The influence of hydrolysis time on the crystallinity degree of cellulose and $\alpha$ – cellulose of oil palm wood (*Elais guinensis* Jack)

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**Abstract.** The research to observe the influence of hydrolysis time towards the degree of crystallinity owned by oil palm wood (*Elais guinensis* Jack) based cellulose and $\alpha$–cellulose had been conducted. Cellulose was extracted from oil palm wood by means of alkali treatment as the first stage then it was bleached with NaOCl 5% , 10 drops of CH$_3$COOH glacial, and heated 70°C while stirred for an hour. The residue was added with HNO$_3$ 0.05N at 70°C while stirred for an hour to produced cellulose. After dissolved into NaOH 17.5%, cellulose will yield $\alpha$-cellulose and then it was hydrolyzed by HCl 2N for 20, 40, and 60 minutes. Functional group analysis using FT-IR showed the functional group of O-H, C-H, and C-O-C in the molecules of cellulose and $\alpha$–cellulose. Degree of crystallinity from cellulose and $\alpha$–cellulose were analyzed using x-ray diffraction. The highest degree of crystallinity of cellulose and $\alpha$ – cellulose are 79.538 % and 80.036 % respectively for 40 minutes hydrolysis time.

1. **Introduction**

Oil palm is one of Indonesia's mainstay commodities that grows very rapidly, especially in Sumatra and Borneo. Oil palm is one of the plantation waste and it needs large cost to recycle it. In general, to overcome these things are usually done by poisoning, accumulating, and burning it. This, of course, also will cause emissions that can pollute the air and impacts to the environmental sustainability [1].

The moisture content in wet oil palm is 40%, its density ranges from 0.2-0.6 g/mL with an average density of 0.37 g/mL. In constant dry state, oil palm wood contains cellulose (30.77%), pentose (20.05%), lignin (17.22%), hemicelluloses (16.81%), water (12.05%), ash (2,25%), and SiO$_2$ (0.84%) [2,3].

Cellulose polymers are composed of two parts, those are regular (crystalline) and irregular (amorphous) chain. The degree of crystallinity of polymer greatly affects to the polymer properties associated with the utilization. In general, cellulose is relatively in crystalline form [4].

Crystallinity is an important property in polymers that exhibits a bond between molecular chains so that producing a more ordered array of molecules. The high properties of crystallinity cause high and rigid stress. Polymer and synthetic chain structures have different crystallinity. The crystallinity of the polymer is influenced by the type of chain structure and bond type [5].

The acid hydrolysis method is a simpler method, without having to go through several stages such as enzymatic hydrolysis. Acid hydrolysis requires a relatively shorter processing time, simpler technology, easier setting conditions, and relatively lower cost [6].
The hydrolysis process using acid is influenced by material size, stirring rate, acid concentration, material ratio, heating temperature, and heating time. The smoother the size of the surface of the material, the higher the reaction rate and it will increase the convection of the reaction. The higher the hydrolysis temperature the hydrolysis will take place more quickly [1].

Rini (2016) has conducted a study on the preparation and characteristics of microcrystalline cellulose from HVS paper waste using 2.5 N HCl solution with varieties of hydrolysis time of 5, 10, 15, 20, and 30 minutes. From the research, it can be concluded that the longer of the acid hydrolysis time, the amount of yield is much more produced [1].

Veronicha (2017) studied about the production of microcrystalline cellulose from cellulose of empty fruit bunches of oil palm (Elaisguinnensis) using hydrochloric acid. The XRD results showed the presence of two relatively maximum peaks of cellulose microcrystals, i.e. 20° and 22° at 20 angle. The degree of crystallinity of the cellulose microcrystals was 72.9% [6].

A study on the analysis of the effect of hydrolysis time on the mechanical properties of crystalline cellulose from a mixture of sawdust, bengkirai wood, teak wood, and meranti wood had been also conducted by Arini in 2015. The study was carried out by hydrolyzing cellulose using 37% HCl and hydrolysis time variations of 30, 45, and 90 minutes. The optimum degree of crystallinity which was 74.49%, was obtained from the hydrolysis process for 30 minute [7].

2 Materials and Methods
2.1 Material
In this study, the materials used in this research where oil palm wood which was harvested from oil palm plantation in Kutacane, Aceh. NaOH, HCl, NaOCl, HNO₃, and CH₃COOH were supplied by Merck Indonesia.

2.2 Procedure
2.2.1. Extraction of cellulose from oil palm wood powder
A total of 50 g of oil palm powder is inserted into a glass beaker, then added aquades until the oil palm powder is completely submerged and stirred at 50°C for 2 hours then filtered. The residue was added with 500 mL of 2% NaOH solution and stirred at 80 °C for 2 hours then filtered and washed until the filtrate was neutral and resulting pulp of oil palm. The pulp was dried in oven at 50°C. The dried pulp from the alkali process was added with 250 ml of 5% NaOCl and 10 drops of glacial acetic acid while continuously stirring at 60-70°C for 1 hour then cooled, washed with aquadest and filtered. The residue was added with 250 mL of 0.05 N HNO₃, stirred at 70°C for 1 hour then filtered and washed until the filtrate was neutral. The washed residue is known as cellulose

2.2.2. Isolation of α-cellulose
The cellulose was dissolved with 17.5% NaOH solution, filtered and the residue washed with aquadest repeatedly until the pH of the filtrate was neutral. The resulting α-cellulose was dried in an oven at 60 °C and then analyzed by FTIR

2.2.3. Cellulose and α-cellulose hydrolysis using HCl 2 N
Respectively 4 gr of cellulose and α-cellulose was inserted into the neck flask. It was added by 80 mL HCl 2 N and then assembled in reflux apparatus for 20 minutes. After that, it was washed with aquadest until the pH was neutral then filtered and dried in the oven. The same experiment was conducted for 40 and 60 minutes. [8]

2.3 Cellulose and α-cellulose characterization
2.3.1. Functional groups analysis using FT-IR spectroscopy.
Firstly, the sample was clamped on the sample place and then placed on the device toward the infrared ray. The result would be recorded into a scale paper that was a curve of the wave number to the intensity.
2.3.2. **Crystallinity degree measurement using X-Ray Diffraction.**

The fundamental principle of x-ray diffraction is to diffract the light through the crystal gap. The diffraction of light by these lattices or crystals can occur when the diffraction comes from a radius having a wavelength equal to the distance between atoms, which is about 1 Angstrom. Radiation used in the form of x-ray radiation, electrons, and neutrons. X-rays are high-energy photons with wavelengths ranging from 0.5 to 2.5 Angstroms. When the X-ray beam interacts with a material, some of the files will be absorbed, transmitted, and partly dissipated. This diffraction scatter is detected by XRD. X-ray files are dissipated there are mutually eliminating because the phase is different and there are also mutually reinforcing because the same phase. Integrating X-ray beams are called diffraction files.

3 Results and Discussions

3.1 **Functional groups analysis by FT-IR spectroscopy.**

Functional group analysis using FT-IR spectroscopy for cellulose and α - cellulose from oil palm wood has been characterized and the result can be seen in Figure 1.

![Figure 1. FT-IR spectra of cellulose and α-cellulose from oil palm wood](image)

The spectra showed the functional groups cellulose and α-cellulose are in the range of wave number 4000-500 cm\(^{-1}\). Based on the figure above, the O-H peaks on cellulose and α-cellulose are showed at the wave number of 3410.15 and 3448.72 cm\(^{-1}\) respectively. The C-H groups are identified at wavelengths of 2900.94 and 2893.22 cm\(^{-1}\). In addition, the wave number of 1373.32 cm\(^{-1}\) indicates the presence of C-O-C group in both samples which indicates the presence of a glycoside bond in the structure of the compounds.

3.2 **Effect of hydrolysis time on degree of crystallinity of cellulose and α – cellulose.**

X-ray diffraction analysis aims to determine the degree of crystallinity of cellulose and α-cellulose that have been hydrolyzed with varieties of hydrolysis time of 0, 20, 40 and 60 minutes. The method is developed by L.Segal, which determines the degree of crystallinity by estimating the amount of crystalline phase in phase 002 and the amorphous (Am) phase in cellulose, the amorphous phase of cellulose is at the angle of 2θ about 18.3°, which is the minimum angle between 002 and 110. The crystallinity index is calculated based on the ratio between the height of 002 (I\(_{002}\)) and the minimum peak height (I\(_{Am}\)). The degrees of crystallinity of cellulose and α - cellulose obtained from this study are shown by Table 1 below.

![Table 1](image)
Table 1. Degree of crystallinity of cellulose and α–cellulose.

| Hydrolysis time (minute) | Degree of crystallinity (%) |
|--------------------------|----------------------------|
|                          | cellulose | α–cellulose |
| 0                        | 74,541    | 74,297     |
| 20                       | 77,966    | 79,463     |
| 40                       | 79,538    | 80,036     |
| 60                       | 78,795    | 79,622     |

From the table above, it can be explained that the highest degree of crystallinity of cellulose and α-cellulose is achieved by using treatment of hydrolysis for 40 minutes, which is respectively 79.538% and 80.036%. In 40 minutes hydrolysis time, the cellulose and α-cellulose are well hydrolysed, where the amorphous portions of cellulose and α-cellulose are lost and leaved only the crystalline regions. The crystalline region of cellulose is formed by hydrolyzing cellulose with acid and due to the presence of hydrogen bonds and van der walls force, cellulose and α-cellulose structures are arranged regularly.

At the time of hydrolysis of 60 minutes, degree of crystallinity of cellulose and α-cellulose decreased, that is equal to 78.795% and 79.622%. It is caused by deformation and irregularity of the cellulose chain. The irregularity of the cellulose is caused by the use of HCl and indicates the opening of cellulose chain arrangement so that the arrangement of polymer chains and cellulose are more easily degraded into glucose. The irregularity affects degree of crystallinity. The more regular chain of cellulose, the greater of degree of crystallinity.[6]

From the measurement of X-ray diffractometer, it is known that cellulose and α-cellulose also contain crystalline phases with high degree of crystallinity. This can be seen on the appearance of specific peaks at 20 angle of 12°, 18°, 20°, and 22°.

The X-ray diffraction results and the 2θ angle at I_{Am} and I_{002} for oil palm wood cellulose in various hydrolysis time are shown in Fig. 2 and Table 2.

![Figure 2. X-ray diffraction of cellulose from oil palm wood.](image)

From figure 2, it shows the diffraction pattern of cellulose with the variation of hydrolysis time 0, 20, 40, and 60 minutes which have the same tendency. The difference only occurs in the sharpness of the peak.
Table 2 2θ angle on I_Am dan I_002 of cellulose.

| Hydrolysis time (minute) | I_Am     | I_002     |
|--------------------------|----------|-----------|
| 0                        | 18.70°   | 22.48°    |
| 20                       | 18.88°   | 22.30°    |
| 40                       | 18.82°   | 22.70°    |
| 60                       | 18.58°   | 22.68°    |

In Table 2 shows the position of the main peak (intensity of crystalline phase (I_002)) of cellulose which varies according to hydrolysis time variation, i.e. 22.48°; 22.30°; 22.70°; 22.68°. This peak shows the distance between hydrogen bonds in cellulose. The amorphous phase minimum peak intensities (I_Am) are at 18.7°; 18.88°; 18.82°; 18.58°.

In addition to cellulose, α-cellulose has also been characterized by XRD analysis and the results are shown in Figure 3.

Figure 3. X-ray diffraction of α–cellulose from oil palm wood.

From Figure 3, it can be seen that 2 sharp peaks are belonged to α–cellulose. this proves that the crystalline phase is contained in α-cellulose. The highest peak is found in hydrolysis process for 40 minutes. 2θ angle of α-cellulose is also obtained and the results are shown in Table 3 below.

Table 3. The angle of 2θ at I_Am and I_002 of α-cellulose.

| Hydrolysis time (minute) | I_Am     | I_002     |
|--------------------------|----------|-----------|
| 0                        | 12.98°   | 20.06°    |
| 20                       | 12.98°   | 20.04°    |
| 40                       | 12.98°   | 20.06°    |
| 60                       | 12.98°   | 20.06°    |

Based on the table, the main peak position (intensity of the crystalline phase (I002)) of the cellulose shows varying results according to the hydrolysis time, that is, respectively, 20.06°; 20.04°; 20.06°; and 20.06°. This suggests that α-cellulose is indeed in crystalline form and characterized by two relatively sharp maximum peaks, proving that there is still a slight amorphous phase in α-cellulose.
due to the acid that hydrolyzes the amorphous part of α-cellulose and only some of the cellulose are penetrated into the α-cellulose molecules. The minimum peak intensities of amorphous phase ($I_{Am}$) are at 12.98°; 12.98°; 12.98°; 12.98°.

4 Conclusion
From this study it can be concluded that cellulose and α-cellulose isolated from oil palm have been successfully done. This is evidenced in the FT-IR spectrum showing the presence of O-H, C-H, and C=O groups in cellulose and α-cellulose. In addition, the variation of time of cellulose hydrolysis and α-cellulose affects the degree of crystallinity, which can increase the degree of crystallinity of cellulose and α-cellulose. The highest degree of crystallinity of cellulose and α-cellulose was obtained at the time of hydrolysis for 40 minutes, i.e. 79.538% and 80.036%.

References
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