The Utilization of Oil Palm Fronds in Producing Oxalic Acid through Oxidation

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Abstract. As one of the solid waste generated by palm oil plantations, Oil Palm Fronds have the potential to be further processed into useful products since the presence of cellulose, hemicellulose and lignin. Hence, the objective of this study was to utilize oil palm fronds in producing oxalic acid through oxidation process using. To achieve the objective, this study assessed conversion of cellulose, yield and quality of oxalic acid produced. Two stages are carried out, namely oxidation and crystallization. Assays on raw materials revealed the cellulose content of 29.2 percent. The largest yield of oxalic acid was 43.31 percent, the highest conversion of cellulose was 58.86 percent. FTIR and melting point analysis were employed in this study. These analyses indicated that the functional groups have reached the standard of oxalic acid with a melting point of 102.1 ^{0}C, which showed that the oxalic acid obtained was oxalic acid dehydrate.

INTRODUCTION

Oil palm plantations continue to expand in almost all provinces in Indonesia and now classified as a second world producer of palm oil after Malaysia's [1]. The area of oil palm plantations is able to produce oil palm fronds waste of 10.14 million tons of which have not been used optimally. The utilization is still on the extent of research for animal food, nitrocellulose and compost. Components of the oil palm frond are content of cellulose, hemicellulose, and lignin, which showed that oil palm fronds are likely to be further processed into useful products and economically valuable. Based on the content contained in the oil palm fronds, it has the potential to be used as raw material in the manufacture of oxalic acid.

The purpose of this research is to utilize oil palm fronds as waste into products that have more value, for instance oxalic acid.

Theory

Oil palm frond is one of the solid wastes from oil palm plantations that can be obtained throughout the year in conjunction with harvesting fresh fruit bunch. The total potential amount of waste in the Indonesian oil palm fronds are 10.14 million tons / year [2]. Oil palm fronds contain of 5.8% crude protein, 1.07% fat, 48.6% crude fiber, 3.3% ash and 29.8% total digestible nutrients. The components of the crude fiber in oil palm fronds are as composed in Table 1 [3].

Table 1. Chemical Composition of Oil Palm Fronds [3]

Chemical Components	(%)
Cellulose	31.5 ± 0.3
Hemicellulose	19.2 ± 0.1
Lignin	14.0 ± 0.5
Ash	12.3 ± 0.2
Protein	9.4 ± 0.1

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Cellulose which is an organic compound of formula ($C_6H_{10}O_5$) n is a straight chain polymer composed of D-glucose subunits linked by β-1,4 glycosidic bond. This long chain is connected due to the hydrogen bonds and Van der Waals forces.

Oxalic acid is one of organic acid that contained in most plants. A large amount of oxalic acid is contained in vegetables, such as spinach, chicory, cabbage, cucumbers and potatoes. [4]. Cellulose that contained in the oil palm fronds fiber can be synthesized into oxalic acid via oxidation reaction by using nitric acid, according to the following reaction [5]:

$$6HNO_3 + C_6H_{10}O_5 \rightarrow 3C_2H_2O_4 + 5H_2O + 6NO$$

Method

The process of making oxalic acid from oil palm fronds is done through several stages, namely: oil palm fronds preparation stage, raw material analysis stage, oxalic acid production stage, and product analysis stage (oxalic acid).

In preparation stage, oil palm fronds are cut into small pieces and dried in the oven at 105 ^{0}C until the weight of the oil palm fronds are constant. Analysis of raw materials such as water content using the oven and cellulose content analysis Chesson method. Oil Palm fronds that had dried pulverized using a ball mill and produce powder sieved with a sieve of 50 mesh.

After that, the powder was inserted into the three-neck flask and nitric acid is added, heated at 75 ^{0}C temperature with a predetermined time and thereafter was filtered. The filtrate was added with $CaCl_2$ 4% solution until the precipitation of calcium oxalate was formed. The precipitate was dissolved in H_2SO_4 2N and then filtered and washed using 96% ethanol. The filtrate is evaporated using a water bath at a temperature of 80 ^{0}C and then cooled to form oxalic acid deposits in the form of a white crystalline needles. The result obtained is purified through the recrystallization process using ethanol 96%.

The product analysis of oxalic acid includes quantitative analysis in the form of yield and qualitative analysis in the form of FTIR and melting points.

RESULTS

Analysis of water content and oil palm fronds cellulose content

Raw material of palm oil that is used in this study contains water content of 46.6%. While cellulose content of the oil palm fronds is 29.2%.

Oxalic Acid Yield

The yield of oxalic acid yield is defined as follows:

$$Yield\ (\%) = \frac{\text{mass of oxalic acid crystals}}{\text{mass of palm oil fronds}} \times 100\ \% \quad (1)$$

The relation between nitric acid concentration with the yield of oxalic acid in various reaction times and reaction temperature of 75 ^{0}C, as well as nitric acid fronds ratio of 1:6 (w/v) can be seen in Figure 1.

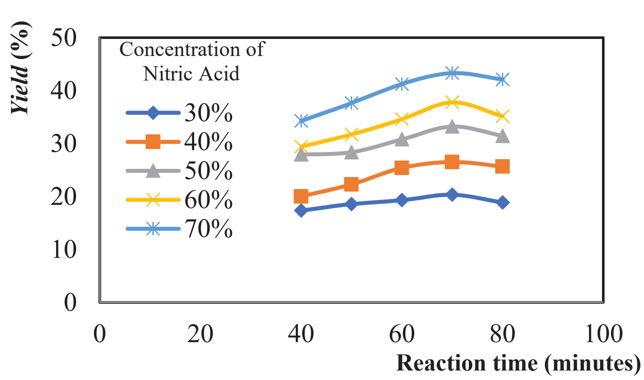

FIGURE 1. Effect of Nitric Acid Concentration and Reaction Time on the Yield of Oxalic Acid

Fig. 1 revealed that there is an increase in the yield of oxalic acid along with the increase of nitric acid concentration and reaction time until there is a decrease in the yield. The increase in yield is due to the increase of oxidizing ability of nitric acid due to rise in concentrations of nitric acid. Meanwhile, the decrease is due to the advanced oxidation reaction that occurs between oxalic acid with residual of nitric acid, forming CO_2, NO, and H_2O [7]. The yield of oxalic acid will increase exponentially with time, until reached a point where the yield will decrease [6]. Further oxidation reaction that occurs can be seen in the following reaction:

$$3C_2H_2O_4\,(aq) + 2HNO_3\,(aq) \rightarrow 6CO_2\,(g) + 4H_2O\,(g) + 2NO\,(g)$$

The best reaction time in this experiment is at 70 minutes, where the yield of oxalic acid that was produced are greater. A decline in the yield was occurred at 80 minutes due to an advanced oxidation reaction. Further oxidation reaction can be avoided by reducing the residence time in order to obtain as much oxalic acid as possible [5].

Cellulose Conversion

Cellulose conversion aims to determine the amount of cellulose that reacts into oxalic acid crystals. This process is expressed as equation 2.

$$X = \frac{S_1 - S_2}{S_1} \tag{2}$$

where:
X = Cellulose conversion
S_1= Contents of cellulose in raw materials
S_2= Contents of cellulose in the residue that has reacted with nitric acid in various concentrations and reaction time

Fig. 2 shows the effect of nitric acid concentration and reaction time to the increase in cellulose conversion. The conversion of cellulose into oxalic acid increases with increasing concentration of nitric acid [8]. This can be seen from the overall results on the above chart, which showed that at every point there is an increase of conversions up to 80 minutes. The conversion of cellulose into oxalic acid increases with increasing nitric acid concentration and reaction time.

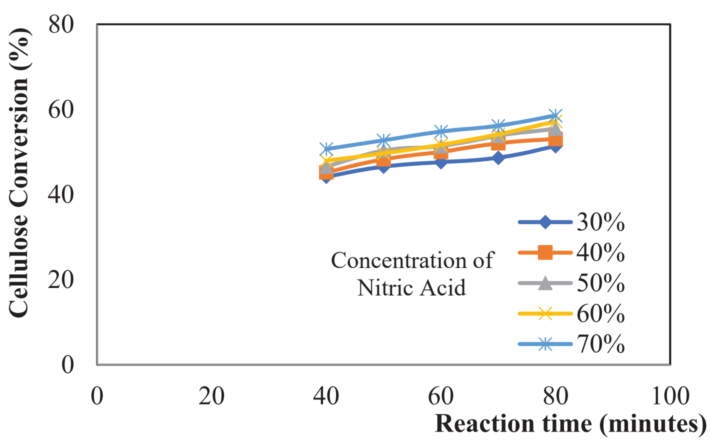

FIGURE 2. Effect of nitric acid concentration and reaction time on the conversion of cellulose in oil palm frond

Relation between Yield and Conversion

The relationship between conversions of cellulose with yield oxalic acid can be seen in Fig. 3.

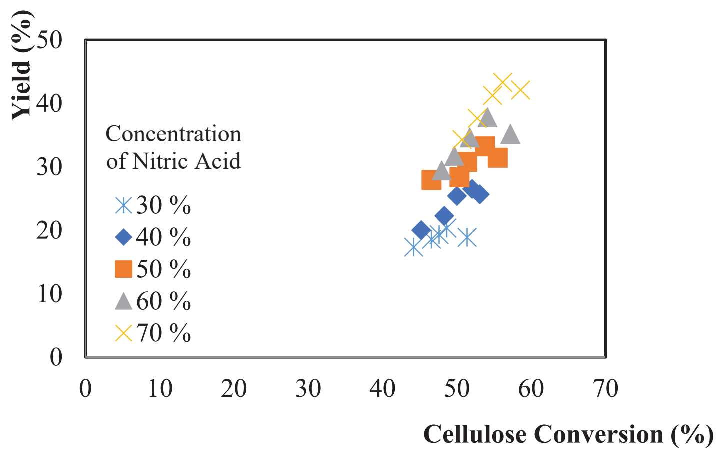

FIGURE 3. Yield vs Cellulose Conversion

Fig. 3 shows a yield decrease with increasing cellulose conversion. The reduction of yield due to the possibility of further oxidation reaction that occurs between oxalic acid with nitric acid residue in the reaction, so that the formation of CO_2, NO and H_2O.

FTIR ANALYSIS

Figure 4 and Figure 5 shows a comparison of characteristics between standard oxalic acid and synthesized oxalic acid.

Strain vibration between standard oxalic acid and synthesized oxalic acid from oil palm fronds has a peak that is not much different as shown in Table 2. It is proven that in this study, the resulting compound is oxalic acid. Other peaks contained in FTIR analysis results indicated that the synthesized oxalic acid obtained is still not pure due to the presence of impurities in the crystals of oxalic acid.

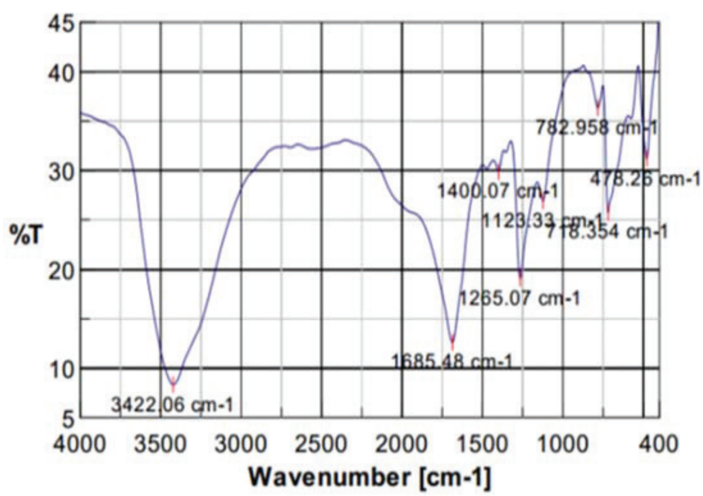

FIGURE 4. Standard Oxalic Acid Infra Red Spectrum [15]

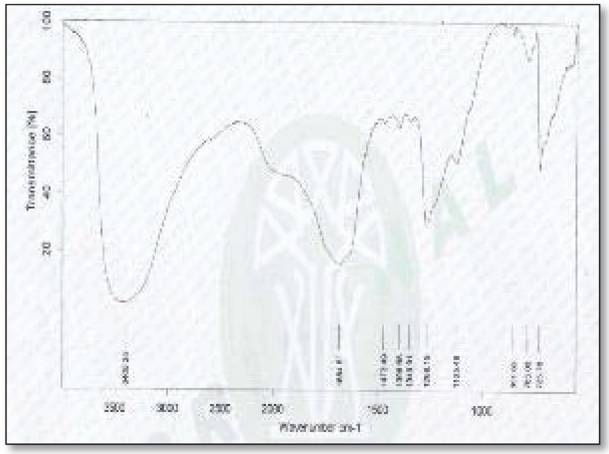

FIGURE 5. Synthesized Oxalic Acid Spectrum from Oil Palm fronds

Table 2. Comparison of Standard Oxalic Acid Infra Red Spectrum with Synthesized Oxalic Acid of Oil Palm Fronds

No	Functional Group	Standard Oxalic Acid	Synthesized Oxalic Acid from Oil Palm Fronds
1.	O-H	3422.06	3405.35
2.	C=C	1685.48	1684.61
3.	C-O	1123.33	1125.48
4.	C-H	718.35	725.78

MELTING POINT ANALYSIS

Melting point analysis was performed to determine the purity as well as to identify solid material [9]. The result of melting point was 102.1 ^{0}C. Furthermore, pure oxalic acid has a melting point of 101.5 ^{0}C [10]. Based on aforementioned analysis, synthesized oxalic acid had as same characteristics as pure oxalic acid. This can be concluded that the product on this research is oxalic acid and can be classified as oxalic acid dehydrate types.

CONCLUSION

The highest yield of oxalic acid from oil palm fronds is obtained on 70% of nitric acid concentration and 70 minutes of reaction time that is equal to 43.31%. The largest cellulose conversion is obtained at 70% of nitric acid concentration and 80 minutes of reaction time that is equal to 58.56%. Oxalic acid that is obtained from the oxidation reaction of oil palm fronds is dehydrate oxalic acid.

The content of cellulose, hemicellulose and lignin on oil palm fronds allows it to be converted into a more useful material.

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