JOURNAL OF CATALYSIS 41, 61–71 (1976)

Effectiveness Factors in Langmuir–Hinshelwood and General Order Kinetics

R. A. RAJADHYAKSHA, K. VASUDEVA

Department of Chemical Technology, University of Bombay, India

AND

L. K. DORAISWAMY

National Chemical Laboratory, Poona 8, India

Received April 29, 1975

The heat and mass balance equations for diffusion accompanied by chemical reaction in a catalyst pellet are solved for reactions following a common class of Langmuir–Hinshelwood kinetics and general-order kinetics. An explicit algebraic expression is developed relating the effectiveness factor to the kinetic, adsorption, and transport parameters under nonisothermal conditions. This equation can be directly used in fixed-bed reactor calculations to take into account the influence of adsorption and intraparticle processes.

NOMENCLATURE

c	dimensionless concentration
C_A	concentration of the reactant A
C_{AS}	concentration of A at the surface of the pellet
D_e	effective diffusivity of A in the pellet
E	activation energy
k	kinetic parameter
$k[T]$	kinetic parameter at temperature T
K	adsorption parameter
$K[T]$	adsorption parameter at temperature T
K_e	thermal conductivity of the pellet
n	reaction order
r	radial coordinate
R	radius of the pellet
R_g	universal gas constant
T	temperature
T_s	temperature at the surface of the pellet
χ	dimensionless radial coordinate, r/R
ΔH	heat of reaction
ω	adsorption factor, K C_{AS}
ϕ	Thiele modulus, $R\ (k[T_s]/D_e)^{1/2}$
ϕ'	modified Thiele modulus
β	$D_e[-\Delta H]C_{AS}/K_eT_s$
γ	Arrhenius factor, E/R_gT_s
η	effectiveness factor.

INTRODUCTION

Simulation of a fixed-bed catalytic reactor involves simultaneous numerical solution of heat and mass balance equations for the reactor. When intraparticle gradients are important the particle equations get coupled with the fluid phase equations. In such instances in order to evaluate the global rate at every grid point in the reactor it also becomes necessary to solve the heat and mass balance equations for the pellet. An analytical solution to the pellet equations can be obtained only for a first order reaction occurring in an isothermal pellet, and a numerical solution becomes necessary when the kinetic expression is nonlinear. Moreover a number of systems of practical importance, such as oxidation

---

[1] N.C.L. Communication No. 1131.

of ethylene and hydrogenation of benzene, exhibit nonisothermal pellet behavior (*1*).

Since the pellet equations constitute a nonlinear boundary value problem, a considerable computational effort will be involved in the fixed-bed calculations. However, the computational time can be significantly reduced by obtaining an algebraic equation expressing the effectiveness factor in terms of system parameters. This approach has been followed by Carberry (*2*), Jouven and Aris (*3*), and Rajadhyaksha and Vasudeva (*4*) for first-order reactions and by Liu (*5*) for first- and second-order reactions.

However, a large number of systems follow nonfirst-order kinetics. The engineering approach to kinetic data fitting involves fitting of a general-order kinetic expression which many times results in a fractional-order equation. In a number of cases where the systems involved intrinsically follow Langmuir–Hinshelwood (L–H) type of kinetics, no single value of reaction order represents the kinetic data satisfactorily over the entire partial pressure range of interest. In such cases resort to L–H type of kinetic expressions becomes necessary. Due to the frequent need to use these nonfirst-order kinetic expressions, it is desirable to obtain algebraic expressions for the effectiveness factor for reaction obeying L–H and general-order kinetics. In the present work such correlations are developed for reactions following a common class of L–H kinetics and those following general-order kinetics.

A large number of numerical solutions for the effectiveness factor over a wide range of parameters is necessary for fitting such correlations. Since the solutions reported in the literature cover only a few special cases, it was necessary to obtain

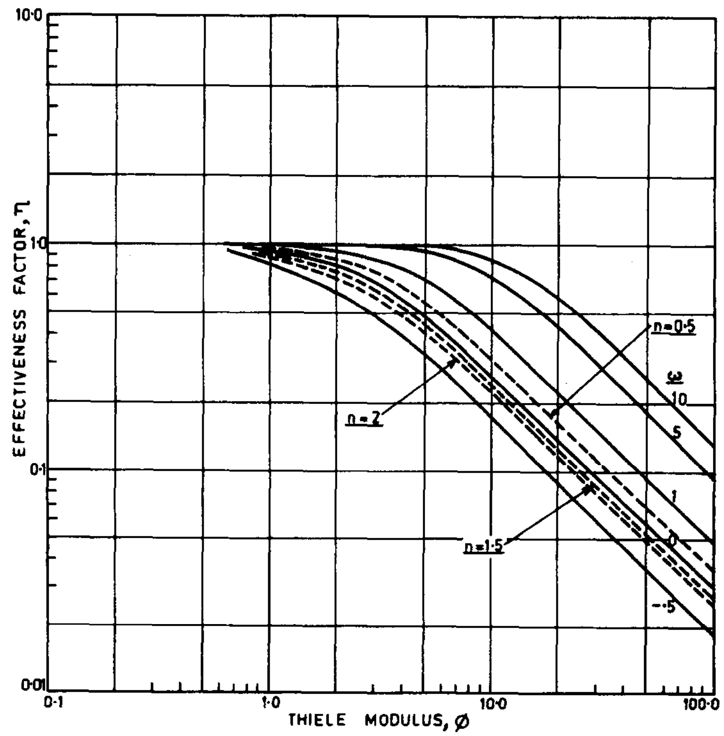

FIG. 1. Effectiveness factor vs Thiele modulus plots for isothermal pellet. (—) Langmuir–Hinshelwood kinetics; (---) general-order kinetics.

the solutions as an essential first step. The results of these computations (expressed as η vs ϕ plots) are also presented since they will serve as useful additions to existing plots and will also bring out certain salient features of the solutions.

EFFECTIVENESS FACTOR SOLUTIONS FOR LANGMUIR-HINSHELWOOD AND GENERAL-ORDER KINETICS

Langmuir-Hinshelwood Kinetics

Even though effectiveness factor solutions for first-order reactions have been studied extensively, very little has been reported (*6–11*) for reactions following L-H type of kinetic expressions. The reason probably is that these kinetic expressions involve many parameters, and each of these expressions needs to be dealt with individually. Roberts and Satterfield (*6*) attempted a generalized approach by classifying these models into two classes. Making use of the fact that the concentrations of various reacting species within the pellet are linearly related to one another, they showed that a class of L-H models can be reduced to the following form:

$$r = (k\, C_A / 1 + K\, C_A). \tag{1}$$

They obtained the effectiveness factor solutions using this kinetic expression assuming isothermal conditions and slab geometry.

Effectiveness factor solutions in the presence of adsorption in a nonisothermal pellet have been reported by Hutchings and Carberry (*9*). But they did not use the generalized kinetic expression given by Roberts and Satterfield (*6*) and hence two

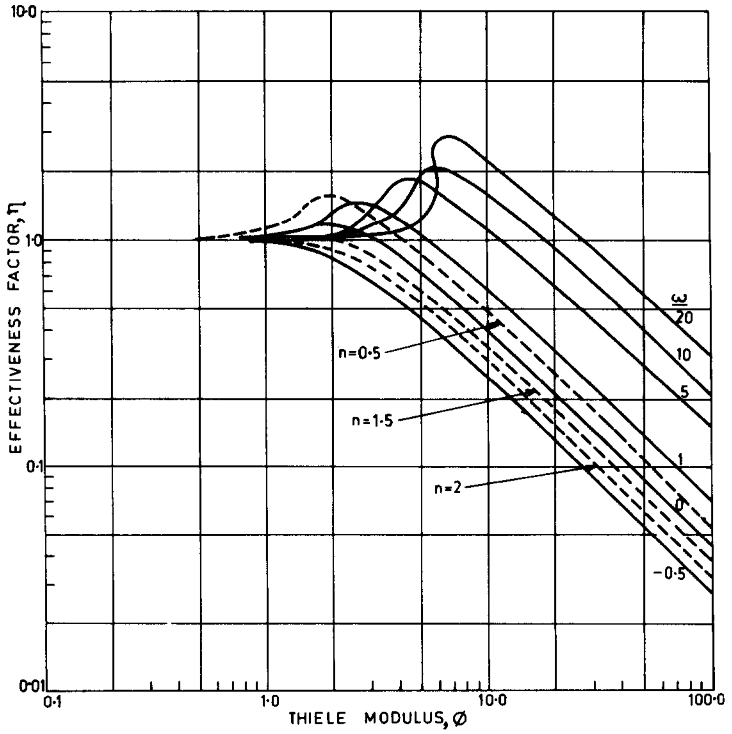

FIG. 2. Effectiveness factor vs Thiele modulus plots; $\gamma = 20$, $\beta = 0.1$. (—) Langmuir-Hinshelwood kinetics; (---) general-order kinetics.

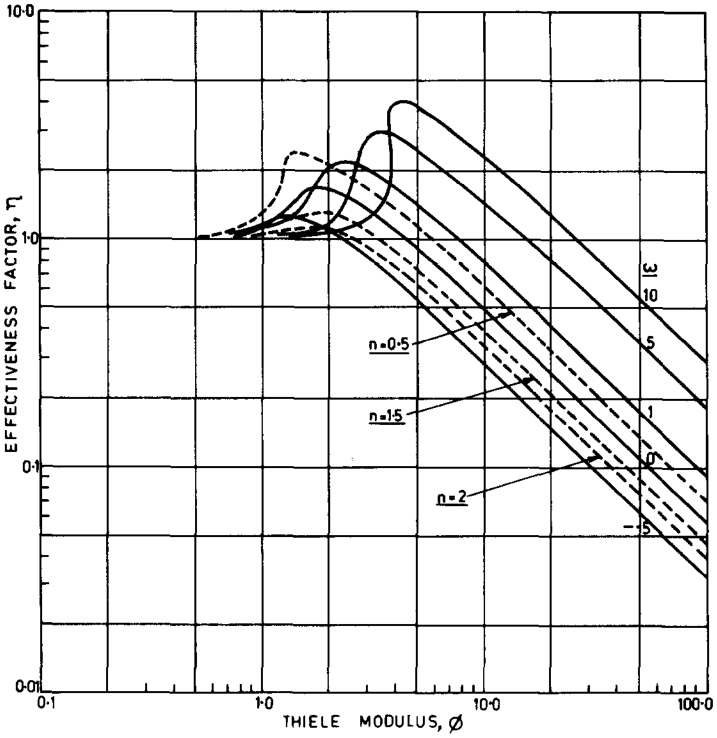

FIG. 3. Effectiveness factor vs Thiele modulus plots; $\gamma = 30$, $\beta = 0.1$. (—) Langmuir–Hinshelwood kinetics; (---) general-order kinetics.

adsorption parameters were involved in the solution. In the present work the general expression given by Eq. (*1*) will be considered.

By using Eq. (1) to represent the reaction rate, the following heat and mass balance equations for the pellet can be readily written for a reaction involving no change in moles:

$$\frac{De}{r^2}\frac{d}{dr}\left[r^2\frac{dC_A}{dr}\right]-\frac{k[T]\,C_A}{1+K[T]\,C_A}=0, \quad (2)$$

and

$$\frac{K_e}{r^2}\frac{d}{dr}\left[r^2\frac{dT}{dr}\right]+\frac{[-\Delta H]k[T]\,C_A}{1+K[T]\,C_A}=0, \quad (3)$$

with boundary conditions:

$$dT/dr=0 \quad d\,C_A/dr=0 \text{ at } r=0, \text{ and} \quad (4)$$

$$T=T_s,\ C_A=C_{AS} \text{ at } r=R. \quad (5)$$

For a rigorous solution of this set of equations both the rate and adsorption constants are required to be expressed as a function of temperature. A considerable degree of simplicity can, however, be introduced by assuming that the effect of temperature on the adsorption constant K is negligible as compared to that on the rate constant k. Thus, the following set of dimensionless equations can be written in which the rate constant k alone is expressed by an Arrhenius type equation:

$$\frac{d^2c}{dx^2}+\frac{2}{x}\frac{dc}{dx}-f[c]\phi^2\exp\frac{\beta\gamma\,[1-c]}{1+\beta\,[1-c]}=0, \quad (6)$$

with

$$\frac{dc}{dx}=0 \quad \text{at } x=0, \text{ and}$$
$$c=1 \quad \text{at } x=1, \quad (7)$$

where

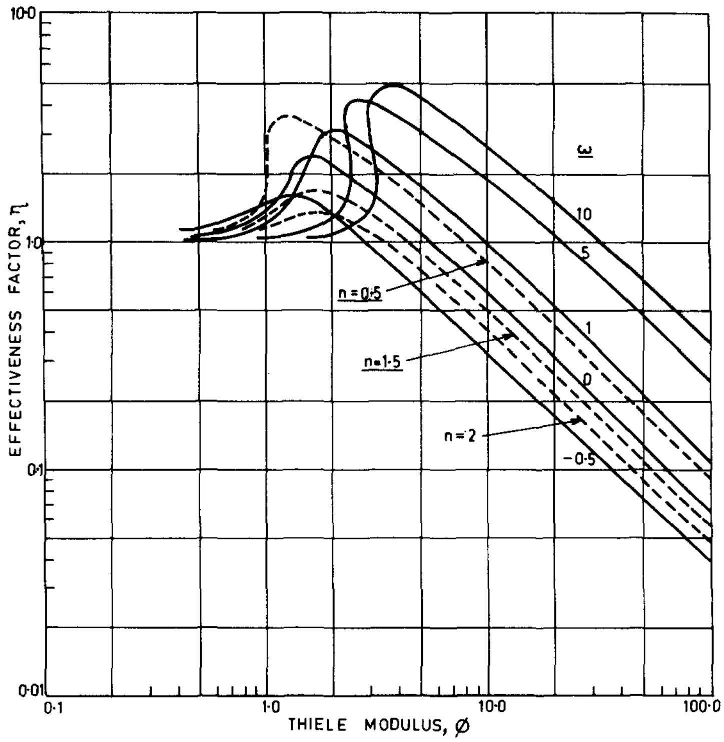

FIG. 4. Effectiveness factor vs Thiele modulus plots; $\gamma = 20$, $\beta = 0.2$. (—) Langmuir-Hinshelwood kinetics; (---) general-order kinetics.

$$f[c] = \frac{c}{1 + \omega c}, \qquad (8)$$

$$\phi = R(k[T_s]/De)^{1/2},$$

$$\alpha = (De[-\Delta H]C_{AS}/K\ T_s),$$

$$\gamma = (E/R_gT_s),\ \omega = K\ C_{AS}.$$

These equations were solved on an IBM-1620 computer by using the Runge–Kutta–Gill procedure. The Newton–Raphson method explained by Hlavacek and Kubicek (*12*) was used for convergence. When this method failed to converge the procedure explained by Weisz and Hicks (*13*) was used.

The correctness of the solutions can be judged by comparing them with the reported solution for certain limiting cases. An analytical solution is available for isothermal first-order reactions (*13*). The solutions obtained for $\beta = 0$ and $\omega = 0$ were compared with those obtained from this expression and the two were found to be identical. Second, nonisothermal solutions for a first-order reaction are reported by Weisz and Hicks (*13*). The solutions obtained for $\omega = 0$, $\gamma = 20$, and $\beta = 0.1$, 0.2 were compared with Weisz and Hick's solutions and were found to coincide completely.

Having established the correctness of the numerical solutions obtained, it would be interesting now to consider the effect of nonisothermicity and adsorption simultaneously. The solutions for a few specific values of the parameters β, γ, and ω are presented in Figs. 1–5. Figure 1 shows the η–ϕ solutions for an isothermal pellet. For a given value of ϕ the effectiveness factor increases with increase in the value of ω. This can be easily conceived as with increase in ω, the fall in the concentration of A has a decreasing influence on the reaction rate and hence diffusional influence

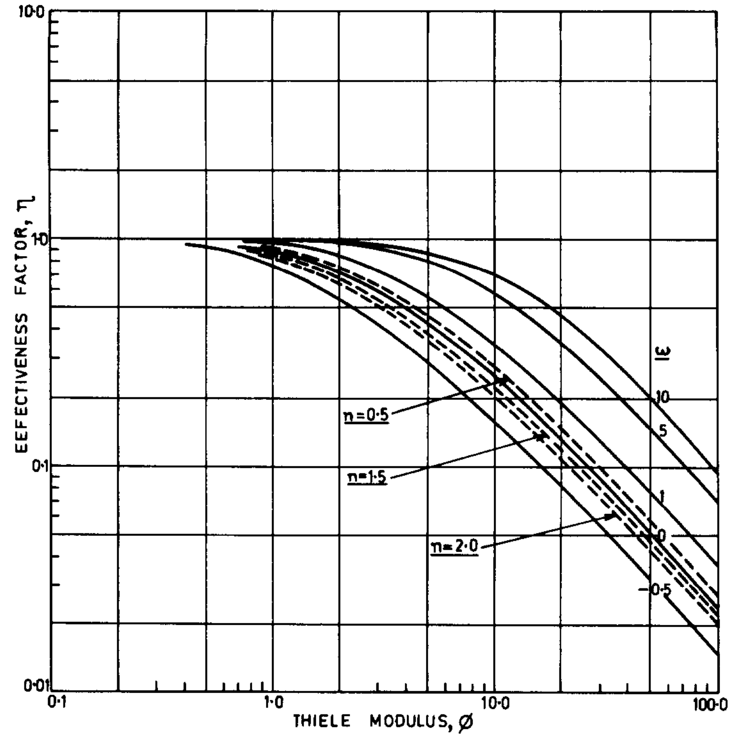

FIG. 5. Effectiveness factor vs Thiele modulus plots; $\gamma = 20$, $\beta = -0.05$. (—) Langmuir–Hinshelwood kinetics; (---) general-order kinetics.

will be less pronounced at higher values of ω.

However, under nonisothermal conditions (Figs. 2–4) while this trend is maintained at higher values of ϕ, there is a reversal of trend in the low ϕ region. The effectiveness factor decreases with the parameter ω at low values of ϕ. As stated earlier, for a given value of ϕ, the reaction rate increases with the decrease in the value of ω. The higher reaction rate at lower values of ω results in steeper temperature gradients. In Table 1, the values of intraparticle temperature rise are illustrated for $\phi = 1$, $\beta = 0.2$, and $\gamma = 20$ assuming the temperature at the surface to be 600°K. The severity of temperature gradients at lower values of ω is responsible for the reversal of the trend. Higher values of $\phi [\phi > 10]$, however, the temperature rise is the same for all values of ω, and hence the trend of variation of η with ω reverts to that under isothermal conditions. Due to these opposing trends at low and high values of ϕ, the curves for different values of ω intersect one another in the intermediate region. From the same consideration, it can be argued that no such reversal should be observed in the case of endothermic reactions. This is apparent from Fig. 5.

TABLE 1

INTRAPARTICLE TEMPERATURE RISE FOR VARIOUS VALUES OF ω AT $\phi = 1$, $\beta = 0.2$, $\gamma = 20$, AND $T_s = 600°K$

ω	−0.5	0.0	1.0	5.0
ΔT[°C]	74.6	33.6	13.2	3.6

General-Order Reactions

The nonisothermal effectiveness factor solutions for reactions following *n*th-order

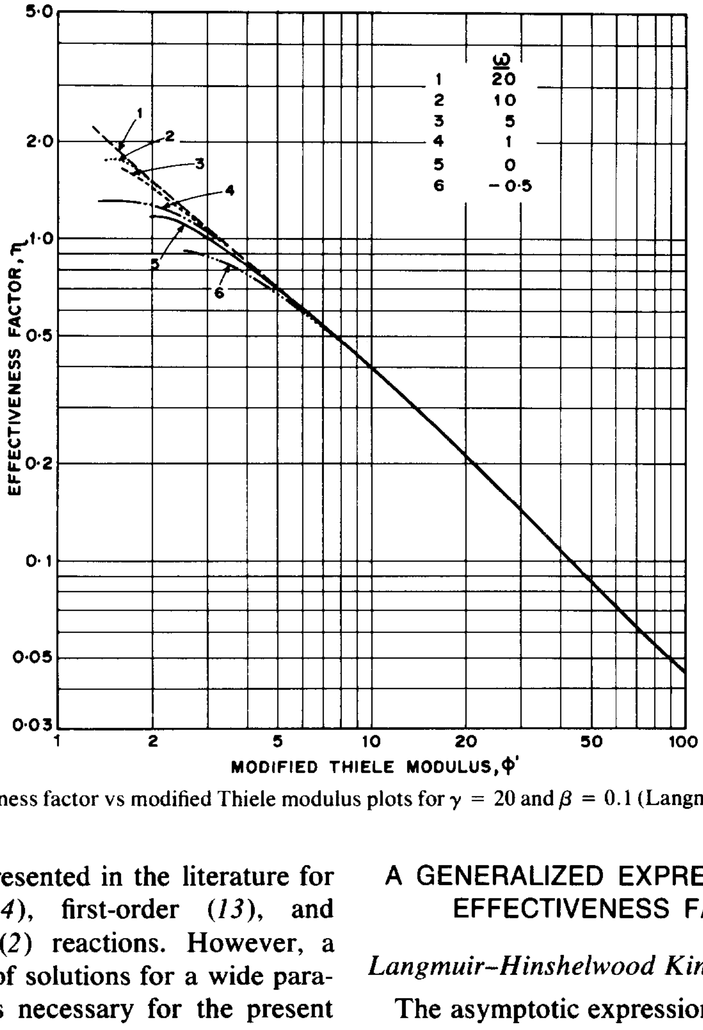

FIG. 6. Effectiveness factor vs modified Thiele modulus plots for $\gamma = 20$ and $\beta = 0.1$ (Langmuir–Hinshelwood kinetics).

kinetics are presented in the literature for zero-order (*14*), first-order (*13*), and second-order (*2*) reactions. However, a large number of solutions for a wide parameter range is necessary for the present analysis. Hence solutions were obtained for orders ½, 1, ³⁄₂, and 2 for different values of the other parameters.

The mass balance equation for the pellet for an *n*th-order reaction can be obtained by substituting

$$f[c] = c^n \tag{10}$$

in Eq. (6). The Thiele modulus will be defined as

$$\phi = R\sqrt{kc_{AS}^{n-1}/D_e} \tag{11}$$

The numerical procedures discussed earlier were used to solve this equation. The results of the computations are included in Figs. 1–5.

A GENERALIZED EXPRESSION FOR EFFECTIVENESS FACTOR

Langmuir–Hinshelwood Kinetics

The asymptotic expression for the effectiveness factor for the kinetic model given by Eq. (1) can be obtained using the expression given by Petersen (*15*). Thus:

$$\nu = \frac{3(\sqrt{2})}{\phi}(1+\omega)\times \left[\int_0^1 \frac{c}{1+\omega c}\exp\frac{\beta\gamma\,[1-c]}{1+\beta\,[1-c]}\,dc\right]^{1/2}. \tag{12}$$

As an approximation, the factor $(1/1+\omega c)$ in the integrand may be replaced by its average value and taken out of the integral sign. The average value of this factor in the interval [0, 1] is given by

$$\int_0^1 \frac{1}{1+\omega c}\,dc = \frac{1}{\omega}\ln\,[1+\omega]. \tag{13}$$

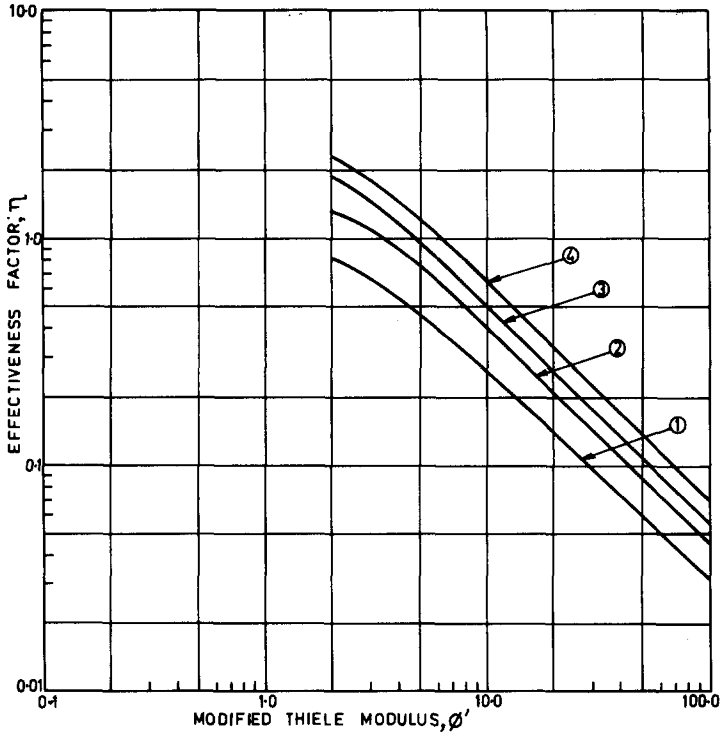

Fig. 7. Effectiveness factor vs modified Thiele modulus plots for Langmuir–Hinshelwood kinetics.

	β	γ
1	Isothermal	
2	0.1	20
3	0.1	30
4	0.2	20

Substituting in Eq. (12),

$$\eta = \frac{3(2)^{1/2}}{\phi'} \left[\int_0^1 c \exp \frac{\beta\gamma\,[1-c]}{1+\beta\,[1-c]}\, dc\right]^{1/2}, \quad (14)$$

where ϕ' is a modified Thiele modulus given by

$$\phi' = \phi \frac{1}{1+\omega} \left(\frac{\omega}{\ln\,[1+\omega]}\right)^{1/2}. \quad (15)$$

Now, it can be seen that Eq. (14) is the same as the asymptotic expression of the effectiveness factor for a first-order reaction. Hence by defining a modified Thiele modulus, the η–ϕ relationship for the model given by Eq. (1) is reduced to that for a first-order reaction in the asymptotic region. Thus the curves for different values of ω should coincide with that for a first-order reaction for given values of β and γ.

To check the validity of this approximation, the effectiveness factor is plotted against the modified Thiele modulus ϕ' in Fig. 6 for $\beta = 0.1$ and $\gamma = 20$. The curves for different values of $\omega > 0$ coincide completely with that for $\omega = 0$ (first order) when $\phi' > 5$ and tend to separate out for ϕ' less than 5. However, they lie within 10% from the mean value up to $\phi' = 2$. For $\omega < 0$, the separation of curves occurs at $\phi' < 6$. Thus the approximation is valid for the following conditions:

[1] $\omega > 0,\ \phi' > 2$;

and

TABLE 2

COMPARISON OF THE VALUES OF EFFECTIVENESS FACTOR FROM NUMERICAL SOLUTION WITH THOSE CALCULATED USING EQUATION (16) FOR THE LANGMUIR–HINSHELWOOD KINETIC MODEL

					Effectiveness factor	
γ	β	ω	ϕ	ϕ'	From numerical solution	From Eq. (16)
20	0.2	1	3.5	2.10	2.30	2.299
20	0.2	1	9.8	5.9	1.01	1.081
20	0.2	1	20.0	12.0	0.55	0.548
20	0.2	1	50.0	30.0	0.22	0.220
20	0.2	5	7.5	2.1	2.20	2.299
20	0.2	5	10.6	3.0	1.70	1.898
20	0.2	5	21.0	5.9	1.00	1.081
20	0.2	10	11.3	2.1	2.42	2.299
20	0.2	10	31.6	5.9	1.071	1.081
20	0.2	−0.5	3.5	5.9	0.92	1.081
20	0.2	−0.5	7.1	12.0	0.51	0.548
20	0.2	−0.5	29.4	50.0	0.126	0.134
30	0.1	5	8.6	2.40	1.62	1.567
30	0.1	5	17.9	5.0	0.90	0.934
30	0.1	5	43.0	12.0	0.40	0.416
30	0.1	10	26.9	5.0	0.97	0.934
30	0.1	10	64.5	12.0	0.43	0.416
30	0.1	−0.5	2.9	5.0	0.84	0.934
30	0.1	−0.5	7.1	12.0	0.43	0.416
30	0.1	−0.5	19.4	33.0	0.151	0.154
30	0.1	1	4.0	2.4	1.69	1.567
30	0.1	1	20.0	12.0	0.42	0.416
30	0.1	1	33.4	20.0	0.26	0.256

[6] $\omega < 0, \phi' > 6$.

Similar behavior was observed for the other sets of values of β and γ, i.e.,

$\beta = 0.2$, $\gamma = 20$; $\beta = 0.1$, $\gamma = 30$; and isothermal. Fig. 7 shows the mean η–ϕ' curves for these sets of values of β and γ over the range of ϕ' given above.

The following correlation between η and ϕ has been obtained by Rajadhyaksha and Vasudeva (*4*) for a first order reaction valid for $\phi < 2, \gamma > 8, \beta\gamma < 6$:

$$\begin{aligned}\eta = (\exp\,[1.172\,\beta(\sqrt{\gamma - 8}\,)] - 1)\\ (\exp\,[X] - 1) + X, \quad (16)\end{aligned}$$

where

$$X = \frac{3}{\phi}\left[\coth \phi - \frac{1}{\phi}\right]. \quad (17)$$

Since the η–ϕ' curves have been shown above to coincide with the first-order curves over the specified range, Eq. (16) should also represent the relation between η and ϕ'. Thus values of the effectiveness factor were computed using Eq. (16) replacing the Thiele modulus in Eq. (17) by the modified Thiele modulus ϕ'. The computed values are compared with those obtained from numerical solution in Table 2. The average absolute deviation is 4.43% and maximum deviation 11.4%. Thus Eq. (16) with ϕ replaced by ϕ' can be used as an expression for the effectiveness factor which takes into account the effect of nonisothermicity as well as adsorption.

General-Order Reaction

The asymptotic expression for the effectiveness factor for *n*th order kinetics is

$$\eta = \frac{3(\sqrt{2})}{\phi}$$
$$\left[\int_0^1 c^n \exp \frac{\beta\,\gamma\,[1-c]}{1+\beta\,[1-c]}\,dc\right]^{1/2}. \quad (18)$$

The factor c^{n-1} may be replaced by its average value over the interval [0, 1] and taken out of the integral sign. By following a procedure similar to that for L–H kinetic models, a modified modulus can now be defined as

$$\phi' = (\sqrt{n})\phi. \quad (19)$$

Liu (*5*) has used the empirical relation

$$\phi' = 1.33\ \phi \quad (20)$$

for a second-order reaction. However, according to Eq. (19), ϕ' should be given by 1.41 ϕ.

The correlation given by Eq. (16) can thus be extended to general-order kinetics by incorporating the modified modulus defined by Eq. (19) in Eq. (15). The values of the effectiveness factor computed from the correlation are compared with those ob-

TABLE 3

COMPARISON OF THE VALUES OF EFFECTIVENESS FACTOR OBTAINED FROM NUMERICAL SOLUTION WITH THOSE CALCULATED USING THE CORRELATION GIVEN BY EQUATION (16) FOR GENERAL-ORDER KINETICS

				Effectiveness factor	
γ	β	η	ϕ	From Eq. (16)	From numerical solution
20	0.1	2.0	4	0.710	0.640
20	0.1	2.0	6	0.495	0.465
20	0.1	2.0	8	0.378	0.360
20	0.1	2.0	10	0.306	0.306
20	0.1	2.0	30	0.104	0.105
20	0.1	1.5	4	0.802	0.720
20	0.1	1.5	8	0.433	0.420
20	0.1	1.5	10	0.351	0.350
20	0.1	1.5	30	0.121	0.121
20	0.1	0.5	3	1.390	1.300
20	0.1	0.5	8	0.710	0.630
20	0.1	0.5	30	0.206	0.180
20	0.2	0.5	3	2.292	2.300
20	0.2	0.5	8	1.12	1.000
20	0.2	0.5	30	0.315	0.295
20	0.2	2.0	6	0.77	0.660
20	0.2	2.0	10	0.47	0.420
20	0.2	2.0	30	0.158	0.150
30	0.1	2.0	4	0.837	0.750
30	0.1	2.0	8	0.442	0.420
30	0.1	2.0	20	0.181	0.180
30	0.1	0.5	4	1.425	1.420
30	0.1	0.5	8	0.837	0.800
30	0.1	0.5	20	0.356	0.345
	0	0.5	3	0.788	0.770
	0	0.5	5	0.609	0.560
	0	0.5	9	0.397	0.360
	0	0.5	20	0.134	0.120

tained from numerical solution in Table 3. The correlation predicts the values of the effectiveness factor to within 15% in the range $\phi' > 4$.

An inspection of Eqs. (15) and (19) shows that they can be combined to give the following general expression for the modified Thiele modulus:

$$\phi' = \phi \frac{(\sqrt{n})}{1 + \omega} \left(\sqrt{\frac{\omega}{\ln[1 + \omega]}} \right). \quad (21)$$

For L–H kinetics $n = 1$ and this equation reduces to Eq. (15), while for general-order kinetics $\omega = 0$ and this reduces to Eq. (19).

CONCLUSIONS

The η–ϕ plots for general order and a class of L–H kinetic models can be made to coincide with one another by defining a modified Thiele modulus in terms of the usual Thiele modulus and an excess term characteristic of the kinetic expression. In L–H kinetics this excess term is defined in terms of the adsorption parameter ω, the definition of the modified modulus being given by Eq. (15). On the other hand, for general-order kinetics, the excess term is merely the square root of the reaction order and the modified modulus is given by Eq. (19).

By making use of the modified modulus as defined above, the effectiveness factor can be calculated for given values of β, γ, and ϕ from a simple algebraic equation, Eq. (16). This equation is valid for

$$\phi' > 2, \beta\gamma < 6, \gamma > 8 \quad \text{for } \omega > 0$$
$$\phi' > 6, \beta\gamma < 6, \gamma > 8 \quad \text{for } \omega < 0$$
$$\text{and } \phi' > 4, \beta\gamma < 6, \gamma > 8 \quad \text{for } 0.5 < n < 2.$$

As can be seen from the values reported in the literature (*1*) for various systems, the range of parameters β and γ covered by the correlation is realistic. Parameters ϕ' and ω depend upon the kinetic constants which vary over a wide range and the correlation covers a major part of this range. Thus by making use of the equations and procedures outlined in this paper, it is possible to describe the effectiveness factor for a variety of reactions by a simple algebraic expression which can be incorporated in any procedure for the design and simulation of fixed-bed reactors.

REFERENCES

1. Hlavacek, V., Kubicek, M., and Marek, M., *J. Catal.* **15**, 17 (1969).

2. Carberry, J. J., *AIChE J.* **7**, 350 (1961).

3. Jouven, J. G., and Aris, R., *AIChE J.* **18**, 403 (1972).

4. Rajadhyaksha, R. A., and Vasudeva, K., *J. Catal.* **34,** 321 (1974).

5. Liu, S. L., *AIChE J.* **16,** 742 (1970).

6. Roberts, G. W., and Satterfield, C. N., *Ind. Eng. Chem. Fundam.* **4,** 289 (1965).

7. Roberts, G. W., and Satterfield, C. N., *Ind. Eng. Chem. Fundam.* **5,** 317 (1966).

8. Knudsen, G. W., Roberts, G. W., and Satterfield, C. N., *Ind. Eng. Chem. Fundam.* **5,** 325 (1966).

9. Hutchings, J., and Carberry, J. J., *AIChE J.* **12,** 20 (1966).

10. Chu, C., and Hougen, O. A., *Chem. Eng. Sci.* **17,** 167 (1962).

11. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," M.I.T. Press, Cambridge, Mass., (1970).

12. Kubicek, M., and Hlavacek, V., *Chem. Eng. Sci.* **25,** 1833 (1970).

13. Weisz, P. B., and Hicks, J. S., *Chem. Eng. Sci.* **17,** 265 (1962).

14. Marek, M., and Hlavacek, V., *Chem. Eng. Sci.* **23,** 865 (1968).

15. Petersen, E. E., "Chemical Reaction Analysis," Prentice Hall, Englewood Cliffs, N.J., (1965).