

## Dynamic Effectiveness Factor for Catalyst Particles

José Álvarez-Ramírez,\* J. Alberto Ochoa-Tapia, and Francisco J. Valdés-Parada

*División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana—Iztapalapa, Apartado Postal 55-534, Mexico D.F. 09340, Mexico*

*Received: January 17, 2005; In Final Form: March 31, 2005*

The effectiveness factor (EF) is a nondynamic concept that has been demonstrated to be useful for the analysis and design of reaction–diffusion systems (e.g., catalyst particles). The aim of this paper is to introduce a dynamic EF factor (DEF) concept that extends the existing nondynamic one. In the first step, the standard EF is interpreted as a scaling factor that transforms total reaction rates from surface/bulk to catalyst particle conditions. Through the use of Fourier transform (i.e., frequency domain) to deal with time variations, the above interpretation is extended to dynamic conditions by defining the DEF as a linear operator transforming total reaction rate signals from surface/bulk to catalyst particle conditions. It is shown that the classical nondynamic EF concept is recovered in the steady-state limit of the DEF definition. Interestingly, the DEF can be easily computed from the nondynamic EF expressions by introducing a complex Thiele modulus. Results show that for reaction–diffusion processes where the diffusion mechanism is governed by Fick's law the magnitude of the DEF decreases with the frequency. This means that the best reaction rate performance is obtained when the process operates at steady-state (i.e., nondynamic) conditions. However, when a diffusion model with relaxation time is assumed to hold, resonant peaks at nontrivial frequencies can be displayed. Physically, this behavior implies that dynamic (e.g., periodic) operation of the reaction–diffusion process can yield better performance when compared with its nondynamic counterpart.

### 1. Introduction

In most practical heterogeneous reaction systems involving catalyzed chemical reactions, catalyst particles are made large enough to minimize the pressure drop in the packed bed such that intraparticle resistance to mass transfer becomes significant. By departure from mass and energy balances, the description of reaction–diffusion phenomena in a heterogeneous reaction system commonly involves distributed parameter models (e.g., partial differential equations (PDEs)) for both a fluid and catalyst particles. Despite its quite good accuracy, this type of model is rarely used for design and/or simulation purposes because of the difficulty to find a computationally nonexpensive solution. For instance, excessive computational burden can occur within an optimization framework where the distributed parameter model of the catalyst particle should be solved at each optimization trial. A commonly used approach to avoid the drawback of solving the catalyst particle model is the use of an effectiveness factor (EF) concept.<sup>1</sup> In fact, the EF reduces the dimensionality of the heterogeneous reactor model and makes the solution easier to obtain. The idea is to express the reaction rate in a catalyst particle by its rate under surface/bulk conditions multiplied by a functional factor, namely, by the effectiveness factor. By serving as the functional factor, the EF gives some information on the effectiveness of a single catalyst particle. Also, the EF can be seen as a measure of the effective usage of the catalyst particle space. In this form, the EF is a useful concept to design catalyst particles in the face of a trade-off situation between the pressure drop across the reaction–diffusion process pack and the effective catalyst particle space usage.

The EF concept used so far concerns nondynamic conditions.<sup>1</sup> This is because most practical chemical reaction systems are designated to operate at steady-state conditions. In fact, the steady-state (i.e., nondynamic) conditions design is based on average values of fluctuating input components. Though the system operation is maintained around a steady state, some of the input components, such as composition, flow rate, etc., vary continuously with time, and thus, industrial chemical reactions do not operate at a steady state. The process performance may improve or deteriorate as a result of dynamic operation. It was suggested over a decade ago that certain features of chemical systems, e.g., the continuous control over the phase shift between fluxes and forces through periodic perturbations, can be exploited for superior dynamic operation in terms of efficiency compared to nondynamic states. Theoretical and experimental studies<sup>2–5</sup> have shown that sometimes working at dynamic conditions gives higher productivity, conversion, selectivity, and efficiency, provides better distribution, and enhances catalyst activity. For instance, studies on trickle bed reactors<sup>6</sup> and Fischer–Tropsch synthesis<sup>7</sup> have shown improvements in the process performance by using periodic operation. Gulari et al.<sup>8</sup> have reviewed the research results for the catalytic oxidation of carbon monoxide, showing improved catalytic system performance under periodic operation. The idea of improving the efficiency of a reaction–diffusion system by means of periodic perturbations has also been explored in the context of electrochemical energy conversion devices.<sup>9</sup> The above results show that the dynamic operation of reaction–diffusion (e.g., catalyst) systems is an exciting research field that requires novel analysis and design methodologies.

In summary, two important facts that should be considered for design and operation of processes involving both chemical reactions and diffusion are the following:

\* Author to whom correspondence should be addressed. Phone: +52-55-57244648. Fax: +52-55-58044900. E-mail: jjar@xanum.uam.mx.

• The EF concept has been demonstrated to be useful for analysis and design. However, the existing EF concept has been limited to nondynamic conditions.

• Studies have shown that the performance of a reaction–diffusion process is sometimes improved when it is operating dynamically.

These facts promote the problem of extending the EF concept to dynamic conditions. In principle, the use of a dynamic EF (DEF) concept would allow us to analyze the improvement or deterioration of the performance for reaction–diffusion processes in the face of external dynamic perturbations or periodic operation. For instance, it would be interesting to use a DEF concept to evaluate the effectiveness of a single catalyst particle when the surface/bulk concentration varies periodically.

It should be mentioned that, although not explicitly, the introduction of a dynamic effectiveness factor associated with a dynamic Thiele modulus has already been anticipated.<sup>10</sup> In fact, while such earlier work was devoted to frequency modulation of adsorption and diffusion processes, the analogy between the perturbing frequency and a first-order rate constant in chemical reactions and its implications on the particle performance was noted. Motivated by the work of Reyes et al., the aim of this paper is to introduce a DEF concept that extends the existing nondynamic EF definition. In the first step, the classical EF is interpreted as a scaling factor that transforms the total reaction rates from surface/bulk to catalyst particle conditions. Through the use of Fourier transform (i.e., frequency domain) to deal with time variations, the above interpretation is extended to dynamic conditions by defining the DEF as a linear operator transforming the total reaction rate signals from surface to catalyst particle conditions. It is shown that the classical nondynamic EF concept is recovered in the steady-state limit of the DEF definition. Interestingly, the DEF can be easily computed from the nondynamic EF expressions by defining a suitable complex Thiele modulus. Results show that for reaction–diffusion processes, where the diffusion mechanism is governed by Fick's law, the magnitude of the DEF decreases with the frequency. This means that the best reaction rate performance under diffusional resistance is obtained when the process operates at steady-state (i.e., nondynamic) conditions. However, when a diffusion model with relaxation time is assumed to hold,<sup>11,12</sup> resonant peaks at nontrivial frequencies can be displayed. Physically, this behavior implies that dynamic operation of the reaction–diffusion process can yield better performance when compared with its nondynamic counterpart.

## 2. Dynamic Effectiveness Factor Concept

The aim of this section is to introduce a DEF concept that extends the classical one based on nondynamic conditions. Since we are concerned with fundamental concepts rather than with EF computations for general cases, analytic solutions for reaction–diffusion processes will be required. In this way, simple isothermic reaction–diffusion processes leading to linear differential equations will be used in the following.

**2.1. Classical EF Concept.** As mentioned previously, the classical EF concept is concerned with nondynamic operating conditions. To recall the classical EF concept, consider an isothermic catalyst particle where a single first-order chemical reaction is taking place. For chemical reactions with a nonlinear reaction rate, the obtained results should be of a local nature in the sense that only hold around steady-state conditions.

For a general geometry, by assumption of constant diffusivity  $\mathcal{D}$  and a Fickian diffusion mechanism  $\mathbf{J} = -\mathcal{D}\nabla c$ , the nondynamic process can be modeled as follows (in the following

overbars denote nondynamic conditions)

$$\mathcal{D}\Delta\bar{c} - k\bar{c} = 0 \quad (1)$$

where  $x \in \mathbb{R}^3$  is the system coordinate vector,  $\bar{c}$  is the nondynamic reactive concentration,  $k$  is the reaction constant, and  $\Delta = \partial^2/\partial x_1^2 + \partial^2/\partial x_2^2 + \partial^2/\partial x_3^2$ .

The space domain  $D \subset \mathbb{R}^3$  of the catalyst particle is assumed to be compact and simply connected. The boundary conditions for eq 1 are given as

$$\begin{aligned} \bar{c}(x) &= \bar{c}_b \text{ for all } x \in \partial D \\ \bar{c}(x) &\text{ is finite for all } x \in D \end{aligned} \quad (2)$$

where  $\bar{c}_b$  is a constant boundary concentration and  $\partial D$  denotes the boundary of the domain  $D$ . The linear eq 1 has a unique solution  $\bar{c}(x)$  satisfying the boundary conditions (eq 2) (i.e.,  $\bar{c}(x) = \bar{c}_b$  for all  $x \in \partial D$ ). The EF expresses the total reaction rate in a catalyst particle by its rate under surface/bulk conditions.<sup>1</sup> That is, the classical nondynamic EF (denoted by  $\bar{\eta}$ ) is defined as follows

$$\bar{\eta} \equiv \frac{\int_D k\bar{c} \, dV}{\int_D k\bar{c}_b \, dV} \quad (3)$$

where  $dV = dx_1 \, dx_2 \, dx_3$ . Analytic solutions of the problem (eqs 1 and 2) can be obtained for simple geometries, and the EF expression can be computed by direct integration of the solution  $\bar{c}(x)$  according to eq 3. Let

$$\Phi \equiv \sqrt{\frac{kL^2}{\mathcal{D}}} \quad (4)$$

be the Thiele modulus, where  $L$  is a characteristic length depending on the geometry. In fact,  $L$  is the slab length for rectangular geometry, and  $L$  is the cylinder and sphere radius for cylindrical and spherical geometries, respectively. The EF depends only on the Thiele modulus  $\Phi$ . For common particle geometries, one has the following well-known expressions<sup>1</sup>

$$\bar{\eta}(\Phi) = \begin{cases} \frac{\tanh(\Phi)}{\Phi} & \text{for rectangular geometry} \\ \frac{2I_1(\Phi)}{\Phi I_0(\Phi)} & \text{for cylindrical geometry} \\ 3\left[\frac{1}{\Phi \tanh(\Phi)} - \frac{1}{\Phi^2}\right] & \text{for spherical geometry} \end{cases} \quad (5)$$

where  $I_1$  and  $I_0$  are the first- and zero-order modified Bessel functions of the first kind, respectively.

The importance of the EF for analysis and design of reaction–diffusion systems relies on the relationship  $\int_D k\bar{c} \, dV = \bar{\eta}[\int_D k\bar{c}_b \, dV]$ . In principle, to compute the total reaction rate  $\int_D k\bar{c} \, dV$  provided by the catalyst particle, one should solve the boundary-value problem (eqs 1 and 2). Standard efficient finite-element and finite-differences numerical methods can be used to this end. However, if such a computation has to be made iteratively, as in optimization-based designs, then excessive and sometime prohibitive computational burden could be introduced. If the EF  $\bar{\eta}$  is known in advance, the computation of  $\int_D k\bar{c} \, dV$  can be easily performed since the computation of  $\int_D k\bar{c}_b \, dV$  is straightforward depending only on the design parameter  $\bar{c}_b$  and the underlying geometry. In this way, computational effort is drastically reduced since instead of solving a boundary-value

problem for each design iteration, only simple algebraic operations are carried out. However, from the analysis viewpoint, the EF provides information on the effective usage of the catalyst particle space for reaction purposes. For instance, small EF values denote that only a reduced fraction of the particle is acting as a reacting space.

**2.2. Extension of the Effectiveness Factor Concept for Dynamic Conditions.** As discussed in the Introduction, industrial processes are subject to external dynamic perturbations that can improve or deteriorate their performances. In this way, it would be desirable to impose a DEF concept to analyze the effects of external perturbations in the performance of reaction–diffusion processes. For a natural extension of the classical EF concept to dynamic conditions, we will interpret the EF as a scaling factor between two reaction rate functions. In fact, let  $\bar{R}_{T,b} = \int_D k \bar{c}_b \, dV$  be the total reaction rate at the boundary conditions. Notice that  $\bar{R}_{T,b} = V k \bar{c}_b$  depends only on the boundary conditions, where  $V = \int_D dV$ . However, let  $\bar{R}_T = \int_D k \bar{c} \, dV$  be the total reaction rate at actual reaction–diffusion conditions. From eq 3, one has that  $\bar{R}_T = \bar{\eta} \bar{R}_{T,b}$ . Hence, the EF  $\bar{\eta}$  can be seen as a steady-state operation that transforms the reaction rate values at the boundary conditions  $\bar{R}_{T,b}$  into reaction rate values at catalyst particle reaction–diffusion conditions  $\bar{R}_T$ ; that is

$$\bar{\eta}: \bar{R}_{T,b} \rightarrow \bar{R}_T \quad (6)$$

This feature of the classical EF has been exploited to reduce the dimensionality of heterogeneous reactor models. In fact, the relationship (eq 6) is used to avoid repeated solutions of the distributed parameter catalyst particle model in, for example, optimization-based designs of chemical reactors.

An extension of the EF concept to dynamic conditions should retain the following salient characteristics:

(a) It should be a linear transformation between the dynamic reaction rate functions at the boundary conditions and the dynamic reaction rate functions at the catalyst particle (reaction–diffusion) conditions.

(b) A dynamic EF seen as an operator between such reaction rate functions should converge uniformly to the steady-state operator  $\bar{\eta}$ .

To introduce the DEF concept as a linear transformation between dynamic reaction rate functions, similar to frequency modulation methods for diffusion and adsorption measurements in porous solids,<sup>10</sup> we resort to Fourier domain methods. Recall that if  $f(x,t)$  is a time function, then its Fourier transform  $F(x,\omega) = \mathcal{F}[f(x,t)]$  is given by  $F(x,\omega) = 1/2\pi \int_{-\infty}^{+\infty} e^{-i\omega t} f(x,t) \, dt$ , where  $\omega$  denotes the frequency and  $i = \sqrt{-1}$ . If  $c_b(t)$  is a dynamic boundary condition, then its Fourier transform is  $C_b(\omega) = \mathcal{F}[c_b(t)]$  and the corresponding dynamic total reaction rate at the boundary conditions is  $R_{T,b}(\omega) = V k C_b(\omega)$ . The dynamic total reaction rate at particle conditions  $R_T(\omega)$  is computed as

$$R_T(\omega) = \int_D k C(x,\omega) \, dV \quad (7)$$

where  $C(x,\omega)$  is the solution of the dynamic boundary-value problem (notice that  $i\omega C$  is the Fourier transform of the accumulation term

$$\mathcal{D}\Delta C - kC = i\omega C \quad (8)$$

with boundary conditions

$$\begin{aligned} C(x,\omega) &= C_b(\omega) \text{ for all } x \in \partial D \\ C(x,\omega) &\text{ is finite for all } x \in D \end{aligned} \quad (9)$$

Similar to the steady-state EF concept, we define the DEF as a linear operator  $\eta(\omega)$  that transforms dynamic total reaction rates at boundary conditions  $R_{T,b}(\omega)$  into dynamic total reaction rates at particle conditions  $R_T(\omega)$ , namely

$$\eta(\omega): R_{T,b}(\omega) \rightarrow R_T(\omega) \quad (10)$$

In other words, the DEF is a linear operator satisfying the relationship  $R_T(\omega) = \eta(\omega) R_{T,b}(\omega)$ . It is expected that  $\eta(\omega) \rightarrow \bar{\eta}$  as  $\omega \rightarrow 0$ . By serving as the functional factor, the DEF should give some information on the effectiveness of a single catalyst particle when it is subjected to external perturbations in the surface/bulk conditions. Notice that while the nondynamic EF  $\bar{\eta}$  is a real number, the DEF  $\eta(\omega)$  is a complex number for each frequency  $\omega$ .

**2.3. Computation of the DEF.** To compute the DEF  $\eta(\omega)$ , one should find the solution  $C(x,\omega)$  of the boundary-value problem (eqs 8 and 9) and use it to calculate  $R_T(\omega)$  via the integral operation in eq 7. An expression for the DEF can be easily obtained from the nondynamic EF expressions (for instance, eq 5) by noticing that eq 8 can be written as

$$\mathcal{D}\Delta C - \kappa(i\omega)C = 0 \quad (11)$$

where  $\kappa(i\omega) = k + i\omega$  can be interpreted as a complex reaction rate constant. By considering the boundary condition (eq 9), eq 11 can be solved in a similar way as in the nondynamic case (eqs 1 and 2). To this end, let us introduce the dynamic Thiele modulus

$$\Psi(\omega) \equiv \sqrt{\frac{\kappa(i\omega)L^2}{\mathcal{D}}} \quad (12)$$

Hence, if

$$\bar{\eta} = \phi(\Phi)$$

is the expression for the nondynamic EF, then the expression for the DEF is obtained by a formal substitution  $\Phi \rightarrow \Psi(\omega)$ . That is, the DEF is obtained as

$$\eta(\omega) = \phi(\Psi(\omega)) \quad (13)$$

Since  $\Psi(0) \rightarrow \Phi$ , one obtains the desired convergence  $\eta(0) = \bar{\eta}$  in the nondynamic conditions. It should be stressed that the expression for the Thiele modulus given by eq 12 and the DEF given by eq 13 hold for any reaction–diffusion dynamics as long as it can be described as in eq 11. In this way, for a given geometry, the expression  $\eta = \phi(\Psi(\omega))$  becomes a type of universal scaling function describing the effectiveness factor for any reaction–diffusion dynamics of the form in eq 11. In particular, the nondynamic case is recovered when  $\kappa(0) = k$ .

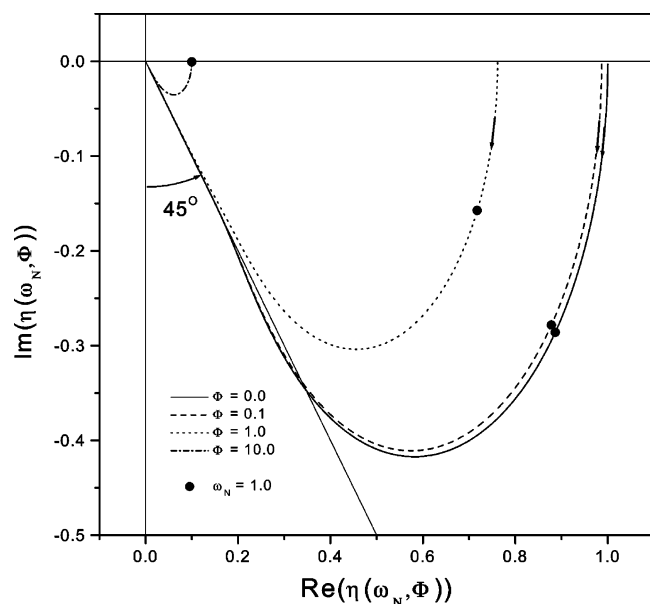
The DEF can be expressed in terms of a normalized frequency as follows. Let  $\omega_d = \mathcal{D}/L^2$  be the diffusion characteristic frequency. Introduce the normalized frequency as

$$\omega_N = \frac{\omega}{\omega_d} \quad (14)$$

Then, for  $\kappa(i\omega) = k + i\omega$ , the dynamic Thiele modulus can be written as

$$\Psi(\omega_N) = \sqrt{\Phi^2 + i\omega_N} \quad (15)$$

where  $\Phi = \sqrt{kL^2/\mathcal{D}}$  is the nondynamic Thiele modulus. In this way, in terms of the normalized frequency, the DEF expressions



**Figure 1.** Nyquist plot for the Fickian diffusion law and four different values of the Thiele modulus  $\Phi$ . Observe the high-frequency convergence of the Fickian diffusion behavior  $\eta(\omega_N, \Phi) \approx (i\omega_N)^{-1/2}$ .

for common geometries are the following

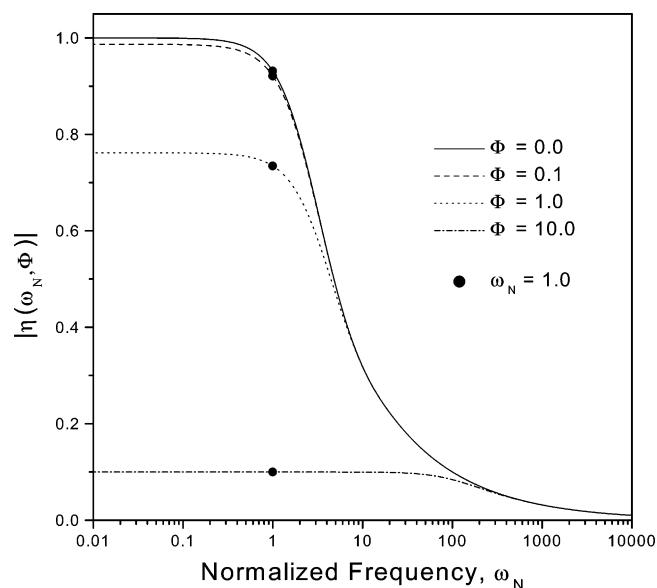
$$\eta(\omega_N, \Phi) = \begin{cases} \frac{\tanh(\Psi(\omega_N))}{\Psi(\omega_N)} & \text{for rectangular geometry} \\ \frac{2I_1(\Psi(\omega_N))}{\Psi(\omega_N)I_0(\Psi(\omega_N))} & \text{for cylindrical geometry} \\ 3 \left[ \frac{1}{\Psi(\omega_N) \tanh(\Psi(\omega_N))} - \frac{1}{\Psi^2(\omega_N)} \right] & \text{for spherical geometry} \end{cases} \quad (16)$$

Notice that the DEF is parametrized only by the nondynamic Thiele modulus  $\Phi$ .

**2.4. Discussion.** In this part of the paper, the behavior of the DEF  $\eta(\omega)$  is discussed and illustrated for rectangular geometry. Similar results are obtained for cylindrical and spherical geometries. Figures 1 and 2 show, respectively, the Nyquist plot  $\text{Re}(\eta(\omega_N, \Phi))$  versus  $\text{Im}(\eta(\omega_N, \Phi))$  and the magnitude Bode plot  $|\eta(\omega_N, \Phi)|$  for three different values of the Thiele modulus  $\Phi$ . For comparison, the limiting case  $\Phi = 0$  corresponding to a purely diffusion process is also included. The following salient features are observed:

- For each Thiele modulus  $\Phi$ , the Bode plot displayed in Figure 1 shows that the DEF magnitude  $|\eta(\omega_N, \Phi)|$  is a monotonically decreasing function of the frequency  $\omega_N$ . This means that the best reaction rate performance of a catalyst particle is obtained in the nondynamic conditions. That is, the largest reaction rate  $R_T(\omega_N)$  is obtained when the reaction–diffusion process operates at steady-state conditions. Dynamic perturbations will deteriorate the performance of the catalyst particle. In this form, this is an incentive to introduce control actions aimed to reduce dynamic perturbation effects on the system performance.

- For nondynamic conditions, one has that  $\bar{\eta}(\Phi_1) < \bar{\eta}(\Phi_2)$  for  $\Phi_1 > \Phi_2$ . That is, the nondynamic EF is a decreasing function of the classical Thiele modulus  $\Phi$ . For each frequency  $\omega_N$ , this property is maintained for the magnitude of the dynamic



**Figure 2.** Magnitude Bode plot corresponding to the conditions of Figure 1. Notice that  $|\eta(\omega_N, \Phi)|$  is a decreasing function of the frequency  $\omega_N$ .

effectiveness factor  $\eta(\omega_N, \Phi)$ . In fact, Figure 2 shows that  $|\eta(\omega_N, \Phi_1)| < |\eta(\omega_N, \Phi_2)|$  for  $\Phi_1 > \Phi_2$  and all  $\omega_N$ . As a consequence, the reaction-free case  $\Phi = 0$  becomes an upper boundary for the DEF  $\eta(\omega_N, \Phi)$ . That is, the largest DEF is obtained for reaction-free conditions. The Nyquist plot in Figure 1 shows that the curve  $\Phi = 0$  surrounds the curves for  $\Phi > 0$ .

- Recall that the diffusion characteristic frequency  $\omega_d$  has been used to normalize the frequency variable. In this way,  $\omega_N = 1$  corresponds to  $\omega = \omega_d$ . Figure 2 shows that the DEF magnitude  $|\eta(\omega_N, \Phi)| \approx \bar{\eta}(\Phi)$  for  $\omega_N < 1$ . That is, dynamic perturbations with frequencies lower than the diffusion characteristic frequency  $\omega_d$  do not have a significant effect on the performance of a catalyst particle. As a consequence, the Nyquist plot of  $\eta(\omega_N, \Phi)$  approaches the unit circle behavior for  $\omega_N < 1$ . This is illustrated in Figure 1 where the point corresponding to  $\omega_N = 1$  is marked. From the physical viewpoint, the behavior  $|\eta(\omega_N, \Phi)| \approx \bar{\eta}(\Phi)$  for  $\omega_N < 1$  can be explained from the fact that since surface concentration fluctuations with  $\omega < \omega_d$  are relatively slow when compared with diffusion dynamics reactant supply into the catalyst particle bulk is not decreased. This allows the reaction–diffusion process to perform similarly to steady-state conditions.

- For  $\omega_d > 1$ , the magnitude of  $|\eta(\omega_N, \Phi)|$  decreases quickly to achieve values close to zero at high frequencies. This behavior is reflected in the Nyquist plot (Figure 1) as a fast convergence of the curve  $\eta(\omega_N, \Phi)$  with the origin. The drastic deterioration of the catalyst particle performance when the perturbation frequency is increased beyond the diffusion characteristic frequency  $\omega_d$  is due to a reduction of the effective usage of the particle space. In fact, when the frequency of the perturbation is large,  $|\eta(\omega_N, \Phi)|$  approaches zero because molecules cannot penetrate the particles during one perturbation period. At high frequencies, the catalyst particle appears as a semi-infinite particle because of the limited penetration of the diffusion wave. In this form, for high-frequency perturbations the EF is close to zero because a significant space of the catalyst particle is unused.

- For high frequencies, Figure 1 shows that the Nyquist plot  $\eta(\omega_N, \Phi)$  approaches a 45° slope in the fourth quadrant, which corresponds to a plot of the form  $\eta(\omega_N, \Phi) \approx (i\omega_N)^{-1/2}$ . This behavior can be easily derived by analyzing the reaction-free



case  $\Phi = 0$ . For  $\Phi = 0$ , one has that  $\eta(\omega_N, \Phi) = \tanh((i\omega_N)^{1/2})/(i\omega_N)^{1/2}$ . For high frequencies, it can be shown that  $\tanh((i\omega_N)^{1/2}) \approx 1$ , such that  $\eta(\omega_N, \Phi) \approx (i\omega_N)^{-1/2}$ . Hence, the high-frequency behavior  $\eta(\omega_N, \Phi) \approx (i\omega_N)^{-1/2}$  corresponds to a regime where dynamics is controlled by the diffusion mechanism.

In summary, the better performance for the reaction–diffusion process (eqs 8 and 9) is found for steady-state (i.e., zero frequency) operating conditions. Besides, two regimes separated by the characteristic diffusion frequency  $\omega_d$  are observed in the behavior of the DEF  $\eta(\omega_N, \Phi)$ . (a) One is a low-frequency regime where the performance of the reaction–diffusion process is not seriously deteriorated. Disturbances with frequencies  $\omega < \omega_d$  do not have a significant effect on the supply of reactant to the reaction mechanism. (b) The other is a high-frequency regime where the performance is seriously depleted. Because of the high-frequency perturbations, the reactant is unable to penetrate the particle, such that the total reaction rate is seriously affected.

### 3. Dynamic Effectiveness Factor for a Non-Fickian Diffusion Process

In the above section, it has been assumed that, even in dynamic conditions, the diffusion process is governed by a Fickian law of the form  $\mathbf{J} = -\mathcal{D}\nabla c$ , where  $\mathbf{J}$  denotes the mass flux. Such an assumption yields unsurprising DEF results as described above. In this section, we will study the DEF for non-Fickian diffusion processes that can yield nonmonotonic behaviors of the DEF magnitude  $|\eta(\omega_N, \Phi)|$ . Specifically, we will describe a diffusion process for which  $|\eta(\omega_N, \Phi)|$  displays resonant peaks.

Fick's law of mass diffusion is only valid for low-rate steady-state transfer processes. Physically, there exists a time where the relationship  $\mathbf{J} = -\mathcal{D}\nabla c$  is not valid. This is because Fick's law implicitly assumes an infinite speed of mass propagation in any media. In reality, mass travels at a large but finite velocity. For heat-transfer processes, Cattaneo<sup>11</sup> and Vernotte<sup>12</sup> proposed a modified constitutive law to fix the problem of infinite transfer speed, which when combined with energy balance results in a hyperbolic damped wave PDE. By analogy, the Cattaneo–Vernotte non-Fickian diffusion law is the following

$$t_r \frac{\partial \mathbf{J}}{\partial t} = -(\mathcal{D}\nabla c + \mathbf{J}) \quad (17)$$

where  $t_r$  is a diffusion relaxation time, such that  $\omega_r = t_r^{-1}$  can be seen as a diffusion relaxation frequency. Equation 17 states that if  $\nabla c \rightarrow 0$ , then the mass-transfer flux decays as  $\mathbf{J}(t) = \exp(-t/t_r)\mathbf{J}(0)$ . Essentially, the Cattaneo concept describes the transition from ballistic to diffusion propagation. The analysis and modeling proposals for non-Fickian diffusion processes are based on generalizations of the Chapman–Kolmogorov equation. As a result, diffusion equations of fractional order are obtained to describe an observed mean displacement of the form  $\langle x^2 \rangle \approx t^\alpha$ , which is the distinguishing feature of anomalous diffusion, with subdiffusion corresponding to  $0 < \alpha < 1$  and superdiffusion to  $\alpha > 1$ . Readers interested in the physical basis of this process are referred to the work by Metzler et al.<sup>13,14</sup> Notice that in the infinite speed limit  $\omega_r \rightarrow \infty$  eq 17 reduces to Fick's law  $\mathbf{J} = -\mathcal{D}\nabla c$ . The diffusion model (eq 17) can be seen as a first-order approximation of more sophisticated anomalous diffusion models in the macroscopic limit.<sup>15</sup> There, the random walkers, representing molecular movements, wait after each jump a period of time drawn from a broad power

law distribution. Such waiting times can be due to, for example, obstacles avoiding or catching sites as in electron diffusion. The effect is that some particles remain stuck for a long time and the diffusion is slower (subdiffusion). This is the situation that would correspond to the carrier diffusion in the amorphous modeled materials.<sup>16</sup>

Under the assumptions that led to the reaction–diffusion eq 1, the mass balance is given by

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} - kc \quad (18)$$

By taking the second time derivative of eq 18 and taking into account that  $\partial(\nabla \cdot \mathbf{J})/\partial t = \nabla \cdot \partial \mathbf{J}/\partial t$ , it is possible to arrive at the following expression for the concentration dynamics

$$t_r \frac{\partial^2 c}{\partial t^2} + (1 + t_{N,r} \Phi^2) \frac{\partial c}{\partial t} = \mathcal{D}\Delta c - kc \quad (19)$$

where  $t_{N,r} = t_r \omega_d$  is a normalized relaxation time. In the infinite propagation speed limit reflected by  $t_r = 0$ , eq 19 reduces to the usual reaction–diffusion equation  $\partial c/\partial t = \mathcal{D}\Delta c - kc$ . Similarly to eq 11, to write eq 19 in the Fourier domain as  $\mathcal{D}\Delta C - \kappa(i\omega)C = 0$ , one can define the complex reaction rate constant  $\kappa(i\omega)$  as follows

$$\begin{aligned} \kappa(i\omega) &= k + t_r(i\omega)^2 + (1 + t_{N,r} \Phi^2)i\omega \\ &= (k - t_r \omega^2) + i(1 + t_{N,r} \Phi^2)\omega \end{aligned} \quad (20)$$

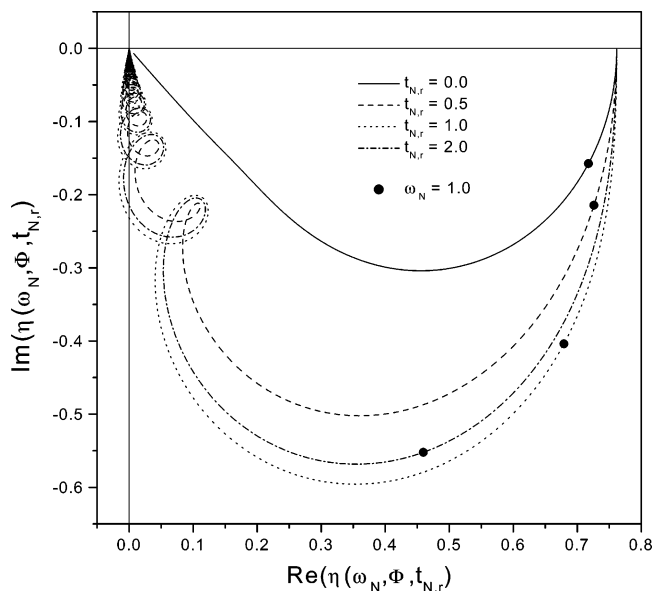
The dynamic Thiele modulus  $\Psi(\omega) = \sqrt{\kappa(i\omega)L^2/\mathcal{D}}$  can be rewritten as follows

$$\Psi(\omega) = \sqrt{(\Phi^2 - t_{N,r} \omega_N^2) + i(1 + t_{N,r} \Phi^2)\omega_N} \quad (21)$$

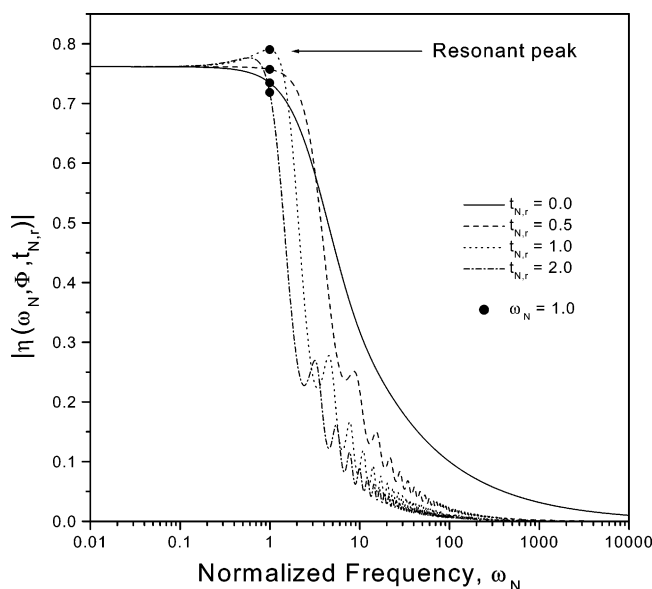
The dynamic modulus  $\Psi(\omega)$  depends only on two parameters, namely, the nondynamic modulus  $\Phi^2$  and the normalized diffusion relaxation time  $t_{N,r}$ . Consequently, the DEF is computed as  $\eta(\omega_N, \Phi, t_{N,r}) = \phi(\Psi(\omega))$  where  $\Psi(\omega)$  is given by eq 21. For common geometries,  $\eta(\omega_N, \Phi, t_{N,r})$  is given by the expressions in eq 16. The following can be observed: (i) When  $t_{N,r} = 0$ , the DEF for Fickian diffusion is obtained, and (ii) when both  $t_{N,r} = 0$  and  $\omega_N = 0$ , the equation  $\eta(\omega_N, \Phi, t_{N,r}) = \phi(\Psi(\omega))$  reduces to the classical nondynamic EF.

We have used two examples to illustrate the behavior of the DEF  $\eta(\omega_N, \Phi, t_{N,r})$ . Figures 3 and 4 show, respectively, the Nyquist and magnitude Bode plots for  $\Phi = 1.0$  and four different values of the normalized relaxation time  $t_{N,r}$  including the Fickian diffusion case  $t_{N,r} = 0$ . The same plots are displayed in Figures 5 and 6 for  $\Phi = 0.25$ . In comparison with the results obtained for the Fickian diffusion case, the following salient features can be noted:

- Similar to the Fickian diffusion case, at sufficiently low frequencies quite below  $\omega_d$ ,  $|\eta(\omega_N, \Phi, t_{N,r})| \approx \bar{\eta}(\Phi)$ . This means that low-frequency perturbations have no significant effects on the performance of the reaction–diffusion process. This is because Cattaneo–Vernotte's law (eq 17) approaches Fick's law at conditions close to the steady state (i.e., at conditions where  $\omega$  is sufficiently small compared to  $\omega_d$ ). However, one has that  $|\eta(\omega_N, \Phi, t_{N,r})| \rightarrow 0$  for sufficiently high frequencies. Contrary to the Fickian case, the decrease of  $|\eta(\omega_N, \Phi, t_{N,r})|$  is not monotonically decreasing, and some decorating oscillations are observed. This oscillation behavior appears because Cattaneo–Vernotte's law (eq 17) acts as a spring between the concentration  $c$  and the mass flux  $\mathbf{J}$  dynamics.



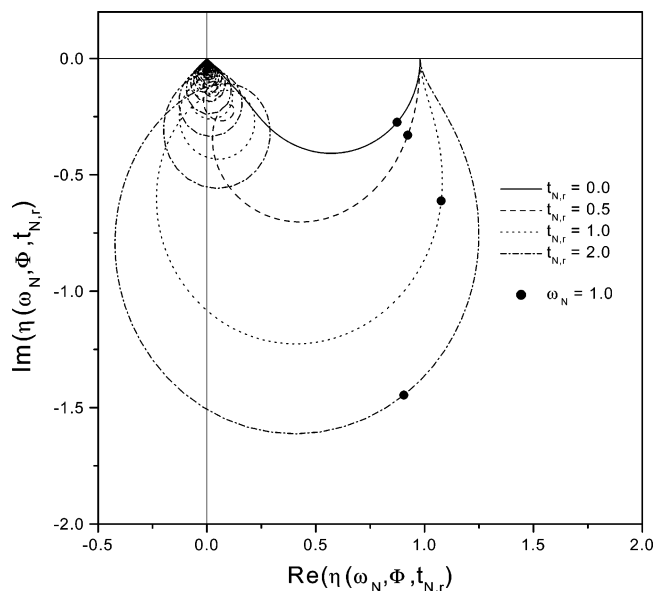
**Figure 3.** Nyquist plot for a diffusion model with relaxation time. The results correspond to  $\Phi = 1.0$  and four different values of the normalized relaxation time  $t_{N,r}$ . Notice that the high-frequency behavior  $\eta(\omega_N, \Phi) \approx (i\omega)^{-1/2}$  for the Fickian diffusion mechanism is no longer displayed.



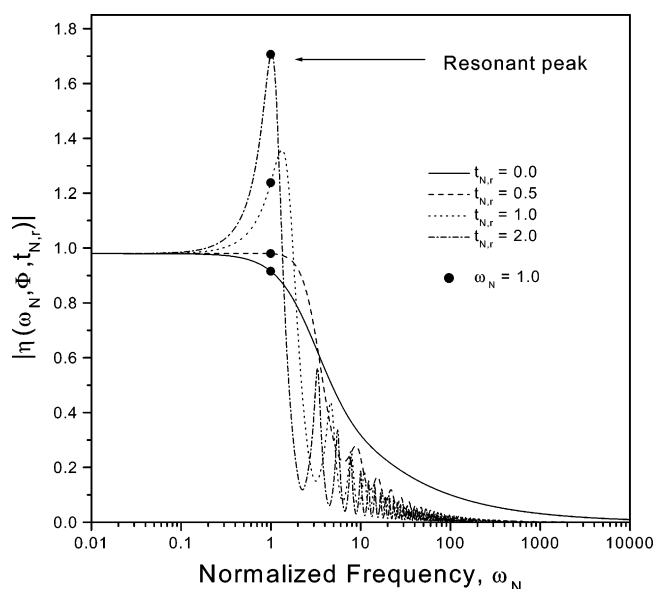
**Figure 4.** Nyquist plot corresponding to the conditions of Figure 3. Observe the resonant peak at frequencies around the characteristic diffusion frequency  $\omega_d$ .

- For each Thiele modulus  $\Phi$ , the maximum value of the DEF was found at nondynamic conditions  $\omega \rightarrow 0$ . This is not the case for the Cattaneo–Vernotte’s diffusion law (eq 17). In fact,  $|\eta(\omega_N, \Phi, t_{N,r})|$  can display a maximum value at a nonzero resonant frequency. From Figures 3 and 5, one can observe that the resonant frequency is around the characteristic diffusion frequency  $\omega_d$  (i.e., around  $\omega_N = 1$ ). From a physical viewpoint, the existence of nontrivial resonant peaks implies that the better reaction rate performance of the reaction–diffusion process is obtained at dynamic conditions. Contrary to the Fickian case where optimal operation is found at steady-state conditions, the total reaction rates  $R_T(\omega)$  can be obtained when the surface concentration  $c_s(t)$  oscillates at frequencies around the characteristic diffusion frequency  $\omega_d$ .

- It has been shown that for the Fickian diffusion case, the Nyquist plot approaches the behavior  $\eta(\omega_N, \Phi) \approx (i\omega_N)^{-1/2}$  at



**Figure 5.** Nyquist plot for a diffusion model with relaxation time. The results correspond to  $\Phi = 0.25$  and four different values of the normalized relaxation time  $t_{N,r}$ . Notice that the high-frequency behavior  $\eta(\omega_N, \Phi) \approx (i\omega)^{-1/2}$  for the Fickian diffusion mechanism is no longer displayed.



**Figure 6.** Nyquist plot corresponding to the conditions of Figure 5. Observe the resonant peak at frequencies around the characteristic diffusion frequency  $\omega_d$ .

sufficiently high frequencies. This behavior characteristic of Fickian diffusion is no longer found for Cattaneo–Vernotte’s diffusion law (eq 17). In fact,  $\eta(\omega_N, \Phi, t_{N,r})$  approaches the origin of the complex plane with an oscillatory behavior. On average, the convergence behaves like an anomalous diffusion  $(i\omega_N)^{-\beta/2}$  with  $\beta > 1$ . Although Cattaneo–Vernotte’s diffusion law (eq 17) approaches Fick’s law at low frequencies, it departs strongly from Fick’s law behavior at sufficiently high-frequency conditions where the storage capacities of the particle are seriously decreased. This can be detected in the Nyquist plot as the curve of  $\eta(\omega_N, \Phi, t_{N,r})$  is closer to the imaginary axis. Similar behavior has been observed in anomalous electron diffusion in a thin layer.<sup>17</sup>

- It was observed that the smaller the Thiele modulus  $\Phi$ , the larger the resonant peak  $|\eta(\omega_N, \Phi, t_{N,r})|_{\max}$ . That is, stronger resonances are found for small Thiele moduli  $\Phi$  where the

process is controlled by the diffusion mechanism. This means that the resonant peak  $|\eta(\omega_N, \Phi, t_{N,r})|_{\max}$  is caused by resonances between the surface concentration dynamics and diffusion dynamics.

- Cattaneo–Vernotte’s law (eq 17) corresponds to an anomalous diffusion process with a Fickian steady-state limit. In this way, the corresponding DEF  $\eta(\omega_N, \Phi, t_{N,r})$  converges to the well-known EF expressions (eq 3) in the steady-state limit. Such a convergence does not necessarily hold for reaction–diffusion processes that, in the absence of a reactive term, correspond to a real steady-state subdiffusion.<sup>13,14</sup> In fact, in such cases the corresponding DEF should have a different steady-state limit, namely, the (steady-state) EF corresponding to reaction–diffusion process with a stationary subdiffusion mechanism. To the best of the authors’ knowledge, computations of effectiveness factors, either numerical or analytical, have not been reported yet, even for steady-state conditions. This is a problem that should be addressed given their importance for the performance analysis of highly structured catalysts.<sup>17</sup>

The above results show that there are performance incentives for the dynamic operation of reaction–diffusion processes with anomalous diffusion. Further exploration of these results is required for a better understanding of the mechanism leading to dynamic resonances in reaction–diffusion processes.

#### 4. Conclusions

An extension of the classical effectiveness factor (EF) concept to dynamic conditions was introduced in this paper. To do this, the EF is interpreted as an operator that transforms reaction rates from surface to particle conditions. On the basis of this interpretation, a dynamic EF (DEF) was defined as a linear operator that transforms reaction signals from surface to catalyst particle conditions. In this way, the DEF retains some information on the performance of a particle under dynamic perturbations. For common geometries, the computation of the DEF can be easily obtained from the nondynamic expression by a direct

substitution of the Thiele modulus for a suitably defined dynamic Thiele modulus. For Fickian diffusion mechanisms, dynamic perturbations deteriorate the performance of the reaction–diffusion process. However, for anomalous (i.e., non-Fickian) diffusion mechanisms, resonant peaks at nontrivial frequencies can be found. Interestingly, this shows that there are reaction–diffusion conditions for which enhanced performance can be obtained under dynamic operating conditions.

Our results showed that the DEF concept can be a useful tool to analyze the performance of reaction–diffusion processes under dynamic perturbations. In particular, they can provide some insights to the optimal operation of catalyst particles where periodic operation leads to enhanced performance compared to nondynamic states.<sup>8,9</sup>

#### References and Notes

- (1) Aris, R. *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*; Clarendon Press: Oxford, 1975; Vol. 1.
- (2) Silveston, P. L.; Hudgins, R. R.; Renken, A. *Catal. Today* **1995**, 25, 91.
- (3) Vernikovskaya, N. V.; Zagoruiko, A. N.; Chumakova, N. A.; Noskov, A. S. *Chem. Eng. Sci.* **1999**, 54, 4639.
- (4) Jianqiang, S.; Ray, A. K. *Chem. Eng. Technol.* **2000**, 23, 1115.
- (5) Kouris, Ch.; Neophytides, St.; Vayenas, C. G.; Tsamopoulos, J. A. *Chem. Eng. Sci.* **2001**, 56, 2897.
- (6) Turco, F.; Hudgins, R. R.; Silveston, P. L.; Sicardi, S.; Manna, L.; Bancho, M. *Chem. Eng. Sci.* **2001**, 56, 1429.
- (7) Adesina, A. A.; Hudgins, R. R.; Silveston, P. L. *Catal. Today* **1995**, 25, 127.
- (8) Gulari, E.; Zhou, X.; Zse, C. *Catal. Today* **1995**, 25, 145.
- (9) Schell, M.; Albahadily, F. N.; Safar, J. J. *Electroanal. Chem.* **1993**, 353, 303.
- (10) Reyes, S. C.; Seinfeld, J. H.; DeMartin, G. J.; Ernst, R. H. *J. Phys. Chem. B* **1997**, 101, 614.
- (11) Cattaneo, C. *Acad. Sci. Paris, C. R.* **1958**, 247, 431.
- (12) Vernotte, P. *Acad. Sci. Paris, C. R.* **1958**, 246, 3154.
- (13) Metzler, R.; Klafter, J. *J. Phys. Chem. B* **2000**, 104, 3851.
- (14) Metzler, R. *Phys. Rev. E* **2000**, 62, 6233.
- (15) Compte, A.; Metzler, R. *J. Phys. A: Math. Gen.* **1997**, 30, 7277.
- (16) Montroll, E. W.; Scher, H. *J. Stat. Phys.* **1973**, 9, 101.
- (17) Bisquert, J.; Compte, A. *J. Electroanal. Chem.* **2001**, 499, 112.