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Estimation of Effectiveness Factor for Arbitrary Particle Shape and Non-Linear Kinetics

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A one-dimensional model, called generalized cylinder (GC), is employed to analyze the diffusion−reaction problem in catalytic pellets of different shapes and nonlinear kinetics. The fitting parameter (σ) of the GC model was adjusted by matching the behavior of the actual pellet at high reaction rates. The errors of the GC model, considering five different kinetic expressions (isothermal zero and second order, isothermal Langmuir−Hinshelwood−Hougen−Watson type, first order exothermic, and first order endothermic) and four different catalytic pellet shapes turned out to be less than 3.5%.

1. Introduction

The analysis of the diffusion−reaction problem in catalytic pellets should be carried out by considering three spatial coordinates (3D) in the general case. 2D geometries are also frequent, due to axial symmetry and in the case of noncircular channels in monoliths.[1,2] Numerical simulation of a catalytic reactor involves the repeated evaluation of reaction rate up to thousands of times and even higher orders will be needed for reactor optimization or a plant simulation as a whole. The occurrence of multiple reactions will further increase the amount of numerical calculations. Moreover, the numerical approach for solving 3D or 2D problems does not warrant getting a final solution, because convergence problems often arise.

Thus, numerical procedures on multiple (3D or 2D) spatial coordinates turn out to be a nonpractical option. In this context, a feasible alternative is to employ models that reduce the spatial dimension of the problem. A very simple approach to reduce 3D or 2D problems into a 1D problem was provided many years ago by several authors [e.g., ref 3] by showing that at large values of the Thiele modulus the effectiveness factor for a single reaction does not depend on the pellet shape but just on the ratio of pellet volume to external surface area, l. To perform approximate evaluations at low and intermediate values of Thiele modulus, any geometry satisfying the actual value of l could be adopted, as a simple slab of half-width l. The expected precision with this approximation is on the order of 20% for relatively simple kinetics. However, for more complex kinetics expressions like Langmuir−Hinshelwood−Hougen−Watson (LHHW) type, the errors can rise up to approximately 40%.

A more convenient 1D model was formerly proposed by Burghardt and Kubaczka.[4] This model, hereafter called the generalized cylinder (GC) model, is based on a hypothetical body in which mass and heat transfer take place along a single coordinate z' with variable cross section according to $(z'/L)^{\sigma}$, where $z' = L$ defines the external surface and $z' = 0$ the symmetry center. The value of L (effective diffusion length) will result from matching the value of l of the actual pellet, while σ (shape factor) can be obtained by matching a geometrical feature of the actual pellet. Therefore, the main challenge is to formulate an adequate criterion for the model to properly predict the catalytic behavior of the actual pellet.

Series expressions for the effective reaction rate can be obtained from the limit of either slow or fast reactions. Second terms of those series contain pellet-shape related parameters, identified as γ and Γ, respectively, that can be straightforwardly employed to evaluate σ. Both criteria have been employed [5,6] with success for a large variety of pellet geometries and isothermal linear kinetics, but the final formulation for parameter Γ of the fast kinetic regime is considerably simpler, as only basic geometric quantities of the pellet are needed. On the contrary, obtaining the value of parameter γ of the slow kinetic regime requires the solution of a Poisson's type differential equation in the actual pellet.

The main objective of this contribution is to validate the predictive capacity of the GC model when σ is evaluated by matching the parameter Γ of the actual pellet. To this end, four typical pellet shapes with some nonlinear kinetics expressions (isothermal zero and second order, isothermal Langmuir−Hinshelwood−Hougen−Watson type, first order exothermic, and first order endothermic) were considered. The type of kinetics tested in this work corresponds to those behaving in a normal way (i.e., effectiveness factor is always equal to or less than 1).

The paper is organized as follows. The GC model is introduced in section 2. The criterion proposed in this paper to evaluate its free parameter σ is presented in section 2.1. In section 3, we first describe the 3D pellets employed to test the GC model and the different kinetic expressions used to that end. A brief description of the numerical procedures follows, and we finally present and analyze the comparison between values of effectiveness factor estimated by the GC model and calculated for the actual 3D pellets.

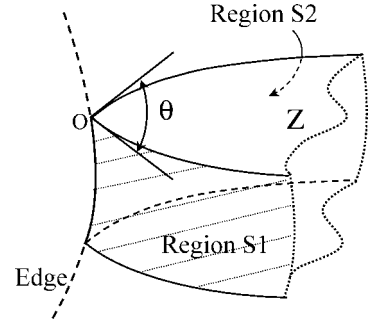

Figure 1. Sketch showing the intersecting angle θ.

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2. 1D Model Formulation

The generalized cylinder (GC) 1D model can be envisaged by means of a solid body that allows material and heat transport in only one spatial coordinate z' and presents a variable cross-section S^{CG} according to

$$S^{CG}=S_p(z'/L)=S_p z$$

where S_p is the permeable external area of the actual pellet and L (diffusion length) and σ (shape factor) are the model parameters.

The external surface is at $z = 1$ and the geometric center of the body is at $z = 0$, where symmetry conditions apply for the state variables. The model cross section exactly coincides with the external surface area of the actual pellet at $z = 1$ [$S^{CG}(1) = S_p$].

In addition, the volume V^{CG} of the model body,

$$V^{GC}=\int_0^L S_p\left(\frac{z'}{L}\right)^{\sigma} dz' = \frac{S_p L}{\sigma+1}$$

is made equal to the actual pellet volume V_p. Hence, the diffusion length becomes defined by

$$L=(\sigma+1)l \tag{1}$$

where $l = V_p/S_p$ is the characteristic length of the actual pellet.

The conservation balance of the GC model for a single reaction, uniform activity ($a = 1$), and uniform diffusion coefficient (D_A) of the key species A (usually the limiting reactant), using variable Y as a dimensionless concentration, leads to

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

$$Y=1 \quad \text{at} \quad z=1 \tag{2b}$$

$$dY/dz=0 \quad \text{at} \quad z=0 \tag{2c}$$

where

$$Y=(C_A-C_{Ae})/(C_{As}-C_{Ae}) \tag{2d}$$

$$r=\pi_A/\pi_{As} \tag{2e}$$

C_A and π_A are the concentration and the net consumption rate of the A species, respectively; the subscript "s" denotes that the variable should be evaluated on the pellet surface S_p, and likewise "e" refers to equilibrium conditions.

The Thiele modulus Φ is defined as

$$\Phi^2=l^2\frac{\pi_{As}}{D_A(C_{As}-C_{Ae})} \tag{3}$$

Values of σ are restrained by eq 1 to be greater than (-1). In addition, it is worth noting that the model exactly encompasses the classical 1D problems in a slab ($\sigma = 0$), an infinitely long circular cylinder ($\sigma = 1$), and a sphere ($\sigma = 2$). The effectiveness factor is expressed as

$$\eta^{GC}=(1+\sigma)\int_0^1 r(Y)z^{\sigma}\,dz \tag{4}$$

Extending the procedure proposed by Wedel and Luss[7] for a sphere to any value of σ, the effectiveness factor can be approximated for large values of Φ with the first two terms of a series in powers of $(1/\Phi)$:

$$\eta^{GC}_{high}=\frac{I_1}{\Phi}\left[1-\frac{I_{12}}{\Phi}\left(\frac{\sigma}{1+\sigma}\right)\right] \tag{5a}$$

where

$$I(Y)=2\int_0^Y r(Y')\,dY' \tag{5b}$$

$$I_1=[I(1)]^{1/2} \tag{5c}$$

$$I_2=\frac{1}{I_1}\int_0^1 [I(Y)]^{1/2}\,dY \tag{5d}$$

$$I_{12}=\frac{I_2}{I_1} \tag{5e}$$

2.1. Criterion for Adjusting σ. As can be appreciated in the expansion eq 5a, the second order term contains the factor $\sigma/(1 + \sigma)$ that just depends on the shape exponent σ. Provided that a similar expansion as eq 5a is available for the actual catalyst shape, the matching of the second order term will provide the value of σ. Keegan et al.[8,9] 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 regions, that is, pieces with continuous curvature radii, separated by N_w edges. In the cited works,[8,9] Keegan et al. expressed the second term by adding the contributions of each region and each edge. The formulation for η_{high} is presented here for the specific case of uniform catalytic activity:

$$\eta_{high}=\frac{I_1}{\Phi}\left[1-\frac{I_{12}}{\Phi}\Gamma\right] \tag{6}$$

where

$$\Gamma=\frac{l}{S_p}\left[\sum_{\nu=1}^{N_s}\overline{\Psi}_\nu S_\nu+\sum_{\mu=1}^{N_w}\overline{\omega}_\mu W_\mu\right] \tag{7}$$

$$\overline{\Psi}_\nu=\frac{\int_{S_\nu}\Psi\,dS}{S_\nu};\quad \overline{\omega}_\mu=\frac{\int_{W_\mu}\omega\,dW}{W_\mu}$$

The contribution of each smooth region ν of area S_ν is given by the curvature parameter $\bar{\Psi}_\nu$, which is the average on S_ν of the sum Ψ of principal curvatures of the region. In terms of the local principal radii of curvature R_a and R_b

$$\Psi=\frac{1}{R_a}+\frac{1}{R_b}$$

The sign of a radius of curvature is positive if the center of curvature is oriented toward the inside of the catalyst, and it is negative for the opposite sense.

Similarly, the contribution of each edge μ of length W_μ is given by $\bar{\omega}_\mu$, which is the average along W_μ of a coefficient ω fully formulated in ref 9.

The coefficient ω depends very weakly on the type of reaction rate expression but strongly on the *intersecting angle* θ that a pair of smooth regions defines when they meet at the edge. The angle θ can be visualized in Figure 1, where the pair of smooth

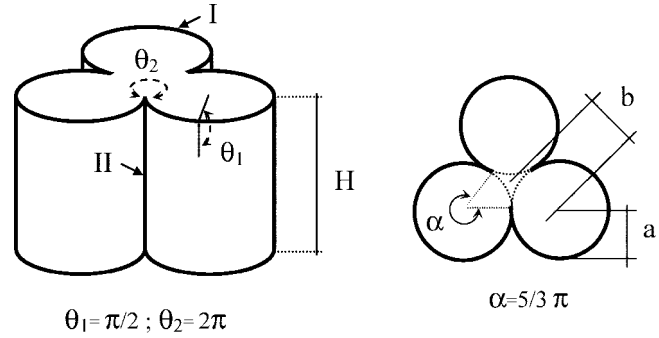


Figure 2. Sketch of a trilobe particle

Table 1. Contributions to Γ for a Trilobe Particle (Figure 2) Considering $r(Y) = Y^2$

regions	S_ν	$\bar{\Psi}_\nu$	$[\bar{\Psi}\ S]_\nu$	dimensions
lateral surface (3)	$(5/3)\pi aH$	$1/a$	$(5/3)\pi H = 13.1$	
flat base (2)	S_B (cross section area)	0.0	0.0	$a = 1$, $b = 1.155$, $H = 2.5$
edge	W_μ	$\bar{\omega}_\mu(\theta)$	$[\bar{\omega}\ W]_k$	derived quantities
I (6)	$(5/3)\pi a$	$\omega(\pi/2) = 2.46$	$(5/3)\pi a\omega(\pi/2) = 12.9$	$S_p = 58.4$, $V_p = 24.0$, $l = 0.410$, $\theta_1 = \pi/2$, $\theta_2 = 2\pi$
II (3)	H	$\omega(2\pi) = -2.06$	$H\omega(2\pi) = -5.15$	
sum			101	
Γ			0.71	($\sigma = 2.45$)

regions is denoted by S1 and S2. For curved regions θ will in general vary with the position on the edge; in Figure 1 the angle θ corresponds to the point O of the edge and Z is the plane normal to the edge at O.

The coefficient ω can be precisely evaluated from the following approximation:[9]

$$\omega(\theta) = \begin{cases} \dfrac{b_0}{\theta}\left[1 - \left(\dfrac{\theta}{\pi}\right)^{\pi^2/b_0}\right], & \text{if} \quad 0 \le \theta \le \pi \\ \dfrac{\pi^2 A}{(\pi - A)\theta + \pi(2A - \pi)}\left[1 - \dfrac{\theta}{\pi}\right], & \text{if} \quad \pi < \theta \le 2\pi \end{cases} \tag{8}$$

where

$$b_0 = 5.2 I_1^{0.3}/I_2^{0.1}$$

$$A = -\omega(2\pi) = 1.9(I_1/I_2)^{0.07}$$

An expression for Γ more general than eq 7, allowing nonuniform catalytic activity and a general transport model, has been formulated by Keegan et al.[8,9]

It is clear from eqs 5a and 6 that the same asymptote $\eta \to I_1/\Phi$ will be obtained as $\Phi \to \infty$ (i.e., for the limiting regime) for both the GC model and the actual pellet.

In turn, if we wish to match the behavior up to the second term in the series of eqs 5a and 6, the parameter σ should be defined as

$$\sigma = \frac{\Gamma}{1 - \Gamma} \tag{9}$$

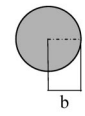
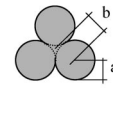
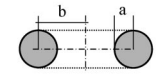
Equation 9 states the criterion proposed in this work to approximate the behavior of a given pellet by means of the 1D GC model. By construction, the criterion guarantees that the GC model will be highly accurate at relatively large values of Φ. Also, differences will tend to zero if $\Phi \to 0$ as $\eta \to 1$ for both the GC model and the actual pellet. The expectation, to be assessed in the next section, is that eq 9 imposed to the GC model will allow it to reproduce the behavior of the actual pellet at intermediate values of Φ.

Example of Evaluation of Γ. Let us consider a trilobe pellet depicted in Figure 2. We can identify five smooth regions corresponding to the two flat bases and the three lateral surfaces (cylindrical envelopes of the lobes). The curvature is uniform on each of the five regions: zero for the flat bases and $(1/a)$ for the lateral surfaces.

There are nine edges: six curved edges, denoted by I in Figure 2, corresponding to the intersection of each lateral surface with each flat base, and three straight edges (II) from the intersection of each pair of lateral surfaces. The intersecting angle θ of each of the nine edges is uniform: $\theta_1 = \pi/2$ for the I edges and $\theta_2 = 2\pi$ for the II edges (see Figure 2).

The contributions to Γ (eq 7) from the geometrical elements from the five smooth regions and nine edges just described are displayed in Table 1 for second order kinetics, $r(Y) = Y^2$. For this kinetic expression $I_1 = 0.8165$ and $I_2 = 0.400$ from eqs 5c and 5d; these parameters are needed to evaluate ω (eq 8).

Table 2. Cross Section of the Analyzed Particles[a]

Particle	Cylinder	Trilobe	Wagon wheel	Toroid
Cross section				
Dimensions	x= 0.286	y=0.866 x=0.684	e=0.2 b x=0.477	y=0.5

[a] $y = a/b$, $x = H/(H + b)$; H is the pellet length.

3. Results and Discussion

This section is devoted to evaluating the predictive capacity of the GC model to estimate effectiveness factors for the four catalytic particles shown in Table 2. All the particles in Table 2, except the toroid, are cylinders with different cross sections. Their relative dimensions were taken from manufacturer catalogues (e.g., Haldor Topsoe, Criterion, etc.). These shapes were selected because of being representative of many applications; trilobular particles are usually employed for liquid phase reactions, wagon wheels are used for fast gas phase reactions, and cylindrical extrudates are widely used in almost every type of catalytic system. A variety of processes can employ those shapes, like hydrogenations, isomerizations, oxidations, hydrotreatments, steam reforming, naphtha reforming, and so forth.

To our knowledge, the toroidal pellet is not presently commercialized. Nevertheless, it was included as a case study because the toroidal shape shows interesting features: most of the external surface could be easily accessible to reactants in either gas or liquid phase and a bed packed with toroids will show a relatively high voidage and hence a low pressure drop.

It should be pointed out that the GC model has been previously tested for a much wider collection of commercial pellet shapes with isothermal linear kinetics.[10] Effective reaction rates were estimated with very good precision (i.e., errors less than 3%).

The application of the GC model for particles in Table 2 was carried out for five types of nonlinear kinetic expressions (isothermal zero and second order, isothermal Langmuir−Hinshelwood−Hougen−Watson type, first order exothermic, and first order endothermic). The studied expressions can be gathered in the following general form:

$$r(Y) = Y^n e^{\delta(1-Y)}\left(\frac{1+K}{1+KY}\right)^d \tag{10}$$

The exponential factor in eq 10 arises from the dependence of the kinetic coefficient with temperature according to Arrhe-

Table 3. Shape Exponents (σ) and Maximum Errors (ε_{max}) for the Analyzed Particles

	particle							
	cylinder		trilobe		wagon wheel		toroid	
kinetic expression	σ	ε_{max}	σ	ε_{max}	σ	ε_{max}	σ	ε_{max}
isothermal zero order $r = \begin{cases} 1, & \text{if } Y > 0 \\ 0, & \text{if } Y \le 0 \end{cases}$	1.34	3.50%	3.00	2.32%	0.55	3.02%	1.00	0.29%
isothermal second order $r = Y^2$	1.19	0.94%	2.44	0.29%	0.39	0.65%	1.00	0.10%
exothermic first order $r(Y) = Ye^{(1-Y)}$	1.28	1.75%	2.78	1.01%	0.47	0.86%	1.00	0.23%
endothermic first order $r(Y) = Ye^{-(1-Y)}$	1.19	1.00%	2.47	0.38%	0.43	0.50%	1.00	0.15%
isothermal LHHW $r(Y) = Y\left(\frac{2}{1+Y}\right)^2$	1.30	2.00%	2.85	1.25%	0.47	1.02%	1.00	0.25%

nius law and the relation between concentration and temperature that can be derived by combining the mass and energy conservation balances (see, e.g., ref 11). Strictly, the exponential factor becomes $\exp[\delta(1 - Y)/(1 + \beta(1 - Y))]$, where $\delta = \beta\gamma$, γ is the Arrhenius number, and β is the Prater number.[11] As in practice, β is small (being a representative range $0.01 < |\beta| < 0.1$; we simplified the denominator and took directly $\exp[\delta(1 - Y)]$ in eq 10, for the purposes of the present manuscript.

The apparent reaction order at the external surface is defined as

$$n_S = \left(\frac{\partial \ln r(Y)}{\partial \ln Y}\right)_{Y=1}$$

The parameters in eq 10: δ, n, d, and K, have been chosen so $r(Y)$ shows a "normal" behavior, that is, that $n_S \ge 0$ for $0 \le Y \le 1$ (consequently, $\eta \le 1$). The exothermic first order reaction tested in this work is $r = Y\exp(1 - Y)$, which corresponds to $n = 1$, $d = 0$, and $\delta = 1$ in eq 10, renders $n_S = 0$. The isothermal LHHW kinetics is $r = Y(2/(1 + Y))^2$, defined by $n = 1$, $d = 2$, $\delta = 0$, and $K = 1$ in eq 10, and also renders $n_S = 0$. The first order endothermic expression is $r = Y\exp[-(1 - Y)]$, which corresponds to $n = 1$, $d = 0$, and $\delta = -1$, and we obtain $n_S = 2$. Strictly, the definition of the isothermal zero-order reaction, in addition to eq 10 with $n = d = \delta = 0$, requires stating that $r = 0$ when $Y = 0$. Finally, the isothermal second order reaction $r = Y^2$ arises from eq 10 by defining $n = 2$, $d = \delta = 0$.

Recalling that for each pellet geometry the parameter Γ (eq 7) should be calculated to define the GC parameter σ (eq 9), it is convenient to remark that for the three cylinders in Table 2 the smooth regions in which S_p is decomposed show uniform curvature Ψ. Considering that flat bases present no curvature, the only contributions to the first summation in eq 7 correspond to circular sectors of the cylindrical envelopes, that is, $\Psi_\nu = 1/R_\nu$, where R_ν is the circle radius (the other principal curvature radius is ∞). In addition, the edges for the cylindrical particles in Table 2 always show a constant intersection angle θ, either for the longitudinal edges or for the edges of the bases (in this case, $\theta = \pi/2$). Consequently, eq 7 becomes (for finite cylinders)

$$\Gamma = \frac{V_p}{S_p^2}\left[H\sum_{\nu=1}^{N_c}\varphi_\nu + \sum_{\mu=1}^{N_w} W_\mu \omega(\theta_\mu)\right]$$

Where φ_ν is the angle sustained by the circular sector ν. The toroidal particle shows a single smooth region (without edges) with nonuniform curvature. Then, from eq 7

$$\Gamma = l\bar{\Psi}_S \tag{11}$$

From the Appendix in ref 12, $\bar{\Psi}_S = 1/a$ (the radius a is defined in Table 2). Besides, $l = a/2$. Taking into account eqs 11 and 9, we obtain for the torus $\Gamma = 1/2$ and $\sigma = 1$. These are the values corresponding to an infinitely long circular cylinder.

To validate the predictive capacity of the GC model, the errors in η estimation were analyzed for every particle shape and kinetic expression. The relative error is defined as

$$\varepsilon = 100\frac{|\eta^{GC} - \eta|}{\eta}$$

where η stands for the effectiveness factor of any of the actual 3D pellets shown in Table 2 and η^{GC} for the value obtained from the GC model employing the corresponding values of σ, which are given in Table 3 for each shape and each kinetic expression. It can be appreciated that the effect of kinetics on σ is weak, as already mentioned in section 2.1.

The solution of the mass conservation equation to obtain the effectiveness factor η for the shapes in Table 2 was carried out by means of the software Femlab v3.1 of Comsol Inc. (numerical solution of differential equations by the finite elements method). Instead, a routine written by us, which uses a shooting procedure to solve an integral formulation of the 1D conservation equation, was employed for evaluating η^{GC}. In either case, for the evaluation of η or η^{GC}, the size of the mesh for numerical evaluation was adjusted to guarantee accuracy of about 0.1%.

Figure 3 shows the behavior of ε while varying Φ for the trilobe particle with isothermal LHHW, exothermic first order, and isothermal first order kinetics (the latter included for reference). It can be appreciated that for the three kinetic expressions the maximum errors take place at values of Φ of approximately 1; these kind of curves are typical for all particles and reaction rate expressions studied in this contribution. Hence, hereinafter the attention will be focused on the analysis of the maximum errors defined as

$$\varepsilon_{max} = \max_{\Phi}\{\varepsilon\}$$

It can be concluded from Figure 3 that the GC model leads to greater values for ε_{max} for the exothermic first order and isothermal LHHW kinetics than for the isothermal first order kinetics. This trend can be generalized: the lower the apparent reaction order, the lower precision.

Nonetheless, the level of errors arising from the use of the GC model is most satisfactory in all cases, as becomes evident

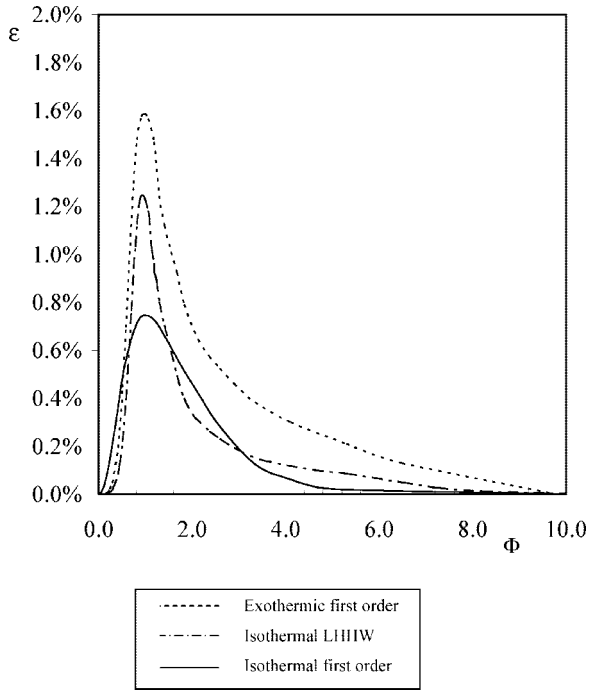


Figure 3. ε vs Φ for the trilobe particle ($y = 0.866$, $x = 0.684$, Table 2).

from the complete set of results summarized in Table 3. It can be appreciated that ε_{max}, for all shapes and kinetic expressions here studied, is kept below approximately 3.5%.

It is worth mentioning that the toroidal pellet behaves almost exactly as an infinitely long circular cylinder: the maximum error from Table 3 is lower than 0.3% (i.e., similar to the intrinsic level of precision of the numerical evaluations).

The cylindrical extrudates present, on average for all kinetic expressions, the maximum values of ε_{max} in Table 3. These results deserve a comment. Cylindrical extrudates are commercialized in a great variety of sizes (different values of x in Table 2), and the aspect ratio employed in this contribution ($x = 0.286$) corresponds to the value for which the maximum value of ε_{max} ($= 1.5\%$) was detected in the estimation of the effectiveness factor for an isothermal first order reaction.[6] Hence, the ratio $x = 0.286$ is nearly the most awkward case to test the GC model performance for nonlinear kinetics.

The values resulting for σ (see Table 3) range from $\sigma = 0.39$ (for the wagon wheel with an isothermal second order expression), that is, slightly larger than for a slab ($\sigma = 0$), to $\sigma = 3$ (for the trilobe particle with isothermal zero order), that is, larger than the exponent of a sphere ($\sigma = 2$).

4. Conclusions

In the present contribution the one-dimensional GC model was employed to estimate effectiveness factors in catalytic pellets of different shapes and nonlinear kinetics.

Some catalyst shapes employed in commercial processes were studied to demonstrate that the GC is a useful numerical tool for practical purposes. Specifically, trilobe pellets, typically used in a number of hydrorefining processes, seven-hole cylinders (wagon wheel) employed in dry/wet reforming of low hydrocarbons/oxygenates, and the well-known cylindrical extrudates broadly used in many processes were considered. A toroidal pellet was also included, in spite of not being a typical commercial shape, because it presents interesting geometrical features for its potential application.

The GC model was applied for five types of nonlinear kinetic expressions (isothermal zero and second order, isothermal Langmuir−Hinshelwood−Hougen−Watson type, first order exothermic, and first order endothermic).

The GC model-free parameter (σ) is fitted so as to reproduce the behavior of the actual pellet at high reaction rates. The shape factor Γ (eq 7) governs such behavior for a pellet of arbitrary shape, and eq 9 provides the fitting value of σ. The shape parameter Γ (eq 7) can be easily calculated for any 2D or 3D geometry from the curvatures of the external surface S_p and the intersecting angles defining its edges.

The maximum deviation between the actual effectiveness factors and values calculated with the GC model for the whole set of particles and kinetic expressions was lower than 3.5%, which can be considered completely satisfactory for any practical application.

A number of aspects deserve further study 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. 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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Nomenclature

C_A = molar concentration of species A [mol m^{-3}]
D_A = diffusion coefficient of species A [m^2 s^{-1}]
H = length of a cylindrical pellet [m]
I_1 = coefficient defined in eq 5c [dimensionless]
I_2 = coefficient defined in eq 5d [dimensionless]
$l = V_p/S_p$, characteristic length [m]
L = diffusion length of the GC model [m]
N_s = number of smooth regions
N_w = number of edges
I_{12} = coefficient defined in eq 5e [dimensionless]
R_a, R_b = principal radii of curvature [m]
$r(Y)$ = relative reaction rate defined in eq 2e [dimensionless]
S_p = external surface area of the catalytic body accessible to reactants [m^2]
S_ν = area of the νth smooth region [m^2]
S^{GC} = cross section of the GC model body [m^2]
V_p = volume of the catalytic body [m^3]
V^{GC} = volume of the GC model body [m^3]
W_μ = length of μth edge [m]
Y = dimensionless concentration defined in eq 2d
z = dimensionless coordinate in the GC model

Greek letters

Γ= coefficient defined in eq 7 [dimensionless]
$\Psi = (1/R_a) + (1/R_b)$, sum of local principal curvatures on S_ν [m^{-1}]
$\bar{\Psi}_\nu$ = average value of Ψ on S_ν [m^{-1}]
π_A = specific consumption rate of A species [mol m^{-3} s^{-1}]
Φ = Thiele modulus defined in eq 3 [dimensionless]
η^{GC} = GC model effectiveness factor [dimensionless]

η = effectiveness factor [dimensionless]
σ = shape factor − GC model parameter [dimensionless]
θ = intersecting angle [rad]
ω = parameter defined in eq 8 [dimensionless]
Subscripts
e = chemical equilibrium
s = value at S_p

Literature Cited

(1) Papadias, D.; Edsberg, L.; Björnbom, P. Simplified method for effectiveness factor calculations in irregular geometries of washcoats. *Chem. Eng. Sci.* **2000**, *55*, 1447–1459.

(2) Hayes, R. E.; Liu, B.; Moxom, R.; Votsmeier, M. The effect of washcoat geometry on mass transfer in monolith reactors. *Chem. Eng. Sci.* **2004**, *59*, 3169–3181.

(3) Bischoff, K. B. Effectiveness factor for general reaction rate forms. *AIChE J.* **1965**, *11*, 351–355.

(4) Burghardt, A.; Kubaczka, A. Generalization of the Effectiveness Factor for Any Shape of a Catalyst Pellet. *Chem. Eng. Proc.* **1996**, *35*, 65–74.

(5) Mariani, N. J.; Keegan, S. D.; Martínez, O. M.; Barreto, G. F. A One-Dimensional Equivalent Model to Evaluate Overall Reaction Rates in Catalytic Pellets. *Chem Eng. Res. Des., Part A* **2003**, *81*, 1033–1042.

(6) Mariani, N. J.; Keegan, S. D.; Martínez, O. M.; Barreto, G. F. On the evaluation of effective reaction rates on commercial catalyst by means of a one-dimensional model. *Cat. Today* **2008**, *133*−*135*, 770–774.

(7) Wedel, S.; Luss, D. A Rational Approximation of the Effectiveness Factor. *Chem. Eng. Commun.* **1980**, *11*, 245–259.

(8) Keegan, S. D.; Mariani, N. J.; Martínez, O. M.; Barreto, G. F. Behavior of smooth catalyst at high reaction rates. *Chem. Eng. J.* **2005**, *110*, 41–56.

(9) Keegan, S. D.; Mariani, N. J.; Martínez, O. M.; Barreto, G. F. Behavior of Catalytic Pellets at High Reaction Rates. The Effect of the Edges. *Ind. Eng. Chem. Res.* **2006**, *45*, 85–97.

(10) Mariani, N. J.; Mocciaro, C.; Keegan, S. D.; Martínez, O. M.; Barreto, G. F. *Chem. Eng. Sci.* **2008**, Submitted.

(11) Froment, G. F.; Bischoff, K. B. *Chemical Reactors Analysis and Design*; John Wiley & Sons Inc.: New York, 1990.

(12) Buffham, B. A. The size and compactness of particles of arbitrary shape: application to catalyst effectiveness factors. *Chem. Eng. Sci.* **2000**, *55*, 5803–5811.

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