Application of Fast Fourier Transform to Nonlinear Fixed-Bed Adsorption Problems

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

In the previous studies (Chen and Hsu, 1987; Hsu and Chen, 1987), the fast Fourier transform (FFT) has been demonstrated to be a very powerful technique to solve linear fixed-bed adsorption problems by inverting the Laplace domain solution into the time domain. However, the direct application of the FFT technique is subject to two limitations. First, the Laplace domain solution should be obtainable, i.e., a linear system. Second the function to be inverted should start and end at zero over a period of interest.

The objective of this paper is to develop a methodology to overcome these two limitations. The first limitation is overcome by a new iterative technique, while the second is solved by a proper modification of the input condition. In this work, a packed column adsorption problem with second-order kinetics, presented in Thomas' article (1944), is chosen as the example to be studied. Since the analytical solution of this problem has also been given elsewhere (Hiester and Vermeulen, 1952; Chase, 1984), a rigid basis of comparison is available. This newly developed technique can be extensively applied to systems with much more complicated kinetics and input conditions.

Method

Consider an adsorber packed with a non-porous adsorbent, where the flow pattern is assumed to be plug-flow and without axial dispersion. The material balance of solute in the mobile phase can be written as

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial z} + \alpha\frac{\partial \theta}{\partial t} = 0 \tag{1}$$

where V is the interstitial velocity, θ is the fraction of surface coverage, and α is the maximum adsorption capacity of the adsorbent per unit bed void volume. In terms of the bed void fraction, ϵ, the density of the solid particle, ρ_p, and the adsorption concentration at complete coverage of surface, q_m, α is expressed as

$$\alpha = \frac{(1-\epsilon)\rho_p q_m}{\epsilon} \tag{2}$$

For a reversible adsorption process, the adsorption kinetics can be assumed to obey the second-order rate equation

$$\frac{d\theta}{dt} = k_1 C(1-\theta) - k_2\theta \tag{3}$$

As a general case, the initial and boundary conditions are given as follows:

$$C(t=0, z) = 0 \tag{4}$$

$$\theta(t=0, z) = 0 \tag{5}$$

$$C(t, z=0) = g(t) \tag{6}$$

where $g(t)$ is the column input condition. To solve this problem by the FFT technique, the Laplace domain solution must first be obtained. Because of the nonlinear term $C\theta$, the exact solution in the Laplace domain is not feasible; nevertheless this problem can still be solved by an iterative method.

The Laplace transformation of Eq. 3 yields

$$\bar{\theta} = \frac{k_1}{k_2 + s}(\bar{C} - \overline{C\theta}) \tag{7}$$

where $\overline{C\theta}(s, z)$ is the Laplace transform of $C\theta(t, z)$. After combining with Eq. 7, the Laplace transform of Eq. 1 is

$$\frac{d\bar{C}}{dz} + \frac{1}{V}\left(s + \frac{k_1\alpha s}{k_2 + s}\right)\bar{C} = \frac{k_1\alpha s}{V(k_2+s)}\overline{C\theta} \tag{8}$$

Correspondence concerning this paper should be addressed to J. T. Hsu.
The permanent address of T. L. Chen is at the Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, R.O.C.

By regarding $\overline{C\theta}$ as a function of z, Eq. 8 is a linear first-order ordinary differential equation with respect to z. Its solution is

$$\bar{C}(s, z) = G(s)\exp(-\lambda_1 z) + \exp(-\lambda_1 z)\int_0^z \exp(\lambda_1 z)\lambda_2 \overline{C\theta}\, dz \quad (9)$$

where

$G(s) = L[g(t)]$, the Laplace transform of $g(t)$

$$\lambda_1(s) = \frac{1}{V}\left(s + \frac{k_1 \alpha s}{k_2 + s}\right) \quad (10)$$

$$\lambda_2(s) = \frac{k_1 \alpha s}{V(k_2 + s)} \quad (11)$$

To solve this problem, we still need information concerning $G(s)$ and $\overline{C\theta}(s, z)$.

One of the limitations of applying the FFT to the inversion of Laplace transforms is that the function considered should start and end at zero. The step input, $g(t) = C_0$, results in a breakthrough curve which does not end at zero; therefore, the direct application of the FFT can not be implemented. In order to obtain a qualified elution curve, the column input condition is first modified to include a tail part of zero concentration. By doing this, the elution curve can be made to end at zero. The tail of the modified elution curve (concentration from C_0 to 0) has no meaning in reality, but it is necessary for the application of the FFT technique. Although the problem in the elution curve is solved by this modification, another problem is still existing: the input condition is not feasible for the FFT technique. Therefore, the column input is modified again to start from zero and still has the feature of a step input (with a small lag time) as discussed later. In this way, both the column input condition and the elution curve start and end at zero, and are eligible for the direct application of the FFT technique. It should be noted that, instead of the exact analytical expression, the Laplace transform of the column input condition, $G(s)$, will be obtained numerically by transferring the digital time domain data into the frequency domain.

The first step of the FFT technique to invert a function in the Laplace domain into the time domain is to transfer this function into the frequency domain (by setting $s = i\omega$ and $\omega = k\pi/T$). One of the features of the FFT technique is that the frequency and time domain data can be interchanged. The numerical data of $C(t, z)$ and $\theta(t, z)$ can be combined to obtain $C\theta(t, z)$; $C\theta(t, z)$ can therefore be transferred into the frequency domain. The corresponding $\overline{C\theta}(s, z)$ in the frequency domain can then be combined with other functions and transferred back into the time domain to obtain the desired solution. This procedure can be repeated a number of times. In the iteration, the initial guess of $C(t, z)$ and $\theta(t, z)$ can be obtained from the linear approximation ($C\theta = 0$), where the Laplace domain solutions are

$$\bar{C}(s, z) = G(s)\exp\left[-\frac{1}{V}\left(s - \frac{k_1 \alpha s}{k_2 + s}\right)z\right] \quad (12)$$

and

$$\bar{\theta}(s, z) = \bar{C}(s, z)\frac{k_1}{k_2 + s} \quad (13)$$

Results and Discussion

The analytical solution of Eqs. 1 and 3 with step input, $g(t) = C_0$, can be obtained by modifying those presented elsewhere (Hiester and Vermuelen, 1952; Chase, 1984). The elution concentration measured at a time t_s, after a nonadsorbed component would have emerged from the column is given by

$$\frac{C(t_s, L)}{C_0} = \frac{J(n/r, nM)}{J(n/r, nM) + [1 - J(n, nM/r)]\exp[(1 - r^{-1})(n - nM)]} \quad (14)$$

where

$$r = 1 - \frac{C_0 k_1}{k_2} \quad (15)$$

$$n = \frac{\alpha k_1 L}{V} \quad (16)$$

$$M = \frac{t_s\left(\frac{k_2}{k_1} + C_0\right)V}{\alpha L} \quad (17)$$

$$J(a, b) = 1 - e^{-b}\int_0^a e^{-x} I_0(2\sqrt{bx})\, dx \quad (18)$$

In Eq. 18, I_0 is a modified Bessel function of the first kind. The value of J can be calculated by an asymptotic expression when a and b are both greater than 10 (Hiester and Vermeulen, 1952):

$$J(a, b) = \frac{1}{2}\left\{1 - \operatorname{erf}(\sqrt{a} - \sqrt{b}) - \frac{\exp[-(\sqrt{a} - \sqrt{b})^2]}{\sqrt{\pi}[\sqrt{b} + (ab)^{1/4}]}\right\} \quad (19)$$

Equation 19 is accurate to within 1% when $ab > 36$. This analytical solution provides a means for examining the validity of applying the FFT technique to solve nonlinear fixed-bed problems.

In order to solve this problem by the FFT technique, the column input condition, $g(t)$, is modified as

$$g(t) = \begin{cases} C_0 \exp\left[-\frac{1}{2}\left(\frac{t - \tau}{\sigma}\right)^2\right] & 0 \le t < \tau \\ C_0 & \tau \le t < t_e - \tau \\ C_0 \exp\left[-\frac{1}{2}\left(\frac{t - t_e + \tau}{\sigma}\right)^2\right] & t_e - \tau \le t < t_e \\ 0 & t_e \le t < 2T \end{cases} \quad (20)$$

where the concentration profiles in the time ranges 0 to τ and ($\tau_e - \tau$) to t_e are characterized by the normal distribution (τ is the mean and σ is the standard deviation). The standard deviation, σ, should be carefully selected. If σ is too large, the input condition will deviate from a step input; if too small, t at τ and ($t_e - \tau$) will become points of discontinuity, and oscillations will occur (the Gibbs phenomenon in the Fourier integral). By adequately setting the values of τ and σ, such as $\tau = 5$ s and $\sigma = 0.2$ s, a block shape of input can be obtained. Such a column input can be regarded as a step input with a lag time of τ. From the digital data of Eq. 20, the corresponding frequency domain data can be obtained numerically by using the FFT subroutines. It is interesting to note that this modified step input with normal distribution at both ends is actually similar to a real system in which dispersion occurs inside the sample injection loop.

In addition to τ (= 5 s) and σ (=0.2 s), other parameters used in the simulation were assigned as follows: $C_0 = 1.0 \times 10^{-6}$ mol/cm^3, $k_1 = 1.0 \times 10^4$ cm^3/mol · s, $k_2 = 0.1$ s^{-1}, $V = 0.1$ cm/s, $L = 10$ cm, $\alpha = 1.0 \times 10^{-5}$ mol/cm^3, $t_e = 300$ s, $T = 400$ s. In order to compare the result from the analytical solution, Eq. 14, with that from the FFT technique, the time scale used has to be consistent. Since this column input can be considered as a step input with a lag time τ, it is obvious that $t_s = t - 105$ is a very good approximation ($105 = L/V + \tau$). The number of sample points used to obtain the elution peaks from the FFT technique is 1,024. To integrate Eqs. 9 and 18, the number of points of integration used are 6 and 12, respectively. The value of $J(a, b)$ in the analytical solution is obtained from Eq. 19 when $ab > 36$. The agreement in the iterated data and the analytical solution, as shown in Table 1, indicates that the present iterative technique is workable. Besides the iterated solution converges to the exact solution very rapidly. The reason for this fast convergence can be attributed to the use of the corresponding linear solution as an initial guess.

In addition to being extended to systems with axial dispersion and intraparticle diffusion, this method can also be applied to many chemical systems with complicated column inputs since only their digital data in the time domain are needed, and to systems with complicated kinetics because the nonlinear terms can be handled by iteration. The accuracy and high computing speed of this FFT technique make it feasible to perform parameter estimation of nonlinear systems in the time domain (fewer sample points can still be used to reduce the execution time); and the large number of sample points obtained provides a suitable means to analyze highly skewed elution curves.

Notation

C = solute concentration in mobile phase, mol/cm^3
C_0 = inlet concentration of solute, mol/cm^3
$C\theta = C(t, z) \times \theta(t, z)$
g = column input function
G = Laplace transform of $g(t)$
k_1 = forward rate constant, cm^3/mol · s
k_2 = backward rate constant, s^{-1}
L = column length, cm
M = paramter, Eq. 17
n = parameter, Eq. 16
q_m = adsorption concentration at complete coverage of surface, mol/g
r = parameter, Eq. 15
s = Laplace Transfer variable, s^{-1}
T = half period of the function interested, s
t = time, s
t_e = the time when the input concentration is back to zero, s
t_s = time measured after a non-adsorbed component has emerged, s
V = interstitial velocity, cm/s
z = distance in flow direction, cm

Greek letters

α = maximum adsorption capacity of adsorbent per unit bed void volume, mol/cm^3
ϵ = bed void fraction
θ = fraction of surface coverage
λ_1 = parameter, Eq. 10
λ_2 = parameter, Eq. 11
ρ_p = density of solid particle, g/cm^3
σ = standard deviation of the normal distribution, s
τ = mean of the normal distribution, s

Table 1. Numerical Data from FFT Technique and Analytical Solution*

Time s	FFT Technique Linear Approx.	First Iteration	Second Iteration	Analyt. Solution
125	0.011	0.011	0.011	0.011
150	0.092	0.102	0.103	0.102
175	0.273	0.313	0.316	0.316
200	0.502	0.578	0.582	0.580
225	0.705	0.794	0.797	0.790
250	0.846	0.923	0.922	0.912
275	0.928	0.980	0.977	0.967
300	0.969	0.999	0.996	0.989
325	0.988	1.002	1.000	0.997
350	0.996	1.002	1.000	1.000
Execution time, s: CDC Cyber 850 (1,024 Points)				
	0.227	2.508	5.365	0.405

*Normalized concentration, C/C_0.

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