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APPROXIMATE EFFECTIVENESS FACTOR ESTIMATION FOR WAVE SHELL CATALYST

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The estimation of effectiveness factor for the case of wave shell catalyst is attempted through an approximated procedure developed by the authors for other kind of catalytic pellets. It is shown that the approximate scheme can be used even with this kind of important catalysts and that the results so obtained are very accurate. The analysis is only restricted to the case of single reaction although it can be used even for those cases where non-isothermal conditions could prevail. The estimation avoid the solution of the governing mass and heat balance differential equations by numerical procedures. Finally a set of algebraic equations must be solved through an iterative scheme which is illustrated for the case of isothermal systems.
KEYWORDS Effectiveness factor Wave shell catalyst Catalysis.

INTRODUCTION

In a recent contribution Papa and Shah[1] presented an approximate expression to estimate the effectiveness factor (η) for the specific case of a bimolecular L-H intrinsic kinetics equation in a shell square wave catalyst pellet. Their expression was

$$\eta_\rho = \tanh(\Phi)/\Phi \tag{1}$$

where Φ stands for a suitable modified Thiele modulus which takes into account internal and external mass diffusion limitation and which was deduced from the asymptotic behavior of the system when $\Phi \gg 1$. It must be stressed however that Eq. (1) was first adopted by Petersen[2] in an attempt to produce very rough estimations of η values for non-linear kinetic equations. It follows naturally from the analytical expression derived for first order reaction in slab geometry. The error due to using Eq. (1) can be as higher as 30% in the mixed control regime when the apparent reaction order approaches zero. However it is quite clear that Eq. (1) will not be able to predict η values greater than one as in the case of bimolecular L-H kinetics equations as shown by Satterfield.[3]

In the early 80's Gottifredi[4] *et al* presented a rather simple procedure to build up a suitable expression to estimate η values but where the involved coefficients must be determined from the asymptotic solutions of the governing differential mass and heat balance equations valid for low and large values of the corresponding Thiele modulus (h). Moreover it was shown that this procedure

was able to predict η values greater than one. Although the technique takes into account the case of non-uniform catalyst activity inside the pellet, the particular case where discontinuities arise and where a portion of the catalyst pellet near the surface is not active such the case of wave shell catalyst pellet, were not investigated.

The purpose of this contribution is to extend our previous finding, which have been used with success to the case of wave shell like catalytic pellet due to the increasing importance of these type of catalyst. On the other hand, there is a recognized need to predict η with great accuracy due to important improvements in the field of theoretical estimation of transport parameters and also on the experimental determination of intrinsic kinetic parameters. Quick and accurate predictions of η allow reliable reactor calculations and on time control design.

THEORY

It will be assumed that the active phase is supported on a shell located in some region within the pellet ($x_i \leq x \leq x_P$) that the intrinsic kinetic expression can be expressed as a function of the concentration of the key component (unique reaction) and temperature. The dimensionless mass and energy balances can be written in the following fashion

$$\frac{d}{dx}\left(x^n \frac{dC}{dx}\right) = h^2 R(C, T) x^n f(x)$$
$$\frac{d}{dx}\left(x^n \frac{dT}{dx}\right) = \beta h^2 R(C, T) x^n f(x) \qquad (2a,b)$$

to consider the particle shape ($n = 0,1,2$ slab, cylindrical and spherical geometry respectively) and where

$$C = (C'/C'_b); \quad T = (T'/T'_b); \quad R(C, T) = r(C', T')/r(C'_b, T'_b)$$
$$\beta = D_{\text{eff}} C'_b(-\Delta H)/(K_{\text{eff}} T'_b); \quad h^2 = (r(C'_b, T'_b)/C'_b) L^2/D_{\text{eff}} \qquad (3a,b,c,d,e)$$

D_{eff} and K_{eff} being the effective diffusivity and thermal conductivity of the pellet. r the dimensional rate of reaction, L the characteristic dimension of the particle and the primes to denote dimensional variables $f(x)$ denotes the catalytic activity distribution inside the shell which can be uniform in this region or being a given function of the position. The usual case on square wave shell catalyst is

$$f(x) = \delta \quad (x_i \leq x \leq x_P) \qquad (4)$$

and $f(x) = 0$ elsewhere. However the assumption of constant load to compare results requires

$$(n+1) \int_0^1 x^n f(x)\, dx = 1 = \delta(x_P^{n+1} - x_i^{n+1}) \qquad (5)$$

Nevertheless in a more general case δ, in Eq. (4), can also be taken as a given function of x when required without any extra effort.

It should be noticed that Eqs. (2a, b) must be solved subject to the following

conditions:

$$C = C_P; \qquad T = T_P \quad \text{at} \quad x = x_P$$
$$\frac{dC}{dx} = \frac{dT}{dx} = 0 \qquad \text{at } x = x_i \tag{6a,b}$$

Under these circumstances as usual, it can be shown that

$$T = T_P + \beta(C_P - C) \tag{7}$$

By replacing this expression into $R(C, T)$ the dimensionless rate of reaction becomes a general function of C, C_p and T_P, namely $R(C, C_P, T_P)$. On the other hand in the outer region ($x_P \leq x \leq 1$) there will be no reaction so that

$$x_P^n \frac{dC}{dx}\bigg|_{x_P} = \frac{B_i(1 - C_P)}{(1 + \lambda B_i)}$$
$$x_P^n \frac{dT}{dx}\bigg|_{x_p} = -\beta x_P^n \frac{dC}{dx}\bigg|_{x_P} = \frac{Bi_e(1 - T_P)}{(1 + \lambda Bi_e)} \tag{8a,b}$$

where

$$\lambda = \int_{x_P}^{1} x^{-n}\, dx \tag{9}$$

$$Bi = k_g L/D_{\text{eff}}; \qquad Bi_e = h_e L/K_{\text{eff}} \tag{10a,b}$$

k_g and h being the mass and heat transfer film coefficients are Bi and Bi_e the Biot numbers for mass and heat transfer defined in relation to the effective diffusivity and thermal conductivity respectively. These equations will be used to estimate η since

$$\eta = \frac{(n+1)}{h^2} x_p^n \frac{dC}{dx}\bigg|_{x_P} \tag{11}$$

In the reaction shell when $h \ll 1$ a general asymptotic series solution can be assumed

$$C = C_P(1 + A_1(x)h^2 + A_2(x)h^4 + O(h^6) \tag{12}$$

which after being replaced into Eq. (2a), equating terms of like power of h and solving leads to

$$(n+1)x_0^n \frac{dC}{dx}\bigg|_{x_P} = R_P\{h^2 - R'_P \alpha h^4 + O(h^6)\} \tag{13}$$

where R_P and R'_P denote the dimensionless rate of reaction derivative with respect to C evaluate at $C = C_P$, $T = T_P$, and

$$\alpha = (n+1) \int_{X_i}^{X_P} x^{-n} \left(\int_{X_i}^{X} \epsilon^n f(\epsilon)\, d\epsilon \right)^2 dx \tag{14}$$

On the other hand when $h \gg 1$ the classical asymptotic solution can be found for this particular case following the same procedure of Bishoff[6] resulting:

$$\frac{dC}{dx}\bigg|_{x_P} = \left(2f(x_P) \int_0^{C_P} R(C)\, dC \right)^{1/2} h = \sigma h R_P \tag{15}$$

A suitable expression to match Eqs. (13) and (15) was proposed by Gottifredi[6] *et al.* It can be shown that:

$$\eta = (h_M^2 + \exp(-ah_M^2))^{-1/2} R_P \tag{16}$$

where

$$h_M = ((n+1)x_P^n \sigma)^{-1} h \tag{17}$$

and the parameter "a" is given by

$$a = 1 - 2\alpha R_P'(\sigma(n+1)x_P^n)^2 \tag{18}$$

By combining Eqs. (8), (11) and (16) the following relations are derived

$$(1 + \lambda Bi_e)\{h_M^2 + \exp(-ah_M^2)\}^{-1/2} R_P h^2 = (n+1)Bi(1 - C_P) \tag{19}$$

$$-\beta(1 + \lambda Bi_e)\{h_M^2 + \exp(-ah_M^2)\}^{-1/2} R_P h^2 = (n+1)Bi_e(1 - T_P) \tag{20}$$

and the values of C_P, and T_P for any particular set of parameters, can be easily estimated by a suitable trial and error procedure. The final solution can be found with great precision with no more than two or three trials unless the initial guess are too far from the true value. Along the reactor this will not be the case since the previous value on the grid can be used as first guess. Nevertheless when $h \leq 1$ a good initial guess could be $C_P = T_P = 1$. When isothermal conditions are considered it was found most convenient, for increasing convergence to use the following scheme:

$$C_P(i+1) = (n+1)B_i/((n+1)B_i + V(C_P(i)) \tag{21}$$

where

$$V = (1 + \lambda B_i)\{h_M^2 + \exp(-ah_M^2)\}^{-1/2} h^2 R(C_P)/C_P \tag{22}$$

"i" being the internal counter for the iteration procedure. When non-isothermal conditions are met a double iteration technique is involved but after two or three iterations desirable results are obtained as shown by Gonzo and Gottifredi.[8]

It must be stressed that the method presented here is more general than Papa and Shah[1] previous contribution. It can be used for any geometrical shape regardless of the intrinsic kinetics equation and of the activity distribution function. Moreover it can be used in those cases where non-isothermal conditions prevail. It can be seen that η values greater than one are not precluded as in the case of Papa and Shah.[1] The necessary (not sufficient) condition for such a case is $a > 1$ which implies $R_P' < 0$. In fact this case should have been met by Papa and Shah[1] since their kinetic equation was

$$R(C) = (1 + \gamma)^2 C/(1 + \gamma C)^2 \tag{23}$$

even if isothermal conditions were considered.

DISCUSSION OF RESULTS

A comparison of the obtained results for first order isothermal reaction is presented in Table I for slab ($n = 0$) and spherical ($n = 2$) geometries for $Bi = 1$.

TABLE I

Comparison of the effectiveness factor values for first order reaction

	$n=0$			$n=2$		
h^2	η_P	η_A	η_E	η_P	η_A	η_E
0.1	0.9970	0.9063	0.9063	0.9974	0.9667	0.9667
0.3	0.9319	0.7634	0.7634	0.9876	0.9064	0.9064
0.5	0.8564	0.6594	0.6594	0.9732	0.8531	0.8531
0.7	0.7746	0.5803	0.5803	0.9552	0.8058	0.8058
1.0	0.6588	0.4919	0.4919	0.9228	0.7438	0.7438
2.0	0.4032	0.3262	0.3262	0.7926	0.5922	0.5922
4.0	0.2161	0.1949	0.1949	0.5374	0.4089	0.4088
10.1	0.0901	0.0876	0.0876	0.2531	0.2218	0.2217

Conditions: $B_i = 1$; $x_P = 1.0$; $x_i = 0.9$; $\gamma = 1$.

It is clearly seen that our approximate results (η_A) are extremely accurate when compared with exact values (η_E) derived from analytical solution in the case of square wave catalyst pellet located on the surface ($x_P = 1$, $x_i = 0.9$). The difference between pairs of η_A and η_E values are negligible. When these results are compared with those calculated by Papa et Shah[1] Eq. (1) the differences among their estimates (η_P) and the corresponding exact values (η_E) are significant and it can be concluded that their procedure is not reliable in the mixed-control regime.

In Figure 1 a comparison is presented among Papa and Shah[1] results and our

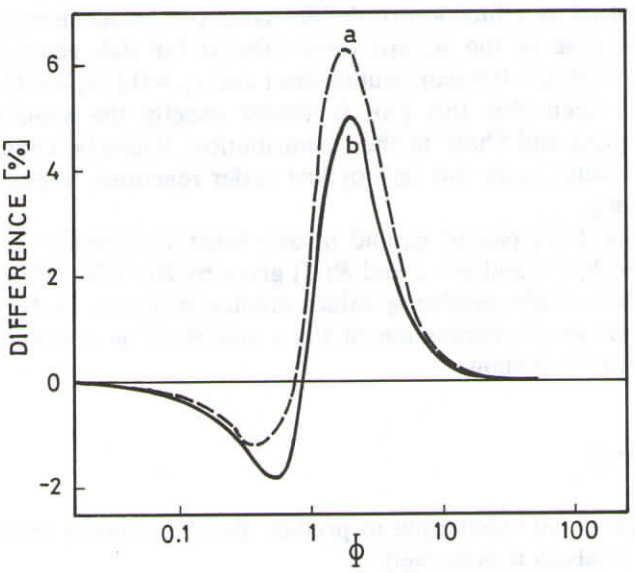

FIGURE 1 Wave shell position effect for slab geometry. Wave width = 0.1, $Bi = 1$, $\gamma = 1$, $n = 0$. a) $x_P = 0.1$, $x_i = 0.0$. b) $x_P = 1.0$, $x_i = 0.9$.

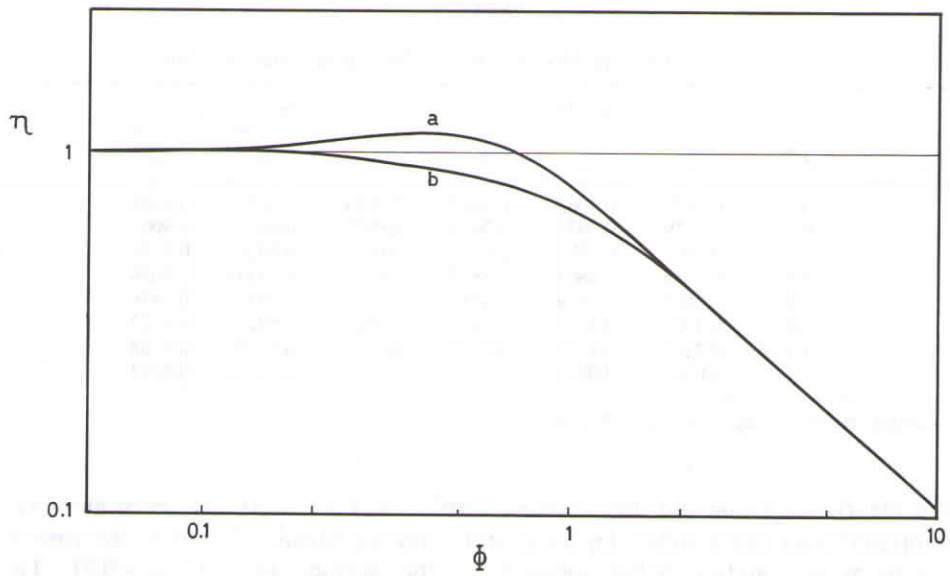

FIGURE 2 Comparison of effectiveness factor estimations versus modified Thiele module for $n = 0$, $x_P = 1.0$, $x_i = 0.8$, $Bi = 1$, $\gamma = 2$ and $R(C)$ as Eq. (23) a) This work, b) Papa and Shah work.

approximate results for exactly the same conditions as those presented in their contributions, namely isothermal conditions and $R(C)$ given by Eq. (23). By defining

$$D(\%) = 100(\eta_P - \eta_A)/\eta_A \tag{24}$$

$D(\%)$ was plotted as a function of Φ (the same parameter defined by Papa and Shah[1]) for the case of the square wave catalyst for slab geometry and $\gamma = 1$, $B_i = 1$ and $x_P = 10$; $x_i = 0.9$ (continuous line) and $x_P = 0.1$; $x_i = 0$ (broken line). It can be clearly seen that this plot is almost exactly the same graph as that presented by Papa and Shah[1] in their contribution. It can be concluded that our approximate results, as in the case of first order reactions, almost coincide with numerical finding.

Finally Figure 2 is a plot of η_A and η_P as a function of Φ for the case of $n = 0$, $x_P = 1$; $x_i = 0.9$; $B_i = 1$ and $\gamma = 2$ and $R(C)$ given by Eq. (23). While, as expected, our approximate results predict η values greater than one in the mixed control region the approximate expression of Papa and Shah[1] is not able to follow the true behavior of the system.

CONCLUSIONS

A general approximate technique to predict the effectiveness factor for the case of wave shell catalysts is presented.

The produced results obtained with this approximated procedure are shown to be extremely accurate. The differences between approximate and exact results

are always less than 1% even when rather strong non-linear kinetics equations were used to test the differences between approximate and exact results.

It can be concluded that our general procedure presented in this contribution can be safely used to produce η estimates when these kind of catalyst pellets are to be considered. They can be particularly useful for reactor and control design compiting with numerical schemes which are too much time consuming. Due to its simplicity and accuracy can be safely used even in the case of kinetics parameter estimation as in the case analyzed by Papa[7] *et al.*, avoiding the numerical integration of the mass balance equation.

On the other hand the procedure herewith presented can be used for predicting non-isothermal effectiveness factors even if a double trial and error technique must be settled to achieve final results (see Gonzo and Gottifredi[8]).

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NOMENCLATURE

a	dimensionless parameter defined by Eq. (18)
A_i	auxiliary functions (see Eq. (12))
B_i	Biot numbers defined by Eq. (10)
C	dimensionless concentration Eq. (3a)
C'	dimensional concentration [kmol/m^3]
D_{eff}	effective diffusivity [m^2/s]
$D(\%)$	auxiliary function defined by Eq. (24)
$f(x)$	catalytic activity distribution function
h	Thiele modulus Eq. (3e)
h_e	heat transfer film coefficient [kJ/m^{2}s]
h_M	Modified Thiele modulus Eq. (17)
i	iteration integer counter
k_g	mass transfer film coefficient [m/s]
L	dimensional characteristic length of the catalyst pellet [m]
n	dimensionless geometric parameter
r	dimensional rate of reaction [kmol/m^3]
R	dimensionless rate of reaction defined by Eq. (3c)
R'	derivative of R respect to C

T dimensionless temperature
V auxiliary variable defined by Eq. (22)
x dimensionless diffusion coordinate

Greek Letters

α auxiliary variable defined by Eq. (14)
β dimensionless parameter defined by Eq. (3d)
γ dimensionless kinetic parameter
δ activity within the shell Eq. (4)
ΔH heat of reaction [kJ/kmol]
K_{eff} effective thermal conductivity [kJ/ms]
η effectiveness factor
λ auxiliary parameter defined by Eq. (9)
σ parameter dependent on C_p and T_P defined by Eq. (15)
Φ modified Thiele modulus defined by Eq. (14) (Papa and Shah[1])

Subscripts

i refers to the inner wall of the catalyst shell
p refers to the outer wall of the catalyst shell
b refers to bulk flow conditions

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