Prediction of Breakthrough Curves by the Application of Fast Fourier Transform

Teh-Liang Chen, J. T. Hsu
Department of Chemical Engineering
Lehigh University
Bethlehem, PA 18015

The fast Fourier transform (FFT) was discovered by Cooley and Tukey (1965) to compute the Fourier integral. The most popular areas of its applications have been spectral analysis and digital signal processing. Fast Fourier transform is also a powerful method of numerical inversion of Laplace transform. Villermaux (1974) used this method to calculate chromatographic peaks. Hsu (1979) and Hsu and Dranoff (1987) described in detail the application of this method to invert certain Laplace transforms. The purpose of the present work is to show how this method can be applied to the prediction of breakthrough curves of a fixed-bed adsorber, and how powerful this method is by comparing the accuracy and computation time with the exact analytical solution and the orthogonal collocation method.

Mathematical Model and Method

We consider the fixed-bed adsorber model of Rasmuson and Neretnieks (1980) to describe an isothermal adsorption column packed with porous spherical particles of radius b. At time zero, a step change in the concentration of an adsorbable species was introduced to the flowing stream. The adsorption column was subjected to axial dispersion, pore diffusion resistance, and external film diffusion resistance. After introducing dimensionless groups as in the work of Raghavan and Ruthven (1983), the fixed-bed adsorber can be described by the following set of equations:

Mass balance in the flowing phase:

$$\frac{\partial U}{\partial \tau} + \psi\theta\frac{\partial U}{\partial x} - \frac{1}{P_e}\psi\theta\frac{\partial^2 U}{\partial x^2} = -3\psi\xi\left(U - \frac{Q|_{\eta=1}}{K}\right) \tag{1}$$

Particle diffusion:

$$\frac{\partial Q}{\partial \tau} = \frac{\partial^2 Q}{\partial \eta^2} + \frac{2}{\eta}\frac{\partial Q}{\partial \eta} \tag{2}$$

Initial and boundary conditions:

$$U(x, \tau = 0) = 0 \tag{3}$$

$$U(x = 0, \tau) = 1 \tag{4}$$

$$U(x = \infty, \tau) = 0 \tag{5}$$

$$Q(\eta, x, \tau = 0) = 0 \tag{6}$$

$$Q(\eta = 0, x., \tau) \neq \infty \tag{7}$$

$$\frac{1}{K}\frac{\partial Q}{\partial \eta}\bigg|_{\eta=1} = \xi\left(U - \frac{Q|_{\eta=1}}{K}\right) \tag{8}$$

where $U = C/C_0$. $Q = C_p/C_0$, $x = z/L$, $\tau = Dt/b^2$, $\eta = r/b$, $\psi = K/m$, $\theta = Vb^2m/LDk$, $\xi = k_fb/DK$, $P_e = LV/D_L$.

In this problem, the Laplace domain solution of U can be obtained without much effort. It is

$$\bar{U}(x, s) = \frac{1}{s}\exp\left\{\left[\frac{P_e}{2} - \sqrt{\frac{P_e^2}{4} + \frac{P_e s}{\psi\theta} + \frac{3\xi P_e\phi(s)}{\theta}}\right]x\right\} \tag{9}$$

where

$$\phi(s) = \frac{\sqrt{s}\cosh\sqrt{s} - \sinh\sqrt{s}}{\sqrt{s}\cosh\sqrt{s} - \sinh\sqrt{s} + \xi\sinh\sqrt{s}}$$

Equation 9 is the transfer function of the described system. If we take $1/s$ off, then we obtain a transfer function $F(s)$ of the corresponding chromatography system.

$$F(s) = \exp\left\{\left[\frac{P_e}{2} - \sqrt{\frac{P_e^2}{4} + \frac{P_e s}{\psi\theta} + \frac{3\xi P_e\phi(s)}{\theta}}\right]x\right\} \tag{10}$$

Correspondence concerning this paper should be addressed to J. T. Hsu.

If the inverse of $F(s)$, named $f(\tau)$, can be found, then U at bed length x and time τ can be obtained by integrating $f(\tau)$ from zero to τ with respect to τ.

The inversion of $F(s)$ by FFT is described by Hsu (1979) and Hsu and Dranoff (1987). The desired formula for this computation is

$$f(t) = f(j\Delta T) = \frac{1}{2T}\sum_{k=0}^{N-1} F\left(ik\frac{\pi}{T}\right)\exp\left(i\frac{2\pi jk}{N}\right) \qquad (11)$$

$$j = 0, 1, 2, \ldots, N-1.$$

The calculation of Eq. 11 can be achieved by the use of fast Fourier transform subroutines, which are generally available in a computer library. For example, there is a fast Fourier transform subroutine FFT2C in IMSL (International Math. and Stat. Libraries) that can be used for this purpose. To use this subroutine, N must be a power of 2.

Before executing the calculation, the operating period $2T$ must be chosen to cover the range of the chromatographic peak. To obtain an adequate period, we tested various T and observed the resulting elution curves. Figure 1 shows an elution curve with a suitable period. If the chosen period is too large or too small, it will cause numerical errors in the elution curves. The breakthrough curves can easily be obtained by integrating the elution curves using Simpson's rule.

Results and Discussion

An exact analytical solution to this problem has been derived by Rasmuson and Neretnieks (1980). In their solution, there was an integrand remainer, and additional numerical computations were needed. Raghavan and Ruthven (1983) solved this problem with different column boundary conditions by the orthogonal collocation method. Instead of Eq. 5, they used $\partial U/\partial x|_{x=1} = 0$. This difference in boundary conditions leads to a significant difference in the solutions only when the Peclet number and column length are both small.

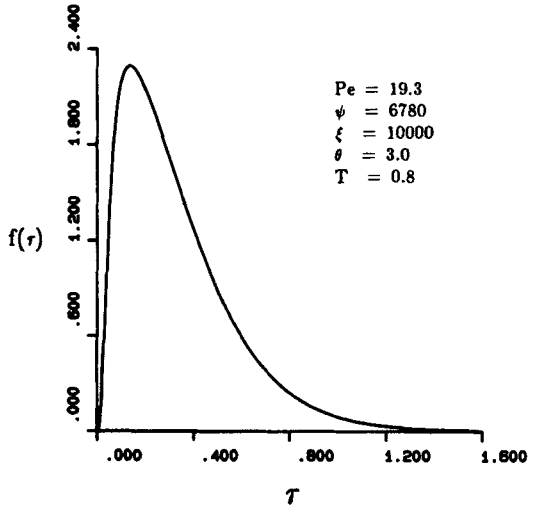

Figure 1. Elution curve of the corresponding chromatographic system.

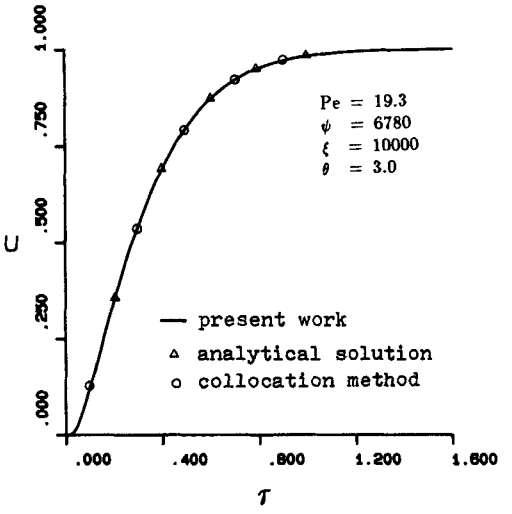

Figure 2. Comparison of breakthrough curves.

Figure 2 shows the comparison of the numerical solution of the present study with the analytical and orthogonal collocation solutions. It is evident that the numerical solution obtained by the FFT technique agrees well with both methods. Based on 128 points on an elution curve, the computer execution time for the breakthrough curve in Figure 2 is 0.053 on a CDC Cyber 850. Tables 1 and 2 show the comparison of execution time and accuracy for a breakthrough curve with various numbers of sample points. For larger Peclet numbers (Pe = 19.3 and 200), N = 128 is sufficient to give accurate results. For a small Peclet number (Pe = 1.93), however, the elution curve is very skewed and the peak apex appears near $\tau = 0$, as shown in Figure 3. This situation requires a larger number of sample points to obtain accurate results.

In order to compare the speed of this technique with the

Table 1. Execution Time and Accuracy for a Breakthrough Curve at Large *Pe*

	No. of Sample Points, N			
τ	64	128	256	1,024
0.1	0.1211	0.1219	0.1220	0.1220
0.2	0.3458	0.3468	0.3469	0.3469
0.3	0.5404	0.5415	0.5416	0.5416
0.4	0.6898	0.6909	0.6911	0.6911
0.5	0.7972	0.7984	0.7985	0.7985
0.6	0.8707	0.8720	0.8721	0.8721
0.7	0.9192	0.9205	0.9206	0.9206
0.8	0.9503	0.9516	0.9517	0.9517
0.9	0.9698	0.9711	0.9712	0.9712
1.0	0.9818	0.9830	0.9831	0.9831
1.1	0.9890	0.9902	0.9904	0.9904
1.2	0.9934	0.9945	0.9947	0.9947
1.3	0.9960	0.9971	0.9972	0.9972
1.4	0.9975	0.9985	0.9987	0.9987
1.5	0.9985	0.9994	0.9995	0.9995
1.6	0.9996	0.9999	1.000	1.000
Execution time, s CDC Cyber 850	0.038	0.053	0.086	0.290

Pe = 19.3; ψ = 6,780; ξ = 10,000; θ = 3.0

Table 2. Execution Time and Accuracy for a Breakthrough Curve at Small *Pe*

	No. of Sample Points, N			
τ	128	512	1,024	2,048
0.125	0.3829	0.3774	0.3764	0.3762
0.250	0.5797	0.5726	0.5714	0.5713
0.375	0.7096	0.7015	0.7003	0.7001
0.500	0.7983	0.7895	0.7883	0.7881
0.625	0.8595	0.8503	0.8490	0.8489
0.750	0.9023	0.8928	0.8916	0.8914
0.875	0.9326	0.9230	0.9217	0.9216
1.000	0.9544	0.9447	0.9434	0.9433
1.125	0.9702	0.9605	0.9592	0.9591
1.250	0.9816	0.9722	0.9709	0.9708
1.375	0.9900	0.9808	0.9796	0.9795
1.500	0.9961	0.9874	0.9861	0.9860
1.625	1.000	0.9923	0.9911	0.9910
1.750	1.003	0.9960	0.9949	0.9947
1.875	1.004	0.9989	0.9978	0.9977
2.000	0.9956	1.000	1.000	1.000
Execution time, s CDC Cyber 850	0.053	0.152	0.290	0.584

$Pe = 1.93$; $\psi = 6{,}780$; $\xi = 10{,}000$; $\theta = 3.0$

results of previous investigators (Raghavan and Ruthven, 1983), we performed the computations on an IBM 4381 computer and then converted the execution times to that of an IBM 3032 computer by dividing by a factor of 1.31, which was provided by the IBM Corporation (Tobin, 1987). The comparison results are summarized in Table 3. It is obvious that the present method is more than two orders of magnitude faster than the results from the orthogonal collocation method. For small Peclet numbers, the comparison results are even better.

Although the application of fast Fourier transform to solve a fixed-bed adsorption problem is very powerful, two limitations of this method should be mentioned. First, the Laplace domain solution of the system considered should be obtainable. Second, the solution could be represented by a continuous periodic function with a period of interest.

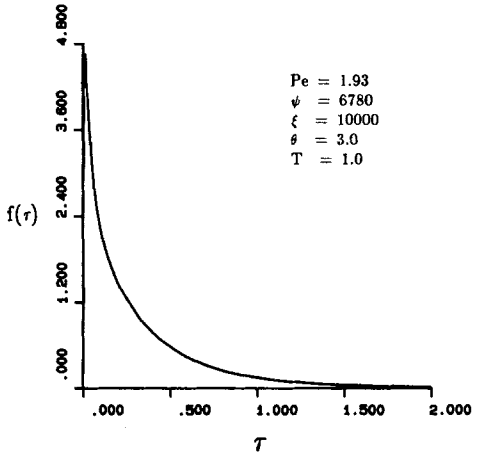

Figure 3. Elution curve of a system with small Peclet number.

Table 3. Comparison of Execution Times

Parameter Values	Execution Time Required: Present Method IBM 4381*	Present Method IBM 3032**	Orthogonal Collocation IBM 3032†	Analytical Solution IBM 3032†
$Pe = 200$ $\psi = 10{,}000$ $\xi = 10{,}000$ $\theta = 3.0$	0.050 s ($N = 128$)	0.038 s	23 s	10 min
$Pe = 19.3$ $\psi = 6{,}780$ $\xi = 10{,}000$ $\theta = 3.0$	0.050 s ($N = 128$)	0.038 s	26 s	18 min
$Pe = 1.93$ $\psi = 6{,}780$ $\xi = 10{,}000$ $\theta = 3.0$	0.379 s ($N = 1024$)	0.289 s	5 min	>20 min

*IBM 4381-P13 vs. Fortran, OPT = 0.
**Average computing time ratio of IBM 4381/IBM 3032 = 1.31 (Tobin, 1987)
†Raghavan and Ruthven (1983).

Acknowledgment

The authors express their thanks to J. Tobin of IBM for the IBM 4381 and IBM 3032 simulation data.

Notation

b = particle radius, m
C = concentration in fluid, mol/m^3
C_0 = inlet concentration in fluid, mol/m^3
C_p = internal concentration in particles, mol/m^3
D = intrapore diffusivity, m^2/s
D_L = axial dispersion coefficient, m^2/s
K = volume equilibrium constant, m^3/m^3
k_f = mass transfer coefficient, m/s
$m = \epsilon/(1-\epsilon)$
N = number of sample points
$P_e = LV/D_L$, Peclet number
$Q = C_p/C_0$, internal concentration in particles
q = volume-averaged concentration in particles, mol/m^3
r = radial distance from center of spherical particles, m
s = Laplace transform variable
t = time, s
T = half-period of function being considered
$U = C/C_0$, fluid phase concentration
$\bar{U}$ = Laplace domain solution of U
V = average linear pore velocity, m/s
$x = z/L$, axial distance
z = axial distance coordinate, m

Greek letters

$\theta = Vb^2m/LDK$, bed length parameter
ϵ = bed porosity, m^3/m^3
$\eta = r/b$, radial distance in particle
$\xi = k_fb/DK$, film resistance parameter
$\psi = K/m$, distribution ratio
$\tau = Dt/b^2$, contact time parameter

Literature Cited

Cooley, J. W., and J. W. Tukey, "An algorithm for the Machine Calculation of Complex Fourier Series," *Math. Comput.*, **19**, 297 (1965).
Hsu, T., "Computer Automation of Cascade Chromatography and the Application of Fast Fourier Transform to Distributed-Parameter

Model Problems," Ph.D. Thesis, Northwestern Univ. Evanston, IL (1979).
Hsu, J. T., and J. S. Dranoff, "Numerical Inversion of Certain Laplace Transforms by the Direct Application of Fast Fourier Transform (FFT) Algorithm," *Comput. Chem. Eng.*, (1987).
Raghavan, N. S., and D. M. Ruthven, "Numerical Simulation of a Fixed-Bed Adsorption Column by the Method of Orthogonal Collocation," *AIChE J.*, **29**, 922 (1983).
Rasmuson, A., and I. Neretnieks, "Exact Solution of a Model for Diffusion in Particles and Longitudinal Dispersion in Packed Beds," *AIChE J.*, **26**, 686 (1980).
Tobin, J., IBM local systems engineer, private communication (1987).
Villermaux, J., "Deformation of Chromatographic Peaks Under the Influence of Mass Transfer Phenomena," *J. Chromatogr. Sci.*, **12**, 822 (1974).

Manuscript received Nov. 3, 1986, and revision received Feb. 28, 1987.