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Transient effectiveness factor in porous catalyst particles. Application to kinetic studies with batch reactors

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ABSTRACT

The actual transient characteristics of the effectiveness factor for reactions in porous catalyst particles were considered in a model for kinetic studies in gradientless batch reactors. The transient effectiveness factor depends both on the Thiele modulus and the system's adsorption capacity, a function of the catalyst mass. After the injection of reactant, the transient effectiveness factor reaches a stable value, which is always larger than the conventional factor based on the assumption of steady state in the concentrations in the particle. The steady state approach on classical pseudo-homogeneous models can be used if the adsorption capacity of the system is low. A new pseudo-homogeneous model, where the accumulation of mass in the particle and the transient effectiveness factor approach are considered, extend this limit to systems with medium or high adsorption capacity. The usual interpretation of the Weisz-Prater parameter was reformulated based on this approach, showing that kinetic constants can be determined precisely if the transient effectiveness factor is employed, thus avoiding the errors induced by the accumulation of mass in the catalyst particles. Proper experimental conditions for kinetic studies were suggested.

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1. Introduction

In order to determine kinetics, diffusion and adsorption parameters in heterogeneous reaction systems over porous catalysts, it is a common laboratory practice to use batch reactors where reactants are injected (see, e.g., Ma and Roux, 1973; Ma and Lee, 1976; Oberoi et al., 1980; Biswas et al., 1986; Bidabehere and Sedran, 2006). With this aim, gradientless reactors are used in various configurations (Weekman, 1974). An advantage of using these reactors is the lack of the reactor space variable. However, the mass balances in the particles are partial differential equations (PDE) coupled to the ordinary differential equations (ODE) in the fluid phase, their solutions requiring the use of complex mathematical tools or laborious numerical calculations. The number and complexity of the calculations in the design of het-

erogeneous chemical reactors with such catalysts can be decreased if approximate descriptive models are used. The most common approach is to consider that the concentration of reactants and products inside the catalyst particles operate following a steady state situation (Aris, 1975), and the classical effectiveness factor defined by Thiele (1939), which has been developed extensively as shown in textbooks (Aris, 1975; Froment and Bischoff, 1979; Fogler, 1999), is used. Other approximations are based on the consideration of “linear driving forces” (LDF) (Kim, 1989; Szukiewicz, 2000; Álvarez-Ramírez et al., 2005; Kim, 2009; Lee and Kim, 2011) which, even though they simplify the analysis in converting the partial differential equations corresponding to the mass balances in the catalyst particles into ordinary differential equations, they do not decrease the number of differential equations to be solved. First order kinetics expressions can be assumed in many cases (Froment and Bischoff, 1979; Bidabehere and Sedran, 2001), or linearizations of more complex kinetics can be performed (Dursun and Tepe, 2005).

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Nomenclature

Symbols

C	Reactant concentration (gmol/m ³)
D	Diffusivity (m ² /s)
E	Relative error corresponding to the approximate effectiveness factor in comparison to the exact value (dimensionless)
I _a	Correction factors in Eq. (16) (dimensionless)
K	Henry's constant (dimensionless)
k	Reaction rate constant (s ⁻¹)
Q	Concentration in the solid phase, adsorbed compound (gmol/m ³)
R	Catalyst particle radius (m)
r	Radial distance (m)
r	Reaction rate per unit volume of porous catalyst particles (gmol/m ³ s)
s	Coefficients of expansion in Eq. (11), defined in Eq. (12) (dimensionless)
t	Time (s)
V	Volume (m ³)

Greek symbols

α	System's adsorption capacity defined by Eq. (8)
χ	Dimensionless concentration in the fluid phase
ε	Porosity (dimensionless)
φ	Thiele modulus (dimensionless)
η	Effectiveness factor (dimensionless)
λ	Eigenvalues in Eq. (11), defined by Eq. (12) (dimensionless)
θ	Weisz–Prater parameter (dimensionless)
ρ	Dimensionless radial distance
σ	Tortuosity in catalyst particles (dimensionless)
τ	Dimensionless time
ξ	Dimensionless concentration in the particle

Subscripts

approx	Approximate
e	Equivalent or effective
f	Fluid phase
i	Order of coefficients s _i in Eqs. (11) and (12)
k	Knudsen
n	Order of the eigenvalues in Eqs. (11) and (12)
m	Molecular
obs	Observed
p	Particle
pE	Pseudo-equilibrium state

Superscripts

–	Volume averaged variable
*	Extrapolation to time zero (dimensionless concentration in the fluid phase defined by Eq. (19))
o	Initial
ss	Steady state
ts	Transient state

Recently, the use of an approximation to the effectiveness factor preserving the original concept by Thiele (1939) was proposed, which acknowledges that the true effectiveness factors, by definition, are subjected to the transient states in the concentrations of reactants and products in the reacting system. Thus, the usual assumption of steady states in the catalyst particles leading to classical effectiveness factors is only a particular case which corresponds to very slow or

imperceptible changes in the medium where the catalyst particles are immersed (Bidabehere et al., 2015). On the other hand, the magnitude of the difference between the actual (transient) and steady state effectiveness factors depends on both the inertia in the changes of concentration in the particles (due to diffusion resistances) and the rate of change of concentration in the fluid phase. The clearest examples for which this transient analysis, in opposition to the conventional steady state approach, is recommended, are all the cases where strong adsorption of reactant molecules, previous to surface reaction, exists. Among them, the cracking of hydrocarbons on various zeolites (Bidabehere and Sedran, 2001; Al-Khattaf et al., 2002; Atias and de Lasa, 2004; Konno et al., 2012) and biodegradation of phenol by bacteria (Dursun and Tepe, 2005) can be noticed. This methodology, which can be applied to both flow or batch reactors, considers the effect of the changes in the concentration of reactant at the external surface of the particles on the simultaneous processes of diffusion, adsorption and reaction in the porous network of the catalyst. The model was formulated for isothermal systems with linear adsorption equilibrium ($Q = KC$, with two phases that can be distinguished inside the particles: one diffusing in the pores, and the other one adsorbed), diffusion into the pores following the Fick's law, spherical geometry, negligible mass transfer resistance in the film outside the particles and first order reaction. The concentration of reactant should be low in order to reach linear conditions in kinetics and adsorption equilibrium. In spite of the restrictions, when an initial period is elapsed, the approach greatly simplifies the analysis of the transient response of reactors with porous catalysts, because it leads to pseudo-homogeneous models whose approximate effectiveness factors are much closer to the exact ones than those from the steady state assumptions.

It is the objective of this work to determine the accuracy of the approximate form of the transient effectiveness factor, comparing it with the true (exact) effectiveness factor and the one which is calculated with the classical assumptions of steady state in the catalyst particles. The validity of its application to the simulation of the dynamic response of well stirred batch reactors used in pulse injection kinetic techniques, which produces a pseudo-homogeneous model, will be determined by comparison with the exact solutions of the differential equations system which include the mass balances in the particles. The approach's comparative advantages in the assessment of kinetic constants in systems with high adsorption capacity will be verified by means of the error analysis in the use of the Weisz–Prater criterion (Weisz and Prater, 1954) when the time changes in concentrations in the catalyst are not taken into account.

2. Theory

The dimensionless reactant mass balances in a batch reactor where a reactant is injected and in the catalyst particles are

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

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

which are subjected to the initial and boundary conditions

$$\chi_{(\tau=0)} = 1 \quad (3)$$

$$\xi_{(\rho,0)} = 0 \quad (4)$$

$$\left. \frac{\partial \xi}{\partial \rho} \right|_{\rho=0} = 0 \quad (5)$$

$$\xi_{(1,\tau)} = \chi_{(\tau)} \quad (6)$$

The dimensionless variables and parameters are defined as

$$\tau = \frac{tD_e}{R^2}, \quad \rho = \frac{r}{R}, \quad \xi = \frac{C}{C_f^0}, \quad \chi = \frac{C_f}{C_f^0}, \quad (7)$$

$$\phi = R\sqrt{\frac{k_e}{D_e}}, \quad \alpha = \frac{V_p K_e}{V_f} \quad (8)$$

ϕ being the Thiele modulus for the reaction and α the system's adsorption capacity, respectively.

$$D_e = \frac{D_p}{K_e}, \quad k_e = \frac{(1 - \varepsilon_p)Kk_s}{K_e} \quad K_e = \varepsilon_p + (1 - \varepsilon_p)K \quad (9)$$

K is the Henry's constant, k_s is the reaction rate constant and D_p is the diffusivity in the particle, which can be evaluated from the estimation of the porosity, the tortuosity and the molecular and Knudsen diffusion coefficients (Satterfield, 1981).

The system of Eqs. (1)–(6) was solved numerically (exact solution) for a wide range of ϕ (Thiele modulus) and α (system's adsorption capacity) values in Bidabehere and Sedran (2006), where more details can be found. It is interesting to stress the meaning of the parameter α , which relates the solid and fluid phase volumes and can be considered as an indication of the system's adsorption capacity. As it will be shown later, the discrepancy between the approximation to the true effectiveness factor and that based on the assumption of steady states strongly depends on its magnitude.

The effectiveness factor for a first order chemical reaction, which is obviously a function of time, is coincident with the relationship between the average reactant concentration in the particles and the concentration in the external surface of the particles

$$\eta(\tau) = \frac{\int_0^1 4\pi\rho^2 k_e \xi(\rho, \tau) d\rho}{\frac{4}{3}\pi k_e \chi(\tau)} = \frac{\bar{\xi}(\tau)}{\chi(\tau)} = \eta^{ts}. \quad (10)$$

Particularly, the exact solution for the reactant's volume average concentration in the particles, $\bar{\xi}$, obtained from Eqs. (2), (4)–(6), is (Kim, 1989)

$$\begin{aligned} \bar{\xi} = & s_1 \chi - s_2 \frac{d\chi}{d\tau} + s_3 \frac{d^2\chi}{d\tau^2} - \dots + \sum_{n=1}^{\infty} \left(\frac{e^{-\lambda_n \tau}}{\lambda_n} \right) \left(-\chi(\tau=0) \right. \\ & \left. + \frac{1}{\lambda_n} \frac{d\chi}{d\tau} \Big|_{(\tau=0)} - \frac{1}{\lambda_n^2} \frac{d^2\chi}{d\tau^2} \Big|_{(\tau=0)} + \dots \right) \end{aligned} \quad (11)$$

where

$$s_i = \sum_{n=1}^{\infty} 6/\lambda_n^i, \text{ and } \lambda_n = \phi^2 + n^2\pi^2. \quad (12)$$

Eq. (10) provides the exact solution to the actual, transient effectiveness factor. It was shown that the relationship between the concentrations averaged in the particles and in the fluid become constant, a pseudo-equilibrium state being reached, after a certain dimensionless time (τ_{pE}) has elapsed, which depends on the ϕ and α values (Bidabehere and Sedran, 2006).

An analytical solution to the system of Eqs. (1)–(6) would reduce the number of calculations to solve it and simplify the analysis. It was shown in Bidabehere et al. (2015) that an

approximation to the effectiveness factor can be defined after a certain dimensionless time τ_{\min} has elapsed, which is also a function of time.

$$\eta_{approx}^{ts} = s_1 \left(1 - \frac{s_2}{s_1} \frac{1}{\chi} \frac{d\chi}{d\tau} \right) \text{ valid for } \tau > \tau_{\min} = \frac{1}{\pi^2 + \phi^2} \quad (13)$$

After time τ_{\min} has elapsed, η^{ts} becomes constant ($\eta^{ts} = \eta_{pE}^{ts}$), and then the relative change of the concentration of reactant in the fluid phase, $\frac{1}{\chi} \frac{d\chi}{d\tau}$, is constant. In this way, the semilogarithmic representation of the observed evolution of the dimensionless concentration in the fluid phase as a function of the dimensionless time,

$$\frac{1}{\chi} \frac{d\chi}{d\tau} = \frac{d \ln \chi}{d\tau} = -\tau_{obs}^{-1} \quad (14)$$

is linear, its slope being $\frac{-1}{\tau_{obs}}$. Note that s_1 is equal to the steady state effectiveness factor (Kim, 1989; see also Eqs. (12) and (17)). The value of s_2/s_1 , which represents the dimensionless time constant for the diffusion-adsorption-reaction processes in the particles (τ_p , Bidabehere et al., 2015) can be calculated from Eq. (12). τ_p is the minimum time at which the equilibrium would be reached inside the catalyst particles if a step change occurs in the concentration of the external surface, its highest value, 1/15, corresponding to situations where no chemical reaction proceeds (Glueckauf, 1955). Moreover, τ_p decreases monotonically if ϕ is increased (Kim, 1989). Then, Eq. (13) can be written

$$\eta_{approx}^{ts} = \eta^{ss} \left(1 + \frac{\tau_p}{\tau_{obs}} \right). \quad (15)$$

Eq. (13) can be used in the mass balance in the reactor (1) together with the consideration that $3 \frac{\partial \xi}{\partial \rho} \Big|_{\rho=1} = \frac{d\bar{\xi}}{d\tau} + \phi^2 \bar{\xi}$ (Appendix A, Eq. (A.3)), while the average concentration in the particle and its first derivative can be obtained from Eq. (11), by neglecting the derivatives of order higher than one. Thus, it can be shown (Bidabehere et al., 2015) that

$$\eta_{approx}^{ts} = s_1 I_a \quad I_a = 1 + \frac{\alpha s_1 (s_2/s_1) \phi^2}{1 + \alpha s_1 (1 - (s_2/s_1) \phi^2)} \quad (16)$$

$$s_1 = \frac{3}{\phi^2} (\phi \coth \phi - 1) = \eta^{ss} \quad (17)$$

and I_a is the diffusion-adsorption-reaction correction factor which is always larger than one and a complex function of the Thiele modulus and the system's adsorption capacity. For a given ϕ , I_a increases with α (Bidabehere et al., 2015). Eq. (16) predicts a constant value of the approximated effectiveness factor, which can be calculated from the classical effectiveness factor and the correction factor I_a .

The correction factor $I_a = \frac{\eta_{approx}^{ts}}{\eta^{ss}}$ (compare Eqs. (15) and (16)) shows proportionality with the relationship between the particle's inertia (τ_p , process of diffusion, adsorption and reaction, that is, changes in the average reactant concentration given in the light of changes in the external surface of the particles) and the overall process' inertia (τ_{obs} , changes observed in the fluid phase after the injection of a pulse of reactant). η_{approx}^{ts} is close to η^{ss} , that is, $I_a \cong 1$, if $\tau_p/\tau_{obs} \ll 1$. Since τ_p decreases as a function of ϕ (Bidabehere et al., 2015) and τ_{obs} is high in systems with low reactivity and adsorption capacity, the differences between η_{approx}^{ts} and η^{ss} , as it will be shown later, will

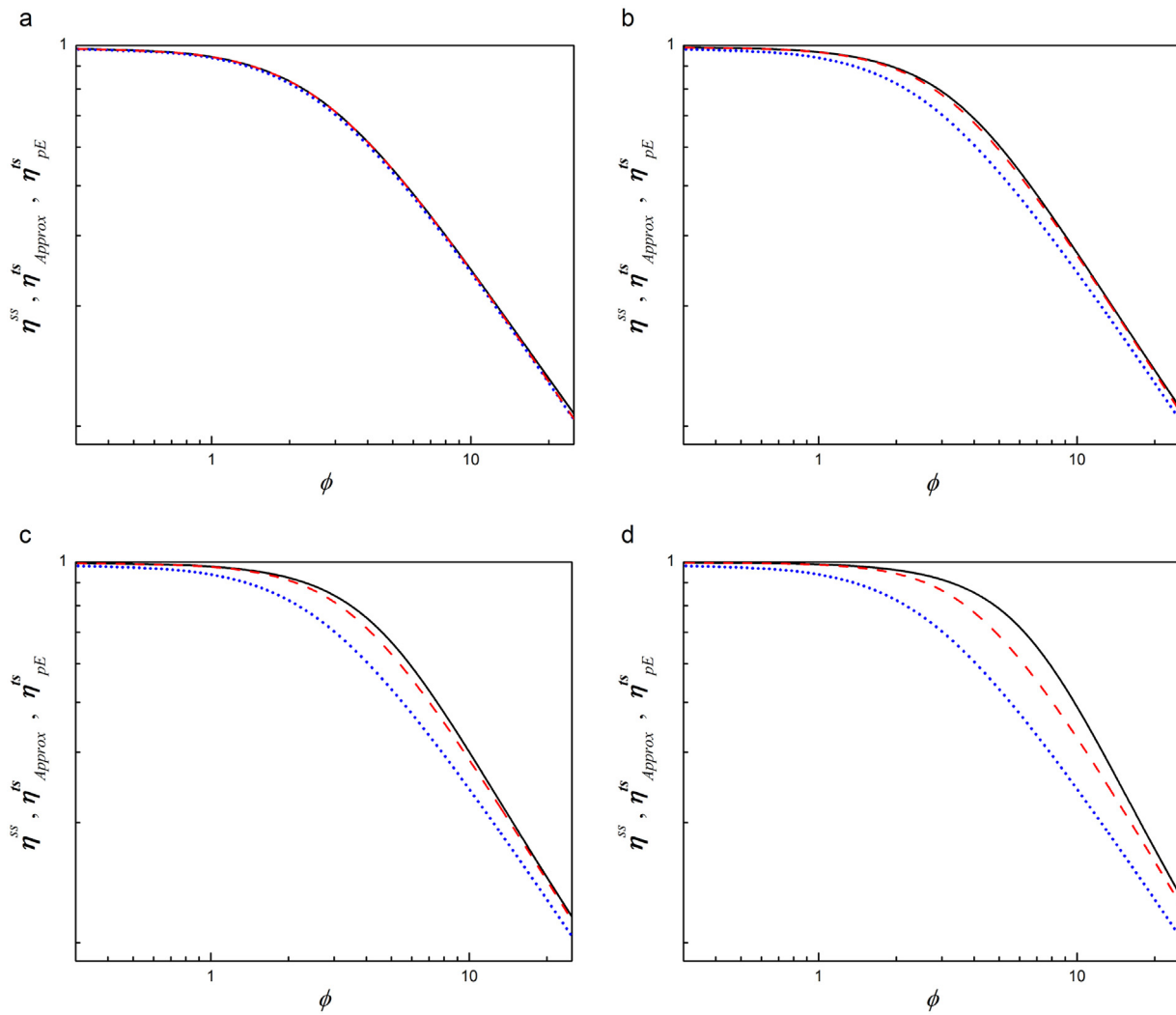


Fig. 1 – Effectiveness factors as a function of the Thiele modulus (ϕ) for different values of the system’s adsorption capacity (α). (η_{pE}^{ts} (solid), η_{approx}^{ts} (dash), η^{ss} (dot). $\alpha = 0.1$ (a), 1 (b), 2 (c), 5(d)).

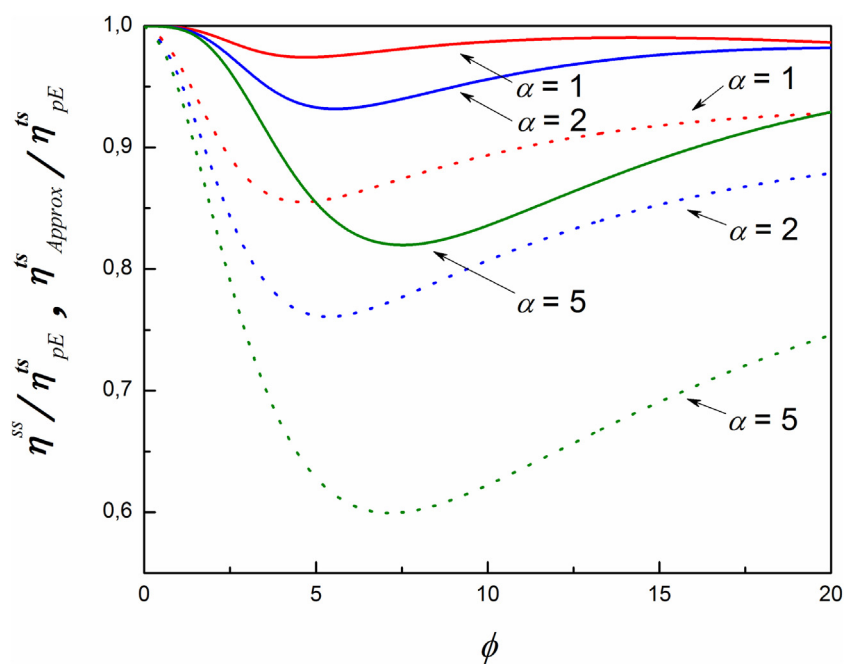


Fig. 2 – Relationships $\eta_{approx}^{ts} / \eta_{pE}^{ts}$ (solid lines) and $\eta^{ss} / \eta_{pE}^{ts}$ (dotted lines) as a function of the Thiele modulus (ϕ) for different values of the system’s adsorption capacity (α).

be significant in systems with medium and high adsorption capacities and medium ϕ values.

3. Results and discussion

3.1. Accuracy of the approximation to the transient effectiveness factor

Fig. 1 shows the value of the exact effectiveness factor after time τ_{pE} has elapsed (η_{pE}^{ts} , Eq. (10)), the proposed approximation ($\eta_{approx}^{ts} = \eta^{ss} I_a = s_1 I_a$, Eq. (16)) and the effectiveness factor assessed under the assumption of steady state in the particles ($\eta^{ss} = s_1$, Eq. (17)), as a function of the Thiele modulus for various values of α . In the case of systems with $\alpha \ll 1$ (low adsorption capacity), the profiles of both η_{approx}^{ts} and η^{ss} are coincident with that of the exact effectiveness factor; as it can be seen in Fig. 1a, even if $\alpha = 0.1$, closeness is apparent. When $\alpha \cong 1$ (Fig. 1b), η_{approx}^{ts} is still satisfactorily close to the exact effectiveness factor, but η^{ss} differs significantly. If α is higher, the divergence between η_{approx}^{ts} and η_{pE}^{ts} is apparent, but it is still lesser than that corresponding to η^{ss} .

In the injection of reactant to a batch reactor, then, as it can be deduced from the correction given by Eqs. (15) and (16) and confirmed in Fig. 1, the effectiveness factor (either exact or approximated) is always larger than the one provided by the classical approach which considers the steady state for the concentration inside the catalyst particles. Fig. 2 shows that the relative errors corresponding to the approximate effectiveness factor in comparison to the exact value ($E = (\eta_{pE}^{ts} - \eta_{approx}^{ts}) / \eta_{pE}^{ts}$) are lower than 2.4%, 5.0% and 15.0% for the corresponding α values of 1, 2 and 5, respectively. It can also be seen that in case of using η^{ss} the errors are significantly larger in the same cases.

It can be concluded that the accuracy of η_{approx}^{ts} is acceptable for the study of dynamic systems where α is not much larger than one. The mass of catalyst used in the experiments, which conditions the system's adsorption capacity (see Eq. (8)), should allocate an adequate parametric sensibility. A brief discussion on typical values of the experimental parameters is presented in Section 3.3.

3.2. Analytical solution

The mass balances for the reactant in the reactor and the catalyst particles can be combined so as to obtain an analytical solution for the evolution of the observed reactant concentration in the reactor's fluid phase, χ , which is the variable to be observed in the experiments. Considering that the flux of reactant to the solid equals its accumulation, diffusion and reaction in the particles ($3 \frac{\partial \xi}{\partial \rho} \Big|_{\rho=1} = \frac{d\bar{\xi}}{d\tau} + \phi^2 \bar{\xi}$, see Appendix A, Eq. (A.3)), and that when the time τ_{pE} is evolved, the average reactant concentration in the particle can be expressed by means of Eq. (10) as $\bar{\xi} = \eta_{pE}^{ts} \chi$, the mass balance in the reactor is

$$\frac{d\chi}{d\tau} = -\alpha \left[\eta_{pE}^{ts} \frac{d\chi}{d\tau} + (\eta_{pE}^{ts} \phi^2) \chi \right]. \quad (18)$$

The general solution of this equation, which defines a pseudo-homogeneous model, is (see Appendix A)

$$\chi = \chi_0^* \exp(-\tau/\tau_{obs}) \quad \tau > \tau_{pE} \quad (19)$$

where

$$\chi_0^* = \frac{\exp(\tau_p/\tau_{obs})}{1 + \alpha \eta_{pE}^{ts}} \quad \tau_{obs}^{-1} = \frac{\alpha \eta_{pE}^{ts} \phi^2}{1 + \alpha \eta_{pE}^{ts}}. \quad (20)$$

The extrapolation of the solution to time zero, χ_0^* , is the result of considering that, when $\tau = \tau_p$, the amount of reactant in the reactor's fluid phase and adsorbed or diffusing inside the particles, is much larger than the amount which has reacted which can consequently be disregarded (see Appendix A).

When $\alpha \rightarrow 0$ the asymptotic solutions of χ tend to the results provided by the steady state assumption in the calculation of the effectiveness factor. Certainly, it can be verified that for a given ϕ , if $\alpha \ll 1$ (low adsorption capacity), $I_a \rightarrow 1$, $\eta_{approx}^{ts} \rightarrow \eta^{ss}$, $\tau_{obs}^{-1} \rightarrow \alpha \eta^{ss} \phi^2$, the value of τ_{obs} is large and $\tau_p/\tau_{obs} \ll 1$. Then, $\chi_0^* \rightarrow 1$ and the solution is coincident with that obtained when the steady state assumption in the particles is used. In dimensionless terms, the concentration of reactant in the fluid phase of the reactor is given by the very well known expression

$$\chi = \exp(-\alpha \eta^{ss} \phi^2 \tau). \quad (21)$$

3.3. Comparison of the solution of the pseudo-homogeneous model with the exact solution

Fig. 3 shows the evolutions of χ , which is obtained exactly, that is, the solution of the system of Eqs. (1)–(6), and the analytical solution of the pseudo-homogeneous model (Eqs. (19) and (20)), for $\phi = 5$ and different values of α . The evolutions of the average reactant concentration in the particles are also included, which at very short times increase very fast and then pass through a maximum value; after the time τ_{pE} is evolved, it maintains a constant relationship with the concentration in the reactor's fluid phase, which is equal to the effectiveness factor (Eq. (10)). It can be seen that, as long as $\tau > \tau_{min} \cong 0.03$, the evolutions of χ are very close, even though $\alpha \gg 1$.

In order to realize the range of values of α which is appropriate to achieve a proper parametric sensitivity in laboratory experiments with catalytic reactors, it is useful to analyze the time spans involved. It can be considered that for many chemical species, both gas and liquid, the range of diffusivities is in the order of about 10^{-5} and $10^{-9} \text{ m}^2 \text{ s}^{-1}$ respectively (Satterfield, 1981). That means that in systems with strong adsorption (K about 10^3 or larger (Ruthven, 1984; Yang, 1987), for typical porosities of 0.4 and tortuosity factors of 3 in particles of about 1 mm radius, the resulting values of D_e/R^2 are in the order of 10^{-3} and 10^{-7} s^{-1} for gases and liquids, respectively. It can be seen in Fig. 3 that the changes in the fluid phase reactant's concentration which are significant occur at times which, if considered dimensionally, are in the order of minutes for systems with fast diffusion or even weeks for systems with slow diffusion. This could be inconvenient in slightly reactive systems, since the observed concentration changes would be extremely slow (see inlet in Fig. 3a); if possible, smaller particle sizes would be helpful. On the contrary, the concentration profiles decrease abruptly at $\tau < 0.1$ in highly reactive systems (see Fig. 3d), thus making difficult to follow the evolution of the reaction due to limitations in the analytical methods.

Then, the amount of catalyst used in the experiments, impacting on the definition of the system's adsorption capacity (see Eq. (8)), must provide an adequate parametric sensitivity. If it is too low ($\alpha \ll 1$, even though the consideration of steady state in the particles is applicable, η^{ss}), the

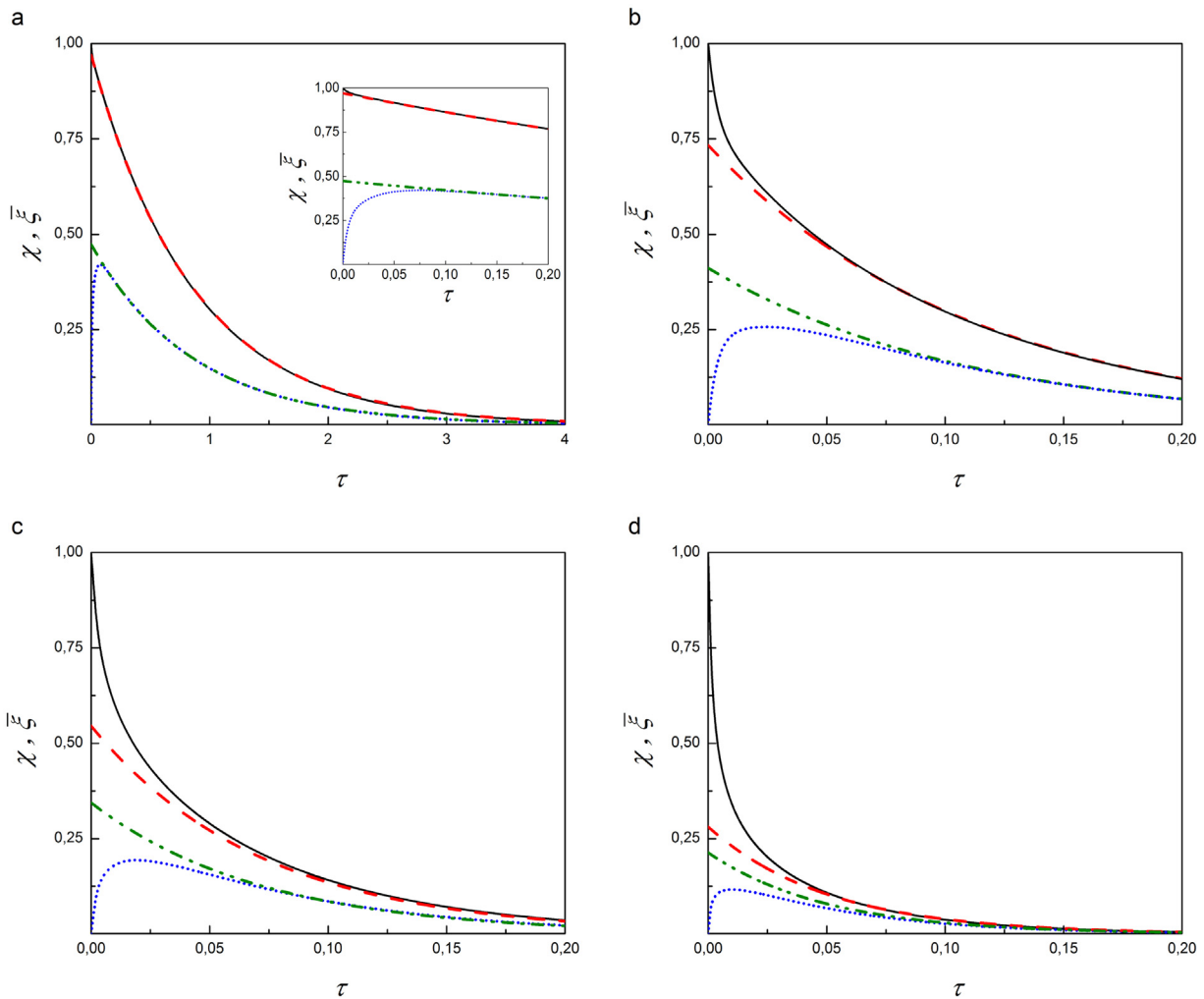


Fig. 3 – Transient responses in a batch reactor after the injection of a pulse of reactant. Lines: solid, χ (exact solution); dot, $\bar{\xi}$ (exact solution); dash, χ (analytical solution); dash dot dot, $\bar{\xi}$ (analytical solution) ($\phi = 5$; $\alpha = 0.1$) (a), 1 (b), 2 (c), 5(d).

changes observed in the concentration of reactant could be not perceived in a reasonable time in slow diffusion systems. If it is too high ($\alpha \gg 1$), the initial rate of change of concentration could be excessively fast to follow, thus inducing extensive tailing of extremely low concentrations and a larger error in the quantifications.

Consequently, in terms of adequate parametric sensitivity in kinetic studies in batch reactors, the mass of catalyst used should lead to α values in the range from 1 to 2, although values lower than 1 could be admitted in fast diffusion systems. It is precisely in that range that the approximated transient effectiveness factor η_{approx}^{ts} is sufficiently accurate, with errors lower than 5% (see Fig. 2).

3.4. Use of the transient effectiveness factor in the determination of kinetic constants

The classical criterion proposed by Weisz and Prater (Weisz and Prater, 1954; Weisz, 1957) estimates the effect of the diffusion resistances in a catalyst with certain particle size by means of the experimental measurement of the rate of consumption of the reactant. The Weisz–Prater parameter is defined as (Weisz and Prater, 1954)

$$\theta = \frac{R^2}{D_p C_f} r_{obs} \quad (22)$$

where $D_p = \frac{\varepsilon_p (D_m^{-1} + D_k^{-1})^{-1}}{\sigma}$, and r_{obs} is the observed reaction rate per unit volume of catalyst ($V_p r_{obs} = -\frac{d(V_f C_f)}{dt}$), which equals the flux to the particles (see Appendix A)

$$r_{obs} = \frac{3}{R} D_e \frac{\partial C}{\partial r} \Big|_{r=R} = \frac{d\bar{C}}{dt} + k_e \bar{C}. \quad (23)$$

Note that the original definition by Weisz and Prater (1954) considered $C_{(r=R)}$ instead of C_f , but external resistances to mass transfer are considered nil in this model. Moreover, as a general rule, if $\theta < 1$ diffusional limitations are negligible.

Then Eq. (22) results

$$\theta = \frac{R^2}{D_p} \frac{V_f}{V_p} \frac{1}{t_{obs}} = \frac{1}{\alpha t_{obs}} \quad (24)$$

where $t_{obs}^{-1} = \frac{-1}{C_f} \frac{dC_f}{dt}$ is an observable quantity.

The original approach by Weisz and Prater ignores the term of accumulation of reactant in the catalytic solid in Eq. (23), thus making θ represent a steady state situation in the particles ($\theta = \theta^{ss}$), which is only a function of the Thiele modulus (see Appendix B, Weisz and Prater, 1954; Weisz, 1957; Weisz and Hicks, 1962; Froment and Bischoff, 1979):

$$\theta^{ss} = \eta^{ss} \phi^2. \quad (25)$$

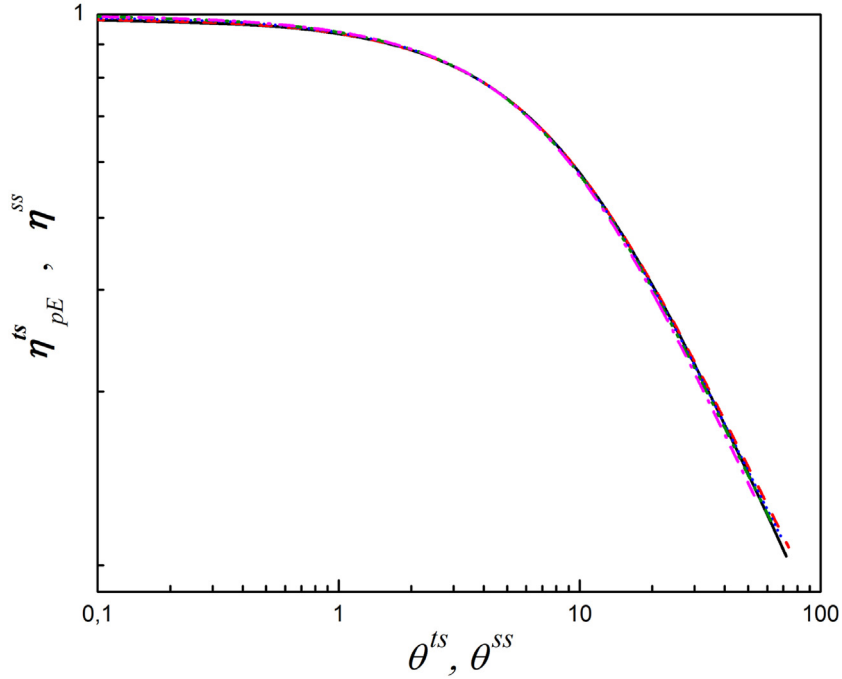


Fig. 4 – Transient (η_{pE}^{ts}) and steady state (η_{pE}^{ss}) effectiveness factors as functions of the Weisz–Prater parameters (θ^{ts} and θ^{ss}) for different values of the system’s adsorption capacity (α). Lines: solid, $\alpha \rightarrow 0$ (η^{ss}); dash, $\alpha = 0.1$; dot, $\alpha = 1$; dash dot dot, $\alpha = 2$; dash dot, $\alpha = 5$.

On the contrary, if the accumulation term in the mass balance equation for the reactant in the particles is taken into account, the corresponding result is (see [Appendix B](#)):

$$\theta^{ts} = \frac{\eta_{pE}^{ts} \phi^2}{1 + \alpha \eta_{pE}^{ts}}, \quad (26)$$

which, obviously, not only depends on the Thiele modulus but also on the parameter α , which includes the mass of catalyst. The η_{pE}^{ts} effectiveness factor in Eq. (26) is provided by Eq. (10) after time τ_{pE} has elapsed.

In this way, the experimental determination of the Weisz–Prater parameter, which is usually employed to calculate Thiele modulus according to Eq. (25), can lead to errors, because, actually, Eq. (26) should be used.

Fig. 4 shows the relationship between η_{pE}^{ts} and θ^{ts} , which was calculated by using Eq. (26) and is the same for every value of α . Moreover, the same dependency is observed for the representation of η_{pE}^{ss} as a function of θ^{ss} (Eq. (25)); indeed, it represents a limiting case ($\alpha \ll 1$) in the approach considering the occurrence of transient states. It is interesting to note that, provided the experiments to determine t_{obs} and, consequently, θ (Eq. (22)), were performed, then the effectiveness factor which can be read from Fig. 4 is indeed the transient state (exact) one. The possibility of serious misinterpretation is shown below.

Once the value of θ is determined experimentally, the effectiveness factor can be evaluated from Fig. 4, and it can be used to assess the kinetic constant. If the classical approach (Eq. (25)) is used,

$$\theta = \frac{1}{\alpha \left(\frac{D_e}{R^2}\right) t_{obs}} = \eta_{pE}^{ss} k_e^{ss} \left(\frac{R^2}{D_e}\right) = \theta^{ss} \quad (27)$$

and the constant is

$$k_e^{ss} = \frac{1}{t_{obs}} \left(\frac{1}{\alpha \eta_{pE}^{ss}}\right). \quad (28)$$

The kinetic constant could also be calculated from the value of the Thiele modulus. Since it is easy to show from Eq. (25) that $\theta^{ss} = 3(\phi \coth \phi - 1)$, then $k_e^{ss} = \phi^2 \frac{D_e}{R^2}$ (Weisz and Prater, 1954; Froment and Bischoff, 1979).

If, however, it is considered that indeed the concentration profiles inside the catalyst’s pores follow transient states, then the calculation of the kinetic constant must be performed following Eq. (26). Thus, by replacing ϕ according to Eq. (8) into Eq. (26),

$$\theta = \frac{1}{\alpha \left(\frac{D_e}{R^2}\right) t_{obs}} = \frac{\eta_{pE}^{ts} k_e^{ts} \left(\frac{R^2}{D_e}\right)}{1 + \alpha \eta_{pE}^{ts}} = \theta^{ts} \quad (29)$$

and then

$$k_e^{ts} = \frac{1}{t_{obs}} \left(\frac{1 + \alpha \eta_{pE}^{ts}}{\alpha \eta_{pE}^{ts}}\right) \quad (30)$$

where η_{pE}^{ts} can be obtained from its relationship with the parameter θ (Eq. (26) or Fig. 4), which is unique for a given experiment and can be calculated with experimental data.

The parameter θ is of great importance in kinetic studies, but if the classical approach is used, it could lead to seriously incorrect values of k_e . For example, if the experimental data determine that θ is equal or lower than 0.75, it can be seen from Fig. 4 that either the steady or the transient effectiveness factor would be larger than 0.95 and close to one. Then, the kinetic constant in the absence of diffusional restrictions, is

$$k_e^{ss} = \frac{1}{t_{obs}} \left(\frac{1}{\alpha}\right) \quad (\text{from Eq. (28), classical approach}) \quad (31)$$

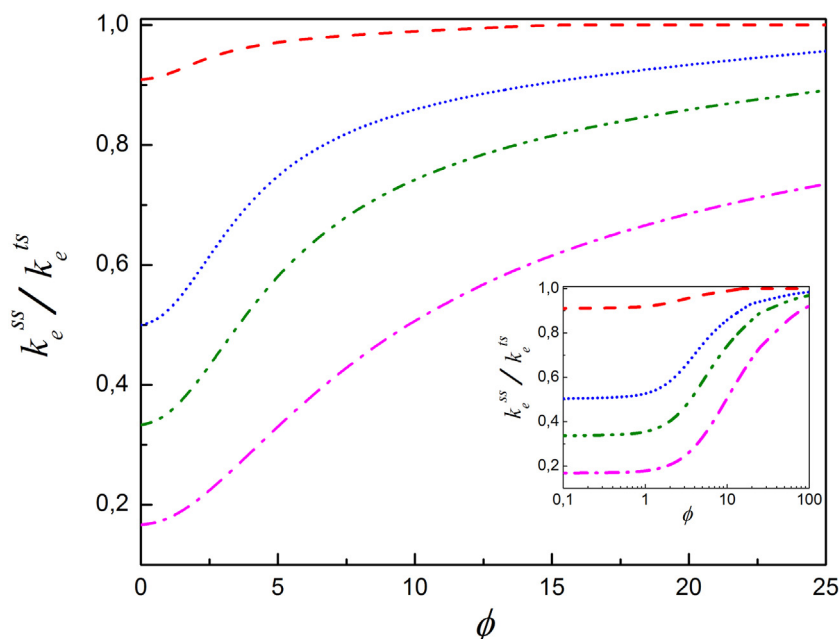


Fig. 5 – Relationship $\frac{k_e^{ss}}{k_e^{ts}}$ as a function of the Thiele modulus (ϕ) for different values of the system's adsorption capacity (α). (Lines: dash, $\alpha = 0.1$; dot, $\alpha = 1$; dash dot dot, $\alpha = 2$; dash dot, $\alpha = 5$).

or

$$k_e^{ts} = \frac{1}{t_{obs}} \left(\frac{1 + \alpha}{\alpha} \right) \quad (32)$$

(from Eq. (30), transient concentration profiles).

This means that in a laboratory experiment performed without diffusion restrictions where $\alpha = 1$, the kinetic constant calculated assuming steady state in the reactant concentration in the particles, k_e^{ss} , will be half the true kinetic constant k_e^{ts} . Moreover, it is easy to see that the larger the load of catalyst in the reactor, the larger the difference between constants.

This is consistent with the analysis which can be performed based on the evidences in Fig. 1 for a given α . For example, for $\alpha = 1$ and effectiveness factors 0.95 (see Fig. 1b), the Thiele modulus corresponding to the assumption of steady state in the particles is 0.89, while the one corresponding to the transient state model is 1.25. Thus, their relationship is 0.71 and, since both modulii are calculated for the same values of R and D_e , they only differ in how the kinetic constants are calculated. Consequently, $\sqrt{\frac{k_e^{ss}}{k_e^{ts}}} \cong 0.71$, which confirms that $\frac{k_e^{ss}}{k_e^{ts}} \cong 0.5$.

The relationship between the kinetic constants calculated from the Weisz–Prater parameter, but following the two different criteria, can be seen in Fig. 5 as a function of ϕ for various values of α . The relationship is the lowest when there exist chemical control of the overall process rate, its value being $\frac{k_e^{ss}}{k_e^{ts}} = \frac{1}{1+\alpha}$ when $\phi \rightarrow 0$, remaining approximately constant until $\phi = 1$ and tending to $\frac{k_e^{ss}}{k_e^{ts}} = 1$ when $\phi \rightarrow \infty$, independently of the value of α . Therefore, if the mass of catalyst and the contribution of the accumulation term in the mass balances in the particle are not taken into account in the experiments, the classical steady state approach can lead to serious errors, consequently affecting, for example, any reactor design effort or comparison between catalysts.

4. Conclusions

Given its definition, the effectiveness factor η^{ts} is inherently transient and, in the case of batch reactors, it was shown that it not only depends on the Thiele modulus ϕ but also on the adsorption capacity of the system α , a function of the load of catalyst in the reactor.

After a certain time has elapsed following the injection of a pulse of reactant, a stable relationship between the average reactant concentration in the particle and that in the fluid is achieved, thus defining a pseudo-equilibrium state in which $\eta^{ts} = \eta_{pE}^{ts}$ is constant.

An approximation to the effectiveness factor, η_{approx}^{ts} , can be defined after simple considerations. It is always closer to η_{pE}^{ts} and larger than the classical effectiveness factor, η^{ss} , which is determined assuming a steady state in the concentrations inside the catalyst particles. η_{approx}^{ts} can be determined from η^{ss} , correcting it with a factor which is a function of ϕ and α and considers the simultaneous diffusion-adsorption-reaction processes in the particles.

The advantages of this approach can be demonstrated in its application to usual kinetic studies, since the accuracy of η_{approx}^{ts} is completely adequate (for example, for $\alpha = 1$, it differs less than 2.4% from η_{pE}^{ts}) under practical and typical experimental conditions. By means of using η_{pE}^{ts} it is possible to derive pseudo-homogeneous analytical models, their solutions being coincident with the exact one in a wide range of conditions.

It was shown that η_{pE}^{ts} can also be determined from the experimental observation of the changes in the concentration of reactant in the fluid phase, following the approach developed by Weisz and Prater (use of the parameter θ), and that the kinetic constants can be calculated even with the classical η^{ss} versus θ relationships, that is, obtained with assumptions of steady state in the particles, provided the concepts of η_{pE}^{ts} are taken into account. On the contrary, significant errors can be introduced.

The recognition of the parameter α as a controlling factor in kinetic analysis experiments clearly sustains that the mass of catalyst used should lead α to be in the approximate range

1–2 for systems with slow diffusion and fast changes in the fluid phase, where the steady state approach in the particles is not adequate.

A quantitative practical criterion for the use of effectiveness factors in kinetic studies was determined: the classical steady state approach and pseudo-homogeneous models can be used if the adsorption capacity of the system is low ($\alpha \leq 0.1$). The new pseudo-homogeneous model, which includes the mass accumulation in the particle and, consequently, the transient effectiveness factor, extends this limit and can be used in systems with medium ($\alpha = 1$) or high ($\alpha > 1$) adsorption capacity.

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Appendix A.

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

$$\frac{d\bar{\xi}}{d\tau} = \frac{1}{V_p} \int_{V_p} \nabla \cdot (\nabla \xi) dV - \phi^2 \bar{\xi}. \quad (\text{A.1})$$

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

$$\frac{1}{V_p} \int_{V_p} \nabla \cdot (\nabla \xi) dV = 3 \frac{\partial \bar{\xi}}{\partial \rho} \Big|_{\rho=1}. \quad (\text{A.2})$$

By replacing in Eq. (A.1)

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

If Eq. (A.3) is introduced in Eq. (1)

$$\frac{d\chi}{d\tau} = -\alpha \left[\frac{d\bar{\xi}}{d\tau} + \phi^2 \bar{\xi} \right]. \quad (\text{A.4})$$

After time τ^{pE} has elapsed a constant relationship is established between the average reactant concentration in the particles and the concentration in the external surface of the particles

$$\eta_{pE}^{ts} = \frac{\bar{\xi}}{\chi}. \quad (\text{A.5})$$

If $\bar{\xi}$ from Eq. (A.5) is replaced in Eq. (A.4)

$$\frac{d\chi}{d\tau} = -\alpha \left[\eta_{pE}^{ts} \frac{d\chi}{d\tau} + \eta_{pE}^{ts} \phi^2 \chi \right] \quad (\text{18})$$

or

$$\frac{d\chi}{d\tau} = - \left[\frac{\alpha \eta_{pE}^{ts} \phi^2}{1 + \alpha \eta_{pE}^{ts}} \right] \chi. \quad (\text{A.6})$$

When $\tau = \tau_p$ (minimum time at which the equilibrium can be reached inside the catalyst particles), the amount of reactant in the reactor's fluid phase, and adsorbed or diffusing inside the particles, is much larger than the amount which

has reacted, and which can consequently be disregarded. In dimensional terms,

$$C_f^0 V_f = C_f V_f + \left[V_p \varepsilon_p \bar{C} + V_p (1 - \varepsilon_p) K \bar{C} \right] \quad (\text{A.7})$$

or, in dimensionless terms,

$$1 = \chi(\tau_p) + \alpha \bar{\xi}(\tau_p). \quad (\text{A.8})$$

The solution to Eq. (A.6) is simply

$$\chi = \chi_0^* \exp(-\tau/\tau_{obs}) \quad (\text{19})$$

where

$$\tau_{obs}^{-1} = \frac{\alpha \eta_{pE}^{ts} \phi^2}{1 + \alpha \eta_{pE}^{ts}} \quad (\text{A.9})$$

and the extrapolation of the solution to time zero,

$$\chi_0^* = \frac{\exp(\tau_p/\tau_{obs})}{1 + \alpha \eta_{pE}^{ts}} \quad (\text{A.10})$$

is obtained by replacing Eq. (A.8) into the general solution, Eq. (19).

Appendix B.

The very well known Weisz–Prater parameter is defined as

$$\theta = \frac{R^2}{D_p C_f} r_{obs} = \frac{R^2}{D_p} \frac{V_f}{V_p} \left(-\frac{1}{C_f} \frac{dC_f}{dt} \right) \quad (\text{B.1})$$

which can be written in dimensionless terms as

$$\theta = \frac{1}{\alpha} \left(-\frac{1}{\chi} \frac{d\chi}{d\tau} \right). \quad (\text{B.2})$$

If Eq. (14) is introduced into Eq. (B.2), then

$$\theta = \frac{1}{\alpha \tau_{obs}}. \quad (\text{B.3})$$

If the concentrations inside the catalyst particles are not assumed to be in a steady state, the corresponding mass balance in the reactor is given by Eq. (18) and, consequently, τ_{obs} is given by Eq. (20), that is,

$$\theta^{ts} = \frac{\eta_{pE}^{ts} \phi^2}{1 + \alpha \eta_{pE}^{ts}}. \quad (\text{26})$$

If, on the contrary, the concentrations inside the catalyst particles are assumed to be in a steady state, the accumulation terms in the mass balance equations (that is, $\frac{d\bar{\xi}}{d\tau}$ in Eq. (A.4), $\eta_{pE}^{ts} \frac{d\chi}{d\tau}$ in Eq. (18) and $\alpha \eta_{pE}^{ts}$ in Eq. (20)) are nil and, moreover, the effectiveness factor will be that corresponding to the mentioned condition (steady state in the catalyst particles, $\eta^{ts} = \eta^{ss}$). Then,

$$\theta^{ss} = \eta^{ss} \phi^2. \quad (\text{25})$$

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