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Conference Paper *in* AIP Conference Proceedings · January 2020

DOI: 10.1063/1.5140896

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Cite as: AIP Conference Proceedings **2197**, 030004 (2020); https://doi.org/10.1063/1.5140896

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AIP Conference Proceedings **2197**, 030004 (2020); https://doi.org/10.1063/1.5140896 **2197**, 030004

Optimization Based on Kinetic of Dilute-Acid Hydrolysis of Sugar Cane Bagasse in Bio-Ethanol Production

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Abstract. Hydrolysis is an important step in the degradation of holo-cellulose to monohydrates for bio-ethanol production. Ethanol from sugarcane bagasse is very prospective, because the cellulose content is high (40.27%) and its amount is very abundant. The purpose of this study was to study the optimization of hydrolysis conditions of sugarcane bagasse with dilute sulfuric acid catalyst based on reaction kinetics. The hydrolysis of sugarcane bagasse was carried out at various sulfuric acid concentrations (0.3, 0.4, 0.5, 0.6 mol/L), temperatures (70, 80, 90, 100 °C), and times (15, 30, 45, 60, 75 min). The hydrolysis kinetics are solved by a homogeneous reaction approach accompanied by sugar degradation. The results showed that the catalyst concentrations, temperatures, and times greatly influenced the hydrolysis of sugarcane bagasse. The higher the temperature and catalyst concentration, the higher the hydrolysis reaction and sugar degradation will be. As a result, the longer the hydrolysis, the lower the sugar concentration will be. The degradation of sugar began to be seen at 90 °C and the catalyst concentration was 0.5 mol/L. The simulation results showed that the order of hydrolysis reaction is 1 and sugar degradation is 2. The correlation between the activation energy and the catalyst concentration can be expressed by the equation $\ln (E_{hyd}) = 11.593 - 0.0329C_{cat}$ and $\ln (E_{deg}) = 10.869 - 0.0785C_{cat}$ for hydrolysis and sugar degradation, respectively. The optimum sugar concentration obtained was 0.002 mol/L at 100 °C, catalyst concentration 0.567 mol/L and 40 min.

INTRODUCTION

Bio-ethanol is produced from sugar fermentation and can be used as an alternative source of energy to replace fuel oil which is running low [1]. The development of bio-ethanol has reached the 4th generation; the 1st generation is from sugar and starch [2]; 2nd generation from lignocellulose [3]; 3rd generation from marine organisms such as algae [4] and 4th generation from algae that are genetically and nano technologically modified [5]. One of the raw materials that can be used to make the 2nd generation bio-ethanol is sugarcane bagasse, because it contains about 40.27 cellulose, 30.3 hemicellulose, and 27.14% lignin [6].

Several stages in making lignocellulose-based bio-ethanol are hydrolysis, fermentation and purification [7]. Hydrolysis is the initial stage which aims to convert polysaccharides into simple sugar monomers [8]. Chemical and enzymatic methods are generally used to hydrolyze lignocellulose. However, in terms of cost, chemical hydrolysis is more advantageous than enzymatic because of the high cost of producing enzymes [9]. From the various types of acids used, hydrolysis using sulfuric acid is more efficient, because it has many advantages; the price is cheaper and available in large quantities [10,11].

Hydrolysis using acid is influenced by its operating conditions, such as time, acid concentration, and temperature. The hydrolysis of sugarcane bagasse using sulfuric acid was carried out at a temperature of 80-120 °C, the

Proceedings of 2nd International Conference on Chemical Process and Product Engineering (ICCPPE) 2019
AIP Conf. Proc. 2197, 030004-1–030004-7; https://doi.org/10.1063/1.5140896
Published by AIP Publishing. 978-0-7354-1948-3/$30.00

concentration of sulfuric acid was 0.1-0.9 mol/L, and the time was 30-120 min. The results showed that the optimum operating conditions were at 120 °C, 0.1 mol/L of sulfuric acid concentration, and 120 min. In those optimum operating conditions, the sugar concentration obtained was 452.27 mg/g [12]. Meanwhile, Dussan et al has carried out hydrolysis of sugarcane bagasse using a sulfuric acid catalyst (2-6% w/v), at a temperature of 155-175 °C, and for 10-30 min. The maximum sugar concentration obtained was 22.74 g/L in sulfuric acid 2% w/v, 155 °C, and for 30 min [13].

The optimum operating conditions that produce high sugar concentrations are important to know. Variable optimization process can be done using statistical methods, such as Surface Response Methodology (RSM) [14], Artificial Neural Network (ANN) [15], and Monte Carlo [16]. In this study, optimization of the hydrolysis of sugarcane bagasse using sulfuric acid catalyst was kinetics based which is new and unique.

MATERIALS AND METHODS

Dilute-acid Hydrolysis of Sugar Cane Bagasse

The sugarcane bagasse used was obtained from a sugarcane juice company in Semarang and sulfuric acid (Merck, Art 713) from the Chemical Engineering laboratory of Semarang State University. The research variables used were catalyst concentrations (0.3, 0.4, 0.5, 0.6 mol/L), temperatures (70, 80, 90, 100 ºC) and times (0-75 min). Before being used, the sugarcane bagasse was dried and then milled to get a size of 20 mesh. The hydrolysis was done by mixing sugarcane bagasse with sulfuric acid solution (0.3 g/L) into an autoclave (Tomy model ES-315). The sugar concentrations in the sample were analyzed using Fehling method conducted at the Chemical Engineering Laboratory, Universitas Negeri Semarang.

Kinetics of Sugarcane Bagasse Hydrolysis Reaction

Hydrolysis reactions accompanied with degradation of sugar can be written as Eq (1), with B = potential sugar in sugarcane bagasse (mol/L), C = sugar hydrolysis yield (mol/L), U = sugar degradation yield (mol/L), k_{hyd} (1/min) as hydrolysis reaction rate constants, and k_{deg} (L/mol.min) as degradation reaction rate constant. Accordingly, the hydrolysis of sugarcane bagasse follows a series reaction; sugarcane bagasse is hydrolyzed to glucose, and glucose is degraded into side compounds [17]. The rate constants of hydrolysis reactions and the rate of degradation reactions are influenced by temperature, expressed in the Arrhenius equation [18], with A_{hyd} (1/min) and A_{deg} (L/mol.min) as the frequency factors, E_{hyd} (J/mol) and E_{deg} (J/mol) energy activation of hydrolysis and sugar degradation, R (J/(K.mol)) as gas ideal constant, and T (K) as temperature of reaction which can be written as Eq. (2) and (3).

$$B \xrightarrow{k_{hyd}} C \xrightarrow{k_{deg}} U \tag{1}$$

$$k_{hyd} = A_{hyd} exp\left(\frac{-E_{hyd}}{RT}\right) \tag{2}$$

$$k_{deg} = A_{deg} exp\left(\frac{-E_{deg}}{RT}\right) \tag{3}$$

The optimization of hydrolysis conditions was carried out based on kinetics. This kinetic equation was arranged based on the balance of the initial and final sugar mass. Eq. (4) and (5) are the balance of initial and final sugar mass [8], with m and n as the hydrolysis order and sugar degradation order, C_B is the sugar concentration potential in sugarcane bagasse, and C_D is sugar concentration, respectively. Eq. (4) and (5) can be solved using Runge-Kutta.

$$\frac{d(C_D)}{dt} = k_{hyd} C_B^m - k_{deg} C_D^n \tag{4}$$

$$\frac{d(C_B)}{dt} = -k_{hyd} C_B^m \tag{5}$$

The optimization stages can be explained as follows. The values of m, n, k_{hyd} and k_{deg} were calculated through curve fitting. The effect of time on sugar concentration produced from hydrolysis is clearly seen in equation (4) and

(5). The effect of temperature and catalyst concentration on the concentration of sugar produced from hydrolysis and sugar degradation can be expressed through k_{hyd}, and k_{deg} values, based on the Arrhenius equation, in equation (2) and (3). Furthermore, from these values, the frequency factor and activation energy for hydrolysis and sugar degradation can be obtained. The frequency factor was not affected by the concentration of the catalyst, but the activation energy. These effects can be expressed empirically using equation (6) and (7), with x_{hyd}, x_{deg}, y_{hyd}, and y_{deg} as the constants, C_{cat} (mol/L) as the catalyst concentration.

$$\ln\left(E_{hyd}\right) = E_{hyd} + y_{hyd}C_{cat} \tag{6}$$

$$\ln\left(E_{deg}\right) = E_{deg} + y_{deg}C_{cat} \tag{7}$$

Using the values of m, n, x_{hyd}, x_{deg}, y_{hyd}, and y_{deg}, the temperature variables, catalyst concentration, and hydrolysis time variables optimization were performed using a solver tool in Microsoft Excel software to produce the maximum sugar concentrations based on equation (2) – (7).

RESULTS AND DISCUSSION

The effect of temperature on sugar concentration is very strong (see Figure 1-4). At an acid concentration of 0.6 mol/L, the higher the temperature, 70-100 °C, the higher the sugar concentration will be, from 100.8 to 318.6 mg/L. Every increase of 10 °C, the sugar concentration also increases from 70-80 °C by 77%, 80-90 °C by 40 and 90-100 °C by 26%. According to Tizazu and Moholkar, the effect of temperature on the hydrolysis of sugarcane bagasse is also very strong. Their research showed that at 100-130 °C, the sugar concentration rose from 1800-3400 mg/L (every increase of 10 °C sugar concentration increased by 29.63%) [6].

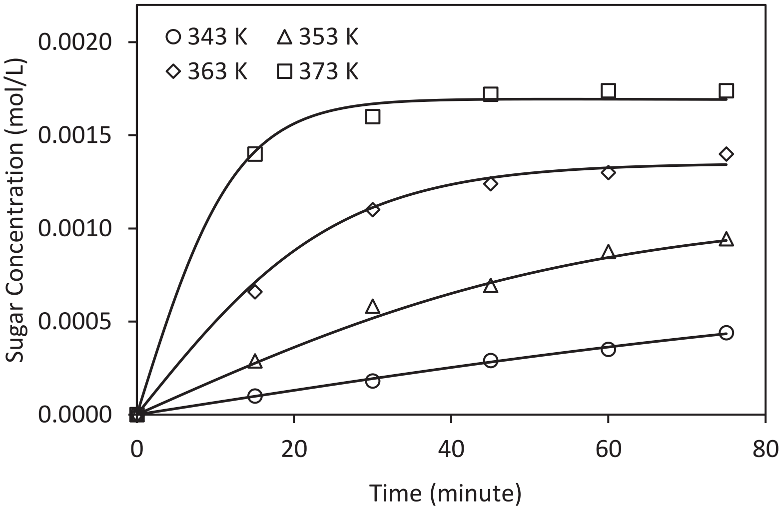

FIGURE 1. The Effect of Temperature towards Sugar Concentration in the Sugarcane Bagasse Hydrolysis using 0.3 mol/L Sulfuric Acid as Catalyst (operating conditions: material size = 20 mesh, material/solution ratio = 0.3 g/L)

Besides temperature, the catalyst concentration also has a positive effect. In this study, at a temperature of 100 °C, the higher the catalyst concentration (0.3-0.6 mol/L) the higher the sugar concentration will be (313.2-318.6 mg/L). Meanwhile, according to Muhaimin et al, the sugar concentration rose (421.143-1035.998 mg/L) when the catalyst concentration increased (0.1-1 mol/L) [19].

The effect of time can be investigated at a catalyst concentration of 0.3-0.4 mol/L and a temperature of 70-100 °C. The sugar concentration increases during the hydrolysis. However, at a catalyst concentration of 0.5-0.6 mol/L and a temperature of 90-100 °C, the sugar concentration does not increase steadily, but will stabilize at 60 min. This means that the degradation of sugar begins to form. Thus, it can be concluded that sugar degradation is very sensitive at high temperatures and catalyst concentrations. Muhaimin et al, for 150 min, the sugar concentration continued to rise from 304.089-468.401 mg/L at 60 °C and the catalyst concentration was 0.1 mol/L [19].

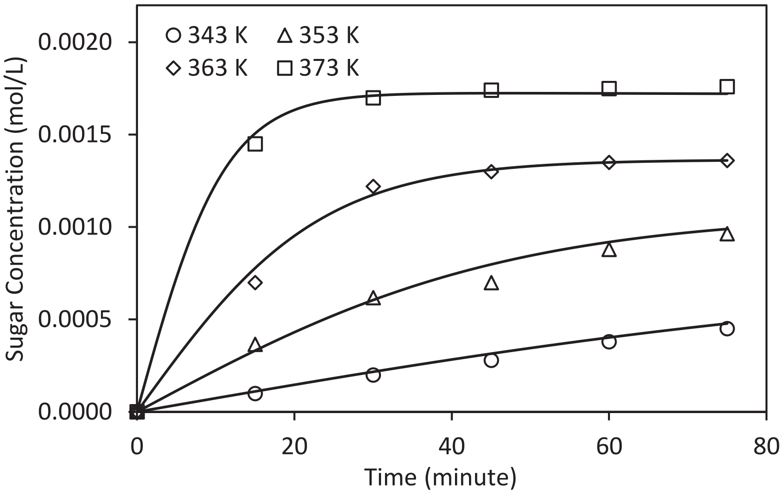

FIGURE 2. The Effect of Temperature towards Sugar Concentration in the Sugarcane Bagasse Hydrolysis using 0.4 mol/L Sulfuric Acid as Catalyst (operating conditions: material size = 20 mesh, material/solution ratio = 0.3 g/L)

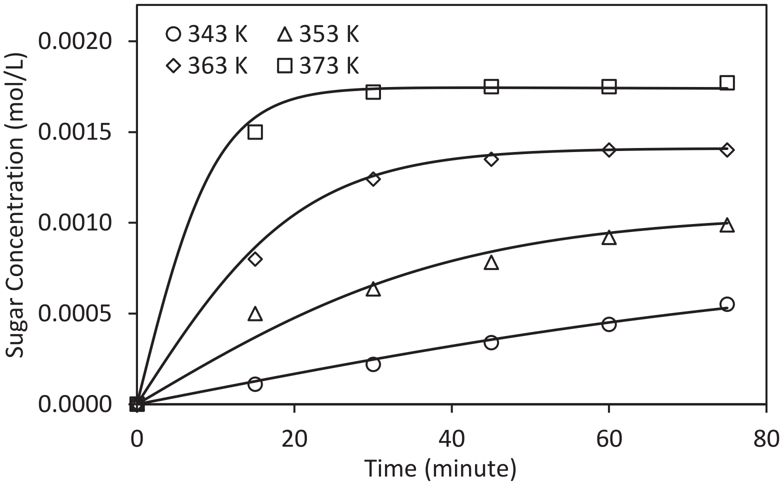

FIGURE 3. The Effect of Temperature towards Sugar Concentration in the Sugarcane Bagasse Hydrolysis using 0.5 mol/L Sulfuric Acid as Catalyst (operating conditions: material size = 20 mesh, material/solution ratio = 0.3 g/L)

The higher the temperature, the faster the hydrolysis and sugar degradation will be. In this study, at a catalyst concentration of 0.4 mol/L, in average, every increase of 10 degrees, the hydrolysis constant rate increased by 31.73 and sugar degradation by 25.44%. According to Tizazu and Moholkar, at the sulfuric acid catalyst concentration of 2% v/v, as the temperature increased from 120 to 130 K, the hydrolysis rate constant would also increase from 8.17×10^{-3} to 8.37×10^{-3} 1/min and the degradation rate constant from 5.53×10^{-5} to 7.75×10^{-5} 1/h [6]. Meanwhile, the higher the catalyst concentration, the faster the hydrolysis and sugar degradation will be. In this study, at a temperature of 373 K and catalyst concentration of 0.5-0.6 mol/L, the hydrolysis rate constant increased by 6% and the rate of sugar degradation increased by 25%.

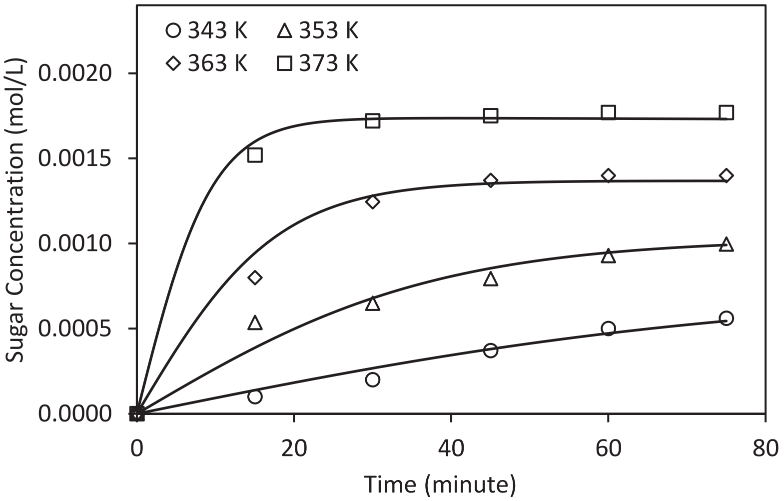

FIGURE 4. The Effect of Temperature towards Sugar Concentration in the Sugarcane Bagasse Hydrolysis using 0.6 mol/L Sulfuric Acid as Catalyst (operating conditions: material size = 20 mesh, material/solution ratio = 0.3 g/L)

TABLE 1. Reaction Rate Constants on Sugar Cane Bagasse Hydrolysis using Dilute Sulfuric Acid in Temperature Variations and Catalyst Concentrations

Temperature (K)	Catalyst Concentration (mol/L)	k_{hyd} (1/min)	k_{deg} (L/(mol.min))
343	0.3	0.000576	11.3802
353		0.001644	15.8772
363		0.004598	28.7001
373		0.011826	46.7362
343	0.4	0.000650	12.1955
353		0.001998	19.7035
363		0.005152	31.4751
373		0.013505	51.5102
343	0.5	0.000744	13.1328
353		0.002245	23.2075
363		0.005870	33.5497
373		0.015216	56.7176
343	0.6	0.000818	17.2657
353		0.002379	25.5510
363		0.006760	41.0067
373		0.016130	71.0044

The linearization results of Eq (6) and (7) to study Arrhenius parameters are presented in Figure (5) and (6). The calculation result showed that the hydrolysis frequency factor was $1.28\text{x}10^{13}$ 1/min and sugar degradation $6.8\text{x}10^{8}$ L/(mol. Min). Meanwhile, the activation energy for each hydrolysis and degradation can be seen in Table (2). The activation energy of hydrolysis and degradation decreases as the catalyst concentration increases [20]. At a catalyst concentration of 0.3 to 0.6 mol/L, the activation energy of hydrolysis decreased from 107.4 to 106.3 kJ/mol and the activation energy of degradation decreased from 51.3 to 50 kJ/mol. Therefore, the higher the catalyst concentration used, the faster the hydrolysis and sugar degradation will be. This shows that the catalyst concentration optimization to maximize the sugar production is very important. In addition, in this study, hydrolysis activation energy (106.3 kJ/mol) is greater than the sugar degradation (50 kJ/mol). It means that the sugar degradation tends to occur compared to hydrolysis. This phenomenon increasingly shows that catalyst concentration optimization is very important. According to Kumar et al, the activation energy of sugarcane bagasse hydrolysis and sugar degradation using sulfuric acid 18% w/w was 84.7 and 56.5 kJ/mol [11].

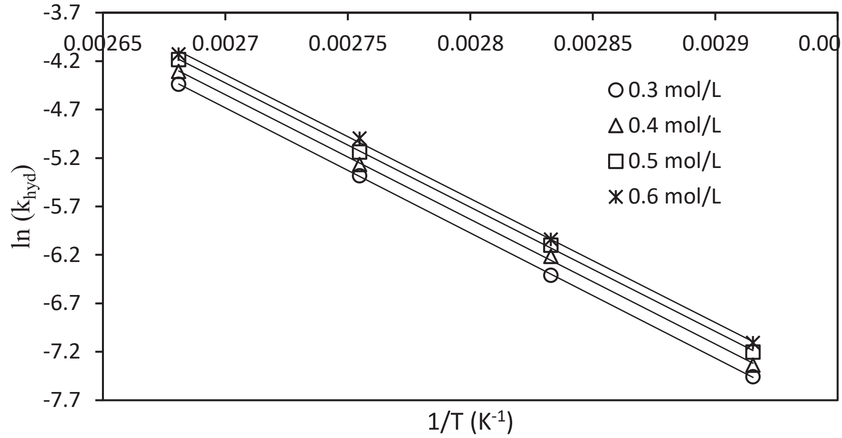

FIGURE 5. Plot ln (k_{hyd}) to 1/T on the sugarcane bagasse hydrolysis using sulfuric acid as catalyst

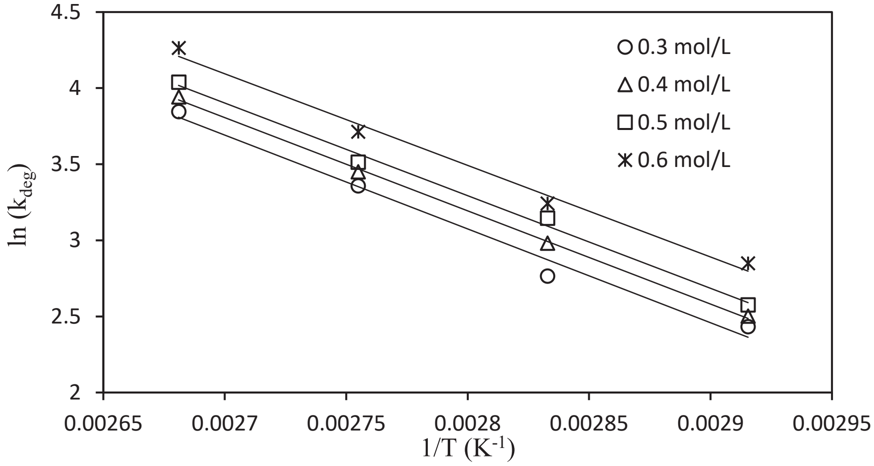

FIGURE 6. Plot ln (k_{deg}) of 1/T in the reaction of sugar degradation in sugarcane bagasse using Sulfuric acid as catalyst

TABLE 2. Activation energy of sugarcane bagasse hydrolysis and sugar degradation in catalyst concentration variations

Catalyst Concentration (mol/L)	E_{hyd} (J/mol)	E_{deg} (J/mol)
0.3	107359	51257
0.4	106943	50925
0.5	106569	50609
0.6	106311	50037

Changes in catalyst concentrations affect both hydrolysis and degradation activation energy [20]. Therefore, to find the activation energy of hydrolysis and sugar degradation at certain catalyst concentrations, we need to know the correlation. The correlation can be expressed by Eq (8) and (9).

$$\ln(E_{hyd}) = 11.593 - 0.0329C_{cat} \tag{8}$$

$$\ln(E_{deg}) = 10.869 - 0.0785C_{cat} \tag{9}$$

The optimization results based on the kinetic parameters mentioned above showed that the optimal conditions were at the catalyst concentration of 0.567 mol/l, 100 °c, and 40 min, with the maximum sugar concentration obtained at 340.2 mg/l. The optimization of the sugarcane bagasse hydrolysis process using sulfuric acid was also carried out by kamalu et al. This optimization was carried out using response surface methodology (RSM), with temperature of 76-144 °c and sulfuric acid concentration of 0.24-0.57 mol/l [21] as the variables. The optimum conditions were at a temperature of 90.41 °C, acid concentration of 0.53 mol/l, and time of 44.84 min, in which the sugar concentration obtained was 217.38 mg/l. The optimization results of this study and the literature are similar.

CONCLUSION

The sulfuric acid concentration as a catalyst, temperature, and time greatly influence sugarcane bagasse hydrolysis. At an acid concentration of 0.6 mol/L, a temperature of 70-100 °C, the sugar concentration continues to increase, from 100.8 to 318.6 mg/L. At a temperature of 100 °C, the higher the catalyst concentration (0.3-0.6 mol/L) the higher the sugar concentration is (313.2-318.6 mg/L). At a catalyst concentration of 0.5-0.6 mol/L and temperature of 90-100 °C, the sugar concentration does not increase steadily, but will stabilize at 60 min. The higher the temperature and catalyst concentration, the higher the hydrolysis reaction and sugar degradation will be. As a result, as the sugarcane bagasse hydrolysis takes more time, the sugar concentration decreases due to the degradation. The sugar degradation began to be seen at 90 °C and the catalyst concentration was 0.5 mol/L. The simulation results showed that the order of hydrolysis and degradation reactions were 1 and 2, respectively. The relationship between catalyst concentration and hydrolysis activation energy and degradation can be expressed using the equation $\ln(E_{hyd}) = 11.593 - 0.0329C_{cat}$ dan $\ln(E_{deg}) = 10.869 - 0.0785C_{cat}$. From the optimization, the optimum conditions obtained were at the catalyst concentration of 0.567 mol/L at 100 °C and 40 min with the maximum sugar concentration obtained at 0.002 mol/L.

ACKNOWLEDGMENTS

The author would like to thank Semarang State University and Indonesian Ministry of State of Research and Technology-Indonesian Directorate General of Higher Education (Kemenristek-Dikti) for research grant 2019.

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