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Approximation of the effectiveness factor in catalytic pellets

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Abstract

The 1D model proposed by Burghardt and Kubaczka [Chem. Eng. Proc. 35 (1996) 65] to approximate the behavior of 3D catalytic pellets has been recently found able to provide accurate results for evaluating effective reaction rates when its parameter σ is suitable adjusted [Chem. Eng. Res. Des., submitted for publication]. This parameter represents the contraction of the cross-section available for diffusion. A formulation coupling a first-order Galerkin approximation with a truncated asymptotic expansion is proposed here to evaluate the effectiveness factor of single reactions in the range of interest $-1/5 < \sigma < 5$ [Chem. Eng. Res. Des., submitted for publication]. The formulation provides a 3% level of precision for essentially all normal kinetics of practical interest and a large range of abnormal kinetics. In particular, this conclusion includes reaction rates approaching a zero-order reaction, for which large deviations arise from the use of previous approximations proposed in the literature. On the other hand, the extent of abnormal kinetics being accurately approximated is significantly enlarged.

Keywords: Effectiveness factor; One-dimensional model; Diffusion-reaction

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1. Introduction and literature survey

Burghardt and Kubaczka [1] proposed a 1D geometric model, hereafter called GC model, to approximate the behavior of 3D catalytic pellets. The GC model consists in a body allowing mass flux on a single dimensionless coordinate z, $0 \leq z \leq 1$, and presenting a cross-section of variable area proportional to (z^σ). According to the value of the *shape power* σ, the model reduces to a slab ($\sigma = 0$), an infinitely long circular cylinder ($\sigma = 1$) or a sphere ($\sigma = 2$).

To approximate the behavior of a generic 3D pellet shape, the external surface area and volume of the model body are assumed to equal those of the actual pellet, S_p and V_p, and according to Mariani et al. [2], σ is evaluated by matching the behavior of the actual pellet at low reaction rates. Some simple particle shapes can lead to high values of σ, as a circular cylinder with a height to diameter ratio 0.85 ($\sigma = 3.25$) or a cube ($\sigma = 4.3$). Values $\sigma < 0$ are not likely for catalytic pellets, but the important case of monolith reactors with catalytic washcoat on channels shows this feature [3]. The range of interest can be set as $-1/5 < \sigma < 5$. In this range, Mariani et al. [2] found that the GC model is precise up to 0.7% for linear kinetics and they estimated that the deviations will not rise above 2% for non-linear kinetics outside the range of steady state multiplicity. Therefore, the GC model seems to be an accurate mean to avoid 3D evaluations for effective reaction rates.

For actual application, the GC model will be most valuable in the case of multiple reactions, as it avoids the heavy computational burden of having to solve a set of conservation equations in 3D. Nonetheless, we will restrain ourselves in this contribution to a single reaction, with the purpose of presenting an approximation to evaluate the effectiveness factor without resorting to the numerical solution of the conservation equation.

Numerical codes and computer facilities have been developed up to such an extent that the evaluation of effective reaction rates is far from being a numerically challenging problem, provided that a few isolate calculations should be made. However, it should be realized that relatively novel catalytic reactors, as reverse-flow reactors and reactive distillation processes, or more sophisticated models for traditional reactors, including CFD simulations, can demand thousands, or higher orders, of spatial and temporal discretization points, in which the effective reaction rates should be evaluated. Besides, the overall solution will most

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often have to be found iteratively. If in addition, operating conditions or design parameters are being optimized, the number of such evaluations will be augmented by a large factor. It seems clear that a suitable approximation for evaluating effective reaction rates will be desirable, even considering nowadays computer speed.

A number of approximations for η have been presented in the literature (e.g. [4–15]). Some of them have specific purposes, as those of Szukiewicz [11,12] intended to evaluate transient, in addition to steady state, solutions and those of Ochoa and co-workers [13,14] intended to provide a fast evaluation for low and intermediate Thiele modulus (Φ). They are not suitable to cover the whole range of Φ. For this reason, they will not further discussed. All the quoted contributions were originally intended to deal with any or all of the discrete values $\sigma = 0$, 1, 2. Except the contribution of Hong et al. [15] that can only be employed for $\sigma = 2$, the other approximations can be readily adapted for continuous values of σ. However, only some of them can be used for the whole range of interest $-1/5 < \sigma < 5$ for a given reaction rate expression. Each approximation shows some other distinguishing features, but some common conclusions can be drawn.

For kinetics showing effective reaction orders ($n_e = d \ln r/d \ln C$) higher than around 0.5, most of the approximations provide a good estimation of η in the applicable range of σ values. Instead, when $0 \le n_e < 0.5$ the error increases for all the approximations. In the limit, for the so-called zero-order isothermal reaction (actually, a step function of the reactant concentration) none of them can guarantee errors less than 20% in the range $0 < \sigma < 5$. It is recalled that low values of n_e do not only arise from power-law rate expressions, but also for the very important case of some LHHW rate expression with significant inhibition effects.

For abnormal kinetics the approximations of Wedel and Luss [4]; Gottifredi et al. [6], Gottifredi et al. [8] and Yin and Li [10] can be employed, although the errors rapidly increase as the magnitude of the maximum rate increases. This is expectable, as these approximations join, by means of a suitable expression, the limiting behavior of η as $\Phi \to 0$ and $\Phi \to \infty$ and, therefore, the position and magnitude of the maximum can hardly be predicted from such information.

The aim of this work is to present for the whole range $-1/5 < \sigma < 5$ a procedure capable to approximate the effectiveness factor η for essentially all normal kinetics of practical interest and for a wide range of abnormal kinetics. Special emphasis has been put in establishing the precision level and the limit of application of the proposed formulation.

From the previously summarized analysis, it was concluded that knowing the limiting behavior of η at $\Phi \to 0$ and $\Phi \to \infty$ is not enough to deal with strongly abnormal kinetics. Based on this observation, the first-order Galerkin (FOG) approximation is adopted. It is well known that the FOG approximation is accurate and computationally efficient [16] from low to intermediate values of Φ. A critical value $\hat{\Phi}$ is defined for the application of the FOG approximation and for $\Phi > \hat{\Phi}$ a truncated expansion in terms of $1/\Phi$ is employed.

2. The formulation to approximate η

The problem to solve for a single reaction is:

$$z^{-\sigma} \frac{\mathrm{d}}{\mathrm{d}z}\left(z^{\sigma} D_{\mathrm{A}}(C_{\mathrm{A}}) \frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}z}\right) = L^2 r_{\mathrm{A}}(C_{\mathrm{A}}) \tag{1}$$

$$C_{\mathrm{A}} = C_{\mathrm{As}} \quad (z = 1); \qquad \frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}z} = 0 \quad (z = 0) \tag{2}$$

where A is the limiting reactive species and L is the diffusion length, $L = \ell(1+\sigma)$, $\ell = V_{\mathrm{p}}/S_{\mathrm{p}}$.

A dimensionless dependent variable Y is defined as

$$Y = \frac{1}{J_{\mathrm{A}}} \int_{C_{\mathrm{Ae}}}^{C_{\mathrm{A}}} D_{\mathrm{A}}(C_{\mathrm{A}})\,\mathrm{d}C_{\mathrm{A}};$$

$$J_{\mathrm{A}} = \int_{C_{\mathrm{Ae}}}^{C_{\mathrm{As}}} D_{\mathrm{A}}(C_{\mathrm{A}})\,\mathrm{d}C_{\mathrm{A}} \tag{3}$$

where C_{Ae} is the equilibrium concentration. In the case that $D_{\mathrm{A}}(C_{\mathrm{A}})$ is constant, $J_{\mathrm{A}} = D_{\mathrm{A}}(C_{\mathrm{As}} - C_{\mathrm{Ae}})$ and $Y = (C_{\mathrm{A}} - C_{\mathrm{Ae}})/(C_{\mathrm{As}} - C_{\mathrm{Ae}})$. Eqs. (1) and (2) become

$$z^{-\sigma} \frac{\mathrm{d}}{\mathrm{d}z}\left(z^{\sigma} \frac{\mathrm{d}Y}{\mathrm{d}z}\right) = (1+\sigma)^2 \Phi^2 r(Y) \tag{4}$$

$$Y(1) = 1; \qquad Y'(0) = 0 \tag{5}$$

where $r = r_{\mathrm{A}}/r_{\mathrm{As}}$, and

$$\Phi^2 = \ell^2 \frac{r_{\mathrm{As}}}{J_{\mathrm{A}}} \tag{6}$$

It is noted that with the given definition of Y, $r = 0$ at $Y = 0$.

The effectiveness factor is the average dimensionless rate

$$\eta = (1+\sigma) \int_0^1 r\, z^{\sigma}\,\mathrm{d}z \tag{7}$$

The formulation employed in this work to evaluate η is presented in Table 1. The two approximations employed will be described in the following paragraphs.

The first-order Galerkin method is employed in the lower range of Φ. The formulation described in Chapter 2 of [16] is used for FOG. It is based on the approximation

$$Y = 1 + (Y_0 - 1)(1 - u) \tag{8}$$

where $u = z^2$ and $Y_0 = Y(0)$ is the parameter to be determined. The integral of the residuals of Eq. (4) weighted by $(1-u)$ over the pellet volume is evaluated by a Gauss–Jacobi (weighting function $[(1-u)u^{(\sigma-1)/2}]$) quadrature. Then, the quadrature points are the zeros $\{u_i\}$ of the Jacobi polynomials $P_N(u)$ defined by

$$\int_0^1 [(1-u)u^{(\sigma-1)/2}] u^j P_N(u)\,\mathrm{d}u = 0; \qquad j = 0, \ldots, N-1 \tag{9}$$

Table 1
Formulation of the proposed approximation

First-order Galerkin approximation (used when $\Phi \le \hat{\Phi}$)

$$\eta_G(\Phi) = 1 - \frac{2}{3+\sigma}\sum_{i=1}^{N}\omega_i \frac{1-r(Y_i)}{1-u_i} \tag{T1}$$

where

$$Y_i = 1 + (Y_0 - 1)(1-u_i) \tag{T2}$$

$$1 - Y_0 = \tfrac{1}{2}(1+\sigma)\Phi^2 R(Y_0); \qquad R(Y_0) = \textstyle\sum_{i=1}^{N}\omega_i r(Y_i) \tag{T3}$$

$$\hat{\Phi} = \min[\Phi_0, \Phi_M] \tag{T4}$$

where

$$\Phi_0^2 = \frac{2}{(1+\sigma)R(0)}; \qquad \Phi_M^2 = 9\frac{(1+\sigma/5)}{(1+\sigma)^2}\eta_G(\Phi_0) \tag{T5}$$

Asymptotic approximation (used for $\sigma \le 3$, $\Phi > \hat{\Phi}$)

$$\eta_B(\Phi) = \frac{\beta_1}{\Phi} + \frac{\beta_2}{\Phi^2} + \frac{\hat{\beta}}{\Phi^3} \tag{T6}$$

where

$$\beta_1 = [P(1)]^{0.5}; \qquad \beta_2 = -\frac{\sigma}{(1+\sigma)\beta_1}\int_0^1 [P(\lambda)]^{0.5}\,\mathrm{d}\lambda; \qquad P(\lambda) = 2\int_0^{\lambda} r(Y)\,\mathrm{d}Y \tag{T7}$$

$$\hat{\beta} = \hat{\Phi}^3\eta_G(\hat{\Phi}) - \beta_1\hat{\Phi}^2 - \beta_2\hat{\Phi} \tag{T8}$$

Eq. (T3) in Table 1 is the resulting expression that allows the evaluation of Y_0. $\{\omega_i\}$ is the set of weighting factors of the quadrature just described, normalized to $\sum \omega_i = 1$. For $N = 2$ (FOG$_2$)

$$u_{1,2} = \frac{(3+\sigma) \mp \sqrt{12(3+\sigma)/(7+\sigma)}}{9+\sigma};$$
$$\omega_1 = \frac{u_2 - (1+\sigma)/(5+\sigma)}{u_2 - u_1}; \qquad \omega_2 = 1 - \omega_1 \tag{10}$$

Once Y_0 is evaluated, η from Eq. (7) is calculated by a Radau (end-point $u = 1$)–Jacobi (weighting function $u^{(\sigma-1)/2}$) quadrature. The same set $\{u_i\}$ of quadrature points applies, and the corresponding weighting factors can be written in terms of $\{\omega_i\}$. Recalling that $r(1) = 1$, the final result is that in Eq. (T1).

If $N = 1$ is chosen, the method becomes the one-point orthogonal collocation (1POC) method described by Villadsen and Michelsen [16]. The general case with N quadrature points will be referred as FOG$_N$ method. It is anticipated that FOG$_2$ will be the recommended choice in most cases, on the basis of results obtained from numerical experiments.

The solution from FOG, η_G, is used up to $\Phi = \hat{\Phi}$, Eq. (T4), where Φ_0 (Eq. (T5)) makes $Y_0 = 0$ in the solution of Eq. (T3). Note that the evaluation of $\eta_G(\Phi_0)$ from Eq. (T1) does not require any iteration, as it corresponds to $Y_0 = 0$ and thus $r(Y_i) \equiv r(u_i)$ (Eq. (T2)). Further remarks about FOG in general and the definition of $\hat{\Phi}$ in particular can be found in Keegan et al. [17].

At $\Phi > \hat{\Phi}$, the proposed approximation η_B (Eq. (T6) in Table 1) is a truncated expansion of η in terms of $(1/\Phi)$. The coefficients β_1 and β_2 (Eq. (T7)) are evaluated analytically (e.g. from Gonzo and Gottifredi [18]), while $\hat{\beta}$ (Eq. (T8)) provides continuity with the FOG approximation.

For a zero-order reaction or normal LHHW kinetics behaving alike, η_B shows a small maximum shortly after $\hat{\Phi}$ ($=\Phi_0$ in these cases) when $\sigma > 3$. Although not very important in magnitude, this kind of errors is undesirable. In the present range of interest, $3 < \sigma \le 5$, we suggest using the solution for $\sigma = 3$ with a suitable scaled Thiele modulus, as follows. Define

$$\Phi_S^2 = \Phi^2\left[\frac{S_0(\hat{\Phi})^2_{\sigma=3} + \Phi^2}{S_\infty(\hat{\Phi})^2_{\sigma=3} + \Phi^2}\right];$$
$$S_0 = \frac{96}{(1+\sigma)(3+\sigma)}, \qquad S_\infty = \frac{64}{(1+\sigma)^2} \tag{11a}$$

Then,

$$\eta = \eta(\Phi_S)_{\sigma=3} \quad (3 < \sigma \le 5) \tag{11b}$$

where $(\hat{\Phi})_{\sigma=3}$ is the value of $\hat{\Phi}$ (Table 1) calculated with $\sigma = 3$ and $\eta(\Phi_S)_{\sigma=3}$ is the value from the algorithm in Table 1 at Φ_S and $\sigma = 3$.

It is worth recalling the number of times that $r(Y)$ should be calculated for the algorithm in Table 1. When $\Phi \le \hat{\Phi}$, $\eta_G(\Phi_0)$ demands N calculations of $r(Y)$ and the iterative process for $\eta_G(\Phi)$ demands about $3N$ calculations. For FOG$_2$, this implies eight evaluations in all.

When $\Phi > \hat{\Phi}$, β_1 and β_2 (Eq. (T7)) should be numerically evaluated, for which 10 calculations $r(Y)$ were employed. These should be added to the N calculations for $\eta_G(\Phi_0)$ and, just in the case $\hat{\Phi} = \Phi_M$ (Eq. (T4)), the $3N$ calculations for $\eta_G(\Phi_M)$. More details about computational aspects are discussed by Keegan et al. [17].

3. Accuracy of the proposed formulation

We will consider for $r = r_A/r_{As}$ expressions of the following form,

$$r = \frac{(1+A)^d}{(1+AC)^d}\exp\left(\frac{\gamma\beta(1-C)}{1+\beta(1-C)}\right) \times \left(\frac{C^n - C_e^n(Q/Q_e)^m}{1 - C_e^n(Q_s/Q_e)^m}\right). \tag{12}$$

C is the limiting-species dimensionless concentration, $C = C_A/C_{As}$, and Q represents the dimensionless concentration of a product, $Q = C_Q/C_{As}$, that is assumed to be stoichiometrically related to C according to $Q = Q_s + 1 - C$. The equilibrium concentration $C = C_e$ is taken as a parameter and Q_e follows from stoichiometry. The diffusivity D_A will be taken as a constant, so variables C and Y are related by $C = Y(1 - C_e) + C_e$. The reaction orders n, m are parameters which should be assigned to complete the definition of the driving force in Eq. (12).

The inhibition term $(1+AC)^d$ involves two further parameters, the dimensionless adsorption constant $A = K_A C_{As}$

Table 2
Maximum errors for FOG approximation (FOG_2, unless otherwise stated) and conditions at which they take place

Group	Type of kinetic expression and parameter ranges	Maximum ε (%)	Conditions
A	*Irreversible nth order endothermic reactions*: $n = 0$–3, $(\gamma\beta) = -5$, $\beta = -0.2$	2.8	$\sigma = 4$; $n = 0$
B	*Irreversible LHHW reactions*: $n = d = 1, 2$; $A = 0$–30; isothermal and endothermic $(\gamma\beta) = -5$; $\beta = -0.2$ cases.	2.4	$\sigma = 4$; $n = d = 2$; $A = 20$; endothermic
C	*Reversible reactions*: $n = m = 0.5$; $Q_s = 0$; $C_e = 0.5, 0.9$; isothermal, endothermic $(\gamma\beta) = -5$; $\beta = -0.2$ and exothermic $(\gamma\beta) = 5$; $\beta = 0$ cases.	3.1	$\sigma = 1$; $C_e = 0.9$; endothermic
D	*Irreversible exothermic nth order reactions*, $D_{\mathrm{MAX}} \cong 1$: $n = 0$–3.	2.8	$\sigma = 0$; $n = 2$
E	*Irreversible LHHW reactions* $(d > n)$, $D_{\mathrm{MAX}} \cong 1$: isothermal $(n, d, A) = (1, 2, 4.3; 0.5, 1, 8)$ and exothermic $(n, d, A) = (0.5, 1, 4.6)$; $(\gamma\beta) = 0.3$; $\beta = 0$ cases.	3.2	$\sigma = 5$; $(n, d, A) = (1, 2, 4.3)$
F	*Irreversible nth order exothermic reactions*, $D_{\mathrm{MAX}} \cong 2$ (FOG_3): $n = 0$–3	3.8	$\sigma = 5$; $n = 0.5$
G	*Irreversible LHHW reactions* $(d > n)$, $D_{\mathrm{MAX}} \cong 2$ (FOG_3): isothermal $(n, d, A)=(1, 2, 6.4; 0.5, 1, 13)$ and exothermic $(n, d, A) = (0.5, 1, 9)$; $(\gamma\beta) = 0.3$; $\beta = 0$ cases.	3.6	$\sigma = 5$; $(n, d, A) = (1, 2, 6.4)$

and inhibition exponent d. The Prater (β) and Arrhenius (γ) numbers define the exponential term in Eq. (12) for non-isothermal cases.

Reversibility, inhibition or thermal effects are not accounted for if A, $(\gamma\beta)$ and C_e, respectively, are taken as being zero. In the examples discussed below it will be assumed that a given effect is not included unless the specific parameters are explicitly defined. Note that for the reversibility effect three parameters should be stated: m, C_e and Q_s.

Some restrictions for the values of some parameters are taken from the outset, in order to keep realistic values. The reaction orders will be taken within $0 \le n, m \le 3$. The specific case identified with $n = 0$ actually means the zero-order reaction, $C^n = 1$ if $C > 0$; $C^n = 0$ if $C = 0$. The non-isothermal parameters will be constrained by $\gamma \le 25$ and $|\beta| \le 0.2$.

Given the set of parameters defining $r(Y)$ and the value of σ, the following relative error has been identified

$$\varepsilon = \max_{\Phi} \left| \frac{\eta(\Phi) - \eta_{\mathrm{num}}(\Phi)}{\eta_{\mathrm{num}}(\Phi)} \right|$$

where η is the value from the approximate formulation and η_{num} arises from the numerical solution of Eqs. (4) and (5). From the way in which the approximate formulation has been built up, ε always corresponds to some intermediate value of Φ. The results for a number of cases of practical interest will be discussed next. Due to space limitations, most of the results are summarized in Table 2. Further details and comments can be found in Keegan et al. [17].

3.1. Normal kinetics

Normal kinetics are here understood as those in which $\mathrm{d}r/\mathrm{d}Y$ is non-negative in the range $0 \le Y \le 1$. The use of FOG_2 is assumed, unless the contrary is stated.

For irreversible, isothermal nth order reactions, the values of ε are displayed in Fig. 1 as a function of σ. For $n = 0$, the values of η from the proposed approximation are exact for the specific values $\sigma = 1$ and $\sigma = 3$. For the remaining values of σ, the approximation behaves very well, with a maximum value (1.67%) at $\sigma = 5$. In general, ε keeps below 2% for all n and σ.

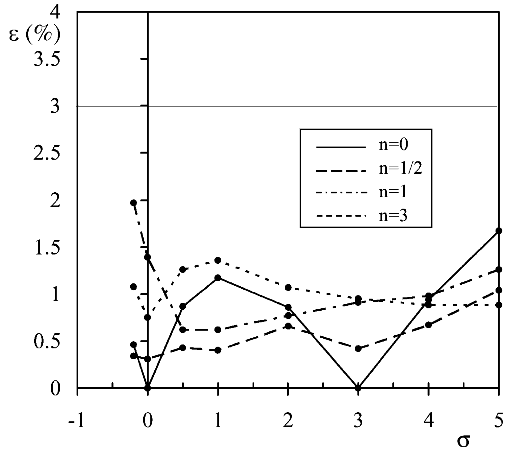

Fig. 1. Error ε (%) for irreversible nth order isothermal reactions.

The errors adding an endothermic effect ($\gamma\beta = -5$) to irreversible nth order reactions were somewhat higher than for the isothermal case, although not exceeding 3% (Table 2, Group A).

Inhibition effects (LHHW kinetics) with $d \le n$ do not introduce much variation in precision respect to power law kinetics. A number of examples were tried, either at isothermal conditions or with endothermic effects (Group B of results in Table 2).

As far as $m > 1$, the effect of the reversibility term in Eq. (12) on the level of accuracy of the proposed approximation is not significant. However, if $m < 1$ and $Q_s = 0$, the derivative $\mathrm{d}r/\mathrm{d}Y$ tends to infinity at $Y = 1$, causing fast variations of r close to the pellet surface. The deviations for a highly limited reaction ($C_e = 0.9$), keeping $n = m = 0.5$, at isothermal, endothermic ($\gamma\beta = -5$; $\beta = -0.2$) and exothermic ($\gamma\beta = 5$; $\beta \to 0$) conditions, are in general bounded by 3%, except for some values slightly higher (see Table 2, Group C). Temperature variations become restrained by the strong reversibility, even for the large value $|\gamma\beta| = 5$. When lower values of C_e are tried ($C_e = 0.5$), the errors become smaller than for $C_e = 0.9$. Nonetheless, the case $C_e = 0.5$, $(\gamma\beta) = 5$ is particularly interesting as $r(Y)$ shows a minimum and a maximum within $0 < Y < 1$ (this is actually an example of abnormal kinetics). Consequently, the corresponding curve η versus Φ also shows a minimum and a maximum.

3.2. Abnormal kinetics

It is very well known that strong exothermic or inhibition effects producing $\mathrm{d}r/\mathrm{d}Y < 0$ lead to values $\eta > 1$ and eventually to multiple solutions. The maximum value of $(-\mathrm{d}r/\mathrm{d}Y)$ occurring within $0 \le Y \le 1$, denoted as D_{MAX}, has been found a suitable criterion to establish up to what extent the approximation can be used with adequate level of precision [17].

Exothermic and irreversible nth order kinetics and values of the product $(\gamma\beta)$ such that $D_{\mathrm{MAX}} \cong 1$ were tested leading to ε always below 3% (Table 2, Group D). Smaller values of $(\gamma\beta)$ produce smaller values of ε, on average, and always less than 3%.

Two cases of isothermal and irreversible kinetics ($D_{\mathrm{MAX}} \cong 1$) with significant inhibition effects $n < d$ and one case combining exothermic and inhibition effects were also analised. The parameter A was again taken such that $D_{\mathrm{MAX}} \cong 1$ results. The error ε remains below 3%, except for a few cases showing slightly higher values (see Table 2, Group E).

The examples shown up to this point allow to conclude that FOG$_2$ is able to approximate normal and abnormal kinetics showing values of $D_{\mathrm{MAX}} \le 1$ within a precision of around 3%.

On the other hand, rate expressions showing values of D_{MAX} increasingly larger than one lead to errors consistently larger than 3%. It has been tried if higher values of N could enlarge the value of D_{MAX}, while maintaining the precision around 3%. The approximation FOG$_3$ can be judged as able to maintain the desired level of precision up to $D_{\mathrm{MAX}} = 2$, if some tolerance is allowed (up to 4%, see Groups F, G in Table 2). Higher values of N do not succeed to extend the value of D_{MAX} above 2, showing that the FOG approximation (Eq. (8)) becomes limiting, rather than the precision of the quadrature to evaluate the integrated residuals.

It is interesting to disclose the behaviour of the approximation for abnormal kinetics beyond the analysed values of D_{MAX}. The effect of A on ε for the already considered LHHW isothermal cases $(n, d) = (1, 2)$ and $(n, d) = (0.5, 1)$ can be appreciated in Fig. 2, using FOG$_2$ and $\sigma = 2$ (sphere). At the largest A in Fig. 2, D_{MAX} equals 4.48 and 3.71 for $d = 2$ and $d = 1$, respectively. In spite of these values largely exceeding the safe limit $D_{\mathrm{MAX}} = 1$ for FOG$_2$, the errors are still moderate, around 8.0% ($d = 2$) and 3.7% ($d = 1$), and perhaps acceptable for some purposes. The exact maximal η is 1.62 for $(n, d, A) = (1, 2, 10)$, while FOG$_2$ predicts $\eta = 1.66$.

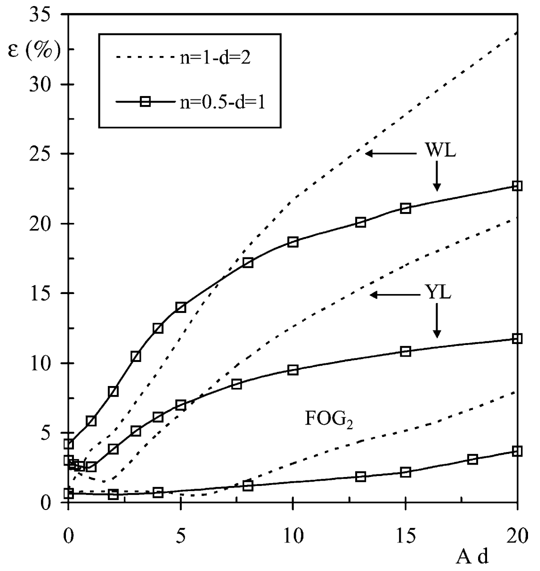

Fig. 2. Comparison of errors (%) from Wedel and Luss (WL) [4] and Yin and Li (YL) [10] expressions and FOG$_2$, for LHHW reactions with $d > n$ and $\sigma = 2$.

Also shown in Fig. 2 are the results from Wedel and Luss [4] and Yin and Li [10] approximations, specially developed for $\sigma = 2$. The errors from both expressions rapidly increase as A increases, although for this particular value of σ, Yin and Li [10] approximation behaves better. The Gottifredi et al. [6,8] approximations have been also tried for the conditions in Fig. 2. They present similar results as those from Wedel and Luss [4] approximation in the upper range of A, but the latter is more suitable at small A.

4. Conclusions

A formulation coupling a first-order Galerkin approximation with a truncated asymptotic expansion is proposed to evaluate the effectiveness factor of single reactions in the range $-1/5 < \sigma < 5$ of the GC geometrical model (Table 1). The formulation introduces an empirical criterion to shift from the FOG to the asymptotic approximation, expressed by Eq. (T4) in Table 1. In the range $3 < \sigma < 5$, the formulation is not directly applied, but the results from $\sigma = 3$ are employed along with a scaled Thiele modulus, Eq. (11a).

The FOG$_2$ option, employing two quadrature points, is suggested for general purposes. FOG$_2$ provides a 3% level of precision for essentially all normal kinetics of practical interest and abnormal kinetics restrained by a maximum negative slope $(-\mathrm{d}r/\mathrm{d}Y) = D_{\mathrm{MAX}} \cong 1$. In this way, FOG$_2$ allows very precise predictions for reaction rates approaching a zero-order reaction, for which large deviations arise from the use of former approximations. On the other hand, the extent of abnormal kinetics being accurately approximated is significantly enlarged.

If some errors between 3 and 4% can be accepted, the use the FOG_3 approximation allows dealing with kinetics showing up to $D_{MAX} = 2$.

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