Production Nanocellulose from Raw Materials For Oil Palm Empty Bunches (TKKS) with Hydrolysis and Freeze Drying Methods

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Abstract. Accumulation Oil Palm Empty Bunches (TKKS) cause environmental problems if not solved. TKKS has a high cellulose composition, so it can be used as nanocellulose which has a higher value. The process of making nanocellulose from TKKS through the isolation stage of α-cellulose with a delignification process using Sodium Hydroxide (NaOH) 17.5% (b / v) at 80°C, bleaching using Hydrogen Peroxide (H₂O₂) 10% (v / v), hydrolysis using sulfuric acid and drying using freeze drying at a heating temperature of 53°C for 7 hours. Cellulose yield produced from the isolation process of α-cellulose from TKKS was 20.8%. The results of drying process will reduce the aggregation of particles in the nanocellulose produced, so that nanocellulose is produced at 160-298 nm. Keywords: nanocellulose, hydrolysis, freeze drying.

1. Introduction

Oil palm is one of the plants that thrives in the territory of Indonesia. The main products of oil palm is kernels (palm kernel), side products of oil palm processing is oil palm empty fruit bunches (TKKS) in the range of 20-23% [22]. Components of the TKKS shown in Table 1.

Table 1. Composition of TKKS (Source : a [16] and b [15])

| Composition        | Content (%)   |
|--------------------|---------------|
| Lignin⁰           | 21.27 - 36.68 |
| Cellulose⁰        | 35.66 - 57.75 |
| Hemicellulose⁰    | 6.61 – 15.96  |
| Water content⁰    | 8.56          |
| Tannin, alkaloids,| 4.19          |
| etc⁰              |               |

This large amount of TKKS waste will cause problems for the environment. High cellulose content in TKKS has the potential to be used as nanocellulose. Cellulose is the main component in lignocellulosic biomass which consists of linear homopolysaccharide from the D-anhydroglucosa unit with β-1,4-glucoside bonds.

Nanocellulose has a higher value than TKKS. The purpose of this research was to make nanocellulose from TKKS and determine the yield and diameter of nanocellulose that produced by the hydrolysis method and freeze drying.
The anhydroglucose unit has a hydroxyl group which forms strong hydrogen bonds with intamolecular glucose units and with intamolecular hydrogen [10]. X-ray analysis proves that cellulose is a long parallel chain that is bound together by hydrogen bonds. Cellulose in the form of long fibers as seen in Figure 1 [3].

![Figure 1. Structure Of Cellulose (Source : [14])](image)

Nanocellulose is a new type of cellulose material that has increased crystallinity, aspect ratio, surface area, and increased dispersion ability and biodegradation. With this capability, nanocellulose can be used with good quality for polymer reinforcement fillers, additives for biodegradebale products, membrane reinforcement, dispersion thickener and drug and implant carrier media [5]. Composite cellulose nanofiber is one application of nanocellulose, by adding polymers to strengthen the physical properties of the polymer [11].

Production nanocellulose by isolation process of α-cellulose was carried out from TKKS and acid hydrolysis. The isolation process of α-cellulose is carried out by the alkalization process using NaOH solution to remove the content of hemicellulose and lignin contained in the TKKS which has an alkali soluble nature (delignification process) and followed by H₂O₂ solution to produce purer α-cellulose [20]. The NaOH solution used has a concentration of 17.5% which aims to increase the purity of α-cellulose, which is based on the degree of polymerization and solubility in the compound of sodium hydroxide (NaOH) 17.5%. Cellulose is divided into three types [17]:

- α-cellulose is a long-chain cellulose and does not dissolve in 17.5% NaOH solution or strong base with 600-1500 polymerization degrees.
- β-cellulose is a part of cellulose which dissolves in 17.5% NaOH solution or strong base with a polymerization degree of 15-90.
- γ-Cellulose has a degree of polymerization of less than 15 which easily dissolves in 17.5% NaOH solution and no precipitate will form after the solution is neutralized.

Bleaching using hydrogen peroxide (H₂O₂) for bleach the fiber and eliminate the content of lignin, hemicellulose, and impurity [18]. The use of H₂O₂ was chosen because it was efficient, low cost, and environmentally friendly [12]. The concentration of H₂O₂ used is 10% (b / v) with optimum conditions at temperature 70-80°C for 1 hour which can produce a constant brightness of cellulose [9].

Production nanocellulose is carried out by various methods such as acid hydrolysis, ultrasonic techniques, and enzymatic hydrolysis [23]. The method of acid hydrolysis often used because it produces small size nanocellulose. Strong acids that used such as H₂SO₄, has purpose to break down the glycoside bonds in cellulose [2]. The acid hydrolysis process to remove the amorphous part of the cellulose chain so that cellulose crystal isolation can be carried out [6]. The scheme of acid hydrolysis on cellulose shown in Figure 2.

![Figure 2. Acid Hydrolysis can Eliminate Amorphous Parts from Cellulose (Source : [6])](image)

According to Dong et al in Börjesson (2015), hydrolysis process using 64% -weight H₂SO₄ with optimal conditions at temperature 45°C with a ratio of 8.75 ml / gr due to stable nanocellulose obtained [1]. The result of nanocellulose is dried using a freeze drying method through two stages of the process, formation of ice crystals (freeze) and sublimation ice molecules (drying). This sublimation process occurs where solid water is converted into steam without passing through the
liquid phase which is carried out under triple water properties in the range 20°C-50°C, to reduce the aggregation of particles in the nanocellulose [21].

Morphology of nanocellulose can be analyzed by SEM (Scanning Electron Microscope). SEM is one type of electron microscope that uses electron beams to describe the surface shape of the material being analyzed. The function of SEM is focus the fine beam of electrons into the sample. This test has a function to determine the morphology, particle size, pore and particle shape material [19].

2. Experimental Details

2.1 Research Procedures
2.2 Chemical and Materials
The material that used in this research is Oil Palm Empty Bunches (TKKS) from the Bogor Palm Oil Plantation. Chemicals that used in this research is NaOH 17.5% (b/v), H₂O₂ 10% (v/v), CH₃COOH 10% (v/v), aquadest and H₂SO₄ 64%.

2.3 Tools
The tools that used in this research is four neck squash, thermometer 0-250°C, stirring motor, stirrer, water bath, hotplate, condenser, water circulator, freeze drying.

3. Result and Discussion
3.1 Pre-Treatment TKKS
In the preparation stage, TKKS are washed using aquadest to remove impurities that still attached at TKKS until clean and dry use sunlight for ± 2 days. Dry TKKS is downsized used grinding and sizing up to 230 mesh in size. TKKS at the pre-treatment stage shown in figure 4.

3.2 Isolation of α-Selulosa from TKKS
Isolation of α-cellulose from TKKS is done by alkalizing treatment using NaOH [8] that purpose to eliminate content of hemicellulose, waxes, pectin and some lignin monomers ([7] and [13]). NaOH 17.5% is used to increase the purity of α-cellulose. α-cellulose has an insoluble nature in 17.5% NaOH [17]. In this research, 17.5% (b / v) NaOH solution was used temperature 70-80 °C for 30 minutes. As a result of this process, there is a layer of blackish brown and residue. This blackish brown layer is lignin and hemicellulose which dissolves in NaOH. This blackish brown coating is also produced from previous research, according to Sudiyana, et al (2016) which states that the layer contains lignin, hemicellulose and residual NaOH from the process [28], that’s shown in Figure 5.
Bleaching process used hydrogen peroxide ($\text{H}_2\text{O}_2$) solution to bleach the fiber by removing content of lignin, hemicellulose, and impurity [18]. Theoretically, perhydroxyl (-OOH) ions are produced from decomposition of hydrogen peroxide into alkaline solutions which can absorb chromophoric groups from lignin and cellulose (carbonyl and conjugated carbonyl groups and quinones) [18]. Bleaching process using $\text{H}_2\text{O}_2$ at concentration 10% has been carried out by Dewanti (2018), which results in a brighter cellulose color which shows that lignin has dissolved, resulting in high purity cellulose [27]. The results of the bleaching process in this research using 10% (v/v) $\text{H}_2\text{O}_2$ solution produced brighter colors. Figure 6 shows the results of the bleaching process carried out for three times.

![Figure 6. Bleaching Result one time (A), twice (B), and three times (C)](image_url)

Bleaching process was carried out three times, because the cellulose results were still dark. Figure 6c shows that the color changes produced after bleaching three times produce brighter cellulose. The isolation process of $\alpha$-cellulose from this TKKS produced cellulose with a yield of 20.8%. The result has a smaller value compared to the research conducted by Dewanti (2018) of 34%. The use of 12% NaOH carried out by Dewanti (2018) allows the content of $\beta$-cellulose and $\gamma$-cellulose to be obtained so that the high purity of $\alpha$-cellulose has not been obtained [27]. Based on the results of SEM analysis, $\alpha$-cellulose produced was 31.5 µm with $\alpha$-morphology of cellulose in the form of fibers on its surface. The results of SEM, $\alpha$-cellulose are shown in Figure 7.

![Figure 7. Results of SEM $\alpha$-cellulose](image_url)

### 3.3 Production nanocellulose using Acid Hydrolysis and Freeze Drying Method

Cellulose was hydrolyzed using $\text{H}_2\text{SO}_4$ 64% for 45 minutes at 45°C by reflux. Hydrolysis of sulfuric acid in cellulose is a heterogeneous process, in which acid diffuses into cellulose and cuts the glycosidic bonds in cellulose polymers. Based on reaction time, hydrolysis can occur in the crystalline region and some hydroxyl groups on the surface of the crystalline area will turn into sulfate groups (-OH groups on cellulose to cellulose -OSO$_3$) [4]. The results of this hydrolysis process have a pH of 2, so that the neutralizing process is needed on nanocellulose formed using distilled water. The results of acid hydrolysis are shown in Figure 8.
Nanocellulose was produced by freeze drying method, which was first put into freeze for 24 hours and continued with the freeze drying process at a heating temperature of 53°C for 7 hours. Freeze drying process has purpose to eliminate the water content of nanocellulose which has been frozen with the principle of sublimation [24]. The results of drying process will reduce the aggregation of particles at nanocellulose [21]. The results of the SEM analysis of nanocellulose by hydrolysis and freeze drying method showed that the nanocellulose morphology was still agglomerated, but the diameter produced was small at 160 - 298 nm. According to Othman et al in Lani et al (2014), agglomeration generally occurs due to the presence of Van der Waals forces that interact between nanoparticles [26]. The results of SEM nanocellulose analysis are shown in Figure 9.

The effect of the freeze drying process on the resulting diameter is quite significant, when compared with the research conducted by Julianto et al (2017) the resulting diameter is 291.4 nm - 8242 μm [25]. This study without the freeze drying process, the freeze drying process is needed to reduce the aggregation of particles in the nanocellulose [21].

4. Conclusions
Production nanocellulose from TKKS by the hydrolysis and freeze drying method has been successfully made with the following yield characteristics: cellulose yield produced from the isolation process of α-cellulose from TKKS was 20.8%, with the size / diameter of nanocellulose produced at 160-298 nm.

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