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ESTIMATION OF THE KINETIC PARAMETERS FOR H_2O_2 ENZYMATIC DECOMPOSITION AND FOR CATALASE DEACTIVATION

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Abstract - Catalase is a potentially useful biocatalyst in various industrial bioprocesses (textile industry, food processing, and pulp and paper) that require removal of hydrogen peroxide. This process can be achieved in such reactors even under isothermal conditions. However, it is usually connected with a long duration of the process or with spending a considerable amount of biocatalyst for a unit mass of the transformed substrate, which in turn leads to an increase in operating costs. They can be limited by applying the optimal temperature control, which requires the values of the thermodynamic parameters -the activation energy for reaction and the activation energy for deactivation must be known. This work reports these parameters for hydrogen peroxide decomposition and *Aspergillus niger* catalase deactivation at temperatures ranging from 35°C to 50°C.

Keywords: Aspergillus niger catalase; Deactivation; The activation energy for deactivation.

INTRODUCTION

Catalase (EC 1.11.1.6) decomposes hydrogen peroxide to water and oxygen

$$2H_2O_2 \xrightarrow{catalase} O_2 + H_2O \qquad (1)$$

The catalytic reaction takes place in two steps. The first hydrogen peroxide molecule oxidizes the heme to an oxyferryl species in which one oxidation equivalent is removed from the iron and one from the porphyrin ring to generate a porphyrin cation radical (reaction 2a). The second hydrogen peroxide is then used as a reagent with compound I - *Enz(Por$^{+\bullet}$- Fe^{IV}= 0)* to regenerate the resting state enzyme, water, and oxygen - reaction 2b (Switala and Loewen, 2002).

$$Enz(Por - Fe^{III}) + H_2O_2 \rightarrow H_2O + Enz(Por^{+\bullet} - Fe^{IV} = 0) \qquad (2a)$$

$$Enz(Por^{+\bullet} - Fe^{IV} = 0) + H_2O_2 \rightarrow H_2O + O_2 + Enz(Por - Fe^{III}) \qquad (2b)$$

Industrial applications for catalase include removal of hydrogen peroxide after cold sterilization steps in food processing (Farkye, 2004; Lee, 2004; Tarhan, 1995). Catalase has also been used in the manufacturing of semi-conductors (Akyilmaz and Kozgus, 2009; Liu *et al.* 2016) and in the textile industry (Arabaci and Usluoglu, 2013; Costa *et al.* 2002). Moreover, catalase is indispensable for carrying out biotransformation processes with the use of oxidases to cause decomposition of hydrogen

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peroxide being formed in the reaction (Ene and Maria, 2012; Maria *et al.* 2012).

Deactivation of catalase by the substrate is a significant limitation for any broader use of catalase. Previous attempts to stabilize *Aspergillus niger* catalase by immobilization have not been successful enough as yet (Grigoras, 2017; Hooda, 2014; Miłek *et al.* 2011; Yoshimoto *et al.* 2005).

In the present study the deactivation of catalase by hydrogen peroxide was examined. It is not possible to analyze catalase deactivation by hydrogen peroxide decomposition in a batch reactor without knowing the enzymatic reaction kinetics. Catalase from *Aspergillus niger* appears to show the dependence of reaction rate ν_R on concentration C_S observed for the Michaelis-Menten equation:

$$v_R = \frac{v_{\max} c_s}{k_m + c_s} \tag{3}$$

where: $V_{max} = k_R C_E$ is the maximum reaction rate, K_m is the apparent Michaelis-Menten constant. K_m values, as determined for catalase from *Aspergillus niger*, are in the range 0.322-0.465 mol/L (Lardinois *et al.* 1996; Switala and Loewen, 2002). Hence, for typical applications of catalase in decomposition of residual hydrogen peroxide, for which the concentration is lower than 0.02 mol/L (Arvin and Pedersen, 2015; Herdt, 2012; Ghadermarzi and Moosavi-Movahedi, 1996) Eqn (3) is simplified and assumes the following form:

$$v_R = k_R C_E C_S \tag{4}$$

where k_R is the reaction rate constant, L/(mol·h).

When conducting the study of decomposition kinetics of hydrogen peroxide by catalase we need to take into account the phenomenon of deactivation. Georg (1947) was the first to propose the following experimental kinetic equation which describes the catalase deactivation rate ν_D:

$$v_D = C_E\left(\frac{aC_S}{b + C_S} + cC_S\right) \tag{5}$$

where *a, b,* and *c* are experimental constants.

The above equation for hydrogen peroxide concentrations $C_S << b$ is simplified to obtain a first order reaction with respect to the substrate and the enzyme concentrations:

$$v_D = k_D C_E C_S \tag{6}$$

where k_D is the deactivation rate constant, L/(mol·h).

The value of the *b* constant, as established by Georg (1947) for catalase from erythrocytes, was 0.15 mol/L, which means that, for substrate concentrations below 0.015 mol/L Eqn (5) can be well approximated Eqn (6). This kinetic equation of deactivation was used a number of times in studies on immobilized catalase of either animal or microbiological origin (DeLuca *et al.*, 1995; Herdt, 2012; Miłek and Wójcik, 2011; Tarhan, 1995; Tse and Gough, 1987, Vasudevan and Weiland, 1990).

Vasudevan and Weiland (1990) studied deactivation of catalase from beef liver and from *Aspergillus niger* by hydrogen peroxide. Experiments were conducted in a continous stirred tank reactor (CSTR) at a temperature of 25ºC and initial concentration of hydrogen peroxide in the range from 0.05 to 1 mol/L.

DeLuca *et al.* (1995) studied deactivation of native catalase from beef liver and from *Aspergillus niger*. They used Eqn (6) for analysing hydrogen peroxide decomposition at a temperature of 25ºC and at hydrogen peroxide initial concentration 0.02 mol/L. The reaction rate constant for deactivation of catalase from *Aspergillus niger* k_D equals 0.00851 L/(mol·s), 17 times lower than that for beef catalase.

Lardinois et al. (1996) also confirmed that the deactivation of catalase from *Aspergillus niger* proceeded according to Eqn (6). Agreement of experimental data with this kinetic equation was obtained for a very wide range of hydrogen peroxide concentrations (0.01- 2 mol/L) but at the temperature of 25ºC.

The effect of the deactivation of *Aspergillus niger* catalase by hydrogen peroxide in a wider range of temperatures has not been shown in the literature yet. The present studies were conducted with the concentration of hydrogen peroxide lower than 0.015 mol/L at temperatures ranging from 35ºC to 50ºC. The obtained parameters for deactivation of *Aspergillus niger* catalase by hydrogen peroxide can be used in modeling and optimization of batch bioreactors (Grubecki, 2016; Vasić-Rački *et al.*, 2011).

MATERIALS AND METHODS

Reagents

Catalase (E.C. 1.11.1.6) from *Aspergillus niger* was purchased from Sigma-Aldrich (No. catalog C3515). Perhydrol (30% hydrogen peroxide) was procured from POCH, Poland. All other chemicals used were of analytical quality.

Reaction study procedure

Assay of the rate reaction for the decomposition hydrogen peroxide was measured at the temperatures 20°C, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C. In the spectrophotometer tank (isothermal batch reactor) was placed 2 mL of hydrogen peroxide of concentration 0.015 mol/L, pH 6.9, and catalase added (30 U/mL). The mixture was gently homogenized and incubated at the reaction temperature for 1 min. Catalase activity was monitored by observing the rate of decomposition of hydrogen peroxide using a spectrophotometer UV - VIS JASCO V -530. Absorbance of H_2O_2 was measured at a wavelength of 240 nm (Bayramoglu *et al.*, 2016). From the change of the concentration of hydrogen peroxide in the time from 0 s to 15 s, which has a linear relationship, the values of reaction rate constant were determined.

Deactivation study procedure

Assay of the rate of deactivation catalase by hydrogen peroxide was measured at the temperatures 35°C, 40°C, 45°C and 50°C, respectively. The reaction was carried out in Erlenmeyer flasks (250 mL) in a water bath shaker (250 rpm). Reaction volume was 200 ml hydrogen peroxide at an initial concentration of 0.015 mol/L and pH 6.9 and different amounts of catalase were used (2.5 U/mL or 5.0 U/mL).

All the deactivation experiments were pre-incubated (1.5 h) in the water bath shaker to set the reaction conditions. Samples of the reaction solution were taken out at intervals of 20 minutes and the conversion of hydrogen peroxide by catalase was measured spectrophotometrically. Deactivation rate constants k_D were determined on the basis of the conversion of hydrogen peroxide at an initial concentration of 0.015 mol/L and pH 6.9 at temperatures of 35ºC, 40ºC, 45ºC and 50ºC.

Kinetic model

Based on an analysis that was conducted in the theoretical part it was assumed that a kinetic equation for the reaction (Eqn 4) and a kinetic equation for deactivation (Eqn 6) may be applied for the description of hydrogen peroxide decomposition at an initial concentration of 0.015 mol/L. The mass balance for the substrate and active catalase in an isothermal batch reactor leads to a system of two ordinary differential equations:

$$\frac{dC_S}{dt} = -k_R C_E C_S \tag{7}$$

$$\frac{dC_E}{dt} = -k_D C_E C_S \tag{8}$$

Initial conditions were defined as follows:
$C_S\ (t = 0) = C_{S_0}$ and $C_E\ (t = 0) = C_{E_0}$.
When the dimensionless activity of catalase is $a = C_E / C_{E0}$ then Eqs (7) and (8) become:

$$\frac{dC_S}{dt} = -k_R^* a C_S \tag{9}$$

$$\frac{da}{dt} = -k_D a C_S \tag{10}$$

where: $k_R^* = C_{E0} k_R$, initial conditions $C_S\ (t = 0) = C_{S0}$ and $a\ (t = 0) = 1$

Further, it is convenient to introduce the fractional conversion $X = (C_{S0} - C_S)/C_{S0}$ and the system of eqs. (9)-(10) can be written:

$$\frac{dX}{dt} = k_R^* a (1 - X) \tag{11}$$

$$\frac{da}{dt} = -k_D a C_{S0} (1 - X) \tag{12}$$

with initial conditions: $X(t = 0)=0$ and $a\ (t = 0)=1$.

Dividing eq. (11) by (12) and using $a(t=0)=1$ and $X(t=0)=0$ for a reaction that proceeds in a batch reactor, it defines the relationship between activity and conversion

$$a(X) = 1 - \frac{k_D}{k_R^*} C_{S_0} X \tag{13}$$

where $k_R^* = k_R C_{E_0}$.

A change in the conversion with time, t, is described by the following relationships:

$$X = \frac{1 - \exp[(k_R^* - k_D \cdot C_{S_0})t]}{C_{S_0}\frac{k_D}{k_R^*} - \exp[(k_R^* - k_D \cdot C_{S_0})t]} \qquad for\ k_D C_{S_0} \neq k_R^* \tag{14a}$$

$$X = 1 - \frac{1}{(k_R^* \cdot t + 1)} \qquad for\ k_D C_{S_0} = k_R^* \tag{14b}$$

Preliminary analysis of the experimental data showed that the reaction rate constant k_R^* and deactivation rate constant k_D in Equations (14a) and (14b) are strongly correlated and the reaction rate constant k_R^* changes much less with changes in temperature than do the rate constants for typical enzymatic reactions. Therefore, independent spectrophotometric measurements of the rates of hydrogen peroxide decomposition for reaction times below 1 minute were made, using many times as high catalase concentrations. Such conditions enable enzyme deactivation by the substrate to be practically eliminated. The reaction rate constant k_R^* at the initial

concentration of hydrogen peroxide of 0.015 mol/L and in the temperature range from 20°C to 50°C and changed every 5°C, was thus established.

For known values of k_R^* , based on Equation (14a) the values of k_D were found using nonlinear regression with the Levenberg-Marquardt procedure (Freitas *et al.* 2012; Frutiger *et al.* 2016). It is a standard technique used to solve nonlinear equation by the least squares method and is the most popular alternative to the Gauss-Newton method of finding the minimum of the sum of the squares. If experimental values are expected to vary along the curve, then the points should be weighted differentially. The most often used weighting method is called "weighting by $1/y^2$" and in this case it is described as follows:

$$SEE(k_D) = \sum_{i=0}^{n} \frac{1}{(X_{emp})_i^2}\left((X_{\exp})_i - X_{cal}(k_D, t_i)\right)^2 \quad (15)$$

where $(X_{\exp})_i$ is the conversion of hydrogen peroxide by *Aspergillus niger* catalase determined experimentally; $X_{cal}(k_D, t_i)$ is the conversion of hydrogen peroxide by *Aspergillus niger* catalase calculated by Eqn (14a).

Eqn (15) allows one to find the objective function with a given set of parameters. The obtained values of the parameters were calculated using nonlinear regression with SigmaPlot 12.3.

RESULTS AND DISCUSSION

The present study shows the effect of temperature on the process of hydrogen peroxide decomposition by catalase from *Aspergillus niger* to complete limited information on the subject in the literature. Tse and Gough (1987) and also DeLuca *et al.* (1995) analyzed hydrogen peroxide decomposition by *Aspergillus niger* catalase at the temperatures of 25ºC and 37ºC, respectively. However, the researchers did not report data for higher temperatures of the process, which are commonly used in industry.

On the basis of this study, the reaction rate constants k_R^* were determined for temperatures 20ºC, 25ºC, 30ºC, 35ºC, 40ºC, 45ºC and 50ºC. The rate of decomposition of 0.015 mol/L hydrogen peroxide was measured during 15 seconds. The dependence between the k_R^* constant and temperature was in agreement with the Arrhenius equation and this dependence is presented in Figure 1.

The value obtained for the activation energy for the reaction, E_a, equals 12.9±0.7 kJ/mol. This value is similar to the activation energy for decomposition of hydrogen peroxide by catalase, found earlier for catalase Terminox Ultra (Miłek and Wójcik, 2011). The activation energy was a little lower than that

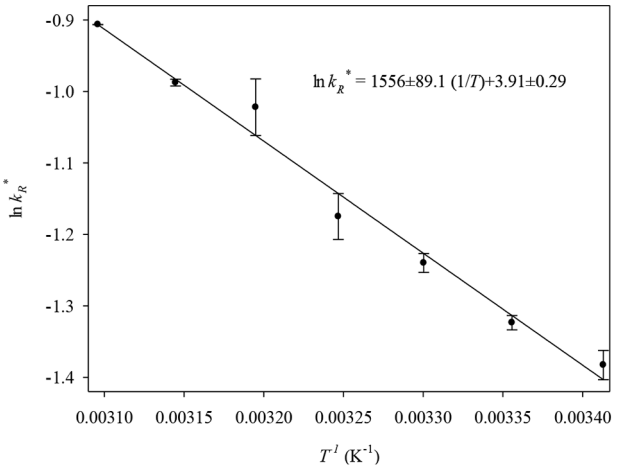

Figure 1. Arrhenius plot for decomposition 0.015 mol/L hydrogen peroxide by *Aspergillus niger* catalase (30 U/mL).

reported in the literature (19.7 kJ/mol) by Altamore (1974). Hooda (2014) reported that the value of the activation energy for decomposition of hydrogen peroxide equals 23.5 kJ/mol. However, the value of E_a was also evaluated from an Arrhenius plot by plotting the inverse of temperature vs. the log of enzyme activity. The temperature of the reaction mixture was varied from 15°C to 75°C and, above the temperature of 35°C, the deactivation of catalase influenced the value of the activation energy E_a .

On the basis of the deactivation study, the deactivation rate constants k_D were determined for temperatures of 35°C, 40°C, 45°C and 50°C. The rate of the decomposition of 0.015 mol/L hydrogen peroxide was measured during 1.5 h. Measurement of the hydrogen peroxide decomposition was carried out at a temperature higher than 35°C because, as shown in previous work (Miłek and Wójcik, 2011), catalase was deactivated above this temperature.

Figure 2 shows a comparison between experimental data (40ºC) and those calculated from Eqn (14a) using two quantities of the enzyme. Good agreement between the experimental and the calculated data is observed. Data shown in Fig. 2 confirm that, at the temperature of 40ºC, an increase in the conversion to 0.95 is impossible using 5.0 U/mL catalase during 1.5 h of hydrogen peroxide decomposition.

Rate constants for deactivation of catalase, k_D, were determined for the entire studied range of temperature (35-50ºC), using nonlinear regression with the Levenberg-Marquardt optimization procedure. The obtained k_D values have been collected in Table 1. Comparison between calculated conversion and experimental conversion for all temperatures in the range from 35°C to 50°C was made and the standard errors of estimate *SSE* were lower than 0.07.

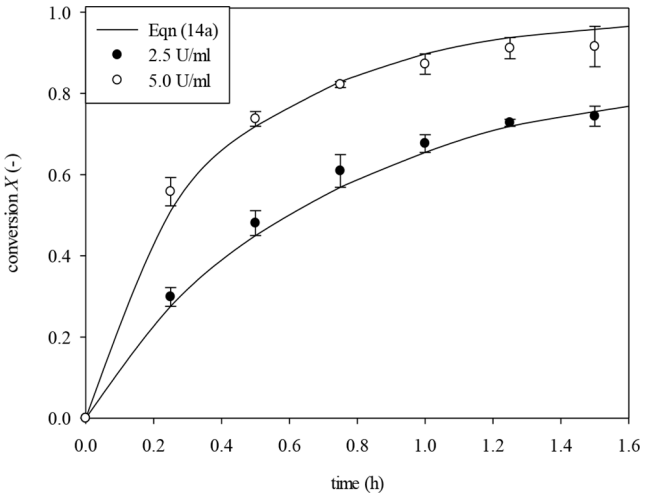

Figure 2. Dependence of the conversion on time for 0.015 mol/L hydrogen peroxide decomposition at 40ºC by catalase 2.5 U/mL (●); 5.0 U/mL (○).

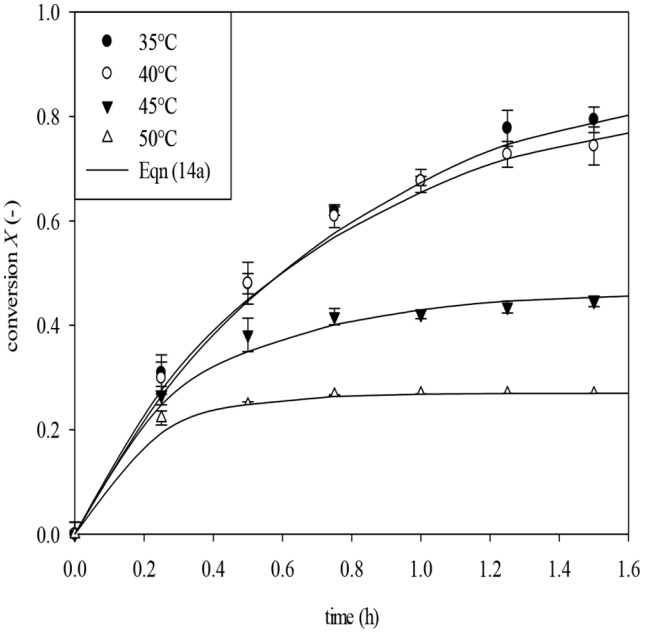

Figure 3. Effect of temperature on the rate of conversion for 2.5 U/mL catalase during the decomposition of 0.015 mol/L hydrogen peroxide.

The increase in temperature caused an increase in the value of the rate constant for deactivation k_D. This value almost doubled at 40°C compared to the value obtained for the temperature 35°C. For the decomposition of hydrogen peroxide at 45°C, the value of k_D was four times higher than the value k_D obtained for the temperature 40°C.

The Pearson correlation coefficient r for the obtained parameters was higher than 0.994 and the determination coefficient (correlation coefficient squared, r^2) was higher than 0.988. Figure 3 shows a comparison between experimental conversions and those found with the use of the deactivation constants given in Table 1. All the data relate to the same quantity of catalase (2.5 U/mL), which enables their direct comparison.

The first order model is able to fit adequately all the kinetic data at all the temperatures. The enzyme is totally deactivated at the end of the reaction at 50ºC. Figure 4 shows the comparison of the experimental conversion data with the calculated conversion for temperatures ranging from 35ºC to 50°C by catalase from *Aspergillus niger*.

Data in Table 1 were used for making the Arrhenius plot (Figure 5).

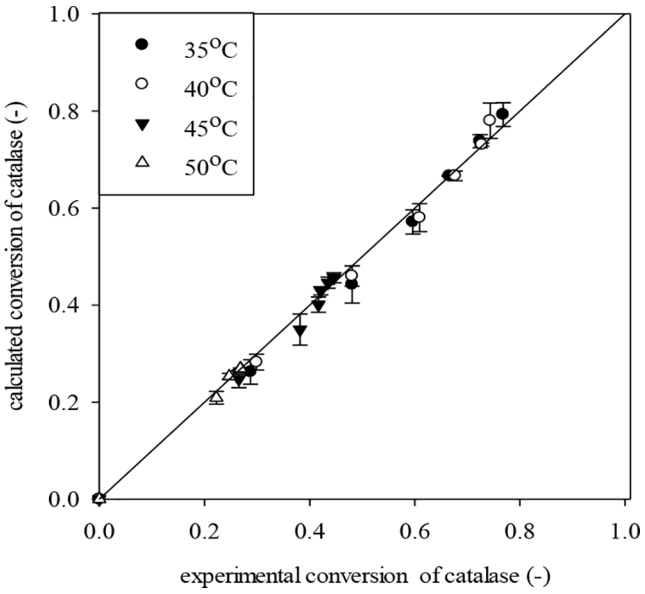

Figure 4. Comparison between calculated conversion and experimental conversion for *Aspergillus niger* catalase during the decomposition of 0.015 mol/L hydrogen peroxide.

Table 1. Deactivation rate constants for catalase from *Aspergillus niger* for an initial concentration of 0.015 mol/L hydrogen peroxide.

Temperature	35ºC	40ºC	45ºC	50ºC
k_D (L/(mol·h))	30.5±2.98	58.6±5.71	235.9±6.23	469.5±4.99
SEE	0.066	0.022	0.018	0.006
r	0.997	0.997	0.994	0.998
r^2	0.992	0.993	0.988	0.996

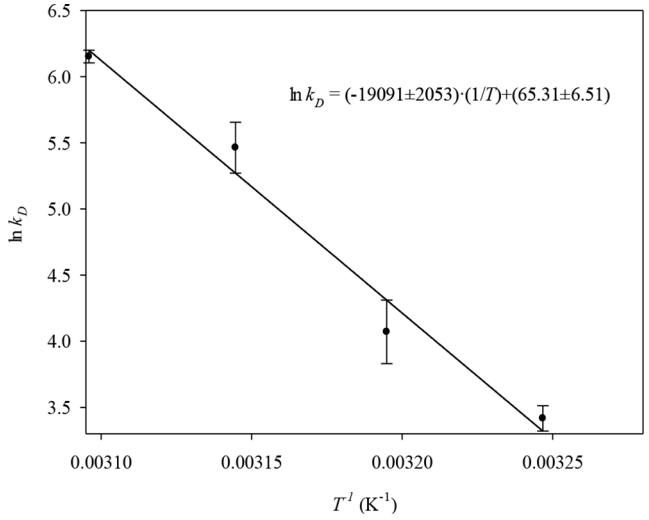

Figure 5. Arrhenius plot for estimation of the activation energy for deactivation of *Aspergillus niger* catalase during the decomposition of 0.015 mol/L hydrogen peroxide.

Deactivation rate constants varied depending on temperature in accordance with the Arrhenius equation. The activation energy for deactivation of *Aspergillus niger* catalase was calculated to be 158.7±1.7 kJ/mol. The correlation between the data obtained from the mathematical model and experimental data was high (correlation coefficients higher than 0.988). The value of the activation energy for deactivation of catalase *Aspergillus niger* was 3.4 times higher than the value of the activation energy for deactivation of catalase Terminox Ultra (Miłek and Wójcik, 2011).

The established values of rate constants for reaction and rate constants for deactivation k_D, based on equation (13) allow definion of the change of catalase activity during the decomposition of hydrogen peroxide with the initial concentration of 0.015 mol/L. Figure 6 shows the change of enzyme activity with time calculated at 40ºC, using two quantities of the enzyme.

From the data shown in Figure 6, it was observed that the activity of catalase (2.5 U/ml) during hydrogen peroxide decomposition at time 1.6 h and at the temperature 40°C decreased to about 50% of the initial activity of catalase.

Figure 7 shows the changes in the activity of the enzyme, which depends on temperature ranging from 35°C to 50°C using 2.5 U/mL catalase. Figure 7 shows that, during decomposition of hydrogen peroxide at 45°C, the catalase activity falls to 20% of the initial activity after 0.58 h. On the other hand, during decomposition of hydrogen peroxide at 50°C, the catalase activity falls to 20 % of the initial activity after 0.26 h.

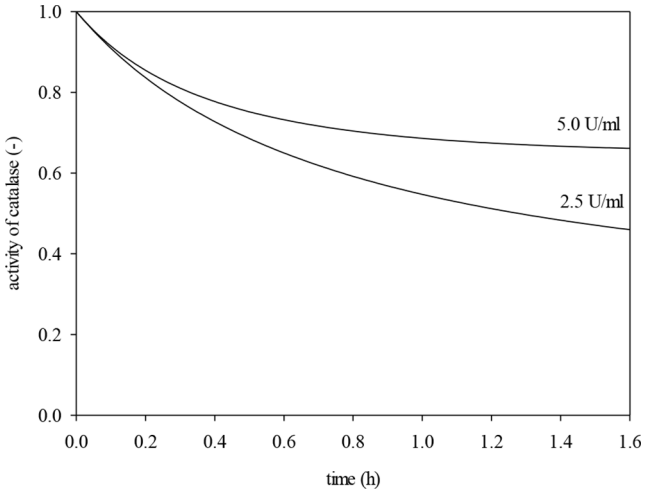

Figure 6. Dependence of catalase activity on reaction time at 40ºC during the decomposition of 0.015 mol/L hydrogen peroxide.

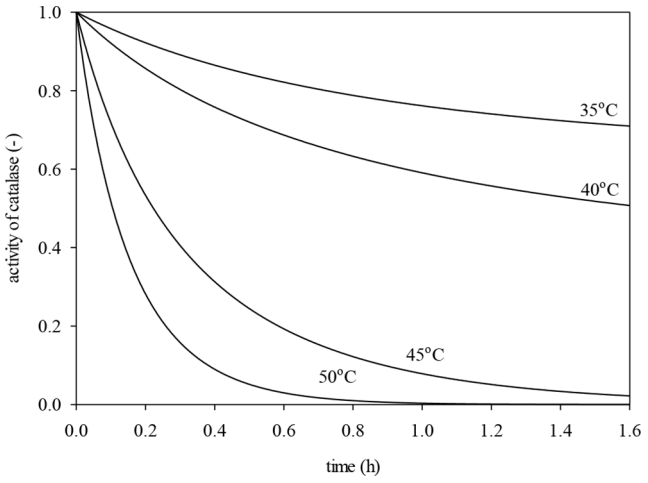

Figure 7. Effect of temperature on the change of dimensionless activity for *Aspergillus niger* catalase during the decomposition of 0.015 mol/L hydrogen peroxide.

Thus, due to the significant deactivation of catalase at temperatures above 40°C, it is recommended to use larger quantities of enzyme during the course of the reaction of hydrogen peroxide decomposition by catalase.

Table 2 shows values of the deactivations constant k_D for catalase of different origins at hydrogen peroxide concentrations lower than 0.02 mol/L, which are presented in the literature.

The effect of temperature on the deactivation of catalase from *Aspergillus niger* by hydrogen peroxide so far has not been the object of systematic research. In the literature only the values of k_D for *Aspergillus niger* catalase for the temperatures 25°C and 37°C are presented: 30.6 L/(mol·h) and 54.0 L/(mol·h), respectively (DeLuca *et al.* 1995; Tse and Gough, 1987).

Table 2. Values of deactivations constant kD for catalase of different origins.

Temperature	k_D [L/(mol·h)]	catalase	Authors
25ºC	30.6	*Aspergillus niger*	DeLuca *et al.*(1995)
	532.8	bovine liver	
27ºC	410.1	bovine liver	Ghadermarzi and Moosavi-Movahedi(1996)
37ºC	54.0	*Aspergillus niger*	Tse and Gough (1987)

The kinetic deactivation parameters obtained for the *Aspergillus niger* catalase allow the calculation with the Arrhenius equation of the deactivation rate constants k_D for specific temperatures. The calculated value k_D of 3.54 L/(mol·h) for *Apergillus niger* catalase at the temperature of 25ºC is lower than that determined by DeLuca *et al.* (1995). The calculated value of k_D of 42.7 L/(mol·h) for *Apergillus niger* catalase at 37°C is lower by about 21% than that determined by Tse and Gough (1987). However, it appears that there is a divergence in the results when enzymes of different origins are used. Comparing the calculated values of k_D for *Aspergillus niger* catalases with k_D values for bovine liver catalase (DeLuca *et al.*, 1995), it can be concluded that microbial catalases are more stable than those obtained from animal tissues.

However, the inactivation constant is reported to be strongly influenced by the other enzymes and reactions producing hydrogen peroxide, e.g., an oxidation reaction catalyzed by an oxidase (Ene and Maria, 2012; Maria *et al.* 2012). So it is necessary in the future to study and estimate kinetic parameters for deactivation of catalase in bi-enzymatic reactions.

The parameters obtained for deactivation of *Aspergillus niger* catalase by hydrogen peroxide can be used in modeling and optimization of batch bioreactors (Grubecki, 2016; Vasić-Rački *et al.*, 2011).

CONCLUSIONS

Hydrogen peroxide decomposition in the concentration range from 0.001 mol/L to 0.015 mol/L by catalase from *Aspergillus niger* is associated with a noticeable deactivation of the enzyme by the substrate at temperatures ranging from 35ºC to 50ºC. Good agreement between experimental data and the model simulations was obtained. The deactivation rate is described by a first-order kinetic equation in relation to the enzyme and the substrate concentrations. The parameters, namely, the deactivation rate constants in this mathematical model, were estimated by the Levenberg-Marquardt method. Dependence of the reaction rate constant for deactivation on temperature is in agreement with the Arrhenius equation. The activation energy obtained for decomposition of hydrogen peroxide equals 12.9±0.7 kJ/mol. The activation energy for deactivation of *Aspergillus niger* catalase was 158.7±1.7 kJ/mol.

In summary, the results obtained could be very useful in order to improve the application of *Aspergillus niger* catalase in industrial processes. The kinetic deactivation parameters that were determined and the appropriate mathematical model could be used to significantly optimize hydrogen peroxide decomposition by using *Aspergillus niger* catalase. In the future, it is necessary to determine the kinetic parameters for the reaction of *in situ* production H_2O_2 by another enzyme.

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NOMENCLATURE

$a = C_E / C_{E_0}$ dimensionless activity of catalyst
C_E concentration of enzyme (mol/L)
C_S concentration of hydrogen peroxide (mol/L)
E_D activation energy for deactivation (kJ/mol)
E_R activation energy for reaction (kJ/mol)
k_D deactivation rate constant (L/(mol·h)
k_{D0} pre-exponential deactivation rate constant (L/(mol·h))
k_R reaction rate constant (L/(mol·h))
$k_R^* = C_{E_0} k_R$ reaction rate constant (1/h)
SEE standard error of estimate
T temperature (ºC)
t time (h)
X fractional conversion

REFERENCES

Akyilmaz, E. and Kozgus, O., Determination of calcium in milk and water samples by using catalase enzyme electrode. Food Chemistry, 115(1), 347-351 (2009).

Altomare, R. E., Greenfield, P. F. and Kittrell, J. R., Inactivation of immobilized fungal catalase by hydrogen peroxide. Biotechnology and Bioengineering, 16(12), 1675-1680 (1974).

Arabaci, G. and Usluoglu, A., Catalytic properties and immobilization studies of catalase from *Malva sylvestris L*. Journal of Chemistry, 2013, 1-7 (2013).

Arvin, E. and Pedersen, L.-F., Hydrogen peroxide decomposition kinetics in aquaculture water. Aquacultural Engineering, 64, 1-7 (2015).

Bayramoglu, G., Arica, M. Y., Genc, A., Ozalp, V. C., Ince, A. and Bicak, N., A facile and efficient method of enzyme immobilization on silica particles via Michael acceptor film coatings: immobilized catalase in a plug flow reactor. Bioprocess and Biosystems Engineering, 39(6), 871-881 (2016).

Costa, S.A., Tzanov, T., Carneiro, A. F., Gűbitz, G. M. and Cavaco-Paula, A., Recycling of textile bleaching effluents for dyeing using immobilized catalase. Biotechnology Letters, 24, 173-176 (2002).

DeLuca, D., Dennis, R. and Smith, W. G., Inactivation of an animal and a fungal catalase by hydrogen peroxide. Archives of Biochemistry and Biophysics, 320(1), 129-134 (1995).

Ene, M. D. and Maria, G., Temperature decrease (30-25°C) influence on bi-enzymatic kinetics of D-glucose oxidation. Journal of Molecular Catalysis B: Enzymatic 81, 19-24 (2012).

Farkye, N. Y., Cheese technology. International Journal of Dairy Technology, 57(2-3), 91-98(2004).

Freitas, F. F., Marquez, L. D. S., Ribeiro, G. P., Brandão, G. C., Cardoso, V. L. and Ribeiro, E. J., Optimization of the immobilization process of β-galatosidase by combined entrapment-cross-linking and the kinetics of lactose hydrolysis. Brazilian of Journal Chemical Engineering, 29(1), 15-24 (2012).

Frutiger, J., Marcarie, C., Abildskov, J. and Sin, G., A comprehensive methodology for development, parameter estimation, and uncertainty analysis of group contribution based property models an application to the heat of combustion. Journal of Chemical Engineering Data, 61(1), 602-613 (2016).

Grigoras, A. G., Catalase immobilization - A review. Biochemical Engineering Journal, 117, 1-20 (2017)

Ghadermarzi, M. and Moosavi-Movahedi, A. A., Determination of the kinetic parameters for the "suicide substrate" inactivation of bovine liver catalase by hydrogen peroxide. Journal of Enzyme Inhibition, 10(3), 167-175 (1996).

Grubecki, I., How to run biotransformations. At the optimal temperature control or isothermally? Mathematical assessment. Journal of Process Control, 44, 79-91 (2016).

Herdt, B. L., Magnuson, J. P., Mcsherry, D. D., Li, J. and Owens, K. L., United States Patent No. US 8,241,624 B2 United State Patent and Trademark European Patent Office (2012).

Hooda, P. V., Immobilization and kinetics of catalase on calcium carbonate nanoparticles attached epoxy support. Applied Biochemistry and Biotechnology, 172(1), 115-130 (2014).

Lardinois, O. M., Mestdagh, M. M. and Rouxhet, P. G., Reversible inhibition and irreversible inactivation of catalase in presence of hydrogen peroxide. Biochimica et Biophysica Acta, 1295(2), 222-238 (1996).

Lee, C. H., The role of biotechnology in modern food production. Journal of Food Science, 69(3), CRH92- CRH95 (2004).

Liu, F., Zhong, A., Xu, Q., Cao, H. and Hu, X., Inhibition of 2,4-dichlorophenoxyacetic acid to catalase immobilized on hierarchical porous calcium phosphate: Kinetic aspect and electrochemical biosensor construction. Journal of Physical Chemistry. C, 120(29), 15966-15975 (2016).

Maria, G., Ene, M. D. and Jipa, I., Modelling enzymatic oxidation of D-glucose with pyranose 2-oxidase in the presence of catalase. Journal of Molecular Catalysis B: Enzymatic 74, 209-218 (2012).

Miłek, J.,Kwiatkowska-Marks, S. and Wójcik, M., Immobilization of catalase from *Aspergillus niger* in calcium alginate gel. Chemik, 65(4), 305-308 (2011).

http://www.chemikinternational.com/pdf/2011/04_2011/CHEMIK%202011_65_4_305-308.pdf.

Miłek, J. and Wójcik, M., Effect of temperature on the decomposition of hydrogen peroxide by catalase Terminox Ultra. Przemysł Chemiczny, 90(6), 1260-1263 (2011)

http://sigma-not.pl/publikacja-60227-wplyw-temperatury-na-rozklad-nadtlenku-wodoru-przez-katalaze-terminox-ultra-przemysl-chemiczny-2011-6.html (in Polish).

Switala, J. and Loewen, P. C., Diversity of properties among catalases. *Archives of Biochemistry and Biophysics*, 401(2), 145-154 (2002).

Tarhan, L., Use immobilized catalase to remove H_2O_2 used in the sterilization of milk. *Process Biochemistry*, 30(7), 623-628 (1995).

Tse, P. H. S. and Gough, D., Time-dependent inactivation of immobilized glucose oxidase and catalase. Biotechnology and Bioengineering, 29(6), 705-713 (1987).

Vasić-Rački, Đ., Findrik, Z. and Presečki, A. V., Modelling as a tool of enzyme reaction engineering for enzyme reactor development. Applied Microbiology and Biotechnology, 91(4), 845-856 (2011).

Vasudevan, P. T. and Weiland, R. H., Deactivation of catalase by hydrogen peroxide. Biotechnology and Bioengineering, 36(8), 783-789 (1990).

Yoshimoto, M., Wang, S., Fukunaga, K., Fournier, D., Walde, P., Kuboi, R. and Nakao, K., Novel immobilized liposomal glucose oxidase system using the channel protein OmpF and catalase. Biotechnology and Bioengineering, 90, 231-238 (2005).