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Characterization of cellulose from oil palm empty fruit bunches by fast delignification process with different solvents

Karakterisasi selulosa dari tandan kosong kelapa sawit melalui proses delignifikasi cepat menggunakan pelarut yang berbeda

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Abstrak

Ekstraksi selulosa umumnya diawali dengan reaksi delignifikasi yang dilakukan menggunakan cara konvensional yaitu perlakuan basa. Proses delignifikasi dengan menggunakan perlakuan basa membutuhkan waktu yang cukup lama yaitu lebih dari 6 jam untuk proses pemasakan, sehingga biaya untuk memproduksi selulosa cukup besar. Pendekatan delignifikasi menggunakan berbagai pelarut diperlukan untuk menjawab permasalahan saat ini, yaitu mempersingkat waktu reaksi. Pada penelitian ini, dibandingkan dua jenis pelarut untuk proses delignifikasi TKKS yaitu NaOH (basa) dan H_2O_2 (asam), sedangkan waktu yang digunakan untuk proses delignifikasi kedua pelarut tersebut adalah 15 menit. Parameter pengamatan penelitian meliputi kadar lignin, selulosa, dan hemiselulosa. Ekstraksi selulosa dari TKKS menggunakan H_2O_2 dan NaOH menghasilkan kandungan selulosa berturut-turut yaitu sebesar 52,76% dan 66,46%. Namun, secara visual hasil perlakuan NaOH masih berwarna coklat yang menandakan lignin masih terkandung dalam TKKS. Hasil karakterisasi sebelum dan sesudah delignifikasi menggunakan Fourier Transform Infra Red (FTIR) dan X-Ray Diffraction (XRD) menunjukkan bahwa puncak 3301,75 cm^{-1} yang menunjukkan senyawa selulosa mendominasi gugus fungsi, dengan indeks kristalinitas tertinggi sebesar 12,43% pada perlakuan H_2O_2. Hasil analisis Thermogravimetry Analysis (TGA) dan Scanning Electron Microscopy (SEM) menunjukkan bahwa TKKS sebelum dan sesudah perlakuan menunjukkan adanya perbedaan, dilihat dari struktur lignin yang hilang dan nilai TGA yang mulai terdegradasi pada suhu 351,78°C. Oleh sebab itu, berdasarkan penelitian ini pelarut terbaik untuk delignifikasi cepat TKKS adalah H_2O_2 dengan waktu hanya 15 menit.

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[Kata kunci: hidrogen peroksida, lignin, sodium hidroksida, FTIR, XRD]

Abstract

Cellulose extraction typically begins with a delignification reaction using conventional methods, namely alkaline treatment. So far, the delignification process using alkaline treatment requires quite a long time, which is over 6 hours of the cooking process, so the cost to produce cellulose is quite large. The delignification approach using a variety of solvents is needed to answer the current problem, which is to shorten the reaction time. In this study, two types of solvents were carried out for the delignification process of EFB, namely NaOH and H_2O_2, while the time used for the delignification process was 15 minutes. Parameters of research observations included levels of lignin, cellulose, and hemicellulose. Extraction of cellulose from EFB using H_2O_2 and NaOH produced cellulose content of 52.76% and 66.46%, respectively. However, based on visual results of treatment using NaOH are still brown in color which indicates that lignin is still remained in the EFB. The Fourier Transform Infra Red (FTIR) and X-Ray Diffraction (XRD) characterization results before and after delignified EFB showed that a peak of 3301.75 cm^{-1} dominated the functional group that show cellulose, with the highest crystallinity index of 12.43% in the H_2O_2 treatment. The results of Thermogravimetry Analysis (TGA) and Scanning Electron Microscopy (SEM) analyses showed that EFB before and after treatment were different, which can be observed from the loss of lignin structure and TGA values which began to degrade at 351.78°C. Therefore, based on this research the best solvent for fast delignification of EFB was H_2O_2 that only need 15 min.

[Keywords: hydrogen peroxide, lignin, sodium hydroxide, FTIR, XRD]

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Introduction

Empty Fruit Bunches (EFB) of oil palm have been widely used by the community, especially for the extraction of cellulose, which has many derivative products. EFB has a cellulose content of 30-40%. EFB-based cellulose has been widely converted into many products, including paper (Rafidah et al., 2017), helmets (Nikmatin et al., 2017), fire retardant composites (Suriani et al., 2021), and bioplastics (Isroi et al., 2016). However, the cellulose extraction process used to make these products still employ alkaline treatment. Cellulose is a linear chain of anhydroglucose monomer units connected via chains 1–4β-linkage and has amorphous and crystalline materials. Different sources of cellulose will produce different structures, properties, and sizes of cellulose (Razali et al., 2017).

Plants are the primary potential source of cellulose as it is abundant and inexpensive. Oil palm empty fruit bunches are solid waste, which amounts to one-fifth of fresh fruit bunches (FFB). Empty palm fruit bunches are approximately 3.5 kg in mass, up to 130 mm in thickness, 300 mm in width, and 300 mm in length (Chang et al., 2014). In palm oil processing, FFB undergoes steam sterilization so that EFB has high humidity of around 60% (Loh et al., 2017). This humidity affects the next step to obtain cellulose from EFB. The cellulose content in EFB is comparable to other non-wood lignocellulosic sources. Cellulose extraction is usually carried out by alkaline treatment and acid treatment. The treatment during cellulose extraction usually has the following flow: delignification using NaOH and bleaching using chlorine, ozone, and hydrogen peroxide (Leh et al., 2008). Based on research by Leh et al. (2008) and Rosli et al. (2013), the yield of cellulose produced from EFB was 97%, while the time required was more than 6 hours. Chemical pretreatment can be carried out using alkaline or acidic agents, or a combination thereof, under moderate temperature operating conditions.

The alkaline pretreatment method is more widely used because it is a simple yet effective method for converting lignocellulosic biomass (Kim et al., 2016). The pretreatment process using NaOH must be completely in contact with the NaOH compound so that the lignocellulosic pores can be opened. Mechanisms of transporting chemicals for EFB pretreatment can be classified into two. First, it involves the penetration of liquid into the capillaries. Second, it involves the diffusion of liquid substances through the EFB cell wall, the membrane holes, and the diffusion of the interface (Ng et al., 2021). Penetration refers to liquid flow into the air-filled pores of lignocellulose, which is assisted by hydrostatic pressure. However, the process requires a long time, so innovation is needed to speed up cellulose extraction from EFB.

Further research is needed to reduce the costs and chemicals required to extract cellulose from EFB. This study aimed to compare the solvents NaOH (alkaline) and H_2O_2 (acidic) used to obtain cellulose in a short time, 15 minutes from EFB. The results of cellulose extraction were characterized using FTIR, XRD, and SEM.

Materials and Methods

Materials

EFB biomass was obtained from the PTPN VIII Cikasungka-Banten plantation. In this study, the reagents used were NaOH (technical), 30% H_2O_2 (technical), and deionized water.

Pretreatment EFB

EFB fibers chopped into 3-5 cm size were washed thoroughly using deionized water. The clean EFB were ground to a size of 100 mesh. Then the EFB was filtered and ovened at 80°C for 24 hours.

Isolation process of α-cellulose

Five-gram pretreatment EFB after getting constant weight, were added with 12% NaOH or 30% H_2O_2 solution. The mixture then heated to 90°C and stirred at 400 rpm for 1 hour. The precipitate was filtered with Whatman No.40 and washed to a neutral pH with deionized water. The residue was then dried in an oven at 60°C for 24 hours. The α-cellulose sample was measured for the α-cellulose content based on SNI 0444:2009 (Indonesian National Standard, 2009).

Characterization of X-Ray Diffraction (XRD)

Characterization using XRD looks at the residue left from treatment using chemicals which can be seen using D8 Advance. XRD is supported by the position of the Lynx Eye detector and monochromatic Cu Kα with radiation (λ= 0.154 nm). Step mode can be done at 5° to 50° and a range of 2θ. This equipment operates on 40kV and 40mA. The sample's crystallinity index (CrI) can be calculated based on Segal et al. (1959) in the following formula.

$$CI = \frac{I_{002} - I_{amp}}{I_{002}} x100$$

I002 is the maximum diffraction intensity associated with (002) lattice crystallinity at 22 to 23 at 2θ degrees, and Iamp is the minimum diffraction associated with the amorphous portion at 18 to 19 at 2θ degrees.

Characterization of Fourier Transform Infrared (FTIR)

Characterization using FTIR spectra was carried out on CPH and cellulose materials. This analysis was carried out to monitor changes in the structural characteristics of CPH samples before and after chemical treatment. Approximately 15 mg of each sample was placed in the sample holder. A gentle force was applied to the sample using adjustable knob with the sample holder to facilitate the collection of infrared spectrum data. Infrared data was collected by scanning a sample from 4000 to 650 cm^{-1}.

Characterization of Thermogravimetric Analysis (TGA)

Thermogravimetry measures thermal stability and characteristic degradation of EFB before and after delignification. This analysis was performed using TGA Q500 thermogravimetric series analyzer (Perkin Elmer thermal analyzer). This analysis will provide basic information about material thermal stability when measuring its nitrogen flow rate below 30 mL/min and keeping heating constant.

Characterization of Scanning Electron Microscopy (SEM)

The sample was placed and affixed to the SEM specimen holder using a carbon double tip with the cross-section pointing vertically up or facing the objective lens. SEM was operated with standard operating parameters: voltage = 20 kV, point size = 50, and working distance 10 mm high. The distance of 10 mm was chosen as a compromise to the settings for signal acquisition so that the X-ray detection and enumeration are optimal.

Results and Discussion

Delignification of EFB

The delignification process chemically affects the chemical composition of the fiber. These alkaline and acid treatment conditions affect the morphology of the subsequent materials. The advantage of fast delignification using H_2O_2 was more environmentally friendly than NaOH. This can be seen in Figure 1, which shows quantitative results for the delignification process with various treatments. The results showed that EFB with peroxide treatment and longer reaction time increased α-cellulose levels and decreased lignin levels. These results are better when compared to research by Li et al. (2009) and Sheltami et al. (2012) using mulberry leaf biomass with delignification alkaline treatment at 130°C for 2 hours. The treatment in this study used 12% NaOH and 30% H_2O_2 and the control was EFB which not treated.

The composition of cellulose, hemicellulose and lignin after the delignification process using various treatment was shown in Figure 1. Overall, the delignification treatment using acids and alkalines (peroxide and NaOH) caused the hemicellulose and cellulose content to increase while the lignin content decrease. Hemicellulose content increased by 30%, cellulose increased by 40%, while lignin significantly reduced by 75%. This is caused by the cleavage of ester-linked hemicellulose (Palamae et al., 2014; Nomanbhay et al., 2013). The analysis results of lignin, hemicellulose, and α-cellulose EFB that have been delignified can be seen in Table 1.

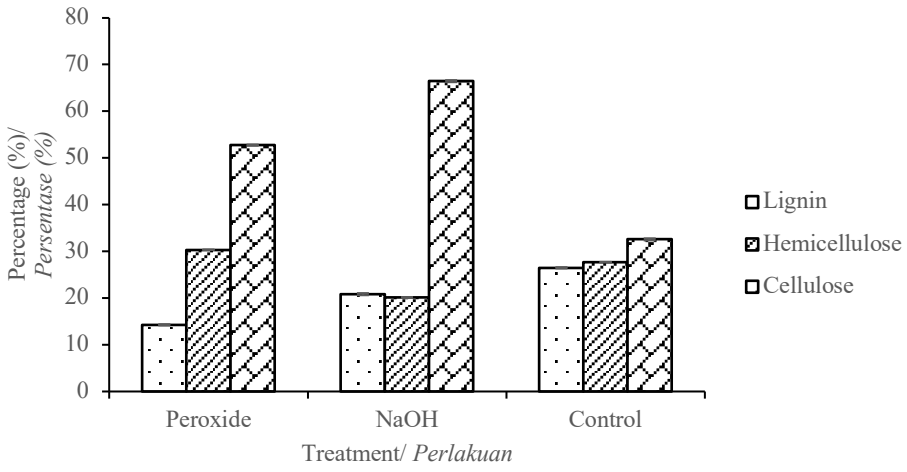

Figure 1. Composition of lignin, hemicellulose, and cellulose after pretreatment
Gambar 1. Komposisi lignin, hemiselulosa, dan selulosa setelah pra-perlakuan

The results of the ANOVA test showed significantly different results between the different solubility treatments. The lowest lignin content was 14.28% in the H_2O_2 treatment for 15 minutes. In heated by H_2O_2, it will split into H_2O and O_2, where O_2 is a strong oxidizing agent to enter the EFB layer and degrade lignin (Suriyatem et al., 2020). The highest hemicellulose content was 30.36% in the H_2O_2 treatment for 15 minutes. Then the highest cellulose content was 66.46% in the NaOH treatment for 15 minutes. Cellulose content with NaOH treatment produces higher levels than H_2O_2 but visually the EFB is brown in color, indicating that the lignin has not been completely released from EFB. The treatment using peroxide produced a brighter EFB color, the lignin content was lower than the NaOH treatment. Calculate the delignified EFB's dry weight and its depreciation of 40% (Figure 2). This can be used as a benchmark if the scaling-up process is carried out to determine the desired yield and visual results (Figure 3), which may affect the next stage.

Table 1. Lignin, hemicellulose, and cellulose content of EFB
Tabel 1. Kandungan lignin, hemiselulosa, dan selulosa dari TKKS

Treatment *Perlakuan*	Lignin content (%) *Kandungan lignin (%)*	Hemicellulose content (%) *Kandungan selulosa (%)*	Cellulose content (%) *Kandungan selulosa (%)*
Peroxides	14.28 [a*)]	30.36 [a]	52.76 [a]
NaOH	20.84 [c]	20.13 [b]	66.46 [b]
Control	26.49 [a]	27.70 [b]	32.57 [c]

*) Note : the same letter in the same column is not significantly different in the DMRT (Duncan's Multiple Range Test) test with a significance level of 5%

**) Catatan: huruf yang sama pada kolom yang sama menunjukkan tidak berbeda nyata pada uji DMRT (Duncan's Multilple Range Test) dengan taraf nyata 5 %*

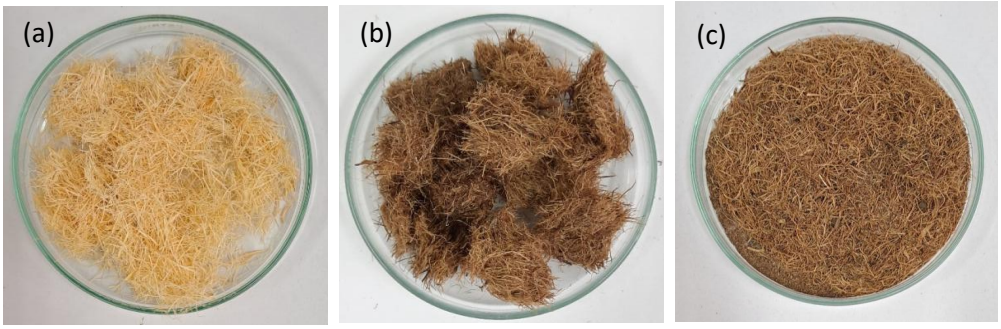

Figure 2. The dry weight of EFB before and after delignification using: (a) peroxide 15 minutes; (b) NaOH 15 minutes; (c) EFB before delignification (control)

Gambar 2. Berat kering TKKS sebelum dan sesudah delignifikasi menggunakan: (a) peroksida 15 menit; (b) NaOH 15 menit; (c) TKKS sebelum delignifikasi (kontrol)

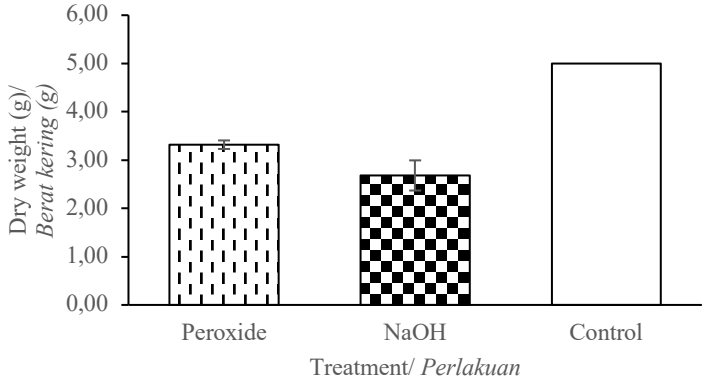

Figure 3. Dry weight of EFB after delignification for 15 minutes using: (a) peroxide; (b) NaOH; (c) control

Gambar 3. Hasil delignifikasi TKKS selama 15 menit menggunakan: (a) peroksida; (b) NaOH; (c) kontrol

EFB cellulose characterization using FTIR

The functional groups in Figures 4, 5, and 6, delignified with H_2O_2 and NaOH, can be seen to have similar functional groups. All functional groups are dominated by a peak at a wavelength between 3275.58 to 3301.75 cm^{-1} caused by the vibration of the OH group. The tendency of the material to be hydrophilic is also reflected in the peak of 3100 to 3700 cm^{-1}. The presence of OH bonds is related to the water content or hydroxyl groups present in cellulose, hemicellulose, and lignin (Nadiratuzzahra et al., 2020).

Lignin aromatic hydrocarbons are present at peaks of 1509.45 to 1511.21 cm^{-1} and 1428.92 to 1418.94 cm^{-1}, according to the stretching of carbon-carbon bonds in aromatic compounds. The peak was found in the delignified EFB using H_2O_2 and the control EFB. This result was in accordance with the cellulose and lignin content which showed that the cellulose content from delignified NaOH had the highest level, namely 66.46%. The absorption peaks at 3300 and 2900 cm^{-1} are the hydroxyl and CH groups of lignin and cellulose. This is in accordance with research by Shanmugarajah et al. (2015).

Figure 4 shows a peak between 2900.30 to 2927.22 $cm^{-1,}$ an aliphatic CH stretching associated with the methylene group in cellulose (Nadiratuzzahra et al., 2020). As is known, lignin is a multifunctional natural polymer built by oxidative compounds from C6-C3 chains with phenylpropanoid units, forming random structures in a three-dimensional network with certain interunit bonds.

Characterization of EFB cellulose using XRD

Overall, the crystallinity index for EFB before and after delignification increased (Figure 5). This shows the characteristic properties of EFB, which were originally amorphous and gradually became crystalline. When compared with research by Lani et al. (2014) and Ching & Ng (2014), the crystallinity produced after 15 minutes of the delignification process was still below the crystallinity of EFB that had become cellulose or nanocrystalline, namely 59% and 69%. This is in accordance with the pretreatment goal of rapid delignification of EFB, which is to weaken the lignin bond so that the components in EFB are easily decomposed (Lamaming et al., 2015). Table 2 shows the crystallinity index of EFB before and after delignification using various solvents.

In addition, the increase in the crystallinity index was also affected by the removal of non-cellulosic polysaccharides such as hemicellulose and lignin matrices attached to the cellulose fibers. According to Hattori et al. (2016), under conditions of drastic acid hydrolysis, the amorphous and crystalline regions may only partially disintegrate due to erosion caused by high acid concentrations. Figure 5 shows the X-ray diffractogram obtained for all samples, showing a peak at 2θ at 22°. This shows the crystal structure of cellulose because lignin is amorphous. Along with the chemical treatment, the intensity of the peak cellulose increases (Figure 5).

Peaks detected in Figure 5 showed a peak shift from EFB before and after delignification. In Figure 5, besides the 2θ peak at 22°, there are also peaks at 34.63 and 39, which indicate the presence of lignin-covered cellulose. This is in accordance with what was reported by Akinjokun et al. (2021), who characterized the cocoa pod shell. The EFB structure on the XRD diffractogram reads amorphous and crystalline because cellulose has a partially crystalline and partially amorphous structure (Muna et al., 2019).

Characterization of EFB cellulose using TGA

Thermal stability study and decomposition process on EFB samples, determined by thermogravimetric analysis (TGA). This process is needed to observe the differences in the EFB material decomposition characteristics caused by the delignification treatment.

Although not very significant, there was an increase in thermal stability in the delignified EFB, indicating the removal of hemicellulose, pectin, and lignin during the chemical treatment process. The initial decomposition temperature increased to 248.99 and 281.73 ºC for treatment with peroxide and NaOH, respectively. The final temperature also increased to 380.37 and 368.92 ºC. This increase in thermal stability is affected by the increased crystal structure of cellulose due to chemical treatment and heating. Similar results have been reported previously that EFB fiber has better thermal stability after the delignification process (Ching & Ng, 2014).

Table 2. EFB crystallinity index before and after delignification
Tabel 2. Index kristalinitas TKKS sebelum dan sesudah delignifikasi

Treatment (Code) *Perlakuan (kode)*	Amorphous index (%) *Indeks amorf (%)*	Crystallinity index (%) *Indeks kristalinitas (%)*
Peroxides	85.52	12.43
NaOH	77.46	10.30
Control	53.05	7.32

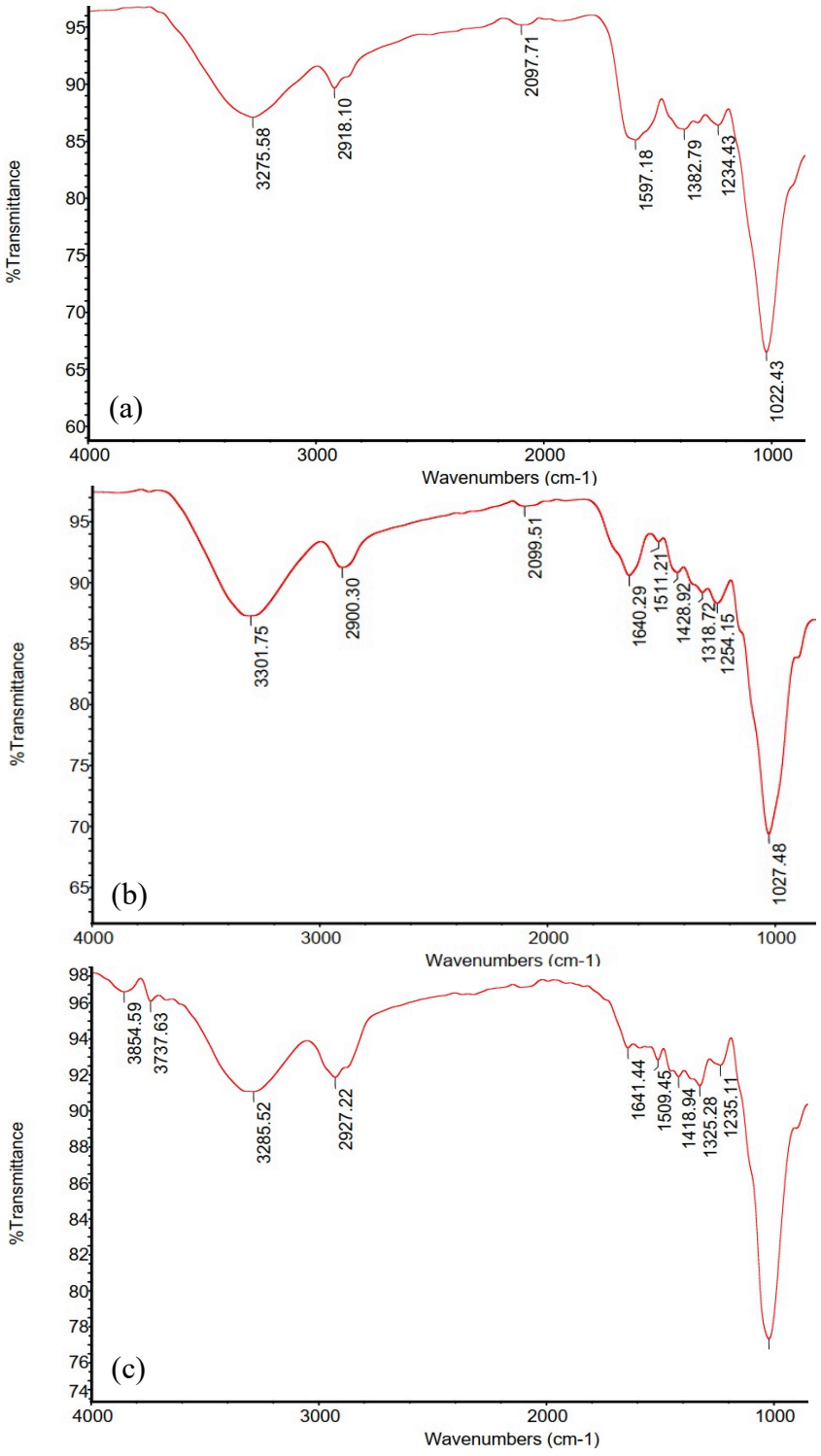

Figure 4. The result of FTIR from delignified EFB using: (a) peroxide; (b) NaOH; (c) control

Gambar 4. Hasil FTIR dari TKKS yang sudah didelignifikasi menggunakan: (a) peroksida; (b) NaOH; (c) kontrol

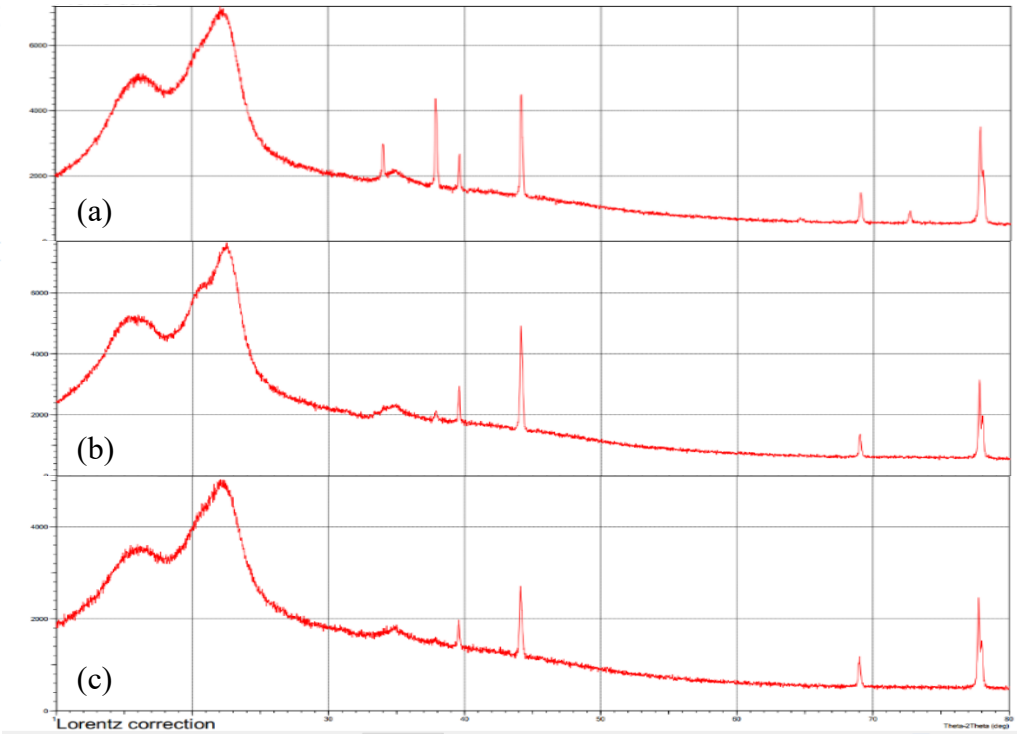

Figure 5. XRD analysis of delignified EFB using: (a) peroxide; (b) NaOH; (c) control

Gambar 5. Analisis XRD dari TKKS yang sudah didelignifikasi menggunakan: (a) peroksida; (b) NaOH; (c) kontrol

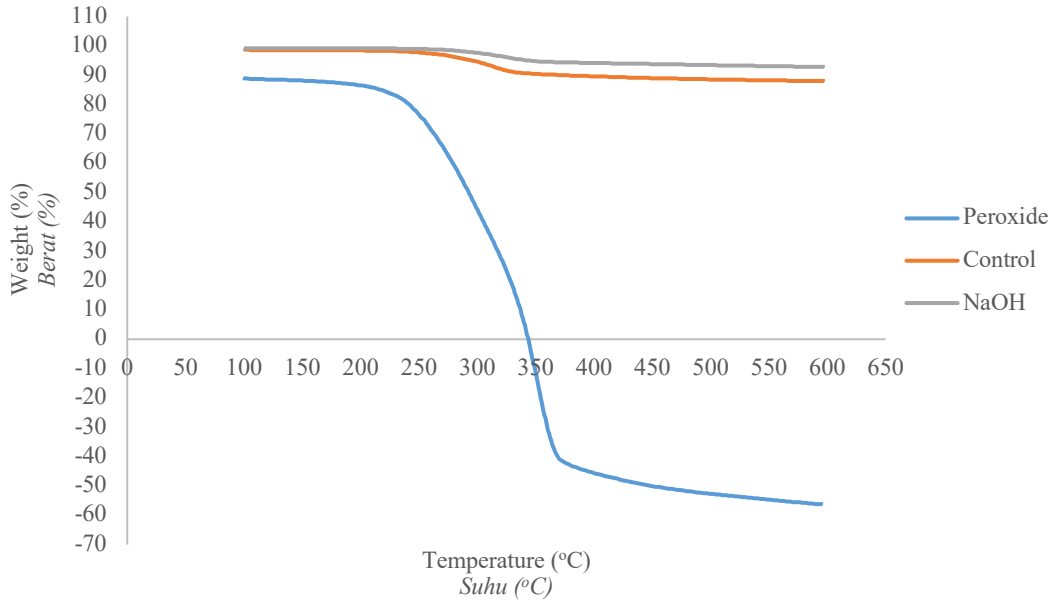

Figure 6. TGA analysis from delignified EFB with peroxide and NaOH

Gambar 6. Analisis TGA dari TKKS yang sudah didelignifikasi menggunakan peroksida dan NaOH

In general, as shown in Figure 6. EFB material undergoes rapid thermal degradation from 200ºC to around 400ºC (Hajaligol et al., 2001). The process of thermal degradation of lignocellulosic materials begins with the initial decomposition of hemicellulose, followed by the initial stages of lignin pyrolysis, depolymerization of cellulose, active flame combustion, and oxidation of charcoal (Lee et al., 2004). The thermal stability of the control EFB (Figure 6-c) shows a lower value, where the transition temperature of the initial decomposition process is around 247.3 ºC, and the final one is at 351.78 ºC. This happened because the content of hemicellulose and pectin, which are lignocellulose components, was still high in the EFB control. These two components had the lowest thermal stability and began decomposing at around 180 ºC. The lack of crystallinity may also be one of the reasons for this low thermal stability (Beall et al., 1971). Inthe peroxide treatment it was found negative weight loss for degradation. It might be because it refers to oxidation, where the hydrocarbons oxidize, acquiring some oxygen to get carboxylic acids.

Characterization of delignified EFB using SEM

SEM analysis of EFB before and after delignification showed that the surface structure of EFB had changed due to chemical treatment (Figure 7). Chemical treatment affects fiber morphology in terms of fiber size and surface smoothness.

The morphology of EFB biomass in various solvent treatments showed the lignocellulosic structure of EFB before delignification (Fig. 7c) still coated by lignin, hemicellulose, and other impurities indicated by arrow. Lignin is visible in the form of spheres found in EFB cellulose fibers. Delignification using acidic and alkaline solvents can remove lignin and hydrophobic layers. Removal of this hydrophobic coating increases the accessibility of cellulose to chemical attack (Mazlita et al., 2016). SEM micrographs with acid (a) and alkali (b) treatment appear smoother and different compared to the control.

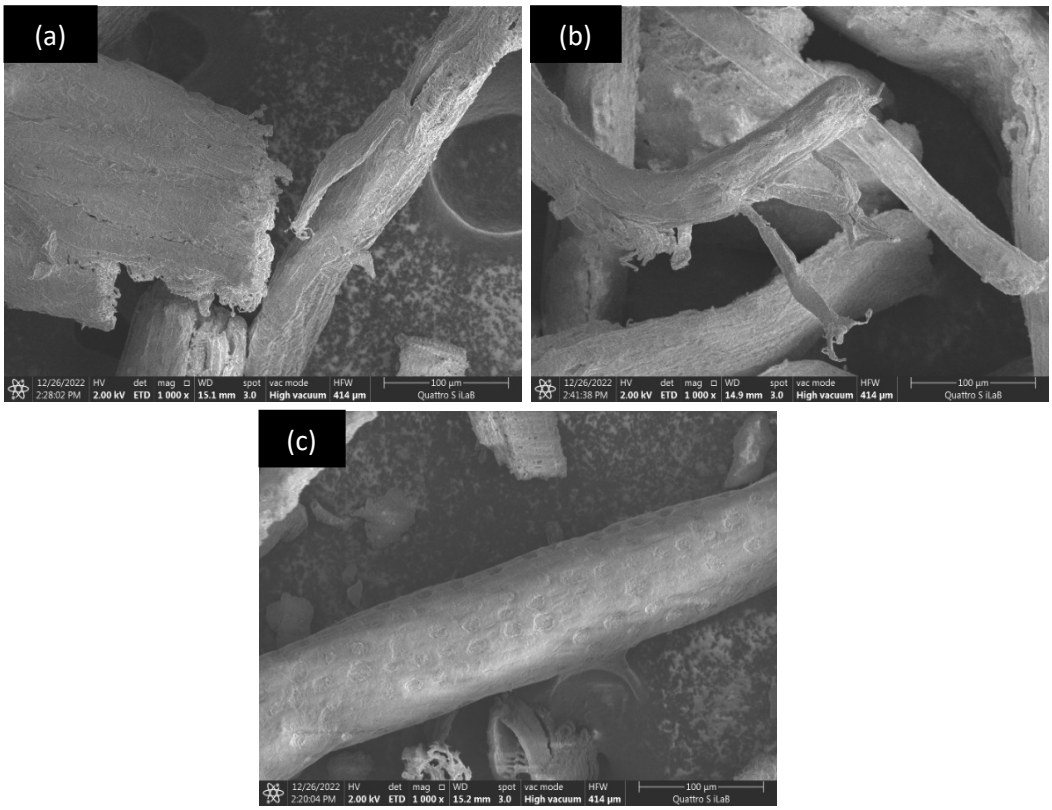

Figure 7. SEM micrograph analysis of delignified EFB using: (a) peroxide; (b) NaOH; (c) control
Gambar 7. Mikrograf SEM dari TKKS yang sudah didelignifikasi menggunakan: (a) peroksida; (b) NaOH; (c) kontrol

Conclusion

The fast delignification process using H_2O_2 produces cellulose with lower lignin content than NaOH, respectively 14.28% and 20.84%. The delignification process with H_2O_2 also produces a higher crystallinity index than NaOH, respectively 12.43% and 10.30%. The result indicates that the EFB delignification process using 30% H_2O_2 is better than 12% NaOH solvent. However, the cellulose extraction process from EFB using NaOH produces a higher cellulose content 66.46%, but visually it is still brown which indicates that there is still lignin content. Characteristics of cellulose delignified by NaOH or H_2O_2 almost have the same functional groups, dominated by OH bonds from hydroxyl groups found in lignin, hemicellulose, and cellulose.

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