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DEACTIVATION OF PALLADIUM CATALYST SUPPORTED BY ALUMINA IN THE PRODUCTION OF GLYPHOSATE

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During the production process of glyphosate from n-phosponomethyl iminodiacetic acid (NPMIDA) and hydrogen peroxide (H_2O_2), deactivation of the catalyst used may occur, which will decrease the production of glyphosate. To controll the rate of production the deactivation process of the catalyst needs to be evaluated.

Five grams of NPMIDA, 0.3 grams of fresh palladium catalyst, and 85 mL of H_2O were put into a three neck flask. One mL of H_2O_2 was added into the mixture every ten minutes, so that the total amount of H_2O_2 added was 9 mL. The reaction was kept going for another 15 minutes. The catalyst was filtered and its filtrate collected in a 500 mL erlenmeyer glass. The filtrate was then naturally cooled to room temperature and 130 mL of technical grade ethanol was added to it. The solution was left overnight for the crystal formation. The glyphosate crystal formed was then separated from the solution and washed with 40 mL of technical grade ethanol, followed by 40 mL of technical grade ether. Finally the glyphosate crystal was dried in open air. The amount of crystal glyphosate produced was weighed and its purity was analyzed using UV/Vis spectrophotometer. The catalyst was then reused in the next experiments using the same procedure.

The activity as a function of temperature and time can be expressed as follows:

$$\varphi(T,t) = at^{(-n)}$$

where $a = 0.027T - 7.99$ and $(-n) = 0.005T + 1.62$. These parameters hold for temperatures (T) of 333K to 363K. At 363K, the rate of deactivation of the catalyst is the fastest. Experiments that were run at 348K resulted in higher glyphosate productivity compared to other temperatures.

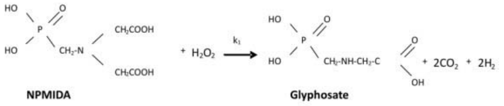
Keyword: *deactivation, glyphosate, hydrogen peroxide, n-phosphonomethyl iminodiacetic acid, palladium catalyst.*

INTRODUCTION

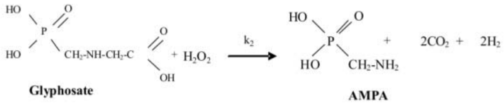
Background Problem

Glyphosate herbicide available in Indonesia is imported from China. Since Indonesia is an agricultural country, it is necessary to produce glyphosate in Indonesia. In 2003 a Research and Development Group, Biro Litbang PT Petrosida conducted a preliminary survey and concluded that the production of technical glyphosate from NPMIDA and H_2O_2 in Indonesia would enhance the glyphosate herbicide.

The reaction of glyphosate production from NPMIDA and H_2O_2 is as follow *(*U.S.Patent 3,950,402, 1976*):*



(1)



(2)

The reaction of NPMIDA and H_2O_2 produces glyphosate, carbon dioxide, and hydrogen, as shown in Equation (1). In addition there is a side reaction between glyphosate and hydrogen peroxide to form aminomethyl phosponic acid (AMPA), carbon dioxide, and hydrogen, as in Equation (2). Generally the selectivity of the reaction can be increased by using a proper catalyst. The catalysts that have been evaluated were acid, metal, and activated carbon (U.S.Patent 3,950,402, 1976). The use of some acid catalysts for producing glyphosate from NPMIDA and hydrogen peroxide have been studied by Rahayuningsih et al. (2008) and it was found that sulfuric acid was better than both nitric acid and asetic acid.

Evaluation of constant rates of the main reaction (k_1) and of the side reaction (k_2) in producing glyphosate from NPMIDA and H_2O_2 using activated carbon catalyst have been performed by Angkasa and Rahayuningsih (2008) and the evaluation palladium catalyst supported by activated carbon was evaluated by Rahayuningsih et al. (2009b). It was found that, in the first 180 minutes the side reaction could be neglected for reactions catalyzed by activated carbon and palladium. The experimental results show that the value of k_1 using palladium catalyst supported by activated carbon is higher than the value of k_1 for activated carbon catalyst. Meanwhile, the value of k_2 using palladium catalyst supported by activated carbon was lower than that of activated carbon catalyst. Therefore it can be concluded that the selectivity of palladium catalyst supported by activated carbon is higher than the selectivity of activated carbon catalyst.

Solid catalysts frequently lose an important fraction of their activity while in operation or in other words they experience deactivation process. As has been widely known, there are three causes for deactivation, namely, sintering, poisoning, and coking or fouling. The fraction of sites remaining active or the activity, φ, is given by:

$$\varphi = \frac{C_t - C_{pi}}{C_t} \qquad (3)$$

where C_t and C_{pi} are respectively the total sites and the fraction of sites covered with poison or carbon. A decrease of the active sites causes a decline in the reaction rate. By assuming the system to be heterogeneous and the rate of reaction to be pseudo first order with respect to hydrogen peroxide (C_B) the activity can be defined as follows:

$$\varphi = \frac{r_t}{r_{t=0}} = \frac{k^*_{1,(t)} C_B}{k^*_{1,(t=0)} C_B} = \frac{k^*_{1,(t)}}{k^*_{1,(t=0)}} \tag{4}$$

or

$$k^*_{1,(t)} = \varphi k^*_{1,(t=0)} \tag{5}$$

where, $k^*_{1,(t=0)}$ is the constant rate of reaction using fresh catalyst (t=0), $k^*_{1,(t=t)}$ is the constant rate of reaction at time t, $r_{t=0}$ is the reaction rate using fresh catalyst, and r_t is the reaction rate at time t. The value of φ decreases as the time increases and can be expressed empirically as a function of temperature and time. One of them follows the power law (Fogler, 1999).

$$\varphi(T,t) = at^{-n} \tag{6}$$

where $a = f(T)$ and $n = f(T)$. Palladium catalyst is very expensive, therefore it is necessary to study palladium deactivation during its use in order to optimize its utilization.

Reaction Rate Constants Evaluation

The constant rates of reaction cannot be determined directly from the experimental work in the laboratory. Assuming the reaction rate follows elementary reactions, mole balance of glyphosate in a batch process can be expressed as follows,

$$\frac{dC_C}{dt} = k_1 C_A C_B - k_2 C_C C_B \tag{7}$$

where C_A, C_B and C_C are respectively the concentration of NPMIDA (mole/L), H_2O_2, and glyphosate. Experimental data shows that the glyphosate formation from NPMIDA and H_2O_2 is better conducted in the first 180 minutes in order to eliminate the side reaction (Rahayuningsih et al., 2009a). Rahayuningsih et al. (2009b) found that the constant rate of the main reaction (k_1) is 100 times the value of the constant rate of the side reaction (k_2), when using the palladium catalyst supported by active carbon to catalyze the glyphosate formation. Consequently, the adverse side reaction can be neglected, and Equation (7) becomes,

$$\frac{dC_C}{dt} = k_1 C_A C_B \tag{8}$$

The concentration of NPMIDA in the solution during the experiments was assumed constant and equal to its saturated concentration. This is, because the availablity of NPMIDA crystal in the solution is higher than its solubility which is equal to 2 % w/w at 348K. According to the Equation (1), the moles H_2O_2 in the reaction is equal to the moles of glyphosate formed. As a result, Equation (8) can be expressed as follows:

$$\frac{dC_C}{dt} = -\frac{dC_B}{dt} = k_1^* C_B \tag{9}$$

where $k_1^* = k_1 C_A$.

In order to avoid H_2O_2 evaporating and decomposing, H_2O_2 was added drop by drop to the reactor already containing NPIMDA solution. Every 10 minutes the volume of H_2O_2 added to the reactor was 1 mL, and each run was lasted for 90 minutes. Therefore, the boundary conditions of Equation (9) for the ten minute interval are as follows: at t=10(m) minutes the concentration of hydrogen peroxide (C_B) was $C_{B,(10(m))}$ mole/L, and at t=(10(m+1)-0.1) minutes the concentration of hydrogen peroxide was $C_{B,(10(m+1)-0.1)}$ mole/L. Integrating Equation (9) with its given boundary conditions give

$$\ln \frac{C_{B,(10(m+1)-0.1)}}{C_{B,(10(m))}} = -k_1^*((10(m+1)-0.1)-10(m)) \tag{10}$$

or

$$C_{B,(10(m+1)-0.1)} = C_{B,(10(m))} \exp(-k_1^*((10(m+1)-0.1)-10(m)) \tag{11}$$

where m=0,1,2,...,9.

The concentration of H_2O_2 in the

solution after the drops can be evaluated using Equation (12)

$$C_{B,(10(m+1))} = \frac{0.0177}{V_{Solution}} + C_{B,(10(m))} \exp(-k_1^*((10(m+1)-0.1)-10(m))) \quad (12)$$

Volume solution $(V_{Solution}) = (0.085 + m(0.001))Liters$. The total mole of H_2O_2 in the reaction with NPMIDA is calculated using Equation (13)

Total mole of H_2O_2 in the reaction after 90 minutes =
Total mole of H_2O_2 added in 90 minutes − (13)
Total moles of H_2O_2 in the solution at 90 minutes

From the experiments the amount of glyphosate produced was found, therefore the total mole of H_2O_2 in the reaction could be determined. Then k_1^* can be evaluated from Equation (13). When, using fresh catalyst the value of k_1^* is equal to $k_{1,(t=90)}^*$ while with reused catalyst the value of $k_{1,(t=l(90))}^* = \varphi_{(t=l(90))} k_{1,(t=90)}^*, l = 1,2,3,\ldots,15$. When the deactivation occurs the value of φ, as shown in Equation (6), declines with respect to time, if n is positive. The value of the reaction rate constant is affected by temperature, which in turn, it will have an impact on the value of φ. Generally the value of φ can be stated as a function temperature and time, $\varphi = f(T,t)$.

EXPERIMENTAL METHOD

Five grams of NPMIDA, 0.3 grams of fresh palladium catalyst supported by activated carbon of Fluka brand, and 85 mL of H_2O were put into a three neck flask. The NPMIDA ($C_5H_{10}NO_7P$) was supplied by PT Petrokimia Gresik, its purity is 98 %, and the solubility in water at temperature of 348K is 2 %(w/w). Every 10 minutes 1 mL of 50% hydrogen peroxide (H_2O_2) (purchased from Bratako Chemical Shop), was added into the mixture, and the total amount of H_2O_2 added was 9 mL. The total time for adding H_2O_2 into the system was 90 minutes. The reaction was kept for another 15 minutes. The catalyst was filtered and the filtrate was collected in an erlenmeyer glass. The filtrate was cooled to room temperature. The solution was then added with 130 mL of technical grade ethanol and the erlenmeyer glass was covered properly with plastic sheets and finally was left overnight for crystal formation. The glyphosate crystal formed was separated from the solution and then washed with 40 mL of technical grade ethanol and 40 mL of technical grade ether. The washing process was repeated several times to obtain glyphosate crystals free of reactant solution. Then, the crystal was dried in open air. The amount of crystal glyphosate produced was weighed and the purity was analyzed using UV/Vis spectrophotometer. The experiments were carried out 14 times using the same method and similar condition, but utilizing used Palladium catalyst. The experiments were performed for three different temperatures, namely 333K, 348K, and 363K.

Equipment schematics is shown in Figure 1.

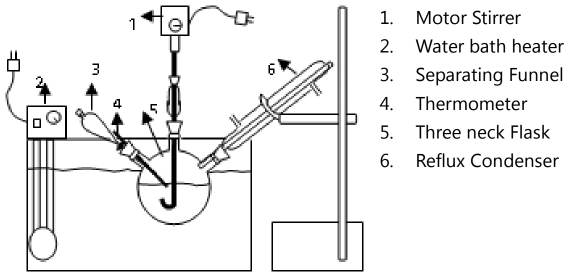


Fig. 1 : The experimental set-up for glyphosate production

RESULT AND DISCUSSION

Figure 2 shows glyphosate concentration versus time for temperatures of 333K, 348K, and 363K respectively. The concentration of glyphosate that was resulted in the first of 90 minutes using fresh catalyst for temperature of 363K was the highest compared to the other temperatures (333K and 348K). These results are in good agreement with the previous study (Rahayuningsih et al., 2009b).

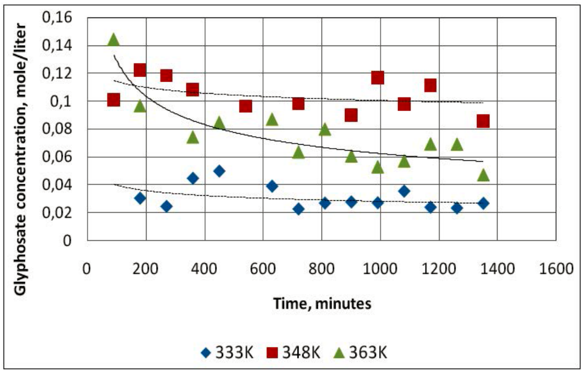


Fig. 2 : The concentration of glyphosate as a function of time at various temperatures

From Figure 2, it can be seen that up to 200 minutes, the amount of glyphosate formation for temperature of 363K decreases very sharply and then decreases gradually. This is because the activity of catalyst decreases. The amount of glyphosate formation at temperature of 348K is higher than that of 363K. This is due to at temperature of 363K, the side reaction could take place simultaneously. As a result the glyphosate formation decreases. As shown in Figure 2, at temperature of 333K the amount of glyphosate produced is the lowest one, due to the solubility of NPMIDA is low.

By curve fitting method the value of $k^*_{1,(t=90)}$for the fresh catalyst and $k^*_{1,(t=l(90))}$ for the reused catalyst fo the various times and temperatures of 333K, 348K, and 363K can be evaluated. Based on calculated values of $k^*_{1,(t=90)}$ and $k^*_{1,(t=l(90))}$, the values of activity $(\varphi(T,t))$ can be calculated. The results are shown in Table 1, Figure 3, and Figure 4.

From Figure 4, it can be stated that catalyst deactivation fits Equation (6).

Table 1. The value of main reaction rate constants using fresh catalyst and used catalyst for consecutive processes at the reaction temperatures of 333K, 348K, and 363K

No. of reaction	Time Period, minutes	Temperature 333K		Temperature 348K		Temperature 363K	
		k_1^*	φ	k_1^*	φ	k_1^*	φ
1= fresh	90	0.0822	1.0000	0.1365	1.0000	0.1529	1.0000
2	180	0.0818	0.9951	0.1294	0.9479	0.1062	0.6945
3	270	0.0814	0.9900	0.1232	0.9021	0.1025	0.6706
4	360	0.0811	0.9858	0.1146	0.8394	0.0991	0.6482
5	450	0.0803	0.9770	0.1102	0.8070	0.0965	0.6312
6	540	0.0796	0.9688	0.1062	0.7781	0.0936	0.6121
7	630	0.0790	0.9610	0.1053	0.7711	0.0908	0.5941
8	720	0.0780	0.9485	0.1042	0.7633	0.0885	0.5787
9	810	0.0770	0.9361	0.1031	0.7552	0.0870	0.5693
10	900	0.0760	0.9244	0.1022	0.7486	0.0855	0.5589
11	990	0.0751	0.9130	0.1017	0.7446	0.0840	0.5497
12	1080	0.0745	0.9066	0.1011	0.7407	0.0835	0.5463
13	1170	0.0741	0.9011	0.1006	0.7369	0.0828	0.5417
14	1260	0.0739	0.8990	0.1002	0.7339	0.0824	0.5389
15	1350	0.0738	0.8978	0.0993	0.7272	0.0818	0.5351

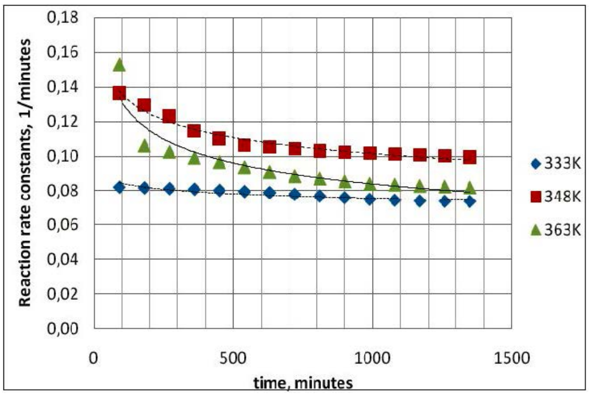


Fig. 3 : The value of main reaction rate constants using fresh catalyst and used catalyst for consecutive processes at the reaction temperatures of 333K, 348K, and 363K

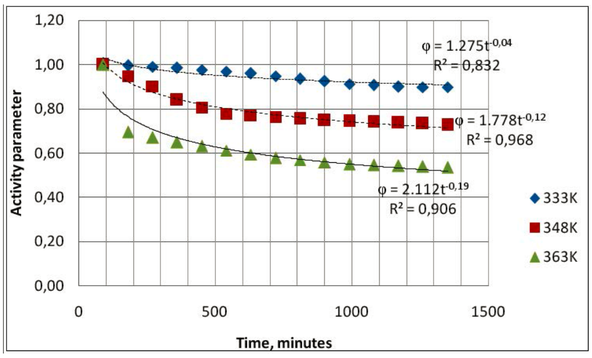


Fig. 4 : The value of activity parameter (φ) with used catalyst for consecutive processes at the reaction temperature of 333K, 348K, and 363K

The empirical correlations between the value of activity and time, at the temperatures of 333K, 348K, and 363K are as follows:

$$\varphi(333K,t) = 1.275t^{-0.04} \tag{14}$$

$$\varphi(348K,t) = 1.778t^{-0.12} \tag{15}$$

$$\varphi(363K,t) = 2.112t^{-0.19} \tag{16}$$

Equation (14), (15), and (16) match the power law model (Fogler, 1999). This model shows that deactivation of catalyst might be caused by poisoning and/or fouling. Equation of (14), (15), and (16) shows that the constant values of a and n, of the equation can be stated as a function of temperature (T), as shown in Figure 5 and Figure 6.

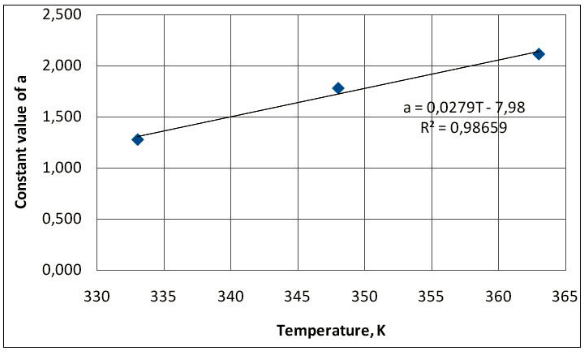


Fig. 5 : The relationship between the constant value of a and temperature

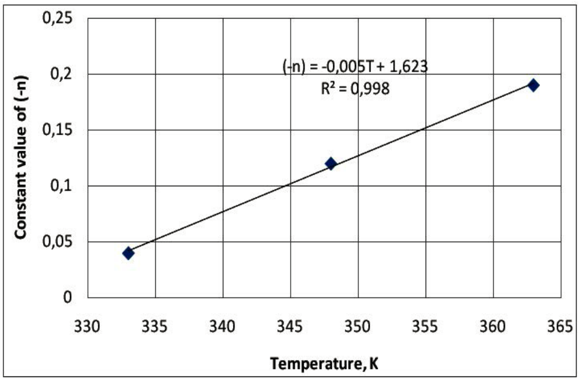


Fig. 6 : The relationship between the constant value of n and temperature

Figure 5 shows that the relationship between a and temperature is linear. Figure 6 shows that n is also linear with respect to temperature. They can be correlated as follows:

$$a = 0.027T - 7.99 \tag{17}$$

or

$$(-n) = -0.005T + 1.62 \tag{18}$$

These equations hold for the temperature (T) of 333K to 363K. Equations

(17) and (18) show that the higher the temperature, the higher the value of a and n, therefore the value of deactivation also increases.

CONCLUSION

From the experimental results, it can be concluded that:

1. The activity parameter (φ) can be expressed as a function of temperature (T) and time (t):
   $\varphi(T,t) = at^{(-n)}$
   where a= $0.027T - 7.99$ and
   $(-n) = 0.005T + 1.62$
   They hold for T of 333K to 363K and t from 90 to 1350 minutes .
2. The deactivation of the catalyst might be caused by poisoning and/or fouling.
3. At 348K, the amount of technical glyphosate produced is higher than the other temperatures (333K and 363K).

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