

Trickle-Bed Effectiveness Factors for Liquid-Phase Reactants

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In cocurrent downflow of liquid and gas over a fixed bed of catalyst particles, the outer surface of the particles may not be completely covered by flowing liquid, that is, by liquid rivulets. The fraction of the outer surface so covered, the wetting efficiency f , affects the global rate of reaction or overall effectiveness factor, η_o . Tan and Smith (1980) proposed a weighting-factor approximation which closely approached the theoretical solution for a cubical particle (Herskowitz et al., 1979).

The question arises of whether the weighing-factor model is suitable when the rate of reaction is determined solely by the concentration of non-volatile, liquid reactant. This situation could

$$B'_{mn} = \frac{\frac{1}{\delta_m \lambda_m} (\sin \lambda_n)(\sin 2\delta_m)}{(\cosh V_{mn} + \frac{V_{mn}}{Nu_L} (\sin V_{mn}))} \times \frac{1}{\left(\frac{1}{2} + \frac{\sin 2\lambda_n}{4\lambda_n}\right) \left(1 + \frac{\sin 4\delta_m}{4\delta_m}\right)} \quad (3)$$

and

$$B''_{mn} = \frac{\frac{1}{\lambda_n \lambda_m} (\sin \lambda_n)(\sin \lambda_m)}{\left[\cosh 2V'_{mn} + \frac{V'_{mn}}{Nu_L} (\sinh 2V'_{mn}) \right] \left[\left(\frac{1}{2} + \frac{\sin 2\lambda_n}{4\lambda_n}\right) \left(\frac{1}{2} + \frac{\sin 2\lambda_m}{4\lambda_m}\right) \right]} \quad (4)$$

with λ_n , λ_m , and δ_m determined by the solutions of the equations

$$\lambda_n \tan \lambda_n = Nu_L \quad (5)$$

$$\lambda_m \tan \lambda_m = Nu_L \quad (6)$$

$$\delta_m \tan 2\delta_m = Nu_L \quad (7)$$

for $n = 1, 2, \dots, \infty$ and $m = 1, 2, \dots, \infty$.

The parameters V_{mn} and V'_{mn} are defined as

$$V_{mn} = (\phi^2 + \lambda_n^2 + \delta_m^2)^{1/2} \quad (8)$$

$$V'_{mn} = (\phi^2 + \lambda_n^2 + \lambda_m^2)^{1/2} \quad (9)$$

Effectiveness factors calculated from Eq. 2 and similar equations for other f values are shown, labeled "cubic model," in Figures 1 and 2.

WEIGHTING-FACTOR MODEL EFFECTIVENESS FACTORS

Tan and Smith (1980) proposed that the total amount of reaction was equal to the sum of contributions due to mass transfer of reactant to the liquid-covered and gas-covered outer surfaces. For our case of nonvolatile, liquid limiting reactant, the resultant equation for a spherical particle, and including mass transfer from bulk liquid to particle surface, is

$$\eta_{os} = \frac{\frac{3f}{\phi_s} \left(\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right)}{1 + \frac{\phi_s}{Nu_{Ls}} \left[\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right]} \quad (10)$$

where

$$Nu_{Ls} = \epsilon_p k_{Ls} r_p / D_e \quad (11)$$

$$\phi_s = r_p (k \rho_p / D_e)^{1/2} \quad (12)$$

Equation 10 shows that η_o and the global reaction rate is directly proportional to f . This is a reasonable result only if mass transfer from liquid to particle surface controls the global rate. Hence, when the intrinsic rate affects the global rate, Eq. 10 would not be a suitable approximation.

arise, for example, in the removal of very small amounts of sulfur-containing compounds by oxidation or hydrogenation. In this situation the amount of reaction is equal to the transport of liquid reactant to the liquid-covered part of the particle surface. In this report the exact results formulated from the cubic model are compared with the weighting-factor approach. Also a new, more accurate model, based upon the suggestion of Dudukovic (1977), is presented.

CUBIC-MODEL EFFECTIVENESS FACTORS

Consider a first-order, isothermal reaction in liquid-filled pores of a cubical catalyst particle of side L . The concentration C_d of reactant in the pores is described by the dimensionless equation

$$\frac{\partial^2 C_d}{\partial X^2} + \frac{\partial^2 C_d}{\partial Y^2} + \frac{\partial^2 C_d}{\partial Z^2} = \phi^2 C_d \quad (1)$$

where $C_d = C/C_L$, $X = x/(L/2)$, $Y = y/(L/2)$, $Z = z/(L/2)$ and $\phi = (L/2)(\rho_p k / D_e)^{1/2}$. Suppose five faces of the cubical particle are covered by liquid and the other face (at $x = -L/2$) is covered by gas, corresponding to $f = 5/6$. Then Eq. 1 can be solved with appropriate boundary conditions and used to determine the overall effectiveness factor, defined by the equation

$$R = \eta_o k C_L$$

Here the reaction rate R is equal to the mass transfer rate of the reactant on the five liquid-covered faces of the cubical particle. The solution is different from that of Herskowitz et al. (1979) because the boundary conditions for a nonvolatile reactant are different from those for a gaseous reactant. In dimensionless form the resultant expression (for $f = 5/6$) is

$$\eta_o = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \left\{ B'_{mn} \frac{(\sin \lambda_n)(\sin 2\delta_m)(\sinh V_{mn})}{\lambda_n \delta_m V_{mn}} + \frac{1}{2} B''_{mn} \frac{(\sinh 2V'_{mn})(\sin \lambda_n)(\sin \lambda_m)}{\lambda_n \lambda_m V'_{mn}} \right\} \quad (2)$$

The quantities B'_{mn} and B''_{mn} are given by

PROPOSED MODEL FOR EFFECTIVENESS FACTORS

A less complex solution than Eq. 2, but more accurate than Eq. 10, is needed. Such an approximation can be developed by incorporating Dudukovic's suggestion (1977) that, for a nonvolatile liquid-phase reactant in a trickle-bed, the proper Thiele modulus for a spherical particle is ϕ'_s , defined as

$$\phi'_s = \phi_s / f \quad (12a)$$

Here ϕ_s is the conventional modulus given by Eq. 12. The effectiveness factor in terms of ϕ'_s is the usual expression

$$\eta_L = \frac{3}{\phi'_s} \left(\frac{1}{\tanh \phi'_s} - \frac{1}{\phi'_s} \right)$$

or, in terms of ϕ_s and f ,

$$\eta_L = \frac{3}{\phi'_s} \left[\left(\frac{1}{\tanh(\phi_s/f)} \right) - \frac{1}{\phi_s/f} \right] \quad (13)$$

When mass transfer resistance from bulk liquid to particle is included, the overall effectiveness-factor expression becomes

$$\eta_{om} = \frac{\frac{3f}{\phi_s} \left(\frac{3}{\tanh(\phi_s/f)} - \frac{1}{\phi_s/f} \right)}{1 + \frac{\phi_s}{Nu_{Ls}} \left(\frac{3}{\tanh(\phi_s/f)} - \frac{1}{\phi_s/f} \right)} \quad (14)$$

Equation 14 is a much closer approximation of the rigorous cubic model expression (Eq. 2) than is Eq. 10.

COMPARISON OF η_o FROM DIFFERENT MODELS

In the cubic model it is possible to calculate overall effectiveness factors only for $f = 1/6, 2/6, 3/6, 4/6, 5/6$, and 1. For $2/6, 3/6$, and $4/6$ there are two possible arrangements for the liquid-covered faces, that is, faces either perpendicular or parallel to each other. The maximum deviation between the values for the two arrangements is for low values of ϕ and for $f = 2/6$, and is about 13%. Over a range of ϕ the average deviation is about 5%. Since the differences are small, results in Figures 1 and 2 for the cubic model are for averages of the parallel and perpendicular cases.

Figure 1 is for a relatively small amount of liquid-to-particle mass transfer resistance corresponding to Nu_L (or Nu_{Ls}) = 15. The weighting-factor method gives results that deviate greatly from those for the cubical model whenever the Thiele modulus is 5 or less, that is, when the reaction is intrinsically slow. When reaction resistance is negligible, corresponding to ϕ_s of 10 or more, the

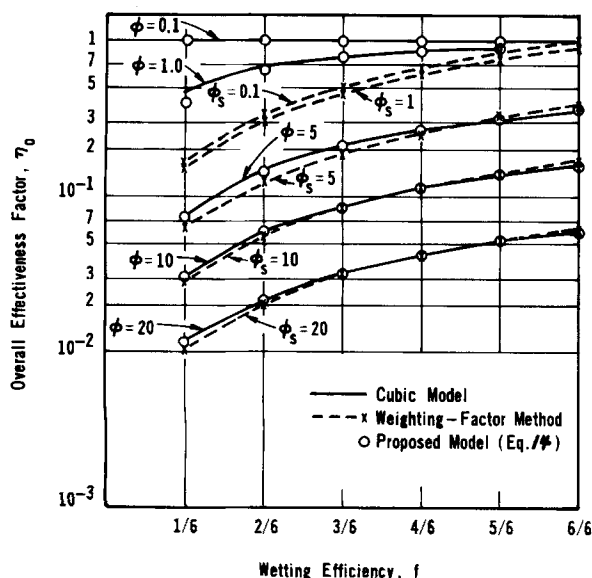


Figure 1. Comparison of Effectiveness Factors Predicted by Different Methods for Nu_L (or Nu_{Ls}) = 15.

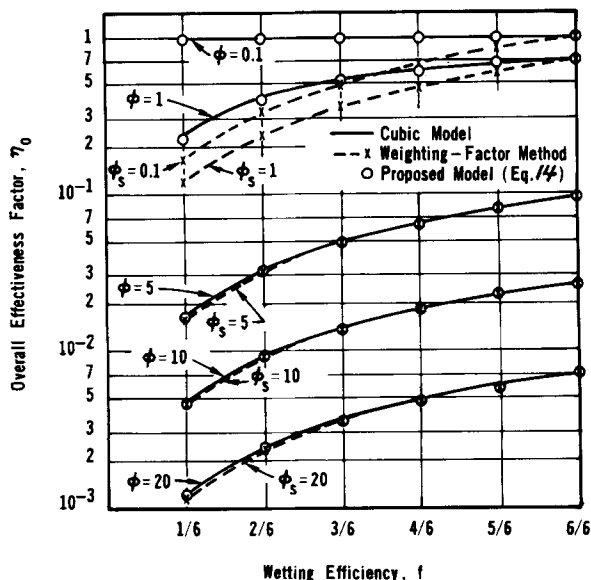


Figure 2. Comparison of Effectiveness Factors Predicted by Different Models for Nu_L (or Nu_{Ls}) = 1.

weighting-factor method gives accurate results. For any value of ϕ_s , the overall effectiveness factors predicted by the proposed, new method, Eq. 14, are in good agreement with those obtained by the cubic model.

Figure 2 shows η_o for the case of more liquid-to-particle mass transfer resistance corresponding to Nu_L (or Nu_{Ls}) = 1.0. Now the weighting-factor model gives slightly more accurate results, but the deviations are still significant for $\phi_s \leq 1.0$. Again, effectiveness factors from the proposed model are in good agreement with the cubic model results for all levels of ϕ_s .

It is concluded that the proposed model, Eq. 14, is a useful approximation over a wide range of conditions [Nu_{Ls} from 10^{-6} to 15, and ϕ_s from 0.01 to 20]. In this range the largest deviation from the cubic model was about 10%, with an average difference of 2%. The weighting-factor method can lead to large deviations except for large ϕ_s or very low Nu_{Ls} .

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NOTATION

B'_{mn}	= parameter defined by Eq. 3
B_{mn}	= parameter defined by Eq. 4
C	= intraparticle concentration of reactant, kmol/m ³
C_d	= dimensionless intraparticle reactant concentration, C/C_L
C_L	= Concentration of reactant in the bulk liquid, kmol/mg ³
D_e	= effective diffusivity of reactant in liquid-filled pores, m ² /s
f	= wetting efficiency; fraction of external surface of catalyst particle covered by liquid rivulets
k	= intrinsic, first-order, reaction, rate constant, m ³ /(kg)(s)
k_{Ls}	= liquid-to-particle mass transfer coefficient, m/s
L	= length of cubical catalyst article, m

Nu_{Ls}	= liquid-to-particles, defined	selt number for spherical particles, defined
R	= global rate of	11
r_p	= radius of sphere	1, kmol/(kg)(s)
V_{mn}, V'_{mn}	= parameters defined by Eqs. 8 and 9	alyst marticle, m
x, y, z	= rectangular coordinates	es, m
X, Y, Z	= dimensionless	sular coordinates

Greek Letters

δ_m	= constant defined by Eq. 7
ϵ_p	= porosity of particles
λ_m, λ_n	= constants defined by Eqs. 5 and 6
η_o	= overall effectiveness factor calculated by the cubical model, Eq. 2 and similar expressions
η_{om}	= overall effectiveness factor calculated from Eq. 14
η_{os}	= overall effectiveness factor calculated by the weighting-factor model (Eq. 10)
η_L	= conventional effectiveness factor based upon ϕ_s and given by Eq. 13 for a spherical catalyst particle

ρ_p	= density of particle, kg/m ³
ϕ	= Thiele modulus for cubical particle
ϕ_s	= Thiele modulus for spherical particle, defined by Eq. 12
ϕ'_s	= modified Thiele modulus for spherical particle, defined by Eq. 12a

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Two-Step Catalytic Reactions: Pitfalls in the Prediction of Transient Behavior by Global Kinetics

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INTRODUCTION

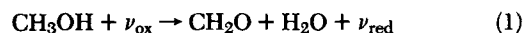
In heterogeneous catalysis chemical reactions occur through a sequence of elementary steps which involve highly reactive intermediates called active centers. The complete description of every single step of the sequence usually leads to rather complicated rate expressions. The most important general technique applied to simplify such expressions is the steady-state approximation of the active sites, which allows to formulate a global rate expression. Moreover, other approximations such as the rate-determining step and the most abundant surface intermediate (which replaces the first one when the elementary reactions of the sequence are irreversible) can be introduced to further simplify the global rate expression by decreasing the number of the involved adjustable parameters (Boudart, 1968).

The steady-state approximation is obviously correctly applicable only to the reacting system in stationary conditions, while the transient requires to describe the entire sequence of elementary steps. For example, this is done in the interpretation of oscillations in surface catalyzed reactions (Sheintuch and Schmitz, 1977), and in the discrimination among rival kinetic models performed exploiting the superior information content of transient experimental data (Bennet, 1976).

This paper points out the pitfalls associated with the application of rate expressions obtained using the steady-state approximation for the description of the transient behavior of a chemical reactor, which is of crucial importance to the definition of the reactor

steady-state stability character. Some of the parameters which characterize the dynamic behavior of the reactor do not affect its steady-state performance. Thus, global rate expressions calibrated on steady-state experiments do not allow the correct design of chemical reactors, which includes the definition of their steady-states stability character.

We will focus here on the redox mechanism which is a quite common example for two-step reactions (Boudart, 1972; Carrà and Forzatti, 1977). We consider the oxidation of methanol to formaldehyde over catalysts of iron molybdate, recently investigated by Santacesaria et al. (1981):



The reaction rates of the two elementary steps are

$$f_1 = k_1 C_M \nu_{\text{ox}} \quad (3)$$

$$f_2 = k_2 C_O^{1/2} \nu_{\text{red}} \quad (4)$$

Recalling that $\nu_{\text{red}} = 1 - \nu_{\text{ox}}$ and using the active sites steady state approximation, from Eqs. 3 and 4 it follows

$$\nu_{\text{ox}} = k_2 C_O^{1/2} / (k_1 C_M + k_2 C_O^{1/2}) \quad (5)$$

Substituting Eq. 5 in Eq. 3, the global rate expression of the process can be derived

$$f = k_1 C_M k_2 C_O^{1/2} / (k_1 C_M + k_2 C_O^{1/2}) \quad (6)$$

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