



## An approximate expression for predicting concentration and temperature profiles inside a catalyst pellet

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### INTRODUCTION

Many contributions have been presented in the past to predict accurately the effectiveness factor ( $\eta$ ) when a single reaction is taking place inside a catalyst pellet. The major contributions are due to Wedel and Luss (1980) and Gottifredi *et al.* (1981a,b, 1986). With these techniques, however, the concentration profile of the key component, inside the catalytic pellet, remains unknown. By knowing this profile, the temperature within the pellet can be predicted, which can be important information when side reactions have to be avoided. Even in the case of isothermal reactions, the knowledge of concentration profiles can be crucial to avoid series and parallel reactions that can cause catalyst inhibition.

The scope of this contribution is to develop an approximate expression based on the available information, since  $\eta$  values are related to the slope of concentration in a region near the surface. Since  $\eta$  values can be accurately predicted, it is possible to build up an approximate expression that also describes the profiles inside the particle.

### APPROXIMATE EXPRESSION DEVELOPMENT

It will be assumed that a single reaction is taking place inside the catalytic pellet of characteristic length  $L$ . It is well known that the dimensionless temperature and concentration profiles are related by

$$T = 1 + \beta(1 - C) \quad (1)$$

when the dependent variables are normalized with respect to their surface values. The continuity equation for the dimensionless key component concentration can be written as

$$\frac{d}{dx} \left( x^n \frac{dC}{dx} \right) = h^2 x^n f(x) R(C) \quad (2)$$

where

$$\begin{aligned} C &= (C'/C'_s), \quad T = (T'/T'_s), \quad R(C) = r(C, T')/r_s(C'_s, T'_s) \\ h^2 &= [r_s(C'_s, T'_s)/C'_s] L^2 / D_{\text{eff}} \quad (3a-c) \\ \beta &= D_{\text{eff}} C'_s (-\Delta H) / (K_{\text{eff}} T'_s) \end{aligned}$$

$D_{\text{eff}}$  and  $K_{\text{eff}}$  being the effective diffusivity and thermal conductivity of the pellet,  $r$  the dimensional rate of reaction,  $\Delta H$  the heat of reaction,  $f(x)$  the normalized catalytic activity function and  $n = (0, 1, 2)$  a geometrical parameter. The prime is used to denote dimensional variables and the subscript  $s$  to denote the surface properties ( $x = 1$ ). The effectiveness factor ( $\eta$ ) is defined as

$$\eta = \int_0^1 (n+1)x^n f(x) R(C) dx = \frac{(n+1)}{h^2} \left. \frac{dC}{dx} \right|_s \quad (4)$$

Gottifredi *et al.* (1986) have shown that  $\eta$  can be predicted through approximate procedures with great accuracy.

However, the concentration and temperature profiles remain unknown when these predictions are used. No attempts have been made to predict these profiles through an approximate expression. Most of the results found in the literature are obtained through the application of numerical schemes that can become unstable when  $h^2 > 1$ . The purpose is to derive an approximate expression and then to compare produced results with numerical findings reported in the literature.

In the most general case there will be a value of  $C = C^*$  such that  $R(C^*) = 0$ . Thus, it is most convenient to define an auxiliary variable:

$$A = \frac{C - C^*}{(1 - C^*)} \quad (5)$$

As shown by Villadsen and Michelsen (1978), a good approximation for the concentration profile when  $h^2 \ll 1$  is the so-called one collocation point expression:

$$A = 1 - \lambda(1 - x^2)/2 \quad (h^2 < 1) \quad (6)$$

where the parameter  $\lambda$  should be found through the application of some reasonable criterion for minimizing the residual over the continuity equation. However, the best choice should be that by which  $\eta$  values are accurately predicted. By applying this assumption,

$$\lambda = h^2 \eta / [(n+1)(1 - C^*)] \quad (7)$$

On the other hand, when  $h^2 \gg 1$  the only known analytical procedure is based on the Clairaut substitution and the perturbation technique used by Petersen (1965). However, with this procedure only the flux can be analytically found:

$$\left. \frac{dC}{dx} \right|_s \approx \left[ 2 \int_0^1 f(1) R(C) dC \right]^{1/2} h = \frac{h^2 \eta}{(n+1)} \quad (8)$$

The concentration profiles for a first-order reaction are a superposition of exponentials. Therefore, near the surface a reasonable approximation would be

$$A \approx \exp[bh(1 - x)] \quad (h^2 \gg 1) \quad (9)$$

From eq. (9) the value of  $b$  is estimated as

$$b = h\eta / [(n+1)(1 - C^*)] = (\lambda/h) \quad (10)$$

It should be noticed that in the region  $0 \leq x \leq 1/h$ , eq. (9) does not predict the concentration accurately.

A suitable general expression for the reduced concentration that matches the profiles predicted by eqs (6) and (9), when  $h^2 \ll 1$  and  $h^2 \gg 1$  respectively, would be

$$A = \exp \left[ -\lambda(1 - x^2) / \left\{ 2 - \frac{[1 - x \cdot g(x)]}{(1 + 2/\lambda)} \right\} \right] \quad (11)$$

where

$$g(x) = [1 - \exp(-\lambda x)] / [1 - \exp(-\lambda)] \quad (12)$$

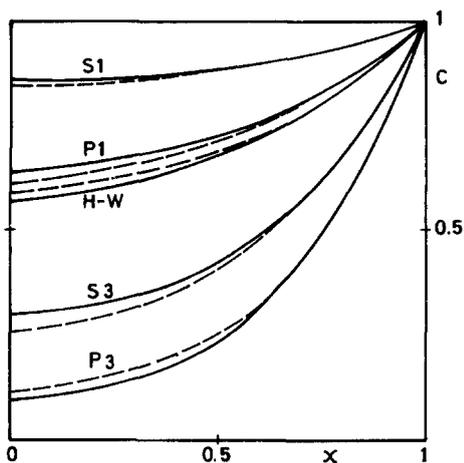


Fig. 1. Comparison between predicted (---) and exact (—) concentration profiles for a first-order irreversible reaction. Spherical shape: S1 ( $h = 1$ ); S3 ( $h = 3$ ); slab shape: P1 ( $h = 1$ ); P3 ( $h = 3$ ). Hougen–Watson kinetics: slab shape (H–W) [ $R = (1 + K)C/(K + C)$ ;  $K = 0.5$ ;  $h = 1$ ].

The function  $g(x)$  was introduced in eq. (11) to ensure that the derivative of  $A$  vanishes at  $x = 0$ .

#### COMPARISON

Figure 1 presents a comparison between predicted and exact concentration profiles obtained from the analytical solutions when first-order reactions were considered. The agreement is very good. As expected, the deviation increases towards the region  $x \rightarrow 0$ . The effect of reversible reaction is too mild, the differences due to the fact that the base value of  $C^*$  absorbs the deviations when  $h^2 \gg 1$ . Figure 1 also presents the comparison between approximate and numerical profiles of  $C$  for the particular case of a H–W (Hougen–Watson) type of kinetics assuming isothermal conditions. This case was studied by Varma and Amundson (1973). A fair agreement is also observed in this case. They also investigated the first-order nonisothermal reaction and the resulting temperature profile for the particular case where  $\eta = 1.56$ . The comparison between our temperature approximate profile and their numerical reported results is fairly acceptable (see Fig. 2).

The case of benzene hydrogenation studied by Irving and Butt (1967) was also analyzed. They measured the temperature profile inside a cylindrical catalyst pellet ( $L = 0.635$  cm). Our approximate expression is able to reproduce the experimental finding with great accuracy (see Fig. 2). It should be noticed that our procedure predicts a central pellet ( $x = 0$ ) temperature of 428.1 K while the experimental extrapolated value was 426.6 K. The surface temperature was 408 K. In the same figure the comparison between computed and approximate concentration profiles, for this case, is also shown.

An interesting case is the dehydrogenation of *n*-butene to butadiene studied by Dumez and Froment (1976). The kinetic expression at 600°C is given by

$$r = \frac{0.824[p_B - (1/K_{eq})p_H p_D]}{(1 + 1.727p_B + 3.593p_H + 38.028p_D)^2} \quad (13)$$

$r$  is the rate of reaction (kmol/kg cat h) and  $p_B$ ,  $p_H$  and  $p_D$  denote the partial pressure (atm) of *n*-butene, hydrogen and butadiene, respectively. Dumez and Froment (1976) present concentration profiles within a particle ( $L = 0.23$  cm) when

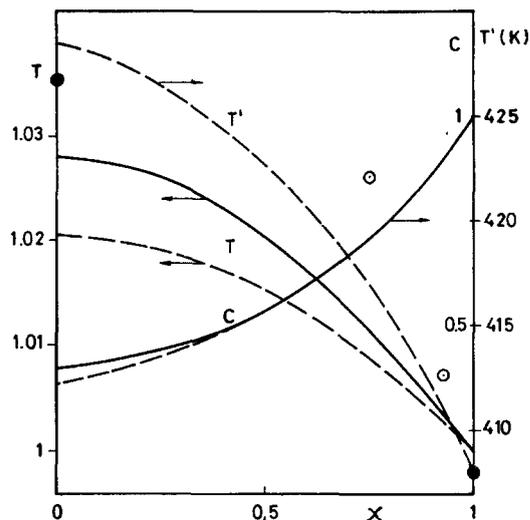


Fig. 2. Comparison between predicted (---) and exact (—) temperature and concentration profiles. Varma and Amundson (1973):  $T$  [first-order kinetics; slab shape ( $\beta = 0.2$ ;  $h = 0.4$ ;  $\eta = 1.56$ )]. Irvine and Butt (1967): [first-order kinetics; cylindrical shape ( $\beta = 0.08$ ;  $h = 1.86$ ;  $\eta = 0.79$ )];  $T'$  (temperature profile); ○ experimental values ( $K$ );  $C$  (concentration profile).

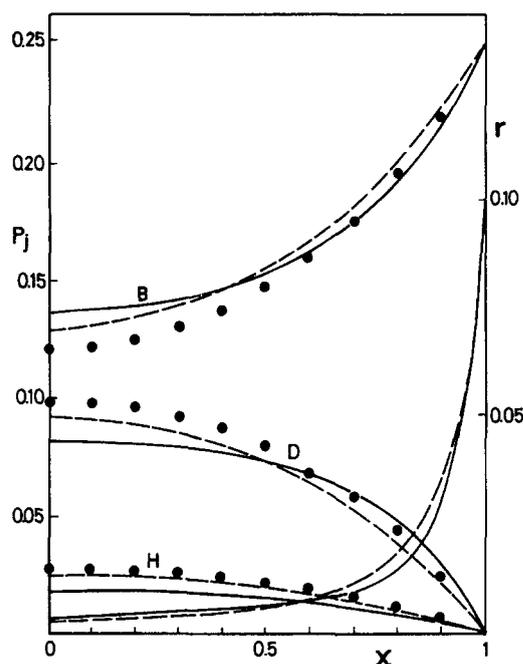


Fig. 3. Butene dehydrogenation. Partial pressures and reaction rate profiles inside a spherical catalyst particle. (—) numerical results (Dumez and Froment, 1976). (---) approximate values (spherical pellet) (this work). (●●●) approximate values (slab pellet) (this work).

the surface partial pressure of  $B$  is equal to 0.25 atm which coincides with the total pressure. In this case,  $h = 2.80$  and

$$R = \frac{2.08[C_B - 0.413(1 - C_B)^2]}{[1 + 0.442C_B + 7.503(1 - C_B)]^2} \quad (14)$$

$C_B = (p_B/0.25)$ . From thermodynamics  $K_{eq} = 0.1 \text{ atm}^{-1}$ . The ratio of effective diffusivities for  $H$  and  $D$  with respect to  $n$ -butene, 4.66 and 1.3 respectively, were taken constant at the values in the center of the particle.

A comparison between approximate and numerical results is presented in Fig. 3. The points refer to the concentration profiles assuming slab instead of spherical geometry. In both cases, a good agreement is obtained. The calculated value of  $\eta$  was 0.17. It was obtained using the general procedure of Gottifredi *et al.* (1986) and it is very close to the value (0.135) obtained by numerical procedure (Dumez and Froment, 1976).

It can be concluded that the approximate expression proposed here, for estimating concentration and temperature profiles inside a catalyst particle, in which a single reaction takes place, produces fairly accurate results. Moreover, due to the fact that the concentration profile of the key component is related to temperature and concentration profiles of the other components, these profiles can also be estimated with a reasonable degree of accuracy. Of particular importance is the agreement achieved for the more complex and representative H-W type kinetics.

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#### NOTATION

$A$	reduced concentration defined by eq. (5) related to $C$
$b$	parameter related to $h$ and $E$ [see eq. (10)]
$C$	dimensionless concentration
$C'$	dimensional concentration
$C^*$	pseudo-equilibrium concentration $R(C^*) = 0$
$D_{\text{eff}}$	effective diffusivity coefficient of key component in the particle
$f(x)$	catalytic activity distribution function
$g(x)$	function of $x$ and $\lambda$ defined by eq. (12)
$h$	Thiele modulus [see eq. (3d)]
$K_{\text{eff}}$	effective thermal conductivity of the pellet
$L$	characteristic length of the particle
$n$	geometry parameter
$r$	rate of reaction, kmol/kg cat h

$R$	dimensionless rate of reaction ( $= r/r_s$ )
$T$	dimensionless temperature
$T'$	dimensional temperature
$X$	dimensionless position inside the pellet

#### Greek letters

$\beta$	dimensionless parameter [see eq. (3e)]
$\lambda$	auxiliary parameter [see eq. (7)]
$\Delta H$	heat of reaction
$\eta$	effectiveness factor

#### Subscripts

$B$	butene
$D$	butadiene
$S$	surface value ( $x = 1$ )
$H$	hydrogen

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