



0009–2509(94)E0066–Y

DIFFUSION AND REACTION INSIDE A CATALYST PELLET FOR A PARALLEL–CONSECUTIVE REACTION SCHEME

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(Received 10 September 1993; accepted for publication 11 March 1994)

Abstract—An analytical solution is presented for the concentration profiles inside a catalyst particle with uniform activity for a parallel-consecutive reaction scheme containing a reversible step and in which the reactions are all of the first order.

An accurate approximate solution for the surface fluxes was developed for the case of non-uniform activity.

The effects of the degree of reversibility of the first step of the consecutive chain and of the ratio of the surface concentrations of the intermediate and feed component are illustrated. The influence of a non uniform catalyst activity is shown to be important, particularly in the mixed control regime.

1. INTRODUCTION

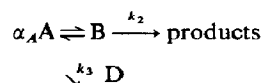
Many catalytic processes are carried out under conditions in which the rate is diffusion limited. The phenomenon of simultaneous diffusion and reaction inside a catalyst particle has received considerable attention (Petersen, 1965), but mainly for single reactions and simple kinetics, for which analytical solutions are possible.

The introduction of the generalized modulus (Aris, 1965; Petersen, 1965; Bischoff, 1965) has allowed one to deal in a semi-analytical way with more complex kinetic equations, of the Hougen–Watson type (Satterfield, 1970), but the technique is still limited to single reactions. For more complex reactions no analytical solution of the continuity equations for the key components is available. The numerical solution is not always trivial and is always time consuming, in particular when it has to be carried out in each point of the grid used in the integration of the continuity equations of the species flowing through the reactor. Xu and Froment (1989) and Soliman (1992) have used spline collocation for this purpose and discussed the problems encountered in real situations. There is, in spite of the progress in numerical techniques and computer power, still a need for a rapid solution of the reaction–diffusion problem.

The present paper deals with analytical and approximate solutions for reaction schemes comprising parallel and consecutive steps taking place inside a catalyst particle with distributed activity.

2. PARALLEL–CONSECUTIVE REACTION SCHEME. CONCENTRATION PROFILES FOR UNIFORM ACTIVITY AND APPROXIMATE SOLUTION FOR SURFACE FLUXES AND SELECTIVITY, VALID FOR ANY ACTIVITY DISTRIBUTION

Consider the parallel–consecutive reaction scheme



in which all the reactions are of the first order.

This is a scheme of relative complexity already, likely to be of use in the simulation of industrial processes. Hydrocarbon oxidation processes correspond to such a scheme, but in that case the first step in the consecutive chain is not reversible. The above scheme was analyzed by Do (1982) through a complicated analytical procedure. The solution presented here is very simple.

The porous catalyst particle is considered to have either a planar, cylindrical spherical shape ($n = 0, 1, 2$, respectively) with characteristic length R and with an activity distribution function $f(x)$.

The dimensionless continuity equations for A and B in an isothermal pellet can be written as

$$\frac{d}{dx} \left(x^n \frac{dC_A}{dx} \right) = h^2 x^n f(x) \left[C_A - \left(\frac{p}{\gamma} \right) C_B \right] \quad (1)$$

$$\frac{d}{dx} \left(x^n \frac{dC_B}{dx} \right) = h^2 x^n f(x) [(w + p) C_B - \gamma C_A] \quad (2)$$

where x is the spatial coordinate, C the concentration, normalized with respect to the corresponding surface value of component A, and indexes 1 and 2 refer to the first step, $\alpha_A A \rightleftharpoons B$, and to the second step, $B \rightarrow$ products, of the consecutive chain, respectively. The groups h^2 , w , p , q and γ are defined as follows:

$$\begin{aligned} h^2 &= (k_1 R^2 / q D_A), & w &= (k_2 D_A q / k_1 D_B) \\ p &= \gamma q / K, & \gamma &= \frac{D_A / D_B}{\alpha_A} \\ q &= \frac{1}{1 + (k_3 / k_1)} \end{aligned} \quad (3)$$

where D represents the effective diffusivity, K the thermodynamic equilibrium constant for the first reaction and k_i the reaction rate coefficient. Equations (1) and (2) must be solved subject to the following boundary conditions:

$$C_A = 1, \quad C_B = C_B^0 \quad \text{at } x = 1 \quad (4a)$$

$$\frac{dC_A}{dx} = \frac{dC_B}{dx} = 0 \quad \text{at } x = 0. \quad (4b)$$

The analytical solution of this system can be found for the case of uniform activity distribution [$f(x) = 1$]. It can be shown that

$$C_A = (1 + \lambda X^0) \frac{\cosh(\epsilon h x)}{\cosh(\epsilon h)} - \lambda X^0 \frac{\cosh(\beta^{1/2} h x)}{\cosh(\beta^{1/2} h)} \quad (5)$$

$$X = X^0 \frac{\cosh(\beta^{1/2} h x)}{\cosh \beta^{1/2} h} \quad (6)$$

where

$$C_B = X - \Gamma C_A \quad (7)$$

$$X^0 = \Gamma + C_B^0 \quad (8)$$

$$\epsilon^2 = (1 + w + p - \beta) \quad (9a)$$

$$\eta = \frac{(1 + \lambda X^0) \epsilon^2 [(H_1 + \exp(-aH_1))^{-1/2} - \lambda X^0 \beta [H_2 + \exp(-aH_2)]^{-1/2}]}{[1 - (p/\gamma) C_B^0]} \quad (17)$$

$$\lambda = \frac{(p/\gamma)}{(\beta - \epsilon^2)} \quad (9b)$$

$$\beta = \frac{1}{2} \{ (1 + w + p) - [1 - (p + w)] \delta \} \quad (10)$$

$$\delta = \left\{ 1 + \frac{4pq}{[1 - (p + w)]^2} \right\}^{1/2} \quad (11)$$

$$\Gamma = \frac{\gamma q}{(1 - \beta)} = \frac{\gamma}{p} (w + p - \beta). \quad (12)$$

When the activity distribution is not uniform there is no analytical solution but the procedure proposed by Gottifredi *et al.* (1986) can still be used to estimate the fluxes at the interface. It can be shown that, for the case of first-order reactions suitable matching expressions valid in the whole range of h values can be written as

$$(n + 1) \left(\frac{dX}{dx} \right)_{x=1} = \beta X^0 h^2 [H_2 + \exp(-aH_2)]^{-1/2} \quad (13)$$

$$\begin{aligned} (n + 1) \left(\frac{dC_A}{dx} \right)_{x=1} &= (1 + \lambda X^0) (h\epsilon)^2 \\ &\times [H_1 + \exp(-aH_1)]^{-1/2} \\ &- \lambda h^2 X^0 \beta [H_2 + \exp(-aH_2)]^{-1/2} \end{aligned} \quad (14)$$

where the parameters H_1 , H_2 and a must be determined from the following expressions:

$$H_1 = \frac{[\epsilon h / (n + 1)]^2}{f(1)}, \quad H_2 = \frac{[h / (n + 1)]^2 \beta}{f(1)} \quad (15)$$

$$a = 1 - 2f(1)(n + 1) \left\{ \int_0^1 x^{-n} \left[\int_0^x x^n f(x) dx \right]^2 dx \right\}.$$

H_1 , H_2 and a are functions of the pellet geometry and catalyst activity distribution inside the pellet. A table with the value of the integral in the bracket multiplied by $(n + 1)$ is given by Gottifredi *et al.* (1986) for two distribution functions (linear and parabolic) and for three particle shapes.

Sutradhar *et al.* (1986) also solved this problem following a similar procedure, but the asymptotic solutions were not matched and their results are only valid in the region where $h \leq 1$, i.e. where the influence of diffusion is small.

It should be noticed that the approximate solution does not yield the profiles inside the particle, only the surface fluxes, which is sufficient for most purposes, anyway.

Given the kinetics of the reaction network considered here, an effectiveness factor, η , for the consumption of A can be obtained from the definition:

$$\eta = \frac{(n + 1) \left(\frac{dC_A}{dx} \right)_{x=1}}{h^2 [1 - (p/\gamma) C_B^0]} \quad (16)$$

Substituting $(dC_A/dx)_{x=1}$ in eq. (16) by its value given by eq. (14) yields the expression for η :

The selectivity for the component B, taken over the whole pellet, can now be predicted from its usual definition as the ratio of the rate of formation of component B to the rate of consumption of component A:

$$S = - \frac{(dC_B/dx)_{x=1}}{(dC_A/dx)_{x=1}} = \Gamma - \frac{(dX/dx)_{x=1}}{(dC_A/dx)_{x=1}} \quad (18)$$

By combining eqs (16) and (17), the flux of A at the surface can be calculated as a function of η . The flux $(dX/dx)_{x=1}$ is obtained from eq. (13), so that

$$S = \Gamma - \frac{X^0 \beta [H_2 + \exp(-aH_2)]^{-1/2}}{\eta [1 - (p/\gamma) C_B^0]} \quad (19)$$

Limit values of S , represented by $S(0)$ when $h^2 \ll 1$ and by $S(\infty)$ when $h^2 \gg 1$, can be derived from eq. (19):

$$S(0) = \gamma - (w + p) C_B^0 \quad (20)$$

$$S(\infty) = \frac{\gamma - (w + p + w^{1/2}) C_B^0}{[1 + w^{1/2} - (p/\gamma) C_B^0]} \quad (21)$$

Table 1. Comparison between exact values of $(\eta)_E$ and S_E with their respective approximate values $(\eta)_A$ and S_A

h	$(\eta)_E$	$(\eta)_A$	S_E	S_A	$(\eta)_E$	$(\eta)_A$	S_E	S_A
$C_B^0 = 0, w = 0.50, \gamma = 1, p = 0.1$				$C_B^0 = 0, w = 0.50, \gamma = 1, p = 10$				
0.1	0.9964	0.9964	1.0	1.0	0.9649	0.9650	1.0	1.0
0.5	0.9177	0.9180	0.96	0.96	0.5699	0.5724	0.97	0.97
1.0	0.7477	0.7494	0.87	0.87	0.3224	0.3228	0.91	0.91
2.0	0.4705	0.4725	0.70	0.70	0.1796	0.1796	0.81	0.81
4.0	0.2453	0.2455	0.60	0.59	0.1036	0.1037	0.69	0.69
10.0	0.0983	0.0983	0.59	0.59	0.0469	0.0470	0.59	0.59
20.0	0.0492	0.0492	0.59	0.59	0.0237	0.0238	0.59	0.59
$C_B^0 = 0, w = 2, \gamma = 1, p = 10$				$C_B^0 = 0.4, w = 0.5, \gamma = 1, p = 1$				
0.1	0.9651	0.9652	0.99	0.99	0.9945	0.9945	0.66	0.66
0.5	0.5947	0.5968	0.88	0.88	0.8860	0.8866	0.60	0.60
1.0	0.3764	0.3766	0.72	0.72	0.6995	0.7015	0.46	0.46
2.0	0.2404	0.2406	0.54	0.54	0.4647	0.4656	0.25	0.25
4.0	0.1442	0.1446	0.44	0.44	0.2679	0.2687	0.11	0.11
10.0	0.0607	0.0607	0.41	0.41	0.1101	0.1101	0.09	0.09
20.0	0.0303	0.0303	0.41	0.41	0.0551	0.0551	0.09	0.09

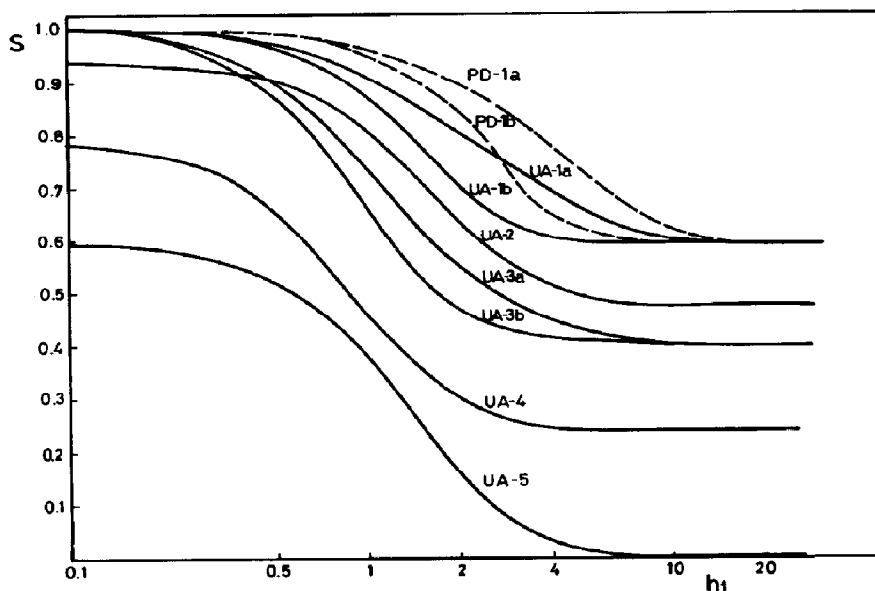


Fig. 1. Selectivity S vs Thiele modulus h for a purely consecutive scheme ($q = 1$): (—) uniform catalyst activity inside the pellet (UA-1a: $C_B^0 = 0, w = 0.5, \gamma = 1, p = 10$; UA-1b: $C_B^0 = 0, w = 0.5, \gamma = 1, p = 0.1$; UA-2: $C_B^0 = 0.1, w = 0.5, \gamma = 1, p = 1$; UA-3a: $C_B^0 = 0, w = 2, \gamma = 1, p = 10$;

UA-3b: $C_B^0 = 0, w = 2, \gamma = 1, p = 0.1$; UA-4: $C_B^0 = 0.1, w = 2, \gamma = 1, p = 1$; UA-5: $C_B^0 = 0.45, w = 0.5, \gamma = 1, p = 1$); (---) parabolic activity distribution $f(x) = 3x^2$ (PD-1a: $C_B^0 = 0, w = 0.5, \gamma = 1, p = 10$; PD-1b: $C_B^0 = 0, w = 0.5, \gamma = 1, p = 0.1$).

The solution for the purely consecutive scheme is completely identical, but some of the parameters take on different values, of course.

An evaluation of the accuracy of the approximate solution is possible by comparing its results for uniform activity with those of the exact analytical solution. This is done in Table 1, for $q = 1$. The approximate solution is extremely accurate: the maximum difference between both solutions for η and S is always lower than 1%.

3. APPLICATION OF THE EQUATIONS TO REACTOR DESIGN

The application of the equations derived here to problems of practical interest is extremely convenient. Consider a plug flow catalytic reactor. One problem encountered with a consecutive or parallel-consecutive reaction scheme is the distance in the reactor beyond which there is a net consumption of the intermediate product, B, instead of a net production. As shown in Fig. 1, profiles of the concentration of the

intermediate B inside the pellet typically exhibit a maximum. It follows from eqs (20) and (21) that the location of the maximum shifts towards the surface ($x = 1$) as the surface concentration C_B^0 increases. The maximum reaches the surface for a C_B^0 value which can be derived from either eq. (20) or eq. (21). The most conservative value, $(C_B^0)_M$, which can be used as a design criterion, is the one obtained from eq. (21):

$$(C_B^0)_M \leq \gamma/(w + p + w^{1/2}). \quad (22)$$

The effect of the Thiele modulus, h , on the selectivity for B is shown in Fig. 1 for the purely consecutive scheme ($q = 1$). S varies between the asymptotic values $S(0)$ and $S(\infty)$, as expected. For given w and γ and $C_B^0 = 0$ the selectivity $S(0) = 1$ and neither $S(0)$ nor $S(\infty)$ depend on p , as can be seen from a comparison of UA-1a, b and UA-3a, b. For intermediate values of h , however, there is a significant influence of p on S . As p is increased (i.e. K decreased), the consumption of A and the net production of B are both reduced, but the selectivity increases, due to less pronounced concentration profiles.

For $C_B^0 \neq 0$, both $S(0)$ and $S(\infty)$ decrease with increasing C_B^0 , as can be seen from a comparison of the curves UA-2, 4, 5, and the same is true, of course, for S at intermediate h . The choice of a reactor length that would avoid the selectivity to drop below a certain value, set by economics, is easily arrived at by means of the equations derived here. The effect of w is illustrated by curves UA-2, 4: the higher the w , the lower the selectivity, and this is more pronounced the higher the h .

For the reaction schemes considered here a nonuniform catalyst activity may favor the selectivity. An activity profile descending from the surface towards the center increases the selectivity for B, as can be seen from a comparison of PD-1a, b with UA-1a, b, but only for intermediate values of h . For very strong diffusional limitations the reaction takes place in a very narrow zone close to the surface, so that the activity distribution is not felt. For reaction control the activity distribution operates on the local fluxes of A and B, but for the kinetics considered here the effect cancels out in the selectivity. The effect of $f(x)$ on the selectivity was investigated in detail by Juang *et al.* (1980) for a consecutive scheme with irreversible reactions only, but by means of a numerical technique. Overall, their results are in line with those shown in Fig. 2, but their $S(\infty)$ are not properly calculated, as the analytical solution of the present paper revealed.

4. CONCLUSIONS

An analytical solution is presented for concentration profiles inside a catalyst particle for a parallel-consecutive reaction scheme with first-order reactions, but in which the first step of the consecutive chain is reversible. The solution is limited to a uniform activity of the catalyst.

An approximate solution is obtained for the case of an activity distribution inside the pellet. It does not

yield the concentration profiles, but only surface fluxes. This is sufficient for most practical applications. A comparison with the analytical solution for uniform activity establishes the accuracy of the approximate solution.

The exact analytical solution and the approximate solution considerably simplify the evaluation of the performance or the design of reactors operating under conditions in which diffusional limitations are of importance. The reaction scheme considered here is relatively complex already and representative for a number of commercial processes. The solutions can be easily extended to schemes containing more irreversible consecutive steps and also to situations whereby external diffusion limitations have to be accounted for. It would be extremely valuable to further extend them to nonlinear kinetics.

Acknowledgement—The authors are grateful for the support provided by CONICET, Argentina, and the Belgian "National Fonds Voor Wetenschappelijk Onderzoek".

NOTATION

a	parameter defined by eq. (27)
C	dimensionless concentration
D	effective diffusivity, $m^2/m_p s$
f	activity distribution function
h	Thiele modulus defined by eq. (3)
H_1, H_2	modified Thiele modulus defined by eq. (27)
k_1, k_2, k_3	intrinsic kinetic constant for forward reactions, s^{-1}
K	thermodynamic equilibrium constant
n	parameter characterizing the pellet geometry
p	parameter defined by eq. (3)
q	parameter defined by eq. (3)
R	characteristic length of the particle, m
S	selectivity defined by eq. (30)
w	ratio of h_2 to h [see eq. (3)]
x	dimensionless coordinate
X	pseudocomponent dimensionless concentration defined by eq. (5)

Greek letters

α	stoichiometric coefficient
β	parameter, see eq. (8)
γ	parameter defined by eq. (3)
Γ	parameter defined by eq. (7)
δ	parameter defined by eq. (9)
ϵ	parameter defined by eq. (12)
η	effectiveness factor, defined by eq. (28)
λ	parameter defined by eq. (13)

Subscripts

A	a component
B	a component

Superscript

0	pellet surface conditions
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