

Representation of Breakthrough Curves for Fixed-Bed Adsorbers and Reactors using Moments of the Impulse Response

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Abstract

An approximate expression for breakthrough curves (step responses) in isothermal packed-bed adsorbers and reactors is obtained by using the first two moments of the impulse response in a leading term of a Laguerre polynomial series expansion. The approximation is expressed in terms of an incomplete gamma function which can readily be obtained either by Romberg integration or from tabulated values. The approximation agrees well with analytical solutions for both long and short packed-beds. It is shown that the leading term of the Laguerre series is a better approximation to analytical solutions for short beds than the Hermite polynomial expansion and is at least equal to the latter in case of long columns.

INTRODUCTION

Evaluation of breakthrough curves is important in predicting the desired adsorption-regeneration cycle time for fixed-bed adsorbers, in assessing the start-up and dynamics of fixed-bed reactors and in scale-up procedures of laboratory or pilot plant data. A model for the adsorber or reactor is generally postulated, its parameters estimated either *a priori* or from bench, pilot or plant scale data; and the solution to the model, subject to step input in the feed, is obtained analytically or by numerical means. A number of elegant analytical solutions for various basic models of fixed-bed adsorption have been reported in the literature [1 - 3], among them the pioneering work of Amundson [4, 5] and Vermeulen and co-workers [3, 6, 7]. The adsorption diffusion phenomena in solid

particles are examined in detail in these models but plug flow is most frequently assumed for the fluid flow pattern. When the dispersion phenomena in the bed are coupled with inter- and intra-particle diffusion, adsorption and reaction in solid particles, the models become more complex and analytical solutions are rarely reported. However, the moments of the impulse response can be evaluated for linear systems as shown by Smith and co-workers [8, 9]. Moment analysis is often used for parameter estimation [8, 9] *i.e.* the unknown parameters are evaluated from the calculated moments for the experimentally obtained curves since the first few moments of the impulse response usually contain all the parameters of the system (dispersion coefficient, diffusivity, adsorption and reaction rate constants, *etc.*).

As already mentioned, some of the models for fixed-bed adsorbers and reactors are rather complex. Analytical solutions are sometimes feasible but they are frequently expressed in terms of slowly convergent series or contain higher transcendental functions which have to be evaluated numerically *via* proper sub-routines. Numerical solutions are always possible but frequently different numerical schemes and special algorithms have to be used for different models in order to guarantee convergence and accuracy. Thus, it is desirable to have a method which allows a rapid computation of breakthrough curves for any model of a fixed-bed and uses systematically the same features of the solution in computing the approximation. Since the moments of the impulse response are generally available in terms of the parameters of the model an approximation that utilizes the moments is of particular interest. Such an approach was suggested by Razavi *et al.* [10].

The objective of this paper is to demonstrate that an approximation which utilizes the moments of the impulse response can be obtained in terms of a Laguerre polynomial series expansion of the impulse response. It is desired to show that the leading term of such a series, containing only the first two moments, leads to a good approximation of analytical solutions. Finally, this approximation will be compared to the one obtained by expanding the impulse response in a series of Hermite polynomials as suggested by Razavi *et al.* [10].

DEVELOPMENT OF THE APPROXIMATION

This development extends the approach of Hulburt and Katz [11] used in representation of probability density functions of crystal sizes to approximations of impulse and step responses. A concentration impulse response can be represented by the following series:

$$C_\delta(t) = \frac{b}{a} p^b \left(\frac{b}{a} t\right) \sum_{n=0}^{\infty} k_n L_n^b \left(\frac{b}{a} t\right) \quad (1)$$

where:

$$p^b(\tau) = \tau^{b-1} e^{-\tau} / \Gamma(b) \quad (2)$$

$$L_n^b(\tau) = \sum_{i=0}^n (-1)^i \frac{n! \Gamma(n+b) \tau^{n-i}}{i! (n-i)! \Gamma(n+b-i)} \quad (3)$$

The Laguerre polynomials $L_n^b(\tau)$, as defined by eqn. (3), are orthogonal on the interval $(0, \infty)$ with respect to the weighting function $p^b(\tau)$.

$$\int_0^{\infty} p^b(\tau) L_m^b(\tau) L_n^b(\tau) d\tau = \frac{n! \Gamma(n+b)}{\Gamma(b)} \delta_{mn} \quad (4)$$

where δ_{mn} is the Kronecker delta. Since an actual impulse response in chemical engineering systems is defined only on the interval $(0, \infty)$, one would expect that the Laguerre polynomials would provide a uniformly better approximation than the Hermite polynomials which are orthogonal on the interval $(-\infty, \infty)$.

The absolute moments of the concentration impulse response are defined by eqn. (5) where the term on the right hand side of the second equality sign represents convenient means for evaluation of the moments from

the transfer function of the system (Laplace transform of the impulse response) in terms of system parameters.

$$M_n = \int_0^{\infty} t^n C_\delta(t) dt = (-1)^n \left. \frac{d^n \bar{C}_\delta(s)}{ds^n} \right|_{s=0} \quad (5)$$

for $n = 0, 1, 2, \dots$

The constants k_n are evaluated by requiring that the series given by eqn. (1) matches the impulse response best in the least squares sense *i.e.* by minimizing the sum of the squares of the errors with respect to the proper choice of the constants k_n .

$$k_n^{\min} \int_0^{\infty} \left[C_\delta(t) - \frac{b}{a} p^b \frac{bt}{a} \sum_{m=0}^{\infty} k_m L_m^b \left(\frac{bt}{a}\right) \right]^2 dt \quad (6)$$

This results in the following linear equations:

$$\int_0^{\infty} \left[C_\delta(t) - \frac{b}{a} p^b \frac{bt}{a} \sum_{m=0}^{\infty} k_m L_m^b \left(\frac{bt}{a}\right) \right] L_n^b \frac{bt}{a} dt = 0 \quad (7)$$

for $n = 0, 1, 2, \dots$

These linear equations by virtue of the orthogonality property given by eqn. (4) are reduced to:

$$\int_0^{\infty} C_\delta(t) L_n^b \frac{bt}{a} dt = k_n \frac{n! \Gamma(n+b)}{\Gamma(b)} \quad (8)$$

$n = 0, 1, 2, \dots$

Making use of eqns. (3) and (5) the series coefficients are evaluated in terms of the moments of the impulse response:

$$k_n = \sum_{i=0}^n \frac{(-1)^i \Gamma(b) (b/a)^{n-i}}{i! \Gamma(n+b-i) (n-i)!} \quad (9)$$

$n = 0, 1, 2, \dots$

The constants a and b are now selected in such a manner as to postpone making the corrections to the leading term for as long as possible by making $k_1 = k_2 = 0$. This yields:

$$a = \frac{M_1}{M_0} = \mu_1 \quad (10)$$

$$b = \frac{(M_1/M_0)^2}{(M_2/M_0) - (M_1/M_0)^2} = \frac{\mu_1^2}{\sigma^2} \quad (11)$$

The approximation to the normalized impulse response $C_\delta^*(t) = C_\delta(t)/M_0$ can be written as:

$$C_\delta^*(t) = \left(\frac{b}{a}\right)^b \frac{t^{b-1} e^{-bt/a}}{\Gamma(b)} \times \left\{ 1 + \sum_{n=3}^{\infty} k_n^* L_n^b \left(\frac{b}{a} t\right) \right\} \quad (12)$$

with a and b being defined by eqns. (10) and (11) respectively and k_n^* being defined by eqn. (9) with μ_{n-i} replacing M_{n-i} .

The approximation to the step response (breakthrough curve) is obtained by using the convolution integral of the impulse response

$$C_u^*(t) = \int_0^t C_\delta^*(\tau) d\tau = P\left(\frac{\mu_1^2}{\sigma^2}, \frac{\mu_1}{\sigma^2} t\right) + \sum_{n=3}^{\infty} k_n \sum_{i=0}^n \frac{(-1)^i n! \Gamma(n+b)}{i! (n-i)! \Gamma(b)} P\left(b+n-i, \frac{b}{a} t\right) \quad (13)$$

where $P(c, x)$ is the incomplete gamma function [12] defined as:

$$P(c, x) = \frac{1}{\Gamma(c)} \int_0^x \tau^{c-1} e^{-\tau} d\tau = 1 - \frac{1}{\Gamma(c)} \int_x^{\infty} \tau^{c-1} e^{-\tau} d\tau \quad (14)$$

Expression (13) at first sight does not seem to offer a particular advantage since it contains a series of incomplete gamma functions which are not as extensively tabulated as, for example, error functions. However, only the leading term of the series is required for a simplified approximation:

$$C_u^*(t) \approx P\left(\frac{\mu_1^2}{\sigma^2}, \frac{\mu_1}{\sigma^2} t\right) = P\left(b, \frac{b}{a} t\right) \quad (15)$$

This expression is advantageous in that only the parameters that affect the first and second moments of the impulse response are required to approximate the breakthrough curve of any particular model. Expression (15) represents a generalization of the step response for the tank in series model.

In evaluating $P(b, tb/a)$ required by expression (15) tabulated values of $\Gamma(b)$ can be used [12]. The asymptotic expansion for $\ln \Gamma(b)$ is particularly useful in evaluating $\Gamma(b)$ for large values of the argument. Upon change of variables Romberg integration can be used to evaluate the integrals in eqn. (14). For large values of $x = tb/a$ and $c = b$, the second form of eqn. (14) should be used. Once programmed the evaluation of incomplete gamma function $P(a, tb/a)$ can be accomplished with sufficient accuracy using a hand calculator of the TI-59 or HP-67 type.

It should be noted that polynomial expansions and moments have also been used along similar lines to those presented in this paper in a variety of chemical engineering areas and in particular in the applications of the theory of chromatography [13] and in numerical inversion of Laplace transforms [14].

RESULTS AND DISCUSSION

To illustrate the utility of eqn. (15) in predicting breakthrough curves, this approximation is compared to the analytical solutions for two selected examples. The case of interphase mass transfer in a plug flow packed-bed adsorber is considered first followed by the transient response of the axial dispersion model for a packed-bed reactor with first order reaction. The parameter values selected by Razavi *et al.* [10] are used in order to also compare the present approximation with the one based on a series of Hermite polynomials.

Packed-bed adsorber — plug flow with interphase mass transfer

This case has been studied extensively in the literature [16, 17] and the analytical solution is presented in terms of Goldstein J functions [17]. Using the notation of Razavi *et al.* [10], which is described in the Nomenclature, one can show that the parameters for evaluation of the incomplete gamma function are:

$$a = \frac{z}{v} \left(1 + \frac{k'}{mk}\right); \quad b = \frac{z}{2vk'} (mk + k')^2 \quad (16)$$

In Fig. 1 the comparison between the exact solution, the leading term of the Hermite polynomial approximation and of the

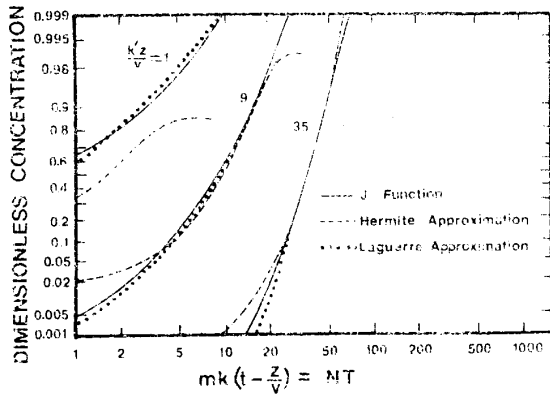


Fig. 1. Comparison of the approximate solutions with the analytical solution for the adsorber.

Laguerre approximation (eqn. (15)) is shown. It is apparent that eqn. (15) gives a good representation of the exact solution even at small values of the Stanton number, $k'z/v$, (corresponding to a short column) in contrast to the Hermite polynomial approximation. This is not surprising since the leading term of eqn. (12) can readily approximate non-symmetrical functions. At higher values of $k'z/v$ both approximations are very good with eqn. (15) being slightly more accurate. In this situation the impulse response is symmetric and the leading term of both approximations predicts it accurately. In Fig. 2 the breakthrough curve for a short column is illustrated. The exact solution of the model is compared to the leading term of the Laguerre series (incomplete gamma function) and to the leading term of Hermite series (error function). The J-function predicts no response until the mean transit time is reached. The incomplete gamma function predicts the start of the

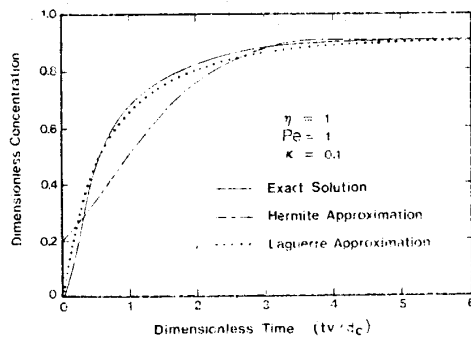


Fig. 2. Approximate and analytical breakthrough curves for the adsorber.

response to occur at time $t = 0$. The Hermite polynomial approximation predicts that some of the response has occurred before $t = 0$ when the step input was made. This paradox is caused by the interval of orthogonality for Hermite polynomials and the error is significant for short columns like the one considered here in Fig. 2.

Fixed-bed reactor — dispersion model with first order reaction

This case has also been studied extensively in the literature [18, 19]. The parameters a and b can now be evaluated in terms of the moments for the dimensionless concentration response which is a function of dimensionless time $\tau = vt/d_c$ and dimensionless distance $\eta = z/d_c$

$$a = \eta \left(1 + \frac{4\kappa}{Pe} \right)^{1/2}, \quad b = \frac{\eta Pe}{2} \left(1 + \frac{4\kappa}{Pe} \right)^{1/2} \quad (17)$$

It should be noted that Peclet number is based on column diameter in order to compare directly the results with those of Razavi *et al.* [10] rather than on particle diameter or bed length which is customary. Figure 3 represents the step response of a short bed (length equal to diameter) with relatively large degree of backmixing and low particle Peclet number. In this situation the leading term of the Laguerre series is a superior approximation. In case of very small degree of backmixing, which is equivalent to having a longer bed, both approximations match the analytical solution extremely well as shown in Fig. 4.

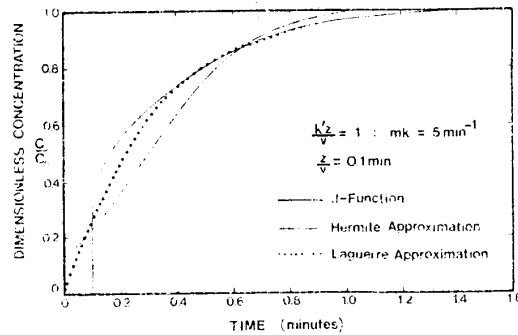


Fig. 3. Approximate and analytical breakthrough curves for the dispersion model (large backmixing).

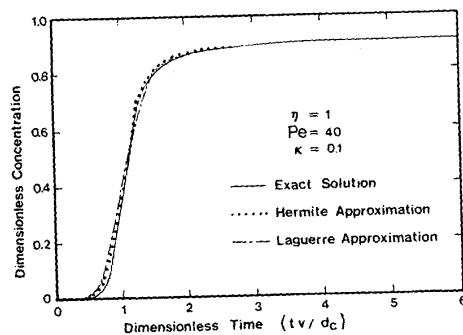


Fig. 4. Approximate and analytical breakthrough curves for the dispersion model (small backmixing).

CONCLUSIONS

The representation of an impulse response by a leading term of a series of Laguerre polynomials results in an approximation for the breakthrough curve (step response) in terms of an incomplete gamma function. This approximation contains only the first and second normalized moments of the impulse response and can be computed based on the knowledge of parameters which determine these moments. The approximation is adequate for various models of fixed-bed adsorbers and reactors for all bed lengths. Its advantage over an approximation based on a series of Hermite polynomials is particularly apparent for short beds.

NOMENCLATURE

a	constant defined by eqn. (10), s
b	constant defined by eqn. (11), dimensionless
C	concentration in the effluent as a result of a step input, mol cm ⁻³
C_0	concentration in the feed, mol cm ⁻³
C_δ	concentration in the effluent as a result of an impulse injection in the feed (impulse response), mol cm ⁻³
C_δ^*	normalized impulse response, s ⁻¹
\bar{C}_δ^*	Laplace transform of the normalized impulse response, dimensionless
C_u^*	= C/C_0 , normalized step response, dimensionless
d_c	column diameter, cm
D	dispersion coefficient, cm ² s ⁻¹
k	mass transfer coefficient based on area

	per unit volume of the flowing phase, s ⁻¹
k'	mass transfer coefficient based on area per unit volume of the stationary phase, s ⁻¹
k_r	first order reaction rate constant based on unit reactor volume, s ⁻¹
k_n	coefficients in the series of Laguerre polynomials defined by eqn. (9), mol cm ⁻³ s
k_n^*	normalized coefficients of the Laguerre polynomial series, s
$L_n^b(\tau)$	Laguerre polynomials defined by eqn. (3)
m	linear adsorption equilibrium constant, dimensionless
M_n	n th moment of the concentration impulse response defined by eqn. (5), mol cm ⁻³ s ⁿ⁺¹
$p^b(\tau)$	weighting function defined by eqn. (2)
$P(c, x)$	incomplete gamma function defined by eqn. (16)
Pe	Peclet number based on column diameter, vd_c/D , dimensionless
s	Laplace transform variable, s ⁻¹
t	time, s
\bar{t}	mean residence time, s
v	interstitial velocity of the fluid, cm s ⁻¹

Greek symbols

$\Gamma(b)$	gamma function
δ_{mn}	Kronecker delta
η	dimensionless axial position z/d_c
κ	= $k_r d_c/v$, Damköhler number for first order reaction, dimensionless
μ_n	n th moment of the normalized impulse response, M_n/M_0 , s ⁿ
σ^2	variance of the normalized impulse response, s ²
τ	dimensionless time

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