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The Effect of Alkali Concentration and Hydrolysis Time on the Production of Oxalic Acid from Wood Sawdust Waste by Alkali Hydrolysis Process

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Mahogany wood is a type of wood often found in sawmills because the wood grows faster than other types of wood, so a lot of mahogany sawdust is wasted and not utilized in a product that is discarded and has economic value. The wood residue from removal is then used as a raw material for oxalic acid ($C_2H_2O_4$) products through an alkali hydrolysis process. This study aims to determine the effect of sodium hydroxide (NaOH) and reaction time on the quantity and quality of $C_2H_2O_4$ formed in the NaOH extraction reaction on mahogany sawdust. In this process, the mahogany sawdust was reacted with NaOH concentrations of 1 N and 3 N with variations of coarse and fine mahogany sawdust and reaction times of 60 min and 120 min. To obtain $C_2H_2O_4$, this research was carried out with several stages of pre-treatment, hydrolysis with NaOH, precipitation with calcium chloride ($CaCl_2$), acidification with sulfuric acid (H_2SO_4), and crystallization. The quality of the $C_2H_2O_4$ obtained was analyzed by High-performance Liquid Chromatography (HPLC). The best conditions for producing $C_2H_2O_4$ from mahogany sawdust were NaOH at a concentration of 1 N with a reaction time of 60 min and a yield of 15.67 % from coarse mahogany sawdust.

1. Introduction

Wood is a forest product that is widely used in large and small industries. Wood is used as the main raw material in the industry, but not all parts of wood can be processed into finished materials. In industry, most wood waste is produced in the form of sawdust 15% and wood palm 25%. Sawdust is a waste when sawing wood by machine or hand. The sawmill industry produces wood waste in sawdust and shavings (Krisdianto A, 2016). Waste from the sawmill industry is still not optimally utilized. Sawdust processing will only rot, accumulate and burn, all of which have a negative impact on the environment (Saptari et.al, 2016). One solution is to turn this waste into a valuable product using simple technology (Mulana et.al 2011). Sawdust contains a substance that can decompose. These substances include cellulose, hemicellulose, and lignin (Mohan et al. 2006). Each of these substances is degraded during alkali hydrolysis.

Oxalic acid is used in several industrial activities in Indonesia, including as a dye in the textile industry, anodizing, bleaching agent, neutralizing alkali in the washing process, etc. One of the raw materials for making Oxalic acid is cellulose biomass. Cellulose is a long-chain carbon compound that can be broken down into simpler carbon compounds using a solid base or alkaline hydrolysis. Oxalic acid is a chemical compound with the formula $C_2H_2O_4$ and its systematic name is ethanedioic acid. This simplest dicarboxylic acid is often written by the formula HOOC-COOH. $C_2H_2O_4$ acts as a natural preservative and supports energy production in the body's cells. In addition, $C_2H_2O_4$ is used industrially to remove rust and as a reagent in manufacturing paints.

Mufid et al. (2018) made $C_2H_2O_4$ from teak sawdust using an alkali catalyst of 1 N, 2 N, and 3 N NaOH. The results showed the most significant yield of 20 % at 60 min of hydrolysis with a concentration of 1 N NaOH using coarse teak sawdust. Mufid et al. (2018) produce $C_2H_2O_4$ from materials containing cellulose using the NaOH-catalyzed hydrolysis method includes several stages, namely hydrolysis, filtration, precipitation with $CaCl_2$, acidification with H_2SO_4, and crystallization.Cellulose is one of the raw materials for making $C_2H_2O_4$. Mahogany wood was chosen as the main material because it contains a high number of cellulose which is 35 – 50 % cellulose and the other are 20 – 30 % hemicellulose and 25 – 30 % lignin. Another reason for choosing

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mahogany wood is because it is one of a kind of hardwood that is popular in Indonesia. This wood is widely used in the field of furniture, so in the process manufacturing, a lot of waste is generated production (Wijayanti, 2018). This study aims to know the effect of NaOH concentration and hydrolysis time on the production of $C_2H_2O_4$ by alkali hydrolysis using mahogany wood sawdust waste to know which condition can reach the best yield.

2. Methodology

2.1 Equipment and materials

The tools used in this study were a hot plate mixer, reflux condenser, magnetic stirrer, 500 mL three-neck flask, 250 mL beaker, 250 mL Erlenmeyer, filter paper, crusher, oven, dropper pipette, 100 mL measuring cup, stirrer, 250 mL glass funnel, 100 mL volumetric flask, foil, digital scale, petri disk, spatula, and sterile gloves. While the materials used were: Mahogany sawdust was obtained from local carpenter; 1 N sodium hydroxide (NaOH), 3 N sodium hydroxide (NaOH), distilled water, calcium chloride ($CaCl_2$), and 98 % sulfuric acid (H_2SO_4) were purchased from local chemical store.

2.2 Pretreatment

The first process in this study was the pretreatment or treatment of mahogany sawdust with NaOH solution. Mahogany wood sawdust size that was used in this treatment process was coarse sawdust and fine sawdust. To make fine mahogany wood sawdust, mahogany wood sawdust was dried in an oven at 100 °C. Then mahogany wood sawdust was blended until it resembles powder, then fine mahogany wood sawdust was weighed 15 g and put into a three-neck flask, then 200 mL of NaOH solution was added.

2.3 Hydrolysis of mahogany sawdust

Each sample was made in duplet with a variable concentration of 1 N and 3 N NaOH. The hydrolysis time variable when hydrolyzing mahogany wood sawdust with NaOH was 60 min and 120 min, and the third variable was the variation in mahogany wood sawdust size where the mahogany wood sawdust that we use was fine mahogany wood sawdust and coarse mahogany wood sawdust.

The use of NaOH solution as a hydrolyzing agent is so that the lignin in mahogany sawdust will release its bonds with cellulose. At the same time, on further heating, it will undergo oxidation and decomposition into sodium oxalate ($Na_2C_2O_4$) and sodium acetate (CH_3COONa). At this stage, the hydrolysis was carried out in a three-neck flask with 15 g of mahogany sawdust and the addition of 200 mL of two different NaOH concentrations of 1 N and 3 N at a constant temperature of 70 °C and stirred by a magnetic stirrer with a speed of 600 rpm with heating times of 60 min and 120 min. Furthermore, after the hydrolysis was stopped, the solution was cooled to room temperature. Then the solution was filtered to separate the filtrate and precipitate using filter paper.

2.4 Precipitation and acidification

The precipitation process was carried out by adding saturated $CaCl_2$, and the acidification process was carried out by adding 2 M H_2SO_4. The first step in this process was to add saturated $CaCl_2$ to a beaker containing mahogany sawdust filtrate and NaOH, which had been hydrolyzed beforehand until a white precipitate of calcium oxalate (CaC_2O_4) was obtained. Then the solution was filtered to separate the filtrate and precipitate using filter paper. Then the precipitate was taken and put into a beaker glass, and 200 mL of 2 M H_2SO_4 was added to decompose the precipitate into $C_2H_2O_4$ and calcium sulfate ($CaSO_4$). The solution was then filtered again using filter paper to separate the filtrate and precipitate.

2.5 $C_2H_2O_4$ crystallization

At this crystallization stage, the filtrate that had gone through precipitation and acidification processes was then heated using a hot plate at a constant temperature of 70 °C for 1 h. Then the solution was cooled to room temperature for 24 h to form a precipitate of white needle crystals. Next, the filtrate and crystal precipitate was separated using filter paper. Then precipitate white needle crystals in the oven to remove the water content at 85 °C for 10 min. Next, the dried $C_2H_2O_4$ was weighed using a digital scale and the mass of $C_2H_2O_4$ was calculated.

2.6 Test for $C_2H_2O_4$ content

The $C_2H_2O_4$ content analysis intends to see how much $C_2H_2O_4$ content is in mahogany sawdust using Shimadzu LC 2030 High-Performance Liquid Chromatography (HPLC). For testing the $C_2H_2O_4$ content in the HPLC device, an HPX 87H aminex biorad column was monitored by a UV – vis detector at 210 nm and the mobile phase was H_2SO_4 5 mM with a flow rate of 0.6 cm/min. The first stage in this test was to make a standard solution of 0.5 g of $C_2H_2O_4$ by mixing it with 50 mL of distilled water. After the standard solution was made, it was taken to measure its value using HPLC with a UV – vis detector at a wavelength of 210 nm. To analyze the hydrolyzate sample, the first step was to take a 0.5 g hydrolyzate sample and then dissolve it using 50 mL of hot distilled water. Then the solution was taken to measure its value using HPLC with a UV – vis detector at a wavelength of 210 nm.

Figure 1: Oxalic acid

2.7 Calculation of $C_2H_2O_4$ theoretical yield (%)

After the mass of $C_2H_2O_4$ was obtained from the results of the hydrolyzate, then a graph was made using Microsoft Excel from the theoretical data. As a result, an increase in yield (%) of $C_2H_2O_4$ and an increase in the resulting hydrolysis time were obtained. The theoretical experimental data was calculated using Eq(1) (Hong et al., 2012):

$$Yield\ (\%) = \frac{Mass\ of\ oxalic\ acid\ (g)}{Mass\ of\ wood\ sawdust\ (g)} \times 100\% \quad (1)$$

After experimental theoretical data was obtained, calculate theoretical yield data for $C_2H_2O_4$ with a cellulose content in mahogany (Eq(2)), which is 35 %. The theoretical data of $C_2H_2O_4$ was calculated using Eq(3).

$$Cellulose\ (\%) = \frac{Mass\ of\ oxalic\ acid\ (g)}{Mass\ of\ sawdust\ sample\ (g)} \times 100\% \quad (2)$$

$$Theoretical\ Yield\ of\ Oxalic\ Acid\ (\%) = \frac{Mass\ of\ sawdust\ sample\ (g)}{Theoretical\ mass\ of\ oxalic\ acid\ (g)} \times 100\% \quad (3)$$

3. Results and discussions

3.1 $C_2H_2O_4$ hydrolysis process

In this study, mahogany sawdust containing cellulose would be hydrolyzed with various concentrations of NaOH (1 N and 3 N) and variations in hydrolysis time (60 min and 120 min). Cellulose that was being hydrolyzed with NaOH at 70 °C will undergo the breakdown of cellulose molecules to form $Na_2C_2O_4$ (Eq(4)). The addition of $CaCl_2$ is so that $Na_2C_2O_4$ will bind to Ca^- ions, forming a CaC_2O_4 precipitate (Eq(5)). Then H_2SO_4 was added as a donor of H^- to form $C_2H_2O_4$ (Eq(6)). The reaction of this process can be shown with:

$$(C_6C_{10}O_5)_n + 4n\ NaOH + 3n\ O_2 \rightarrow n\ (COONa)_2 + n\ (CH_3COONa) + 5n\ H_2O + CO_2 \quad (4)$$

$$(COONa)_2 + CaCl_2 \rightarrow (COO)_2Ca + 2\ NaCl \quad (5)$$

$$(COO)_2Ca + H_2SO_4 \rightarrow C_2H_2O_4 + CaSO_4 \quad (6)$$

3.2 The effect of mahogany wood sawdust size

Sawdust has strong potential as a raw material for making $C_2H_2O_4$ and contains cellulose, where cellulose has two reactive groups, namely the hydroxyl group and the reducing group. Reducing groups play a role in reactions with alkali. One of the raw materials for making $C_2H_2O_4$ is cellulose biomass. Wijayanti (2018) states that mahogany wood contains 35-50 % cellulose, 20-30 % hemicellulose, and 25-30 % lignin. This study used 15 g of mahogany sawdust as a raw material in coarse and fine sawdust for each time and concentration of NaOH. The raw material for mahogany wood sawdust in coarse and fine form can be seen in Figure 2.

Table 1 and Table 2 show that some sample from coarse mahogany wood sawdust obtained more results than some sample from fine mahogany wood sawdust. This is different from the research that was done by Obum (2019), where the smaller the particle size, the greater the surface area, the more reactive contact (NaOH) there is, and the results obtained also increase. According to Gaban et al. (2013), one of the possible causes is that in the pretreatment of raw materials, there is a process of reducing the particle size of the material, which is carried out by cutting with a crusher which damages the cellulose structure, causing the cellulose structure to become damaged so that it can turn into other carbohydrate compounds and does not react with NaOH. Thus reducing the formation of $C_2H_2O_4$ as a product.

(a) (b)

Figure 2: Picture of (a) coarse mahogany wood sawdust, and (b) fine mahogany sawdust

3.3 The effect of NaOH solution concentration

The concentration of NaOH and hydrolysis time can affect the production of $C_2H_2O_4$. It was observed that at higher concentration of NaOH, longer hydrolysis time was needed to reach the optimum point. After reaching the optimum yield point, the yield. Precipitation by NaOH produced $Na_2C_2O_4$, which is obtained by filtering the sample solution. In the hydrolysis stage of cellulose, NaOH solution was used as a hydrolysis material, the lignin in mahogany sawdust was released from its bonds with cellulose, and when heated, it was oxidized and decomposed into $Na_2C_2O_4$ and CH_3COONa. In this study, 200 mL of NaOH solution with concentrations of 1 N and 3 N was used, which was hydrolyzed with 15 g of mahogany sawdust.

Table 1: Data from the result of $C_2H_2O_4$ synthesis using coarse mahogany wood sawdust

Hydrolysis Time (min)	NaOH Concentration(N)	$C_2H_2O_4$ Mass (g)		Average $C_2H_2O_4$ Mass (g)	Average Yield (%)	$C_2H_2O_4$ Theoretical Yield (%)
		Sample I	Sample II			
60	1	2.1	2.6	2.35	15.67	0.40
60	3	1.7	1.8	1.75	11.67	0.30
120	1	1.4	1.2	1.3	8.67	0.22
120	3	2.1	1.5	1.8	12	0.30

Table 1 shows that hydrolysis using 1 N NaOH has an optimum time at 60 min with a yield of 15.67 %. But, when hydrolysis time was extended to 120 min, there was a decrease in yield to 8.67 %. This could be due to the further decomposition of $Na_2C_2O_4$ into carbon dioxide (CO_2). At the concentration of 3 N NaOH solution, the yield of $C_2H_2O_4$ increased with longer hydrolysis time but the yield produced at hydrolysis time at 60 min was below 1 N NaOH. This could be caused by the degradation of $C_2H_2O_4$ due to the concentration of NaOH used being too high (Sunarti, 2016).At hydrolysis time of 60 min, it can be seen that yield using 1 N NaOH was higher than using 3 N NaOH. That could happen because at that time the 1 N NaOH already dissolved in water and effectively decomposed lignin. But, at hydrolysis time of 120 min, 1 N NaOH already evaporated so there's no further lignin decomposition. Meanwhile, 3 N NaOH has not yet evaporated and still effectively decomposed lignin (Elwin et al., 2014).

From Table 2, a longer reaction time can increase the contact of the reactant, so a relatively large amount of $C_2H_2O_4$ was obtained. Fine sawdust mahogany wood with NaOH concentrations of 1 N and 3 N experienced an increase in hydrolysis time at 120 min. The higher concentration of NaOH solution also increased the yield obtained. However, an additive concentration that is too high could result in the decomposition of $Na_2C_2O_4$ back into CO_2 and water vapor, thereby reducing the yield of oxalate (Sunarti, 2016).

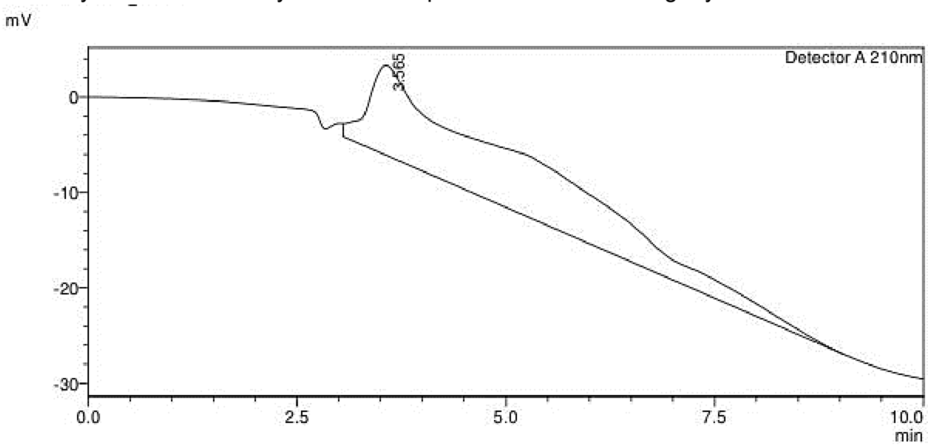
Table 2: Data from the result of $C_2H_2O_4$ synthesis using fine mahogany wood sawdust

Hydrolysis Time (min)	NaOH Concentration(N)	$C_2H_2O_4$ Mass (g)		Average $C_2H_2O_4$ Mass (g)	Average Yield (%)	$C_2H_2O_4$ Theoretical Yield (%)
		Sample I	Sample II			
60	1	1.8	1.5	1.65	11	0.28
60	3	1.5	1.2	1.35	9	0.23
120	1	1.4	2.3	1.85	12.33	0.31
120	3	1.8	1.5	1.65	11	0.28

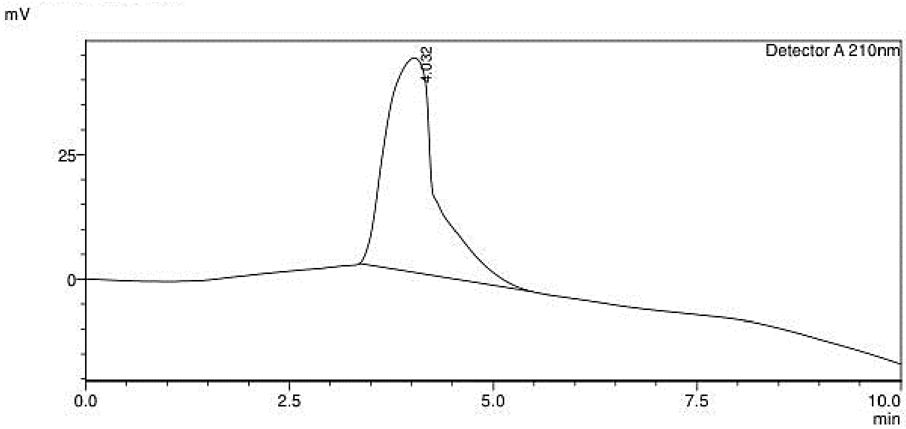
In this study, the highest yield of 15.67 % was obtained using 1 N NaOH with a hydrolysis time of 60 min on the raw material of coarse mahogany sawdust. After that, the yield was decreased to 8.67 % when the hydrolysis time reached 120 min with 1 N NaOH. This could be due to the further decomposition of $Na_2C_2O_4$ into CO_2.
In a study by Mufid et al. (2018), the same thing was also observed where the optimal conditions for producing $C_2H_2O_4$ from teak wood sawdust with a yield of 20% were obtained using 1 N NaOH with a hydrolysis time of 60 min on the raw material of coarse teak sawdust. However, when the hydrolysis time was increased to 70 min, the yield decreased to 16.27 %. Several factors can cause this, including the type of wood, filtering process that not optimal, and the influence of temperature.

3.4 HPLC (High-Performance Liquid Chromatography) analysis result

HPLC analysis aims to identify $C_2H_2O_4$ compounds found in mahogany wood sawdust.



(a)



(b)

Figure 3: HPLC chromatography on (a) standard $C_2H_2O_4$, and (b) $C_2H_2O_4$ from mahogany wood sawdust

For testing $C_2H_2O_4$ content in the Shimadzu LC 2030 HPLC device, an HPX 87H aminex biorad column was monitored by a UV – vis detector at 210 nm and the mobile phase was H_2SO_4 5 mM with a flow rate of 0.6 cm/min. The results of the analysis using HPLC obtained a retention time value of 3.565 min on standard $C_2H_2O_4$. While the retention time on $C_2H_2O_4$ from mahogany sawdust obtained a result of 4.032 min.

If the retention time standard $C_2H_2O_4$ solution and $C_2H_2O_4$ solution from mahogany wood sawdust are the same or close, it can be concluded that the compounds are the same (Willard et al., 1988).

4. Conclusions and recommendations

Mahogany wood contains 35 – 50 % cellulose, 20 – 30 % hemicellulose, and 25 – 30 % lignin. Hence, it can be used as a raw material for synthesis of $C_2H_2O_4$. The concentration of NaOH and hydrolysis time can affect the production of $C_2H_2O_4$. It was observed that at higher concentration of NaOH, longer hydrolysis time was needed to reach the optimum point. The highest yield of 15.67 % was obtained using 1 N NaOH with a hydrolysis time of 60 min on the raw material of coarse mahogany sawdust. After reaching the optimum yield point, the yield decreased when using 1 N NaOH with a hydrolysis time of 120 min. The decreased yield can be caused by several factors, namely the concentration of solvent or hydrolyzing agent, time, temperature, and speed of the stirring process. The HPLC analysis indicated a result for standard $C_2H_2O_4$ with a retention time of 3.565 min and $C_2H_2O_4$ from mahogany wood sawdust with a retention time of 4.032 min. The close retention time result shows that both compounds are the same compound. For future study, it is recommended that the temperature is controlled in constant conditions to minimize its effects on the results obtained. This is because the temperature could significantly affect the results obtained. In addition, it is recommended to explore the potential of Mahogany wood dust for synthesis of other ingredients besides oxalic acid. There is a need to ensure the quality of the materials used to be consistent in the process.

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