FAST CALCULATION OF ELUTION CURVES OF A SLURRY ADSORBER WITH NONLINEAR KINETICS

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Introduction

The fast Fourier transform (FFT) algorithm can be used to numerically invert certain Laplace transforms.[3] Recently, it has been successfully applied to the prediction of elution curves of fixed-bed adsorbers with linear kinetics and pore diffusion,[1,4,5] and with nonlinear kinetics but without pore diffusion.[2] The results illustrated that this method has the advantages of computing speed and accuracy.

The purpose of the present study is to investigate the utilization of FFT to simulate the elution curves of slurry adsorbers in which nonlinear adsorptions proceed over porous adsorbents, and to evaluate its validity in terms of calculating speed and accuracy.

1. Descriptions of Model and Method

Consider an isothermal slurry adsorber where a reversible and nonlinear adsorption process is carried out over a porous spherical adsorbent. The adsorber is assumed to be perfectly mixed and there is no external film resistance. The initial concentration of adsorbate is zero. At time zero, a step input of adsorbate is introduced to the inlet of the adsorber, which can then be described by the following equations:

$$\frac{dC}{dt} = \frac{1}{\tau}(C_{in} - C) - \varepsilon_p D_p A_s \left(\frac{\partial C_p}{\partial r}\right)_{r=R} \tag{1}$$

$$\varepsilon_p D_p \left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r}\frac{\partial C_p}{\partial r}\right) - n_T \frac{\partial \theta}{\partial t} = \varepsilon_p \frac{\partial C_p}{\partial t} \tag{2}$$

$$\frac{\partial \theta}{\partial t} = k_1 C_p(1 - \theta) - k_2 \theta \tag{3}$$

$$C(t=0) = C_p(t=0, r) = \theta(t=0, r) = 0 \tag{4}$$

$$C_p(t, r=0) = \text{finite} \tag{5}$$

$$C_p(t, r=R) = C(t) \tag{6}$$

Direct use of the FFT technique has two limitations; the function involved should be a continuous one, and

should start and end at zero. Therefore, a step input is not valid, and a modified input function proposed in a previous work[2] is employed:

$$C_{in}(t) = \begin{cases} C_0 \exp\left[-\frac{1}{2}\left(\frac{t-t_i}{\sigma}\right)^2\right] \\ \qquad 0 \le t < t_i \\ C_0 \qquad t_i \le t < t_e - t_i \\ C_0 \exp\left[-\frac{1}{2}\left(\frac{t-t_e+t_i}{\sigma}\right)^2\right] \\ \qquad t_e - t_i \le t < t_e \\ 0 \qquad t_e \le t \le 2T \end{cases} \tag{7}$$

where the concentration profiles in the time ranges 0 to t_i and $(t_e - t_i)$ to t_e are characterized by the normal distribution. The function described by Eq. 7 is continuous and can approach a block function if t_i and σ are carefully selected; for example, if t_i is small compared with t_e and σ is small enough. In this situation, the concentration profile desired for a step input can be obtained from the input function of Eq. 7 after ignoring the time lag (time from 0 to t_i) and the tailing part (after saturation) of the elution curve.

The solutions of the above system of equations in the Laplace domain can be solved as

$$\bar{\theta} = \frac{k_1}{k_2 + s}(\bar{C}_p - \overline{C_p \theta}) \tag{8}$$

$$\bar{C}_p = \frac{A}{\beta_1 \sinh(\Phi_1 R) + \beta_2 \cosh(\Phi_1 R)} \frac{\sinh(\Phi_1 r)}{r}$$
$$+ \frac{\cosh(\Phi_1 r)}{r} \int_0^r \frac{\Phi_2}{\Phi_1} r \sinh(\Phi_1 r)\overline{C_p \theta}dr$$
$$- \frac{\sinh(\Phi_1 r)}{r} \int_0^r \frac{\Phi_2}{\Phi_1} r \cosh(\Phi_1 r)\overline{C_p \theta}dr \tag{9}$$

$$\bar{C} = \bar{C}_p\big|_{r=R} \tag{10}$$

where

$$A = \frac{1}{1+\tau s} \bar{C}_{in} - [\beta_1 \cosh(\Phi_1 R) + \beta_2 \sinh(\Phi_1 R)]$$

$$\int_0^R \frac{\Phi_2}{\Phi_1} r \sinh(\Phi_1 r) \overline{C_p \theta} dr$$

$$+ [\beta_1 \sinh(\Phi_1 R) + \beta_2 \cosh(\Phi_1 R)] \int_0^R \frac{\Phi_2}{\Phi_1}$$

$$r \cosh(\Phi_1 r) \overline{C_p \theta} dr \tag{11}$$

$$\Phi_1 = \left[\frac{1}{\varepsilon_p D_p} \left(\frac{n_T k_1 s}{s + k_2} + \varepsilon_p s \right) \right]^{1/2} \tag{12}$$

$$\Phi_2 = \frac{n_T k_1 s}{\varepsilon_p D_p (s + k_2)} \tag{13}$$

$$\beta_1 = \frac{1}{R} - \frac{\varepsilon_p D_p A_s \tau}{R^2 (1 + \tau s)} \tag{14}$$

$$\beta_2 = \frac{\varepsilon_p D_p A_s \tau \Phi_1}{R(1 + \tau s)} \tag{15}$$

The time-domain elution curve can then be obtained by adapting the FFT algorithm with the iterative procedure described below. It should be noted that the Laplace variable s is calculated by setting $s = ik\pi/T$, where $k = 0, 1, 2, \cdots, N-1$. The linear adsorption process was assumed to start the calculation, i.e., C_p and θ are first calculated from Eqs. 8, 9, and 11–15 by setting $C_p \theta$ equal to zero. The nonlinear term, $\overline{C_p \theta}$, needed for iteration is then calculated numerically from C_p and θ with the aid of FFT.[2] All integrals involved in the present work were obtained by the Newton-Cotes method. To calculate the integrative terms numerically, data of $\overline{C_p \theta}$ at different positions inside the particle must be obtained first. For this purpose, five equal-spaced points were taken along the radius of the particle. When the calculations were made at the center of the spherical adsorbent, $r = 0$, or when the Laplace variable s equaled zero, an infinite value was encountered. To overcome these problems, L'Hospital's rule was applied. The expression of $\bar{C}_p$ under these special conditions was obtained as:

when $s = 0$

$$\bar{C}_p = \begin{cases} A & r = 0 \\ A + \frac{\cosh(\Phi_1 r)}{r} \int_0^r \frac{\Phi_2}{\Phi_1} r \sinh(\Phi_1 r) \overline{C_p \theta} dr \\ \quad - \frac{\sinh(\Phi_1 r)}{r} \int_0^r \frac{\Phi_2}{\Phi_1} r \cosh(\Phi_1 r) \overline{C_p \theta} dr & r \neq 0 \end{cases} \tag{16}$$

when $r = 0$ and s is nonzero

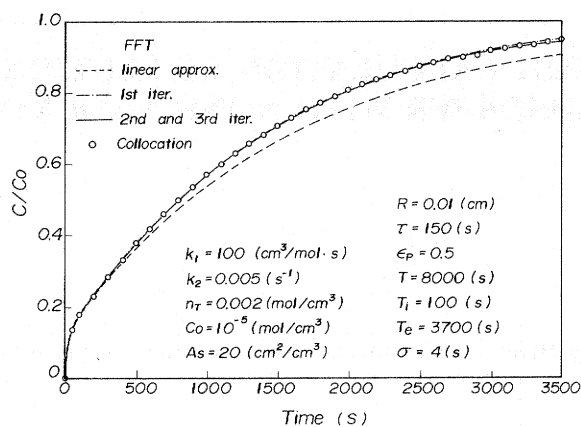$$\bar{C}_p = \frac{A \Phi_1}{\beta_1 \sinh(\Phi_1 R) + \beta_2 \cosh(\Phi_1 R)} \tag{17}$$

Fig. 1. Elution curves from the FFT method and the orthogonal collocation method

2. Results and Discussion

The number of sample points, N, used in the FFT method is critical in the aspects of accuracy and computing speed. The adequate sample size depends on the sharpness of the function encountered, i.e., larger N for sharper function. To solve a nonlinear system by the FFT method, the number of iterations should be determined first. A relatively large number of sample points ($N = 1024$) were employed to ensure good accuracy during the determination of the iteration number. Since the iterative process of the present method converges very fast, only two iterations were needed, as shown in **Fig. 1**. After determining iteration number, the sample size N was then examined. It was found that $N = 256$ was sufficient for the present case, and the execution time on a CDC Cyber 840 computer was 2.398 seconds.

Since the analytical solution for the present system has not yet been established in the literature, the result calculated from the FFT method was compared with the result from the orthogonal collocation method, which is widely used to solve partial differential equations. In the method of orthogonal collocation, step input was employed and four interior collocation points were taken. The resulting equations are a set of ordinary differential equations that are initial-value problems. The Runge-Kutta method was then chosen for the time integration. The results obtained from these two methods were in good agreement, as shown in Fig. 1. The execution time for the orthogonal collocation method (terminated at C/C_0 around 0.95) was found to be 2250 seconds. Thus the computing speed the computing speed of the FFT method is three orders of magnitude faster than the orthogonal collocation method.

In this study, the FFT technique was successfully applied to a slurry adsorber with a nonlinear kinetics and pore diffusion, without losing the elegance of computing speed and accuracy. Since the calculation

is so rapid, the present method is believed to be suitable for use as an auxiliary tool for parameters estimation in the time domain. For the case of existing external film resistance, the transfer functions can also be derived with the same mathematical manipulation, and the same numerical iteration procedure is also applicable. Extending this technique to fixed-bed adsorption problems with nonlinear kinetics and diffusion effects and to other chemical reactor systems, which might need further modification of this technique, is attractive future work.

Nomenclature

A	= parameter, Eq. 11	[—]
As	= specific surface area	[cm²/cm³]
C	= adsorbate concentration in bulk fluid phase	[mol/cm³]
C_{in}	= adsorber input function	[—]
C_0	= inlet concentration of adsorbate	[mol/cm³]
C_p	= adsorbate concentration in pore fluid phase	[mol/cm³]
$C_p\theta$	= $C_p(t, r) \times \theta(t, r)$	[—]
D_p	= pore diffusivity of adsorbate	[cm³/s]
k_1	= adsorption rate constant	[cm³/mol·s]
k_2	= desorption rate constant	[s⁻¹]
N	= number of sample points	[—]
n_T	= adsorption concentration at complete coverage of surface	[mol/cm³]
R	= radius of spherical adsorbent	[cm]
r	= radial distancce in particle	[cm]
s	= Laplace transfer variable	[s⁻¹]
T	= half period of the function of interest	[s]
t	= time	[s]
t_e	= time when the input concentration returns to zero	[s]
t_i	= mean of the normal distribution	[s]
β_1	= parameter, Eq. 14	[—]
β_2	= parameter, Eq. 15	[—]
ε_p	= void fraction in particles	[—]
θ	= fraction of surface coverage	[—]
σ	= standard deviation of the normal distribution	[s]
τ	= space time	[s]
Φ_1	= parameter, Eq. 12	[—]
Φ_2	= parameter, Eq. 13	[—]

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