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# MICROWAVE-ASSISTED ALKALIZATION PRETREATMENT OF CELLULOSE NANOFIBERS DERIVED FROM SUGAR PALM FIBER

**M. Lubis[1,✉], M. Sartika[1], M. H. S. Ginting[1] and D. L. Lestari[2]**

[1]Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan-20155, Indonesia

[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Riau, Tampan, Pekanbaru-28293, Indonesia

✉Corresponding Author: maulida@usu.ac.id

**ABSTRACT**

Microwave-assisted alkalization was used to successfully isolate cellulose nanofibers from sugar palm fibers. Microwave-assisted alkalization pre-treatment is expected to be the best option in the production of cellulose nanofibers from various cellulose sources. Microwave radiation can be used instead of conventional heating because it can take place at milder reaction conditions, resulting in reaction acceleration and higher yields. The Fourier Transform Infrared (FTIR) result shows that microwave-assisted alkalization can successfully remove components such as lignin and hemicellulose. This is indicated by the absence of absorption peaks at wave numbers 1030 to 1060 $cm^{-1}$, which correspond to the C=C- and C-O (strain cyclic) strain groups in cellulose nanofibers. This result is in accordance with X-ray Diffraction (XRD) results that show a high crystallinity of cellulose nanofibers at 74.7% with a crystallite size of 0.011 nm. The Particle Size Analyzer (PSA) results show that cellulose nanofibers have a particle size of about 10-25 nm and an average diameter of 24.95 nm. Cellulose nanofibers produced with microwave-assisted alkalization have potential applications in a variety of fields, particularly as reinforcing agents in bio-nanocomposites.

**Keywords:** Alkalization, Cellulose Nanofiber, Microwave, Pretreatment, Sugar Palm Fiber.

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## INTRODUCTION

Cellulose is one of the bio-based materials that has gained popularity in recent decades due to its excellent biocompatibility, biodegradability, and low toxicity in a variety of applications.[1] They are low density, semicrystalline, and can be easily obtained from a variety of natural fibers[2] such as sugar palm[3], bamboo[4], sugarcane bagasse[5], roselle[6], pine wood, and corncob.[7] Sugar palm fiber has a high percentage of cellulose content (56.8% by weight) and can be used for industrial purposes. This fiber is typically underutilized and has the potential to be transformed into a high-value nano product.[8] The use of cellulose to develop bio-composite materials is currently highly favored by researchers due to its hierarchical structure, which can produce micro- or nano-sized dimensions mechanically, chemically, or by combining the two. One of them is cellulose nanofiber (CNF), which has gotten a lot of attention because of the potential for strengthening that its inherent strengths provide.[2,9] Nanofibers are commonly used in the manufacture of nanostructured biocomposites.[10,11] There are numerous methods for extracting CNFs, each of which produces a unique type of fibrillar material with properties that differ depending on the cellulose source, pre-treatment, and disintegration process.[12] For isolating nanofibers of cellulose from plant fibers, pre-treatment is typically a required process.[11] Mechanical treatments such as ultrasonication[13], high-pressure homogenization[14], and chemical treatments such as acid[15], TEMPO-mediated oxidation[16], alkali[17], and enzymatic hydrolysis[12] are used in the pre-treatment process. Though the aforementioned technologies were successful in isolating cellulose nanofibers, and the results were promising, disadvantages such as high temperatures or high operating pressures, time-consuming, energy requirements, and equipment continue to limit these methods for practical applications. There is still a need for advanced techniques for producing low-cost, environmentally friendly, and time-efficient cellulose nanofibers.[11,18] Microwave radiation can be used instead of conventional heating it can take place at milder reaction conditions, resulting in reaction acceleration and higher yields.[18] Microwave energy penetrates and generates a heat source that is distributed


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throughout the material, resulting in faster heating rates and improved kinetics.[19] Mercerization has a significant role in improving the characteristics of resulting CNFs. It can improve reinforcement properties by increasing surface roughness; it can improve mechanical behavior, such as strength and stiffness; and it can increase the percentage of crystallinity index of alkali-treated fibers.[20] As a result, mercerization has a significant impact on the final CNFs product produced. The use of microwaves in the mercerization process in this work is expected to provide NFC with high crystallinity while also saving energy and time. The disposal of the amorphous form using a combination of both treatment methods significantly improves the crystallinity and purity of the CNFs obtained. Higher crystallinity is associated with higher tensile strength in chemically treated fibers. As a result of using these nanofiller-treated fibers, the properties of the nano-composite material can be improved.[21]

## EXPERIMENTAL

### Materials and Chemical Preparation

The sugar palm fibers were collected from Padang Bulan, Medan, Indonesia. Sodium hydroxide, hydrogen peroxide (50% purity), hydrochloric acid (37% purity Merck, Germany), and sulphuric acid (98% purity Merck, Germany) were supplied by CV. Rudang Jaya Medan, Medan, Indonesia. The microwave-assisted alkalization process was carried out at the Organic Chemical Laboratory at Universitas Sumatera Utara's Department of Chemical Engineering in Indonesia.

### Methods and Characterization

Cellulose was extracted by the methods described by Singh *et al.* (2017) and Chowdhury and Hamid (2016) with some modifications. The fiber was cleaned, sun-dried, and cut into small pieces. After that, the fiber was alkalized in a 2.5 M solution of NaOH with a fiber-to-solvent ratio of 1:30 (w/v). Twenty-five grams of fiber and 750 ml of solvent were put into an Erlenmeyer and heated in the microwave at various power levels; medium, medium-high, and high. The fiber is alkalized and heated in the microwave for 45, 55, and 65 minutes. The washing and filtering processes are carried out until the filtrate is neutral. The bleaching process was carried out using 30% $H_2O_2$ at a medium microwave power level for 60 minutes. The washing and filtering processes were carried out. The samples then were dried to a constant weight in an oven set to 55°C.[22,23] Cellulose nanofibers were obtained by the methods described by Ayu *et al.* (2021) with some modifications. Alpha-cellulose was hydrolyzed at 60°C for 2 hours with 5% HCl and 5% $H_2SO_4$ mixtures, followed by 30 minutes of ultrasonication after washing and filtering.[14] Thermo Fisher Scientific was used to analyze the functional groups of the CNFs produced. X-Ray Diffraction (XRD) was used to determine the crystallinity index of CNFs, and the particle size distribution of CNFs was determined using the FRITSCH ANALYSSETTE 22 Nanotec.

## RESULTS AND DISCUSSION

### The yield of Alpha-cellulose after Alkalization Treatment with Microwave

Variations in microwave power level and alkalization time have a significant effect on the resulting alpha-cellulose yield. Table-1 shows the yield of alpha-cellulose obtained at various power levels and alkalizing times. According to the results, increasing the power level and alkalization time generally reduces the yield of alpha-cellulose produced. The increase in microwave power level and alkalization time causes extreme disruption and degradation of the tissue structure in the crystalline regions of cellulose.[24] However, the highest alpha-cellulose yield of 36.92% was obtained at a medium-high power level with an alkalization time of 55 minutes. This demonstrates that the alkalization process yields the highest yield at medium-high power levels in 55 minutes. The alpha cellulose obtained at that power level and time was then hydrolyzed to produce CNFs.

Table-1: Yield of Alpha-Cellulose Obtained After Alkalization Treatment with Microwave

| Power levels | Sugar Palm Fibers (g) | Alkalization Time (minutes) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Alpha-cellulose (g) | | | Yield (%) | | |
| | | 45 | 55 | 65 | 45 | 55 | 65 |
| Medium | 25 | 8.86 | 8.95 | 6.39 | 35.44 | 35.8 | 25.56 |
| Medium High | 25 | 8.16 | 9.23 | 6.68 | 32.64 | 36.92 | 26.72 |
| High | 25 | 8.95 | 8.78 | 4.95 | 35.8 | 35.12 | 19.8 |

**Functional Groups Analysis of CNFs**

FTIR characterization can be done by analyzing the resulting spectra according to the peaks formed by a functional group. Figure-1 depicts the FTIR spectra of sugar palm fiber, alpha-cellulose, and NFCs obtained by microwave-assisted alkaline pretreatment. The chemical composition of natural fiber's main components revealed cellulose, lignin, and hemicellulose. There were three types of natural fibers: ester, aromatic ketone, and alcohol groups, with the oxygen content in the functional groups varying.[25] Cellulose compounds are characterized by the stretch groups O-H, C-H, and C-C, as well as the $CH_2$ bending groups.[14] According to Fig.-1, a similar absorption peak was obtained by sugar palm fiber, alpha-cellulose, and CNFs between 3319 -3345 $cm^{-1}$ which indicated the O-H stretching group, this band is particular to cellulose material.[12] CNFs on the other hand, showed the sharpest peak at this region, indicating the highest cellulose content after alkalization pre-treatment. The absorption at 2875 to 2918 $cm^{-1}$ for sugar palm fiber, alpha-cellulose, and CNFs indicated the C-H stretch group. This band was formed by stretching vibrations of C-H bonds found in hemicellulose and cellulose.[12] The absorption peak around 1030 to 1060 $cm^{-1}$ corresponds to C=C stretch groups and stretch cyclic C-O, which was reduced for the CNFs after the treatment. The aromatic ring vibration of lignin is represented by the observed peak at 1500 to 1594 $cm^{-1}$ for sugar palm fiber and alpha-cellulose.[22] However, this peak intensity was not found in the CNFs. This helped to confirm that microwave-assisted alkaline pretreatment can remove the lignin and hemicellulose fragments efficiently, improving the quality of the resulting cellulose nanofibers.

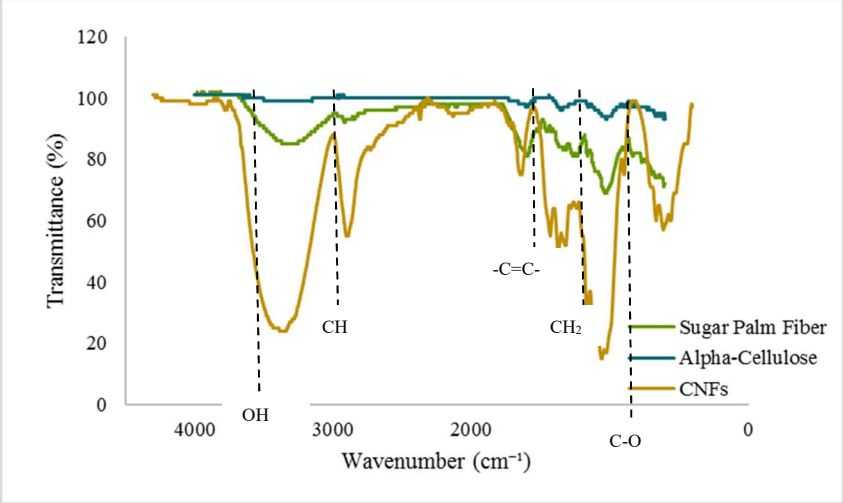


Fig.-1: Characterization of NFCs using FTIR (Fourier Transform Infra Red)

**Crystallinity Index of CNFs**

The purpose of this characterization is to examine the crystallinity index and crystallite size of CNFs. The index of crystallinity (CrI) of cellulose is determined by the proportion of crystalline to amorphous regions, which influences the mechanical properties of cellulose fibers as well as the orientation of the crystalline and amorphous subject areas in the fibers.[26] Figure-2 displays the X-ray diffraction pattern of NFCs produced. According to the ratio of crystalline to amorphous regions, cellulose nanofibers had a crystallinity index (CrI) of 74.7% and a crystallite size of 0.011 nm. This finding also corresponds with the findings of Ilyas *et al.* (2019), who discovered that cellulose nanofibrils produced from sugar palm fibers using conventional heating and methods have a crystallinity index of 75%.[27] Chowdhury and Hamid (2016) demonstrate that microwave-irradiated NaOH solution behaves as an intra-crystalline swelling agent, selectively penetrating and swelling the amorphous region of cellulose, resulting in partial delignification of the sample.[22]

**Particle Size Analysis of CNFs**

PSA characterization of cellulose nanofibers aims to determine the particle size distribution of materials. The results of characterization using a Particle Size Analyzer (PSA) are shown in Figure-3. The results of PSA characterization show that CNFs have a particle size of about 10-25 nm with an average diameter of

24.95 nm. Similar results for the diameters were reported by Balea *et al.* (2021). CNFs have a typical length of >1 m, a width of 20 to 100 nm, and aspect ratios ranging from 10 to 100, with particle morphology, surface chemistry, and charge determined by the mechanical shear process, pretreatment, and cellulose source.[28]

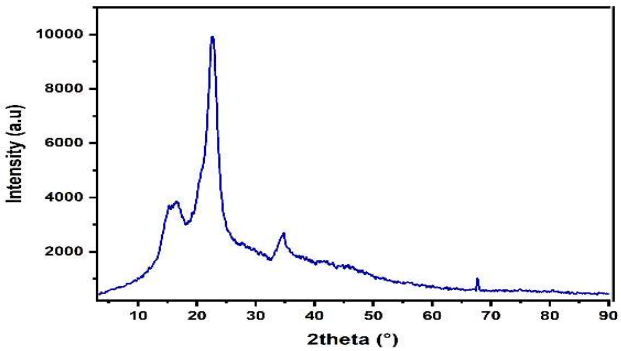


Fig.-2: Characterization of CNFs using XRD

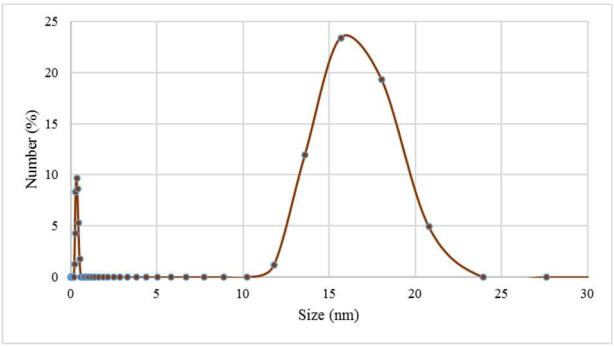


Fig.-3: Characterization of CNFs using PSA

## CONCLUSION

This research shows that cellulose nanofiber can be successfully extracted from sugar palm fiber. Microwave-assisted alkalization and ultrasonication were used in two different treatment combinations. Chemical treatments combined with microwaves can successfully remove amorphous structures such as hemicellulose and lignin, according to FTIR results. This result is consistent with the XRD result, which showed that the crystallinity index of cellulose nanofibers can even be higher when compared to cellulose nanofibers produced by conventional heating. The PSA results show that the average diameter of cellulose nanofiber is 24.95 nm. All of these cellulose nanofibers produced with microwave-assisted alkalization have potential applications in a variety of fields, particularly as reinforcing agents in bio nanocomposites.

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## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

M. Lubis http://orchid.org/0000-0002-0176-4745
M. Sartika http://orchid.org/0009-0003-6821-622X
M.H.S. Ginting http://orchid.org/0000-0002-2741-7135
D.L. Lestari http://orchid.org/0000-0003-1606-2022

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