Chemical Engineering Science 60 (2005) 907–916

Chemical Engineering Science

www.elsevier.com/locate/ces

Analytical expression for the non-isothermal effectiveness factor: the *n*th-order reaction in a slab geometry

Enrique Muñoz Tavera*

Department of Bioengineering, Rice University, Suite 116 Keck Hall, 6100 Main, Houston, TX 77005-1892 USA

Received 25 June 2004; received in revised form 17 September 2004; accepted 28 September 2004
Available online 23 November 2004

Abstract

The problem of calculating the effectiveness factor for a porous slab of catalyst pellet under non-isothermal conditions has been revisited. An exact formal analytical solution was obtained for a *n*th-order (integer $n \geqslant 0$), exothermic and irreversible chemical reaction. Numerical calculations where performed, and an analytical formula was obtained for the very fast reaction limit. In addition, a fairly simple formula, which was called the low beta approximation, was developed and tested to be valid for low values of the *thermicity* group $\beta \leqslant 0.1$.

Keywords: Biocatalysis; Catalysis; Catalyst support; Kinetics; Porous media

1. Introduction

Heterogeneous catalytic reactors constitute an important unit operation in a wide variety of chemical processes. Traditional chemical engineering applications (Lee, 1985; Satterfield, 1970), like hydrogenation of organic compounds, oxidation, dehydrogenation, polymerization and catalytic cracking, among many others, are performed by contacting a fluid (gas or liquid) reacting phase with solid porous particles, which possess a high surface-volume ratio to enhance contact between the fluid phase and the actual catalyst agent, typically a metal (Ni, Pd, Fe, Cu, Pt) or metal oxide. Analogous situation arises in some biochemical engineering processes (Buchholz, 1982; Engasser and Horvath, 1976), in particular in immobilized enzyme reactors, where enzymes are fixed to a porous matrix, like agarose.

From the engineering perspective, only macroscopic variables in the reactor are accessible for both measurement and control. However, in the processes described above, chemical or biochemical catalytic reactions take place at the surface of solid particles, usually at the pore surfaces in the particle interior, and consequently they depend on microscopic distributed parameters, as concentration and temperature, which are related to the macroscopic values through a combination of mass and heat transfer resistances, in addition to the chemical reaction itself. A simplified analysis of the real situation is to consider two resistances in series (Lee, 1985; Satterfield, 1970), the first one for transport through the external boundary layer which surrounds the particle, and the second one due to the combination of diffusion and reaction at the interior of the pores. In steady state, the overall reaction rate will be controlled by the higher resistance, i.e., the slowest step. For the case in which reaction and diffusion at the interior of the pores controls, the theory of effectiveness factors can be applied. Originally developed independently by Damköhler (1935), Thiele (1939) and Zeldovitch (1939), this theory has become an important and useful concept in heterogeneous reactor analysis, design and control for many years.

Extensive theoretical studies have been performed for the calculation of effectiveness factors assuming isothermal conditions and different reaction rates (Bischoff, 1965), and analytical expressions can be obtained for typical cases: simple *n*th-order, Langmuir isotherm (Chu and Hougen, 1962) assuming simple slab one-dimensional geometries. Other shapes (spheres, cylinders) have been studied (Amundson and Luss, 1967) in the context of the first-order reaction.

---

* Tel.: +71 33483050; fax: +71 33485877.
E-mail address: munozt@rice.edu (E. Muñoz Tavera).

0009-2509/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2004.09.053

Under conditions when intra-particle thermal resistance becomes important, i.e., non-isothermal pellet, the analysis becomes more complicated due to the unavoidable coupling between heat and mass transfer equations. Much theoretical work has been performed to study questions related to uniqueness and stability of solutions (Aris, 1969; Drott and Aris, 1969; Hlaváček et al., 1969a,b; Luss, 1968), and in particular analytical expressions for the exothermic first order reaction rate have been developed by Drott and Aris (1969), who reported trifurcation points for certain combinations of the parameters involved in the model.

Despite the inherent mathematical complexity of general solutions described above, in many practical cases the internal temperature gradients are comparatively small (Hlaváček et al., 1969a) (but not necessarily negligible), and for very fast irreversible reactions the concentration of reactant at the center of the pellet will be close to zero, so uniqueness of solutions in those cases is guaranteed even on physical grounds. In this context, simple empirical analytical expressions for the temperature dependence of the effectiveness factor in the first-order reaction have been reported (Liu, 1969).

In the present work, an exact formal analytical solution is presented for the nonisothermal effectiveness factor in a plane slab geometry, for the case of irreversible and exothermic *n*th-order reaction rate. This general formal expression is specialized for the limit of very fast chemical reaction, where the concentration at the center of the slab can be assumed close to zero, obtaining an analytical formula suitable for direct calculations. Finally, for the case of very small temperature gradients, a fairly simple analytical formula is derived.

2. Theory

2.1. Definition of the effectiveness factor

For a porous catalyst pellet, where the controlling resistance is assumed to be diffusion and chemical reaction occurring at the interior pores, an expression for the average reaction rate R_{avg} is required as a function of the parameters accessible to measurement and control in the reactor. If the reaction rate at the external pellet surface conditions is given by R_{surf}, the effectiveness factor is defined by the expression:

$$\eta \equiv \frac{R_{\text{avg}}}{R_{\text{surf}}} = \frac{\frac{1}{V_{\text{pellet}}} \int\int\int_{V_{\text{pellet}}} R\,\mathrm{d}V}{R_{\text{surf}}}, \tag{1}$$

where R represents the volumetric reaction rate inside the pellet pores, and V_{pellet} is the total volume of the catalyst pellet.

In what follows, we shall assume that C is the reactant concentration at the interior of the pellet pores. We shall also consider effective transport properties inside the pores: D_{eff} and k_{eff} will be the effective diffusion coefficient and thermal conductivity. The reaction enthalpy will be given by ΔH_R, and the stoichiometric coefficient (negative) for the reactant will be v_c.

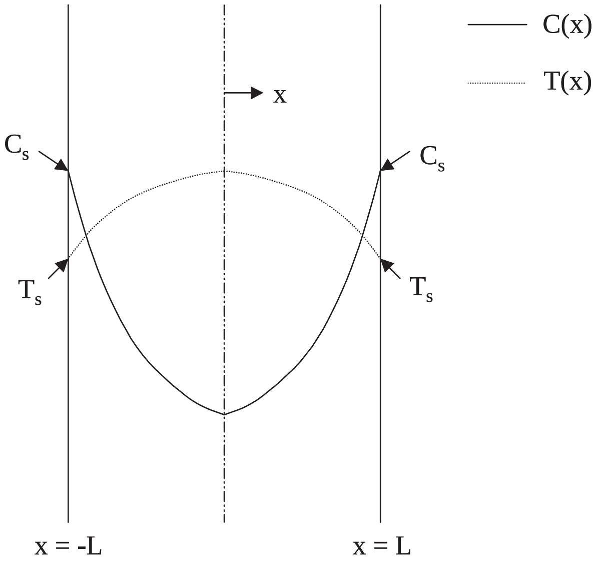

Fig. 1. Sketch of the slab catalyst pellet, showing concentration and temperature profiles for an exothermic chemical reaction.

Under steady-state conditions, the mass and energy balance are

$$\text{Mass balance:}\quad -D_{\text{eff}}\nabla^2 C = v_c R, \tag{2}$$

$$\text{Energy balance:}\quad -k_{\text{eff}}\nabla^2 T = (-\Delta H_R) R. \tag{3}$$

Substituting the reaction rate from Eq. (2) into the effectiveness factor definition (1), and after applying Gauss' Theorem:

$$\eta = \frac{D_{\text{eff}}}{(-v_c) V_{\text{pellet}} R_{\text{surf}}} \oint\!\!\oint_{S_{\text{pellet}}} \nabla C \cdot \hat{n}\,\mathrm{d}S. \tag{4}$$

Expression (4) is in general valid for any geometry. However, in many applications the interesting cases are simple geometries (slabs, cylinders, spheres) whose symmetry allows to assume that the concentration gradient is independent of the position over the surface. Under this last assumption, Eq. (4) can be reduced to:

$$\eta = \frac{D_{\text{eff}} S_{\text{pellet}}}{(-v_c) V_{\text{pellet}} R_{\text{surf}}} \hat{n} \cdot \nabla C_{\text{surf}}. \tag{5}$$

2.2. Pellet with the shape of a slab

Consider a catalyst pellet with the shape of a slab, of thickness $2L$, with $L^2 \ll S_{\text{pellet}}$, as is shown in Fig. 1. For this geometry, the mass and energy balance Eqs. (2) and (3) reduce to the following expressions:

$$\text{Mass balance:}\quad -D_{\text{eff}} \frac{d^2 C}{\mathrm{d}x^2} = v_c R, \tag{6}$$