



Enhancing cellulose fiber properties from *Chromolaena odorata* and *Anana comosus* through novel pulping chemical mixtures

Olayinka Oluwaseun Oluwasina^{a,b}, Mochamad Zakki Fahmi^{b,*}, Olugbenga Oludayo Oluwasina^c

^aDepartment of Marine Science and Technology, Federal University of Technology, P.M.B 704, Akure, Nigeria

^bDepartment of Chemistry, Universitas Airlangga, Kampus C Mulyorejo, Surabaya 60115, Indonesia

^cDepartment of Chemistry, Federal University of Technology, P.M.B 704, Akure, Nigeria

Abstract

The production of cellulose with exceptional properties has led to the modification of chemical pulping methods and the development of newer chemical pulping methods. This study developed mixtures of sodium hydroxide, ethanol, and anthraquinone as new pulping chemicals to produce alpha-cellulose from pineapple leaves and Siam weed stem s. The addition of anthraquinone was noticed to influence the pulp yield positively and the FTIR of all the cellulose has the characteristic cellulose bands. Calculated Total crystallinity index (TCI), (Lateral order index) LOI, and Hydrogen bond intensity (HBI) from the FTIR presented PLSHAEC (68.38 %) and SWSHQEC (67.74 %) having high crystallinity. From the XRD, the 2θ by all the materials is attributed to cellulose I diffraction, and the crystallinity index aligned with FTIR determined crystallinity. The determined particle average diameter using ImageJ software showed that PLSHQEC 3.00 had the smallest value, followed by 5.17 for PLSHQEC, 5.32 for SWSHQEC, and 6.03 for SWSHQEC. From the thermal analysis, the onset of the degradation of all the cellulose occurred at different temperatures: 247.10 °C (PLSHQC), 253.38 °C (PLSHQEC), 240.20 °C (SWSHQEC) and 242.58 °C (SWSHQEC). The increase in yield, higher crystallinity index, and smaller fiber diameter of the cellulose demonstrated anthraquinone as a better additive to produce quality cellulose that would undergo easy chemical modification.

DOI:10.46481/jnsps.2024.2033

Keywords: Cellulose, Characterization, Lignocellulose, Pineapple leaf, Siam weed

Article History :

Received: 02 March 2024

Received in revised form: 25 April 2024

Accepted for publication: 26 April 2024

Published: 08 May 2024

© 2024 The Author(s). Published by the [Nigerian Society of Physical Sciences](#) under the terms of the [Creative Commons Attribution 4.0 International license](#). Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

Communicated by: Emmanuel Etim

1. Introduction

The non-biodegradability and negative environmental greenhouse gas impact of synthetic- based products and global environmental guidelines have led to a vigorous search for year-round, renewable substitutes for fossil-based industrial raw ma-

terials. Lignocellulosic biomass is copious, inexpensive, renewable, and easy to process, with great potential to replace synthetic raw materials. Also, researchers are interested in lignocellulosic resources to protect against persistent and imminent damage to the environment and humanity by synthetic chemicals [1].

Lignocellulosic comprises functional biochemical components like lignin, cellulose, hemicellulose, and extractive. Cellulose is one of the most desirable commodities in the universe because of its properties, such as high aspect ratio, crystallinity,

*Corresponding author: Tel. No.: +62-838-3290-1697

Email address: m.zakki.fahmi@fst.unair.ac.id (Mochamad Zakki Fahmi)

thermal stability, biodegradability, mechanical ability, mixability, and functionalization potential [2]. Because of its exceptional characteristics, cellulose and its derivatives can be used in paper, textile, pharmaceutical, biomedical, food, polymer, biofuel, and other industries.

Various pulping methods, such as Kraft, sulfite, and soda, have been adopted to produce cellulose from lignocelluloses. Pulping methods such as semi-chemical [3], sodium hydroxide and sodium sulfide [4], and organosolv and sulfite acid [5] have been employed in the time past. However, the chemical method has been used extensively to isolate cellulose from plant biomass, and the realization of the direct relationship between the pulping chemicals and the characteristics of the produced cellulose has triggered more research on the use of different chemicals and chemical mixtures for the production of cellulose. Sodium hydroxide solution is mainly used for delignification and cellulose extraction during pulping. However, the low lignin removal and carbohydrate peeling effect of sodium hydroxide pulping are some of its drawbacks. To enhance the properties of cellulose, sodium hydroxide pulping has been modified by adding some other chemicals. The addition of anthraquinone to sodium hydroxide has been reported [2, 6, 7]. Adding ethanol to soda pulping has been reported to increase the lignin removal and yield and produced a better result than using kraft pulping chemicals in ethanol production [8]. The search for chemicals or chemical mixtures that could positively influence the properties of cellulose has been pivotal in various research on chemical pulping. Modifying the soda pulping method could produce cellulose with better properties than cellulose produced with either soda or soda anthraquinone pulping chemical. Ethanol and anthraquinone have been combined singly with soda, but there needs to be more information on the use of soda, ethanol and anthraquinone mixture for cellulose production.

In this study, instrumental investigation using scanning electron microscopy, ImageJ software, X-ray diffraction, Fourier Transform Infrared, and thermogravimetric analysis was carried out to elucidate surface morphology, fiber diameter, crystallinity, the functional group (with FTIR-derived crystallinity), and thermal stability of cellulose produced from pineapple leaf and siam weed (*chromolaena odorata*) stem as influenced by sodium hydroxide-anthraquinone-ethanol and sodium hydroxide-anthraquinone pulping chemicals.

2. Materials and methods

2.1. Preparation of cellulose

The leaves of pineapple (*anas comosus*) were collected at the School of Agricultural Technology, Mini Mat. At the same time, the stem of siam weed (*chromolaena odorata*) was gathered from demonstration farm, both from the federal university of technology akure, nigeria. these plants were validated at the same university's department of crop, soil, and pest management. The materials were freed of foreign matters, and the pineapple leaves were washed with water. The samples were cut to 2 to 3 cm sizes and sun-dried (40 °C) for a month before pulverizing. The material was sieved to obtain 450 µm

particle size and then stored in an air-tight glass mason jar (500 mL, 26 °C, 60 % relative humidity). The leaves of pineapple were coded as "PL" while siam weed was "SW" sodium hydroxide, sodium chlorite, ethanol (98 %), sulfuric acid (95 %), glacial acetic acid, and anthraquinone are all analytical grades obtained from Sigma Aldrich, USA.

2.2. Proximate analysis of materials

Moisture content

The sample's known weight (m_1) was dried (oven, 105 °C 3 h), and the weight (m_2) was determined after the experimental duration [9]. The moisture content was determined using equation (1)

$$\% \text{ moisture} = \left[\frac{m_1 - m_2}{m_1} \right] \times 100. \quad (1)$$

Ash content

A moisture-free sample (3 g) was weighed into an ash crucible and subjected to furnace heating (575 °C, 3 h). After the experiment, the ash weight (AW) was determined, and the ash content [10] was determined using equation (2).

$$\% \text{ ash} = \left(\frac{A_W}{3} \right) \times 100. \quad (2)$$

Lignin determination

Sulphuric acid (15 mL, 72 %) was added to a known weight of extractive free sample (W_{ac}) and subjected to mechanical stirring (2 h, 20 °C). Afterwards, the volume was made up to 575 mL with distilled water and then subjected to heating (100 °C, 4 h). The content was allowed to cool overnight, filtered, the solid residue washed free of acid, oven dried (3 h, 105 °C, and the weight determined (Y) [11]. The acid-insoluble lignin was calculated using equation (3).

$$\text{Klason lignin}(\%) = \frac{Y \times 100}{W_{ac}}. \quad (3)$$

2.3. Holocellulose

A quantified extractive sample (E_e) and distilled water (150 mL) mixture were treated under mechanical stirring in a water bath (80 °C, 1 h), after which NaClO₂ (1 g) and glacial acetic acid (0.2 mL) were added. The Addition of NaClO₂ (1 g) and glacial acetic acid was repeated consecutively for 5 h. The mixture was then cooled, and the solid content was washed free of chlorine before drying (3 h, 105 °C), and the weight was determined (H_s). Holocellulose content was determined using equation (4) [12].

$$\text{Holocellulose content}(\%) = \frac{E_e}{H_s}. \quad (4)$$

2.4. Alpha-cellulose

Holocellulose of pre-determined weight (H_{Ce}) was treated with NaOH (50 mL, 17.5 %, 20 °C) under mechanical stirring (30 min), followed by the addition of distilled water (50 mL), and the reaction continued (5 min). The solid content was obtained, washed free of sodium hydroxide, and oven-dry (105 °C, 3h) [13], and the weight was determined (A_C). The alpha-cellulose was determined using equation (5).

$$\text{Alpha-cellulose(\%)} = \frac{A_C}{H_{Ce}}. \quad (5)$$

2.5. Pulping method

Two pulping solutions were employed following slightly modifying the Oluwasina et al. [9]. method. The first solution was a mixture of NaOH (15 %) and 95 % ethanol (40 %), and for the second solution, anthraquinone (0.1 %) was added to the first solution. All the percentages of the used chemicals are based on the weight of the plant sample. The pulping was carried out in an oil bath autoclave digester (THR-280B), with a solution to a solid ratio of 30:1 (v/w) and 15 psi. Two-stage pulping method was employed; the sample was heated at 70 °C for 1 h before the temperature was raised to 170 °C for another 1 h. The pulp sample was obtained after filtration, washed free of chemicals, and dried (105 °C) to constant weight (6 h).

2.6. Bleaching process

The bleaching method sequentially added sodium chlorite (NaClO_2) and sodium hydroxide (NaOH). An oven-dried pulp sample (10 g) in a beaker was added to hot distilled water (80 °C, 500 mL) in a water bath. Then NaClO_2 (6 g), and acetic acid (2 mL) were added. The sample was filtered after 1 h, then treated with NaOH (5 %, 80 °C, 1:10 solid to chemical ratio) and washed free of NaOH (the process was repeated consecutively for four hours) [9]. The sample was finally washed free of chemicals and dried (105 °C).

2.7. Preparation of alpha-cellulose

Alpha-cellulose was extracted from the bleached pulp using NaOH (17.5 %) at 25 °C with solids to chemical ratio of 1:10. The sample was washed free of the chemical and dried to constant weight (105 °C, 6h) [9]. The sodium hydroxide and ethanol mixture were coded as SHQ, while sodium hydroxide, ethanol, and anthraquinone were coded as SHQE. The alpha celluloses (C) produced were named after the plant-coded names (Pineapple as PL and siam weed as SW). The final celluloses were named as PLSHQ (Pineapple leaf with sodium hydroxide and ethanol cellulose) and SWSHQ (siam weed, with sodium hydroxide and ethanol cellulose), PLSHQEC (pineapple leaf with sodium hydroxide, ethanol and anthraquinone cellulose), and SWSHQEC (siam weed with sodium hydroxide, ethanol and anthraquinone cellulose)

2.8. Instrumental characterization

Fourier Transform Infrared (FTIR) (model Bruker Tensor 27) spectroscopy obtained the functional group analysis. XRD (model Bruker D2 Phaser, 30 kV, 10 mA, and Cu- $K\alpha$ radiation) was employed for the sample X-ray diffraction and crystallinity determination. Sample surface morphology was obtained using a Scanning Electron Microscope (SEM coupled with energy dispersive X-ray (EDX) (FEI FIB/SEM Nova 600 Nanolab). The fiber diameter was determined using ImageJ software. Material thermal firmness was observed using a thermogravimetric analyzer. Using the absorbance peak height of the FTIR spectra, HBI, LOI, and TCI were calculated using equations (6), (7), and (8), respectively.

$$\text{Hydrogen bond intensity (HBI)} = \frac{A_{3336}}{A_{1336}} \text{cm}^{-1}, \quad (6)$$

$$\text{Lateral order index (LOI)} = \frac{A_{1429}}{A_{893}} \text{cm}^{-1}, \quad (7)$$

$$\text{Total crystallinity index (TCI)} = \frac{A_{1372}}{A_{2892}} \text{cm}^{-1}. \quad (8)$$

The material's XRD crystallinity index was determined using peak height ratios of I 200 (the highest spectra peak height) and I_{am} (the lowest spectra peak height). The % CI was calculated using equation (9).

$$\% \text{ CI} = \left(\frac{I_{200} - I_{am}}{I_{200}} \right) \times 100. \quad (9)$$

3. Result and discussion

3.1. Proximate analysis of the plants

The useability of a material hinges on its properties; thus, preliminary proximate analysis was conducted on the selected plant materials to establish their suitability for chemical pulping. Those materials' moisture, ash, lignin, and cellulose contents were determined (Figure 1a). Moisture content can influence the shelf-life of material because wood decay microbes could thrive in a high moisture environment, which could lead to the loss of quality lignocellulosic due to microbe degradation. All the moisture content values observed in this study are lower than the 30 % moisture content expected of wood for microbial degradation [14]; nevertheless, taking a clue from food and storage powdered material with recommended storage moisture content of between 12 % to 15 % [15]. It could be inferred that lower moisture content would be preferred to preserve the chemical composition of powdered lignocellulosic. Thus, the moisture content of 5 % (siam weed) and 6 % (pineapple) are opined to be suitable for preserving the chemical properties of the materials. The ash content of 6.5 % (siam weed) and 9.50 % (pineapple) compete reasonably well with 4.63 % to 6.03 % [16] and 2.9 % to 9.5 % [17] reported for various biomass. A pretreatment process would be needed to reduce the ash content of the plant materials to prevent channel clogging during pulping. The lignin contents are 21.40 % (siam

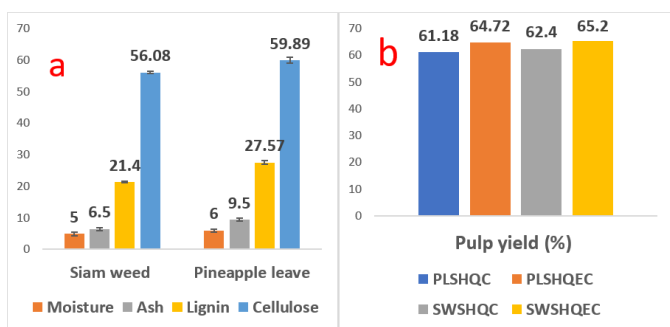


Figure 1. (a) Proximate analysis and (b) pulp yield percentage of biomass.

weed) and 27.57 % (pineapple) indicates the potential of those plant materials as lignin sources for industrial purposes.

The high lignin content in pineapples could have impacted the compactness and glossy nature of the plant material. Lignin is known to be the glue holding plant fiber together, and its aromatic nature could have impacted the glossy character. Similar lignin values have been reported by Alharbi *et al.* [18]. The pineapple leaf recorded 59.89 % alpha-cellulose, higher than 56.08 % of siam weed. The alpha-cellulose values reported here exceed 26 % to 43 % of coir and leave biomass [18]. From the overall proximate results, siam weed stem and pineapple leaf fiber are good pulping candidates for cellulose production.

3.2. Pulp yield

Higher pulp yields were observed when sodium hydroxide, ethanol, and anthraquinone were used as the pulping chemical. Pineapple leaves and siam weed stem recorded 64.7265.20 % yields. Still, lower yields of 61.18 % and 62.40 % were recorded for the same plant material when sodium hydroxide and ethanol were used as the pulping chemicals (Figure 1b). The addition of anthraquinone to sodium hydroxide during pulping has been documented to have increased the yield, improved the chemo-mechanical properties of the products, quickened delignification, prevented redeposition of removed non-cellulosic materials and prevented carbohydrate peeling effect [2, 7, 8]. This study has demonstrated that combining ethanol and anthraquinone can improve pulp yield.

3.3. FTIR result

The prominent peaks expected of cellulose are identifiable in the spectra of all the celluloses (Figure 2). Some exhibited sharp and broad spectra (PLSHQEC and SWSHQEC), while some shifted to low frequency. The spectra at 3293 cm^{-1} , 3283 cm^{-1} , 3296 cm^{-1} , and 3290 cm^{-1} for PLSHQEC, PLSHQ, SWSHQEC, and SWSHQ are attributed to a hydrogen-bonded hydroxyl group holding cellulose fiber together. The spectra band at 2895 cm^{-1} , 2903 cm^{-1} , 2898 cm^{-1} , and 2889 cm^{-1} , for PLSHQEC, PLSHQ, SWSHQEC, and SWSHQ are for C-H stretch of methyl and methylene groups, while 1636 cm^{-1} , 1647 cm^{-1} , 1638 cm^{-1} and 1640 cm^{-1} are for hydrogen bonds associated with absorbed water [19]. Also, spectra at 1422 cm^{-1} (PLSHQEC and PLSHQ), 1425 cm^{-1} , 1418 cm^{-1} and 1313 cm^{-1} (PLSHQEC and SWSHQEC), and 1314 cm^{-1}

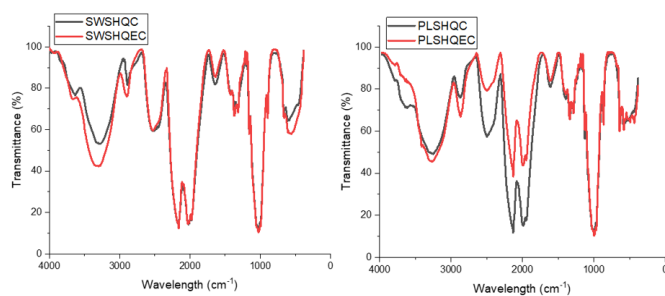


Figure 2. FTIR spectra of cellulose.

(PLSHQC and SWSHQEC) are for CH 2 group bending and wagging. At the same time, band at 1157 cm^{-1} for PLSHQEC and SWSHQEC and 1156 cm^{-1} for PLSHQ and SWSHQ are for C-O-C of the glycosidic linkage [9]. However, compared with their counterparts, the OH peaks of PLSHQEC and SWSHQEC are broader and more intense (though the OH band of PLSHQEC was more visible than that of SWSHQEC). These broad and intense OH peaks of PLSHQEC (3293 cm^{-1}) and SWSHQEC (3296 cm^{-1}) attest to removing most non-cellulosic materials, thereby exposing the OH functional group to FTIR vibration frequency. The smaller fibre diameter (as shown from the ImageJ determination) resulted in a high surface area, thus granting accessibility to the available OH groups. It was noticed that there was an overlapping of peaks between PLSHQEC and PLSHQ, as well as SWSHQEC and SWSHQ. The overlapping of peaks experienced by the celluloses suggests that those materials have the same chemical composition. The overlapping experience reported in this study is similar to the finding of Rafidah *et al.* [20]. Additionally, the empirical crystallinity (TCI, LOI, and HBI) inferences were obtained from the various spectra through the use of Nelson and O'Connor [21] and Nada *et al.* [22] equations.

PLSHAEC and SWSHQEC crystallinity obtained from the FTIR (TCI, LOI, and HBI) and XRD data followed the same order presented in Figure 3. However, there was an interchange in their LOI values because SWSHQEC (1.13) has a higher value than PLSHQEC (1.06). The removal of non-cellulosic matters and reduction in the amorphous cellulose could be responsible for the increase in their crystallinity. The removal of non-cellulosic matters and reduction in the amorphous cellulose could be responsible for the increase in crystallinity of PLSHQEC and SWSHQEC when compared with the SWSHQ and PLSHQ. Kaur *et al.* [23] reported an increase in LOI after removing the water-loving portion of cellulose. The higher HBI recorded for PLSHQEC (0.99) and SWSHQEC (0.67) imply that they contained more ordered cellulose chains than their counterparts. In another study, an increase in TCI and LOI has been credited for cellulose orderliness and crystallinity [24]. The crystallinity values observed from the XRD and FTIR are likely influenced by anthraquinone addition to the SHQ pulping chemical. The anthraquinone helps remove unwanted materials from the lignocellulosic fiber [8], leaving smoother and cleaner cellulose behind. The smoothness and cleanliness could be responsible for the formation of intra- and

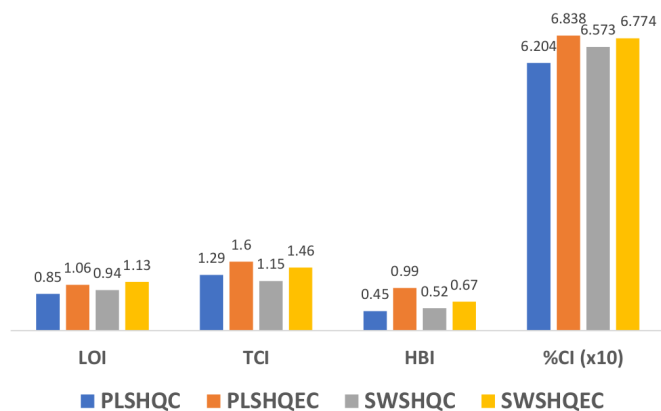


Figure 3. Crystallinity (FTIR and XRD).

inter-hydrogen bonding between the cellulose chain, which in turn influence the crystallinity of the materials.

3.4. XRD

The four distinct peaks (Figure 4) presented by all the cellulose at different 2θ an evidence plant materials reacted differently to the two pulping chemicals.

The 2θ values of all the cellulose PLSHQEC (14.7° , 23.9° , 25.9° and 30.2°), PLSHQC (15.1° , 24.2° , 26.8° and 31.8°), SWSHQEC (14.7° , 24.1° , 26.0° and 40.6°) and SWSHQC (14.6° , 24.0° , 26.1° , 40.5°) can be attributed to cellulose I diffraction peaks [25]. Samples pulped with SHQE have lower crystallinity, while those with added anthraquinone have the highest values. The PLSHQEC had a crystallinity of 68.4 %, while PLSHQC had 62.0 %. Likewise, SWSHQEC had 67.7 % and SWSHQC had 65.7 %. According to the literature, the decrease and increase in crystallinity of cellulose is a function of the amount of the OH group present in the cellulose; a decrease in the OH group would adversely reduce the crystallinity order of cellulose material [25–27]. Soda pulping is synonymous with hydrolysis and peeling reaction of cellulose, affecting the degree of cellulose polymerization because it causes shortness of the chain length and dissolution of cellulose due to glycosidic bond cleavage. However, adding ethanol and anthraquinone to soda-pulping chemicals has produced a unique cellulose with higher delignification and brightness [28]. This reason could be responsible for the higher crystallinity index of cellulose. The crystallinity index (Figure 2) of 62.04 %, 65.7 %, 67.7 %, and 68.4 % recorded in this study compete favourably with some in the literature 60.50 % [29], 67 % [30], 62.54 % [31], 57.85 % [32] and 59 % [33]. The relatively high crystallinity of the cellulose in this study indicates its better tensile strength, modulus, and rigid properties [34]. These are good properties desirable of cellulose that could be used in various industrial applications.

3.5. SEM

The fiber micrograph of the celluloses is presented in Figure 5. The influence of the pulping chemicals was evident from the images. The images of cellulose obtained with soda, ethanol,

and anthraquinone mixture look brighter, smoother, and shining than cellulose obtained with only soda and ethanol pulping chemicals. Ethanol addition to soda chemical can improve lignin selectivity towards degradation and dissolution, thereby reducing the impurity on the fiber surface. However, it is worth noting that lignin dissolution and degradation are enhanced by anthraquinone, which also prevents redeposition of lignin and other impurities (wax, pectin, extractives, hemicelluloses) on cellulose fiber surface [9]. The overlay of long, bundle, firmly glued, and cloudy fiber was more conspicuous in SWSHQC than PLSHQC, testifying that non-cellulose compounds are still present in the fiber. The presence of silica in the EDX spectra (Figure 6 and Table 1) of SWSHQC revealed the existence of non-cellulose materials, which agrees with the findings of Ichwan *et al.* [1]. The removal of that non-cellulosic impurity allowed the proper interaction between the pulping chemical and fiber, leading to defibrillation, causing the PLSHQEC and SWSHQEC to appear as fiber strands instead of a bundle like the SWSHQC [35].

Table 1. Percentage composition of elements in the cellulose.

	Element (%)		
	Carbon	Oxygen	Silica
SWSHQC	51.29	46.74	1.97
SWSHQEC	54.40	45.60	0.00
PLSHQC	49.42	50.58	0.00
PLSHEQC	49.00	51.00	0.00

3.6. ImageJ

The average diameters of the cellulose fiber measured using SEM image and ImageJ software (Figure 7) are 3.00 (PLSHQEC), 5.17 (PLSHQC), 5.32 (SWSHQEC) and 6.03 (SWSHQEC), reflecting the influence of the pulping chemical and non-cellulosic material fibers on the measured diameter. The distribution pattern of the fiber diameter revealed that PLSQHEC has a minor diameter, having recorded the lowest diameter frequency (4 to 10 μm), probably the reason for its highest crystallinity because much of the non-cellulosic impurity might have been removed by the pulping chemical. According to Ichwan *et al.* [1], lignin, hemicellulose, and pectin removal reduce fiber diameter. Conversely, the higher fiber diameter recorded by the SWSHQC and PLSHQC can be linked to an attached impurity, which undoubtedly increases the fiber thickness, leading to a wider diameter. The small fiber diameter of the PLSQHEC and SWSHQEC made them good candidates for the production of cellulose derivatives because their OH functional group would be very much available and accessible for modification.

3.7. TGA

The thermal analysis of the cellulose presents their reaction to heat, which consistently dictates applicability. From Figure 8, all the thermal spectra present three stages of weight loss; however, there are two stages of thermal degradation. All the samples experienced loss of moisture content of 7.78

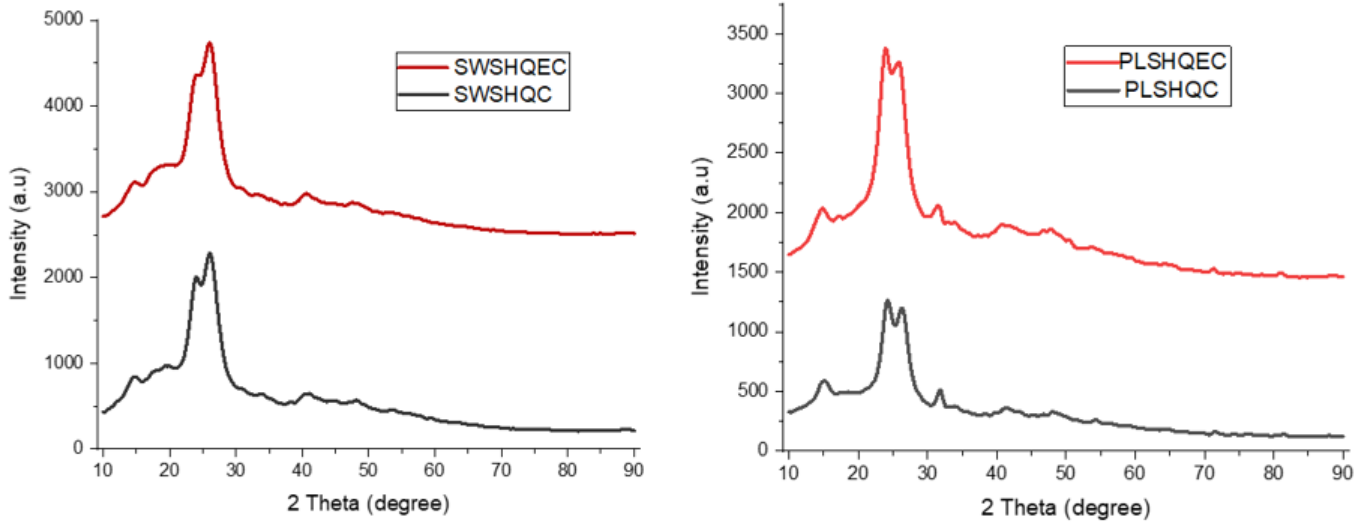


Figure 4. XRD spectra of cellulose.

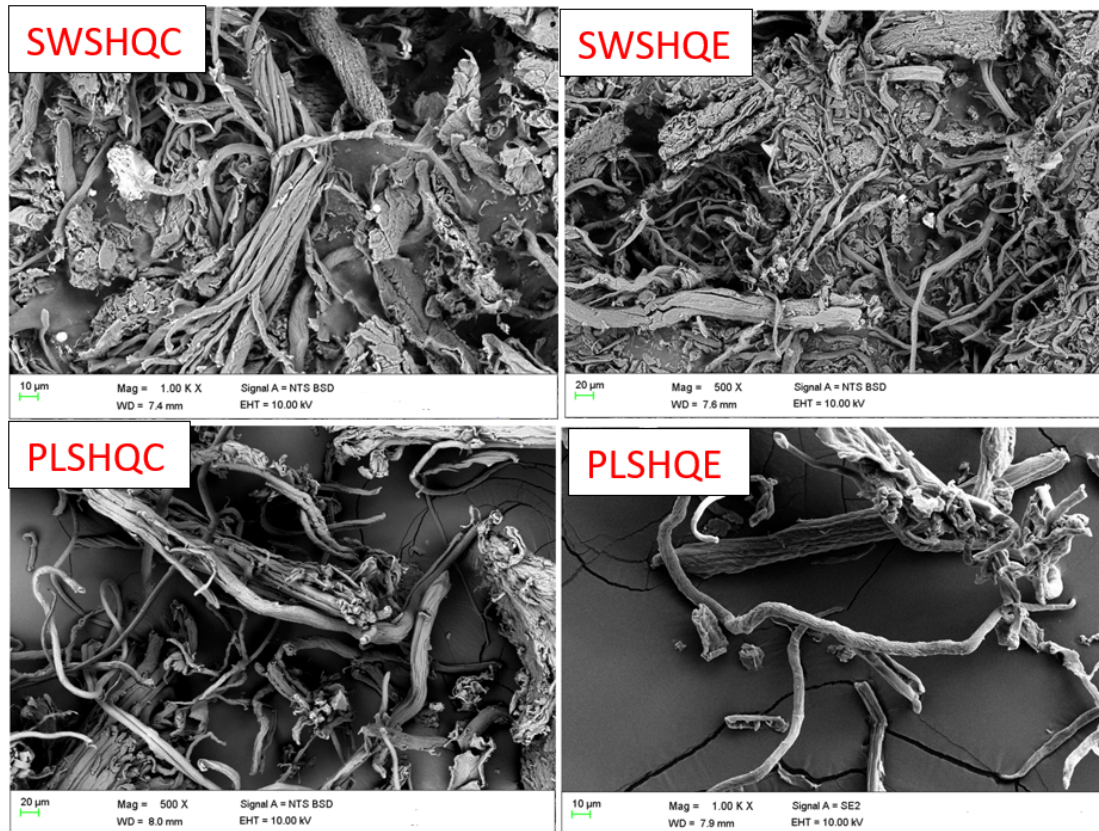


Figure 5. SEM of cellulose.

% (PLSHQC), 22 % (PLSHQEC), 6.68 % (SWSHQ), and 6.32 % (SWSHQEC) depicted by the first peak in the DTG curve. The onset of the degradation of all the cellulose occurred at different temperatures: 247.10 °C (PLSHQC), 253.38 °C (PLSHQEC), 240.20 °C (SWSHQ), and 242.58 °C (SWSHQEC), showing that the cellulose produced using SHQE ex-

hibited resistance to thermal degradation. The XRD results of cellulose can support this because crystallines are known to have better thermal properties. The crystallinity inferences, as determined from the cellulose FTIR spectral, which are higher for PLSHQEC and SWSHQEC, could also attest to the thermal stability of the cellulose [36]. In the first stage of thermal degra-

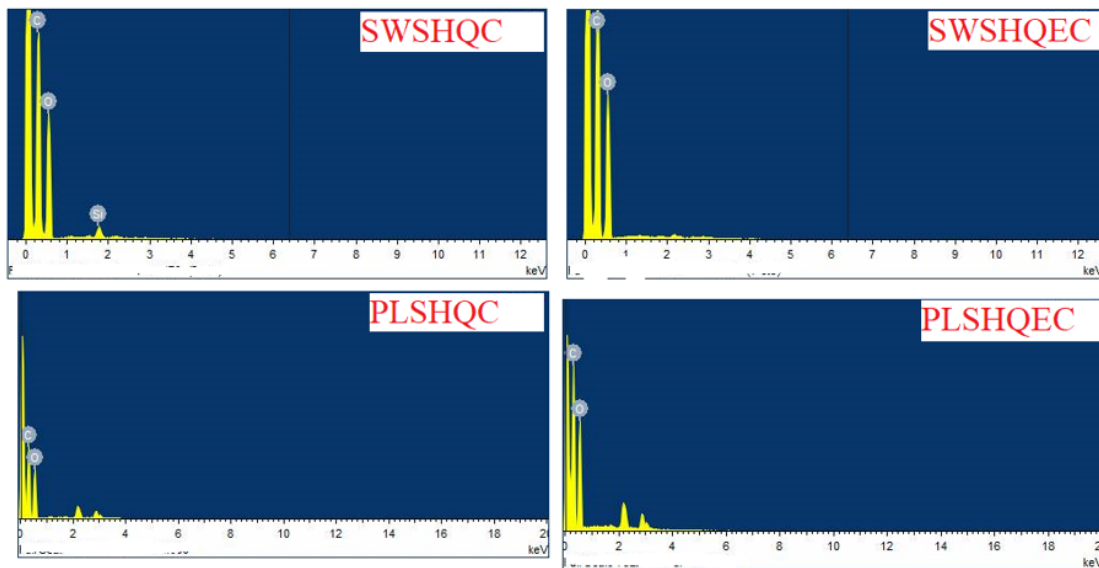


Figure 6. EDX spectra of cellulose.

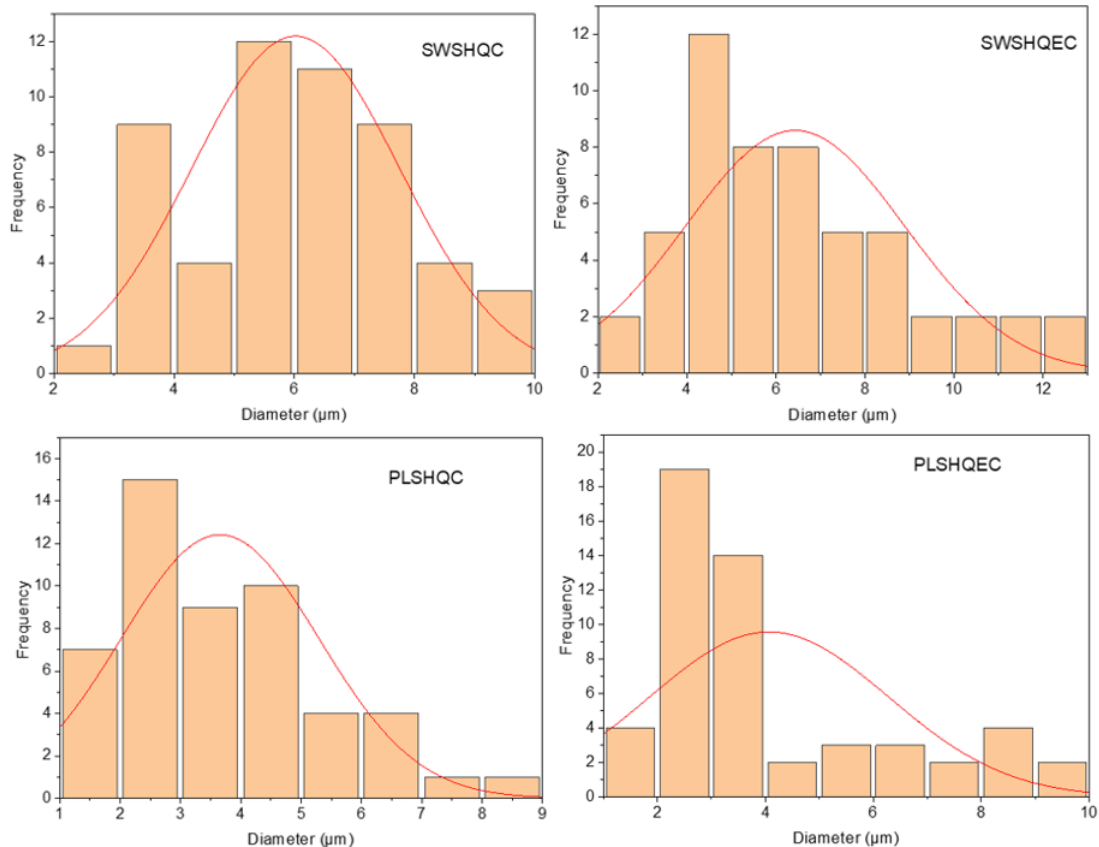


Figure 7. ImageJ average diameter size of the cellulose fiber.

dation between 247.10 °C to 353.79 °C (PLSHQC), 253.38 °C to 361.23 °C (PLSHQEC), 240.20 °C to 383.90 °C (SWSHQC) and 242.58 °C to 387.72 °C (SWSHQEC), the weight loss experienced by the PLSHQEC (65.87 %) and SWSHQEC (72.32 %) was higher than that of PLSHQC (63.38 %) and

SWSHQC (70.31 %). The presence of non-cellulosic materials such as silica and lignin (EDX Table 1 and spectra Figure 6), which are known to have higher degradation temperatures, could be responsible for the reduction in the percentage weight loss of PLSHQC and SWSHQEC. The higher D.T.G. curves

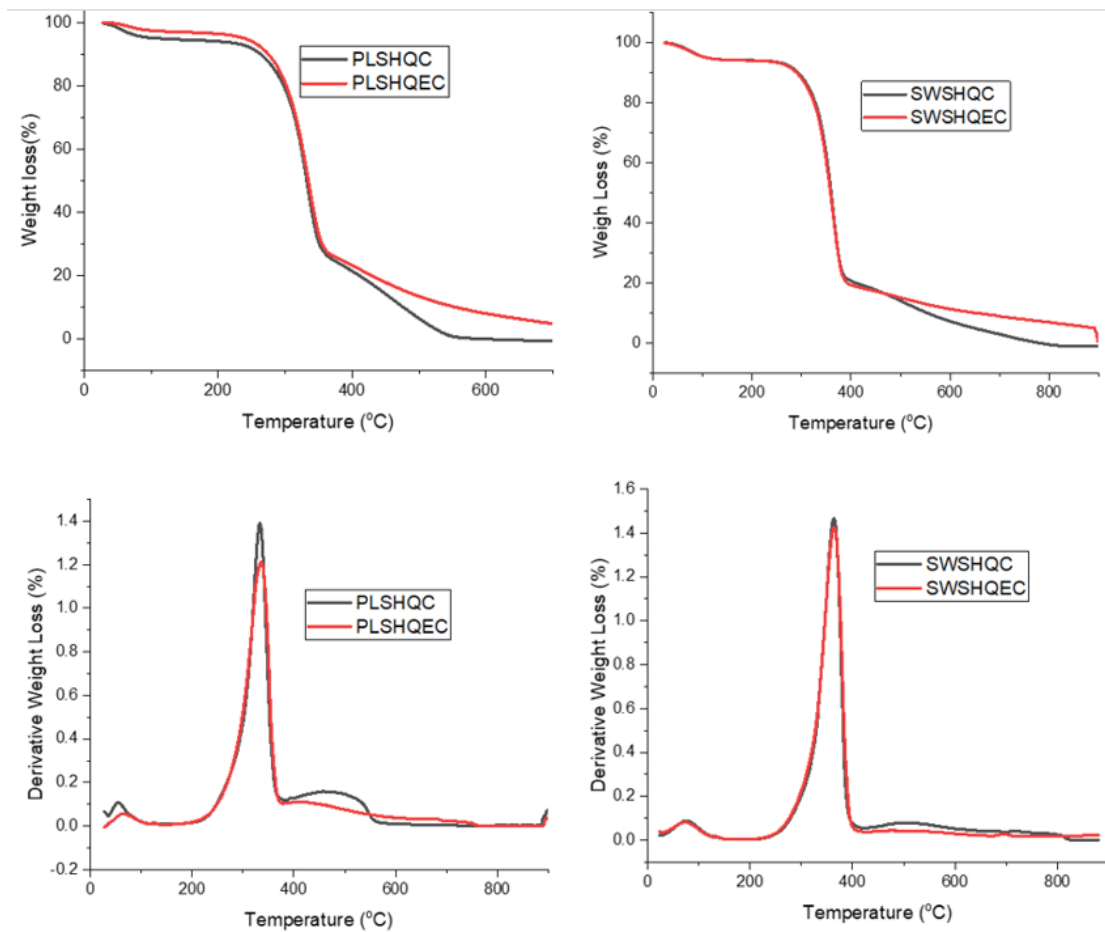


Figure 8. Thermogravimetric analysis of cellulose.

presented by PLSHQ and SWSHQ suggest the presence of non-cellulosic material, which requires a higher thermal degradation temperature. Reflection from the last degradation temperature (353 to 800 °C) experienced by the cellulose materials showed that a higher percentage of weight loss was recorded for PLSHQ (28.26 %) and SWSHQ (23.01 %). A lower percentage was observed for PLSHQEC (23.57 %) and SWSHQEC (15.79 %). Degradation of lignin at higher temperatures [37] could have caused a higher percentage of weight loss experienced by those cellulose materials at the last degradation temperature. The results have revealed that cellulose produced using SHQE is more thermally stable than those produced with SHQ.

4. Conclusion

The proximate results of the raw materials (moisture content of 5 % siam weed and 6 % Pineapple), (ash content of 6.5 % siam weed and 9.50 % pineapple), (lignin contents of 21.40 % siam weed and 27.57 % pineapple), alpha-cellulose of 59.89 % pineapple and 56.08 % of siam weed) suggest them as good pulping candidates for cellulose production. Adding anthraquinone to sodium hydroxide-ethanol pulping chemical has proved to be a better alternative to sodium hydroxide-ethanol.

It produced celluloses with a higher crystallinity index and fiber with a larger surface area due to the reduced fiber diameter determined by the ImageJ software. The celluloses have higher thermal stability than those produced with sodium hydroxide and ethanol. The prominent peaks expected of cellulose are identifiable in the spectra of all the celluloses. The SEM analysis that showed the smaller morphological images of the cellulose by adding ethanol collaborated with the ImageJ and the crystallinity results. The functionalization reaction of those celluloses produced by ethanol addition would be faster and easier because of their larger surfaced area. Because of their crystallinity properties, the cellulose materials could be useful in thermal and strength demanding products. Also, the particle size of the materials could make the materials that can easily be modified to produce various cellulose derivatives.

Acknowledgement

The authors thank the Universitas Airlangga Postdoctoral Fellowship, Indonesia, for the financial support of this work. Ref No.: 1769/UN3.AGE/DI.04/2023.

References

- [1] M. Ichwan, A. J. Onyianta, R. S. Trask, A. Etale & S. J. Eichhorn, "Production and characterization of cellulose nanocrystals of different allomorphs from oil palm empty fruit bunches for enhancing composite interlaminar fracture toughness", *Carbohydrate Polymer Technologies and Applications* **5** (2023) 100272. <https://doi.org/10.1016/j.carpta.2022.100272>.
- [2] S. H. Omer, T. O. Khider, O. T. Elzaki, S. D. Mohieldin & S. K. Shomeina, "Application of soda-AQ pulping to agricultural waste (okra stalks) from Sudan", *B.M.C. Chemical Engineering* **1** (2019) 1. <https://doi.org/10.1186/s42480-019-0005-9>.
- [3] A. Gonzalo, F. Bimbela, J. L. Sánchez, J. Labidi, F. Marín & J. Arauzo, "Evaluation of different agricultural residues as raw materials for pulp and paper production using a semichemical process", *Journal of Cleaner Production* **156** (2017) 184. <https://doi.org/10.1016/j.jclepro.2017.04.036>.
- [4] S. Saini, A. A. Kadam, V. Kumar, K. K. Gaikwad, S. P. Singh & D. Dutt, "Conversion of rice straw into disposable food-serving bowl via refiner mechanical pulping: An environmentally benign approach to mitigate stubble burning and plastic pollution", *Biomass Conversion and Biorefinery* **13** (2023) 6797. <https://doi.org/10.1007/s13399-021-01728-y>.
- [5] L. A. Worku, A. Bachheti, R. K. Bachheti, C. E. Rodrigues Reis & A. K. Chandel, "Agricultural residues as raw materials for pulp and paper production: Overview and applications on membrane fabrication", *Membranes* **13** (2023) 228. <https://doi.org/10.3390/membranes13020228>.
- [6] Q. Han, X. Gao, H. Zhang, K. Chen, L. Peng & Q. Jia, "Preparation and comparative assessment of regenerated cellulose films from corn (*Zea mays*) stalk pulp fines in DMAc/LiCl solution", *Carbohydrate polymers* **218** (2019) 315. <https://doi.org/10.1016/j.carbpol.2019.04.083>.
- [7] A. H. Basta & V. F. Lotfy, "Impact of pulping routes of rice straw on cellulose nanoarchitectonics and their behavior toward indigo dye", *Applied Nanoscience* **13** (2023) 4455. <https://doi.org/10.1007/s13204-022-02714-0>.
- [8] C. M. Imlauer Vedoya, M. C. Area, N. Raffaelli & F. E. Felissia, "Study on soda-ethanol delignification of Pine Sawdust for a Biorefinery", *Sustainability* **14** (2022) 6660. <https://doi.org/10.3390/su14116660>.
- [9] O. O. Oluwasina, L. Lajide & B.J. Owolabi, "Microcrystalline cellulose from plant wastes through sodium hydroxide-antraquinone-ethanol pulping", *BioResources* **9** (2014) 6166. <https://doi.org/10.15376/biores.9.4.6166-6192>.
- [10] T211om-93, *Standard for ash in wood, pulp, paper and paperboard*, Technical association of the pulp and paper industry (TAPPI), 1999. <https://www.tappi.org/content/sarg/t211.pdf>.
- [11] T222om-98, *Standard for acid-insoluble lignin in wood and pulp*, Technical association of the pulp and paper industry (TAPPI), 1999. <https://www.tappi.org/content/sarg/t222.pdf>.
- [12] ASTM D1104-56, *A standard method of test for holocellulose in wood*, ASTM international, 1978. <https://www.document-center.com/standards/show/ASTM-D1104>.
- [13] ASTM D1103-60, *A standards method for alpha-cellulose in wood*, ASTM international, 1978. <https://www.document-center.com/standards/show/ASTM-D1103>.
- [14] B. Goodell, J. E. Winandy & J. J. Morrell, "Fungal degradation of wood: emerging data, new insights and changing perceptions", *Coatings* **10** (2020) 1210. <https://doi.org/10.3390/coatings10121210>.
- [15] *FAO Code of practice for the prevention and reduction of mycotoxin contamination in cereals. CAC/RCP 51-2003: Codex Alimentarius*, Food and Agriculture Organization of the United Nations, 2014. www.fao.org/fao-who-codexalimentarius/standards/en/.
- [16] A. Sahoo, S. Kumar & K. Mohanty, "A comprehensive characterization of non-edible lignocellulosic biomass to elucidate their biofuel production potential", *Biomass Conversion and Biorefinery* **12** (2020) 5087. <https://doi.org/10.1007/s13399-020-00924-6>.
- [17] B. Castells, I. Amez, L. Medic, N. Fernandez-Anez & J. Garcia-Torrent, "Study of lignocellulosic biomass ignition properties estimation from thermogravimetric analysis", *Journal of Loss Prevention in the Process Industries* **71** (2021) 104425. <https://doi.org/10.1016/j.jlp.2021.104425>.
- [18] M. A. H. Alharbi, S. Hirai, H. A. Tuan, S. Akioka & W. Shoji, "Effects of chemical composition, mild alkaline pretreatment and particle size on mechanical, thermal, and structural properties of binderless lignocellulosic biopolymers prepared by hot-pressing raw microfibrillated Phoenix dactylifera and Cocos nucifera fibers and leaves", *Polymer Testing* **84** (2020) 106384. <https://doi.org/10.1016/j.polymertesting.2020.106384>.
- [19] S. Cichosz & A. Masek, "I.R. study on cellulose with the varied moisture contents: Insight into the supramolecular structure", *Materials* **13** (2020) 4573. <https://doi.org/10.3390/ma13204573>.
- [20] M. S. Rafidah, A. Jahimin & S. M. Sani, "Chemical functional groups of extractives, cellulose and lignin extracted from native *Leucaena leucocephala* bark", *Wood Science and Technology* **55** (2021) 295. <https://doi.org/10.1007/s00226-020-01258-2>.
- [21] M. L. Nelson & R. T. O'Connor, "Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part II. A new infrared ratio for estimation of crystallinity in celluloses I and II", *Journal of Applied Polymer Science* **8** (1964) 1325. <https://doi.org/10.1002/app.1964.070080323>.
- [22] A. A. M. Nada, S. Kamel & M. El-Sakhawy, "Thermal behaviour and infrared spectroscopy of cellulose carbamates", *Polymer Degradation and Stability* **70** (2000) 347. [https://doi.org/10.1016/S0141-3910\(00\)00119-1](https://doi.org/10.1016/S0141-3910(00)00119-1).
- [23] P. Kaur, N. K. Bhardwaj & J. Sharma, "A study elucidating the relation between cellulose dissolution and crystallinity after cellulase treatment at different doses", *Biotech* **11** (2021) 371. <https://doi.org/10.1007/s13205-021-02920-7>.
- [24] I. Jankowska, P. Ławniczak, K. Pogorzelec-Glaser, A. Łapiński, R. Pankiewicz & J. Tritt-Goc, "Cellulose microfibrils surface treated with imidazole as new proton conductors", *Materials Chemistry and Physics* **239** (2020) 122056. <https://doi.org/10.1016/j.matchemphys.2019.122056>.
- [25] A. F. Tarchoun, D. Trache, T. M. Klapötke, B. Krumm, K. Khimeche & A. Mezroua, "A promising energetic biopolymer based on azide-functionalized microcrystalline cellulose: synthesis and characterization", *Carbohydrate Polymers* **249** (2020) 116820. <https://doi.org/10.1016/j.carbpol.2020.116820>.
- [26] L. K. Kian, N. Saba, M. Jawaid & H. Fouad, "Characterization of microcrystalline cellulose extracted from olive fiber", *International journal of biological macromolecules* **156** (2020) 347. <https://doi.org/10.1016/j.ijbiomac.2020.04.015>.
- [27] D. Trache, A. F. Tarchoun, S. Chelouche & K. Khimeche, "New insights on the compatibility of nitrocellulose with aniline-based compounds", *Propellants, Explosives, Pyrotechnics* **44** (2019) 970. <https://doi.org/10.1002/prep.201800269>.
- [28] E. Erisir, E. Gumuskaya, H. Kirci & N. Misir, "Alkaline sulphite antraquinone pulping of caucasian spruce (*Picea orientalis* L.) chips with added sodium borohydride and ethanol", *Drewno Prace Naukowe Doniesienia Komunikaty* **58** (2015) 194. <https://doi.org/10.12841/wood.1644-3985.067.07>.
- [29] A. F. Tarchoun, D. Trache & T. M. Klapötke, "Microcrystalline cellulose from *Posidonia oceanica* brown algae: Extraction and characterization", *International journal of biological macromolecules* **138** (2019) 837. <https://doi.org/10.1016/j.ijbiomac.2019.07.176>.
- [30] A. Y. Melikoğlu, S. E. Bilek & S. Cesur, "Optimum alkaline treatment parameters for the extraction of cellulose and production of cellulose nanocrystals from apple pomace", *Carbohydratepolymers* **215** (2019) 330. <https://doi.org/10.1016/j.carbpol.2019.03.103>.
- [31] L. Cheng, X. Hu, Z. Gu, Y. Hong, Z. Li, C. Li, "Characterization of physicochemical properties of cellulose from potato pulp and their effects on enzymatic hydrolysis by cellulase", *International journal of biological macromolecules* **131** (2019) 564. <https://doi.org/10.1016/j.jlp.2021.104425>.
- [32] B. Tsegaye, C. Balomajumder & P. Roy, "Alkali pretreatment of wheat straw followed by microbial hydrolysis for bioethanol production", *Environmental technology* **40** (2019) 1203. <https://doi.org/10.1080/09593330.2017.1418911>.
- [33] M. A. Jmel, N. Anders, G. B. Messaoud, M. N. Marzouki, A. Spiess & I. Smaali, "The stranded macroalga *Ulva lactuca* as a new alternative source of cellulose": Extraction, physicochemical and rheological characterization. *Journal of Cleaner Production* **234** (2019) 1421. <https://doi.org/10.1016/j.jclepro.2019.06.225>.

- [34] R. K. Gond, M. K. Gupta & M. Jawaid, "Extraction of nanocellulose from sugarcane bagasse and its characterization for potential applications", *Polymer Composites* **42** (2021) 5400. <https://doi.org/10.1002/pc.26232>.
- [35] K. O. Reddy, C. U. Maheswari, M. S. Dhlamini, B. M. Mothudi, V. P. Kommula, J. Zhang & A.V. Rajulu, "Extraction and characterization of cellulose single fibers from native african napier grass", *Carbohydrate Polymers* **188** (2018) 85. <https://doi.org/10.1016/j.carbpol.2018.01.110>.
- [36] M. Poletto, V. Pistor, R. M. C. Santana & A. J. Zattera, "Materials produced from plant biomass: part II: evaluation of crystallinity and degradation kinetics of cellulose", *Materials Research* **15** (2012) 421. <https://doi.org/10.1590/S1516-14392012005000048>.
- [37] P. Manimaran, S. P. Saravanan & M. Prithiviraj, "Investigation of physico chemical properties and characterization of new natural cellulosic fibers from the bark of *Ficus Racemosa*", *Journal of Natural Fibers* **18** (2019) 274. <https://doi.org/10.1080/15440478.2019.1621233>.