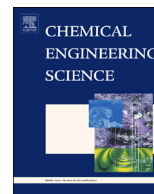




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Transient effectiveness factors in the dynamic analysis of heterogeneous reactors with porous catalyst particles



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HIGHLIGHTS

- A model for the transient effectiveness factor TEF is shown in gradientless reactors.
- The TEF depends not only on the Thiele modulus but also on operational variables.
- The TEF is larger than the steady state effectiveness factor SSEF in pulse injections.
- The SSEF can be corrected by means of two correction factors to yield the TEF.
- This approach is general and embraces the case of the usual steady state assumptions.

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ABSTRACT

A model to calculate the actual transient effectiveness factor in spherical porous catalyst particles in gradientless reactors, where a first order reaction takes place under isothermal conditions, linear equilibrium adsorption and intraparticle diffusion control, was developed. After a certain time has elapsed following a change in the feed's reactant concentration, the transient effectiveness factor can be approximated as a linear combination of the steady state effectiveness factor and the relative rate of change of the concentration in the fluid phase. Oppositely to the well-known steady state effectiveness factor, which depends only on the Thiele modulus ϕ , related to intrinsic properties of the catalysts, the transient effectiveness factor also depends on other two dimensionless numbers: α , the relationship between the capacity of accumulation of reactant in the fluid and solid phases, and ϕ_f , a relationship between the convective flow and the intraparticle diffusion rate. In this way, the catalyst load, the reactor volume and the volumetric flow do impact on the effectiveness factor. The coefficients defined as I_a and I_f are the Diffusion–Adsorption–Reaction Factor and the Flow Factor, respectively, which are complex functions of the Thiele modulus, the convective modulus ϕ_f and the system's adsorption capacity α , and which can be used to correct the steady state effectiveness factor to yield the approximated transient effectiveness factor, which is more exact. In the case of a pulse perturbation in the reactant's concentration, the transient effectiveness factor reaches a constant value which is larger than that from the steady state effectiveness factor and, the larger the catalyst mass and the flow, the larger the difference. Results show the existence of a pseudo-equilibrium state in gradientless reactors.

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1. Introduction

In order to simplify the analysis of chemical reaction systems in heterogeneous reactors with porous catalyst particles, the linearization of adsorption isotherms, the lumping of chemical species and the assumption of steady state for the concentration profiles

in the inner surface of the solid catalyst particles are assumed (Aris, 1975). The immediate consequence is that the steady state effectiveness factor η^{ss} , which is defined as the relationship between the actual chemical reaction rate taking place at the inner pore surface and that at the external particle surface, depends only on the dimensionless Thiele modulus (Thiele, 1939). Moreover, the need of solving the partial differential equations (PDEs) of the mass balances in the particle, which are coupled to the corresponding mass balances in the fluid phase, can be avoided since pseudo homogeneous systems outcomes. An important number of works exists where the effectiveness factor is

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Notation			
<i>Symbols</i>		ϕ	Thiele modulus (dimensionless)
C	reactant concentration (gmol/m ³)	ϕ_f	convective modulus (dimensionless)
D	diffusivity (m ² /s)	η	effectiveness factor (dimensionless)
Da	Damköhler number for first order reaction in a flow reactor (dimensionless)	λ	eigenvalues in Eq. (22), defined in Eq. (23) (dimensionless)
F	volumetric flow (m ³ /s)	ρ	dimensionless radial distance
f	perturbation at the inlet concentration in a well stirred flow reactor (gmol/m ³)	τ	dimensionless time
I	correction factors in Eq. (27) (dimensionless)	ξ	dimensionless concentration in solid phase
K	Henry's constant (dimensionless).	<i>Subscripts</i>	
k	reaction rate constant (s ⁻¹)	a	adsorption
Q	concentration in the solid phase, adsorbed compounds (gmol/m ³)	e	equivalent or effective
R	catalyst particle radius (m)	f	fluid phase, Flow
r	radial distance (m)	i	order of coefficients S_i in Eq. (23)
s	coefficients of expansion in Eq. (22), defined in Eq. (23) (dimensionless)	k	refers to the second term in the right hand side in Eq. (28)
t	time (s)	n	order of the eigenvalues in Eq. (22)
V	volume (m ³)	obs	observed
<i>Greek symbols</i>		p	particle
α	relationship between fluid and solid phase capacities (dimensionless)	s	solid phase
χ	dimensionless concentration in the fluid phase	<i>Superscripts</i>	
δ	Dirac delta function	-	volume averaged variable
ε	porosity (dimensionless)	in	inlet
		o	initial
		ss	steady state
		ts	transient state

studied and approximate expressions are developed to obtain fast estimations, or to extend the approach to different particle geometries or chemical reaction kinetics (Bischoff, 1965; Gonzo et al., 1988; Gottifredi et al., 1981; Gottifredi and Gonzo, 2005; Haynes, 1986; Lee and Kim, 2006; Szukiewicz and Petrus, 2004).

Another option to simplify the mathematical treatment is to apply the concept of linear driving force (LDF), an approximation which transforms the partial differential equations (PDEs) in the particle into ordinary differential equations (ODEs) (Álvarez-Ramírez et al., 2005; Glueckauf, 1955; Goto and Hirose, 1993; Kim, 1989, 2008, 2009; Kim and Lee, 2012; Lee and Kim, 2011, 2013; Szukiewicz, 2000, 2002). Even though the LDF concept produces simpler calculations, the total number of dynamic equations does not reduce and, then, most of the studies devoted to non-linear or complex kinetics, even in cases where the balances are simple (e.g. case of gradientless reactors) use the steady state assumption for the reactants' concentrations in the particle (Al-Sabawi and de Lasa, 2010; Gomez Carrasco et al., 2011; Kim et al., 2013; Wang et al., 2011). It is to be mentioned that the simultaneous solution of the coupled transient mass balances for a reactant in the catalyst particles and the fluid phase has been solved by some authors following different aims (e.g. Frost, 1981; Marroquin de la Rosa et al., 2002; Miró et al., 1986; Oberoi et al., 1980; Schobert and Ma, 1981a, 1981b).

Besides the widespread use of steady state effectiveness factors, and even though evidences exist about their limitations, the confirmation of the applicability of the steady state assumption in the catalyst particles is very unusual. However, it is true that the concentration profiles inside the particles can be similar to the steady state ones only in cases of moderate changes of the concentration in the fluid phase. Nevertheless, in batch systems with high adsorption capacity, the changes in the concentration of

the reactant are significant and the exact solution of the equations which describe mass transport and chemical reaction simultaneously shows that the steady state assumption for the particle is not always appropriate (Bidabehere and Sedran, 2006). Similar conclusions can be obtained through the observation of the changes of reactant concentration in the fluid phase and averaged in the particle when they are calculated for the transient operation of continuous reactors under high flow conditions (Marroquin de la Rosa et al., 2002).

Since the substitution of the reaction term in the reactor's mass balance by the product between the actual effectiveness factor and the chemical reaction evaluated at the external catalyst surface is attractive and easy to use, it is the objective of this work to provide a simple view of this transient effectiveness factor, aimed at maintaining the classic approach. Moreover, it is shown that it is possible to develop an approximate solution in order to represent such a effectiveness factor directly in terms of physical system parameters and truly measurable macroscopic variables, such as reactor volume, catalyst load, volumetric flow and fluid phase concentration, as applied to gradientless reactors with porous particles. The influence of these parameters, as well as the relationship between the steady state and the transient effectiveness factors, is analyzed in batch and continuous operations.

2. Theoretical model

The system under study is a heterogeneous stirred chemical reactor where solid, porous catalyst particles are used. Assumptions in the model are that an isothermal regime occurs, that an adsorption equilibrium of the reactant is reached in the pores, which is linear ($Q = KC$), that the chemical reaction is first order

on the reactant, that the diffusion into the pores obeys Fick's law, and that the mass transfer resistance in the external film of the spherical catalyst particles, which have uniform size, is negligible. In this way, the mass balance for the reactant in the catalyst particles can be written as

$$\varepsilon_p \frac{\partial C}{\partial t} = \varepsilon_p D \nabla^2 C - (1 - \varepsilon_p) \frac{\partial Q}{\partial t} - (1 - \varepsilon_p) k_s Q \quad (1)$$

which, if expressed in terms of the concentration in the fluid phase, is

$$\frac{\partial C}{\partial t} = D_e \nabla^2 C - k_e C \quad (2)$$

subjected to the following initial and boundary conditions:

$$C_{(r,0)} = 0 \quad (3)$$

$$\left. \frac{\partial C}{\partial r} \right|_{r=0} = 0 \quad (4)$$

$$C_{(R,t)} = C_{f(t)} \quad (5)$$

where

$$D_e = \frac{\varepsilon_p D}{\varepsilon_p + (1 - \varepsilon_p) K}, \quad k_e = \frac{(1 - \varepsilon_p) K k_s}{\varepsilon_p + (1 - \varepsilon_p) K} \quad (6)$$

k_s is the reaction rate constant and D is the diffusivity, which can be evaluated from the estimation of the tortuosity and the molecular and Knudsen diffusion coefficients (Satterfield, 1981).

The mass balance in the reactor is

$$V_f \frac{dC_f}{dt} = FC_f^{in} - FC_f - V_p \frac{3}{R} \varepsilon_p D \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (7)$$

where C_f^{in} is an arbitrary function of time

$$C_f^{in} = f(t) \quad (8)$$

subjected to the following initial condition:

$$C_f(t=0) = 0. \quad (9)$$

If dimensionless variables are introduced according to

$$\tau = \frac{t D_e}{R^2}, \quad \rho = \frac{r}{R}, \quad \xi = \frac{C}{C_f^0}, \quad \chi = \frac{C_f}{C_f^0} \quad (10)$$

where C_f^0 is a characteristic concentration, the following parameters can be defined:

$$\phi = R \sqrt{\frac{k_e}{D_e}}, \quad \phi_f = R \sqrt{\frac{F/V_f}{D_e}} = \frac{\phi}{\sqrt{Da}}, \quad \alpha = \frac{V_p [\varepsilon_p + (1 - \varepsilon_p) K]}{V_f} \quad (11)$$

The parameter ϕ is the well-known Thiele modulus, while the convective modulus ϕ_f , which is analogous to the Thiele modulus, is a relationship between the convective flow and the diffusion rate. Da is the Damköhler number for first order reactions occurring in a continuous reactor. The parameter α relates the solid and fluid phase volumes and can be considered an indication of the system's adsorption capacity. Then, the mass balances can be rewritten as

$$\frac{d\chi}{d\tau} = \phi_f^2 (\chi^{in} - \chi) - 3\alpha \left. \frac{\partial \xi}{\partial \rho} \right|_{\rho=1} \quad (12)$$

$$\frac{\partial \xi}{\partial \tau} = \nabla^2 \xi - \phi^2 \xi \quad (13)$$

subjected to the initial and boundary conditions

$$\chi_{(\tau=0)} = 0 \quad (14)$$

$$\xi_{(\rho,0)} = 0 \quad (15)$$

$$\left. \frac{\partial \xi}{\partial \rho} \right|_{\rho=0} = 0 \quad (16)$$

$$\xi_{(1,\tau)} = \chi_{(\tau)}. \quad (17)$$

It is shown in Appendix A that

$$3 \left. \frac{\partial \xi}{\partial \rho} \right|_{\rho=1} = \frac{d\bar{\xi}}{d\tau} + \phi^2 \bar{\xi} \quad (18)$$

where $\bar{\xi}$ is the volume average reactant concentration in the particle, defined according to

$$\bar{\xi} = 3 \int_0^1 \rho^2 \xi \, d\rho. \quad (19)$$

Finally, by introducing Eq. (18) into Eq. (12), the mass balance for the reactant in the reactor can be written

$$\frac{d\chi}{d\tau} = \phi_f^2 (\chi^{in} - \chi) - \alpha \frac{d\bar{\xi}}{d\tau} - \alpha \phi^2 \bar{\xi} \quad (20)$$

with the initial conditions (14) and

$$\bar{\xi}_{(\tau=0)} = 0. \quad (21)$$

On the other hand, the exact solution for the reactant's volume average concentration in the particle, $\bar{\xi}$ (Eq. (19)), from the solution of Eq. (13), is given by Kim (1989)

$$\bar{\xi} = s_1 \chi - s_2 \frac{d\chi}{d\tau} + s_3 \frac{d^2 \chi}{d\tau^2} - \dots + \sum_{n=1}^{\infty} \left(\frac{e^{-\lambda_n \tau}}{\lambda_n} \right) \left(-\chi_{(\tau=0)} + \frac{1}{\lambda_n} \left. \frac{d\chi}{d\tau} \right|_{(\tau=0)} - \frac{1}{\lambda_n^2} \left. \frac{d^2 \chi}{d\tau^2} \right|_{(\tau=0)} + \dots \right) \quad (22)$$

where

$$s_i = \sum_{n=1}^{\infty} \frac{6}{\lambda_n^i}, \quad \lambda_n = \phi^2 + n^2 \pi^2. \quad (23)$$

The transient effectiveness factor is the relationship between the chemical reaction evaluated throughout the particle and the chemical reaction evaluated at the external particle surface, that is

$$\eta_{(\tau)}^{TS} = \frac{\int_0^1 4\pi \rho^2 k_e \xi_{(\rho,\tau)} \, d\rho}{\frac{4}{3}\pi k_e \chi_{(\tau)}} = \frac{\bar{\xi}_{(\tau)}}{\chi_{(\tau)}} \quad (24)$$

The averaged particle concentration in Eq. (24) can be replaced by the solution given by Eq. (22).

Approximations to the exact solution for the dimensionless average concentration in the particle (Eq. (22)), and consequently for the transient effectiveness factor, can be defined. Moreover, they can be studied about their quality in determining the value of the transient effectiveness factor for a given situation. For example, when the product $\lambda_n \tau$ in Eq. (22) is large, the exponential factor tends to be nil. Then, an approximation excluding the summation can be accepted after a certain minimum time (Kim, 1989). This minimum time can be calculated considering the most restrictive condition, that is, the lowest λ_n ($\lambda_1 = \pi^2$), which is obtained with $n = 1$ and $\phi = 0$, that is, when no chemical reaction occurs; then, the exponential factor could be considered extremely small if $\tau > 1/\pi^2 \cong 0.1$. This value is coincident with the limits of applicability of Glueckauf's approximation formulas for diffusion in adsorbents (Glueckauf, 1955). Nevertheless, this condition is unnecessarily severe when chemical reaction occurs, particularly in highly reactive, diffusion controlled systems such as zeolites, where it would be acceptable to consider $\tau > 1/(\pi^2 + \phi^2)$ as the limiting condition. It can be shown that the s_i coefficients decrease more than one order of magnitude with the order of their

derivatives which, in general, also become less important as their order increase (Kim, 1989). Then, a proper approximation for the relationship between the dimensionless average concentration in the particle and that in the fluid phase, that is, the transient effectiveness factor, can be obtained if the series in Eq. (22) is truncated at the second term

$$\eta^{ts} = s_1 \left(1 - \frac{s_2}{s_1} \frac{1}{\chi} \frac{d\chi}{d\tau} \right), \quad \text{valid for } \tau > \frac{1}{\pi^2 + \phi^2}. \quad (25)$$

Eq. (25) is an approximation to the actual effectiveness factor which is more exact than that provided by the steady state effectiveness factor, which can be obtained from Eq. (24) if all the time derivatives in Eq. (22) are nil, thus yielding $\eta^{ss} = s_1$. The reason for this higher accuracy is that the relative changes in the concentration of the reactant in the fluid phase, $(1/\chi)(d\chi/d\tau)$, are affected by the proportionality factor $\tau_p = (s_2/s_1)$. The meaning of s_2/s_1 can be understood from the linear driving force (LDF) formulae derived by Kim (1989) in extending the pioneering work by Glueckauf (1955), which has been extensively used in chromatography and adsorption systems without chemical reactions. Starting from a refinement of Eq. (22), the simplest formula obtained by Kim for diffusion–adsorption–reaction systems in porous media shows that the rate of accumulation of the reactant in the particles is proportional to the difference between the mean concentration and that obtained at the surface of the particle,

$$\frac{d\bar{C}}{dt} = \frac{s_1 D_e}{s_2 R^2} (s_1 C_f - \bar{C}). \quad (26)$$

The value of s_1/s_2 can be calculated from Eq. (23). It is 15 if $\phi = 0$ and increases with increasing ϕ . This increase can be explained considering that the proportionality constant in the LDF approximation is the mass transfer coefficient (Kim, 1989). At large ϕ values, the concentration profiles in the particle fall abruptly near the external surface, resulting in a fast mass transfer rate, a fact which is reflected in a high LDF coefficient. The inverse of this coefficient is the time constant associated to the overall diffusion, adsorption and reaction process $t_p = (s_2/s_1)(R^2/D_e)$. Then the relationship $\tau_p = (s_2/s_1)$ is the dimensionless time constant for diffusion–adsorption–reaction in the particles.

It is interesting to note that Eq. (25) also shows that the transient effectiveness factor can be equal, larger or smaller than the steady state effectiveness factor, according to different situations:

- $\eta^{ts} \rightarrow \eta^{ss}$ if $d\chi/d\tau \rightarrow 0$, or, more appropriately, $(s_2/s_1)(1/\chi)(d\chi/d\tau) < 1$ (which corresponds to a low relationship between the relative change in the concentration of reactant in the fluid phase, $(1/\chi)(d\chi/d\tau)$, and the rate for diffusion–adsorption–reaction in the particles, s_1/s_2).
- $\eta^{ts} > \eta^{ss}$ if $d\chi/d\tau < 0$ (which corresponds, for example, to the response of a batch system, particularly with high adsorption capacity, after the injection of a pulse of reactant).
- $\eta^{ts} < \eta^{ss}$ if $d\chi/d\tau > 0$ (which corresponds, for example, to the initial stages of the response to step changes in the concentration of the feed to continuous reactors).

Eq. (25) can be used in Eq. (20) and, moreover, considering that the accumulation term $d\bar{C}/d\tau$ can be approximated by $s_1(d\chi/d\tau)$ if the derivatives of order higher than one are neglected and the time elapsed is sufficiently long, then (refer to Appendix B)

$$\eta^{ts} = \eta^{ss} \left[(I_a + I_f) - I_f \frac{\chi^{in}}{\chi} \right] \quad \text{valid for } \tau > \frac{1}{\pi^2 + \phi^2} \quad (27)$$

where

$$I_a = 1 + \frac{\alpha s_1 (s_2/s_1) \phi^2}{1 + \alpha s_1 (1 - (s_2/s_1) \phi^2)} \quad (28)$$

and

$$I_f = \frac{(s_2/s_1) \phi_f^2}{1 + \alpha s_1 (1 - (s_2/s_1) \phi^2)}. \quad (29)$$

I_a is the Diffusion–Adsorption–Reaction Factor and I_f is the Flow Factor for the reaction system, which are complex functions of the Thiele modulus and the system's adsorption capacity α . The Diffusion–Adsorption–Reaction Factor $I_a = 1 + I_k$ is a correction factor to the steady state effectiveness factor, which is equal to the ratio η^{ts}/η^{ss} when $\phi_f = 0$ (batch reactor). It is also an increasing function of the parameter α , which is proportional to the amount of reactant adsorbed on the catalyst particles. On the other hand, the Flow Factor I_f is a correction factor which is an increasing function of ϕ_f^2 , resulting proportional to the convective flow.

It can be shown that the use of Eqs. (27)–(29) leads to a pseudo homogeneous model which avoids solving the partial differential equations (PDEs) of the mass balances in the particle (Eq. (13)), which are coupled to the corresponding mass balances in the fluid phase (Eq. (12)).

3. Discussion

Fig. 1 shows the I_a factor as a function of the Thiele modulus. It can be seen that the correction factor is always larger than one, a fact which makes the transient effectiveness factor to be larger than the steady state effectiveness factor in batch reactors ($I_f = 0$). Moreover, the higher the system's adsorption capacity α , the higher the correction factor, which in all the cases passes through a maximum value. The fact that the transient effectiveness factor depends on the amount of catalyst in the system (refer to the definition of α , Eq. (11)) in a non-uniform mode (Eqs. (27)–(29)) implies that errors can be introduced in the assessment of the kinetic or adsorption parameters if steady state approximations are assumed.

Fig. 2 shows how the product $I_f (\phi^2/\phi_f^2) = I_f Da$ changes as a function of the Thiele modulus for different values of the parameter α in a stirred flow reactor, thus impacting on the value of the transient effectiveness factor and on its relationship with the steady state effectiveness factor (see Eq. (27)). As seen in Eq.

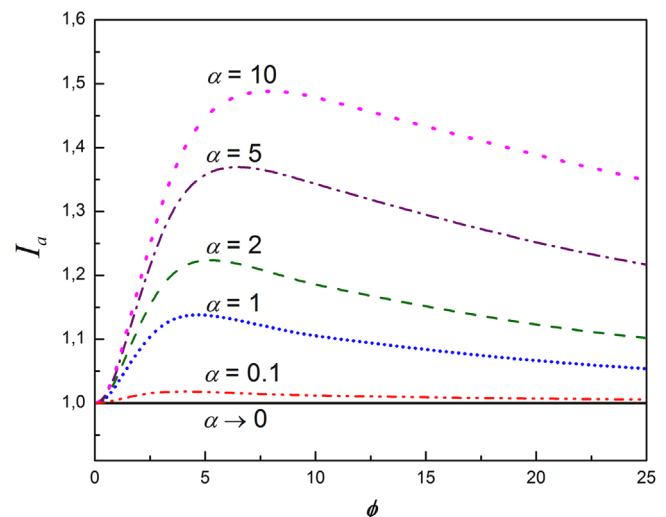


Fig. 1. Diffusion–Adsorption–Reaction Factor I_a as a function of the Thiele modulus.

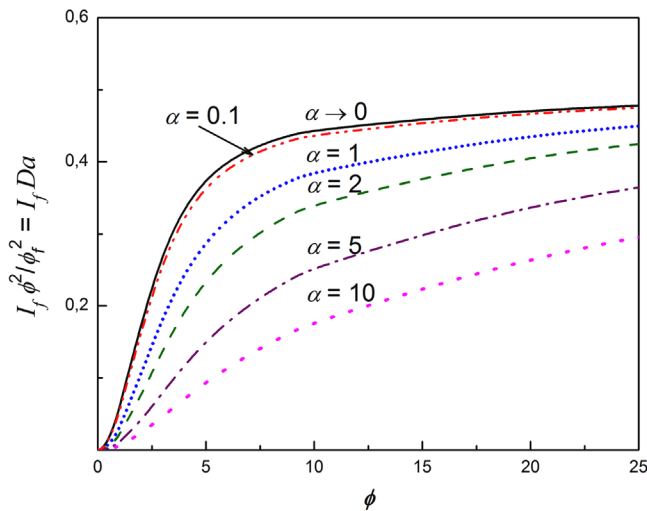


Fig. 2. Product $I_f (\phi^2/\phi_f^2) = I_f Da$ as a function of the Thiele modulus. Stirred flow reactor.

(29), for given values of α and ϕ , I_f increases with ϕ_f^2 , which is proportional to the flow F and inversely proportional to the reactor's volume. The fact that the transient effectiveness factor depends on both the flow and the reactor's volume in a non-uniform mode implies that errors can be introduced in the assessment of the kinetic or adsorption parameters if steady state approximations are assumed. Moreover, it can be seen in Fig. 2 that, for given values of α and ϕ , the value of the Flow Factor I_f is inversely proportional to the Damköhler number $Da = k_e(V_f/F)$. Then, the transient effectiveness factor could increase indefinitely in certain cases (e.g. for pulse injection, see Eq. (27) and discussion below) and values higher than one could be reached, even for isothermal particles, if the flow is sufficiently high. However, this may be not completely convenient in the operation of stirred flow reactors.

Steady state effectiveness factors higher than one could be observed in highly exothermic reactions. Weisz and Hicks (1962) demonstrated that in such a case the increases in the value of the rate constant, would more than offset the decrease in reactant concentration, so that the reaction rate averaged over the particle exceeds that at surface conditions.

4. Analysis of particular cases: pulse perturbation

In order to analyze the meaning of the correction factors I_a and I_f and the issues impacting on them, a perturbation with a pulse of reactant (Dirac delta function) is to be produced, will be considered. In the case of $\chi^{in} = \delta(\tau)$ it can be seen from Eq. (27) that the transient effectiveness factor becomes

$$\eta^{ts} = \eta^{ss} (I_a + I_f) \quad \text{valid for } \tau > \frac{1}{\pi^2 + \phi^2}. \quad (30)$$

It is important to see in Eq. (30) that, for a pulse perturbation, a state exists when the transient effectiveness factor becomes constant, in accordance with the results from a pseudo equilibrium model applied to dynamic techniques in stirred reactors (Bidabehere and Sedran, 2006). The pseudo equilibrium state can be easily observed in Fig. 3 after a certain time has evolved. Eqs. (28)–(30) allow estimating the effectiveness factor of that pseudo equilibrium state. Since the transient effectiveness factor does not change after a certain time has elapsed, the changes in the fluid and particle concentrations after the injection of a pulse can be

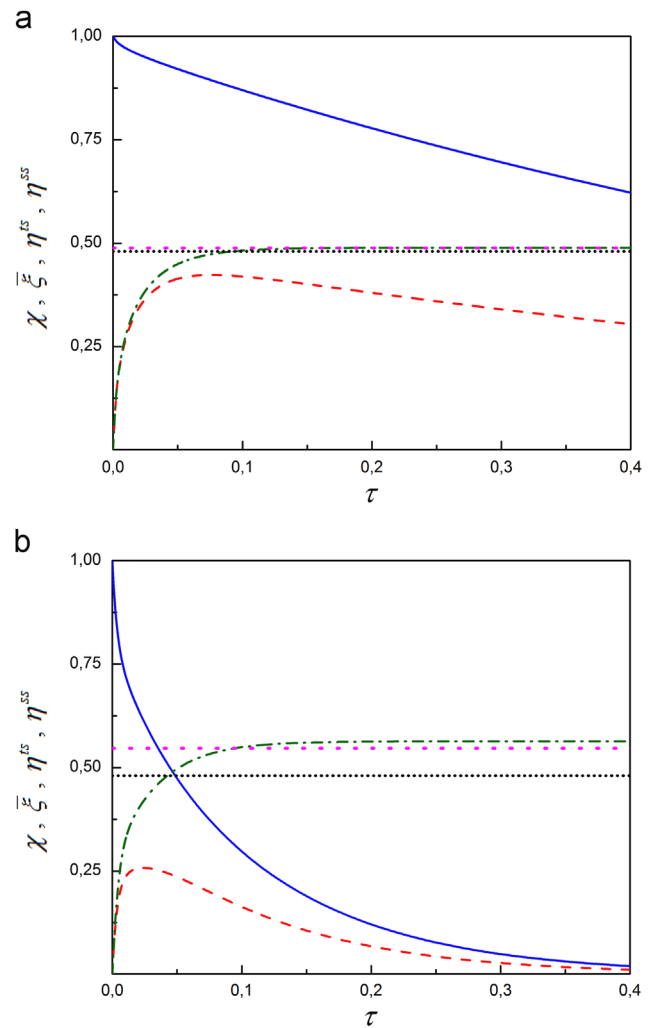


Fig. 3. Transient responses of the fluid (χ) and average particle ($\bar{\xi}$) dimensionless reactant concentrations and the transient (η^{ts}) and steady state (η^{ss}) effectiveness factors for a pulse injection in a well stirred batch reactor. (a) $\phi = 5, \alpha = 0.1$; (b) $\phi = 5, \alpha = 1$. Lines: **solid**, χ ; **dash**, $\bar{\xi}$; **dash-dot**, Exact η^{ts} (Eq. 24); **short dot**, η^{ss} ; **dot**, η^{ts} (Eq. 30).

obtained easily by replacing the average particle concentration in the reactor mass balance by the product between the approximate transient effectiveness factor and the fluid phase concentration. As a consequence, the evolution of the dimensionless concentration in the fluid phase as a function of the dimensionless time τ in semi-log coordinates is a line, whose slope is the inverse of the observed dimensionless time constant ($(1/\chi)(d\chi/d\tau) = -(1/\tau_{obs})$). This characteristic behavior takes place in various dynamic techniques and, in these cases Eq. (25) can be written as

$$\eta^{ts} = \eta^{ss} \left(1 + \frac{\tau_p}{\tau_{obs}} \right) \quad (31)$$

and then, by comparing Eqs. (30) and (31),

$$I_a + I_f = 1 + \frac{\tau_p}{\tau_{obs}}. \quad (32)$$

Both Eqs. (31) and (32) show that the larger the relationship between the dimensionless time constant for diffusion–adsorption–reaction in the particles (τ_p) and the dimensionless time constant in the system (τ_{obs}), the larger the correction to the steady state effectiveness factor.

4.1. Batch reactors

The case of the injection of a pulse of reactant to a well stirred batch reactor will be considered to further demonstrate how the transient and the steady state effectiveness factors differ. Fig. 3 shows the evolution of the dimensionless fluid and average solid reactant concentrations as a function of time for two different values of the system's capacity α , as obtained from Eqs. (12)–(17) and (19) for $\phi_f = 0$ and by considering that $\chi(0) = 1$. The time evolutions of the concentration profiles and the apparent adsorption constant were studied extensively by Bidabehere and Sedran (2006). The exact transient effectiveness factor $\eta^{ts} = (\bar{\xi}/\chi)$ (Eq. (24)), the steady state effectiveness factor $\eta^{ss} = s_1$ and the approximation to the transient effectiveness factor given by Eq. (30) are also included. It is clear that the transient effectiveness factor, which can be calculated from the exact solution provided α and ϕ are known, becomes larger than the steady state effectiveness factor after a certain time has elapsed, and finally reaches an asymptotic value; the larger the system's adsorption capacity, the larger the asymptotic value of the transient effectiveness factor.

Moreover, the approximation to the transient effectiveness factor calculated from Eq. (30) is closer to the exact solution (Eq. 24) than that from the steady state in the particle ($\eta^{ss} = s_1$).

As it is shown in Eq. (31) the correction factor I_a , that is, $(1 + (\tau_p/\tau_{obs}))$, leads to transient effectiveness factors larger than the steady state effectiveness factors when the dimensionless time constant for diffusion-adsorption-reaction in the particles is not negligible in comparison to the overall time scale of the process. α values are much smaller than one make I_a to be close to one (see Eq. 28), and finally the effectiveness factors become similar (alternatively, the changes of concentration in the particle are so slow that it behaves essentially in a steady state). For certain particle size and reaction temperature, however, the system's adsorption capacity increases if the mass of catalyst is larger, a fact which does not modify neither the Thiele modulus nor the value of τ_p , but makes the concentration of reactant in the fluid phase to decrease faster (that is, τ_{obs} is smaller), thus increasing the difference between transient and steady state effectiveness factors.

Additionally, the difference between effectiveness factors as a function of both α and ϕ can be observed in Fig. 4, which shows the typical logarithmic representation of the effectiveness factors

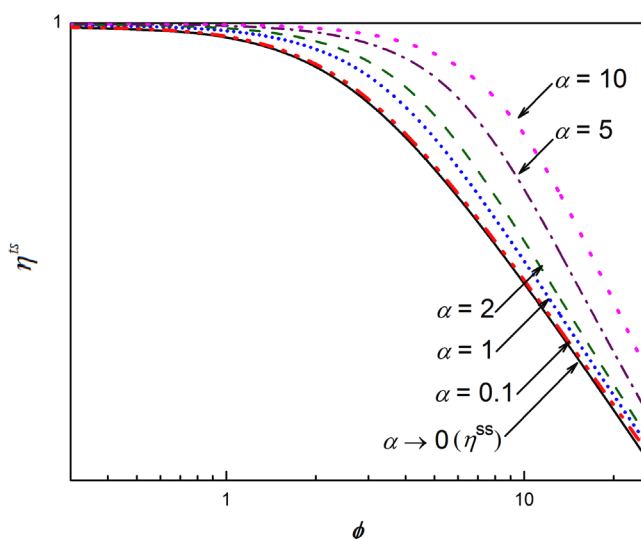


Fig. 4. Asymptotic values of the effectiveness factor (Eq. (24)) as a function of the Thiele modulus. Batch reactor with pulse injection of reactant.

as a function of the Thiele modulus. Fig. 4 was constructed with the help of Eqs. (12), (13) and (24) (asymptotic values). Note that the transient effectiveness factor tends to the steady state effectiveness factor when the system's adsorption capacity tends to zero ($\alpha \rightarrow 0$) as can be observed in Eqs. (27)–(29). It can be seen that the very well known shape of the relationship between effectiveness factor and Thiele modulus is maintained but, in the full range of the modulus, the larger the system's adsorption capacity, the larger the differences between the effectiveness factors.

Fig. 4 shows that the same effectiveness factor can be achieved in catalyst particles with very different sizes. For example, if $\alpha = 1$ and $\phi = 1$ the effectiveness factor is 0.95, the same value for a particle which is two times larger ($\phi = 2$) when $\alpha = 5$. Moreover, for a given value of the Thiele modulus, the effectiveness factor can be significantly higher provided the mass of catalyst per unit reactor volume, that is, α , is higher. For example, if $\phi = 3$, the effectiveness factor is 0.67 when $\alpha = 1$ and 0.91 when $\alpha = 5$. The previous discussion and Fig. 4 demonstrate that the inappropriate selection of the mass of catalyst in experiments aimed at determining diffusion limitations or kinetics parameters, can lead to erroneous conclusions.

4.2. Gradientless continuous reactors

As previously shown, I_f is a correction to the steady state effectiveness factor which considers the influence of the convective flow. Systems with low adsorption capacity clearly demonstrate this influence. For example, if $\alpha \ll 1$, $I_a \rightarrow 1$, and the Flow Factor $I_f \rightarrow (s_2/s_1)\phi_f^2$ (refer to Eq. (29)). Thus, the relative relationship between the effectiveness factors (see Eqs. (27)–(29)) is

$$I_f = \frac{\eta^{ts} - \eta^{ss}}{\eta^{ss}} = \frac{s_2}{s_1} \phi_f^2.$$

The correction factor I_f increases if the flow increases at a given reactor volume, temperature and catalyst particle size. Moreover, under these conditions (very small α), it is equal to the product $(s_2/s_1)\phi_f^2 = ((s_2/s_1)(R^2/D_e))/(F/V_f)$, that is, the relationship between the rates of change of the concentration of the reactant in the fluid phase due to the mass transfer to the particles and the convective flow.

It can be seen in Fig. 2 that the smaller the system's adsorption capacity α , the larger the Flow Factor I_f and, consequently, the more important its impact on the transient effectiveness factor. This (a more significant impact of the flow on the transient effectiveness factor when the system's adsorption capacity is smaller) is an expected behavior, since the transient effectiveness factor is proportional to the rate of consumption of the reactant in the fluid phase, subjected to two simultaneous processes which are competitors: the mass transfer to the solid catalyst particles, equal to the adsorption and reaction rates which is proportional to the adsorption capacity, and the convective mass transfer, which is proportional to the flow. If α is larger, the rate of mass transfer to the solid increases, thus governing the overall process and making the impact of the convective mass transfer to be less significant.

Fig. 5 shows the evolution of the dimensionless fluid and average particle reactant concentrations as a function of time in a stirred flow reactor, for the same pair of α and ϕ values and different convective moduli ϕ_f , as obtained from Eqs. (12), (13) and (19), and their relationship, which is the transient effectiveness factor $\eta^{ts} = (\bar{\xi}/\chi)$ (Eq. 24). The steady state effectiveness factor $\eta^{ss} = s_1$ and the approximation to the transient effectiveness factor given by Eq. (30) are also included. It is clear that the transient effectiveness factor (both from Eqs. (24) (exact, asymptotic value) and (30) (approximated)) are larger than the steady state effectiveness factor. It can be seen that, as already discussed, for given α

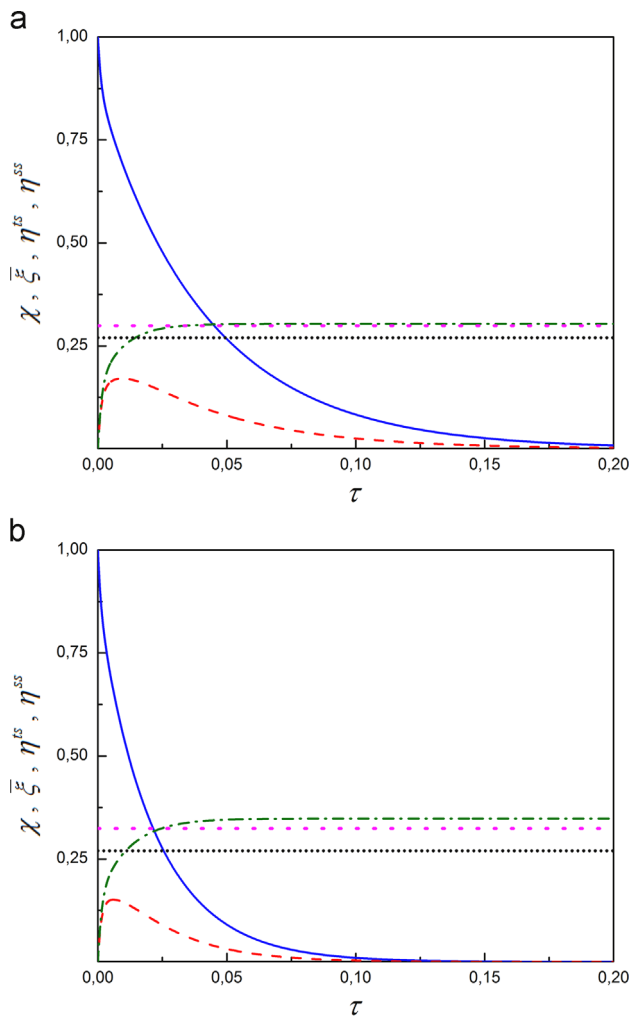


Fig. 5. Transient responses of the fluid (χ) and average particle ($\bar{\xi}$) dimensionless reactant concentrations and the transient (η^{ts}) and steady state (η^{ss}) effectiveness factors for a pulse injection in a well stirred flow reactor. $\phi = 10$, $\alpha = 1$. (a) $\phi_f = 1$; (b) $\phi_f = 5$. Lines: **solid**, χ ; **dash**, $\bar{\xi}$; **dash-dot**, Exact η^{ts} (Eq. 24); **short dot**, η^{ts} ; **dot**, η^{ss} (Eq. 30).

and ϕ , the larger ϕ_f , the larger the transient effectiveness factor. Moreover, the approximation to the transient effectiveness factor calculated from Eq. (30) is closer to the exact solution (Eq. 24) than that from the steady state in the particle ($\eta^{\text{ss}} = s_1$).

It can be shown that the approach can be applied to the study of not only stirred reactors, but also other configurations such as fluidized and fixed bed reactors. Moreover, Eq. (27) is also applicable to different perturbations on the reactor's operation.

5. Conclusions

It is possible to develop exact or approximate expressions which describe the actual transient effectiveness factor in systems where a chemical reaction proceeds catalyzed by porous catalysts particles, subjected to diffusive restrictions. The usual approach, that is, considering a steady state for the concentration profiles in the catalyst particles, is not always appropriate, because the solution of the mass balances in gradientless reactors show that the transient effectiveness factor also depends on measurable parameters such as catalyst load, reactor volume and flow of reactant. These dependencies are established through two

dimensionless parameters besides the Thiele modulus: the system's adsorption capacity α , which is proportional to the relationship between the capacities of adsorption in the particle and the amount of reactant in the fluid phase, and the convective modulus ϕ_f , analogous to the Thiele modulus, which is proportional to the relationship between the convective and diffusive transports.

It can be shown that the transient effectiveness factor can be smaller, equal or larger than the steady state effectiveness factor, depending on the rate of change of the reactant concentration in the fluid phase. Moreover, the differences between the effectiveness factors can be adjusted by means of two correction factors (the Adsorption factor and the Flow factor) to the steady state effectiveness factor.

Pulse injections of the reactant to both gradientless batch and continuous reactors showed that a constant relationship between the average solid and fluid phase reactant concentrations is reached after a certain time has elapsed, thus defining a pseudo equilibrium state. This relationship is the same than that expected when steady state conditions are assumed in the catalyst particles only if the flow and the adsorption capacity are extremely small.

When the transient effectiveness factor is represented against the Thiele modulus, it is clear that the consequences of the mass transfer limitations on the overall rate of the diffusion–adsorption–reaction process can be different from those predicted from the typical steady state assumptions, and experimental parameters such as the catalyst load and the reactor volume become relevant.

The use of transient effectiveness factors leads to pseudo homogeneous models which avoid solving the partial differential equations of the mass balances in the particle, and the solutions using approximate expressions are more precise than those produced when the steady state assumptions for the effectiveness factors are used.

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Appendix A

If Eq. (2) is averaged in the volume of the particle

$$\frac{d\bar{C}}{dt} = \frac{1}{V_p} \int_{V_p} D_e \nabla \cdot (\nabla C) dV - k_e \bar{C}. \quad (\text{A.1})$$

By applying Gauss' theorem on the first term in the right hand side of Eq. (A.1),

$$\frac{1}{V_p} \int_{V_p} D_e \nabla \cdot (\nabla C) dV = \frac{3}{R} D_e \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (\text{A.2})$$

and then

$$\frac{3}{R} D_e \left. \frac{\partial C}{\partial r} \right|_{r=R} = \frac{d\bar{C}}{dt} + k_e \bar{C} \quad (\text{A.3})$$

If dimensionless variables as defined by Eq. (10) are used, Eq. (A.3) is equivalent to Eq. (18).

Appendix B

If time is long enough, the exponential term in Eq. (22) can be considered negligible and it becomes

$$\bar{\xi} = s_1\chi - s_2\frac{d\chi}{d\tau} + s_3\frac{d^2\chi}{d\tau^2} - \dots \quad (\text{B.1})$$

If Eq. (B.1) is truncated in the second term

$$\frac{d\chi}{d\tau} \cong \frac{1}{s_2}(s_1\chi - \bar{\xi}). \quad (\text{B.2})$$

The time derivative of Eq. (B.1) is

$$\frac{d\bar{\xi}}{d\tau} = s_1\frac{d\chi}{d\tau} - s_2\frac{d^2\chi}{d\tau^2} + s_3\frac{d^3\chi}{d\tau^3} - \dots \quad (\text{B.3})$$

and, neglecting the terms corresponding to the second and higher order derivatives,

$$\frac{d\bar{\xi}}{d\tau} \cong s_1\frac{d\chi}{d\tau}. \quad (\text{B.4})$$

If Eqs. (B.2) and (B.4) are introduced in the mass balance for the reactant in the reactor (Eq. (20)), the dimensionless average reactant concentration in the particle can be obtained,

$$\bar{\xi} = \frac{\phi_f^2 s_2 (\chi^{in} - \chi) + s_1 (1 + \alpha s_1) \chi}{1 + \alpha s_1 - \alpha s_2 \phi_f^2}. \quad (\text{B.5})$$

Alternatively Eq. (B.5) can be written as

$$\bar{\xi} = s_1 \left\{ \left[\frac{(1 + \alpha s_1)}{1 + \alpha s_1 (1 - (s_2/s_1) \phi_f^2)} + \frac{(s_2/s_1) \phi_f^2}{1 + \alpha s_1 (1 - (s_2/s_1) \phi_f^2)} \right] \chi - \left[\frac{(s_2/s_1) \phi_f^2}{1 + \alpha s_1 (1 - (s_2/s_1) \phi_f^2)} \right] \chi^{in} \right\} \quad (\text{B.6})$$

where the definitions of the correction factors I_a and I_f (Eqs. 28 and 29) can be considered to finally yield

$$\bar{\xi} = \eta^{ss} (I_a + I_f) \chi - \eta^{ss} I_f \chi^{in} \quad (\text{B.7})$$

The relationship between Eq. (B.7) and χ , the dimensionless reactant concentration in the fluid phase, leads to Eq. (27).

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