ISOTHERMAL EFFECTIVENESS FACTOR—I

ANALYTICAL EXPRESSION FOR SINGLE REACTION WITH ARBITRARY KINETICS. SLAB GEOMETRY

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Abstract—An analytical simple algebraic expression for isothermal effectiveness factor (η) in a porous pellet is presented. Arbitrary kinetic expressions are investigated and the external mass transfer effect is also considered. The resulting analytical expression is found after matching asymptotic expressions of η valid for large and small values of Thiele modulus.

The agreement between approximated and numerical results is surprisingly good. For most cases analyzed maximum deviation are below 3% for power law type kinetic expressions provided the reaction order is greater than 0.5. More severe limitation arises for Langmuir–Hinshelwood kinetic expressions. In actual facts the proposed analytical expressions is unable to predict effectiveness factor greater than one.

Nevertheless, as will be shown in future works, this very simple procedure can be safely used to predict the effectiveness in more complex situations such as those where activity distribution must be considered or where the kinetic parameters will be function of composition and/or spatial coordinates.

INTRODUCTION

The effectiveness factor(η), defined as the actual rate of reaction divided by the rate which would occur in the absence of mass and heat transfer resistance, is an important parameter in the design of catalytic chemical reactors which use porous particles as catalysts. It plays a fundamental role in the study of the simulation and stability of packed bed reactors and must be taken into account when kinetic parameters are to be measured in this kind of reactors. As recently pointed out by Churchill[1], due to this fact, and also because of the mathematical tractability of the problem, a great number of contributions on the subject have been written. Fortunately, Aris[2] has been able to prepare a concise review in which the outstanding and classical features of the subject are superbly presented. In spite of many efforts, as far as the authors can ascertain, there is still the lack of a generalized analytical expression for the effectiveness factor. analytical relationships are not generally possible for reaction orders different from one. However, Petersen[3] suggested the use of the analytical expression for first order reactions provided the Thiele modulus (h) is replaced by the asymptotic value of ($1/\eta$) when $h \to \infty$. Moreover, after Rester *et al.*[4], and Rester and Aris[5], the simple results obtained in slab geometry can be used for other geometrical shapes with a maximum deviation of 16%, in the case of first order isothermal reactions, provided the Thiele modulus has been properly defined regarding the characteristic length (see Aris[6]).

The puppose of this contribution is to investigate the possibility of existence of a generalized expression for the effectiveness factor for isothermal reaction in porous slab pellets. No other restrictions will be invoked. Since thermal conductivity of catalyst pellets is ordinarily very much higher than the effective diffusivity, the isothermal restriction is not too serious. The analysis of the pellet shape on the existence of a generalized expression will be presented in a future work.

Main results are presented for a reaction of the type $A + \nu B \rightleftharpoons O_P$ but they can be extended very easily to other types of reactions. Basically, the method used to obtain this general expression is rather simple. First, asymptotic analytical expressions for η, at low and high values of the Thiele modulus, are obtained and then they are matched. The resulting analytical expression should produce reasonable estimates of η valid over the full range of the Thiele modulus values. In fact, when these results are compared with numerical values, obtained after solving the corresponding non linear differential equations, a fairly good correlation is found, with a maximum deviation to the order of 3%, exept for very few particular cases.

Finally, it is shown, with a simple example, how to extend our results to other situations in which external mass transfer resistances are to be considered.

ANALYSIS

Let us consider the problem of estimating the effectiveness factor in an isothermal porous slab in which species A, B, C and D diffuse and simultaneously react according to the following stoichiometry:

$$\sum_{i=1} \nu_i S_i = 0 \tag{1}$$

where S_i represents any of the species in a given order and ν_i, the corresponding stoichiometric coefficient. It is

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clearly assumed that a single independent reaction occurs in this system. It will be further assumed that species A is so chosen in eqn (1) that its ν_i will be (-1). The dimensional concentration of any of the species in the bulk of the fluid phase will be denoted by C'_0 while its corresponding value at the pellet surface will be C'_S. To illustrate our procedure, firstly it will be assumed that $C'_0 = C'_S$ for all components of the reacting system, thus neglecting the effect of any external mass transfer resistance; and secondly, that the rate of reaction in the pseudo homogeneous system can be expressed as a power of the concentration of the reacting species. Both restrictions will be analyzed later on by considering the effect of external mass transfer resistances and by also consideing other types of expressions for the rate of reactions such as the Langmuir–Hinshelwood type.

Thus, the rate of reaction per unit volume will be given by the following expression:

$$r_v = k\left(C'_A{}^m C'_B{}^b - \frac{1}{K} C'_C{}^c C'_D{}^d\right) \qquad (2)$$

where K is the equlibrium thermodynamic constant and k the specific rate for the forward reaction. C' being the actual concentration inside the pellet and m, b, c and d the orders of reactions for species A, B, C and D respectively. The dimensionless rate of reaction can be obtained by dividing eqn (2) by its surface value:

$$r_v^* \equiv (r_v/r_{vs}) = C_A{}^m C_B{}^b\left\{1 - \frac{1}{K'}(C_C{}^c C_D{}^d/C_A{}^m C_B{}^b)\right\}$$
$$\times \left[\frac{K'-1}{K'}\right]^{-1} \qquad (3)$$

where

$$K' \equiv K[C'_A{}^m C'_B{}^b/C'_C{}^c C'_D{}^d]_S. \qquad (4)$$

S denotes the surface value of the quantity in the brackets. Clearly, the dimensionless concentration of any of the species C_i has been defined by:

$$C_i \equiv (C'_i/C'_{iS}). \qquad (5)$$

For eqn (3) to be thermodynamically consistent, K' must be subject to the following condition:

$$K'[C_C{}^c C_D{}^d/C_A{}^m C_B{}^b]_{eq} \qquad (6)$$

where the suffix equation denotes the equilibrium value.

Taking into account previous assumptions and considering unidirectional diffusion flow in the absence of a pressure gradient, surface transport and steady state conditions the dimensionless mass balance for each species in the porous slab, can be written, by the following expression:

$$\frac{d^2 C_i}{dx^2} = h^2 \gamma_i r_v^* \qquad (7)$$

where the subindex i applies for any species (A, B, C

and D), x being the dimensionless normalized distance measured from the surface and:

$$h^2 \equiv (r_{v_s} L^2/D_A C'_{A_s})$$
$$\gamma_i \equiv -\frac{D_A}{D_i}\left(\frac{C'_A}{C'_i}\right)_s \nu_i. \qquad (9)$$

D_i being the effective diffusivity coefficient, and L the half thickness of the slab. It must be stressed that $\nu_A = -1$ was assumed.

Equations (7) are subject to the following boundary conditions:

$$C_i(0) = 1; \quad (dC_i/dx) = 0 \quad \text{at} \quad x = 1. \qquad (10a,b)$$

It is clear that A was chosen as a key component since $\gamma_A \equiv 1$. Moreover, the actual key component must be chosen in such a way that $\gamma_B < 1$; otherwise, species B must be taken as key component

$$\eta \equiv \int_0^1 r_v^* \, dx = -\frac{1}{h^2}\left(\frac{dC_A}{dx}\right)_{x=0} \qquad (11)$$

according to mass balance (eqn 7) for species A and boundary conditions (10b). Concentrations of species B, C and D can now be rewritten in terms of C_A:

$$C_i = \gamma_i(C_A - 1 + \gamma_i^{-1}) = \gamma_i(C_A - \Gamma_i). \qquad (12)$$

It should be noted that since, by definition, γ_C and γ_D are negative values, there is no restriction on their absolute values since C_C and C_D are always greater than zero. By replacing eqn (12) in eqn (3) and the resulting expression in the corresponding mass balance for component A:

$$\frac{d^2 C_A}{dx^2} = h^2\left[\frac{K'-1}{K'}\right]^{-1} C_A{}^m (C_A - \Gamma_B)^b \gamma_B{}^b$$
$$\times \left\{1 - \frac{(C_A - \Gamma_C)^c (C_A - \Gamma_D)^d}{K^* C_A{}^m (C_A - \Gamma_B)^b}\right\} \qquad (13)$$

with

$$K^* \equiv K' \gamma_B{}^b \gamma_C{}^{-c} \gamma_D{}^{-d}. \qquad (14)$$

At first sight, the solution to eqn (13) seems a very difficult task. However, it would be easy to solve it by perturbation methods when parameter h is either small or large. In fact, when $h^2 \to 0$, eqn (13) suggests itself the following series as solution:

$$C_A = A_0(x) + h^2 A_1(x) + h^4 A_2(x) + \cdots. \qquad (15)$$

By replacing eqn (15) in eqn (13) and by equating terms of like powers of h, it can be shown that up to terms of h^4, $A_0(x)$, $A_1(x)$ and $A_2(x)$ must satisfy the following uncoupled system:

$$\frac{d^2 A_0}{dx^2} = 0 \qquad (16)$$

$$\frac{d^2A_1}{dx^2} = \left[\frac{(K'-1)}{K'}\right]^{-1} A_0^m (A_0 - \Gamma_B)^b \gamma_B^b$$

$$\left\{1 - \frac{(A_0 - \Gamma_C)^c (A_0 - \Gamma_D)^d}{K^*(A_0 - \Gamma_B)^b A_0^m}\right\} \qquad (17)$$

$$\frac{d^2A_2}{dx^2} = \left[\frac{(K'-1)}{K'}\right]^{-1} \gamma_B^2 A_1 \left\{m A_0^{m-1}(A_0 - \Gamma_B)^b\right.$$

$$+ b A_0^m (A_0 - \Gamma_B)^{b-1}$$

$$- \frac{1}{K^*} (d(A_0 - \Gamma_C)^c (A_0 - \Gamma_D)^{d-1}$$

$$\left. + c(A_0 - \Gamma_C)^{c-1}(A_0 - \Gamma_D)^d)\right\} \qquad (18)$$

subject to the following conditions:

$$A_0(0) = 1; \qquad A_1(0) = A_2(0) = 0 \qquad (19a,b)$$

$$\frac{dA_0}{dx} = \frac{dA_1}{dx} = \frac{dA_2}{dx} = 0 \quad \text{at} \quad x = 1.$$

The analytical solutions to A_0, A_1 and A_2 are so simple that need not to be written. However, since $A_0 = 1$, the effectiveness factor up to term of h^2 results to be:

$$\eta = 1 - \beta_1 h^2 + 0(h^4) \qquad (20)$$

where

$$\beta_1 = \frac{1}{3} \left[\frac{K'-1}{K'}\right]^{-1} \left\{m + b\gamma_B - \frac{1}{K'} (c\gamma_C + d\gamma_D)\right\}. \qquad (21)$$

On the other hand, when $h \to \infty$ the reaction rate is so large that equilibrium concentration is reached at the center of the porous slab and the effectiveness factor can be easily calculated applying the Bishoff[7] transformation. Thus

$$\eta = \frac{\alpha}{h} + 0\left(\frac{1}{h^3}\right) \qquad (22)$$

where

$$\alpha = \left\{2 \frac{(K'-1)}{K'} \int_{C_{Aeq}}^{1} r_v^* dC_A\right\}^{1/2}. \qquad (23)$$

C_{Aeq} being the equilibrium concentration of species A which, according to eqn (6), must be the algebraic solution to:

$$C_{Aeq}^m (C_{Aeq} - \Gamma_B)^b = \frac{1}{K'} (C_{Aeq} - \Gamma_C)^c (C_{Aeq} - \Gamma_D)^d. \qquad (24)$$

In order to match expressions (20) and (22), valid for small and large values of h respectively, the following expression for η is proposed:

$$\eta = a \frac{(r + h^2)^{1/2}}{(s + h^2)}. \qquad (25)$$

In fact, by expanding eqn (25) when $h^2 \to 0$ it is found

that:

$$\eta = ar^{1/2}s^{-1} + a\left(\frac{1}{2}r^{-1/2}s^{-1} - r^{1/2}s^{-2}\right)h^2 + 0(h^4) \qquad (26)$$

while

$$\eta = ah^{-1} + 0(h^{-3}) \qquad (27)$$

when $h^2 \to \infty$. By comparing eqns (26) and (27) with eqns (20) and (22) respectively, the coefficients a, r and s must satisfy the following set of algebraic equations:

$$ar^{1/2}s^{-1} = 1; \quad a\left(\frac{1}{2}r^{-1/2}s^{-1} - r^{1/2}s^{-2}\right) = -\beta_1; \quad a = \alpha. \qquad (28a,b,c)$$

Thus

$$r = (s/\alpha)^2; \quad s = \frac{1}{2\beta_1}\{1 \pm \sqrt{(1 - 2\alpha^2\beta_1)}\}. \quad (29a,b)$$

In this general form a, r and s can be calculated from the coefficients deduced by the asymptotic expressions of η. In order to check the validity of the general expressions (25), specific cases must be analyzed.

SPECIFIC CASES

(1) *Irreversible reactions* $(K' \to \infty)$
    (1a)

$$b = 0; \quad \beta_1 = \frac{1}{3}m; \quad \alpha = \left(\frac{2}{m+1}\right)^{1/2}$$

$$s = \frac{3}{2m}\left\{1 + \sqrt{\left(1 - \frac{4}{3}\left(\frac{m}{m+1}\right)\right)}\right\}.$$

It was found that the positive root produces much better results than the negative one. A solution will exist provided $m \leq 3$, otherwise s should be iminigary. However, $m > 3$ is not a case of interest. Table 1 shows some of the results obtained compared with numerical estimates of $\eta(\eta_N)$ as a function of h. The results for $h < 0.5$ are not presented since the deviations are, in all cases investigated, extremely small. For comparison purposes, in Table 1 values of η_T given by:

$$\eta_T = \tanh(h/\alpha)/(h/\alpha) \qquad (30)$$

are also presented. It can be concluded that eqn (25) gives extremely good results when $m \geq 1$ and they are even better than those given by the empirical eqns (30) as proposed by Petersen[3]. However, when $m = 0.5$, it can be seen that for $h < 2$, our proposed expression gives very accurate results, much better than those given by eqn (30), while the situation is inverted for $h > 2$. For practical purposes, it can be concluded that our proposed expression can be safely used for all range of values of h when $m \geq 0.5$. However, when $m < 0.5$, it should only be used for $h < 1$. Under these conditions, it produces

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Table 1.

m	0.5			1.0			1.5			2.0			3.0		
h \ η	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T
0.5	0.9602	0.9600	0.9419	0.9244	0.9242	0.9242	0.8925	0.8926	0.9074	0.8641	0.8644	0.8913	0.8165	0.8180	0.8611
0.8	0.9048	0.9000	0.8657	0.8309	0.8300	0.8300	0.7735	0.7766	0.7978	0.7283	0.7328	0.7685	0.6623	0.6641	0.7173
1.0	0.8598	0.8495	0.8075	0.7631	0.7616	0.7616	0.6952	0.6996	0.7217	0.6455	0.6525	0.6867	0.5▮	5830	0.6282
1.5	0.7367	0.7062	0.6632	0.6069	0.6034	0.6034	0.5337	0.5400	0.5560	0.4865	0.4951	0.5174	0.42▮	4324	0.4580
2.0	0.6196	0.5774	0.5423	0.4866	0.4820	0.4820	0.4224	0.4313	0.4371	0.3830	0.3900	0.4022	0.333▮	.3364	0.3511
4.0	0.3288	0.2890	0.2883	0.2530	0.2498	0.2498	0.2212	0.2230	0.2235	0.2009	0.2032	0.2041	0.1▮	1757	0.1768

estimates of η, which are generally better than those given by empirical expression (30).

(1b) $b \neq 0$

$$b = 1 \quad \alpha = 2\left\{\frac{(1-\gamma_B)}{m+1}+\frac{\gamma_B}{m+2}\right\}^{1/2}$$

$$b = 2 \quad \alpha = \sqrt{(2)}\left\{\frac{(1-\gamma_B)^2}{(m+1)}+\frac{2\gamma_B}{m+2}(1-\gamma_B)+\frac{\gamma_B^2}{m+3}\right\}^{1/2}$$

$$b \neq 1 \quad \text{or} \quad 2$$

$$\gamma_B \leq 0.3 \quad \alpha = \sqrt{(2)}\left\{\frac{1-b\gamma_B+b(b-1)\gamma_B^2/2}{m+1}\right.$$
$$\left.+\frac{b\gamma_B}{m+2}(1-(b-1)\gamma_B)+\frac{b(b-1)\gamma_B^2}{2(m+3)}\right\}^{1/2}.$$

The following cases were investigated: $m=1$, $b=1$, $\gamma_B=[0.3;0.5;0.8]$; $m=2$, $b=1$, $\gamma_B=[0.3;0.5;0.8]$; $m=0.5$, $b=1$, $\gamma_B=[0.3;0.5;0.8]$; $m=0.5$, $b=0.5$, $\gamma_B=0.5$. In all cases the deviations among approximate and numerical results were very small (maximum 3%) as can be seen in Table 2 for $\gamma_B=0.5$, and values of η esti-

Table 2.

m;b	0.5 ; 0.5			0.5 ; 1.0			1.0 ; 1.0			2.0 ; 1.0		
h \ η	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T
0.5	0.9419	0.9412	0.9354	0.9245	0.9254	0.9286	0.8927	0.8948	0.9107	0.8393	0.8412	0.8780
0.8	0.8657	0.8648	0.8524	0.8315	0.8352	0.8386	0.7745	0.7797	0.8040	0.6934	0.6997	0.7455
1.0	0.8074	0.8057	0.7902	0.7629	0.7683	0.7725	0.6969	0.7040	0.7293	0.6094	0.6170	0.6600
1.5	0.6625	0.6596	0.6399	0.6098	0.6153	0.6170	0.5369	0.5462	0.5647	0.4551	0.4631	0.4895
2.0	0.5408	0.5332	0.5183	0.4910	0.4943	0.4953	0.4263	0.4350	0.4452	0.3575	0.3638	0.3779
4.0	0.2830	0.2799	0.2724	0.2585	0.2578	0.2580	0.2248	0.2263	0.2282	0.1877	0.1886	0.1909

$\gamma_B = 0.5$

mated by eqn (25) much better coincide with the exact results than those calculated by eqn (30). Incidentally, it should be noted that the case $m = 1$; $b = 1$ was previously analyzed by Cunningham and Maymo[8]. According to their work, η should depend upon at least three parameters. However our analysis quite clearly shows that η can only depend upon h and γ_B. In fact, their graphs can be joined all together in a single one, except that which refers to the reversible case.

(2) Reversible reactions

In this case it is very difficult to obtain analytical values of η, mainly due to the lower limits of integration (see eqn (24). In the simplest case of first order reversible reaction it can be shown that ($m = 1$, $b = 0$, $c = 1$, $d = 0$):

$$\beta_1 = \frac{1}{3}\frac{(K' - \gamma_C)}{(K' - 1)} \tag{31}$$

and

$$\alpha = \left[\frac{(K' - 1)}{(K' - \gamma_C)}\right]^{1/2}. \tag{32}$$

These results suggest a redefinition of h under the following modified form:

$$h_m = h\left(\frac{K' - \gamma_C}{(K' - 1)}\right)^{1/2} \tag{33}$$

so that the resulting expressions for β_1, α and so for η are exactly the same as those for first order irreversible reactions if h_m is used instead of h. The analytical expression for η in this case will be:

$$\eta = \tanh (h_m)/h_m. \tag{34}$$

Thus, deviations between approximate and exact results will be the same as those deduced from Table 1 for the case $m = 1$.

Some calculations made by the authors for the case $m = b = c = d = 1$ revealed that the observed deviations between numerical and approximate results are of the same order of magnitude as for the irreversible case $m = 1$, $b = 1$ (maximum deviation less than 3%).

(3) Langmuir–Hinshelwood kinetic expression

Robert and Satterfield[9] have shown that these kind of kinetic expressions can be classified in two main classes. One of them behaves in such a way that η can be even greater than 1. This case cannot be represented by our simple eqn (25). In fact, it would be necessary a second term which implies further terms in both asymptotic expressions, as will be shown in a future work. However, for the case $b = 0$, $m = 1$ and $K \to \infty$ the second class leads to the following dimensionless kinetic expression:

$$r_v^* = \frac{C_A(1 + K_1)}{(1 + K_1 C_A)} \tag{35}$$

where K_1 is the characteristic parameter of the system

which can take any value between $-0.98 < K_1 < \infty$. Negative values are intended to explain the depression in the actual reaction rate caused by products which can be absorbed at the catalyst's surface. In this case, it can be shown, following the above described procedure, that the asymptotic expressions for η are:

$$\eta = 1 - \frac{1}{3}h_1{}^2 + 0(h_1)^4 \tag{36}$$

when $h_1 \to 0$ and

$$\eta = \left[\frac{2}{K_1}\left(1 - \frac{\ln(1 + K_1)}{K_1}\right)\right]^{1/2}\frac{1}{h_1} + 0\left(\frac{1}{h_1{}^3}\right) \tag{37}$$

where $h_1 \to \infty$; where

$$h_1 \equiv h/(1 + K_1)^{1/2}. \tag{38}$$

Thus, if eqns (36) and (37) are matched with:

$$\eta = a_1\frac{(r_1 + h_1{}^2)^{1/2}}{(s_1 + h_1{}^2)} \tag{39}$$

the following relation for a_1, r_1 and s_1 results:

$$a_1 = \left(\frac{2}{K_1}\left(1 - \frac{\ln(1 + K_1)}{K_1}\right)\right)^{1/2} \tag{40}$$

$$s_1 = \frac{3}{2}\left\{1 \pm \sqrt{\left(1 - \frac{2}{3}a_1{}^2\right)}\right\} \tag{41}$$

$$r_1 = (s_1/a_1)^2. \tag{42}$$

In Table 3, values of η calculated with eqn (39) are compared with numerical values obtained by solving the corresponding differential equation and also with values of η generated by eqn (30). In this case η^* was calculated using values of s_1 with the negative root of the discriminant. Clearly, when $K_1 \leqslant 1$, a fair agreement is found among numerical and approximate results and the general procedure can be safely used. However, when $K_1 > 1$, eqn (30) or eqn (39) could give reasonable results if, in this last case, the negative value of the discriminant is used.

(4) Mass transfer external resistances

When $C'_{i0} \neq C'_{is}$, the effectiveness factor calculated with boundary conditions $C'_i = C'_{is}$ at the surface must be corrected, and according to its definition:

$$\eta = \eta_s(r'_{vs}/r'_{v0}) \tag{43}$$

where η_s is the value of η estimated as a function of h as defined by eqn (8). However, the mass balance at the surface for each component can be written in the following dimensionless form as:

$$B_i\left(\frac{C'_{i0}}{C'_{is}} - 1\right) = \gamma_i h^2 \eta_s. \tag{44}$$

B_i being the Biot number for component i ($B_i =$

Table 3.

η\h	K_1 = 0.5			1.0			5.0			η^*
	η_A	η_N	η_T	η_A	η_N	η_T	η_A	η_N	η_T	
0.1	0.9974	0.9968	0.9971	0.9983	0.9970	0.9973	0.9994	0.9970	0.9978	0.9995
0.4	0.9658	0.9638	0.9555	0.9741	0.9650	0.9587	0.9912	0.9875	0.9667	0.9800
0.8	0.8778	0.8695	0.8465	0.8969	0.8922	0.8561	0.9658	0.9609	0.8812	0.8844
1.0	0.8232	0.8058	0.7825	0.8596	0.8350	0.7950	0.9475	0.9250	0.8281	0.8194
2.0	0.5599	0.5183	0.5082	0.6179	0.5539	0.5248	0.8196	0.6207	0.5729	0.5430
5.0	0.2276	0.2130	0.2130	0.2531	0.2216	0.2215	0.4332	0.2482	0.2480	0.2425

$k_{Li} L/D_i$). Equation (44) represents a set of algebraic equations which must be solved simultaneously to find the ratio (C'_{io}/C'_{is}) for each component. Once it is solved, the true value of η can be found with the help of eqn (43).

To solve the system given by eqn (44) some trial and error procedure must be used, since h^2 is not known. Let us take as an example the case of an irreversible reaction of order $(m, 0)$. In this case eqn (44) can be written as:

$$\left(\frac{C'_{A0}}{C'_{As}}\right) = \frac{h^2}{B_i} a \frac{(r+h^2)^{1/2}}{(s+h^2)} + 1. \tag{45}$$

As data we, only have values of B_i and h_0, that is the value of the Thiele modulus evaluated a bulk gas phase conditions. Taking into account the definition of h:

$$h^2 = h_0^2 \left(\frac{r'_{vs} C'_{A0}}{r_{v0} C'_{As}}\right) = h_0^2 (C'_{As}/C'_{A0})^{m-1}. \tag{46}$$

Replacing eqn (46) in eqn (45):

$$\frac{C'_{A0}}{C'_{As}} = 1 + \left(\frac{h_0^2}{B_i} a\right) \left(\frac{C'_{As}}{C'_{A0}}\right)^{m-1} \frac{(r+h_0^2(C'_{As}/C'_{A0})^{m-1})^{1/2}}{(s+h_0^2(C'_{As}/C'_{A0})^{m-1})}. \tag{47}$$

Thus, for each pair of values of h_0 and B_i, (C'_{A0}/C'_{As}) can be solved once the order of reaction is fixed. Then, the corrected true value of η can be calculated from eqn (43).

$$\eta = \eta_s \left(\frac{C'_{As}}{C'_{A0}}\right)^m. \tag{48}$$

Figure 1 shows the results that can be obtained for a second order irreversible reaction. Since the basic expression used for estimating η_s is almost exact (2% maximum deviation), the new values of η should only have a maximum deviation of 2% from their true values.

CONCLUSIONS

A new approach to estimate the effectiveness factor of a single reaction in a slab isothermal catalyst is presented. The method assumes that asymptotic expressions for η, valid at small and large values of the Thiele modulus, can be matched with a unique and simple algebraic expression with only three free coefficients. These coefficients, however, must satisfy a set of three algebraic equations, so that their values are finally determined as a function of the parameter derived from η asymptotic expressions.

When the results so obtained are compared with the corresponding values of η calculated by numerical methods an extremely good agreement is found.

The theoretical analysis was presented for a general kinetic expression of the power law type but it is shown that it can be also used with other type of kinetic expressions. Its unique limitation, is that the results are valid provided the order of the reactive species is greater than 0.5 approximately. A more severe limitation arises when a Langmuir–Hinshelwood kinetic expression is tested. Nevertheless, provided the modified dimension less absorption constant is not too high ($K_i \leqslant 1$) a fair agreement between approximate and numerical results is found.

It can also be concluded that the final expression produces results as good as those obtained by the Petersen[3] criterion which suggests the use of first order analytical expressions with a modified Thiele modulus. However it must be noted that our proposed expressions follows the differences in η vs h curves caused by the effect of reaction order. In fact it is shown that it is impossible to fit with a unique curve (e.g. unique parameter) all the cases. Since the final expression is accurate and simple, the case of external mass transfer resistance can be very easily solved as shown with an example. However, an outstanding feature of this method is the possibility to use it for the analysis of
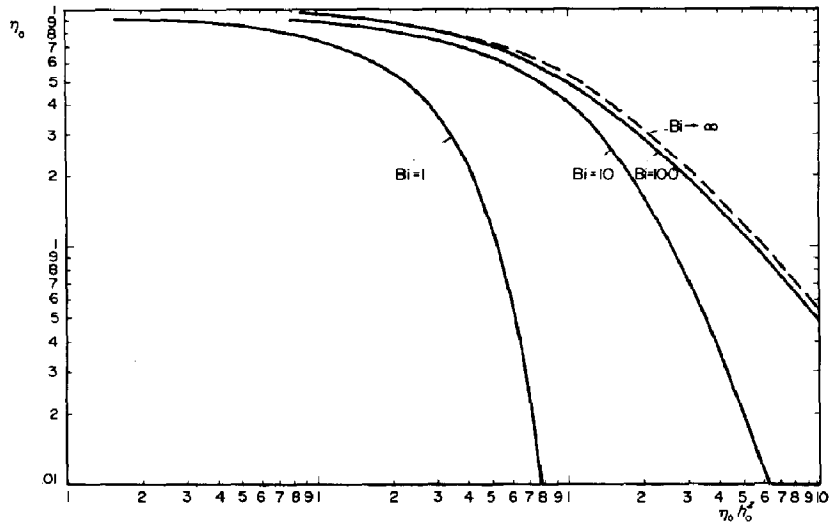
Fig. 1. Effectiveness factor (η) for second order irreversible reactor in an isothermal flat pellet as function of ηh_0^2 with Biot number (Bi) as parameter.

more complex situations such as activity distribution inside the porous pellets, dependence of kinetic parameters, such as diffusivity coefficients, with position or concentration, and finally the analysis of selectivity when more than a single reaction can take place inside the pellets. Another important feature is its simplicity, which renders it suitable for programmed reactor design since once the kinetic expression is know. η can be evaluated step by step through an algebraic equation.

In future works other situations will be analyzed with the purpose to investigate the effect of the geometrical shape of the pellet and its activity distribution in the final expression of η.

Finally, it can be concluded that a unique general expression of η, valid for any reaction order in a slab catalyst, is not possible. In fact, for this to be true the product sa^2 must be equal to one and, in all cases investigated in this work, sa^2 was always greater than 1.3 approximately.

NOTATION

a	parameter defined by eqn (25)
b	order of reaction for species B
B_i	Biot number ($k_{Li} L/D_i$)
c	order of reaction for species C
C'	dimensional concentration
C	dimensionless concentration
d	order of reaction for species D
D	effective diffusivity coefficient
h	Thiele Modulus defined by eqn (8)
h_m	modified Thiele Modulus
k	specific rate for the forward reaction
K_L	mass transfer coefficient
K	equilibrium thermodynamic constant

K'	parameter defined by eqn (4)
K_1	parameter defined by eqn (35)
L	half thickness of slab
m	order of reaction for species A
r	parameter defined by eqn (25)
r_v	rate of reaction per unit volume
r_v^*	dimensionless rate of reaction
s	parameter defined by eqn (25)
x	dimensionless normalized distance measured from the surface

Greek symbols

α	parameter defined by eqn (23)
β_1	parameter defined by eqn (21)
γ	parameter defined by eqn (9)
Γ	parameter defined by eqn (12)
η	effectiveness factor
ν	stoichiometric coefficient

Subindexes

eq	equilibrium value
i	refer to species A, B, C or D
0	bulk fluid phase value
s	surface value

REFERENCES

[1] Churchill S. W., *A.I.Ch.E.J.* 1977 **23** 208.
[2] Aris R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts.* Oxford University Press, London 1975.
[3] Petersen E. E., *Chem. Engng Sci.* 1965 **20** 587.
[4] Rester S., Jouven J. and Aris R., *Chem. Engng Sci.* 1969 **24** 1019.
[5] Rester S. and Aris R., *Chem. Engng Sci.* 1969 **24** 793.
[6] Aris R., *Chem. Engng Sci.* 1956/57 **6** 262.
[7] Bishoff K. B., *A.I.Ch.E.J.* 1965 **11** 351.
[8] Maymó J. A. and Cunningham R. E., *J. Catal.* 1966 **6** 186.
[9] Robert G. W. and Satterfield D., *Ind. Engng Chem. Fundls* 1965 **4** 288.