Chemical Engineering Science Vol. 36, pp. 713–719
Pergamon Press Ltd., 1981. Printed in Great Britain

0009–2509/81/0401–0713/$02.00/0

ISOTHERMAL EFFECTIVENESS FACTOR—II

ANALYTICAL EXPRESSION FOR SINGLE REACTION WITH ARBITRARY KINETICS, GEOMETRY AND ACTIVITY DISTRIBUTION

J. C. GOTTIFREDI,*† E. E. GONZO† and O. D. QUIROGA†
Departamento de Ciencias Tecnológicas, Universidad Nacional de Salta, Buenos Aires 177, 4400-Salta, Argentina

(*Received* 29 *April* 1980; *accepted* 12 *August* 1980)

Abstract—A previously presented method[1], to predict isothermal effectiveness factor with a single complex reaction in isothermal slab pellets is extended to encompass much more complex and general situations. In this work the geometry of the pellet can be arbitrary and a non uniform distribution of the catalyst is considered.

Though the previously presented method[1] has had to be slightly modified to predict with great accuracy the effectiveness factor, (with less than 3% deviation from the exact values), an almost general and very simple algebraic expression is deduced to predict effectiveness factor values within 10% of their respective exact values. Thus for many applications in engineering design and catalytic reactor simulation, this simple general expression can be extremely useful since only one easily generated parameter is needed, as shown throughout the present contribution.

INTRODUCTION

In a previous work, the authors[1] have shown that the isothermal effectiveness factor in a porous slab could be very well predicted by a very simple algebraic equation even in the case of complex non-linear kinetic expressions. This equation was able to satisfactorily match the asymptotic expressions of the effectiveness factor (η) for small and large values of the Thiele modulus.

In this contribution, the effect of the geometrical shape and the activity distribution of the catalytic pellet is investigated. It can be shown that, from a mathematical point of view, these two effects are rather similar since they can be gathered in a unique term with an appropriate change of the spacial coordinate.

Recent studies has shown that impregnated catalyst pellets do not present a uniform distribution of the active species. Chen and Anderson[2] investigated the concentration profiles of chromium and copper salts after being impregnated in γ-alumina spherical pellets. It was concluded that due to complicated mechanisms in the drying step the solute redistributes and rather steep concentration profiles of the active species can result.

Impurities in chemical feedstocks can also cause catalyst deactivation. McArthur[3] found that sulfur and lead concentrations in automotive catalysts decrease hiperbolically towards the particle center. Hegedus and Baron[4] and Su and Weaver[5] found a similar pore mouth poisoning behaviour of lead in noble metal and base metal oxide catalysts. Sato *et al.*[6] showed that vanadium compounds deposited preferentially on the outside of cobalt–molybdenum catalysts while nickel salts penetrate the entire particle.

The question that arises is whether it might be possible to calculate the effectiveness factor under these conditions in a quick approximate analytical way in order to optimize the performance of the catalyst pellet, and also to establish the type of catalyst deactivation mechanism prevailing in a given process. Becker and Wei[7] had to solve numerically the resulting differential equation even for the case of first order reactions when an exponential decaying activity from the catalyst surface was considered. Nyström[8] proposed an infinite series as solution of the concentration profile of a reacting species provided the kinetic expression is a linear function of the concentration, this being a very strong limitation for most catalytic reactions.

The purpose of this work is to investigate the behaviour of the proposed analytical equation previously presented[1] to match asymptotic expressions for the effectiveness factor valid for small and large values of the Thiele modulus. The effect of the geometrical shape of the catalyst is also investigated by assuming that unidirectional diffusion flow occurs in slab, cylindrical, or spherical pellets. Nevertheless, it becomes clear that the method can be used even in those cases where bidimensional diffusion flow takes place.

Once again it is assumed that no convective flow due to a pressure is present, that the diffusivity coefficient is constant, that isothermal and steady state conditions prevail. In this analysis a single reaction of order m is assumed with the condition that $m \geq 0.5$. Negative orders cannot be analyzed with the present method as it was explained previously[1]. Nevertheless, more complex kinetic expressions can be studied under the same procedure thus rendering it as almost general to predict effectiveness factor values when the activity distribution is known, or it is deduced under theoretical considerations, and the geometrical shape of the catalyst is fixed.

*Author to whom correspondence should be addressed.
†Research Member of Consejo Nacional de Investigaciones Cientificas y Técnicas (Argentina).

The analysis follows a pattern similar to that presented in the first contribution[1]. After deriving asymptotic expressions of the effectiveness factor valid for small and large values of the Thiele modulus they are matched with a proposed equation. However, in this case it is shown that the previously presented simple algebraic equation (1) is not able to match asymptotic solutions, and extra terms are needed. Nevertheless, it is shown that an extremely simple equation can be used to estimate the effectiveness factor with maximum deviations of 10% which, for certain engineering applications, proves satisfactory. In any case a procedure to find much more accurate estimates of the effectiveness factor is presented. The external mass transfer resistance effect is not considered in this contribution but it can be very easily taken into account as was previously shown[1].

ANALYSIS

Considering the above stated assumptions, the differential mass balance for species A, that diffuses and reacts according to an mth order irreversible kinetic reaction, can be written in the following dimensionless form:

$$\frac{d^2C_A}{dr^2}+\frac{n}{r}\frac{dC_A}{dr}=h^2f(r)C_A{}^m \qquad (1)$$

where

$$C_A\equiv(C'_A/C'_{AS});\quad r\equiv(r'/R)$$
$$h^2\equiv(k_vC'^{(m-1)}_{AS}R^2/D_A). \qquad (2a,b,c)$$

R being the dimensional characteristic length of the pellet, C'_{AS} the dimensional concentration at the surface, r' the spacial coordinate parallel to the diffusional flow direction, D_A the effective diffusivity coefficient and k_v the specific rate of reaction per unit volume of the pellet. The effect of the geometrical shape in eqn (1) is seen through n (0 slab, 1 cylindrical, 2 spherical geometry) and the activity distribution function by $f(r)$. According to the effectiveness factor definition $f(r)$ should be normalized in such a way that $\eta\to 1$ when $h^2\to 0$. Thus, $f(r)$ can be any function that fits the following condition:

$$\int_0^1(n+1)f(r)r^n\,dr=1. \qquad (3)$$

The appropriate boundary conditions for eqn (1) are:

$$C_A=1 \qquad r=1$$
$$\frac{dC_A}{dr}=0 \qquad r=0 \qquad (4a,b)$$

which implies that a symmetrical plane exists.

Asymptotic solutions can now be very easily found when $h^2\to 0$. Equation (1) suggests itself the following series solution:

$$C_A=A_0(r)+h^2A_1(r)+h^4A_2(r)+\cdots \qquad (5)$$

which after being replaced in eqn (1) and after the terms of like power of h have been equated it gives the following uncoupled system:

$$\frac{d^2A_0}{dr^2}+\frac{n}{r}\frac{dA_0}{dr}=0$$
$$\frac{d^2A_1}{dr^2}+\frac{n}{r}\frac{dA_1}{dr}=f(r)A_0{}^m \qquad (6a,b,c)$$
$$\frac{d^2A_2}{dr^2}+\frac{n}{r}\frac{dA_2}{dr}=mf(r)A_0{}^{m-1}A_1$$

subject to the following conditions:

$$A_0(1)=1 \qquad A_1(1)=A_2(1)=0$$
$$\frac{dA_2}{dr}=\frac{dA_1}{dr}=\frac{dA_2}{dr}=0 \qquad r=0 \qquad (7a,b)$$

$A_0=1$ is the solution to eqn (6a). The other equations can be solved by standard procedures once n and $f(r)$ are chosen. According to the effectiveness factor definition eqn (5), with $A_0=1$, will produce the following results:

$$\eta=1+h^2\beta_1+h^4\beta_2+\cdots \qquad (8)$$

where condition (3) was used and:

$$\beta_1=\int_0^1 mA_1(n+1)f(r)r^n\,dr \qquad (9)$$

$$\beta_2=\int_0^1\left(mA_2+\frac{1}{2}(m-1)mA_1{}^2\right)(n+1)f(r)r^n\,dr$$
$$=\left(m^2+\frac{1}{2}m(m-1)\right)\int_0^1 A_1{}^2(n+1)f(r)r^n\,dr. \qquad (10)$$

On the other hand, when $h^2\to\infty$, it is convenient to introduce the coordinate transformation suggested by Petersen[9]. Thus with:

$$\chi\equiv h(1-r). \qquad (11)$$

Equation (1) can be rewritten in the following form:

$$\frac{d^2C_A}{d\chi^2}-\frac{n}{h\left(1-\frac{\chi}{h}\right)}\frac{dC_A}{d\chi}=f\left(1-\frac{\chi}{h}\right)C_A{}^m. \qquad (12)$$

A series solution in terms of h^{-1} is now possible after expnding the activity distribution function as:

$$f\left(1-\frac{\chi}{h}\right)=f(1)-\left(\frac{df}{dr}\bigg|_{r=1}\right)\left(\frac{\chi}{h}\right)-\cdots. \qquad (13)$$

Clearly, $f(1)$ is the value of f at the surface and $(df/dr)_{r=1}$ also denotes surface value. Now, we can assume the following series solution for C_A when $h\to\infty$

$$C_A=\varphi_0(\chi)+\frac{1}{h}\varphi_1(\chi)+\cdots. \qquad (14)$$

By replacing eqn (14) in eqn (12) and gathering terms of like power of h it results that:

$$\frac{d^2\varphi_0}{d\chi^2} = f(1)\varphi_0{}^m \quad (15)$$

$$\frac{d^2\varphi_1}{dx^2} = f(1)m\varphi_0{}^{m-1}\varphi_1 + n\left(\frac{d\varphi_0}{d\chi}\right) - \chi\left(\frac{df}{dr}\Big|_{r=1}\right)\varphi_0{}^m \quad (16)$$

subject to the following boundary conditions:

$$\varphi_0(0) = 1 \qquad \varphi_1(0) = 0$$

$$\frac{d\varphi_0}{dx} = \frac{d\varphi_1}{dx} = 0 \qquad \chi = h. \quad (17a,b)$$

However, after invoking the usual assumptions ($\varphi_0(\infty) \simeq 0$) the solution to eqn (15) is easily found and need not to be rewritten here. Unfortunately, the same cannot be said of eqn (16). As it is shown in the Appendix, we only found an exact analytical solution to the case of $m = 1$. Nevertheless, a solution can be found after introducing crude approximations into the right hand side of eqn (16). From eqn (14) it becomes clear that η will be now given by the following asymptotic expression:

$$\eta = \alpha\left(\frac{1}{h}\right) + d\left(\frac{1}{h^2}\right) + \cdots \quad (18)$$

where

$$\alpha = -\left(\frac{d\varphi_0}{d\chi}\Big|_{x=0}\right)(n+1)$$

$$d = -\left(\frac{d\varphi_1}{d\chi}\Big|_{x=0}\right)(n+1). \quad (19a,b)$$

At this point, since values of α and β_1 can be easily calculated, we can introduce the previously proposed matching expression for η (see Ref. [1]):

$$\eta = a\frac{(r+h^2)^{1/2}}{(S+h^2)}. \quad (20)$$

Once again it can shown that a, r and S are related to α and β_1 through the following equations:

$$a = \alpha$$

$$r = (S/\alpha)^2 \quad (21a,b,c)$$

$$S = -\frac{1}{2\beta_1}\left\{1 \pm \sqrt{(1+2\alpha^2\beta_1)}\right\}.$$

However, in many cases it could happen that $|2\alpha^2\beta_1| > 1$ and S becomes imaginary thus rendering inconsistent the proposed matching expression. There are two ways to overcome this problem. The first one is the simplest though precision is lost. It is assumed that the second expansion term for η when $h^2 \to 0$ is $\delta_m\beta_1$ instead of β_1 in such a way that:

$$-2\alpha^2\delta_m\beta_1 = 1. \quad (22)$$

Using eqn (22) it can be shown that an extremely simple expression results instead of eqn (20):

$$\eta \simeq (1+(h/\alpha)^2)^{-1/2} = \bar{\eta} \quad (23)$$

which can be compared with the numerical results of η. The ability of eqn (23) to fit true values of η over the entire range of Thiele modulus values will be discussed later though it can be anticipated that it proves fairly good for most engineering purposes.

The second way to overcome the problem, when $|2\alpha^2\beta_1| > 1$ is to use extra terms as matching equation. Thus, instead of eqn (20) the following is proposed:

$$\eta = a\frac{(r+h^2)^{1/2}}{(S+h^2)} + n_1\frac{h^2}{(p+h^2)^2}. \quad (24)$$

After expanding eqn (24) when $h \to \infty$ and by comparing the resulting series with eqn (18) it is shown that:

$$a = \alpha$$

$$n_1 = d. \quad (25a,b)$$

On the other hand, by repeating the expansion procedure with eqn (24) when $h^2 \to 0$ and by comparing it with eqn (8) the following relations result:

$$ar^{1/2}s^{-1} = 1$$

$$\frac{1}{2}ar^{-1/2}S^{-1} + ar^{1/2}S^{-2} + n_1p^{-2} = \beta_1 \quad (26a,b,c)$$

$$1ar^{1/2}S^{-3} - \frac{a}{8}r^{-3/2}S^{-1} - \frac{a}{2}r^{-1/2}S^{-2} - 2n_1p^{-3} = \beta_2.$$

Since a and n are given by eqn (25a,b) a system of three non linear algebraic equations with three unknowns must be solved for r, S and p. After some manipulations this system can be reduced to the following form:

$$\left\{\left(1-\frac{1}{8\gamma^2}-\frac{1}{2\gamma}\right)\frac{1}{\gamma^2a^4}-\beta_2\right\}^2 = \frac{4}{N_1}\left[\beta_1+\left(1-\frac{1}{2\gamma}\right)\Big/\gamma a^2\right]^3 \quad (27)$$

where the auxiliary parameter γ was introduced as:

$$S = \gamma a^2.$$

Once γ is found, by a trial and error procedure, by satisfying eqn (27) p can be found through:

$$p = \left\{\frac{2n_1a^2}{2\beta_1a^2 - [(\gamma^{-1}-1)^2-1]}\right\}^{1/2}. \quad (29)$$

Finally, by combining eqns (28) and (26a) the value of r is found as:

$$r = \gamma^2a^2 \quad (30)$$

As a general rule, the procedure, at least in those cases investigated, gives values of γ encompassed between 0.90 and 2.8 approximately. This short range will speed up the trial and error procedure to find γ.

In terms of $(h/a)^2$ the resulting expression for η can be rewritten in the following form:

$$\eta = \frac{(\gamma^2 + (h/a)^2)^{1/2}}{(\gamma + (h/a)^2)} + \left(\frac{n_1}{a^2}\right)\frac{(h/a)^2}{((p/a^2) + (h/a)^2)^2}. \quad (31)$$

DISCUSSION OF RESULTS

In Table 1, the numerical results of the effectiveness factor as a function of the Thiele modulus when $m = 0.5$, 1.0 and 2.0 are presented. These results are for spherical geometry and $f(r) = 1$ (that is uniform activity distribution). When $m \geq 1$, δ_m (see eqn 22) is less than one so that eqn (24) should be used to calculate η. Nevertheless, values of $\bar{\eta}$ given by eqn (23) are also presented in Table 1 for comparison purposes.

The results obtained after integrating eqn (1) numerically when $m \neq 1$, are also shown in those columns headed by η_N. Values of β_1, β_2, a^2, n, p and γ are also given when necessary. It can be seen that eqn (34) produces results in close agreement with the corresponding numerical values. On the other hand, eqn (23) also produces results which for many engineering design puposes, are accurate enough with the advantage that only parameter, a, needs to be analytically estimated. Maximum deviations when using this expression is about 10% while it is reduced to about 3% when eqn (31) is used.

The results obtained for slab geometry, when $m = 1$ and 2; and 3 different activity distribution functions, are presented in Table 2. Tested functions are:

$$\text{(Linear)} \quad f(r) = \begin{cases} \dfrac{2(r-b)}{(1-b)^2} & r \geq b \\ 0 & 0 \leq r \leq b \end{cases} \quad (32)$$

$$\text{(Parabolic)} \quad f(r) = 3r^2 \quad (33)$$

$$\text{(Exponential)} \quad f(r) = 4\exp(4(r-1))/(1-\exp(-4)). \quad (34)$$

All of them suggested by Kehoe[10] from experimental evidences reported in the literature. The only cases in which there was need to use the whole eqn (31) to estimate η accurately were parabolic and exponential distributions when $m = 2$. In these cases values of the six resulting parameters are reported as well as those values of $\bar{\eta}$ given by the simple expression (23). Once again it is shown that the approximate values of $\eta(\eta_A)$ are in close agreement with the corresponding values obtained by numerical integration (η_N). Maximum deviations are below 3%. However, it seems that for slab geometry, and with those distribution activity functions, the simple expression (23) gives very good estimates of η since the maximum deviation is only about 6%.

Incidentally, it can be shown that the governing mass balance differential equation for species A in a slab pellet with an exponential activity distribution function (see eqn 34) can be easily transformed into the corresponding mass balance with radial diffusion in an infinite long cylindrical pellet with uniform distribution. Thus, the results given in Table 2 for exponential distribution represent a test of our approximate expression in cylindrical pellets with uniform catalyst activity.

Finally, in Table 3, the results obtained in spherical pellets, with linear $(f(r) = (4/3)r)$ and parabolic $(f(r) = (5/3)r^2)$ activity distribution functions, are presented when $m = 1$ and 2. Values of the effectiveness factor, obtained by numerical integration of the corresponding differential equation, (η_N), are compared with those given by eqn (31) and with those calculated with the simple eqn (23) $(\bar{\eta})$. Once again it is shown that the maximum deviation between approximate and numerical values of η is about 3% while in these cases eqn (23) also

Table 1.

m	0.5			1.			2.		
h \ η	η_A	η_N	$\bar{\eta}$	η_A	η_N	$\bar{\eta}$	η_A	η_N	$\bar{\eta}$
1.5	0.9317	0.9253	0.9177	0.8762	0.8761	0.8944	0.8030	0.8000	0.8528
2.0	0.8864	0.8790	0.8660	0.8059	0.8046	0.8321	0.7200	0.7118	0.7746
3.0	0.7837	0.7617	0.7559	0.6714	0.6721	0.7071	0.5870	0.5710	0.6324
4.0	0.6830	0.6470	0.6547	0.5625	0.5661	0.6000	0.4883	0.4695	0.5223
6.0	0.5208	0.4809	0.5000	0.4156	0.4170	0.4472	0.3569	0.3464	0.3780
				β_1 = -0.06667; β_2 = 0.00635			β_1 =-0.13333; β_2 = 0.03175		
				a^2 = 9; γ = 1.772 ; δ_m = 0.833			a^2 = 6; γ = 2.36; δ_m = 0.625		
				n_1 =-3; p = 11.769			n_1 =- 2.4 ; p = 5.559		

Table 2.

	LINEAR				PARABOLIC					EXPONENTIAL				
	m = 1		m = 2		m = 1		m = 2			m = 1		m = 2		
h	η_A	η_N	$\bar{\eta}$	η_N	η_A	η_N	η_A	η_N	$\bar{\eta}$	η_A	η_N	η_A^*	η_N	$\bar{\eta}^*$
0.3	0.9824	0.9824	0.9772	0.9758	0.9874	0.9872	0.9753	0.9752	0.9782	0.9893	0.9893	0.9783	0.9771	0.9835
0.5	0.9531	0.9528	0.9402	0.9364	0.9660	0.9656	0.9358	0.9360	0.9428	0.9711	0.9710	0.9433	0.9442	0.9562
0.8	0.8903	0.8891	0.8652	0.8594	0.9186	0.9184	0.8574	0.8572	0.8704	0.9306	0.9303	0.8730	0.8744	0.8980
1	0.8412	0.8398	0.8090	0.8030	0.8801	0.8791	0.8009	0.8004	0.8165	0.8973	0.8959	0.8214	0.8235	0.8528
1.5	0.7147	0.7110	0.6771	0.6683	0.7746	0.7713	0.6682	0.6671	0.6860	0.8043	0.8000	0.6984	0.6992	0.7365
2	0.6028	0.5968	0.5680	0.5597	0.6730	0.6673	0.5603	0.5594	0.5773	0.7120	0.7037	0.5960	0.5945	0.6325
4	0.3423	0.3392	0.3262	0.3220	0.4054	0.3961	0.3212	0.3244	0.3333	0.4513	0.4372	0.3568	0.3585	0.3780
8	-	-	0.2019	0.2009	0.2132	0.2094	0.2212	0.2249	0.2294	-	-	-	-	-
			δ_m=0.94				β_1=-0.2857; β_2=0.1298 a^2 = 2; γ=2.135; δ_m=0.875 n_1 =-0.6 ; p = 2.3752					β_1=-0.25; β_2=0.1042 a^2 =(8/3); γ=1.927 δ_m = 0.763 n_1 =-0.80 ; p =2.749		

(*) Calculated assuming uniform activity in cylindrical pellets.

Comparison between approximate and numerical values for different activity distribution function in slab pellets.

Table 3.

	LINEAR						PARABOLIC					
m	1			2			1			2		
h \ η	η_A	η_N	$\bar{\eta}$	η_A	η_N	$\bar{\eta}$	η_A	η_N	$\bar{\eta}$	η_A	η_N	$\bar{\eta}$
1.5	0.9070	0.9077	0.9177	0.8432	0.8410	0.8836	0.9253	0.9258	0.9326	0.8704	0.8691	0.9050
2.0	0.8493	0.8494	0.8662	0.7680	0.7636	0.8165	0.8770	0.8775	0.8885	0.8025	0.8006	0.8461
3.0	0.7297	0.7300	0.7559	0.6391	0.6277	0.6859	0.7708	0.7700	0.7904	0.6795	0.6710	0.7254
6.0	0.4699	0.4709	0.5004	0.4020	0.3905	0.4266	0.5144	0.5154	0.5421	0.4399	0.4295	0.4657
8.0	0.3724	0.3737	0.3973	0.3155	0.3111	0.3332	0.4108	0.4124	0.4367	0.3482	0.3463	0.3676
	β_1=-0.04762; β_2=0.003175 a^2 = 12; γ=1.716; δ_m=0,875 n_1 =-3,75; p= 16.524			β_1=-0,09524; β_2=0.01588 a^2=8; γ= 2.392; δ_m=0,656 n_1 =- 3.3 , p= 7.824			β_1=-0,037; β_2=1.899 x 10^{-3} a^2=15; γ=1.762 ; δ_m=0,901 n_1=-4.5; p = 21.319			β_1=-0,074 ; β_2=9.495 x 10^{-3} a^2=10; γ=2.426; δ_m=0,676 n_1= -4.2 ; p=10.09		

produces reasonable estimates of η for engineering purposes.

As a general rule, when $\delta_m > 1$, there is no need to use eqn (31) instead of eqn (20) to estimate η's values, unless extremely accurate predictions are necessary.

CONCLUSIONS

A method which can be safely used to calculate the isothermal effectiveness factor in pellets of arbitrary geometry with non linear expressions and with the effect of non-uniform activity distribution function is presented in this contribution. The obtained results have shown a fairly good agreement between the numerical, almost exact, and approximate values of the effectiveness factor. Maximum deviations are of about 3%.

At the same time it is shown that for many engineering applications a surprisingly simple expression (see eqn 23) can be used to estimate the effectiveness factor with a maximum deviation from the true values of about 10%.

Apart from being a simple one, a unique parameter is needed which can be easily obtained in an analytical way from the well known asymptotic expression of η when $h \to \infty$. Equation (23) has the character of an almost universal expression of η when $1 > \eta > 0$. This case encompasses almost every situation arising in chemical engineering practice rendering eqn (23) in a powerful tool for design purposes and even for kinetic parameters estimation in real chemical reactors.

Though a number of assumptions were introduced, it should be stressed that the method can be easily extended to the analysis of more complex situations and even to estimate the performance of gas solid non-catalitic reactions. Except from those cases where non-isothermal, with exothermic reactions, and negative order kinetic expressions are considered, the method of matching can give extremely good results since the asymptotic expressions of η will always have the same forms as those presented above. Perhaps, this might be the greatest achievement of this contribution.

Acknowledgement—The authors are grateful to Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for partly financing this work.

NOTATION

- a dimensionless parameter given by (21a) or (25a)
- A_0, A_1, A_2 auxiliary expansion function satisfying eqns (6a,b,c)
- b dimensionless parameter defining linear activity distribution function (see eqn (32))
- C_A dimensionless concentration of species A
- C'_A dimensional concentration of species A
- d parameter defined by eqn (19b)
- D_A effective diffusity coefficient for species A
- $f(r)$ activity distribution function inside the pellet
- g auxiliary parameter given by eqn (A13)
- G auxiliary function defined by eqn (A4)
- h Thiele modulus (see eqn 2c)
- k_v specific rate of reaction per unit volume
- m order of reaction for species A
- n geometrical parameter
- n_1 dimensionless parameter given by (25b)
- p dimensionless parameter given by eqn (29)
- q auxiliary parameter used in the Appendix given by eqn (A13)
- r dimensionless spacial coordinate
- R characteristic length
- S dimensionless parameter given by eqn (28)
- w auxiliary variable defined by eqn (A12)
- x spacial coordinate in slab geometry

Greek symbols

- α dimensionless parameter defined by eqn (19a)
- β_1, β_2 dimensionless parameter given by eqns (9) and (10)
- γ auxiliary variable solution to eqn (27)
- δ_m auxiliary parameter given through eqn (22)
- η effectiveness factor
- $\bar{\eta}$ approximate value of η given by eqn (23)
- ξ auxiliary variable defined by eqn (A10)
- φ_0, φ_1 auxiliary expansion variables satisfying eqns (15) and (16)
- χ auxiliary space variable defined by eqn (11)

Subindex

- S refers to surface value

REFERENCES

[1] Gottifredi J. C., Gonzo E. E. and Quiroga O. D., *Chem. Engng Sci.* Ms. No. 1028.
[2] Chen H. C. and Anderson R. B., *J. Catal.* 1976 **43** 200.
[3] McArthur D. P., *Advan. Chem. Ser.* 1975 **143** 85.
[4] Hegedus L. L. and Baron K., Paper presented at *Joint VDIAICHE meeting.* Munich 1974.
[5] Su E. C. and Weaver E. E., *Sae Paper* 730594. Automative Engng Cong., Detroit 1973.
[6] Sato M., Takayama H., Kuritas S. and Kwan T., *Nippon Kagaku Zasshi* 1971 **92** 10.
[7] Becker E. R. and Wei J., *J. Catal.* 1977 **46** 372.
[8] Nyström M., *Chem. Engng Sci.* 1978 **33** 379.
[9] Petersen E. E. *Chemical Reaction Analysis*, p. 62. Prentice Hall, Englewood Cliffs, New Jersey 1965.
[10] Kehoe R., *Chem. Engng Sci.* 1974 **29** 315.

APPENDIX

Here we are concerned with the approximate solution to the following ordinary differential equation:

$$\frac{d^2\varphi_1}{d\chi^2} = mf(1)\varphi_0{}^{m-1}\varphi_1 + n\left(\frac{d\varphi_0}{d\chi}\right) - \chi\left|\frac{df}{dr}\right|_{r=1}\varphi_0{}^m \qquad (A1)$$

φ_0 being the solution to eqn (15) so:

$$\varphi_0 = \begin{cases} \exp(-f(1)^{1/2}\chi) & m = 1 \\ \left[1 - \left(\frac{1-m}{2}\right)\left(\frac{2f(1)}{m+1}\right)^{1/2}\chi\right]^{2/(1-m)} & m \neq 1. \end{cases} \qquad (A2)$$

Equation (A1) is subject to the following boundary conditions:

$$\varphi_1(0) = \varphi_1(\infty) = 0. \qquad (A3)$$

When $m = 1$ an exact analytical solution can be found under the form:

$$\varphi_1 = G(\chi)\exp(-f(1)^{1/2}\chi) \qquad (A4)$$

which after being replaced in (A1) with the corresponding function for φ_0 when $m = 1$ gives:

$$\frac{d^2G}{d\chi^2} - 2\frac{dG}{d\chi}(f(1)^{1/2} = -nf(1)^{1/2} - \chi\left(\left.\frac{df}{dr}\right|_{r=1}\right). \qquad (A5)$$

Thus

$$G(\chi) = \left(\frac{1}{4}\right)\left(\left.\frac{df}{dr}\right|_{r=1}\right)f(1)^{-1/2}\chi^2 + \frac{1}{2}\left(n + \frac{1}{2}\left(\left.\frac{df}{dr}\right|_{r=1}\right)f(1)^{-1}\right)\chi \qquad (A6)$$

is the solution to eqn (A5), and conditions (A3) are satisfied. Finally:

$$-\left.\frac{d\varphi_1}{d\chi}\right|_{\chi=0} = -\frac{1}{2}\left[n + \left(\left.\frac{df}{dr}\right|_{r=1}\right)\frac{f(1)^{-1}}{2}\right]. \qquad (A7)$$

In the case where $m \neq 1$ we have to solve eqn (A1) with::

$$\frac{d\varphi_0}{d\chi} = -\left(\frac{2f(1)}{m+1}\right)^{1/2}\varphi_0\exp\left(\frac{m+1}{2}\right). \qquad (A8)$$

The task seems formidable. However, since the solution to the homogeneous parts of (A1) is $\varphi_1 = 0$, we only need a particular solution to (A1). Here the following expression will be proposed:

$$\varphi_1 = q\chi^2(1+\xi\chi)^{Z-1} + w\chi(1+\xi\chi)^Z \tag{A9}$$

where

$$\xi = \left(\frac{m-1}{2}\right)\left(\frac{2f(1)}{m+1}\right)^{1/2}. \tag{A10}$$

By replacing (A9) into (A1) it is found:

$$Z = -\left(\frac{2}{m+1}\right) \tag{A11}$$

$$w = \frac{\left(n + 0.5\left.\frac{\mathrm{d}f}{\mathrm{d}r}\right|_{r=1} f^{-1}(1)\left(\frac{m+1}{2}\right)\right)}{2(1+0.25(m-1))} \tag{A12}$$

$$q = \left(\frac{2f(1)}{m+1}\right)^{1/2}\left(w - \frac{n}{2}\right). \tag{A13}$$

Clearly (A9) fits boundary conditions (A3) provided $1 < m < 3$, but this is just the range of m's values we need to cover. From (A9):

$$-\left.\frac{\mathrm{d}\varphi_1}{\mathrm{d}\chi}\right|_{\chi=0} = -w \tag{A14}$$

and it can be seen that q reduces itself to expression (A7) when $m = 1$. Thus

$$\alpha = (n+1)\left(\frac{2f(1)}{m+1}\right)^{1/2} \tag{A15}$$

$$d = n_1 = -\left(\frac{n+1}{2}\right)\left\{\frac{\left(n + \frac{1}{2}\left.\frac{\mathrm{d}f}{\mathrm{d}r}\right|_{r=1} f^{-1}(1)\left(\frac{m+1}{2}\right)\right)}{(1+0.25(m-1))}\right\} \tag{A16}$$

are the valid expressions used to estimate the effectiveness factor's tabulated values of this work.