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PREDICTING EFFECTIVENESS FACTOR FOR M-TH ORDER AND LANGMUIR RATE EQUATIONS IN SPHERICAL COORDINATES

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INTRODUCTION

The effectiveness factor is widely used to account for the interaction between pore diffusion and reactions on pore walls in porous catalytic pellets and solid fuel particles. The effectiveness factor is defined as the ratio of the reaction rate actually observed to the reaction rate calculated if the surface reactant concentration persisted throughout the interior of the particle, i.e., no reactant concentration gradient within the particle. The reaction rate in a particle can therefore be conveniently expressed by its rate under surface conditions multiplied by the effectiveness factor.

The generalized steady-state equation in a spherical particle (a catalytic pellet or a solid fuel particle) may be expressed as:

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} - \frac{r'''}{D_e} = 0 \tag{1}$$

where r''' is the intrinsic reaction rate per unit particle volume in mol/cm^3/sec (as a function of C), D_e is the effective diffusivity, C is the local oxygen concentration (as a function of r), and r is the radial distance from the origin. The boundary conditions are

$$C = C_s, \text{ at } r = r_s \tag{2}$$

and

$$\frac{dC}{dr} = 0, \text{ at } r = 0 \tag{3}$$

The intrinsic reaction rate r''' can be in different forms. One way to represent the intrinsic reaction rate is to use an m-th order rate equation:

$$r''' = k_m C^m \tag{4}$$

where k_m is the kinetic coefficient in (mol/cm^3)$^{1-m}$ sec^{-1}, and m is the intrinsic reaction order. Another way is to use a Langmuir rate equation

$$r''' = \frac{k_1 C}{1+KC} = \frac{k_0 KC}{1+KC} \tag{5}$$

where k_1 and K are two kinetic parameters (the physical meanings of these two parameters depend on the mechanism leading to this rate equation), and k_0 is the ratio of k_1 to K. Note that the product of K and C is dimensionless.

The exact analytical solutions for the radial oxygen concentration profile and the effectiveness factor have been well established when the intrinsic reaction rate is first order.[1-3] Assuming that D_e is constant throughout the particle, the exact analytical solution for the effectiveness factor for a first order reaction is

$$\eta = \frac{1}{M_T}\left(\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right) \tag{6}$$

$$M_T = \frac{r_s}{3}\sqrt{\frac{k}{D_e}} \tag{7}$$

where r_s is the radius of the particle, k is the kinetic coefficient in 1/sec, and M_T is the Thiele modulus. Eq. 6 is referred to in this paper as the first order curve.

Bischoff[4] developed (in Cartesian coordinates) a general modulus for an arbitrary reaction rate form:

$$M_T = \frac{Lr'''(C)}{\sqrt{2}}\left[\int_0^{C_s} D(t)r'''(t)dt\right]^{-\frac{1}{2}} \tag{8}$$

where L is the characteristic length of the particle (defined as the volume of the particle/external surface of the particle), t is a dummy integration variable, r''' is the intrinsic reaction rate per particle volume in any form, and D is the effective diffusivity, which can be a function of oxygen concentration, but is assumed to be constant in this study for simplicity. The use of this general modulus in Cartesian coordinates brought all of the curves for various m-th order rate equations and the Langmuir rate equation with different values of K into a relatively narrow band (see Figure 1). In particular, the general modulus for m-th order rate equations was derived from Eq. 8:

$$M_T = L\sqrt{\frac{(m+1)}{2}\frac{k_m C_s^{\,m-1}}{D_e}} \tag{9}$$

For the Langmuir rate equation in Eq. 5, a general modulus can be derived from Eq. 8:

$$M_T = L\sqrt{\frac{k_1}{2D_e}}\frac{KC_s}{1+KC_s}\left[KC_s - \ln(1+KC_s)\right]^{-\frac{1}{2}} \tag{10}$$

If accuracy is not a major concern, all of the η vs. M_T curves in the narrow band can be approximated by the first order curve, as shown in Figure 1. The method of approximating the η vs. M_T curve of a non-first order reaction by the first order curve is referred to in this paper as the first order approximation. The first order approximation method becomes more and more accurate as M_T approaches zero and infinity. However, in the intermediate range of M_T ($0.2 < M_T < 5$), the first order approximation method leads to up to -34% error in Cartesian coordinates, as shown in Figure 1. Note that in Cartesian coordinates the first order curve is

$$\eta = \frac{\tanh(M_T)}{M_T} \tag{11}$$

while in spherical coordinates the first order curve is Eq. 6.

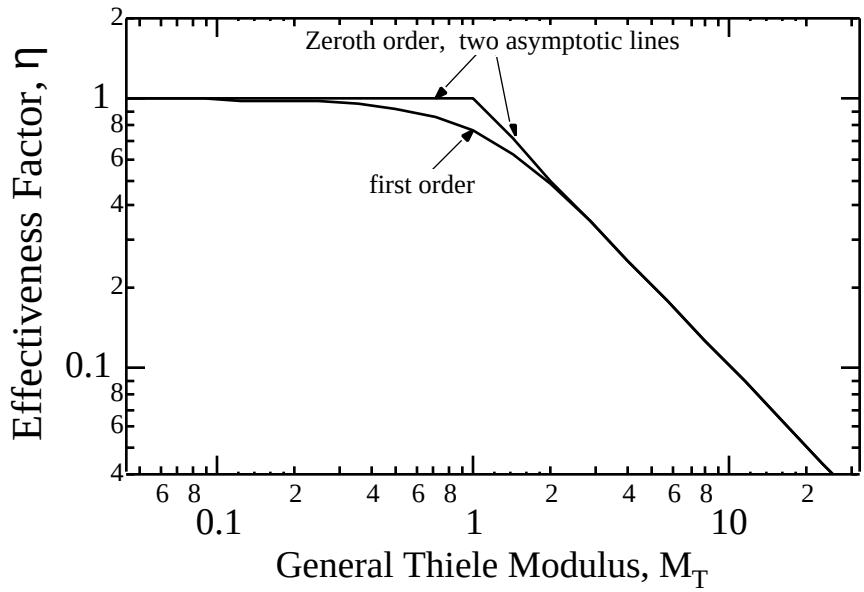

Figure 1. The effectiveness factor curves for first order and zeroth order reactions in Cartesian Coordinates. For reactions between zeroth order and first order extremes ($0 < m < 1$ or $0 < KC_s < \infty$), the curves lie in the narrow band bounded by the first order and the zeroth order curves.

RESULTS AND DISCUSSION

The Effective Reaction Order for An Arbitrary Reaction Rate Form

From the intrinsic m-th order rate equation (Eq. 4), it is easy to get

$$\ln(r''') = \ln(k_m C^m) = \ln(k_m) + m\ln(C) \tag{12}$$

From the above equation, it can be seen that if we plot ln(r''') vs. ln(C), we get a straight line, and the slope of this line is the reaction order m. Eq. 11 can be re-written as:

$$m = \frac{d\ln[r''_{in}(C)]}{d\ln(C)} \tag{13}$$

For a reaction described by a Langmuir-Hinshelwood rate equation, there is no reaction order in an explicit sense. However, the right-hand side of Eq. 12 can be used as the definition of an **effective reaction order m_{eff}** for an arbitrary reaction rate form.

$$m_{eff} = \frac{d\ln[r''_{in}(C)]}{d\ln(C)} \tag{14}$$

We now apply this definition to the Langmuir rate equation. Substitution of the Langmuir rate equation into Eq. 14 gives

$$m_{eff} = \frac{d\ln(\frac{k_1 C}{1+KC})}{d\ln(C)} = \frac{1}{1+KC}. \tag{15}$$

Note that for a Langmuir type reaction the ln(r''') vs. ln(C) curve is not a straight line. The slope of the curve (which is m_{eff}) is dependent on the local oxygen concentration. At the surface oxygen concentration C_s, the effective reaction order is

$$m_{eff,s} = \frac{1}{1 + KC_s} \qquad \text{for the Langmuir rate equation} \qquad (16.L)$$

Note that for an m-th order rate euqation, the effective reaction order is always equal to m. Therefore,

$$m_{eff,s} = m \qquad \text{for an m-th order rate equation} \qquad (16.m)$$

Evaluation of the First Order Approximation in Spherical Coordinates

Since catalytic pellets and porous solid fuel particles can be approximated more or less by spheres, rather than by semi-infinite flat-slabs, it is of more interest to study the performance of the first order approximation method in spherical coordinates. The values of the effectiveness factor predicted by the first order curve (Eq. 6) using the general moduli in Eqs. 9 and 10 were compared to the numerical solutions. It was found that in spherical coordinates, the first order approximation method predicted the effectiveness factor more accurately than in Cartesian coordinates, with errors ranging from -17% to 0% (see Table 1). In other words, all of the curves for various values of $m_{eff,s}$ were brought into a narrower band in spherical coordinates than the band in Cartesian coordinates (see Figures 1 and 2). From Table 1, it can be seen that: 1) as the value of M_T gets away from 0.707 in both directions, the error diminishes rapidly to zero; 2) as $m_{eff,s}$ decreases from unity to zero, the error increases from zero to -17%.

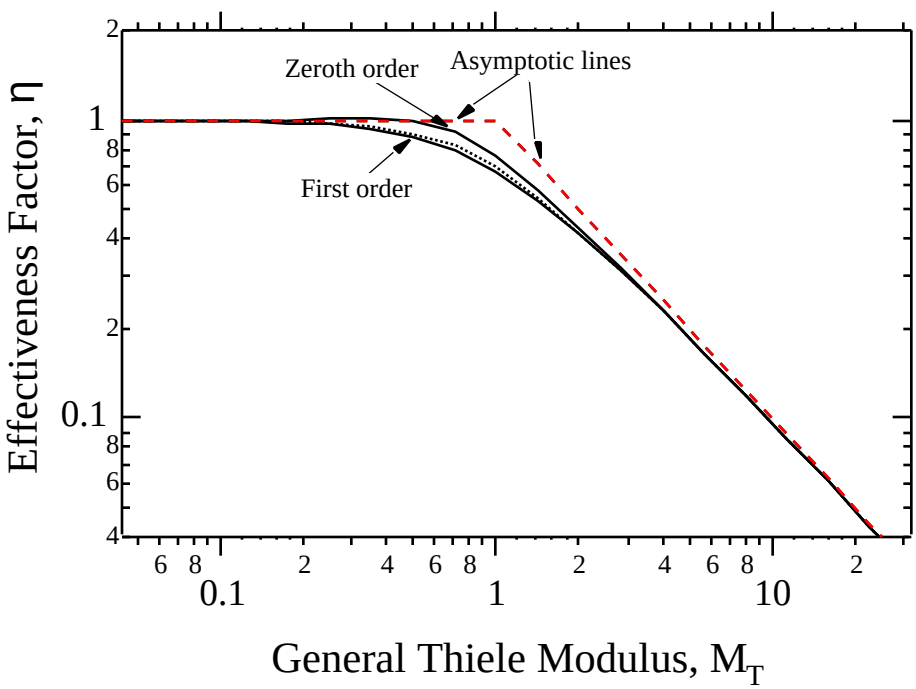

Figure 2. Effectiveness factor curves for first order and zeroth order reactions in spherical coordinates. For reactions described by the Langmuir and m-th order rate equations, the curves lie in the narrow band bounded by the first order and zeroth order curves. The dotted line in the band corresponds to m = 0.5 and corresponds approximately to $KC_s = 1$ ($m_{eff,s}$= 0.5 for both m-th order and Langmuir rate equations).

Table 1. The Errors (%) of the First Order Approximation Method Using the Modulus in Eq. 10

M_T \ $m_{eff,s}$	1.00	0.75	0.50	0.25	0.00
0.125	-0.019	-0.162	-0.342	-0.583	-0.925
0.25	-0.016	-0.588	-1.282	-2.188	-3.560
0.5	-0.013	-1.639	-3.672	-6.557	-12.375
0.707	-0.076	-2.162	-4.802	-8.618	-16.081
1	-0.215	-2.274	-4.756	-8.000	-12.392
2	-0.491	-1.584	-2.813	-4.277	-6.018
4	-0.679	-1.191	-1.774	-2.472	-3.156
8	-0.933	-1.186	-1.473	-1.821	-2.274

Note: The errors of the first order approximation method using the general Thiele modulus in Eq. 9 are almost identical to the values in this table.

Correction Function

It has been shown that in the intermediate range of M_T ($0.2 < M_T < 5$), the first order approximation method leads to up to -17% error. It is desirable to reduce the error using a multiplier with the first order curve (Eq. 6). Two correction functions were constructed to counter the errors associated with the first order approximation methods for m-th order rate equations and the Langmuir rate equation, respectively. By using the effective reaction order evaluated at the external surface oxygen concentration, these two correction functions can be unified into

$$f(M_T, m_{eff,s}) = \left(1 + \frac{\sqrt{1/2}}{\frac{1}{2M^2} + 2M^2}\right)^{\frac{1}{2}(1-m_{eff,s})^2} \tag{17}$$

where $m_{eff,s}$ = m for m-th order rate equations, and

$m_{eff,s} = 1/(1+KC_s)$ for Langmuir rate equations.

The correction function is used as a multiplier before the right-hand-side of Eq. 6:

$$\eta = f\frac{1}{M_T}\left(\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right) \tag{18}$$

Note that this correction function is designed only for correcting the first order approximation in spherical coordinates, but not in Cartesian coordinates.

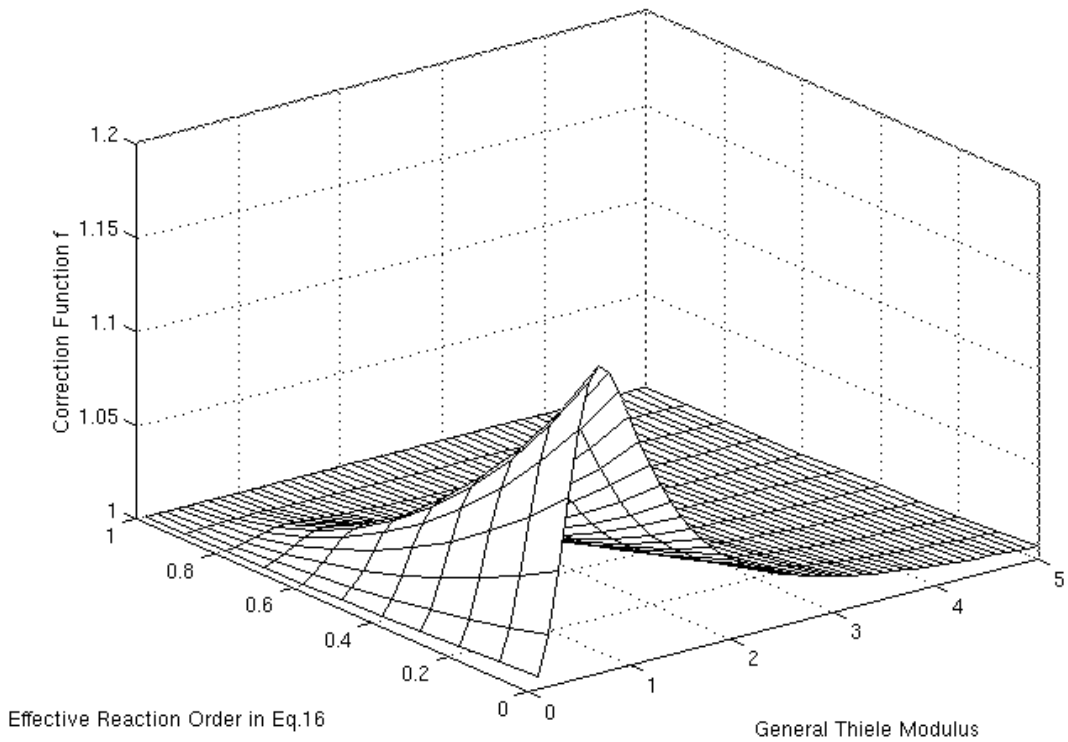

Figure 3. The correction function f vs. Thiele modulus M_T and the effective reaction order at external surface $m_{eff,s}$.

Accuracy of the corrected first order approximation

Compared to numerical solutions, the corrected first order approximation predicts the effectiveness factor within 3.0% errors (see Table 2). After the effectiveness factor is obtained, the overall reaction rate in a spherical particle can be easily calculated using

$$r'''_{obs} = \eta k_m C_s^{\,m} \tag{19}$$

for a m-th order type reaction, and

$$r'''_{obs} = \eta \frac{k_1 C_s}{1 + K C_s} \tag{20}$$

for a reaction described by the Langmuir rate equation.

CONCLUSIONS

Two correction functions were constructed to improve the accuracy of predicting the effectiveness factor for the Langmuir and m-th order rate equations, respectively. By using the

intrinsic effective reaction order evaluated at surface concentration, these two correction functions were unified (see Eq. 17).

The first order curve combined with the correction function developed in this study was able to predict the effectiveness factor for m-th order rate equations and the Langmuir rate equation within 3% in the whole range of M_T (including Zone I, Zone II and especially the transition zone). This "corrected first order approximation method" uses explicit analytical expressions to predict the effectiveness factor, and therefore is particularly suitable for repeated use in comprehensive computer codes.

Table 2. The Errors of the Corrected First Order Approximation Method Using the Proposed Modulus in Eq. 10

M_T \ $m_{eff,s}$	1.00	0.75	0.50	0.25	0.00
0.125	-0.019	-0.030	0.163	0.485	1.133
0.25	-0.016	-0.158	0.375	1.354	0.001
0.5	-0.013	-0.729	-0.113	1.208	1.394
0.707	-0.076	-1.161	-0.849	0.128	-1.246
1	-0.215	-1.387	-1.197	0.076	1.374
2	-0.491	-1.178	-1.136	-0.324	0.545
4	-0.679	-1.068	-1.256	-1.243	-1.144
8	-0.933	-1.153	-1.337	-1.494	-1.743

Note: The errors of the corrected first order approximation method using the general Thiele modulus in Eq. 9 are almost identical to the values in this table.

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