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# Dead-Core Solutions to Simple Catalytic Reaction Problems in Chemical Engineering

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**Abstract**

The catalytic chemical reaction is usually carried out in a pellet where the catalyst is distributed throughout its porous structure. The selectivity, yield and productivity of the catalytic reactor often depend on the rates of chemical reactions and the rates of diffusion of species involved in the reactions in the pellet porous space. In such systems, the fast reaction can lead to the consumption of reactants close to the external pellet surface and creation of the dead core where no reaction occurs. This will result in an inefficient use of expensive catalyst. In the discussed simplified diffusion-reaction problems a nonlinear reaction term is of power-law type with a small positive reaction exponent. Such reaction term represents the kinetics of catalytic reaction accompanied by a strong adsorption of the reactant. The ways to calculate the exact solutions possessing dead cores are presented. It was also proved analytically that the exact solution of the nonlinear two-point boundary value problem satisfies physical a-priori bounds. Furthermore, the approximate solutions were obtained using the orthogonal collocation method for pellets of planar, spherical and cylindrical geometries. Numerical results confirmed that the length of the dead core increases for the more active catalysts due to the larger values of the reaction rate constant. The dead core length also depends on the pellet geometry.

## 1. Introduction

The chemical reactions in the petrochemical and chemical industries are frequently carried out in the fixed-bed reactors filled with catalyst pellets. The catalyst material is distributed throughout the pellet porous structure. The intrinsic rate of chemical reaction and the rate of diffusion of reactant species from the external pellet surface to the pellet interior could both influence the selectivity, yield and productivity of the reactor. In the case of power-law kinetics with the small positive reaction exponent, the so-called dead cores can appear in the pellet where the reactants are fully consumed, and no reaction occurs. This will result in the inefficient use of expansive catalyst material [1, 2]. Recently, core-shell catalysts have been successfully applied for industrially important reactions such as Fischer-Tropsch [3] and steam methane reforming for hydrogen production [4].

In the discussed simplified diffusion-reaction problems there is a nonlinear term of power-law type which represents the kinetics of catalytic reaction accompanied by a strong reactant adsorption. The purpose of this paper is to present the ways to calculate the exact solutions possessing dead cores and their numerical approximations based on the collocation method for planar, spherical and cylindrical geometries [5]. The exact formula is derived analytically for the solution to the dead-core problem in the planar case. The condition which separates the smooth solutions from the dead-core solutions is demonstrated in terms of the reaction rate constant and the reaction exponent.

In Section 2, the model is presented, the dead-core solutions are characterized, and the numerical approach is described. In Sections 3, the analytic and numerical results are illustrated, and in Section 4 the conclusions are drawn.

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## 2. Diffusion-reaction model problem with power-law kinetics

### *2.1. Catalytic diffusion-reaction problem with strong adsorption*

The diffusion-reaction problem is considered for three different pellet geometries. Let $c = c(x)$, $x \in \Omega = (0,1)$ , denote the unknown dimensionless concentration. The mathematical model for diffusion and catalytic reaction in the planar ($n$ = 0), cylindrical ($n$ = 1), and spherical ($n$ = 2) geometry reads as follows

$$\begin{cases} -\frac{1}{x^n}\left(x^n c_x(x)\right)_x + kc_+^p(x) = 0, \quad x \in \Omega, \\ c_x(0) = 0, \quad c(1) = 1 \end{cases} \tag{1}$$

where $k$>0 is the reaction rate constant, $p$>0 denote the reaction exponent and $w_+ = \max\{w, 0\}$ stands for the positive part of $w$. In the case of $p \in (0,1)$ , the strong adsorption of reactant species on the catalyst sites can be faster than the reactant supply from the bulk phase to the sites in the pellets by diffusion across the pellet boundary and in the pellet pores. This can lead to the total vanishing of reactant species in some regions $\Omega_0 := \{x \in \Omega : c(x) = 0\} \subset \Omega$ , the so-called dead cores. In these regions no chemical reaction occurs and the significant amount of the usually expensive catalyst is wasted, so the knowledge of the location of the dead cores plays an important role in chemical engineering.

Notice that a weak solution to the boundary value problem (1) can be also characterized as a minimizer of the following energy functional

$$F[c] = \int_0^1 s^n \left( \frac{1}{2} c_x^2(s) + \frac{k}{p+1} c_+^{p+1}(s) \right) ds \tag{2}$$

in the class of functions satisfying the boundary condition $c(1) = 1$ and whose weak derivative is square integrable. Since the functional (2) is convex, the weak solution to the boundary value problem (1) is unique. In the following lemma a-priori bounds of the solution to the boundary value problem (1) will be stated.

**Lemma 1** Let $c(x)$ be the weak solution to the boundary value problem (1). Then, it holds true

$$0 \le c(x) \le 1 \quad \text{for all} \quad 0 \le x \le 1.$$

**Proof:** Multiplying the differential Eq. (1) by $x^n(c-1)_+$ and integrating by parts over the domain $\Omega = (0,1)$ yields

$$\int_0^1 s^n \frac{\partial(c-1)}{\partial x}(s) \frac{\partial(c-1)_+}{\partial x}(s) ds + \int_0^1 s^n (c(s)-1)_+ c_+^p(s) ds = 0,$$

from which follows

$$\int_0^1 s^n \left[ \frac{\partial(c-1)_+}{\partial x}(s) \right]^2 ds = -\int_0^1 s^n (c(s)-1)_+ c_+^p(s) ds .$$

Consequently, $(c-1)_+ = 0$ due to the fact that the left hand side of the last equation is non-negative but the right hand side is non-positive. This means that $c(x) \le 1$ for all $0 \le x \le 1$. Let $c\_ = \min\{c,0\}$ denote the negative part of $c$. In order to show that the solution $c(x)$ is non-negative for all $0 \le x \le 1$, the differential Eq. (1) is multiplied by $x^n c\_(x)$ and integrated by parts. Then,

$$\int_0^1 s^n \frac{\partial c}{\partial x}(s) \frac{\partial c_-}{\partial x}(s) ds + \int_0^1 s^n c_-(s) c_+^P(s) ds = 0,$$

from which follows

$$\int_0^1 s^n \left[ \frac{\partial c_-}{\partial x}(s) \right]^2 ds = -\int_0^1 s^n c_-(s) c_+^P(s) ds = 0 .$$

This implies that $c\_(x) = const = 0$ due to the boundary condition $c(1) = 1$. Consequently, $c(x) \ge 0$ for all $0 \le x \le 1$.

Next, the monotonicity of solutions to problem (1) will be considered with respect to the reaction rate constant $k$>0.

**Lemma 2** Let $k_1 \ge k_2 > 0$, $p \in (0,1)$ and $c_1$ and $c_2$ be solutions to the boundary value problem (1) with reaction rate constants $k_1$ and $k_2$, respectively. Then, $c_1(x) \le c_2(x)$ for all $0 \le x \le 1$.

**Proof:** Since $c_1$ and $c_2$ solve the boundary value problem (1) with reaction rate constants $k_1$ and $k_2$, respectively, it holds

$$\frac{1}{x^n}\frac{\partial}{\partial x}\left( x^n \frac{\partial c_1}{\partial x} \right) - \frac{1}{x^n}\frac{\partial}{\partial x}\left( x^n \frac{\partial c_2}{\partial x} \right) = k_1[c_1]_+^p - k_2[c_2]_+^p$$

in $\Omega$.

Multiplying the above equation by $x^n\,(c_1-c_2)_+$ and integrating by parts, yields

$$\int_0^1 s^n\left(\frac{\partial c_1}{\partial x}(s)-\frac{\partial c_2}{\partial x}(s)\right)\left(\frac{\partial([c_1-c_2]_+)}{\partial x}(s)\right)ds=-\int_0^1 s^n\left(k_1[c_1]_+^p(s)-k_2[c_2]_+^p(s)\right)(c_1-c_2)_+(s)ds$$

from which follows

$$\begin{aligned}\int_0^1 s^n\left(\frac{\partial([c_1-c_2]_+)}{\partial x}(s)\right)^2 ds &= -\int_0^1 s^n\left(k_1[c_1]_+^p(s)-k_2[c_2]_+^p(s)\right)(c_1-c_2)_+(s)ds\\ &= -\int_0^1 s^n\left(k_1[c_1]_+^p(s)-k_1[c_2]_+^p(s)+k_1[c_2]_+^p(s)-k_2[c_2]_+^p(s)\right)(c_1-c_2)_+(s)ds\\ &= -k_1\int_0^1 s^n\left([c_1]_+^p(s)-[c_2]_+^p(s)\right)(c_1-c_2)_+(s)ds\\ &\quad -(k_1-k_2)\int_0^1 s^n[c_2]_+^p(s)(c_1-c_2)_+(s)ds.\end{aligned}$$

This implies that

$$0\le\int_0^1 s^n\left(\frac{\partial([c_1-c_2]_+)}{\partial x}(s)\right)^2 ds\le -k_1\int_0^1 s^n\left([c_1]_+^p(s)-[c_2]_+^p(s)\right)(c_1-c_2)_+(s)ds\le 0$$

assuming $k_1 \geq k_2 > 0$ and according to the fact that $(u_+^p - v_+^p)(u-v)_+ \geq 0$ for $p\in(0,1)$. Consequently, $[c_1-c_2]_+ = \text{const} = 0$ in Ω due to $[c_1-c_2]_+(1) = 0$. This means that $c_1 \leq c_2$ in Ω. ■

### 2.2. Characterization of exact dead-core solutions

The dead-core solution to the differential Eq. (1) can be obtained analytically using the following ansatz

$$c(x)=\beta(x-a)_+^{\gamma},\qquad x\in[0,1], \tag{3}$$

where $0 \leq a < 1$ is the length of the dead zone, and $\gamma$ and $\beta$ are the real-valued parameters. In the following, the planar case ($n = 0$) will be considered and the unknown parameters $a$, $\gamma$ and $\beta$ in (3) will be determined. Inserting (3) into the differential Eq. (1) and using the boundary condition results in $\beta = (1-a)^{-\gamma}$, and

$$-\frac{\gamma(\gamma-1)(x-a)^{\gamma-2}}{(1-a)^{\gamma}}+\frac{k(x-a)^{\gamma p}}{(1-a)^{\gamma p}}=0\qquad x\in(0,1]$$

Evaluating the last equation for $x = 1$, yields

$$a=1-\sqrt{\frac{\gamma(\gamma-1)}{k}}\,. \tag{4}$$

Multiplying the differential Eq. (1) by $c_x$ and integrating, implies

$$-\frac{1}{2}(c_x)^2+\frac{k}{1+p}c^{p+1}=const=0\,, \tag{5}$$

where the integration constant is zero due to the boundary condition $c_x(0) = 0$ and the necessary condition for the existence of the dead zone, i.e., $c(0) = 0$. Inserting (3) into (5) and evaluating at $x = 1$, yields

$$a=1-\gamma\sqrt{\frac{p+1}{2k}}\,. \tag{6}$$

From (4) and (6) it follows $\gamma=\frac{2}{1-p}$ and

$$a=1-\frac{2}{1-p}\sqrt{\frac{p+1}{2k}}\,. \tag{7}$$

Consequently, the dead-core solution is of the following form

$$c(x)=\begin{cases}\left(\dfrac{x-a}{1-a}\right)^{\frac{2}{1-p}}, & a\le x<1,\\ 0\ , & 0<x<a,\end{cases} \tag{8}$$

where the length of the dead-zone is given by (7). From $a \geq 0$, it can be deduced that

$$k \geq \frac{2(p+1)}{(1-p)^2}, \qquad (9)$$

which constitutes the condition for the existence of the dead-core solution in the case of the planar geometry. Notice that the dead-zone consists of only one point $x = 0$ if $k = \frac{2(p+1)}{(1-p)^2}$. If $0 < k < \frac{2(p+1)}{(1-p)^2}$, the analytic solution possesses no dead zone and can be expressed in terms of hypergeometric functions, c.f. [1]. In the case of cylindrical and spherical geometries, the ansatz (2) leads to complicated algebraic equations for $a$ and γ. In those cases, the dead-core solutions can be obtained numerically.

### 2.3. Numerical approach

Most of the standard numerical schemes based on fixed-point iterations fail when solving the non-linear boundary value problem (1). This shortcoming of standard schemes can be justified by the lack of contraction due to the fact that the non-linear term $r(c) = kc_+^p$ is not differentiable at $c = 0$ if $0<p<1$. In the case of the planar geometry, the solution $c(x)$ is smooth if $0 < k < \frac{2(p+1)}{(1-p)^2}$, and can be approximated numerically without any sophisticated iterations but it can not be expressed by elementary functions. On the other hand, the solution $c(x)$ is not smooth for $k > \frac{2(p+1)}{(1-p)^2}$, and can be given explicitly but its approximation can not be obtained without numerical troubles in the iteration process when using standard finite element or difference schemes [6, 7, 8]. Our numerical approach is based on the collocation method using orthogonal Jacobi polynomials [5].

## 3. Numerical results

Several solution profiles have been calculated by the collocation method for the reaction exponent $p = 0.01$ and reaction rate constants k = 5, 7, 10, 20, 50. The concentration profiles for the problem in the planar geometry are illustrated in Fig. 1. All of them exhibit the dead zones. Similarly, all concentration profiles show the dead zones in the case of the cylindrical geometry, as presented in Fig. 2. Nevertheless, the concentration profile corresponding to the reaction in the spherical pellet does not exhibit a dead zone for the reaction rate constant $k = 5$, as shown in Fig. 3.

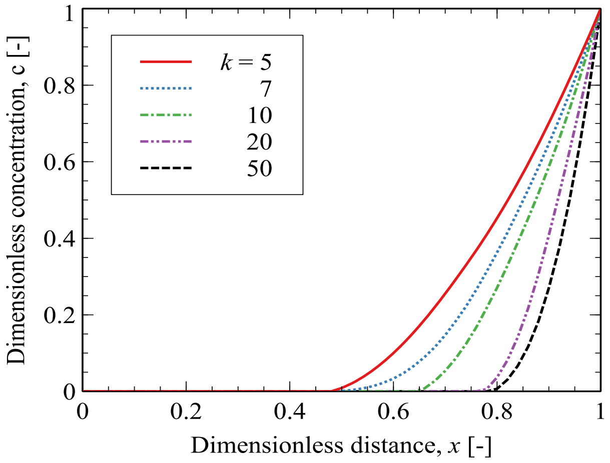


Fig. 1. Solutions for dead-core problem in the case of the planar geometry ($n = 0$) for $p = 0.01$ and various reaction rate constants $k = 5, 7, 10, 20, 50$.

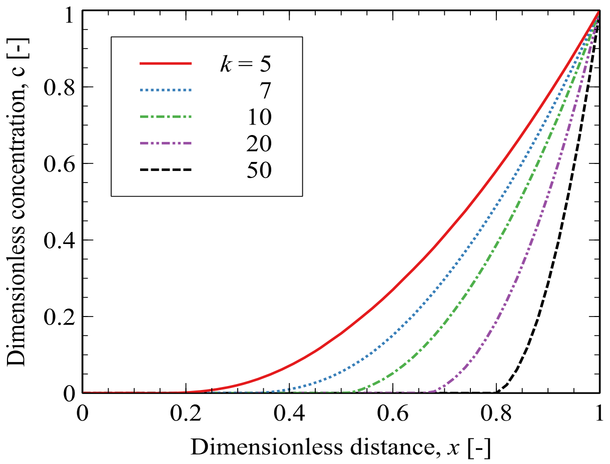


Fig. 2. Solutions for dead-core problem in the case of the cylindrical geometry ($n = 1$) for $p = 0.01$ and various reaction rate constants $k = 5, 7, 10, 20, 50$.

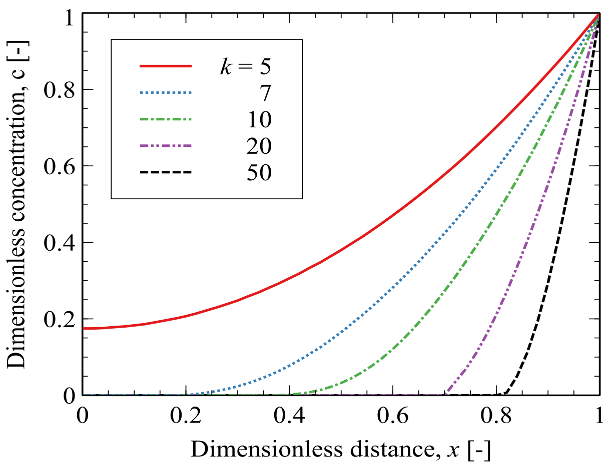


Fig. 3. Solutions for dead-core problem in the case of the spherical geometry ($n = 2$) for $p = 0.01$ and various reaction rate constants $k = 5, 7, 10, 20, 50$.

Notice that the dead zone length depends on the pellet geometry. In the case of cylindrical geometry, the approximate solutions presented in Fig. 2 possess smaller dead zones compared to the corresponding approximate solutions in the case of planar geometry.

Clearly, the length of dead zone increases with an increase in the reaction rate constants $k$. This corresponds to the more active catalyst. Neglecting the discretization errors, this result can be justified by Lemma 2.

## 4. Conclusions

The explicit dead-core solution formula, the specific conditions for the existence of dead-zones and the length of the dead zone are derived for the diffusion-reaction problem in the planar geometry. Numerical illustrations and validations of the dead-core solutions in the cylindrical and spherical geometries are also presented. It was confirmed that the length of the dead zone increases for the more active catalysts corresponding to the larger values of the reaction rate constant. The dead zone length also depends on the pellet geometry. The results obtained in this paper can be useful for the design of catalytic reactors. The finite element collocation schemes with a-posteriori error indicators for localizing dead zones will be published in the forthcoming works.

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