Korean J. Chem. Eng., **22**(6), 960-963 (2005)
SHORT COMMUNICATION

Frequency Response of the Adsorption Vessel Loaded with Inert Core Adsorbents

In-Soo Park†

Department of Energy and Chemical Engineering, Kyungnam University, Masan 631-701, Korea
(*Received 25 July 2005 • accepted 25 August 2005*)

Abstract−An analytical solution for the frequency response of a semi-batch adsorption vessel with sinusoidal modulation of molar flow rate, loaded with inert core adsorbents is obtained for a linear isotherm coupled with intraparticle diffusion and external film diffusion. The low-frequency limiting values of the in-phase and the out-of-phase characteristic functions of the frequency response are found to be explicit functions of the size of the inert core and the external mass transfer parameter. Simulation results of the in-phase and the out-of-phase characteristic functions show that there exist a crossover frequency and overshoot of the in-phase characteristic function when external mass transfer resistance is present.

Key words: Inert Core Adsorbent, Frequency Response, Transfer Function, Adsorption Vessel

INTRODUCTION

Inert core adsorbents were recently developed to improve the separation performance of proteins in the expanded-bed adsorption process [Chanda and Rempel, 1997, 1999; Li et al., 2003]. These inert core adsorbents have increased density by the incorporation of heavier inert core and are reported to be suitable for stable expansion at high flow rates in an expanded-bed. Analytical solutions were reported for the batch adsorption vessel and for the step response of the semi-batch adsorption vessel loaded with inert core adsorbent [Li et al., 2003; Park, 2005]. The analysis of the frequency response for the semi-batch adsorption vessel loaded with conventional adsorbents without inert core and without external mass transfer resistance was reported in the reference [Park, 1998]. The frequency response technique measures the ultimate response of system subjected to small sinusoidal forcing function to estimate system parameters [Park et al., 1998; Jung et al., 2004].

In this study, we will present an analytical solution for the frequency response of a semi-batch adsorption vessel loaded with inert core adsorbents. A general solution for the adsorption vessel with an arbitrary forcing function will be obtained first, from which the particular solution in case of the sinusoidal forcing function will be generated. The linear adsorption isotherm is assumed and the external film diffusion is included.

MAHEMATICAL FORMULATION

Consider an adsorption vessel in which inert core adsorbents are loaded. The inert core adsorbent particle is spherical, which consists of the outer shell layer of radius R and the inert core of radius R_C. The vessel is initially evacuated. At time t=0, a pure gas is introduced into the vessel with a molar flow rate NX(t). The simplifying assumptions for the adsorption vessel loaded with inert core adsorbents are: (1) ideal mixing in the vessel; (2) local linear adsorption equilibrium at the particle surface; (3) homogeneous particle diffusion within the outer shell layer of particle; (4) non-permeable inert core; (5) negligible swelling or shrinking during sorption. The dimensionless mass balances for the adsorption vessel are given in Table 1.

Table 1. Mathematical formulation

Definition of Dimensionless Variables and Parameters
(C_0≡reference concentration)

$$y_b=\frac{C_b}{C_0};\quad y_s=\frac{C_s}{C_0};\quad x=\frac{r}{R};\quad x_C=\frac{R_C}{R};\quad y_\mu=\frac{C_\mu}{KC_0};$$

$$\tau=\frac{D_e t}{R^2};\quad \xi=\frac{k_f R}{KD_e};\quad \beta_0=\frac{V_{\mu 0}}{V}K;\quad \Omega=\frac{R^2/D_e}{VC_0/N};\quad \omega^*=\omega\left(\frac{R^2}{D_e}\right)$$

Mass Balance

Intraparticle Mass Balance in Outer Adsorbent Shell

$$\frac{\partial y_\mu}{\partial\tau}=\left(\frac{\partial^2 y_\mu}{\partial x^2}+\frac{2}{x}\frac{\partial y_\mu}{\partial x}\right)\qquad (x_C\le x\le 1)\tag{1a}$$

$$\text{at }\tau=0\qquad y_\mu=0\tag{1b}$$

$$\text{at }x=x_C\qquad \frac{\partial y_\mu}{\partial x}=0\tag{1c}$$

$$\text{at }x=1\qquad \left[\frac{\partial y_\mu}{\partial x}\right]_{x=1}=\xi(y_b-y_s)\tag{1d}$$

Mass Balance around the Adsorption Vessel

$$\frac{dy_b}{d\tau}+\beta_0(1-x_C^3)\frac{d\langle y_\mu\rangle}{d\tau}=\Omega X(\tau);\qquad \langle y_\mu\rangle=\frac{3}{1-x_C^3}\int_{x_C}^{1}x^2 y_\mu dx\tag{2a}$$

$$\text{at }\tau=0\qquad y_b=0\tag{2b}$$

Linear Adsorption Equilibrium at the Adsorbent Surface

$$y_\mu|_{x=1}=y_s\tag{3}$$

Forcing Function

$$X(\tau)=(1+\nu\sin(\omega^*\tau))U(\tau)\tag{4}$$

SOLUTION IN LAPLACE DOMAIN

The general solution with an arbitrary forcing function in Laplace domain can be expressed as

†To whom correspondence should be addressed.
E-mail: ispark@kyungnam.ac.kr

$$\frac{\bar{y}_b}{\Omega}=G(s)\bar{X}(s) \tag{5}$$

in terms of the overall transfer function G(s), which was reported in the reference [Park, 2005]:

$$G(s)\equiv\frac{\bar{y}_b/\Omega}{\bar{X}}=-\frac{1}{s[1+\beta_0(1-x_C^3)F(s)]} \tag{6a}$$

$$F(s)\equiv\frac{\langle\bar{y}_\mu\rangle}{\bar{y}_b}=\frac{3}{(1-x_C^3)s}\left[\frac{(1-x_C)\sqrt{s}\cosh[(1-x_C)\sqrt{s}]-(1-x_Cs)\sinh[(1-x_C)\sqrt{s}]}{\sqrt{s}\left[x_C+\frac{(1-x_C)}{\xi}\right]\cosh[(1-x_C)\sqrt{s}]+\left[1-\frac{(1-x_Cs)}{\xi}\right]\sinh[(1-x_C)\sqrt{s}]}\right] \tag{6b}$$

The forcing function in Laplace domain is:

$$\bar{X}(s)=\frac{1}{s}+\nu\left(\frac{\omega^*}{s^2+(\omega^*)^2}\right) \tag{7}$$

FREQUENCY RESPONSE

1. In-phase and Out-of-phase Characteristic Functions

We define the in-phase characteristic function δ_R and the out-of-phase characteristic function δ_I of the frequency response as the real and imaginary parts of the vessel transfer function F(s) in the limit of $s\rightarrow i\omega^*$, multiplied by the distribution parameter $\beta_0(1-x_C^3)$, respectively:

$$\delta_R-i\delta_I\equiv\beta_0(1-x_C^3)\lim_{s\rightarrow i\omega^*}F(s) \tag{8}$$

By substitution of Eq. (6b) into Eq. (8), The in-phase and out-of-phase characteristic functions can be obtained as

$$\frac{\delta_R}{\beta_0}=\frac{n_1d_1+n_2d_2}{d_1^2+d_2^2};\quad \frac{\delta_I}{\beta_0}=\frac{n_1d_2-n_2d_1}{d_1^2+d_2^2}; \tag{9a}$$

where parameters in the above equations are:

$$n_1=3[\{\cosh[2u(1-x_C)]-\cos[2u(1-x_C)]\}-u(1-x_C)\{\sinh[2u(1-x_C)]+\sin[2u(1-x_C)]\}] \tag{9b}$$

$$n_2=3[-2u^2x_C\{\cosh[2u(1-x_C)]-\cos[2u(1-x_C)]\}-u(1-x_C)\{\sinh[2u(1-x_C)]-\sin[2u(1-x_C)]\}] \tag{9c}$$

$$d_1=-2u^3\left[\frac{1}{\xi}+\left(1-\frac{1}{\xi}\right)x_C\right]\{\sinh[2u(1-x_C)]+\sin[2u(1-x_C)]\}+\frac{4u^4x_C}{\xi}\{\cosh[2u(1-x_C)]-\cos[2u(1-x_C)]\} \tag{9d}$$

$$d_2=-2u^2\left(1-\frac{1}{\xi}\right)\{\cosh[2u(1-x_C)]-\cos[2u(1-x_C)]\}-2u^3\left[\frac{1}{\xi}+\left(1-\frac{1}{\xi}\right)x_C\right]\{\sinh[2u(1-x_C)]+\sin[2u(1-x_C)]\} \tag{9e}$$

$$u=\sqrt{\omega^*/2} \tag{9f}$$

2. Frequency Response in Terms of In-phase and Out-of-phase Functions

By taking the inverse transform of Eq. (5) for the sinusoidal forcing function, using the method of residues, the frequency response in time domain can be obtained as

$$\frac{y_b}{\Omega}=\left(\frac{y_b}{\Omega}\right)_{\infty,step}+\nu\left\{\frac{1}{\omega^*[1+\beta_0(1-x_C^3)]}+AR\sin(\omega^*\tau+PS)\right\} \tag{10a}$$

where

$$\left(\frac{y_b}{\Omega}\right)_{\infty,step}=\delta_0\tau+\beta_0(1-x_C^3)\delta_0^2(\delta_f+\delta_a) \tag{10b}$$

$$\delta_0=\frac{1}{1+\beta_0(1-x_C^3)} \tag{10c}$$

$$\delta_f=\frac{1-x_C^3}{3\xi} \tag{10d}$$

$$\delta_a=\frac{1}{15}\left(1-\frac{4(1-x_C^2)x_C^3}{1-x_C^3}+\frac{5(1-x_C)x_C^5}{1-x_C^3}\right) \tag{10e}$$

$$AR=\frac{1}{\omega^*\sqrt{\delta_I^2+(1+\delta_R)^2}} \tag{10f}$$

$$PS=\phi-\frac{\pi}{2};\quad \phi=\tan^{-1}\left(\frac{\delta_I}{1+\delta_R}\right) \tag{10g}$$

The first term of RHS of Eq. (10a) is the contribution of the step response (i.e., the contribution of the first term of the forcing function). Since the frequency response is the ultimate response when $\tau\rightarrow\infty$, $(y_b/\Omega)_{\infty,step}$ given by Eq. (10b) is the step response when $\tau\rightarrow\infty$. Note that the step response was reported by Park [2005].

RESULTS AND DISCUSSION

An analytical solution for the frequency response of the adsorption vessel loaded with inert core adsorbents was obtained in terms of the in-phase and the out-of-phase characteristic functions in the previous section. Now we shall discuss about the frequency response by examining some behavior of the characteristic functions.

1. Limiting Behavior

1-1. Case 1: $x_C\rightarrow 0$ & $\xi\rightarrow\infty$

The inert core adsorbent reduces to the traditional adsorbent without inert core when $x_C\rightarrow 0$ and the external film resistance vanishes when $x\rightarrow\infty$. In this limit, the parameters in Eq. (9) reduce to: $n_1=3\{[\cosh(2u)-\cos(2u)]-u[\sinh(2u)+\sin(2u)]\}$; $n_2=-3u[\sinh(2u)-\sin(2u)]$; $d_1=0$; $d_2=-2u^2[\cosh(2u)-\cos(2u)]$. Thus, the characteristic functions are:

$$\frac{\delta_R}{\beta_0}=3\left(\frac{\sinh(\sqrt{2\omega^*})-\sin(\sqrt{2\omega^*})}{\sqrt{2\omega^*}(\cosh(\sqrt{2\omega^*})-\cos(\sqrt{2\omega^*}))}\right);$$

$$\frac{\delta_I}{\beta_0}=3\left(\frac{\sinh(\sqrt{2\omega^*})+\sin(\sqrt{2\omega^*})}{\sqrt{2\omega^*}(\cosh(\sqrt{2\omega^*})-\cos(\sqrt{2\omega^*}))}-\frac{2}{(2\omega^*)}\right) \tag{14}$$

The same equations of characteristic functions for the traditional adsorbent without inert core were reported in the reference [Park et al., 1998].

1-2. Case 2: $x_C\rightarrow 1$

In this limit, the inert core adsorbent reduces to an impermeable sphere and the adsorption vessel becomes a physical filling reservoir without adsorption. Since there is no adsorption in the particle, the change of the bulk concentration in the vessel is purely due to the physical filling with adsorbate. In this limit, the parameters in

Eq. (9) reduce to: $n_1/(1-x_C)=0$; $n_2/(1-x_C)=0$; $d_1/(1-x_C)=-2(\omega^*)^2$; $d_2/(1-x_C)=-2(\omega^*)^2$. Thus, the characteristic functions are:

$$\delta_R=\delta_I=0 \tag{12}$$

In this limit, AR and PS of the frequency response are: AR=1/ω^*; PS=$-\pi/2$. The same equations of AR and PS for the physical filling without adsorption were reported in the reference [Park et al., 1998].

1-3. Case 3: $\omega^*\rightarrow 0$

In this limit, the parameters in Eq. (9) reduce to: $n_1/[(1-x_C)(\omega^*)^2]=0$; $n_2/[(1-x_C)(\omega^*)^2=-2(1-x_C)[3-3(1-x_C)+(1-x_C)^2]$; $d_1/[(1-x_C)(\omega^*)^2]=-2[1-(1-1/\xi)(1-x_C)]$; $d_2/[(1-x_C)(\omega^*)^2]=-2$. Thus, the low-frequency limiting values of the characteristic functions are:

$$\lim_{\omega^*\rightarrow 0}\frac{\delta_R}{\beta_0}=\frac{3(1-x_C)\left[1-(1-x_C)+\dfrac{(1-x_C)^2}{3}\right]}{1+\left[1-\left(1-\dfrac{1}{\xi}\right)(1-x_C)\right]^2};$$

$$\lim_{\omega^*\rightarrow 0}\frac{\delta_I}{\beta_0}=\left[1-\left(1-\frac{1}{\xi}\right)(1-x_C)\right]\left(\lim_{\omega^*\rightarrow 0}\frac{-\delta_R}{\beta_0}\right) \tag{13}$$

When $x_C\rightarrow 0$ & $\xi\rightarrow\infty$, these low-frequency limiting values become: $\lim_{\omega^*\rightarrow 0}\delta_R/\beta_0=1$ and $\lim_{\omega^*\rightarrow 0}\delta_I/\beta_0=0$. The same low-frequency limiting values for the conventional adsorbent without inert core were reported in the reference [Park et al., 1998].

2. Simulation

The reduced characteristic functions relative to the low-frequency limiting value of the in-phase characteristic function given by Eq. (13) are plotted as a function of frequency in Fig. 1 and Fig. 2 to show the effects of the size of inert core and the external film resistance. As we can see in these figures, there exist a crossover frequency at which the two characteristic curves intersect each other and an overshoot of the in-phase characteristic function when ξ is finite. With increasing x_C and with decreasing ξ, the crossover frequency decreases and the overshoot increases, respectively. The

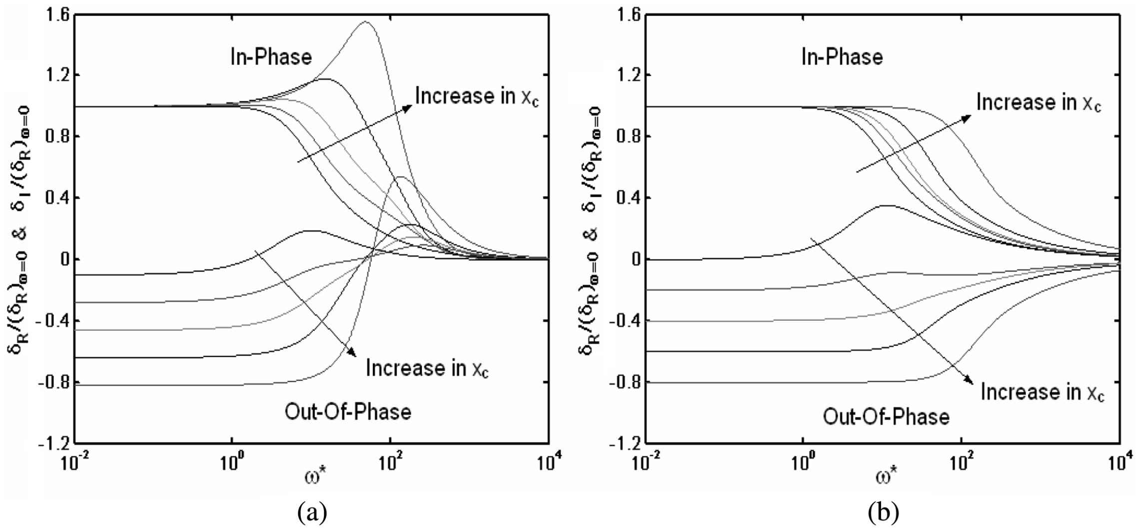

Fig. 1. Effect of x_C on the reduced characteristic function of frequency response (a) ξ=10 (b) $\xi=\infty$: x_C=0, 0.2, 0.4, 0.6, 0.8.

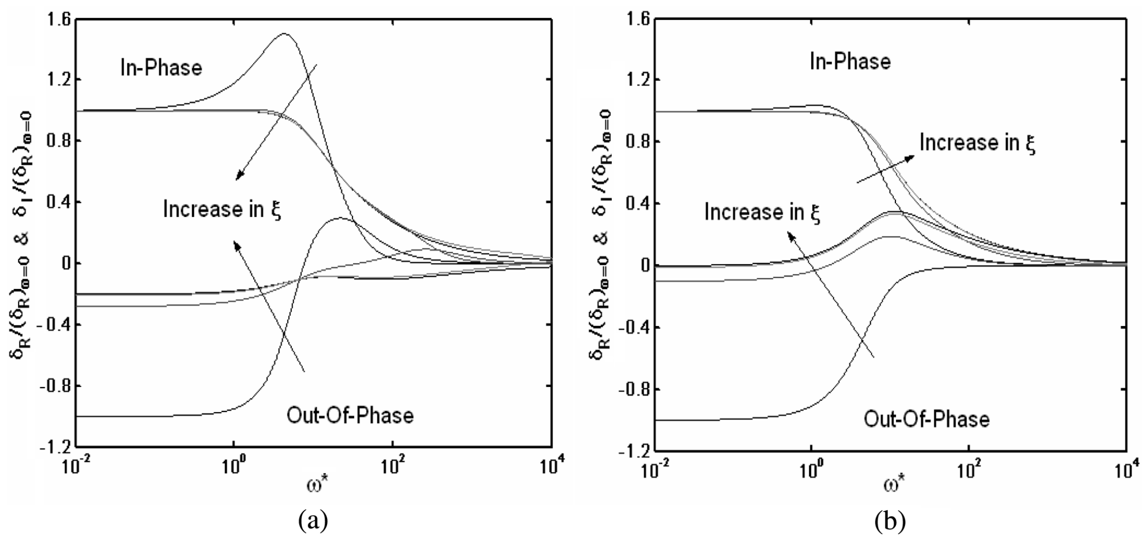

Fig. 2. Effect of ξ on the reduced characteristic function of frequency response (a) x_C=0.2 (b) x_C=0: ξ=1, 10, 100, ∞.

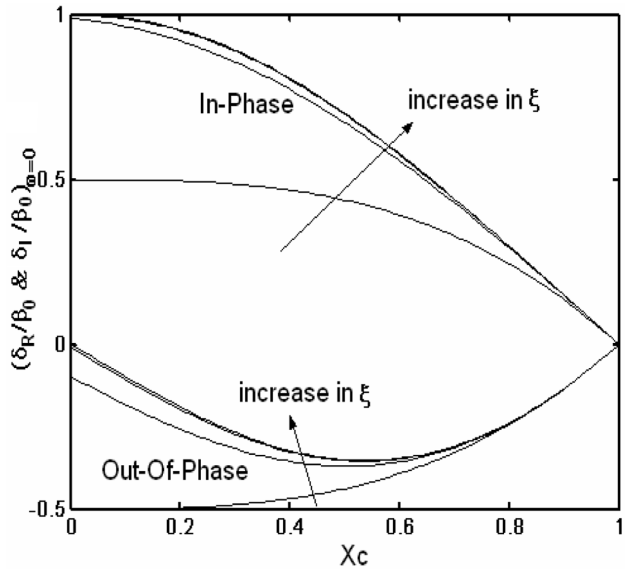

Fig. 3. Low-frequency limiting-value of characteristic function of frequency response: ξ=1, 10, 100, ∞.

overshoot vanishes at x_C=1 (see Eq. (12)) and at $\xi=\infty$, respectively. With larger x_C, the in-phase characteristic function decays from the low-frequency limiting value (when $\xi=\infty$) or from the maximum value (when ξ=finite) at higher frequency. The crossover frequency becomes infinity at x_C=1, at x_C=0 and at $\xi=\infty$, respectively.

The low-frequency limiting values of characteristic functions (i.e., Eq. (13)) are plotted in Fig. 3. The low-frequency limiting value of the in-phase characteristic function increases with decreasing size of inert core and with decreasing external resistance. The low-frequency limiting value of the out-of-phase characteristic function increases with decreasing external resistance. With decreasing size of inert core, however, the low-frequency limiting value of the out-of-phase characteristic function decreases at first and then increases after a minimum value is reached.

CONCLUSION

An analytical solution for the frequency response of the semi-batch adsorption vessel loaded with inert core adsorbents is obtained in terms of the in-phase and the out-of-phase characteristic functions. When the external mass transfer resistance is present, there exist a crossover frequency and an overshoot of the in-phase characteristic function. With increasing x_C and with decreasing ξ, the crossover frequency decreases and the overshoot increases, respectively. The low-frequency limiting value of the in-phase characteristic function increases with decreasing size of inert core and with decreasing external resistance. The low-frequency limiting value of the out-of-phase characteristic function increases with decreasing external resistance. With decreasing size of inert core, however, the low-frequency limiting value of the out-of-phase characteristic function decreases at first and then increases after a minimum value is reached.

ACKNOWLEDGEMENT

This work was supported by the Kyungnam University Research Fund, 2005.

NOMENCLATURE

C_b : concentration in the bulk phase [mol/m^3]
C_s : concentration in the bulk phase at the particle surface [mol/m^3]
C_μ : concentration in the adsorbed phase [mol/m^3]
D_e : effective diffusivity [m^2/s]
k_f : external film mass transfer coefficient [m/s]
K : dimensionless Henry constant of the linear isotherm
N : molar flow rate of adsorbate into vessel [mol/sec]
r : radial variable of adsorbent particle [m]
R : radius of adsorbent particle [m]
R_C : radius of inert core [m]
t : time variable [s]
V, $V_{\mu 0}$: volume of free space and total particles including inert cores within the adsorption vessel [m^3]
ω : angular frequency of sinusoidal forcing function [rad/s]

REFERENCES

Chanda, M. and Rempel, G. L., "Chromium (III) Removal by Epoxy-Cross-Linked Poly(Ethylenimine) Used as Gel-Coated on Silica. 2. A New Kinetic Model," *Ind. Eng. Chem. Res.*, **36**, 2190 (1997).

Chanda, M. and Rempel, G. L., "Gel-Coated Ion-Exchange Resin: A New Kinetic Model," *Chem. Eng. Sci.*, **54**, 3723 (1999).

Jung, H. W., Lee, J. S., Scriven, L. E. and Hyun, J. C., "The Sensitivity and Stability of Spinning Process Using Frequency Response Method," *Korean J. Chem. Eng.*, **21**, 20 (2004).

Li, P., Xiu, G. and Rodrigues, A. E., "Modeling Separation of Proteins by Inert Core Adsorbent in a Batch Adsorber," *Chem. Eng. Sci.*, **58**, 3361 (2003).

Park, I. S., "Analysis of the Constant Molar Flow Semi-batch Adsorber Loaded with Inert Core Adsorbents," *Korean J. Chem. Eng.*, **in press** (2005).

Park, I. S., Petkovska, M. and Do, D. D., "Frequency Response of an Adsorber with Modulation of the Inlet Molar Flow-rate; I. a Semi-batch Adsorber," *Chem. Eng. Sci.*, **53**, 819 (1998).