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Exact analytical solutions of diffusion reaction in spherical porous catalyst

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ABSTRACT

A nonlinear model of coupled diffusion and *n*th-order chemical reaction in a spherical catalyst pellet is revisited in this paper. As we are aware, except for the linear case $n = 1$, no exact solutions of this model have been reported until now. In the present paper several such solutions are given in a closed analytical form. The existence and uniqueness of solutions in the whole range $n \geq 0$ of the reaction order and of the Thiele modulus ϕ is discussed in some detail.

1. Introduction and problem formulation

The main goal of the present paper is to give some exact analytical steady state solutions of a highly nonlinear model of a coupled diffusion and *n*th-order chemical reaction in a spherical porous catalyst. A comprehensive approximate-analytical study of this model, using the Adomian decomposition method, has been reported few years ago by Shi-Bin and co-workers [1]. This latter work is the basic reference for the present paper. A comprehensive review of further reaction-diffusion problems in porous catalysts can be found e.g. [2].

For a first order reaction, $n = 1$, which represents the homogeneous linear case of the mathematical model specified below, an exact analytical solution exists and has already been given by Thiele [3]. However, for $n \neq 1$, to the best of our knowledge, no exact analytical solutions have been reported until now.

At isothermal conditions, the steady regime of the *n*th-order reaction-diffusion process in the spherical geometric pellet is governed by equation [1]

$$D_e\left(\frac{d^2c}{dr^2}+\frac{2}{r}\frac{dc}{dr}\right)=k_v c^n \tag{1}$$

where c is the reactant concentration in pore of catalyst pellet, D_e the effective diffusion coefficient for reactant, r the distance from the pellet core and k_v the reaction rate constant. The admitted range of the reaction order is $n \geq 0$. The boundary conditions assumed are [1]

$$c|_{r=r_0}=c_s \quad \text{(surface of catalyst)} \tag{2}$$

and

$$\left.\frac{dc}{dr}\right|_{r=0}=0 \quad \text{(center of catalyst)} \tag{3}$$

In terms of the dimensionless variables

$$R=\frac{r}{r_0}, \qquad C(R)=\frac{c(r)}{c_s} \tag{4}$$

the boundary value problem (1)–(3) is specified by equations [1]

$$\frac{d^2C}{dR^2}+\frac{2}{R}\frac{dC}{dR}=\phi^2C^n \tag{5}$$

$$C\big|_{R=1}=1, \qquad \left.\frac{dC}{dR}\right|_{R=0}=0 \tag{6}$$

where $\phi=(k_v r_0^2 c_s^{n-1}/D_e)^{1/2}$ denotes the Thiele modulus.

The quantities of physical interest are the concentration in the center of catalyst

$$C(0)\equiv C_0 \tag{7}$$

as well as the concentration gradient at the surface of catalyst $dC/dR|_{R=1}$. The latter quantity is related to the *effectiveness factor* of the spherical catalyst by the relationship [1]

$$\eta=\frac{3}{\phi^2}\left.\frac{dC}{dR}\right|_{R=1} \tag{8}$$

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Nomenclature

c	concentration
c_s	surface concentration (at $r = r_0$)
C	dimensionless concentration, Eq. (4)
C_0	dimensionless concentration in the center of the pellet
D_e	effective diffusion coefficient
k_v	reaction rate constant
n	reaction order
r	radial coordinate
r_0	radius of the pellet
R	dimensionless radial coordinate, Eq. (4)
x	transformed independent variable, Eq. (11)
y	transformed dependent variable, Eq. (11)
Greek symbols	
ϕ	$(k_v r_0^2 c_s^{n-1}/D_e)^{1/2}$, Thiele modulus
ϕ_n	upper bound of ϕ for $0 \le n < 1$, Eq. (33)
η	effectiveness factor, Eq. (8)

For a first order reaction, the solution of the boundary value problem (5) and (6) is well known [3] and reads

$$C(R) = \frac{\sinh(\phi R)}{R \sinh\phi} \quad (n = 1) \tag{9}$$

The corresponding concentration in the center of catalyst C_0 and the effectiveness factor η are obtained in this case as

$$C_0 = \frac{\phi}{\sinh\phi}, \qquad \eta = \frac{3}{\phi^2}\left(\frac{\phi}{\tanh\phi} - 1\right) \quad (n = 1) \tag{10}$$

Hereafter in this paper throughout $n \neq 1$ will be assumed.

2. The autonomous boundary value problem for $n \neq 1$

As a first step of the present approach we transform the governing Eq. (5) of the concentration field, which is a differential equation with variable coefficients on a finite domain, into a differential equation with constant coefficients on a semi-infinite domain. The reason is that such equations in general can more easily be managed than those with variable coefficients. To this end, we change from the old variables R and C to new independent and dependent variables x and y, respectively, which we define by the equations

$$x = -\ln R, \qquad C(R) = R^{2/(1-n)} y(x) \tag{11}$$

Indeed, under the transformations (11), Eq. (5) goes over in the differential equation with constant coefficients

$$y'' - \frac{5-n}{1-n} y' + \frac{2(3-n)}{(1-n)^2} y - \phi^2 y^n = 0 \quad (n \neq 1) \tag{12}$$

where the prime denotes differentiations with respect to the new independent variable x of which range of variation is $x \in [0,+\infty]$. It is also easily shown that in the range $n > 1$ of the reaction order the boundary conditions (6) go over in

$$y(0) = 1, \qquad y'(\infty) = 0 \tag{13}$$

In the range $0 \le n < 1$, however, the transformed problem admits, in addition to solutions satisfying the same boundary conditions (13), also further solutions which correspond to the divergent condition $y'(\infty) = \infty$ in the center of catalyst, while the surface condition $y(0) = 1$ remains still valid also in this case (see Section 3.2).

3. Exact solutions

3.1. Power-law solutions for $0 \le n < 1$

A simple inspection of Eq. (12) shows that this equation admits the constant solution

$$y = \left[\frac{2(3-n)}{(1-n)^2 \phi^2}\right]^{1/(n-1)} \tag{14}$$

Obviously, this solution satisfies the second boundary condition (13) identically. When, in addition, $y = 1$ is required, which happens for

$$\phi^2 = \frac{2(3-n)}{(1-n)^2} \equiv \phi_n^2 \tag{15}$$

then also the first boundary condition (13) is satisfied identically. Therefore, the second Eq. (11) implies that

$$C(R) = R^{2/(1-n)} \tag{16}$$

is a solution of Eq. (5) which satisfies the first boundary condition (6) for all $n \neq 1$. The second boundary condition (6), however, can only be satisfied when the power exponent $2/(1-n)$ is larger than 1. This latter condition requires $-1 < n < 1$. Therefore, Eq. (16) is a solution of the original boundary value problem (5) and (6) only in the range $0 \le n < 1$ of the reaction order for the selected values $\phi = \phi_n$ of the Thiele modulus given by Eq. (15). A remarkable property of the power-law solution (16) is that it yields a vanishing reactant concentration C_0 in the center of the pellet. The effectiveness factor (8) in this case is

$$\eta = \frac{3(1-n)}{3-n} \quad (0 \le n < 1) \tag{17}$$

In the special case of a zeroth order reaction, Eqs. (16), (15) and (17) reduce to

$$C(R) = R^2, \qquad \phi^2 = 6, \qquad \eta = 1 \quad (n = 0) \tag{18}$$

Once the power-law solution (16) is known, it can also be "recovered" from the original equation (5) directly. Indeed, rewriting Eq. (5) in the form

$$\frac{1}{R}\frac{d^2}{dR^2}(RC) = \phi^2 C^n \tag{19}$$

one immediately sees that (16) is an exact solution for any $0 \le n < 1$ when the value of the respective Thiele modulus is given by Eq. (15).

It is worth mentioning here that, similarly to the case of the present spherical porous catalyst, power-law solutions for the concentration field also occur in the reaction-diffusion models of *porous slabs*, as being reported recently by Magyari [4].

3.2. An exact polynomial solution for $n = 0$

In addition to the power-law solution (18), the boundary value problem (5) and (6) admits for the case of zeroth order reactions also a further, more general solution. Indeed, for $n = 0$, Eq. (12) reduces to the linear non-homogeneous differential equation

$$y'' - 5y' + 6y = \phi^2 \tag{20}$$

It is easy to show that

$$y = \frac{\phi^2}{6} + \left(1 - \frac{\phi^2}{6}\right) e^{2x} \tag{21}$$

is a solution of Eq. (20) which satisfies the surface condition $y(0) = 1$. However, this solution violates the asymptotic condition specified by the second Eq. (13), giving $y'(\infty) = \infty$ instead of $y'(\infty) = 0$, as already mentioned at the end of Section 2. Nevertheless, the corresponding concentration

$$C(R) = 1 - \frac{\phi^2}{6}(1 - R^2) \tag{22}$$

obtained from Eq. (21) via Eq. (11), is a proper solution of the original boundary value problem (5) and (6). The corresponding reactant concentration in the center of the pellet is

$$C_0 = 1 - \frac{\phi^2}{6} \quad (n = 0) \tag{23}$$

which requires $\phi^2 \le 6$. The effectiveness factor corresponding to the solution (22) is $\eta = 1$ for all $\phi^2 \le 6$. It is also easily seen that (22) coincides with the power-law solution (18) at the upper bound $\phi_{\max} = \phi_0 = \sqrt{6}$ of its physical existence domain $\phi^2 \le 6$.

It is worth mentioning here that, while the power-law solutions (16) cannot be recovered from the general Adomian decomposition results of [1], the second-order polynomial solution (22) can easily be obtained as the special case $n = 0$ of Eq. (24) of [1]. Indeed, setting in the latter equation $n = 0$, we obtain (in the notations of the present paper) $RC = \beta R + (\phi^2/6)R^3$. Dividing this equation by R and using the surface condition $C\big|_{R=1} = 1$, the constant β is determined to $\beta = 1 - (\phi^2/6)$ and thus the polynomial solution (22) is recovered immediately.

3.3. The exact solution for n = 5

The fifth order reaction is a remarkable special case of the autonomous boundary value problem (12) and (13) since in this case the coefficient of the first order derivative y' becomes zero. As a consequence, Eq. (12) admits for $n = 5$ the first integral

$$y'^2 = \frac{1}{4}y^2 + \frac{\phi^2}{3}y^6 \tag{24}$$

Now, changing in Eq. (24) from y to a new independent variable z according to

$$y = \left(\frac{\sqrt{3}}{2\phi z}\right)^{1/2} \tag{25}$$

we obtain the solution of Eq. (24) in the implicit form

$$x + x_0 = \int \frac{dz}{\sqrt{1+z^2}} = \operatorname{arcsinh}(z) = \operatorname{arcsinh}\left(\frac{\sqrt{3}}{2\phi y^2}\right) \tag{26}$$

which in turn yields

$$y(x) = \left[\frac{\sqrt{3}}{2\phi \sinh(x + x_0)}\right]^{1/2} \tag{27}$$

where x_0 is a constant of integration. The "initial condition" $y(0) = 1$ implies $x_0 = \operatorname{arcsinh}[\sqrt{3}/(2\phi)]$. Thus, bearing in mind that according to Eq. (11) in this case $C(R) = R^{-1/2}y(x) = R^{-1/2}y(-\ln R)$ holds, after some elementary manipulations we obtain the solution for the dimensionless concentration in the form

$$C(R) = \sqrt{2}\left[1 + R^2 + \left(1 + \frac{4}{3}\phi^2\right)^{1/2}(1 - R^2)\right]^{-1/2} \tag{28}$$

For the reactant concentration in the center of the pellet C_0 and the effectiveness factor η we obtain in this case

$$C_0 = \sqrt{2}\left[1 + \left(1 + \frac{4}{3}\phi^2\right)^{1/2}\right]^{-1/2} \tag{29}$$

$$\eta = \frac{3}{2\phi^2}\left[\left(1 + \frac{4}{3}\phi^2\right)^{1/2} - 1\right] \tag{30}$$

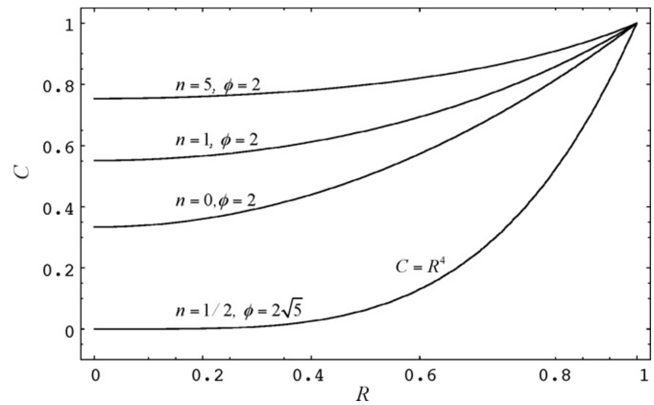

Fig. 1. Plot of the exact power-law solution (16) for $n = 1/2$ and $\phi = 2\sqrt{5}$, as well as the exact solutions for (22), (9) and (28) for $\phi = 2$ and $n = 0$, 1 and 5, respectively.

As an illustration, in Fig. 1 the exact solution (28) is compared to the concentration profiles described by Eqs. (9), (16) and (22) for the reaction orders $n = 1$, 1/2 and 0, respectively, and the indicated values of the Thiele modulus ϕ. It is seen that, for the same value of ϕ, the larger the reaction order n, the larger the concentration C_0 in the center of catalyst. For the power-law solutions (16), which for $n = 1/2$ becomes $C(R) = R^4$ with $\phi = 2\sqrt{5}$, one has $C_0 = 0$.

4. Existence domain and discussion

Except for Thiele's solution (9) and the other solutions reported in Section 3, no further exact analytical solutions of the boundary value problem (5) and (6) were found. In all other cases the problem has to be solved numerically. This latter task can easily be accomplished by a formal transcription of the two-point boundary value problem (5) and (6) in an *initial value problem* with an additional condition. In this sense, we prescribe the *initial conditions*

$$C\big|_{R=0} = C_0, \qquad \frac{dC}{dR}\bigg|_{R=0} = 0 \tag{31}$$

at the "initial instant" $R = 0$ with C_0 as an unknown parameter, and then determine the value of C_0 such that at the "final instant" $R = 1$ the solution $C = C(R;C_0)$ satisfies the additional condition

$$C(R; C_0)\big|_{R=1} = 1 \tag{32}$$

The basic advantage of this approach (which actually is nothing more that the familiar shooting method) consists of the fact that the initial value problem (5), (31) always admits a *unique solution* as a function of the parameter C_0. When the additional condition (32) also admits (for specified values of n and ϕ) a unique solution for C_0, then the solution of the boundary value problem (5) and (6) does exist and is unique. As an example for this procedure, we have calculated the "initial value" C_0 as a function of the Thiele modulus ϕ for the reaction orders $n = 0.4$, 0.6 and 2. The respective numerical results are shown in Fig. 2, together with the exact analytical results for $n = 0$, 1 and 5 as being given by Eqs. (23), (10) and (29), respectively. This figure emphasizes the following features of the solution space which turn out to be generally valid for the present problem:

1. In the range $n \ge 1$ of the reaction order a unique solution exists for any specified value of n and $\phi \ge 0$.
2. In the range $0 \le n < 1$, the boundary value problem admits solutions only in a finite interval of values $0 \le \phi \le \phi_n$ of the Thiele modulus ϕ, where the corresponding solutions are unique.

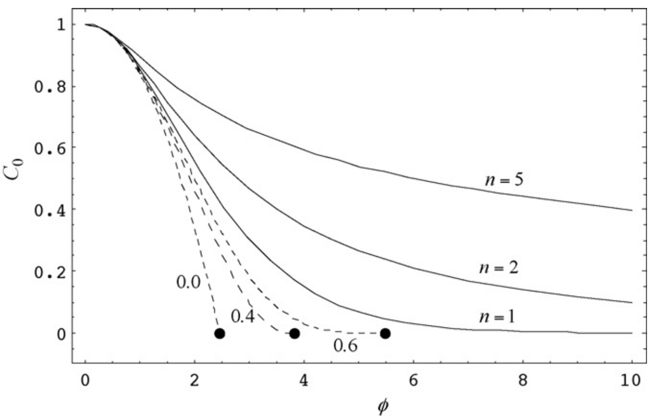

Fig. 2. Shown are the reactant concentrations C_0 in the center of the pellet as functions of the Thiele modulus ϕ for the reaction orders $n = 0$, 0.4, 0.6 (dashed lines) and 1, 2 and 5 (solid lines). The dots denote the upper bounds $\phi_{0.0} = \sqrt{6} = 2.45$, $\phi_{0.4} = \sqrt{130}/3 = 3.80$ and $\phi_{0.6} = \sqrt{30} = 5.48$ of the existence domains of the solutions for $n = 0$, 0.4, and 0.6 as given by Eq. (15). In these points, $C_0 = 0$.

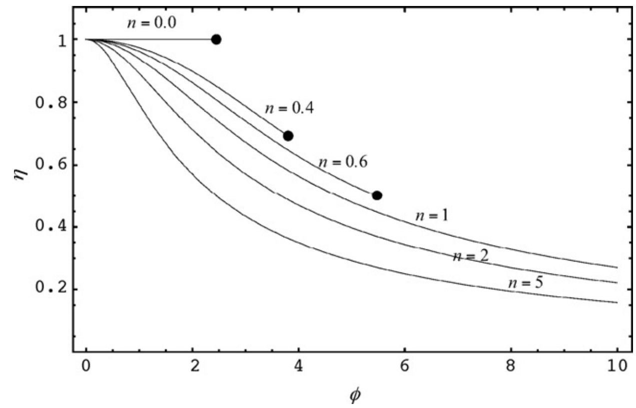

Fig. 3. Shown are the effectiveness factors η as functions of the Thiele modulus ϕ for the reaction orders $n = 0$, 0.4, 0.6, 1, 2 and 5. The dots correspond to the upper bounds $\phi_{0.0} = \sqrt{6} = 2.45$, $\phi_{0.4} = \sqrt{130}/3 = 3.80$ and $\phi_{0.6} = \sqrt{30} = 5.48$ of the existence domains of the solutions for $n = 0$, 0.4, and 0.6 where the values of η, as obtained from Eq. (17), are 1, 0.6923 and 0.5, respectively.

3. For a specified value of n in the range $0 \le n < 1$, the upper bound ϕ_n of the existence domain $0 \le \phi \le \phi_n$ as given by Eq. (15) is,

$$\phi_n = \frac{\sqrt{2(3-n)}}{1-n} \tag{33}$$

   The respective values (33) are marked in Fig. 2 by dots and are associated with the power-law solutions (16) of the boundary value problem. In these points, $C_0 = 0$.
4. The concentration C_0 in the center of the pellet approaches unity for all $n \ge 0$ as $\phi \to 0$.
5. With increasing values of the Thiele modulus, the concentration C_0 decreases monotonically from 1 to zero for all $n \ge 0$.

The property (4) is a direct consequence of the fact that the boundary value problem (5), (6) admits for $\phi = 0$ the constant solution

$$C(R) = 1 \quad (\phi = 0) \tag{34}$$

which is valid for all n. Moreover, Fig. 2 suggests that the concentration C_0 in the center of the pellet possesses not only at $\phi = 0$, but also for all small values, $\phi \ll 1$, of the Thiele modulus a *universal behavior*, i.e. a behavior which does not depend on the reaction order n. When this conjecture is true, the universal dependence of C_0 on ϕ for $\phi \ll 1$ must be given by the exact result (23) obtained for $n = 0$. In other words,

$$C_0 = 1 - \frac{\phi^2}{6} \quad (\text{for all } n \ge 0, \text{ when } \phi \ll 1) \tag{35}$$

must hold for all $n \ge 0$ when $\phi \ll 1$. The exact results (9) and (29) yield the first straightforward arguments speaking for Eq. (35). Indeed, expanding the respective expressions of C_0 in Taylor series to the powers of ϕ, we arrive, up to the leading order in ϕ, precisely to Eq. (35) proving its truth also for $n = 1$ and $n = 5$. The proof of Eq. (35) for arbitrary n can be given as follows. As a first step, we substitute in the governing Eq. (5) $C(R) = 1 - Y(R)$, where $Y(R)$ is a small quantity of the order of magnitude of ϕ^2 when $\phi \ll 1$. In this case, to first order in the small quantities Y and ϕ^2, Eq. (5) becomes

$$-\frac{d^2Y}{dR^2} - \frac{2}{R}\frac{dY}{dR} = \phi^2(1-Y)^n \cong \phi^2(1-nY) \cong \phi^2 \tag{36}$$

The corresponding boundary conditions (6) go over in $Y|_{R=1}$ and $dY/dR|_{R=0} = 0$, respectively. Is easy to see that the solution of the linear non-homogeneous Eq. (36) which satisfies the latter boundary conditions is

$$Y(R) = \frac{\phi^2}{6}(1-R^2) \tag{37}$$

Now, via the equation $C(R) = 1 - Y(R)$, Eq. (37) leads for $R = 0$ precisely to Eq. (35), proving its universal validity for small ϕ.

The dependence of the effectiveness factor η on ϕ, which besides the concentration in the center of catalyst C_0 is an important characteristic of engineering interest, is shown in Fig. 3 for the same values of the reaction order n which have already been selected in Fig. 2. An inspection of Fig. 3 shows that, except for the case $n = 0$ where $\eta = 1$, the effectiveness factor η is a monotonically decreasing function of the Thiele modulus ϕ for all values $n > 0$. Moreover, the larger n, the smaller η for any given value of ϕ (within the domain of existence of the corresponding solutions). In the range $0 \le n < 1$, the curves $\eta = \eta(\phi)$ terminate at the upper bounds ϕ_n of the existence domains of the respective solutions, in a full agreement with Fig. 2. The values of η which correspond to largest admissible values ϕ_n of the Thiele modulus are given by Eq. (17). It is also worth mentioning here that in contrast to $C_0 = C_0(\phi)$, the function $\eta = \eta(\phi)$ does not possess a universal behavior for $\phi \ll 1$. Indeed, expanding the exact results (10) and (30) in Taylor series to the powers of ϕ, to the leading order in ϕ, we arrive to the results

$$\eta = 1 - \frac{\phi^2}{15} \quad (\text{for } n = 1, \text{ when } \phi \ll 1) \tag{38}$$

$$\eta = 1 - \frac{\phi^2}{3} \quad (\text{for } n = 5, \text{ when } \phi \ll 1) \tag{39}$$

When $\phi \to \infty$, on the other hand, both the above effectiveness factors approach zero as $3/\phi$ for $n = 1$, and as $\sqrt{3}/\phi$ for $n = 5$.

5. Summary and conclusions

In the present paper a nonlinear model of coupled diffusion and nth-order chemical reaction in a spherical catalyst pellet has been considered with the aim to report new exact analytical steady state solutions, and to discuss the structure of the solution space in detail. The main results obtained can be summarized as follows:

1. In the range $n \ge 1$ of the reaction order a unique solution exists for any specified value of n and $\phi \ge 0$. For $n = 5$ the solution is available in an exact analytical form (see Eq. (28)).
2. In the range $0 \le n < 1$, the boundary value problem admits solutions only in a finite interval of values $0 \le \phi \le \phi_n$ of the Thiele modulus ϕ, where the corresponding solutions are unique. For a specified value of n, the upper bound ϕ_n of the existence domain is $\phi_n = \sqrt{2(3-n)}/(1-n)$. The solutions associated with these special values of the Thiele modulus are the exact power-law

solutions $C(R) = R^{2/(1-n)}$. In this case the concentration in the center of catalyst is vanishing, $C_0 = 0$ (see Fig. 2).
3. The concentration C_0 approaches unity for all $n \geq 0$ according to the *universal law* $C_0 = 1 - \phi^2/6$, when $\phi \to 0$. With increasing values of the Thiele modulus, the concentration C_0 decreases monotonically from 1 to zero for all $n \geq 0$ (see Fig. 2).
4. The effectiveness factor η is a monotonically decreasing function of the Thiele modulus ϕ for all values $n > 0$. The larger n, the smaller η for any given value of ϕ. In the range $0 \leq n < 1$, the curves $\eta = \eta(\phi)$ terminate at the upper bounds ϕ_n of the existence domains of the respective solutions (see Fig. 3).

The new exact analytical solutions reported in this paper have been obtained by transforming the governing equation for the concentration filed, which is a differential equation with variable coefficients on a finite domain, into a differential equation with constant coefficients on a semi-infinite domain. This procedure shows the usefulness of such variable transformations in the chemical reaction kinetics.

References

[1] S. Yan-Ping, L. Shi-Bin, K. Scott, Analytic solution of diffusion reaction in spherical porous catalyst, Chem. Eng. Technol. 26 (2003) 87–95.
[2] R. Aris, The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, vol. 1. The Theory of Steady State, Clarendon, Oxford, 1975.
[3] E.W. Thiele, Relation between catalytic activity and size of particle, Ind. Eng. Chem. 31 (1939) 916–920.
[4] E. Magyari, Exact analytical solution of a nonlinear reaction-diffusion model in porous catalysts, Chem. Eng. J. 143 (2008) 167–171.