

CONDITIONS OF DEAD ZONE FORMING IN POROUS CATALYST PELLETS

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In the present work the results of the investigations on dead zone formation conditions in catalyst pellet are discussed. A new, simple method of determining the types of kinetic equations for which such a zone can appear was developed on the basis of simple mathematical transformations. It was shown that: (i) pellet geometry has no influence on necessary conditions of the origination of dead zone (ii) only driving-force term (in the sense of Langmuir-Hinshelwood-Hougen-Watson kinetic approach) decides if a dead zone is formed. A new algorithm which allows fast and precise evaluation of critical Thiele modulus Φ_{crit} (in a catalyst pellet for $\Phi > \Phi_{crit}$ the dead zone appears) was proposed and tested.

Keywords: diffusion reaction processes, diffusional limitations, critical Thiele modulus

1. INTRODUCTION

Catalytic reactions are a substantial part of chemical industry. It should be noted that both diffusion of the reactants into the catalyst pellet and the intrinsic reaction rate affect the overall rate of the process. Typical examples of the influence are as follows: methane steam reforming, hydrogenation of benzene to cyclohexane (an intermediate in production of nylon), oxidation of sulfur dioxide (sulfuric acid manufacture), and many other important petrochemical reactions (Jayaraman and Doraiswamy, 1983).

A heterogeneous catalysis is not the only field where the rate of a process is modified by diffusional mass transfer. Other examples of the mentioned processes, i.e. gasification of charcoal, biochemical reactions with enzymes or cells immobilized on porous particles, mass transfer in solid-oxide and proton exchange membrane fuel cells can be easily found in literature (Azimi and Azimi, 2015; Bar-Ziv et al., 2001; Cascaval et al., 2012; Palazzi et al., 2001; Zhang et al., 2014).

If internal diffusion is much slower than reaction rate, the concentration of a reactant inside a pellet decreases rapidly. For sufficiently strong diffusional limitations (when the Thiele modulus is large), the concentration in the pellet center can even drop down to zero – a zone without reaction (the so called “dead zone”) appears in a pellet.

Although a steady-state process of reaction and diffusion in porous catalysts was described in the 1930s (Thiele, 1939), the idea that the mentioned zone could form in catalyst center was first proposed in early

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1950s (Wheeler, 1951), and next studied more extensively by Aris and Temkin (Aris, 1975; Temkin, 1975). Except for a few articles (Fedotov et al., 1985), the ‘dead zone’ concept was completely disregarded in the next years. However, the problem has recently become the subject of further investigation (Andreev, 2013; York et al., 2011).

If a dead zone occurs, a catalyst pellet cannot be fully utilized inevitably resulting in efficiency of a catalytic process decrease. To prevent this, a chemical process should be rerun at different operation conditions (e.g. at lower temperature) or the pellet should be designed in a different way (e.g. smaller pellet radius (Thiele, 1967)).

Moreover if a dead zone occurs, the mathematical description of the process is more complicated. In this case a model with other boundary conditions must be considered. York et al. (2011) showed that using improper boundary conditions can cause large errors. The proper “dead zone” model is presented in the next section.

The task is then to predict whether or not such a zone does occur in a catalyst. Unfortunately, the conditions of dead zone formation are still not fully formulated. Depending on the type of kinetic equation a dead zone could appear (e.g. for the power-law type) or not (e.g. for the Michaelis–Menten type). The necessary conditions of a dead zone formation are present in literature for many types of kinetic equations (Andreev, 2013; Fedotov et al., 1985; York et al., 2011). Satisfying them may not be sufficient to the dead zone formation – diffusional limitations must be sufficiently large i.e. the Thiele modulus should be larger than the critical Thiele modulus Φ_{crit} (Φ_{crit} is the Thiele modulus value for which concentration in the pellet centre decreases to zero). Sufficient conditions, more interesting from a practical point of view, are available only for few simple cases: for the simplest reaction ($A \rightarrow R$) given in (Garcia-Ochoa and Romero, 1988), and for more complex cases (e.g., consecutive parallel reaction) presented by Andreev (2013). One can conclude that, in many practical cases, the sufficient conditions for dead zone formation are unavailable.

In this article, a new, simple method of specifying the necessary conditions for the dead zone formation in a catalysts pellet of the various geometries is presented. The impact of the pellet geometry and adsorption/temperature was examined. Also, in present paper a new, precise algorithm enabling evaluations of the critical Thiele modulus was proposed and tested.

2. CONDITIONS OF DEAD ZONE FORMATION

2.1. Mathematical background

The dimensionless mass-balance equation of the steady-state process of diffusion with a chemical reaction in a catalyst pellet has a form:

$$\frac{1}{x^\alpha} \frac{d}{dx} \left(x^\alpha \cdot \frac{dc}{dx} \right) = \Phi^2 \cdot R(c) \quad (1)$$

where $\Phi = \frac{R_p^2 \cdot R(C_s)}{C_s \cdot D}$ is the Thiele modulus, $R(c)$ is a dimensionless kinetic function and α is a geometry parameter ($\alpha = 0$ slab pellet, $\alpha = 1$ cylindrical pellet, $\alpha = 2$ spherical pellet). If the external mass transfer limitations can be neglected, boundary conditions could be written as follows:

a) dead zone is not formed ($\Phi \leq \Phi_{crit}$)

$$c(1) = 1 \quad (2)$$

$$\left. \frac{dc}{dx} \right|_{x=0} = 0 \quad (3)$$

b) dead zone is formed ($\Phi > \Phi_{crit}$)

$$c(1) = 1 \quad (4)$$

$$c(x_0) = 0 \quad (5)$$

$$\left. \frac{dc}{dx} \right|_{x=x_0} = 0 \quad (6)$$

where x_0 is a dead zone-end coordinate.

If the Thiele modulus Φ is equal to Φ_{crit} , then x_0 is equal to 0, and both models become the same.

If $\Phi_{crit} \rightarrow \infty$, for some kinetic functions, the dead zone does not form.

Multiplying both sides of Eq. (1) by $2 \cdot x^{2\alpha} \cdot \frac{dc}{dx}$ leads to:

$$2 \cdot x^\alpha \cdot \frac{dc}{dx} \cdot \frac{d}{dx} \left(x^\alpha \cdot \frac{dc}{dx} \right) = 2 \cdot \Phi^2 \cdot x^{2\alpha} \cdot R(c) \cdot \frac{dc}{dx} \quad (7)$$

Equation (7) can be easily transformed to:

$$\frac{d}{dx} \left[\left(x^\alpha \cdot \frac{dc}{dx} \right)^2 \right] = 2 \cdot \Phi^2 \cdot x^{2\alpha} \cdot R(c) \cdot \frac{dc}{dx} \quad (8)$$

and then:

$$d \left[\left(x^\alpha \cdot \frac{dc}{dx} \right)^2 \right] = 2 \cdot \Phi^2 \cdot x^{2\alpha} \cdot R(c) \cdot dc \quad (9)$$

The integration of Eq. (9) within the limits from x_0 to x and from 0 to c , respectively, gives:

$$\left(x^\alpha \cdot \frac{dc}{dx} \right)^2 = 2 \cdot \Phi^2 \cdot \int_0^c x^{2\alpha} \cdot R(c) dc \quad (10)$$

and then:

$$\frac{dc}{dx} = \sqrt{2} \cdot \Phi \cdot \sqrt{\frac{\int_0^c x^{2\alpha} \cdot R(c) dc}{x^{2\alpha}}} \quad (11)$$

The separation of variables in Eq. (11) and integration from x_0 to 1 and from 0 to 1, respectively, yields:

$$\sqrt{2} \cdot \Phi \cdot (1 - x_0) = \int_0^1 \frac{dc}{\sqrt{\frac{\int_0^c [x(c)]^{2\alpha} \cdot R(c) dc}{[x(c)]^{2\alpha}}}} \quad (12)$$

where $x(c)$ is the concentration profile in the implicit form.

For $x_0 = 0$ and $\Phi = \Phi_{crit}$ Eq. (12) becomes:

$$\sqrt{2} \cdot \Phi_{crit} = \int_0^1 \frac{dc}{\sqrt{\frac{\int_0^c [x_{crit}(c)]^{2\alpha} \cdot R(c) dc}{[x_{crit}(c)]^{2\alpha}}}} \quad (13)$$

where $x_{crit}(c)$ is a critical concentration profile in the implicit form. Calculating the critical Thiele modulus from Eq. (13) is not simple. For $\alpha = 1, 2$, the implicit critical concentration profile should be known. There will also appear difficulties in the analytical determination of the integrals. The analysis of Eq. (13) leads to the following conclusion: if any of the integrals in Eq. (13) is divergent, the dead zone does not appear and $\Phi_{crit} \rightarrow \infty$. Therefore, the convergence of both integrals in Eq. (13) can be regarded as a necessary condition for dead zone formation. A more detailed description of this problem for slab geometry was presented elsewhere (Król and Szukiewicz, 2013).

2.2. Necessary conditions of dead zone formation

The convergence of both integrals in Eq. (13) could be examined by a comparison test (Leja, 1976). To utilize this test, let us define:

$$I_1 = \int_0^c [x_{crit}(c)]^{2\alpha} \cdot R(c) dc \quad (14)$$

$$I_2 = \int_0^1 \frac{dc}{\sqrt{\int_0^c [x_{crit}(c)]^{2\alpha} \cdot R(c) dc}} \quad (15)$$

$$I_{1p} = \int_0^c R(c) dc \quad (16)$$

$$I_{2p} = \int_0^1 \frac{dc}{\sqrt{\int_0^c R(c) dc}} \quad (17)$$

The integrals I_1, I_2 are convergent if and only if the integrals I_{1p}, I_{2p} are convergent, respectively. The convergence of the integrals I_{1p} and I_{2p} defines the necessary conditions of dead zone formation. Thus, examining the convergence of the integrals I_1 and I_2 is therefore to examine the convergence of integrals I_{1p} and I_{2p} . Interestingly, the integrals I_{1p} and I_{2p} are identical with those studied for catalyst pellets of slab geometry (Król and Szukiewicz, 2013). It follows then that the necessary conditions of dead zone formation for all shapes of pellets are the same. The necessary conditions for the most popular kinetic functions may be received. The data are collected in Table 1 (kinetic equations are presented in dimensionless form).

The analysis of the results presented in Table 1 reveals that both thermal and adsorption terms in the kinetic equations have no influence on the necessary condition of dead zone formation. The conditions valid for isothermal power-law and Langmuir-Hinshelwood kinetics agree with the previous results published in literature (Fedotov et al., 1985; Garcia-Ochoa, 1988; York et al., 2011). It should be noted that our investigations have extended the conditions for the two-reagent reaction reported by Andreev (Andreev, 2013). The method discussed here is much simpler and more precise than that available in literature.

Table 1. Necessary conditions of dead zone formation for any pellet geometry

The dimensionless kinetic rate law		Necessary condition
Power law model	$R(c) = c^n$	$-1 < n < 1$
Monod model	$R(c) = \frac{(1+k) \cdot c}{k+c}$	dead zone does not occur
Moser model	$R(c) = \frac{(1+k) \cdot c^n}{k+c^n}$	$-1 < n < 1$
Michaelis-Menten model	$R(c) = \frac{(1+k_m) \cdot c}{k_m+c}$	dead zone does not occur
Langmuir–Hinshelwood model	$R(c) = \frac{(1+k)^m \cdot c^n}{(1+k \cdot c)^m}$	$-1 < n < 1$
Power law model for non-isothermal reaction	$R(c) = c_n \exp\left(\gamma \cdot \frac{\beta \cdot (1-c)}{1+\beta \cdot (1-c)}\right)$ $\beta = \frac{-\Delta H \cdot D \cdot c_s}{\lambda \cdot T_s}, \quad \gamma = \frac{E_a}{R_g \cdot T_s}$	$-1 < n < 1$
Power law model for non-isothermal reaction under elevated pressure	$R(c) = (c \cdot t)^n \exp\left(\gamma \cdot \frac{\beta \cdot (1-c)}{1+\beta \cdot (1-c)}\right)$ $t = 1 + \beta \cdot (1-c)$	$-1 < n < 1$
Power law model for reaction with rate dependent on concentration of two components	$v_A A + v_B B \rightarrow v_C C$ $R(c) = c_A^n \cdot c_B^m$ $R(c) = c_A^n \cdot (1 - W \cdot (1 - c_A))^m$ $W = \frac{D_A}{D_B} \cdot \frac{v_A}{v_B} \cdot \frac{C_{A,s}}{C_{B,s}}$	<ul style="list-style-type: none"> • dead zone occurs by vanishing of concentration of compound A $W < 1$ and $-1 < n < 1$ • dead zone occurs by vanishing of concentration of both compounds $W = 1$ and $-1 < n + m < 1$ • dead zone occurs by vanishing of concentration of compound B $W > 1$ and $-1 < m < 1$

2.3. Sufficient conditions of dead zone formation – method of Φ_{crit} evaluation

As noted above, the values of the critical Thiele modulus are only available for the simplest case (isothermal power-law type kinetic, non-isothermal zero order power-law type kinetic (York et al., 2011)), so it is purposeful to develop some efficient methods to calculate it for more complex cases. The following algorithm of calculations is proposed:

The multiplication of Eq. (1) by $2 \cdot \frac{dc}{dx}$ and its integration from 0 to 1 and from 0 to 1, respectively, gives us:

$$\left(\frac{dc}{dx}\right)^2 \Big|_{x=1} + 2 \cdot \alpha \cdot \int_0^1 \frac{1}{x} \cdot \left(\frac{dc}{dx}\right) dx = 2 \cdot \Phi_{crit}^2 \cdot \int_0^1 R(c) dc \quad (18)$$

and next:

$$\Phi_{crit} = \sqrt{\frac{\left(\frac{dc}{dx}\right)^2 \Big|_{x=1} + 2 \cdot \alpha \cdot \int_0^1 \frac{1}{x} \cdot \left(\frac{dc}{dx}\right) dx}{2 \cdot \int_0^1 R(c) dc}} \quad (19)$$

The calculations should be performed according to the following scheme (an example included):

1. Assume a form of function $\frac{dc}{dx} = f(x)$ ($f(x)$ could be an arbitrary function).
2. Compute parameters of function f by nonlinear optimization. Use a sum of absolute differences between the left hand and the right hand side of Eq. (1) for at least 101 points from $x = 0$ to $x = 1$ as an objective function. Calculations must be repeated until the objective function reaches a minimum value.

For each optimization step:

- a) Calculate the critical Thiele modulus Φ_{crit} from Eq. (19)
- b) Calculate a value of the objective function – use the estimated value of Φ_{crit}
3. Calculate a real value of the critical Thiele modulus Φ_{crit} by introducing the function $f(x)$ with optimal values of parameters to Eq. (19).
4. Substitute the function $f(x)$ with the optimal values of parameters and the calculated critical Thiele modulus Φ_{crit} to Eq. (1) and calculate the differences between the values of left and right hand side of Eq. (1). If the accuracy is not satisfactory, another type of function $f(x)$ (see point 1) should be assumed.

To test our algorithm, the critical Thiele modulus values for an exemplary kinetic equation (Eq. (20)) and for all pellet geometries were calculated.

For example, for kinetic equation:

$$R(c) = \frac{6 \cdot c^n}{1 + 5 \cdot c} \quad (20)$$

a proposed form of the function f is a polynomial:

$$f(x) = \sum_{i=1}^{10} A_i \cdot x^{i+1} \quad (21)$$

Selected n -parameter values satisfy the necessary condition of dead zone formation (see Table 1): $n = 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.66, 0.7, 0.75$.

Calculations were performed using CAS-type program (Maple®). The results are presented in Fig. 1. The critical Thiele modulus value Φ_{crit} increases as exponent n increases. Moreover, the calculated values of Φ_{crit} are the largest for a spherical pellet and the smallest for a slab pellet, respectively.

The accuracy of the algorithm was tested by a comparison of the results obtained with those using the numerical method presented by Szukiewicz (2016), cf. Figs. 2–4.

For all three geometries of a pellet, the values of Φ_{crit} are in good agreement. Most of the pairs of calculated points coincide in practice, and the relative differences between them are smaller than 2.5% (slab pellet), 3.2% (cylindrical pellet), and 3.6% (spherical pellet). For this reason they can be treated as negligible. The presented results prove that the algorithm proposed here is sufficiently precise. Its application is simple, especially using CAS-type programs.

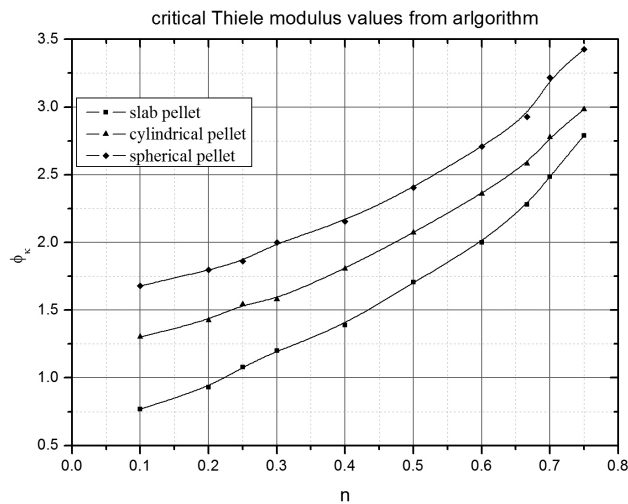


Fig. 1. Comparison of the critical Thiele modulus values for different pellet geometries and different values of exponent n

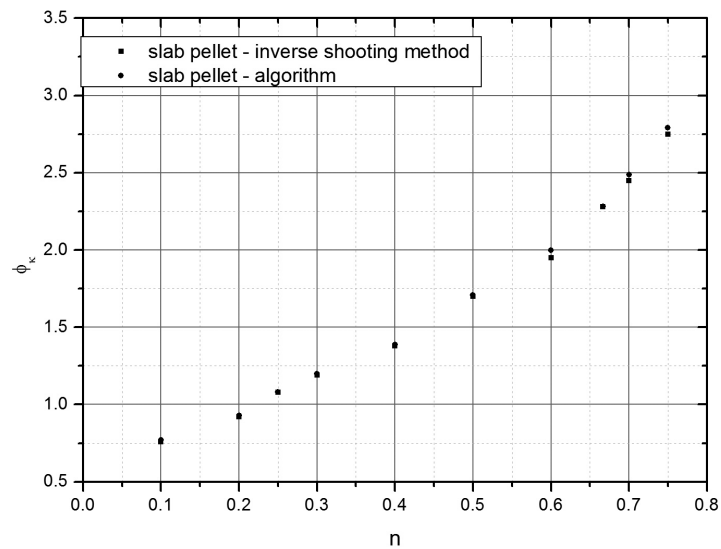


Fig. 2. Comparison of the critical Thiele modulus values for slab pellet obtained from the presented algorithm and by using inverse shooting method

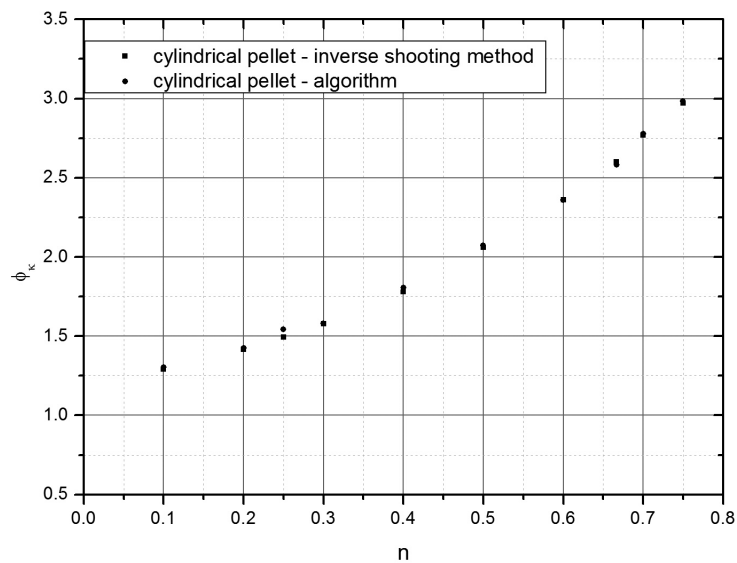


Fig. 3. Comparison of the critical Thiele modulus values for cylindrical pellet obtained from the presented algorithm and by using inverse shooting method

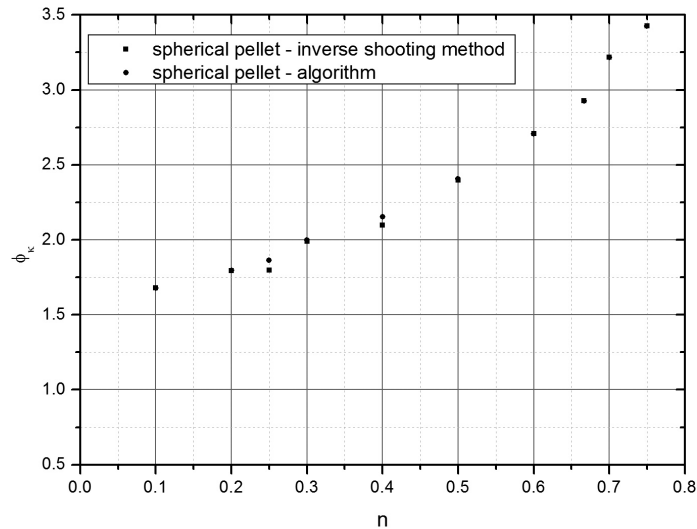


Fig. 4. Comparison of the critical Thiele modulus values for spherical pellet obtained from the presented algorithm and by using inverse shooting method

3. CONCLUSIONS

The main results of the paper can be summarized as follows:

- A method of checking if a dead zone can be formed (necessary conditions) for an arbitrary kinetic equation presented here is simpler than the methods presented so far in literature. Its application requires only elementary mathematical knowledge.
- The necessary conditions of dead zone formation for any shape of pellets are the same.
- A method of calculation of the critical value of the Thiele modulus (sufficient condition) is simple, but somewhat tedious (iterative calculations may be needed). However, its precision fully compensates for this inconvenience.
- Using CAS-type programs makes the task presented in the article much easier.

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SYMBOLS

A_i	parameters in Eq. (21)
C	concentration in a pellet, mol/m ³
$c = C/C_s$	dimensionless concentration in a pellet
D	effective diffusion coefficient, m ² /s
E_a	activation energy of reaction, J/mol
$f(x)$	approximation function for dependence of $\frac{dc}{dx}$ on x
$I_1, I_2, I_{1,p}, I_{2,p}$	integrals defined respectively by Eq. (14), (15), (16) and (17)
k	dimensionless adsorption constant
n, m	exponents in kinetic function
R_g	gas constant, J/(mol K)
R_p	pellet radius, m

$R(C)$	kinetic function
$R(c)$	dimensionless kinetic function
T	temperature in pellet, K
$t = T/T_s$	dimensionless temperature in pellet
x	dimensionless position in pellet
x_0	dimensionless position of dead zone beginning in pellet
W	dimensionless modulus (Table 1)

Greek symbols

α	geometry factor (0 – flat pellet, 1 – cylindrical pellet, 2 – spherical pellet)
β	Prater number (Table 1)
γ	Arrhenius number (Table 1)
ΔH	enthalpy of reaction, J/mol
λ	effective thermal conductivity coefficient of catalyst, W/(m K)
Φ	Thiele modulus
ν	stoichiometric coefficient

Subscripts

A, B, C	relevant specie
crit	value defined for critical diffusional limitations
s	value at the outer surface of pellet

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