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 heterogeneous 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

$$\frac{d\chi}{d\tau} = -3\alpha \frac{\partial \xi}{\partial \rho}\Big|_{\rho=1} \tag{1}$$

$$\frac{\partial \xi}{\partial \tau} = \nabla^2 \xi - \phi^2 \xi \tag{2}$$

which are subjected to the initial and boundary conditions

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

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

$$\frac{\partial \xi}{\partial \rho}\Big|_{\rho=0} = 0 \tag{5}$$

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