A Simple Formula for Estimation of the Effectiveness Factor in Porous Catalysts

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Introduction

In heterogeneous catalysis, the ratio of the observed reaction rate to the intrinsic reaction rate in the absence of intraparticle mass and heat transfer resistances is the effectiveness factor. The effectiveness factor is formally obtained from the solution of the governing equation[1]:

$$\frac{d^2y}{dx^2} + \frac{s}{x}\frac{dy}{dx} - \phi^2 f(y) = 0$$

$$dy(0)/dx = 0, \quad y(1) = 1 \tag{1}$$

Here, s is the shape factor of the catalyst ($s = 0$ for an infinite slab, $s = 1$ for an infinite cylinder, and $s = 2$ for a sphere); x is the dimensionless position variable inside the catalyst in the range of 0 (center) and 1 (external surface); y is the dimensionless reactant concentration normalized with respect to the concentration at the external surface of the catalyst; $f(y)$ is the dimensionless reaction rate, also normalized with respect to the rate at the condition of the catalyst external surface, and, thus, $f(1) = 1$; and ϕ is the Thiele modulus. With the solution of Eq. 1, $y(x)$, the effectiveness factor can be defined by:

$$\eta = \frac{s+1}{\phi^2}\frac{dy(1)}{dx} \tag{2}$$

In general, $f(y)$ is nonlinear, and the analytic solution of Eq. 1 is not available. The numerical solution, however, can be readily obtained with recently proposed methods.[2,3] If the effectiveness factor is evaluated for a relatively small number of times, numerical methods are preferred since they are most accurate in the results. On the other hand, if the factor has to be computed a very large number of times and the desired accuracy is not very high, the computation can be time-consuming. This is the case in simulation of a packed-bed reactor, where the effectiveness factor has to be calculated at every point in the reactor since the reaction conditions such as temperature and concentrations change continuously along the reactor. In this case, it is useful to have an approximation formula that allows a rapid calculation of the effectiveness factor.

For an approximation of the effectiveness factor to be valid for all ϕ, it must, at least, converge to the proper asymptote of the effectiveness factor at either small or large ϕ values. The well-known asymptote at small ϕ is[1,4,5]:

$$\eta_S = 1 + a_1\phi^2,$$

$$a_1 = -\frac{f'(1)}{(s+1)(s+3)} \tag{3}$$

and the asymptote at large ϕ is[4]:

$$\eta_L = \frac{b_1}{\phi} + \frac{b_2}{\phi^2},$$

$$b_1 = (s+1)\sqrt{2\int_0^1 f(\tilde{y})d\tilde{y}}$$

$$b_2 = -\frac{s(s+1)^2}{b_1}\int_0^1 \sqrt{2\int_0^y f(\tilde{y})d\tilde{y}}\,dy \tag{4}$$

Previous approximations of the effectiveness factor reported in the literature are well documented in a recent article.[6] Two

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typical closed-form approximations are discussed in the next section.

Previous Equations

Gottifredi and Gonzo[5] proposed the following approximation:

$$\eta_{GG} = \frac{1}{\sqrt{c_1\phi^2 + \exp(-g\phi^2)}}$$

$$c_1 = 1/b_1^2$$

$$g = 2a_1 + c_1 \tag{5}$$

The formula conforms with the asymptotes, Eqs. 3 and 4, only when $g > 0$. At small ϕ, $\eta_{GG} \approx (1/\sqrt{c_1\phi^2 + 1 - g\phi^2}) \approx 1 - (1/2)(c_1 - g)\phi^2 = 1 + a_1\phi^2$, and at large ϕ, $\eta_{GG} \approx (1/\sqrt{c_1\phi^2}) = (b_1/\phi)$ if $g > 0$. If $g < 0$, however, $exp(-g\phi^2)$ dominates in Eq. 5 as $\phi \to \infty$, and the formula cannot follow the asymptote, Eq. 4. This case can occur for high-order reaction rate function,[6] and modification to avoid this is needed.

Wedel and Luss[4] proposed the following formula for the case of $s = 2$, a spherical catalyst:

$$\eta_{WL} = \frac{1 + \zeta\phi + \dfrac{b_1\zeta - b_1^2 a_1}{b_2 + b_1^2}\phi^2}{1 + \zeta\phi + \dfrac{b_1\zeta - 2b_1^2 a_1 - b_2 a_1}{b_2 + b_1^2}\phi^2 + \dfrac{\zeta - b_1 a_1}{b_2 + b_1^2}\phi^3} \tag{6}$$

where ζ is a tuning parameter. From extensive numerical tests, they recommended:

$$\zeta = \begin{cases} \dfrac{-b_2 - b_2^2/b_1^2 + a_1 b_2^2}{b_2^2/b_1 + 3b_1 b_2 + b_1^3}, & f'(1) \le 1 \\ \dfrac{-(1.2 + 0.2/f'(1))a_1 b_1}{1 + a_1(b_1^2 + b_2)}, & f'(1) > 1 \end{cases} \tag{7}$$

This formula can be shown to follow the corresponding asymptote for either small or large ϕ. For catalyst geometries other than a sphere, such as a slab and a cylinder, Eq. 7 may not be applicable since the tuning parameter ζ has not been defined for such geometries.

Proposed Equation

We propose a simple closed-form formula for approximation of the effectiveness factor:

$$\eta_{LK} = \frac{1}{\sqrt{c_1\phi^2 + \sqrt{c_2\phi^2 + q(\phi^2)}}} \tag{8}$$

where

$$c_1 = 1/b_1^2$$

$$c_2 = 4b_2^2/b_1^6$$

$$c_3 = -(4a_1 + 2c_1 + c_2)$$

$$q(\phi^2) = \begin{cases} \sqrt{1 + 2c_3\phi^2}, & \text{if } c_3 \ge 0 \\ \exp(c_3\phi^2), & \text{otherwise} \end{cases} \tag{9}$$

Equation 8 is one of the simplest forms that comply with the two asymptotes, Eq. 3 for small ϕ and Eq. 4 for large ϕ. It extends η_{GG} of Eq. 5 and removes its limitation. For a small ϕ, η_{LK} can be expanded as:

$$\begin{aligned} \eta_{LK} &= \frac{1}{\sqrt{c_1\phi^2 + \sqrt{c_2\phi^2 + 1 + c_3\phi^2 + \cdots}}} \\ &= \frac{1}{\sqrt{c_1\phi^2 + 1 + \dfrac{1}{2}(c_2 + c_3)\phi^2 + \cdots}} \\ &= 1 - ((2c_1 + c_2 + c_3)/4)\phi^2 + \cdots = 1 + a_1\phi^2 + \cdots \end{aligned} \tag{10}$$

For a large ϕ and $c_3 \ge 0$, Eq. 8 is expanded as:

$$\begin{aligned} \eta_{LK} &= \frac{1}{\phi\sqrt{c_1 + \dfrac{1}{\phi}\sqrt{c_2 + \dfrac{\sqrt{1 + 2c_3\phi^2}}{\phi^2}}}} = \frac{1}{\phi\sqrt{c_1 + \dfrac{\sqrt{c_2}}{\phi} + \cdots}} \\ &= \frac{1}{\sqrt{c_1}}\frac{1}{\phi} - \frac{\sqrt{c_2}}{2c_1\sqrt{c_1}}\frac{1}{\phi^2} + \cdots = \frac{b_1}{\phi} + \frac{b_2}{\phi^2} + \cdots \end{aligned} \tag{11}$$

For a large ϕ and $c_3 < 0$, the expansion becomes:

$$\begin{aligned} \eta_{LK} &= \frac{1}{\phi\sqrt{c_1 + \dfrac{1}{\phi}\sqrt{c_2 + \dfrac{\exp(c_3\phi^2)}{\phi^2}}}} = \frac{1}{\phi\sqrt{c_1 + \dfrac{\sqrt{c_2}}{\phi} + \cdots}} \\ &= \frac{b_1}{\phi} + \frac{b_2}{\phi^2} + \cdots \end{aligned} \tag{12}$$

When $s = 0$, $b_2 = 0$ and $c_2 = 0$. Then Eq. 8 becomes:

$$\eta_{LK} = \frac{1}{\sqrt{c_1\phi^2 + \sqrt{q(\phi^2)}}} \tag{13}$$

When $g > 0$, Eq. 5 and Eq. 13 are identical, and hence Eq. 13 of this study can be regarded as an extension of Eq. 5. With letting $b_2 = 0$, we may use Eq. 13 even for $s \neq 0$. Equation 13 is in general less accurate than Eq. 8, since b_2/ϕ^2 in the asymptote Eq. 4 is not taken into account. Nevertheless, Eq. 13 is a useful first approximation of the effectiveness factor, since it can often yield practically accurate estimates.

Approximation of b_2

For a simpler computation, the term b_2 in Eq. 4 is approximated with utilizing the power series expansion around $y = 1$ as:

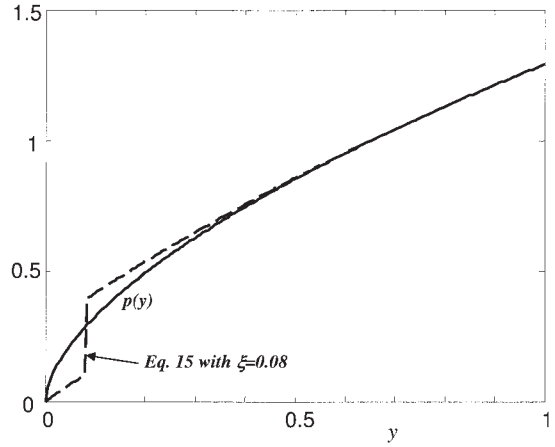

Figure 1. Plot of $p(y)$ and its approximation for $f(y) = y^{0.2}$.

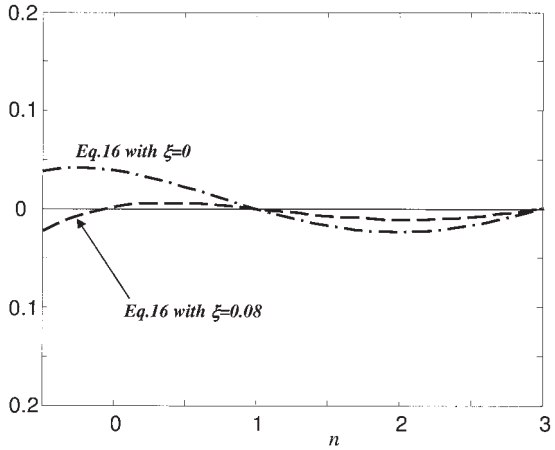

Figure 2. Relative errors of approximations of b_2 for $f(y) = y^n$.

$$p(y) \equiv \sqrt{2\int_0^y f(\tilde{y})d\tilde{y}}$$

$$= p_0 + p_1(y-1) + p_2(y-1)^2 + p_3(y-1)^3 + \cdots$$

$$p_0 = p(1) = \sqrt{2\int_0^1 f(\tilde{y})d\tilde{y}}$$

$$p_1 = \left.\frac{dp(y)}{dy}\right|_{y=1} = \left.\frac{f(y)}{p(y)}\right|_{y=1} = \frac{1}{p_0}$$

$$p_2 = \frac{1}{2}\left.\frac{d^2p(y)}{dy^2}\right|_{y=1} = \left.\frac{f'(y) - p'(y)^2}{2p(y)}\right|_{y=1} = \frac{f'(1) - p_1^2}{2p_0}$$

$$p_3 = \frac{1}{6}\left.\frac{d^3p(y)}{dy^3}\right|_{y=1} = \left.\frac{f''(y) - 3p'(y)p''(y)}{6p(y)}\right|_{y=1}$$

$$= \frac{f''(1) - 6p_1p_2}{6p_0} \quad (14)$$

We truncate the series and modify it to satisfy $p(0) = 0$ as, for a ξ near 0:

$$p(y) \approx \begin{cases} p_0 + p_1(y-1) + p_2(y-1)^2 + p_3(y-1)^3, & \text{if } y > \xi \\ p_1 y + p_2((y-1)^2 - 1) + p_3((y-1)^3 + 1), & \text{otherwise} \end{cases} \quad (15)$$

Then we have $\int_0^1 p(\tilde{y})d\tilde{y} \approx p_0(1-\xi) - p_1((1-2\xi)/2) + p_2((1-3\xi)/3) - p_3((1-4\xi)/4)$ and an approximation for b_2:

$$b_2 = -\frac{s(s+1)^2}{b_1}\left((1-\xi)p_0 - \frac{1-2\xi}{2}p_1 + \frac{1-3\xi}{3}p_2 - \frac{1-4\xi}{4}p_3\right) \quad (16)$$

Numerical tests showed that $\xi = 0.08$ worked fine for most rate expressions. Figure 1 shows the approximation for $p(y)$ when $f(y) = y^{0.2}$ and $\xi = 0.08$. The term b_2 by Eq. 16 is easier to evaluate than b_2 by Eq. 4 and highly accurate, as demonstrated in Figure 2 for $f(y) = y^n$. The error of approximation of b_2 by Eq. 16 was less than 2% for all tested rate expressions.

Examples

The proposed Eqs. 8 and 13 (η_{LK}) were applied to power-law kinetics, nonisothermal first-order kinetics, and Langmuir Hinselwood kinetics, and compared with Eq. 5 (η_{GG})[5] and Eq. 6 (η_{WL}).[4] Equation 16 was used for b_2 in Eq. 8.

Figure 3 shows effectiveness factor plots for power-law kinetics, $f(y) = y^n$ and $s = 2$. Except for a region where effectiveness factors are greater than 1, η_{LK} and η_{WL} approximate the exact values excellently. It is noted that η_{GG} does not follow the asymptote at large ϕ for $n = 1.2$ and η_{WL} is not applicable when $s \neq 2$. When $f(y) = y^{-0.3}$, the exact effectiveness factor shows multiple steady states around $\phi = 2$. The

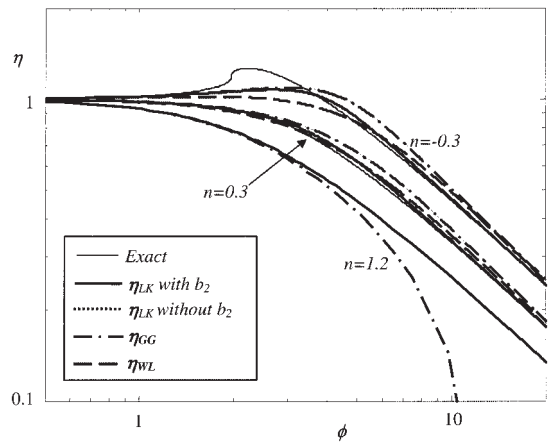

Figure 3. Effectiveness factor plots for $f(y) = y^n$ and $s = 2$.

For $n = -0.3$ and 0.3, η_{LK} *without* b_2 and η_{GG} are identical; and, for $n = 1.2$, η_{WL} and η_{LK} with and without b_2 are not distinguishable to the exact η.

Table 1. Proposed Approximation of Effectiveness Factor

$$\eta_{LK} = \frac{1}{\sqrt{c_1\phi^2 + \sqrt{c_2\phi^2 + q(\phi^2)}}}$$

$$a_1 = -\frac{}{f'(1)\sqrt{(s+1)(s+3)}}$$

$$b_1 = (s+1)\sqrt{2\int_0^1 f(\tilde{y})d\tilde{y}}$$

$$b_2 = -\frac{s(s+1)^2}{b_1}\left((1-\xi)p_0 - \frac{1-2\xi}{2}p_1 + \frac{1-3\xi}{3}p_2 - \frac{1-4\xi}{4}p_3\right),$$

$$\xi = 0.08$$

$$p_0 = \sqrt{2\int_0^1 f(\tilde{y})d\tilde{y}}, \quad p_1 = \frac{1}{p_0}, \quad p_2 = \frac{f'(1) - p_1^2}{2p_0}, \quad p_3 = \frac{f''(1) - 6p_1p_2}{6p_0}$$

$$c_1 = 1/b_1^2$$

$$c_2 = 4b_2^2/b_1^6$$

$$c_3 = -(4a_1 + 2c_1 + c_2)$$

$$q(\phi^2) = \begin{cases} \sqrt{1 + 2c_3\phi^2}, & \text{if } c_3 \geq 0 \\ \exp(c_3\phi^2), & \text{otherwise} \end{cases}$$

single-valued approximations are unable to estimate the multiple effectiveness factors, and their approximation errors are large.

Figure 4 shows the maximum of absolute relative errors of estimated effectiveness factors throughout ϕ, $E_R = \max_{\phi\in(0,\infty)}|(\eta_{estimated} - \eta_{exact})/\eta_{exact}|$, for $f(y) = y^n$. Figures 5 and 6 show the maximum of absolute relative errors of estimated effectiveness factors for $f(y) = (1 + K)^2y/(1 + Ky)^2$ and $f(y) = \{\exp[20b(1 - y)/(1 + b(1 - y))]\}y$, respectively. It is seen that E_R of the proposed approximation is comparable to or smaller than the previous closed-form approximations.

Equation 5 (η_{GG}), whose performances can be found in Gottifredi and Gonzo[5] and Lee and Kim,[6] is identical to the proposed equation when $s = 0$ and $g > 0$. However, when $g < 0$, it fails to follow the asymptote for large ϕ, as shown in Figures 4-6. Equation 6 (η_{WL}) by Wedel and Luss[4] needs a new equation for ζ when $s \neq 2$.

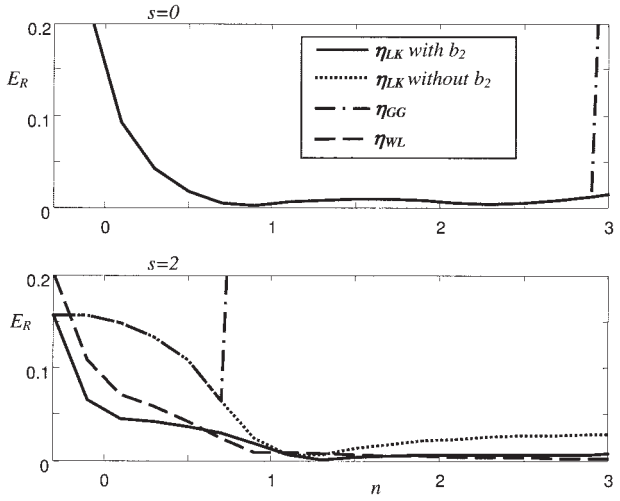

Figure 4. Maximum absolute relative errors for $f(y) = y^n$.

For $s = 0$, η_{WL} is not available, and η_{LK} with and without b_2 are identical.

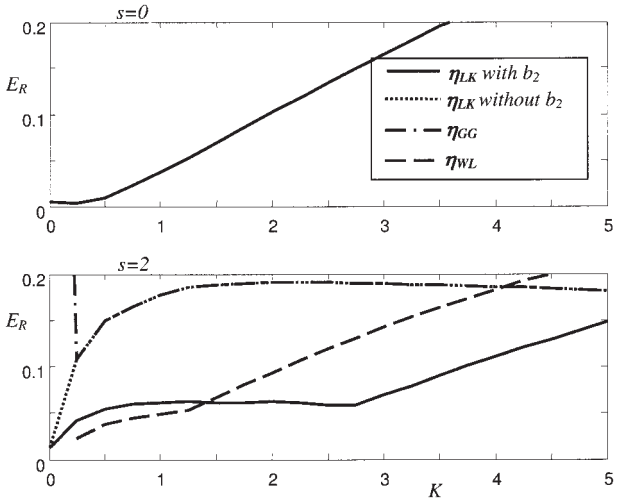

Figure 5. Maximum absolute relative errors for $f(y) = (1 + K)^2y/(1 + Ky)^2$.

For $s = 0$, η_{WL} is not available, and η_{GG} and η_{LK} with and without b_2 are identical.

The proposed Eq. 8 was applied to a realistic example of isothermal methanol steam reforming reactor where the methanol steam reforming reaction occurred over a commercial catalyst. Detailed descriptions of this reactor are in Lee and Kim.[6] The proposed Eq. 8, much simpler than the approximation method of Lee and Kim, provided very accurate results (less than 0.5% relative errors in effectiveness factors and conversions) with much faster computation times than those with the exact numerical methods.[2,3]

In summary, the proposed approximation given in Table 1 is very simple to use and yet provides useful estimates of the effectiveness factor for most reaction rate expressions and catalyst shapes.

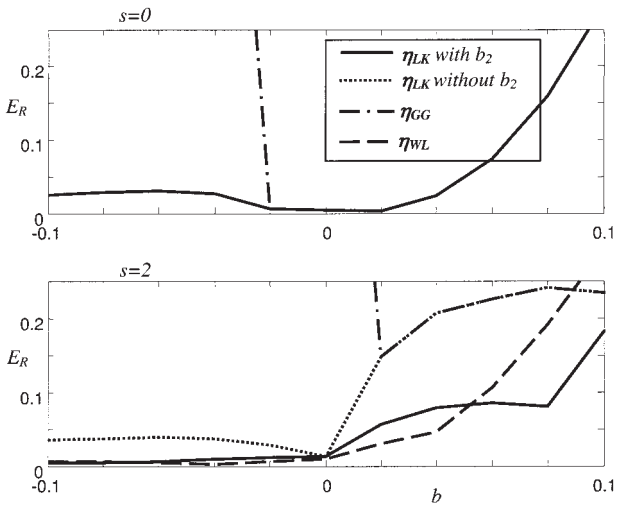

Figure 6. Maximum absolute relative errors for $f(y) = (\exp\frac{20b(1 - y)}{1 + b(1 - y)})y$

For $s = 0$, η_{WL} is not available, and η_{LK} with and without b_2 are identical.

Notation

a_1 = coefficient in the asymptote for small Thiele modulus
b = parameter for nonisothermal first-order kinetics
b_1, b_2 = coefficients in the asymptote for large Thiele modulus
c_1, c_2, c_3 = parameters for Eq. 5
E_R = maximum of absolute relative errors of estimated effectiveness factor throughout ϕ
$f(y)$ = normalized dimensionless reaction rate ($f(1) = 1$)
g = parameter for Eq. 5
K = parameter for Langmuir Hinselwood kinetics
n = order for power-law kinetics
$p(y)$ = function of y defined in Eq. 14
p_0, p_1, p_2, p_3 = coefficients for $p(y)$
$q(\phi^2)$ = function of ϕ^2 for Eq. 5
s = shape factor
x = dimensionless position variable inside the catalyst
y = normalized dimensionless reactant concentration

Subscripts

estimated = value estimated with an approximate analytic formula
exact = exact value calculated by a numerical method
GG = Gottifredi and Gonzo[5]
L = large
LK = Lee and Kim
S = small
WL = Wedel and Luss[4]

Greek letters

ϕ = Thiele modulus
η = effectiveness factor
ξ = parameter for Eqs. 15 and 16
ζ = parameter for Eq. 6

Literature Cited

1. Aris R. *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts. Vol. I: The Theory of the Steady State*. Clarendon: Oxford; 1975.
2. Kim DH, Lee J. A robust iterative method of computing effectiveness factors in porous catalysts. *Chem Eng Sci.* 2004;59:2253-2263.
3. Lee J, Kim DH. An improved shooting method for computation of effectiveness factors in porous catalysts. *Chem Eng Sci.* 2005;60:5569-5573.
4. Wedel S, Luss D. A rational approximation of the effectiveness factor. *Chem Eng Comm.* 1980;7:245-259.
5. Gottifredi JC, Gonzo EE. Approximate expression for the effectiveness factor estimation and a simple numerical method for concentration profile calculation in porous catalyst. *Chem Eng J.* 2005;109:83-87.
6. Lee J, Kim DH. An approximation method of the effectiveness factor in porous catalysts. *Chem Eng Sci.* 2006;61:5127-5136.

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