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On the evaluation of effective reaction rates on commercial catalyst by means of a one-dimensional model

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Abstract

A one-dimensional model (1D), called generalized cylinder (GC), for the diffusion–reaction problem in commercial catalytic pellets is presented. The GC model free parameter (σ) is fitted so as to reproduce the behaviour of the actual pellet at high reaction rates. A simple analytical expression allows obtaining σ straightforwardly and the maximum deviation of the GC model is evaluated at around 2%.

Keywords: Generalized cylinder; Diffusion–reaction process; One-dimensional model

1. Introduction

Usually, the diffusion–reaction process in commercial catalysts takes places along more than one spatial coordinate. The general case is a three-dimensional (3D) problem, while two-dimensional (2D) geometries are frequent, either because of axisymmetry or because of very long catalytic bodies, as for non-circular channels in monolithic reactors. For simulating the behaviour of a catalytic reactor at given operating conditions it becomes necessary to evaluate the effective reaction rate hundreds or thousands of times. For some purposes involving recurrent simulation, as optimization of operating conditions or reactor design, the whole numerical procedure may involve an extremely large number of calculations. Under these conditions, solving numerically the 2D or 3D reaction–diffusion problem will be most probably unaffordable.

A convenient and practical alternative to circumvent this problem is to employ a one-dimensional (1D) geometrical approximation. In particular, the 1D model originally proposed by Burghardt and Kubaczka [1] is simple and conceptually appropriate for such purpose. This model will be hereafter mentioned as the *generalized cylinder* (GC), due to the fact that the solution for a first order reaction is expressed by fractionary order Bessel functions [1], generalizing in this way the very well-known solution for a very long circular cylinder. The diffusion process in this geometrical model is envisaged as taking place along a hypothetical body of length L and variable area for diffusion according to z^{σ}, where z is the dimensionless coordinate and σ (shape exponent) is the relevant geometrical parameter. The length L should be associated with the characteristic length ℓ of the actual catalyst and the shape exponent σ should be chosen to simulate in same way the shape of the actual catalyst.

There is no unique shape factor to identify a given catalyst geometry. Therefore, the accuracy of the GC model will depend on the criterion chosen for adjusting the parameter σ.

One reasonable and systematic approach is to compel the GC model to match the behaviour of the actual 2D or 3D catalyst particle at low reaction rates. Such approach was undertaken in the work of Mariani et al. [2] and the shape exponent σ turned out to be exclusively defined from the shape of the catalyst particle. It was proved for a first order reaction carried out in pellets of various shapes that the GC model produces results with a level of accuracy of about 1% for the

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whole range of Thiele modulus. However, the evaluation of σ involves the solution of a differential equation of the Poisson type for the given 2D or 3D geometry.

From the previously outlined approach, it becomes natural to ask if, instead of analyzing the low reaction rate regime, the high reaction rate regime can be employed for adjusting the shape exponent σ. This alternative approach was preliminarily used in [3] for some simple axisymmetric geometries with promising results.

The aim of this contribution is to further explore the use of the high reaction rate regime approach along with the GC model, by considering several 2D and 3D real shapes, as employed for commercial catalysts.

2. Formulation of the 1D model (GC model)

In the GC model, transport of the reacting species takes place by diffusion on a single coordinate $0 < z' < L$ along which the area of the available cross section varies according to:

$$S_p(z'/L)^\sigma = S_p z^\sigma$$

where S_p is the external area of the actual catalyst pellet that is permeable to the flow of reactants and z is the dimensionless coordinate, $z = z'/L$.

As stated in Section 1, the diffusion length (L) and the shape exponent (σ) are the model parameters.

Assuming that a single reaction takes place, that the diffusion coefficient (D_A) of the limiting reactant is constant and that the catalytic activity is uniform, the conservation balance and the boundary conditions for the limiting species takes the form:

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

$$C = 1, \quad \text{at } z = 1; \qquad \frac{\mathrm{d}C}{\mathrm{d}z} = 0, \quad \text{at } z = 0 \tag{1}$$

where

$$C = \frac{C_A - C_{Ae}}{C_{AS} - C_{Ae}}$$

$$r = \frac{r_A}{r_{AS}}$$

C_A is the molar concentration of species A and r_A is its consumption rate; the suffix "S" denotes the value on S_p and "e" the equilibrium value.

The Thiele modulus Φ is defined as

$$\Phi^2 = \ell^2\frac{r_{AS}}{D_A(C_{AS} - C_{Ae})} \tag{2}$$

where ℓ (characteristic length) is the ratio between the volume of the hypothetical solid represented by the GC model, $S_pL/(1+\sigma)$, and its external surface area

$$\ell = L/(1+\sigma) \tag{3}$$

The GC model reduces to a slab when $\sigma = 0$, to a very long circular cylinder for $\sigma = 1$ and to a sphere when $\sigma = 2$. Admissible values of σ should accomplish $\sigma > -1$, as it becomes evident, for example, from relation (3).

The length L is set by requiring that the characteristic length ℓ (Eq. (3)) of the hypothetical solid equals the value $\ell = V_p/S_p$ of the actual pellet. In this way, the Thiele modulus Φ, Eq. (2), will be the same for both catalytic bodies.

The shape exponent σ will be chosen in order that the GC model can reproduce, as accurately as possible, the asymptotic behaviour of the actual pellet at high reaction rates.

For the GC model the effectiveness factor η is expressed as

$$\eta = (1+\sigma)\int_0^1 r z^\sigma\,\mathrm{d}z \tag{4}$$

Expanding η in powers of $(1/\Phi)$ and truncating at the second term [4], we obtain:

$$\eta_{high} = \frac{I_1}{\Phi} - \left(\frac{\sigma}{1+\sigma}\right)\frac{I_2}{\Phi^2} \tag{5}$$

where

$$I(Y) = 2\int_0^Y r(C)\,\mathrm{d}C$$

$$I_1 = [I(1)]^{1/2}$$

$$I_2 = \frac{1}{I_1}\int_0^1 [I(Y)]^{1/2}\,\mathrm{d}Y$$

2.1. Adjusting σ at high Φ

As can be appreciated in the expansion (Eq. (5)), the second order term contains the factor $\sigma/(1+\sigma)$ that just depends on the shape exponent σ. Provided that a similar expansion can be written out for the actual catalyst shape, the matching of the second order term will provide the value of σ. Keegan et al. [5,6] recently developed a general formulation for the second order term, as follows. Assume that the surface S_p of a catalyst pellet can be composed of N_s smooth sectors, *i.e.* pieces with continuous curvature radii, separated by N_w edges. In the cited works [5,6], Keegan et al. expressed the second term by adding the contributions of each sector and each edge. In order to simplify the notation, the formulation is presented here for the specific case of uniform catalytic activity, uniform curvature radii on each sector and uniform intersection angle θ between both sectors meeting at a given edge. Hence, η_{high} is written as

$$\eta_{high} = \frac{I_1}{\Phi} - \Gamma\frac{I_2}{\Phi^2} \tag{6}$$

where

$$\Gamma = \frac{\ell}{S_p}\left[\sum_{\nu=1}^{N_s} T_\nu S_\nu + \sum_{\mu=1}^{N_w}\omega_\mu W_\mu\right] \tag{7}$$

where S_ν is the area of each sector, W_μ length of each edge and $T = (1/R_a) + (1/R_b)$.

R_a and R_b are the principal radii of curvature. The sign of a radius of curvature is defined here as being positive if the center

of curvature is oriented to the inside of the catalyst body and it is negative for the opposite sense.

The coefficient ω depends strongly on the angle θ and very weakly on the type of reaction rate expression. It can be evaluated from the following approximation, which is strictly valid for first order reactions [5]:

$$\omega(\theta) = \begin{cases} ((8\ln 2)/\theta)[1-(\theta/\pi)^{\pi^2/(8\ln 2)}], & \text{if } 0 \le \theta \le \pi \\ 2\pi^2/((\pi-2)\theta+\pi(4-\pi))[1-\theta/\pi], & \text{if } \pi < \theta \le 2\pi \end{cases}$$

This expression for $\omega(\theta)$ has been developed [5] from the following facts: $\omega(\pi/2) = 8/\pi$, $\omega(\pi) = 0$, $\omega(2\pi) = -2$, $\omega'(\pi) = -1$, $[\theta\omega'(\theta)] \to (8\ln 2)$ as $\theta \to 0$.

An expression for Γ more general than Eq. (7), allowing variable curvature radii on each sector, variable intersection angle θ along each edge, non-uniform catalytic activity and a general transport model, has been formulated by Keegan et al. [5].

Both second order terms, in expression (5) for the GC model and in expression (6) for a general catalytic pellet, will be the same if the shape exponent σ is defined as

$$\sigma = \frac{\Gamma}{1-\Gamma} \tag{8}$$

Using the value of σ given by Eq. (8) along with the GC model ensures that the results from this approximation will be in very good agreement with the actual behaviour at high reaction rates, or equivalently, at high values of the Thiele modulus Φ. As the effectiveness factor will tend to the unity as $\Phi \to 0$ in either case, it is expected that the main differences will occur at intermediate values of Φ. The magnitude of them will be analyzed in the next section.

3. Results and discussion

Except for the case of spherical particles, the vast majority of commercial pellets are cylinders of different cross-section shape.

Therefore, the cross-section shape will be the distinguishing geometrical feature of a given catalyst. However, if the pellet is short ($H \to 0$, being H is the height of the particle), the main component of the molar flux of any reactant will be that in the axial direction, through both bases, and the behaviour will resemble that of a slab, irrespective of the cross-section shape. On the contrary, as $H \to \infty$ the main components of any molar flux will lie on the cross-section and the effect of its shape will be significant. At these conditions, the values of parameter Γ and effective length ℓ will be denoted Γ_∞ and ℓ_∞, respectively. The value of Γ_∞ is determined by the curvatures and edges of the cylindrical surface, as defined by the cross-section shape.

In considering a finite value of H, additional edges arise from the intersection of the cylindrical surface and the two bases. These edges show an intersection angle $\theta = \pi/2$. It turns out from their definitions (Eq. (7) and $\ell = V_p/S_p$) that for finite H the values of both, Γ and ℓ, can be written in terms of Γ_∞ and ℓ_∞, as follows:

$$\Gamma = \frac{\Gamma_\infty + (16/\pi)\ell_\infty/H}{(1+2\ell_\infty/H)^2} \tag{9a}$$

$$\ell = \frac{\ell_\infty}{1+2\ell_\infty/H} \tag{9b}$$

The use of the GC model for some types of commercial catalysts will be carried out by assuming that a first order reaction takes place. Solid circular cylinders ($\Gamma_\infty = 1/2$) and other cylinders whose cross-section shapes are sketched in Table 1 will be considered. The corresponding values of ℓ_∞ and Γ_∞, are also given in Table 1.

Solutions of the mass conservation equation for circular cylinders, Raschig rings and parallelepipeds are available in the form of infinite series [1,7]. They were employed to evaluate the effectiveness factor for those geometries, while for the remaining shapes in Table 1 the software Femlab v3.1 by Comsol Inc. (numerical solution of differential equations by the finite elements method) was employed.

In order to evaluate the level of accuracy allowed by the GC model, the differences in values of the effectiveness factor between the model and the actual catalyst particle were compared for Thiele modulus Φ ranging from zero to sufficiently large values. The maximum difference was identified and denoted as ε_{max}:

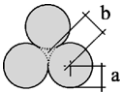
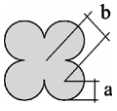
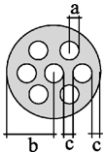
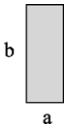
$$\varepsilon_{max} = \max_{\Phi}\left\{\frac{|\eta_{GC}-\eta|}{\eta}\right\} \times 100$$

where η stands for the true effectiveness factor and η_{GC} for the value obtained from the GC model.

For the different geometries, the value of Φ that defines ε_{max} lies typically in the range 1–2.

Values of ε_{max} are plotted in Fig. 1 for Raschig rings against the height parameter defined by $x = H/(H+b)$, for different values of the aspect ratio y (see definition in Table 1). The

Table 1
Cross-sections for the catalyst pellets analyzed in this work; $y = a/b$

Pellet	Raschig ring	Trilobe	Quadrilobe	Seven-hole	Parallelepiped
Cross-section					
Γ_∞	0	0.377 $y = \sqrt{3}/2$	0.410 $y = \sqrt{2}/2$	−0.375 (c = a, y = 1/5)	$(8/\pi)(y/(1+y))$
$2(\ell_\infty/b)$	$1-y$	1.057	1.007	0.300	$y/(1+y)$

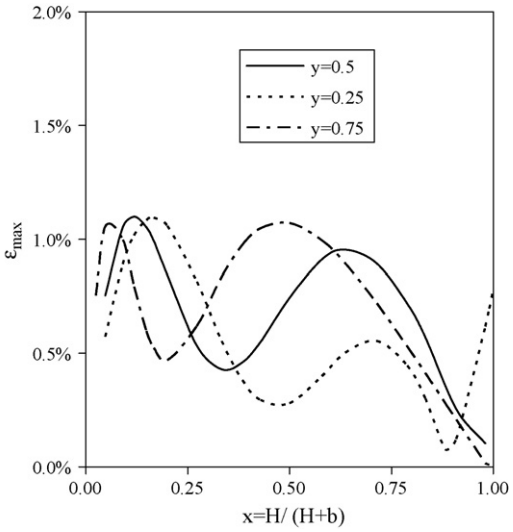


Fig. 1. Error ε_{max} for Raschig rings (aspect ratio y defined in Table 1).

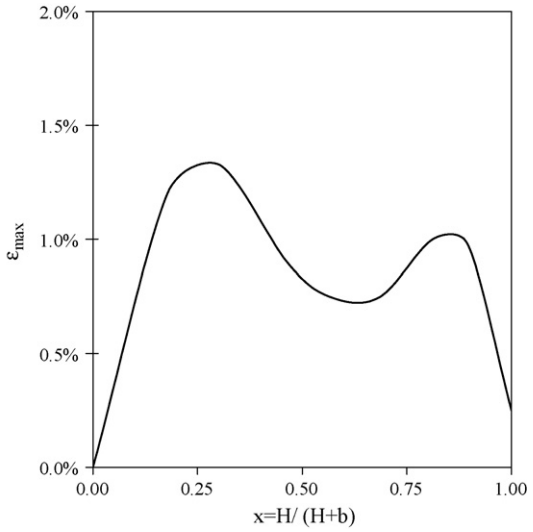


Fig. 3. Error ε_{max} for trilobe pellets (aspect ratio y defined in Table 1).

values of ε_{max} remain less than nearly 1% for any tested combination of parameters.

As already noticed, as $H \to 0$, the behaviour of any cylindrical pellet tends to that of a slab; hence, the GC model can reproduce the exact behaviour with $\sigma = 0$ and, consequently, $\varepsilon_{max} \to 0$ as $x \to 0$.

For solid circular cylinders, the error is zero for both limits, $H \to 0$ and $H \to \infty$. The maximum value of ε_{max} is about 1.5% at nearly height/radius = 0.4.

The performance of the GC model for parallelepipeds can be appreciated in Fig. 2. For the different aspect ratios analyzed (including those not showed in Fig. 2), ε_{max} does not rise above 1.5%.

Trilobe pellets of different heights are analyzed in Fig. 3. The GC model performs similarly as for the previous geometries in all respects. The maximum value found for ε_{max} is about 1.3%.

Nearly the same comments can be made for quadrilobe pellets. The maximum value for ε_{max} is 1.45% in this case, Fig. 4. However, if the curves of ε_{max} in Figs. 3 and 4 are compared, we can distinguish for quadrilobe pellets that the curve of ε_{max} rises again when $x = 1$ is approached (*i.e.* $H \to \infty$). Recalling that the effect of the cross-section shape is stressed for long pellets, that incipient trend prompts to analyze the case of geometries with a larger number of lobes.

The case of eight lobes ($\Gamma_\infty = 0.55$, $\sigma_\infty = 1.2$) was studied in detail. In spite that commercial catalysts with more than five lobes are rare, this case neatly allows confirming the trend, and the maximum value $\varepsilon_{max} = 4.8\%$ is found for $x = 1$. For normal values of H, the values of ε_{max} drop to a level similar to other geometries. For example, $\varepsilon_{max} = 1.4\%$ for $x = 0.28$.

It is theoretically interesting to consider the behaviour of multi-lobe pellets when the number of lobes further increases, as the GC model eventually becomes inapplicable. Thus, if the number of lobes, N_L, is high enough (*i.e.* $y \to 0$, Table 1), the cross-section area tends to the value of the circle of radius b, πb^2, while the perimeter tends to N_L times the perimeter of a semi-circle of radius a, $\pi a N_L$. From these considerations and

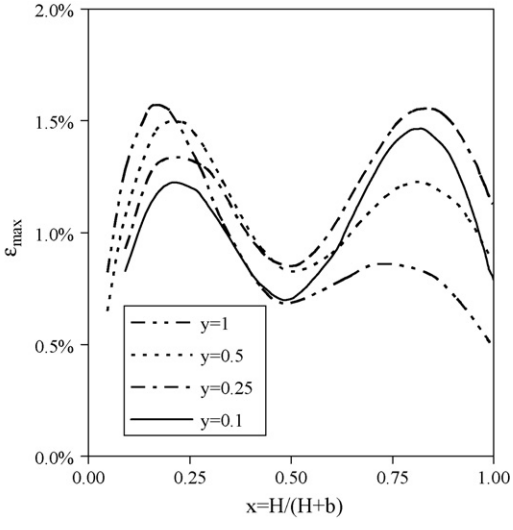


Fig. 2. Error ε_{max} for parallelepipeds (aspect ratio y defined in Table 1).

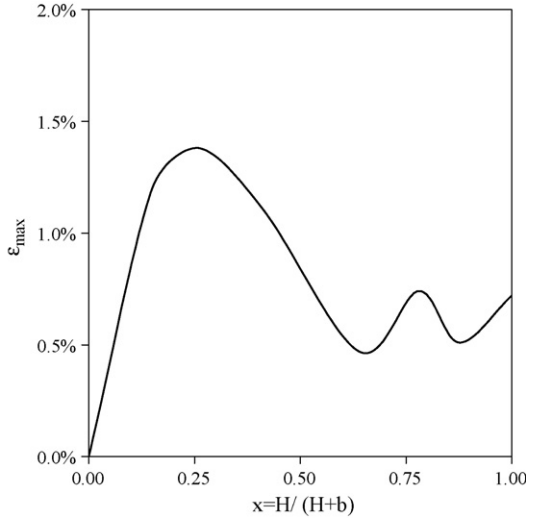


Fig. 4. Error ε_{max} for quadrilobe pellets (aspect ratio y defined in Table 1).

Table 2
Maximum deviations for seven-hole cylinders (Table 1) of different heights H

$x = H/(H + b)$	ε_{max} (%)
0.00	0.00
0.1	0.03
0.20	0.20
0.33	0.82
0.50	1.43
0.65	2.12
0.71	2.45
1.00	3.97

using the definition of Γ in Eq. (7), the following expression arises for Γ_∞:

$$\Gamma_\infty \cong \frac{\pi - 2}{\pi^3} N_L \tag{10}$$

From Eq. (10) Γ_∞ increases linearly with N_L. But, values of Γ_∞ less than 1 are needed to obtain a meaningful value of the shape parameter σ_∞, according to Eq. (8). Hence, the maximum value of N_L for which the GC may be used is the one that makes $\Gamma_\infty = 1$. From Eq. (10) this value would be $N_L = 27$. Actually, as Eq. (10) is an approximation, the true value is $N_L = 20$.

The last shape discussed in this paper corresponds to the seven-hole pellet shown in Table 1. Values of ε_{max} for different H are presented in Table 2; the maximum deviation $\varepsilon_{max} \approx 4\%$ takes place for $H \to \infty$. Nonetheless, the heights of commercial catalyst are in the range $0.5 < x < 0.65$, for which ε_{max} remains lower than 2%. This is the largest error found among the different commercial catalyst investigated in this contribution, but it is definitely tolerable for any practical purpose.

It is interesting to mention that for relatively long seven-hole cylinders, $x > 0.67$, the values of σ turn out to be negative and the minimum is reached at $x = 1$ ($\sigma_\infty = -0.375$). According to the geometrical picture provided by the GC model, negative values of σ means that the cross-section available for diffusion increases towards the interior of the catalyst. As a consequence, values of the effectiveness factor are higher than for a slab ($\sigma = 0$), when compared at the same value of the Thiele modulus. Usually, the values of σ are positive. We recall that a sphere shows $\sigma = 2$, but many cylinders of finite height present higher values, as in the case of the typical commercial circular cylinder. The largest value of σ arisen from the geometries studied here is found for a cube: $\sigma = 5.6$.

4. Conclusions

In a previous work [3], the results of using the one-dimensional GC model to approximate the behaviour of simple 2D or 3D catalyst shapes were presented. For that purpose the shape exponent σ of the GC model was first evaluated by fitting the parameter Γ (Eq. (7)) that characterizes the behaviour of the effectiveness reaction rates at large values of the Thiele modulus. In the present contribution, several other shapes of commercial catalyst catalysts were included to demonstrate the capability of the GC as a useful numerical tool for practical applications. Trilobe and quadrilobe cylinders, typically used in a number of hydrorefining processes and seven-hole cylinders employed in dry/wet reforming of low hydrocarbons/oxygenates have been included in the study.

The maximum difference between values of the effectiveness factor calculated with the GC model and with the actual shapes for a first order reaction was about 2% within the range of usual ratios height/diameter. This is quite a satisfactory level of accuracy for any practical application.

Somewhat larger errors were found when the values of some geometrical parameters are taking away from the usual level. Specifically, very long cylinders with some cross-section geometries make the error of the GC model increase. For example, the maximum errors for eight-lobe and seven-hole cross-sections with $H \to \infty$ are 4.8% and 4%, respectively.

It should also be stressed that the shape parameter Γ (Eq. (7)) used to fix the GC model exponent σ can be easily calculated for any 2D or 3D geometry.

Some aspects should be further explored to appraise comprehensively the virtues of the GC model and the companion criterion to adjust its parameter. Some other shapes of practical interest can be included to detect eventual limitations that in turn may prompt for developing alternative approaches. Non-linear reaction rates and non-isothermal effects should be tested. Preliminary results indicate that the response of the GC model should not be qualitatively different than for a first order reaction, but the level of accuracy should be evaluated. Finally, and perhaps the most important extension of this study will concern the analysis of simultaneous multiple reactions, as the saving in computing efforts when using a one-dimensional approximation will be most significant.

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