Research Article

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Dead zone for hydrogenation of propylene reaction carried out on commercial catalyst pellets

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Abstract: Heterogeneous catalytic processes have for years been of crucial importance in the chemical industry, while biocatalytic processes have become more and more important. For both types of the processes the existence of zones without reactants were reported. Despite the fact that the dead zone can appear in real processes relatively often, the most important problem in practice is the real size of a dead zone inside a catalyst pellet or the real depth of penetration reagents in a biofilm and this is still unsolved. The knowledge of the parameters and some information about the process can allow improvement in yield, and selectivity, reduce consumption of catalyst by reducing the bed size etc. Presented in this work is a simple method of predicting the size of the inactive core of a uniformly activated catalyst pellet. The method is based on a simple mathematical model of catalyst pellet with inactive pellet centre and experimental investigations.

Keywords: dead zone; dead core; diffusional resistances.

1 Introduction

Heterogeneous catalytic processes have for years been of crucial importance in the chemical industry, while biocatalytic processes have become more and more important. For both types of processes the existence of zones without reactants were reported. It should be noted that we don't think about the physical defects of catalysts resulting mainly from imperfections of manufacturing or activation processes such as phase inhomogeneity, improper pellet making, passivation of active sites,

shapes or sizes distributions, improper porosity etc. We are interested in regions of catalysts or biofilms without reactants that arise spontaneously as a result of a fast reaction run, despite the fact that in this area the catalyst is active. Lack of substrata in the zone lessens reactor or bioreactor productivity and influences the process economy. The phenomenon describing this is especially important now, when a lot of institutes work on producing more active and more selective catalysts (e.g. obtained by promotion). On the large scale, formation of zones without reactants can reduce or even destroy effects obtained in the laboratory. Furthermore, the reaction process can be so fast that the reaction only really takes place in the narrow, surface part of the catalyst pellet. In such a case it makes no sense to produce catalysts with active materials placed in non-productive core part of the pellet. For this reason it is especially important to develop methods and tools of the phenomenon analysis.

For heterogeneous catalysis the zone without reactants is called the "dead zone" and it was predicted by Aris [1] and Temkin [2]. While for bio-processes a few terms concerning this phenomena are found e.g. "biological dead zone", "enzymatic inactive region" all mentioned terms are used to describe region where diffusional resistances are sufficiently large and in catalyst appears the zone where reaction rate is equal to zero. The essence of the dead zone concept is presented in Figure 1.

If internal diffusional resistances are small (small Thiele modulus value) concentration of the reagent drops down towards pellet center but it is always larger than zero (solid line in Figure 1). The larger the internal diffusional resistances the smaller the value of substrata concentration in the pellet center and, finally, for critical Thiele modulus value, reagent concentration drops down to zero (dashed line in Figure 1). For larger resistances in the pellet center the zone without reactant the dead zone is formed (dotted line in Figure 1).

It should be noted that solution for the mathematical model of dead zone problem is a harder task than the regular model (model without dead zone, commonly applied and discussed in literature). From a mathematical

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Figure 1: Concentration profiles in catalyst.

point of view the regular model is typical boundary value problem while the dead zone model belongs to the free boundary value problems. More details concerning dead zone model will be presented in **Methods** section.

Previous investigations focused on the theoretical aspects of the dead zone model, for instance mathematical consideration on the existence of free boundary problems for chemical reactions, Diaz and Hernandez [3] or existence and formation of dead core, Bandle and Stackgold [4]. Next Bobisud [5] applied singular perturbation analysis for dead core behavior and Bobisud and Royalty [6] studied formation of dead zone for some diffusion-reaction equations (the generation term could be simplified to Langmuir-Hinshelwood or Michaelis-Menten kinetics). In the 1980s some works were published concerning more practical aspects, e.g. Fedotov et al. [7] investigated the conditions which have to be satisfied for dead zone formation for selected kinetic equations (so-called necessary conditions of dead zone formation) and Garcia Ochoa and Romero [8] presented both necessary and sufficient conditions of dead zone formation for the simplest kinetic equation (power law equation for one-component isothermal reaction). Similar points was raised by Andreev [9] in more recent work. Of course, the dead zone can also be detected in real processes. For instance for methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst (reported by Lee et al. [10]), for hydrogenation of benzene over nickel-alumina catalyst [11], or for acetic acid oxidation [12,13].

For biotechnology the dead zone was reported for limitation created by oxygen diffusion into gel beads for cephalosporin C production processes [14,15], for the process of Penicillin G enzymatic hydrolysis to

6-Aminopenicillanic acid [16] or the process of 3-chloro-1,2-propanediol degradation by Ca-alginate immobilized *Pseudomonas putida* cells [17]. Regions with negligible mass transfer flux in an anaerobic fixed-bed reactor were founded by Zaiat et al. [18] and Pereira and Oliveira [19] analyzed the occurrence of dead core in catalytic particles containing immobilized enzymes for the Michaelis-Menten kinetics.

Despite the dead zone can appearing in real processes relatively often, the most important problem in practice is the real size of a dead zone inside a catalyst pellet or the real depth of penetration reagents in a biofilm and this has not been reported. To our best knowledge, the general method of prediction of these parameters have not been published. The knowledge of the parameters and some information about the process can allow improved yield, selectivity and reduce the consumption of catalyst and reduce the bed size etc.

Advances in computing hardware and algorithms have dramatically improved the ability to simulate complex processes. Presented in the work is a simple evaluation method for estimating size of inactive core of uniformly activated catalyst pellet. The method is based on a mathematical model of catalyst pellet with inactive core and experimental investigations.

2 Methods

The aim of this work is the development of an evaluation method for dead zone size estimate. To do this the following two conditions should be met:

1. A reference reaction that promises formation of dead zone inside the catalyst pellet as well as catalyst itself should be chosen. As a reference reaction for investigation of the dead zone problem we choose propylene hydrogenation reaction. The reaction is easy to carry out and proceeds under mild conditions. As the catalyzer the commercial catalyst produced by New Chemical Syntheses Institute, Catalyst Department, Puławy, Poland was chosen. The physico-chemical properties of substrates and properties of catalyst indicate that the reaction should run very fast and diffusional limitations should be sufficiently large to produce dead zone.
2. Next, a model of sufficient precision for description of the process should be chosen. If reaction zone is narrow, heat generation in the pellet is not very intensive and temperature inside a pellet and in fluid bulk should be almost the same. So, the process

Table 1: Reactor operating conditions.

	Step 1	Step 2
Pressure, Pa	1.2×10^5	1.2×10^5
hydrogen flow rate, $\text{cm}^3 \text{min}^{-1}$	30	30
temperature of the catalyst bed, $^{\circ}\text{C}$	45-85	50-80
propylene flow rate, $\text{cm}^3 \text{min}^{-1}$	3.33 to 7.5	4.0 to 6.6

can be regarded as isothermal. On other hand the mass transfer resistances from bulk phase into catalyst cannot be neglected. In the following it was assumed that the process can be described by the simple isothermal mass transfer model coupled with chemical reaction, taking into account mass transfer resistance.

3 Experiment

The propene hydrogenation reaction was carried out in tubular reactor (Microactivity-Efficient Unit, manufacturer: Process Integral Development Eng&tech, Madrid, Spain) on heterogeneous nickel catalyst (type of KUB-3, manufacturer: New Chemical Syntheses Institute, Catalyst Department, Puławy, Poland). Nickel catalyst was activated in accordance with the manufacturer's instructions. Post reaction mixtures were analysed with gas chromatograph (CALIDUS™ 101 Gas Chromatograph, manufacturer: Falcon Analytical, Lewisburg, WV, USA).

The system was flushed for 30 minutes with a constant flow of hydrogen until a stable right temperature and pressure were obtained. Next, flow of propylene was started. Reaction was carried out for circa 1hr until the stable temperature inside the tubular reactor was reached. The relatively long time was taken to ensure that the steady-state conditions were reached. Next the reaction mixture was analyzed.

Investigations were made in two steps

1. preliminary step, reaction had run on well-crushed catalyst pellet (crushed pellet size was about 40 micrometers)
2. main investigations, reaction had run on spherical catalyst pellet (pellet diameter was about 4.6 mm)

Operating conditions are presented in Table 1. As usually the conditions Step 1 encompass the conditions where model is verified.

4 Mathematical model

Mass balance:

$$\frac{D_e}{RT} \left(\frac{d^2 p_p}{dr^2} + \frac{2}{r} \frac{dp_p}{dr} \right) - r_p = 0 \quad (1)$$

BC:

$$\left. \frac{dp_p}{dr} \right|_{r=R_{dz}} = 0 \text{ and } p_p|_{r=R_{dz}} = 0 \quad (2)$$

$$-\left. \frac{dp_p}{dr} \right|_{r=R_z} = \frac{k_g}{D_e} (p_{p,b} - p_{p,s}) \quad (3)$$

If $\frac{k_g}{D_e} \rightarrow \infty$ eq.(5) becomes

$$p_p|_{r=R_z} = p_{p,s} \quad (3a)$$

where R_{dz} is a radius of inactive core of catalyst pellet.

A comment is required for equation (2). Generally in the literature it is assumed that the derivative of unknown function in the centre of the pellet is equal to zero. It is a simplification which can follow to unphysical solution when concentration in the particle drops to zero at position $0 < r < R_z$. In the general case the correct condition is that which requires the specification in which point the derivative becomes zero (this position is unknown and has to be established in the calculations). It should be noted that conditions (2) cannot be treated as two independent conditions. So the general rule that for second order derivative two boundary conditions should be implemented is fulfilled in this case by Eq.(2) and Eq.(3) or Eq.(3a). This is similar to condition (3) in which there are two unknown parameters namely derivative and the concentration on the pellet surface and they should be calculated simultaneously.

In the following boundary conditions (2) and (3) were applied.

The foundations of engineering mathematics of the diffusion and reaction processes were presented by Aris [1]. The model presented corresponds to the Aris' model for description of dead zone problem. Moreover, the kinetic equation r_p should meet necessary conditions of dead zone formation presented e.g. by Andreev [9]. Presented below Eq.(5) met them.

The model presented is an example of a free boundary problem. In chemical engineering, the most recognizable

problem of this type is the Stefan problem in which a phase boundary can move with time. Solution of the free boundary value problem needs special numerical algorithms. In the present work the method presented by Szukiewicz [20] is used.

Ethical approval: The conducted research is not related to either human or animal use.

5 Results

Kinetic equation of the process was determined on the basis of results obtained in the first step (diffusion limitation was eliminated due to very small size of crushed catalyst). We choose power-law type of kinetic equation:

$$r_p = k_\infty p_p^n e^{\frac{-E}{RT}} \quad [\text{mol}/(\text{m}^3 \text{ s})] \quad (4)$$

Frequency factor, reaction order and activation energy were estimated using Excel, applying multiple linear regression (Equation (4) was previously linearized). The kinetic parameters have high correlation ($R^2=0.963$), the standard error of the regression is equal to 0.063. Values of parameters are presented in Table 2.

For further consideration the following equation was accepted

$$r_p = 44400 p_p^{0.5} e^{\frac{-26500}{RT}} \quad [\text{mol}/(\text{m}^3 \text{ s})] \quad (5)$$

6 Discussion

Before the main investigation were started we had confirmed a assumption about quasi isothermal process conditions. Namely, for inlet propylene concentrations less than 18% vol. and reactor oven temperature less than 85°C the gas temperature increase between reactor inlet and outlet was less than one degree, what justify assumption of quasi isothermal process conditions.

The obtained kinetic equation (5) met necessary condition for appearance of dead zone [9] namely the value of power is inside the range (-1,1). It suggests that appearing of dead zone is very likely for operating conditions presented in Table 1.

To realize the aim of the work, at first it must be concerned with how closely the model reflects the system definition - the domain of applicability for this model should be specified. If the model approximates real processes with sufficient precision then its solution

Table 2: Kinetic parameters.

k_∞ , mol m ⁻³ Pa ⁻ⁿ s ⁻¹	44467±2222
n , -	0.51±0.036
E , J mol ⁻¹	-26513±986

Figure 2: Mathematical model validation. In the region between dashed lines the model fulfills the required accuracy.

determines both the location of dead zone and model applicability region. Then, if calculated and experimental values of effectiveness factor defined by

$$\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions}} \quad (6)$$

are the same (an error is within the specified tolerance), the dead zone with the radius equal to R_{dz} is present inside the pellet.

The results of validation of the model eq.(1)-(3), are presented in Figure 2. Necessary external mass transfer coefficients, were calculated from well-known, recommended in Perry's handbook [21] equation

$$Sh = 0.33 Re^{0.6} Sc^{0.33} \quad (7)$$

It is easy to observe, that inside the operation condition range the proposed model describes the real process very well. Calculated from the model effectiveness factor values varies from experimental ones no more than 10% for 61 of 71 measurements. Selected results of the experiments and computations are presented in details in Table 3. Actual overall reaction rates presented in Table 3 results from experiment. The reference reaction rate that would result if entire interior surface were exposed to the bulk conditions was calculated from Eq.(5) using data presented in Table 1 and Table 3.

Table 3: Model validation and relative volume of dead zone.

No	T	y_p	$r_{p,av,exp}$	D_e	k_g	h_{calc}	h_{exp}	relative radius of dead zone	relative volume of dead zone
	K	—	$\text{mol s}^{-1}\text{m}^{-3}$	m^2s^{-1}	m s^{-1}	—	—	%	%
1	322.3	0.18	18.20	7.30×10^{-8}	2.62×10^{-2}	0.0610	0.0589	93.7	82.4
2	321.4	0.16	17.32	7.30×10^{-8}	2.39×10^{-2}	0.0600	0.0614	93.8	82.6
3	322.6	0.16	17.34	7.30×10^{-8}	2.38×10^{-2}	0.0588	0.0593	94.0	83.0
4	328.3	0.18	21.29	8.16×10^{-8}	2.63×10^{-2}	0.0582	0.0579	94.0	83.1
5	328.5	0.16	20.29	8.16×10^{-8}	2.39×10^{-2}	0.0562	0.0585	94.2	83.7
6	328.4	0.16	18.84	8.16×10^{-8}	2.40×10^{-2}	0.0563	0.0545	94.2	83.7
7	332.2	0.18	22.65	1.01×10^{-7}	2.66×10^{-2}	0.0606	0.0553	93.8	82.5
8	332.7	0.16	22.17	1.01×10^{-7}	2.42×10^{-2}	0.0582	0.0570	94.0	83.1
9	332.4	0.14	20.82	1.01×10^{-7}	2.19×10^{-2}	0.0564	0.0582	94.2	83.7
10	338.1	0.16	26.02	1.27×10^{-7}	2.44×10^{-2}	0.0596	0.0581	93.9	82.7
11	338.2	0.16	25.74	1.27×10^{-7}	2.44×10^{-2}	0.0595	0.0573	93.9	82.8
12	338	0.14	24.27	1.27×10^{-7}	2.20×10^{-2}	0.0575	0.0586	94.1	83.3
13	342.8	0.16	30.00	1.63×10^{-7}	2.46×10^{-2}	0.0624	0.0597	93.6	82.0
14	343	0.16	30.41	1.63×10^{-7}	2.46×10^{-2}	0.0622	0.0602	93.6	82.0
15	343.1	0.14	28.63	1.63×10^{-7}	2.22×10^{-2}	0.0598	0.0611	93.9	82.7
16	348	0.16	33.75	1.99×10^{-7}	2.48×10^{-2}	0.0634	0.0592	93.5	81.7
17	348.1	0.14	31.80	1.99×10^{-7}	2.24×10^{-2}	0.0608	0.0603	93.8	82.4
18	347.9	0.12	29.45	1.99×10^{-7}	2.01×10^{-2}	0.0583	0.0616	94.0	83.1
19	352.7	0.12	34.11	2.54×10^{-7}	2.02×10^{-2}	0.0607	0.0645	93.8	82.4
20	352.9	0.14	35.98	2.54×10^{-7}	2.26×10^{-2}	0.0635	0.0615	93.5	81.7
21	353.1	0.16	38.25	2.54×10^{-7}	2.50×10^{-2}	0.0659	0.0599	93.2	81.0

The very good precision of the model presented in entire range of tested reactor operation conditions follows that the model is applicable in the specified range and predicted sizes of dead zone are trustworthy. The estimated R_{dz} -values are approximately equal to 2.15 mm. It shows that most of catalyst pellet is inactive – reaction runs in the surface shell of the pellet only and circa 80-83% of the pellet volume remains inactive. This is despite the fact that the catalyst pellet was fully active – active places are uniformly distributed in manufacturing process. The only reason for the described situation remains diffusional resistance inside the pellet. Advice for catalyst manufacturing can be proposed to place active material in the outer part of catalyst pellet. Application of so-called “core-shell” type of catalyst should improve yield of reaction and reduce the consumption of an active material.

The results obtained confirm that the choice of reaction and the mathematical model for description of experiment was correct. Inside the pellet exists dead zone. It should be noted that if the regular model (with typical boundary conditions) would be used instead of presented one, the obtained result of simulations would have no physical sense.

7 Conclusions

On the basis of investigations performed the following conclusions can be drawn:

1. The method of estimation of dead zone location is relatively simple, it is able to detect a size of dead zone. It has no limits in their applicability. Only selection of the mathematical model to describe

chemical or biochemical process can be a bit more confused in specific cases because of unclassical boundary condition.

2. The method is universal and it is applicable in more complex cases (e.g. non-isothermal processes or for complex reaction systems). In that case successful result of estimation depends on application of correct mathematical model.
3. The dead zone covers more than 80% of catalyst pellet for propylene hydrogenation (and in consequence 80% of reactor volume). It follows that reaction runs in surface shell of catalyst only. This situation is not optimal and reaction yield can be improved by application of non-uniformly activated catalyst, namely of “core-shell” type.

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Nomenclature

D_e – effective diffusivity ($\text{m}^2 \text{s}^{-1}$)

p_i – partial pressure of a compound (Pa)

P – total pressure

r – distance from the center to a given position in a catalyst pellet (m)

R_g – gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)

r_p – reaction rate in reference to propylene ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$)

R_{dz} – dead zone radius (m)

R_z – pellet radius (m)

T – bulk temperature of gas mixture (K)

x – dimensionless distance from the center to a given position in catalyst pellet, $x=r/R$

y_i – molar fraction of a compound

Greek symbols

η - effectiveness factor

Φ - Thiele modulus

Subscripts

p - propylene

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