A Generalized Expression for the Effectiveness Factor of Porous Catalyst Pellets

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The effectiveness factor, defined as the rate of reaction divided by the rate which would occur with no resistance to component transfer inside or outside the pellet, is an important parameter in the design of reactors using catalysts in the form of porous pellets. For this reason, but perhaps even more because of the mathematical tractability of the problem, a multitude of papers have been written on the subject. For example, Aris (1975), in a compendium of the mathematical nuances, noted that over 100 additional references appeared during the interim while the book was in press.

The objective of this paper is to summarize the most important practical aspects of the dependence of the effectiveness factor on the pertinent variables with a single, simple, empirical equation. Attention is confined to isothermal conditions and to irreversible reactions whose rates can be expressed as a power of the concentration of one component. The pellet is assumed to be pseudo homogeneous.

The isothermal restriction is not too serious, since the effective thermal conductivity of catalyst pellets is ordinarily very much higher than the effective diffusivities for component transfer, thereby minimizing temperature gradients. The restriction on the reaction rate is also not too serious from a practical point of view, since most reactions can be approximated satisfactorily by a simple power dependence, even when adsorption is taken into account. Reference to Aris (1975) is suggested for rigorous treatment of these and other complexities, including nonuniformities in the catalyst pellets and multiple reactions.

The effectiveness factors for no external resistance and a first-order, equimolar reaction in slabs of half thickness δ and in spheres and long cylinders of radius a are given in Table 1 in terms of the Thiele modulus $\tau_1 = l\sqrt{k'S/D_f'}$, where l is the above dimension. The limiting asymptotes for small and large τ and the volume-to-external-surface ratios are included in the table. Aris (1957) was apparently the first to note that the three asymptotes for large τ are identical when expressed in terms of $\tau_1^* = (V_p/lA_p)\tau_1 = (V_p/A_p)\sqrt{k'S/D_f'}$. Rester, Jouven, and Aris (1969) showed that the general expressions for the three geometries differ less than 16% from one another over the entire range when compared in terms of τ_1^*. Rester and Aris (1969) demonstrated that this generality holds for other shapes, such as hollow cylinders, finite cylinders, and parallelepipeds.

External resistance to component transfer by convection in terms of a Biot number $Bi = lk_c/D_f'$ can be combined with the expressions for internal diffusion and reaction to obtain the functional dependences indicated in Table 2. It is apparent that these three expressions will also have identical asymptotes for small and large τ_1 and will differ only slightly for intermediate values, if reexpressed in terms of τ_1^*, as before, and $Bi^* = (V_p/lA_p)Bi = V_pk_c/A_pD_f'$.

These generalized asymptotes for small and large τ_1^* can be rearranged as

$$\frac{1}{\eta_o} - \frac{(\tau_1^*)^2}{Bi^*} = 1 \tag{1}$$

and

$$\frac{1}{\eta_\infty} - \frac{(\tau_1^*)^2}{Bi^*} = \tau_1^* \tag{2}$$

An empirical equation for the intermediate behavior in all geometries then can be written as follows, in the form proposed by Churchill and Usagi (1972):

$$\left(\frac{1}{\eta} - \frac{(\tau_1^*)^2}{Bi^*}\right)^p = 1 + (\tau_1^*)^p \tag{3}$$

Equation (3) with a value of 2.0 for the arbitrary exponent p represents the three general expressions in Table 2, with a maximum error of about 7.5%.

Analytical relationships are not generally possible for other reaction orders, but numerical integrations for the effectiveness factor have been carried out for a series of values of n exceeding all practical interest in their range. Petersen (1965) apparently first noted that the same asymptote for large τ holds for an n^{th}-order reaction in a slab in terms of a generalized Thiele modulus $\tau_n = \delta[(n+1)k'SC_s^{n-1}/2D_f']^{1/2}$. He also noted that values of η for intermediate values of τ_n do not differ greatly for $n \geqq 1$. This result for a slab is readily generalized to other geometries. A simple generalization cannot, however, be developed for the case of external resistance because the linearity in concentration which lead to the additive expressions in Table 2 no longer exists. However,

TABLE 1. EFFECTIVENESS FACTORS FOR FIRST-ORDER REACTION AND NO EXTERNAL RESISTANCE

	Slab	Infinite cylinder	Sphere
τ_1	$\delta(k'S/D_f')^{1/2}$	$a(k'S/D_f')^{1/2}$	$a(k'S/D_f')^{1/2}$
η	$\tanh\{\tau_1\}/\tau_1$	$2I_1\{\tau_1\}/I_o\{\tau_1\}$	$3(\tau_1\coth\{\tau_1\} - 1)/\tau_1^2$
η_o	1	1	1
η_∞	$1/\tau_1$	$2/\tau_1$	$3/\tau_1$
V_p/A_p	δ	$a/2$	$a/3$
τ_1^*	τ_1	$\tau_1/2$	$\tau_1/3$
η	$\tanh\{\tau_1^*\}/\tau_1^*$	$2I_1\{2\tau_1^*\}/I_o\{2\tau_1^*\}$	$(3\tau_1^*\coth\{3\tau_1^*\} - 1)/3(\tau_1^*)^2$
η_∞	$1/\tau_1^*$	$1/\tau_1^*$	$1/\tau_1^*$

TABLE 2. EFFECTIVENESS FACTORS FOR FIRST-ORDER REACTION AND EXTERNAL RESISTANCE

	Slab	Infinite cylinder	Sphere
Bi	$\delta k_c/D_f'$	ak_c/D_f'	ak_c/D_f'
$\frac{1}{\eta}$	$\frac{\tau_1^2}{Bi}+\frac{\tau_1}{\tanh\{\tau_1\}}$	$\frac{\tau_1^2}{2Bi}+\frac{I_o\{\tau_1\}}{2I_1\{\tau_1\}}$	$\frac{\tau_1^2}{3Bi}+\frac{\tau_1^2/3}{\tau_1\coth\{\tau_1\}-1}$

in this case, for large τ

$$r=\frac{k_c(C_b-C_s)}{\delta}=\frac{k'SC_s^n}{\delta[(n+1)k'SC_s^{n-1}/2D_f']^{1/2}}$$

$$\equiv k'SC_b^n\eta_\infty \quad (4)$$

By rearrangement

$$\frac{1}{\eta_\infty}-\frac{k'C_b^{n-1}S\delta}{k_c}=\delta\left(\frac{(n+1)k'C_b^{n-1}S}{2D_f'}\right)^{1/2}\left(\frac{C_b}{C_s}\right)_\infty^{\frac{n-1}{2}} \quad (5)$$

with $(C_s/C_b)_\infty$ determined from the auxiliary equation

$$\left(\frac{C_s}{C_b}\right)_\infty^{\frac{n+1}{2}}\left(\frac{2k'C_b^{n-1}SD_f'}{(n+1)k_c^2}\right)^{1/2}+\left(\frac{C_s}{C_s}\right)_\infty-1=0 \quad (6)$$

Similarly, for small τ

$$r=\frac{k(C_b-C_s)}{\delta}=k'SC_s^n\equiv k'SC_b^n\eta_o \quad (7)$$

and

$$\frac{1}{\eta_o}-\frac{k'C_b^{n-1}S\delta}{k_c}=\left(\frac{C_b}{C_s}\right)_o^{n-1} \quad (8)$$

with $(C_s/C_b)_o$ determined from the auxiliary equation

$$\left(\frac{C_s}{C_b}\right)_o^n\left(\frac{k'S\delta C_b^{n-1}}{k_c}\right)+\left(\frac{C_s}{C_b}\right)-1=0 \quad (9)$$

For nonequimolar reactions which produce $1+\alpha$ moles of product/mole of reactant, the effective diffusivity becomes $D_f'/(1+\alpha x)$, which has the effect of multiplying D_f' in the Thiele modulus for an n^{th}-order reaction by the factor

$$\gamma=\frac{(-1)^n(n+1)}{\omega^{n+1}}\left[\ln(1+\omega)-\omega+\frac{\omega^2}{n}-\ldots\frac{(-1)^n\omega^n}{n}\right] \quad (10)$$

where $\omega=\alpha x_s$. This factor is less than unity, resulting in a decreased rate of reaction for $\omega>0$, and is greater than unity, resulting in an increased rate of reaction, for $\omega<0$.

Substituting the modified values of Bi and τ indicated by Equations (5) and (8) in Equation (3) and then incorporating γ, we get

$$\frac{1}{\eta}-\frac{k'C_b^{n-1}SV_p}{k_cA_p}=\left[\left(\frac{C_b}{C_s}\right)_o^{2n-2}+\frac{(n+1)k'C_b^{n-1}SV_p^2}{2\gamma D_f'A_p^2}\left(\frac{C_b}{C_s}\right)_\infty^{n-1}\right]^{1/2} \quad (11)$$

Equation (11) is proposed for estimation of the isothermal effectiveness factor for irreversible, power law reactions in all geometries. For $n\neq 1$, $(C_s/C_b)_\infty$ and $(C_s/C_b)_o$ must be calculated from Equations (6) and (9), and for $\omega\neq 0$, γ must be calculated from Equation (10). Equation (11) gives a slightly low value for η for intermediate values of τ_n^* with $0<n<1$ and is invalid for $n<0$. However, the error for catalyst pellets of simple shape and for orders of reaction greater than unity is undoubtedly less than the uncertainty ordinarily associated with the indicated, individual variables.

Equation (11) is also applicable for a reversible first-order reaction if k' is taken as the sum of the forward and reverse rate constants. It is adaptable under some circumstances for reactions that follow Langmuir-Hinshelwood kinetics. Reference to Aris (1975) is suggested for a discussion of the necessary modifications in τ and for exceptions.

NOTATION

A_p = external area of catalyst pellet, L^2
a = radius of cylinder and sphere, L
Bi = lk_c/D_f' = Biot number for component transfer
Bi^* = V_pk_c/A_pD_f' = modified Biot number for component transfer
C = concentration of reacting component, M/L^3
C_b = concentration of reacting component in bulk of fluid, M/L^3
C_s = concentration of reacting component in fluid at surface of pellet, M/L^3
D_f' = effective diffusivity of reacting component inside pellet, L^2/θ
I_o = modified Bessel function of zero order
I_1 = modified Bessel function of first order
k' = reaction rate constant for catalytic surface, $L^n/M^{n-1}\,\theta$
k_c = component transfer coefficient from bulk fluid to pellet surface, L/θ
l = characteristic dimension (half thickness or radius), L
n = order of reaction
p = arbitrary exponent in Equation (3)
r = rate of reaction, $M/L^3\,\theta$
S = specific surface of pellet, L^{-1}
V_p = volume of pellet, L^3
x = mole fraction of reacting component
x_s = mole fraction of reacting component at surface of pellet

Greek Letters

α = fractional increase in number of moles
γ = correction factor for nonequimolar reaction
δ = half thickness of slab, L
η = effectiveness factor

η_o = asymptotic effectiveness factor for $\tau \to 0$
η_∞ = asymptotic effectiveness factor for $\tau \to \infty$
τ_1 = $l(k'S/D_f')^{1/2}$ = Thiele modulus for first-order reaction
τ_1^* = $V_p(k'S/D_f')^{1/2}/A_p$ = modified Thiele modulus for first-order reaction
τ_n = $l[(n+1)C_s^{n-1}k'S/2D_f']^{1/2}$ = Thiele modulus for n^{th}-order reaction
ω = $\alpha\, x_s$

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Rectilinear Equation for Binary Azeotropes

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Since Cailletet and Mathias (1886) developed an empirical linear equation to correlate the saturated liquid and vapor densities at the coexistence phases, the so-called Rectilinear Diameter Equation (RDE) has become a convenient way to determine the density at the critical point. The accuracy of the critical density determined by means of RDE has been seriously questioned owing to the relatively poor precision of the measured saturated densities close to the critical state. It is highly important that a theoretical basis for the RDE be established, for then the critical density can be accurately determined from the saturated densities remote from the critical state.

Recently, Zollweg and Mulholland (1972) developed a theoretical model for correlating the saturated densities of the coexisting phases. They have found that within the experimental accuracy the correlated values from the equation derived from the theoretical model of the decorated lattice gas are similar to those from the empirical RDE. It is not the purpose here to strengthen the theoretical foundation for RDE but rather to enlarge its usefulness. The RDE has been applied to correlating the saturated transport properties [Needham and Ziebland (1965) in their correlation of the saturated liquid and vapor thermal conductivities of ammonia in the coexistence phases; Starling, Eakin, Dolan, and Ellington (1962), the rectilinear behavior for the saturated liquid and vapor viscosities of ethane, propane, and n-butane in the critical region].

Most recently, Hall and Eubank (1976) have further demonstrated the use of the RDE in correlating the isochoric slopes from the coexistence curve. These are all limited to the pure components.

Won and Prausnitz (1974) observed that the saturated liquid and vapor densities for some binary mixtures obey analogously the rectilinearity rule such that at constant temperature the arithmetic mean of the molar densities of the saturated vapor and the equilibrium saturated liquid is a linear function of pressure.

This note will show that the rectilinear diameter constant of binary azeotropes can be calculated from the constants of the components, and, furthermore, the saturated vapor densities of the azeotrope can be calculated from the corresponding experimental liquid densities.

The reduced RDE for the i^{th} component can be expressed as (Partington, 1949)

$$\frac{1}{2}\left(\frac{\rho_{li}+\rho_{vi}}{\rho_{ci}}\right) = 1 + \epsilon_i\left(\frac{T_{ci}-T}{T_{ci}}\right) \qquad (1)$$

When

$$\frac{1}{2}\left(\frac{\rho_{li}+\rho_{vi}}{\rho_{ci}}\right) - 1 \text{ -vs.- } \left(\frac{T_{ci}-T}{T_{ci}}\right)$$

is plotted, the rectilinear constant ϵ_i is the linear slope

TABLE 1. RECTILINEAR CONSTANT OF AZEOTROPES

Composition, mole %		Rectilinear constant, ϵ, experimental	calculated [Equation (2)]	%D
CCl_2F_2/CHF_2CH_3(1)		0.9396	0.9405	0.10
CCl_2F_2	60.4	0.8760		
CHF_2CH_3	39.6	1.0390		
$CHClF_2/CClF_2CF_3$(2)		0.9094	0.90943	0.00
$CHClF_2$	63.0	0.9091		
$CClF_2CF_3$	37.0	0.9100		
CH_2ClF/CCl_2F_2(3)		0.9209	0.9139	0.77
CH_2ClF	19.4	1.0714		
CCl_2F_2	80.6	0.8760		
$SF_6/CHClF_2$(3)		0.9500	0.9358	1.50
SF_6	50.0	0.9625		
$CHClF_2$	50.0	0.9091		
$CHClFCF_3/\overline{CF_2CF_2CF_2CF_2}$(4)		1.0233	1.0237	0.04
$CHClFCF_3$	60.0	1.0118		
$\overline{CF_2CF_2CF_2CF_2}$	40.0	1.0417		

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