t = time, s
t_f = cutoff time at which the response curve is exponentially extrapolated, s
u_L = superficial liquid velocity, m/s
V_p = particle volume, m^3
x = axial distance, m

Greek letters

δ_c = maximum magnitude of the added error
ϵ = bed porosity
ϵ_L = liquid holdup
ϵ_P = particle porosity
$\Phi_t(t)$ = modified Thiele modulus defined by Eq. 7
γ = variable defined by Eq. 18
ρ_P = particle density, kg/m^3
τ = mean residence time, s
τ_1 = mean residence time of a single CSTR in a branch of the maldistributed reactor model, s
τ_2 = mean residence time of a single CSTR in a branch of the maldistributed reactor model, s
ω = period of periodic error, s^{-1}

Other

$\mathcal{L}()$ = linear operator for the flowing fluid

Literature Cited

Aris, R., "Residence Time Distribution with Many Reactors and in Several Environments," *Residence Time Distribution Theory in Chemical Engineering*, A. Petho and R. D. Noble, and V. Weinheim, eds., Verlag-Chemie (1982).

Beaudry, E. G., "Modelling of Trickle-Bed reactors at Low Liquid Flow Rates," D. SC. Diss., Washington Univ., St Louis (1987).

Dudukovič, M. P., "Tracer Methods in Chemical Reactors. Techniques and Applications," *Chemical Reactor Design and Technology*, H.I. de Lasa, eds., NATO ASI Series E N0110, Martinus Nijhoff, Dordrecht (1986).

Hanratty, P. J., "Dynamic Modelling of Trickle-Bed Reactors," Masters Thesis, Washington Univ., St. Louis (1988).

Naor, P., and R. Shinnar, "Representation and Evaluation of Residence Time Distributions," *I&EC Fund.*, **2**, 278 (1963).

Ramachandran, P. A., M. P. Dudukovič, and P. L. Mills, "A New Model for Assessment of External Liquid-Solid Contacting in Trickle-Bed Reactors from Tracer Response Measurements," *Chem. Eng. Sci.*, **41**, 855 (1986).

Ramachandran, P. A., and J. M. Smith, "Effectiveness Factors in Trickle-Bed Reactors," *AIChE J.*, **28**, 190 (1982).

Robinson, B. A., and J. W. Tester, "Characterization of Flow Maldistribution Using Inlet-Outlet Tracer Techniques: An Application of Internal Residence Time Distributions," *Chem. Eng. Sci.*, **41**, 469 (1986).

Schneider, P., and J. M. Smith, "Adsorption Rate Constants From Chromatography," *AIChE J.*, **14**, 762 (1968).

Shinnar, R., P. Naor, and S. Katz, "Interpretation and evaluation of multiple tracer experiments," *Chem. Eng. Sci.*, **27**, 1627 (1972).

Shinnar, R., and D. Rumshitzki, "Residence Time Distribution in Heterogeneuous Reactor Modelling Scale-up," AIChE Meeting, San Francisco, paper 139b (Nov., 1984).

Villermaux, J., "Theory of Linear Chromatography," *Percolation Processes: Theory and Application*. A. E. Rodrigues and D. Tondeur, eds., Sijthoff and Noordhoof, Alphen a.d. Rijn, Netherlands (1981).