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Short communication

Approximate expression for the effectiveness factor estimation and a simple numerical method for concentration profile calculation in porous catalyst

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Abstract

The model of steady state diffusion and reaction in a catalyst pellet where a single reaction takes place is analyzed with the scope to predict effectiveness factor through a very simple and practical procedure. Non-linear usual reaction kinetics are used to investigate the agreement among exact or numerical predictions with approximate results. In all cases studied maximum deviations in the whole range of ϕ values are below 4% which turns the procedure attractive and useful. To perform numerical integration of the classical non-linear diffusion and reaction differential equation a new procedure was used that avoid usual instabilities or the introduction of spline collocation methods when concentration profiles are very steep. Concentration resulting profiles are compared with those generated by an early expression proposed by the authors.

Keywords: Diffusion and reaction; Effectiveness factor; Non-linear kinetics; Thiele modulus; Numerical solutions; concentration profiles

1. Introduction

Recently, Sun et al. [1] presented a new procedure, based on the Adomian decomposition method, to obtain approximate solutions for the non-linear diffusion and reaction differential mass balance equation in catalyst pellets. The dimensionless concentration profile inside the catalyst, as well as the effectiveness factor, can be calculated using this procedure. However, three, and even more (up to six), terms of the Adomian polynomial are necessary to obtain concentration (γ) or effectiveness factor (η) values in agreement with numerical or exact prediction. The number of terms depends upon the complexity of the kinetic expression and on the Thiele modulus value. Nevertheless, as the Thiele modulus (ϕ) increases (i.e., $\phi \geq 2$), η deviations in relation to exact values become larger than 100%.

In this contribution a previous developed perturbation and matching procedure [2] is applied to obtain effectiveness factor predictions through a very simple resulting algebraic expression which produces results in close agreement (maximum deviation 4%) for the whole range of ϕ and for kinetic expressions investigated. In addition a new numerical procedure is used to calculate dimensionless concentration profiles and effectiveness factor which is very straightforward and rapidly convergent.

An approximate expression, developed by Gottifredi et al. [3], to estimate dimensionless concentration profiles inside a catalyst pellet, with the knowledge of η is also tested with predictions obtained through the numerical procedure.

2. Theoretical development

It will be assumed that a single reaction is taking place inside the catalyst pellet of characteristic length L and that isothermal conditions prevail. The continuity equation for the

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Nomenclature

a	dimensionless parameter given by Eq. (11)
A	dimensionless variable defined by Eq. (13)
C	dimensional concentration (kmol/m^3)
D	effective diffusivity of key component (m^2/h)
f	auxiliary function defined by Eq. (18)
g	auxiliary function defined by Eq. (13)
K	dimensionless kinetic parameter used in Eq. (22)
L	catalyst particle characteristic dimension (m)
m	parameter used to define geometrical shape
N	reaction order
r	dimensional rate of reaction (kmol/m^3 h)
R	dimensionless rate of reaction defined by Eq. (2)
x	dimensionless coordinate defined by Eq. (2)
x'	dimensional coordinate (m)

Greek letters

γ	dimensionless concentration (see Eq. (2))
ε	auxiliary parameter defined by Eq. (20)
η	effectiveness factor defined by Eq. (4)
λ	auxiliary parameter defined by Eq. (13)
ρ_1	auxiliary parameter defined by Eq. (9)
σ_1	auxiliary parameter defined by Eq. (7)
ϕ	Thiele modulus defined by Eq. (2)
ϕ^*	modified Thiele modulus given by Eq. (8)

Subscripts

c	denotes property calculated at $x = 0$
s	denotes property calculated at $x = 1$

dimensionless key component concentration can be written as

$$x^{-m}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^m\frac{\mathrm{d}\gamma}{\mathrm{d}x}\right) = \phi^2 R(\gamma) \tag{1}$$

where the following dimensionless variables were defined:

$$\gamma = \frac{C}{C_\mathrm{s}}, \qquad x = \frac{x'}{L}, \qquad \phi = L\sqrt{\frac{r_\mathrm{s}}{DC_\mathrm{s}}},$$
$$R(\gamma) = \frac{r(C)}{r(C_\mathrm{s})} \tag{2}$$

Here C represents the dimensional concentration, D the effective diffusivity, $r(C)$ the dimensional rate of reaction and ϕ the Thiele modulus, respectively. $m = 0, 1, 2$ stands for the geometrical shape of the catalyst particle, while subscript ‘s’ denotes values of the corresponding variables evaluated at the outer surface of the pellet.

Assuming negligible external mass transfer resistance Eq. (1) must be solved with the following boundary conditions:

$$\gamma = 1, \quad x = 1, \qquad \frac{\mathrm{d}\gamma}{\mathrm{d}x} = 0, \quad x = 0 \tag{3}$$

Under realistic situations Eq. (1) does not have an analytical solution since $R(\gamma)$ is usually a non-linear function of γ. Most of the results found in the literature are obtained through the application of numerical methods that can become unstable when $\phi^2 \geq 1$. Fortunately, from a chemical engineering point of view, one is not interested in solving Eq. (1) but rather in estimating the effectiveness factor (η) given by:

$$\eta = (m+1)\int_0^1 [R(\gamma)x^m]\,\mathrm{d}x \tag{4}$$

By integrating Eq. (4) once, with boundary condition given by Eq. (3), it can be easily shown that:

$$\eta = \frac{m+1}{\phi^2}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}x}\right)_{x=1} \tag{5}$$

Both Eqs. (4) and (5), can be used to deduce appropriate expressions to predict η values.

2.1. Approximate effectiveness factor estimation

Gottifredi and Gonzo [2] using the perturbation technique have shown that, for small values of ϕ, η depends on ϕ, up to term of the order ϕ^2 as follows:

$$\eta \approx 1 - \sigma_1\phi^2 + \mathrm{O}(\phi^4) \quad (\phi^2 \ll 1) \tag{6}$$

with

$$\sigma_1 = \frac{R'(1)}{(m+1)(m+3)} \tag{7}$$

where $R'(1)$ denotes first derivative with respect to γ, evaluated at $\gamma = 1$.

For large values of ϕ ($\phi \gg 1$), assuming that $\gamma = 0$ in the center of the pellet, the well-known Petersen [4] and Bischoff [5] approximate expression is valid:

$$\eta \approx \frac{\rho_1}{\phi} = \frac{1}{\phi^*} \quad (\phi^2 \gg 1) \tag{8}$$

where the parameter ρ_1 satisfies the following expression:

$$\rho_1 = (m+1)\left[2\int_0^1 R(\gamma)\,\mathrm{d}\gamma\right]^{1/2} \tag{9}$$

Gottifredi et al. [3], proposed an algebraic equation to match Eqs. (6) and (8):

$$\eta = [\phi^{*2} + \exp(-a\phi^{*2})]^{-1/2} \tag{10}$$

By comparing Eqs. (6) and (8) with Eq. (10), the unknown parameter “a” is found to be:

$$a = 1 - 2\sigma_1\rho_1^2 \tag{11}$$

2.2. Dimensionless concentration profile

As will be shown below, the effectiveness factor can be predicted with Eq. (10) with great accuracy. However, the concentration profile remains unknown. Gottifredi and Gonzo [6], using once again the perturbation and matching technique, have shown that the concentration profile could be predicted by the equation:

$$A = \exp\left[\frac{-\lambda(1-x^2)}{2-\frac{1-xg(x)}{1+2/\lambda}}\right] \tag{12}$$

where

$$A = \frac{\gamma-\gamma^*}{1-\gamma^*}, \qquad \lambda = \frac{\phi^2\eta}{(m+1)(1-\gamma^*)},$$
$$g(x) = \frac{1-\exp(-\lambda x)}{1-\exp(-\lambda)} \tag{13}$$

γ^* being the dimensionless concentration that satisfies $R(\gamma^*)=0$.

3. Numerical method

When $m = 1$ (slab geometry) both terms of Eq. (1) can be multiplied by $2(\mathrm{d}\gamma/\mathrm{d}x)$ resulting:

$$2\left(\frac{\mathrm{d}\gamma}{\mathrm{d}x}\right)\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}x}\right) = 2\phi^2 R(\gamma)\frac{\mathrm{d}\gamma}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left[\left(\frac{\mathrm{d}\gamma}{\mathrm{d}x}\right)^2\right] \tag{14}$$

By integrating the last two terms using boundary conditions and $\gamma=\gamma_\mathrm{c}$ at $x=0$:

$$\frac{\mathrm{d}\gamma}{\mathrm{d}x} = \left(2\phi^2\int_{\gamma_\mathrm{c}}^{\gamma} R(\gamma')\,\mathrm{d}\gamma'\right)^{1/2} \tag{15}$$

Thus according to Eq. (5):

$$\eta = \frac{\left(2\int_{\gamma_\mathrm{c}}^{1} R(\gamma')\,\mathrm{d}\gamma'\right)^{1/2}}{\phi} \tag{16}$$

which allows the numerical calculation of η as a function of ϕ, provided γ_c is known. To find the corresponding γ_c value for the given ϕ, Eq. (15) must be integrated once again:

$$\int_{\gamma_\mathrm{c}}^{1}\left(\int_{\gamma_\mathrm{c}}^{\gamma} R(\gamma')\,\mathrm{d}\gamma'\right)^{-1/2}\mathrm{d}\gamma = \sqrt{2}\phi = F(\gamma_\mathrm{c}) \tag{17}$$

As stated, provided the kinetics is know and ϕ given, the only unknown in Eq. (17) is γ_c. However it should be noticed that in most cases:

$$\int_{\gamma_\mathrm{c}}^{\gamma} R(\gamma')\,\mathrm{d}\gamma' = f(\gamma,\gamma_\mathrm{c}) \tag{18}$$

can be found analytically and that it vanishes when $\gamma=\gamma_\mathrm{c}$. To avoid numerical discontinuities it was found convenient to divide the interval in two regions. One very close to γ_c (γ_c and $\gamma_\mathrm{c}+\varepsilon$) and the second between ($\gamma_\mathrm{c}+\varepsilon$) and 1. Thus Eq. (17) can be rewritten in the following fashion:

$$\int_{\gamma_\mathrm{c}}^{1}(f(\gamma_\mathrm{c},\gamma))^{-1/2}\,\mathrm{d}\gamma = \int_{\gamma_\mathrm{c}}^{\gamma_\mathrm{c}+\varepsilon}(f(\gamma_\mathrm{c},\gamma))^{-1/2}\,\mathrm{d}\gamma + \int_{\gamma_\mathrm{c}+\varepsilon}^{1}(f(\gamma_\mathrm{c},\gamma))^{-1/2}\,\mathrm{d}\gamma \tag{19}$$

which is similar, but more simple, than a spline collocation procedure. Both integral were calculated with six points collocations as given by Table 25.8 of Abramowitz and Stegun [7] and the criterion used to establish ε values was:

$$\frac{1-\gamma_\mathrm{c}}{10} = \varepsilon \tag{20}$$

Finally the original second order non-linear differential equation was reduced to a unique algebraic non-linear equation with γ_c as unknown if ϕ is fixed or ϕ can be calculated by fixing γ_c value. In our case γ_c was determined using the standard Polymath [8] non-linear algebraic equation routine which gives excellent results even with an unfair initial guess of γ_c.

Once the pair ϕ and γ_c is determined, concentration profile can be easily calculated by changing the integration limits of Eq. (17):

$$\int_{\gamma_\mathrm{c}}^{\gamma_\mathrm{c}+\varepsilon}(f(\gamma_\mathrm{c},\gamma))^{-1/2}\,\mathrm{d}\gamma + \int_{\gamma_\mathrm{c}+\varepsilon}^{\gamma_\mathrm{A}}(f(\gamma_c,\gamma))^{-1/2}\,\mathrm{d}\gamma = \sqrt{2}\phi x \tag{21}$$

Thus for a fixed value of γ (say $\gamma=\gamma_\mathrm{A}$), x is straightforwardly calculated and the concentration profile is known by applying repeatedly this routine.

4. Results and discussion

4.1. Effectiveness factor

Since agreement is fairly good, with the scope to better show differences among predicted (approximated) (η_A) and numerical (η_N) values of the effectiveness factor for different cases, all the estimations will be presented in tables instead of figures. Maximum deviation for the particular case of first-order irreversible reaction ($n = 1$) is always smaller than 0.5% and Eq. (8) can be safely used when $\phi > 3$.

Tables 1 and 2 show a comparison among η values for the case of a power law kinetic expression: $R(\gamma)=\gamma^n$, with $n = 0.5$ and $n = 2$. It can be seen that Eq. (10) is able to predict η values in excellent agreement with the corresponding numerical values for the entire range of Thiele modulus, since in both tables the asymptotic region (where Eq. (8) is valid) was reached.

To extend the spectra of kinetic expressions, the general case of a reaction with Langmuir–Hinshelwood

Table 1
Approximate and numerical effectiveness factor values for a power law kinetic

ϕ	γ_c	η_N	η_A	E (%)
0.30	0.955003	0.993956	0.984997	0.90
0.60	0.825258	0.962836	0.940426	2.33
1.00	0.561278	0.879014	0.842379	4.17
1.50	0.241401	0.722708	0.693524	4.04
2.00	0.055594	0.573554	0.559991	2.36
2.30	0.011926	0.501717	0.495205	1.30
2.40	0.003490	0.481155	0.476152	1.04

$n = 0.5$, slab geometry, $\rho_1 = 1.1547$.

Table 2
Approximate and numerical effectiveness factor values for a power law kinetic

ϕ	γ_c	η_N	η_A	E (%)
0.30	0.956191	0.965146	0.944864	2.10
0.60	0.848380	0.849162	0.821505	3.26
0.80	0.765435	0.783347	0.757971	3.24
1.00	0.685360	0.672346	0.652817	2.90
1.50	0.519498	0.504733	0.496152	1.70
2.00	0.401616	0.394804	0.391828	0.75
3.00	0.247755	0.270088	0.269944	0.05
4.00	0.137781	0.203857	0.203829	0.01

$n = 2$, slab geometry, $\rho_1 = 0.8165$.

(Michaelis–Menten–Monod) kinetics of the form:

$$R(\gamma) = \frac{\gamma}{1 + K\gamma} \tag{22}$$

is presented in Table 3 for $K = 2$. The agreement is very good. For large values of K ($K \geq 5$), the results are almost those given by a zero order reaction.

The case of more complex Langmuir–Hinshelwood kinetics, leading to apparent negative reaction order, were also investigated showing that η values greater than one are predicted by our approximate expression (10) as well as by the numerical procedure. Maximum deviation are always smaller than 12% in the whole range of ϕ values.

4.2. Dimensionless concentration profile

Fig. 1 shows dimensionless concentration profiles in a catalyst slab with Thiele modulus as parameter. A power law kinetic expression is considered with $n = 0.5$. Comparison between approximate and numerical predictions shows a fair agreement, although the deviation increases as $x \to 0$ and ϕ takes larger values. Same behavior was observed for other values of "n".

Table 3
Estimated and numerical values of the effective ness factor for $R(\gamma) = \gamma/(1 + K\gamma)$, $K = 2$, $\rho_1 = 2.0118$

ϕ	γ_c	η_N	η_A	E (%)
0.6	0.9410	0.9865	0.9860	0.05
1	0.8414	0.9615	0.9586	0.29
2	0.4755	0.8343	0.8198	1.74
4	0.0659	0.5014	0.4995	0.38
5	0.0234	0.4027	0.4024	0.08
6	0.0084	0.3357	0.3356	0.03

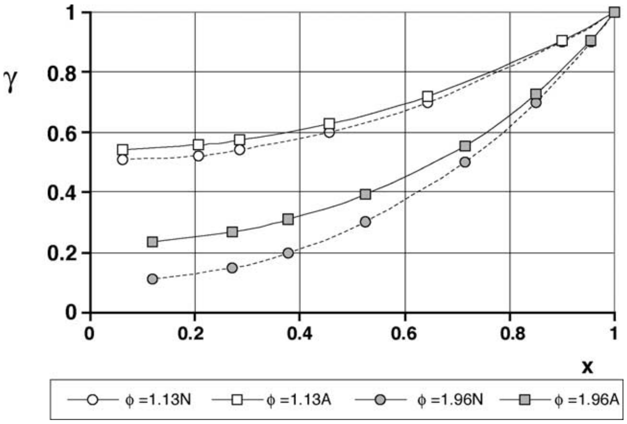

Fig. 1. Dimensionless concentration profiles inside a slab catalytic pellet. Power law kinetic, $n = 0.5$: (A) predicted; (N) numerical results.

5. Conclusions

The semi-analytical procedure, early proposed by Gottifredi et al. [3], is shown very simple and practical to predict very accurate η results when compared with exact or numerical findings even for non-linear kinetic expressions. In the whole range of ϕ values the relative error was always smaller than 4% which is quite acceptable for most engineering purposes. Typical results are presented in tables to better show this behavior.

In order to compare approximate with numerical results a new approach to predict, both concentration profiles and effectiveness factor, was presented. With this method there are no numerical instabilities and there is no need to use spline collocation techniques. The convergence of numerical results is straightforward. Unfortunately this procedure is only fully applicable to slab geometry ($m = 0$). However it can be applied with minor modifications to non-isothermal single reaction models.

It should be stressed that the approximate η results generated with our simple procedure are much better than those recently presented by Sun et al. [1]. Their η deviations can be quite large when compared with numerical findings. Error of 100% or even larger are not acceptable to estimate η values for chemical reactor design purposes. On the other hand the algebra involved in their method can become quite cumbersome to be applicable in chemical engineering practice.

Approximate concentration profile results clearly shown that Gottifredi and Gonzo [6] expression produces very good estimates in the region nearby the catalytic surface and much poor estimates in the central region of the pellet. Nevertheless, it can be useful in most chemical engineering applications as was shown by Gottifredi and Froment [9].

It should be noticed that this approach can be easily extended to consider more complex kinetic expressions, non-isothermal systems and the effect of external mass and heat transfer resistances.

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