

Frequency Response of Adsorption of a Gas onto Bidisperse Pore-Structured Solid with Modulation of Inlet Molar Flow-Rate

In-Soo Park[†], Chul Kwak and Young-Gi Hwang

School of Fine Chemistry and Chemical Engineering, Kyungnam University,
449, Wolyoung-dong, Masan 631-701, Korea

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Abstract—We present a theoretical analysis of the frequency response of a continuous-flow adsorber for adsorption of a gas onto bidisperse pore-structured solid, forced by the periodic modulation of the inlet flow-rate. Spherical macroparticle and spherical microparticle geometries are considered. A local adsorption equilibrium of the gas on the exterior surface of microparticle is assumed. It is confirmed that the in-phase characteristic function of the frequency response of a flow adsorber is independent of the overflow parameter, but that the out-of-phase characteristic function is a strong function of the overflow in the lower frequency region. The overall characteristic functions in the microparticle diffusion regime have information of both microparticle diffusion and macropore diffusion. Hence, in this regime we can extract the macropore diffusion parameter as well as the microparticle diffusion parameter from the experimental data of the overall characteristic functions. In the microparticle diffusion regime the capacity parameter of microparticle affects also the characteristic functions.

Key words: Frequency Response, Characteristic Function, Bidisperse Pore Structure, Adsorption

INTRODUCTION

The frequency response (FR) method in adsorption studies is a relaxation technique in which the equilibrium state of the system is modulated periodically in order to measure the response of the state variables under periodic steady state conditions. Measurement of the response of the system over the modulation frequency spectrum facilitates the identification of the controlling sorption mechanisms and the relevant parameters [Yasuda and Saeki, 1978; Yasuda, 1982, 1989, 1993, 1995; Yasuda and Sugawara, 1984; Yasuda et al., 1995; Jordi and Do, 1992, 1993, 1994; Sun and Do, 1995, 1996].

In the FR method the frequency response is usually investigated in a batch system in which the gas pressure or concentration is changed by a forced periodic modulation of the reservoir volume. Contrary to this conventional FR method, however, the FR method in continuous flow systems was also presented with periodic modulation of the inlet gas concentration [Ngai and Gomes, 1996] or the inlet molar flow rate [Park et al., 1998a, b, 2000]. The main advantages of FR using modulation of the inlet flow-rate over the conventional FR using modulation of the reservoir volume are the following [Park et al., 1998a, b, 2000]:

- High frequencies of the inlet molar flow-rate modulations are easy to obtain in practice on the contrary to volume modulations.
- Large relative amplitudes of the inlet flow-rate can be used.

In addition to the above advantages, Park et al. [1998b] showed in the analysis of the FR of a continuous-flow adsorber, in which monodisperse pore-structured solids were loaded, that the features of the frequency response of a continuous-flow adsorber were highly

dependent on the overflow parameter, which could be exploited in the estimation of adsorption parameters.

In this paper, we will extend the frequency response analysis of Park et al. [1998a, b] to the system of zeolite-like, bidisperse pore-structured pellets. Spherical macroparticle and spherical microparticle geometries will be considered. A linear adsorption isotherm will be assumed.

PROBLEM FORMULATION AND MATHEMATICAL MODEL

We consider a continuous-flow adsorber in which there is a known amount of adsorbent particles with zeolite-like, bidispersed pore structure. At time $t=0$, a stream of pure adsorbate is introduced into the adsorber and at the same time an outlet flow from the adsorber is started. The simplifying assumptions for the mathematical model are as follows:

- (1) negligible gas-to-solid mass transfer resistance
- (2) pore diffusion in macropores within the spherical macroparticle
- (3) equilibrium adsorption on the outer surface of the microparticle
- (4) microparticle diffusion within the spherical microparticle of uniform size (e.g., diffusion within zeolite crystal)
- (5) isothermal condition
- (6) linear adsorption isotherm
- (7) constant equilibrium and dynamic parameters.

Assumption 1 is easily satisfied with rapid stirring in the reservoir. Assumption 2 is reasonable as the surface diffusion in the macropore is negligible compared to the pore diffusion. Assumption 3 is usually satisfied in gas-solid systems as the gas-solid interaction

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

is very fast relative to the diffusion in the macropore as well as the diffusion within the microparticle. Assumption 4 is well satisfied in case of zeolite-like particles because of the molecular dimension of the channels. And assumptions 5, 6, and 7 are reasonable if the pressure during the whole experiment is maintained low.

The mass balance equations based on the above assumptions are given below in terms of dimensionless variables and parameters defined in Table 1:

1. Mass balance equations within the microparticle (with initial and boundary conditions):

$$\frac{\partial A_\mu}{\partial \tau} = \frac{1}{x_\mu^2} \frac{\partial}{\partial x_\mu} \left(x_\mu^2 \frac{\partial A_\mu}{\partial x_\mu} \right) \quad (1a)$$

$$\text{at } \tau=0, A_\mu=0 \quad (1b)$$

$$\text{at } x_\mu=0, \frac{\partial A_\mu}{\partial x_\mu}=0 \quad (\text{or } A_\mu=\text{finite}) \quad (1c)$$

$$\text{at } x_\mu=1, A_\mu=A_a \quad (1d)$$

2. Mass balance in the macropore (with initial and boundary conditions):

$$\frac{\partial A_a}{\partial \tau} = \frac{1}{\alpha x^2} \frac{\partial}{\partial x} \left(x^2 \frac{\partial A_a}{\partial x} \right) - \frac{(1-\varepsilon_a)K \partial \langle A_\mu \rangle}{\varepsilon_a \partial \tau} \quad (2a)$$

$$\langle A_\mu \rangle = 3 \int_0^1 x_\mu^2 A_\mu dx_\mu \quad (2b)$$

$$\text{at } \tau=0, A_a=0 \quad (2c)$$

$$\text{at } x=0, \frac{\partial A_a}{\partial x}=0 \quad (2d)$$

$$\text{at } x=1, A_a=A \quad (2e)$$

where α is the ratio of the macropore time constant to the microparticle time constant (see Table 1). The model is controlled by the macropore diffusion when $\alpha \gg 1$ and controlled by the microparticle diffusion when $\alpha \ll 1$.

3. Mass balance around the reservoir (with initial and boundary conditions):

$$\frac{dA}{d\tau} + \beta_a \frac{d}{d\tau} [e_a \langle A_a \rangle + (1-\varepsilon_a)K \langle \langle A_\mu \rangle \rangle] = \Omega X(\tau) - \gamma A(\tau) \quad (3a)$$

$$\langle A_a \rangle = 3 \int_0^1 x^2 A_a dx \quad (3b)$$

$$\langle \langle A_\mu \rangle \rangle = 3 \int_0^1 x_\mu^2 \langle A_\mu \rangle dx_\mu \quad (3c)$$

$$\text{at } \tau=0, A=0 \quad (3d)$$

where Ω is dimensionless parameter measuring molar supply into

the reservoir, β_a is the volume ratio of adsorbent to reservoir, and γ is the dimensionless overflow parameter (see Table 1). If $\gamma=0$, then we have a semibatch adsorber instead of the continuous-flow adsorber.

In Eq. (3a) $X(\tau)$ is the forcing function, which defines the form of the periodic modulation of the inlet flow rate. We use the sinusoidal wave function:

$$X(\tau) = 1 + v \sin \omega^* \tau \quad (4)$$

where v is the amplitude and ω^* is the dimensionless frequency based on the microparticle time constant (see Table 1).

SOLUTION IN LAPLACE DOMAIN

The solution in the Laplace domain will be given in the form of a transfer function. The overall transfer function in the Laplace domain relating the forcing function to the bulk concentration in the gas phase within the reservoir can be obtained as:

$$G(s) \equiv \frac{\bar{A}}{\Omega \bar{X}} = \frac{1}{s \left[1 + \frac{\gamma}{s} + \beta Q(s) \right]} \quad (5)$$

where β is relative capacity of adsorbent, which is given by

$$\beta = \beta_a [e_a + (1-\varepsilon_a)K] \quad (6)$$

The transfer function $Q(s)$ in Eq. (5) characterizes the adsorption dynamics of the adsorbent particle, which is defined as

$$Q(s) = \frac{\varepsilon_a + (1-\varepsilon_a)KF_\mu(s)}{\varepsilon_a + (1-\varepsilon_a)K} F_a(s) \quad (7)$$

In Eq. (7) $F_a(s)$ is the transfer function relating the bulk concentration to the gas-phase concentration in macropores, which is given by:

$$F_a(s) \equiv \frac{\langle \bar{A}_a \rangle}{\bar{A}} = 3 \left(\frac{q_a \coth(q_a) - 1}{q_a^2} \right) \quad (8)$$

where

$$q_a = \sqrt{\alpha s \left[\frac{\varepsilon_a + (1-\varepsilon_a)KF_\mu(s)}{\varepsilon_a + (1-\varepsilon_a)K} \right]} \quad (9)$$

In Eqs. (7) and (9), $F_\mu(s)$ is the transfer function relating the gas-phase concentration in macropores to the solid-phase concentration within microparticles, which is given by:

$$F_\mu(s) \equiv \frac{\langle \bar{A}_\mu \rangle}{\bar{A}_a} = 3 \left(\frac{q_\mu \coth(q_\mu) - 1}{q_\mu^2} \right) \quad (10)$$

where

$$q_\mu = \sqrt{s} \quad (11)$$

Using the transfer functions $G(s)$, $Q(s)$, $F_a(s)$, and $F_\mu(s)$ defined in this section, the adsorber response to any forcing function can be obtained by using the method of residues and inverse Laplace transform. For the constraints of constant or square-wave forcing, and semibatch operation (i.e., $\gamma=0$), we can arrive at the solution in the real time domain, given by Park and Do [1996].

Table 1. Dimensionless variables and parameters (C_0 denotes a reference concentration)

$A_\mu = \frac{C_\mu}{KC_0}$; $A_a = \frac{C_a}{C_0}$; $A = \frac{C}{C_0}$; $x_\mu = \frac{r_\mu}{R_\mu}$; $x = \frac{r}{R}$; $\tau = \frac{t}{R_\mu^2/D_\mu}$;
$\omega^* = \omega \left(\frac{R_\mu^2}{D_\mu} \right)$; $\beta_a = \frac{V_\mu}{V}$; $\alpha = \frac{R^2/D}{R_\mu^2/D_\mu}$; $\Omega = \left(\frac{\dot{N}}{C_0 V} \right) \left(\frac{R_\mu^2}{D_\mu} \right)$; $\gamma = \left(\frac{q}{V} \right) \left(\frac{R_\mu^2}{D_\mu} \right)$

FREQUENCY RESPONSE

Having obtained the transfer function, we can obtain the FR by substituting $s=i\omega^*$ into $G(s)$. Then the magnitude of $G(i\omega^*)$ becomes the amplitude ratio (AR) of the response and the argument of $G(i\omega^*)$ becomes the phase shift (PS). We can characterize the FR by using the amplitude ratio and the phase shift. However, a more common way to characterize the FR is to use the in-phase and out-of-phase characteristic functions instead of the amplitude ratio and the phase shift.

We define the in-phase characteristic function and the out-of-phase characteristic function as the real part and the negative of the imaginary part of the FR transfer function corresponding to the transfer function $Q(s)$ [defined by Eq. (7)], in the limit of $s=i\omega^*$, respectively. Thus, we have

$$\frac{\eta_R}{\beta} = \operatorname{Re} \left\{ \lim_{s \rightarrow i\omega^*} \left[Q(s) + \frac{\gamma}{\beta s} \right] \right\} \quad (12a)$$

$$\frac{\eta_I}{\beta} = -\operatorname{Im} \left\{ \lim_{s \rightarrow i\omega^*} \left[Q(s) + \frac{\gamma}{\beta s} \right] \right\} \quad (12b)$$

Subsequently, we can obtain the in-phase and the out-of-phase functions as follows:

$$\frac{\eta_R}{\beta} = (1 - \beta_b) f_{aR} + \beta_b (f_{\mu R} f_{aR} - f_{\mu I} f_{aI}) \quad (12c)$$

$$\frac{\eta_I}{\beta} = (1 - \beta_b) f_{aI} + \beta_b (f_{\mu R} f_{aI} + f_{\mu I} f_{aR}) + \frac{\gamma}{\beta \omega^*} \quad (12d)$$

where β_b is the relative capacity of microparticle within adsorbent particle, which is given by

$$\beta_b = \frac{(1 - \varepsilon_a)K}{\varepsilon_a + (1 - \varepsilon_a)K} \quad (13)$$

The functions f_{aR} and f_{aI} in Eq. (12) are given as the real part of f_a ($i\omega^*$) and the negative of the imaginary part of $f_a(i\omega^*)$, respectively:

$$f_{aR} - if_{aI} = \frac{3}{u^2 + v^2} \left\{ \left[\frac{u \sinh(2u) - v \sin(2v)}{\cosh(2u) - \cos(2v)} - \frac{u^2 - v^2}{u^2 + v^2} \right] - i \left[\frac{v \sinh(2u) + u \sin(2v)}{\cosh(2u) - \cos(2v)} - \frac{2uv}{u^2 + v^2} \right] \right\} \quad (14a)$$

where u and v are:

$$u = \operatorname{Re}[q_a]_{s=i\omega^*} = \sqrt{\beta_b \alpha \omega^* / 2} (f_{\mu I} + \sqrt{f_{\mu I}^2 + \{(1 - \beta_b)/\beta_b + f_{\mu R}\}^2})^{1/2} \quad (14b)$$

$$v = \operatorname{Im}[q_a]_{s=i\omega^*} = \sqrt{\beta_b \alpha \omega^* / 2} (-f_{\mu I} + \sqrt{f_{\mu I}^2 + \{(1 - \beta_b)/\beta_b + f_{\mu R}\}^2})^{1/2} \quad (14c)$$

where $f_{\mu R}$ and $f_{\mu I}$ are given as the real part of $f_\mu(i\omega^*)$ and the negative of the imaginary part of $f_\mu(i\omega^*)$, respectively:

$$f_{\mu R} = 3 \left\{ \frac{\sinh(\sqrt{2}\omega^*) - \sin(\sqrt{2}\omega^*)}{\sqrt{2}\omega^* (\cosh(\sqrt{2}\omega^*) - \cos(\sqrt{2}\omega^*))} \right\} \quad (15a)$$

$$f_{\mu I} = 3 \left\{ \frac{\sinh(\sqrt{2}\omega^*) + \sin(\sqrt{2}\omega^*)}{\sqrt{2}\omega^* (\cosh(\sqrt{2}\omega^*) - \cos(\sqrt{2}\omega^*))} - \frac{2}{(2\omega^*)^2} \right\} \quad (15b)$$

The FR to the sinusoidal forcing function [defined by Eq. (4)] in terms of the amplitude ratio (AR) and the phase shift (PS) is [Park et al., 1998a, b]:

$$\frac{A}{\Omega} = \frac{1}{\gamma} + (v)AR \sin(\omega^* \tau + PS) \quad (16)$$

The first term of the RHS of Eq. (16) represents the long time response of the continuous-flow adsorber to the constant term (i.e., unity) of the forcing function. The AR and PS in terms of the in-phase and out-of-phase characteristic functions are given by

$$AR = \left(\frac{1}{\omega^*} \right) \left(\frac{1}{\sqrt{\eta_I^2 + (1 + \eta_R)^2}} \right) \quad (17a)$$

$$PS = \tan^{-1} \left(\frac{\eta_I}{1 + \eta_R} \right) - \frac{\pi}{2} \quad (17b)$$

It should be noted that the in-phase and out-of-phase components and the amplitude ratio and the phase shift satisfy the following relationship:

$$\eta_R - i\eta_I = \frac{1}{(\omega^*)AR} \exp \left[-i \left(PS + \frac{\pi}{2} \right) \right] - 1 \quad (18)$$

SIMULATION OF THE FREQUENCY RESPONSE

We have obtained the FR of a continuous-flow adsorber, in which bidisperse pore-structured solids are loaded. The response is expressed as a function of the AR and the PS. The AR and the PS are expressed as functions of the in-phase and out-of-phase characteristic functions, which are expressed in terms of adsorption equilibrium and dynamic parameters [see Eqs. (16) and (17)]. Therefore, we could extract equilibrium and dynamic parameters by comparing the observed characteristic functions to the theoretical ones. We will simulate the in-phase and the out-of-phase characteristic functions for some cases below to show how each of the system parameters influences the response and to get some ideas how to ex-

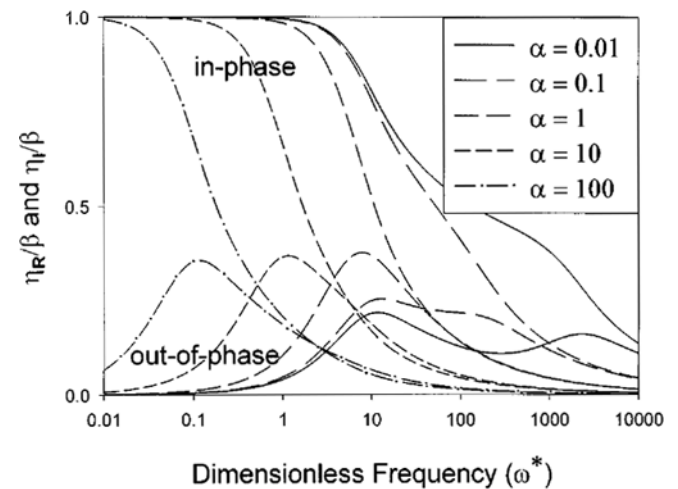


Fig. 1. Effect of the relative magnitude of macropore time constant to microparticle time constant on the characteristic functions for $\beta_b=0.6$ [solid ($\alpha=0.01$), long dash ($\alpha=0.1$), medium dash ($\alpha=1$), short dash ($\alpha=10$), dash-dot ($\alpha=100$)].

tract system parameters effectively.

Fig. 1 shows the in-phase and out-of-phase characteristic functions of the frequency response at different values of α for semi-batchwise operation of the adsorber (i.e., $\gamma=0$). We can see that the characteristic functions start to deviate from the corresponding low-frequency asymptotes and approach to the corresponding high-frequency asymptotes in the lower frequencies, respectively, as the value of α increases. In the macropore diffusion regime (i.e., when $\alpha \gg 1$) the characteristic functions shift nearly parallel to the left along the frequency-axis with increasing α . This is because in the macropore diffusion regime the frequency response is controlled by the macropore diffusion. Since the characteristic functions of the macropore diffusion (i.e., f_{aR} and f_{aI}) are functions of $\alpha\omega^*$ [see Eq. (14)], the parameter α shifts the characteristic functions parallel on the logarithmic scale of the frequency-axis. In the microparticle diffusion regime (i.e., when $\alpha \ll 1$) the shape of the out-of-phase characteristic function is bimodal. This bimodal shape is due to the contribution of the macropore diffusion, which is shown more clearly in Fig. 3. The shape and the characteristic frequencies (e.g., maximum frequency of out-of-phase function) of the FR are different in the different regime. Hence, we can conclude that the discrimination between the macropore diffusion and microparticle diffusion regimes could be achieved by matching the theoretical response to the experiment.

The overall characteristic function (i.e., η_R/β and η_I/β) is expressed as a function of the characteristic functions of the macropore diffusion and the microparticle diffusion [see Eqs. (12)]. To show how the individual characteristic function contributes to the overall function, the overall function of the FR, together with those of macropore diffusion and microparticle diffusion, is plotted in the macropore diffusion regime (i.e., $\alpha=100$) in Fig. 2 and in the microparticle diffusion regime (i.e., $\alpha=0.01$) in Fig. 3, respectively. As shown in Fig. 2, the overall characteristic function in the macropore diffusion regime (e.g., for $\alpha=100$) is nearly consistent with the characteristic function of the macropore diffusion. As we can see in Fig. 3, however, the overall characteristic function in the microparticle diffusion regime (e.g., for $\alpha=0.01$) has both information of the mac-

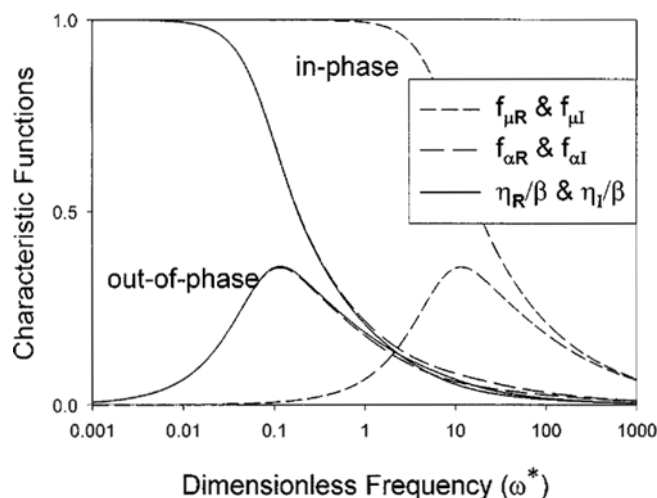


Fig. 2. Behavior of characteristic functions under macropore diffusion control for $\alpha=100$ and $\beta_b=0.6$ [short dash ($f_{\mu R}$ & $f_{\mu I}$), long dash (f_{aR} & f_{aI}), solid (η_R/β & η_I/β)].

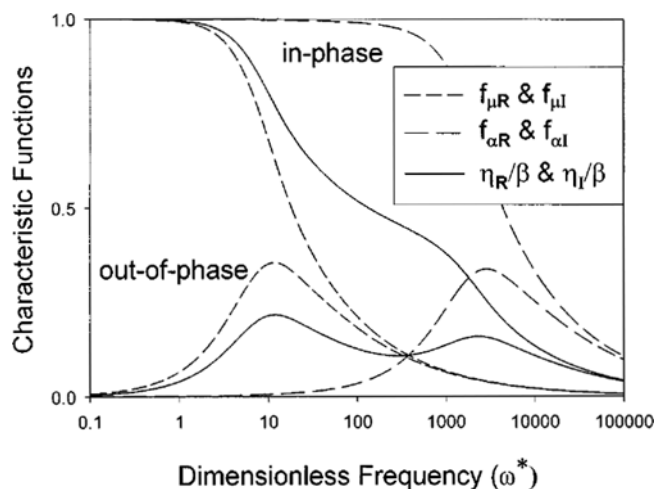


Fig. 3. Behavior of characteristic functions under microparticle diffusion control for $\alpha=0.01$ and $\beta_b=0.6$ [short dash ($f_{\mu R}$ & $f_{\mu I}$), long dash (f_{aR} & f_{aI}), solid (η_R/β & η_I/β)].

ropore diffusion and the microparticle diffusion. Hence, in the microparticle diffusion regime the macropore diffusion time constant as well as the microparticle time constant could be extracted from the overall characteristic function. Since many adsorption processes of gases in zeolites are controlled by the microparticle diffusion [Ruthven, 1984; Park and Do, 1996], this feature of the characteristic function would be very useful in the FR analysis of the zeolitic system.

The effect of the capacity parameter of microparticles on the characteristic function is shown in the macropore diffusion regime ($\alpha=10$) in Fig. 4 and in the microparticle diffusion regime ($\alpha=0.01$) in Fig. 5, respectively. As shown in Fig. 4, in the macropore diffusion regime the existence of the microparticle can hardly affect the overall behavior of the adsorption process. As shown in Fig. 5, however, in the microparticle diffusion regime the overall characteristic functions have both information of the macropore diffusion and the microparticle diffusion.

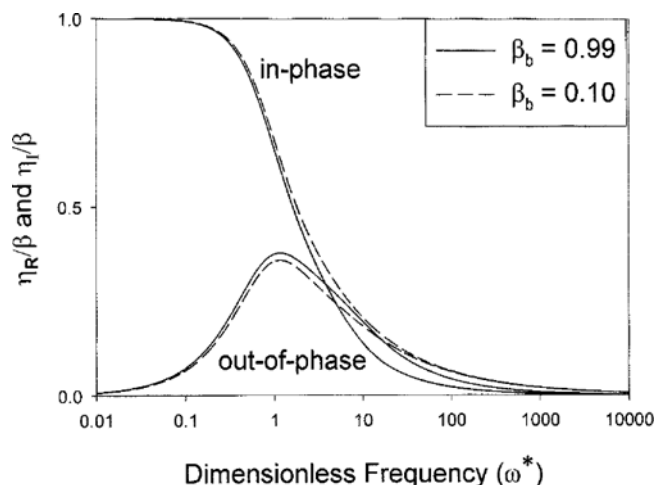


Fig. 4. Effect of the relative capacity of microparticle on the characteristic functions under macropore diffusion control for $\alpha=10$ [solid ($\beta_b=0.99$), dash ($\beta_b=0.1$)].

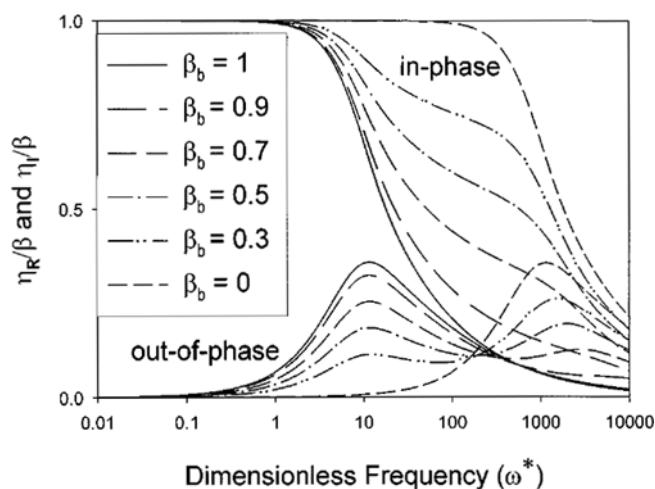


Fig. 5. Effect of the relative capacity of microparticle on the characteristic functions under macropore diffusion control for $\alpha=0.01$ [solid ($\beta_b=1$), long dash ($\beta_b=0.9$), medium dash ($\beta_b=0.7$), dash-dot ($\beta_b=0.5$), dash-dot-dot ($\beta_b=0.3$), short dash ($\beta_b=0$)].

For $0 < \beta_b < 1$, in the microparticle diffusion regime the shape of the out-of-phase function is bimodal (see Fig. 5). For both cases of $\beta_b=0$ and $\beta_b=1$ the shape of the out-of-phase function is unimodal as these cases reduce to the system of monodisperse pore-structured solids.

As we can see in Eq. (12), the in-phase function is independent of the overflow parameter, but the out-of-phase function is a function of the overflow parameter. The effect of the overflow parameter on the out-of-phase function is shown in Fig. 6. On the contrary to the same function of a batch and semibatch adsorber, the out-of-phase characteristic function of a flow adsorber can show a minimum and maximum (for lower values of γ), or no extrema at all (for higher values of γ). As discussed in Park et al. [1998b], the overflow parameter should be kept small to produce the minimum and

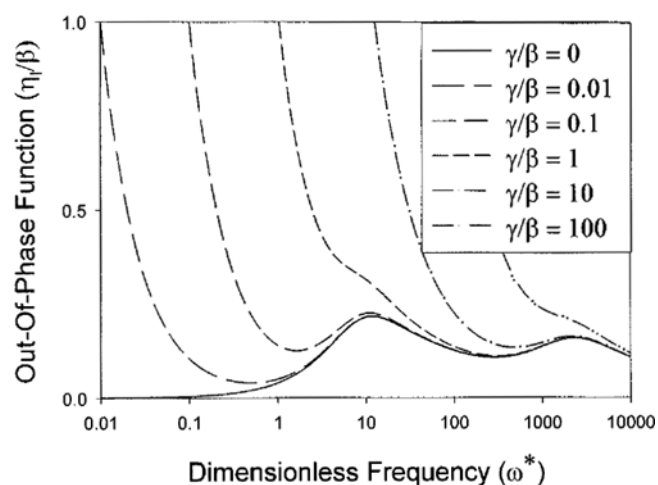


Fig. 6. Effect of the overflow parameter on the out-of-phase characteristic function for $\alpha=0.01$ and $\beta_b=0.6$ [solid ($\gamma/\beta=0$), long dash ($\gamma/\beta=0.01$), medium dash ($\gamma/\beta=0.1$), dash-dot ($\gamma/\beta=1$), dash-dot-dot ($\gamma/\beta=10$), short dash ($\gamma/\beta=100$)].

the maximum which can be useful in parameter estimation from experimental data.

CONCLUSION

In this paper, we presented a theoretical analysis of the frequency response of a continuous-flow adsorber for adsorption of gases onto bidispersed solids, forced by the periodic modulation of the inlet flow-rate. It was confirmed that the in-phase characteristic function of the frequency response of the continuous-flow adsorber is independent of the overflow parameter, but the out-of-phase characteristic function is a strong function of the overflow in the lower frequency region.

Since the shapes and the characteristic frequencies of the FR are different in the different regimes of mass transfer, the discrimination between the macropore diffusion and microparticle diffusion regimes could be achieved by matching the theoretical response to the experiment. The overall characteristic functions in the macropore diffusion regime are nearly consistent with the characteristic functions for the macropore diffusion, while the overall characteristic functions in the micropore diffusion regime have information of both the macropore diffusion and the microparticle diffusion. In this regime we can extract the macropore diffusion parameter as well as the microparticle diffusion parameter from the experimental data of the overall characteristic functions.

The out-of-phase characteristic function of a flow adsorber can show a minimum and maximum, at small values of the overflow parameter. Thus, the overflow parameter should be kept small to produce the minimum and the maximum which can be also useful in parameter estimation.

NOMENCLATURE

- A, A_a, A_μ : dimensionless concentrations in the reservoir, in the macropores, and in the microparticles, respectively, defined in Table 1
- $\langle A_a \rangle$: volumetric average of A_a
- $\langle A_\mu \rangle$: volumetric average of A_μ
- $\langle\langle A_\mu \rangle\rangle$: volumetric average of $\langle A_\mu \rangle$
- AR : amplitude ratio
- C, C_a, C_μ : concentrations in the reservoir, in the macropores, and in the microparticles, respectively [mol/m³]
- D : apparent effective diffusivity in micropores, defined in Table 1 [m²/s]
- D_a : effective diffusivity in macropores [m²/s]
- D_μ : effective diffusivity within microparticles [m²/s]
- f_{aR}, f_{aI} : in-phase and out-of-phase characteristic functions of the macropore diffusion, defined by Eq. (14)
- $f_{\mu R}, f_{\mu I}$: in-phase and out-of-phase characteristic functions of the microparticle diffusion, defined by Eq. (15)
- $F_a(s)$: transfer function, defined by Eq. (8)
- $F_\mu(s)$: transfer function, defined by Eq. (10)
- $G(s)$: overall transfer function, defined by Eq. (5)
- K : adsorption equilibrium constant
- \dot{N} : inlet molar flow rate to reservoir [mol/s]
- PS : phase shift
- q : volumetric overflow rate from reservoir [m³/s]

q_a	: function, defined by Eq. (9)
q_μ	: function, defined by Eq. (11)
$Q(s)$: transfer function for the particle, defined by Eq. (7)
r	: coordinate variable of particle [m]
r_μ	: coordinate variable of microparticle [m]
R	: equivalent radius of particle [m]
R_μ	: equivalent radius of microparticle [m]
s	: Laplace variable [1/s]
t	: time variable [s]
u	: function, defined by Eq. (14b)
v	: function, defined by Eq. (14c)
V, V_μ	: volumes of reservoir and adsorbents, respectively [m ³]
$X(\tau)$: dimensionless forcing function

Greek Letters

α	: relative magnitude of macropore time constant to microparticle time constant
β	: relative capacity of adsorbent, defined by Eq. (6)
β_a	: volume ratio of adsorbent to reservoir, defined in Table 1
β_b	: relative capacity of microparticle within adsorbent particle, defined by Eq. (13)
ε_a	: macropore porosity
γ	: overflow parameter, defined in Table 1
η_R, η_I	: in-phase and out-of-phase characteristic function of frequency response, defined by Eq. (12)
ν	: amplitude of modulation of inlet molar flow rate, defined in Eq. (4)
τ	: dimensionless time, defined in Table 1
ω	: angular frequency of the perturbation in flow rate, rad/s
ω^*	: dimensionless angular frequency of the perturbation in flow rate, defined in Table 1
Ω	: dimensionless molar supply parameter into the reservoir, defined in Table 1

Superscript

—	: variables in the Laplace domain
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