# Arabica Coffee Pulp Cellulose: Isolation, Morphology, and its Capabilities to be Modified into Cellulose Nitrate

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**Abstract.** Cellulose nitrate was a cellulose derivative applied in various applications, from plastics to solid propellants for military ammunition and rocketry. Environmental impact from using cotton linter or wood as a source of cellulose for cellulose nitrate industry promoting attempt to use agricultural waste as an alternative source of cellulose. Utilizing non-wood agricultural waste is also advantageous to reduce waste accumulation and give economical value. However, specific cellulose properties should also considered to achieve optimum cellulose derivation process into cellulose nitrate through nitration reaction. Coffee pulp waste had potential to be used as source of non-wood cellulose for its abundance, considerable fraction of cellulose content, low economical value, and unique cellulose morphology. In this study, the cellulose from the coffee pulp was isolated through sodium hydroxide and hydrogen peroxide bleaching method, which furthermore evaluated in terms of their morphology, physical properties, and its capabilities to be derived into cellulose nitrate. The result showed that coffee pulp cellulose has crystallinity and surface area around 59.63% and 0.5962 $m^2/g$, respectively which is lower than cotton linter, suggesting advantageous properties for nitration reaction. Nitration to coffee pulp-based cellulose resulted in moderate nitrogen content cellulose nitrate which still suitable for non-military application.

## 1 Introduction

In recent decades, the utilization of sustainable and renewable resources for industry and society, as well as the development of environmentally friendly technology and economy, has become a concerning issue [1,2]. Cellulose is considered a suitable resource for these purposes because it was a largely abundant and almost inexhaustible raw material, which is estimated at $10^{11}$ to $10^{12}$ tons produced annually [3]. The capability to be chemically modified into various derivative products with different properties from its original material became one of the appealing features of cellulose. These modifications were possible because of the reactivity of the hydroxyl group present in cellulose [1]. That structure allows it to be utilized in various applications depending on the specific properties of certain cellulose derivative products.

Coffee pulp (CP) was the most prominent coffee post-harvesting waste, encompassing around 28% of the weight of dried coffee cherries. It was estimated that 2 tons of CP were discharged from each 1 ton of coffee produced [4,5]. Because of its abundance, CP has the potential to be utilized as an alternative source of cellulose. CP consisted of 20.7% cellulose, 3.6% hemicellulose, and 14.3% lignin [6]. However, CP waste is currently used as compost or landfilled and is yet to be utilized in highly valued technological or economical applications.

Coffee is Indonesia's third largest agricultural commodity, producing around 761.000 tons annually, making Indonesia the fourth largest coffee producer in the world behind Brazil, Vietnam, and Colombia [7]. A considerable amount of coffee produced resulted in a high amount of coffee pulp as post-harvest agricultural waste, providing available resources.

Despite its potential, extraction or utilization of CP waste was still rarely studied. Achaby (2019) reported cellulose extraction from coffee pulp using three times repetition of alkali treatment using 4% NaOH and three times repetition of sodium chlorite-based bleaching solution. The extracted cellulose was found to have a unique microfibrillar structure with porous and network-like morphology. This condition resulted in cellulose with good accessibility, which allows high absorption properties to water and methylene blue, citing its potential to be used in wastewater treatment [8]. Pudjiastuti (2019) also reported an attempt to extract cellulose from CP by removing lignin using alkali hydrogen peroxide at ambient temperature. However, it still resulted in

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relatively low cellulose purity of around 64%, with residual lignin of about 8.5% [9]. The purity of cellulose was essential, especially in preparing cellulose derivative products, since impurities could disrupt the modification process' effectiveness [10].

Cellulose nitrate (NC) was a derivative product of cellulose obtainable by substituting the hydroxyl group of cellulose to the nitrate group through nitration reaction. The nitration reaction of cellulose is usually conducted using the nitric acid-sulfuric acid-based nitrating mixture. Incorporation of nitrogen-containing group to cellulose resulting in energetic nature of NC. Conventionally, NC was known to be applied in various applications such as for coating agents [11], biofilter material [12], immobilization support for protein [13], and plastics [14], despite in modern day, it mainly used as a solid propellant for firearms ammunition and rocketry for military purposes [2].

Manufacturing cellulose nitrate mainly uses cotton linter or wood-based cellulose, a common source applied in the cellulose industry. However, the usage of both sources raised environmental concerns, such as the alarming rate of deforestation, and high usage of land and water consumption as side effects [15]. Attempts to utilize agricultural waste as a source of cellulose were pursued as an alternative to wood and cotton, which was also advantageous in reducing the accumulation of waste and giving economical value. Efforts were conducted in previous research to seek alternatives to cotton linter for cellulose nitrate; however, we have yet to find satisfactory results. This is affected by the properties of cellulose that could vary depending on its origin and preliminary treatment, which could influence the physicochemical, thermal, and energetic features of the produced NC [16].

The unique microfibrillar structure of CP cellulose is reported to have good accessibility because of its helical and porous morphology [8]. Ease of cellulose accessibility was expected to allow more contact between cellulose and nitrating mixture, thus affecting its reactivity [17]. This aspect became our primary consideration to be studied by the use of CP cellulose, which the aspect of morphology itself was rarely discussed in the selection of a source of cellulose alternative for NC application.

In this study, cellulose extraction from CP was conducted using two-stage processes by NaOH alkali treatment followed by hydrogen peroxide at elevated temperature. Subsequent evaluations of its cellulose properties were conducted afterward. The cellulose obtained was then subjected to a nitration process using a mixture of nitric acid and sulfuric acid as nitration reagents to impart nitrogen-containing nitrate groups into its molecules through a substitution reaction to its hydroxyl group. To the extent of our knowledge, this is yet to be reported. Hydrogen peroxide was considered as it was preferred as a more environmentally bleaching agent than its chlorine-based counterpart [18]. Furthermore, the obtained cellulose with the lowest possible non-cellulosic content was subjected to a nitration reaction to evaluate the effect of its properties to the extent of capabilities to be modified into cellulose nitrate. Through this study, we expect a simpler extraction method that resulted with higher purity of cellulose from CP was developed and contribute to expanding the potential source of cellulose to manufacture cellulose nitrate.

## 2 Materials and Methods

### 2.1 Materials

This study employs natural processed arabica coffee pulp waste (ACP) as a source of cellulose. The coffee pulp waste was provided by Kawung Asli which was obtained from Cikajang Coffee Plantation, Garut Regency, Indonesia. Sodium Hydroxide (NaOH) and Hydrogen Peroxide ($H_2O_2$) used for alkali treatment and bleaching process were supplied by Glatt Chemical, Indonesia. Analytical grade SMART LAB sulfuric acid with a purity of 97% was purchased from CV Quimica Jaya Perkasa, Bandung, Indonesia. Technical grade sulfuric acid 98% and nitric acid 65% were procured from Glatt Chemical and Rofa Laboratory respectively, both based in Bandung, Indonesia. Arnold Grummer's cotton linter was purchased from National Arts Supply, USA.

### 2.2 Isolation of Cellulose From Arabica Coffee Pulp

The cellulose was extracted using two staged processes: NaOH alkali treatment and hydrogen peroxide bleaching. The effect of the process and properties of obtained cellulose were evaluated through lignocellulosic content determination, Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscope (SEM), X-ray diffraction (XRD), and Brunauer-Ernett-Teller (BET).

### *2.2.1 Alkali Treatment Stage*

The obtained ACP is subjected to oven drying at 60°C to constant weight, then milled and sifted using a 2 mm opening sieve to obtain sieved coffee pulp (SCP). Furthermore, the SCP was washed in water at 60°C for 120 minutes under constant stirring to remove its water-soluble substances; the result was dried at ambient temperature, resulting in washed coffee pulp (WCP). The Alkali treatment of WCP was conducted using a method modified from Achaby (2019)[8]. The alkali treatment involves constant stirring of WCP inside the reflux system using a 3% NaOH solution at 80°C for 2 hours with a ratio of WCP to solution conditioned at 1:60 (w/v). The result was filtered and washed to neutral pH, then sieved using 40-grade mesh to separate leftover coffee beans. The filtrate is then dried at ambient temperature. The alkali-treated CP (ATCP) was obtained as result of this process.

### *2.2.2 Bleaching Stage*

The bleaching process was conducted to ATCP to remove residual non-cellulosic content, especially lignin. The bleaching was conducted using hydrogen peroxide solution with a concentration of 2.5%, 5%, 7.5%, and 10%

[9,19] (Designed as BL 2.5, BL 5, BL 7.5, and BL 10, respectively). The process was conducted at temperature 80°C for 2 hours with a ratio of ATCP to solution in 1:60 (w/v). The result is then washed and dried at ambient temperature, designed as bleached CP cellulose (BL).

The resulting bleached cellulose was evaluated through Lignocellulose content measurement using the Chesson Method to determine the hydrogen peroxide concentration that has optimum removal of non-cellulosic content. Further characterization was conducted to result in the lowest non-cellulosic content (cellulose with the highest purity) with Fourier Transform Infrared (FTIR) spectroscopy, electron microscopy (SEM), and Brunauer-Ernett-Teller (BET) Characterization. The extent of hornification to bleached cellulose was also studied by evaluating cellulose dried in two different methods: freeze drying and air drying. The result was designed as BL-FD and BL-AD for freeze-dried and air-dried coffee pulp cellulose, respectively.

## 2.3 Nitration of Arabica Coffee Pulp Cellulose

Arabica coffee pulp cellulose with the lowest impurities obtained in the previous isolation process was subjected to nitration reaction and characterization to evaluate CP-based cellulose's capability for the nitration process. The nitration process was conducted using nitric acid and sulfuric acid as a nitrating mixture. The dried CP cellulose with a 1:45 (w/v) ratio to nitric acid was treated for 30 minutes at 25°C [2,16]. The composition of the mixture was adjusted according to the ratio (v/v) of nitric acid: sulfuric acid that varied in 1:1, 1:2, 1:3, 1:4, and 1:5. The resulting nitrated cellulose was filtered and washed using demineralized water to neutral pH to remove the nitrating mixture and stop the nitration reaction. The washed nitrated cellulose was then stirred in boiled demineralized water for 15 minutes to remove residual nitrating acid trapped within the fiber. Furthermore, acid-purified nitrated coffee pulp cellulose was filtered and dried in ambient conditions. The samples were coded as coffee pulp cellulose nitrate (CPNC) followed by its nitric acid-sulfuric acid ratio. Which are CPNC11, CPNC12, CPNC13, CPNC14, and CPNC15 for CP nitrated with nitric acid : sulfuric acid in 1:1; 1:2; 1:3; 1:4; and 1:5 respectively.

## 2.4 Characterization

The effect of the isolation process properties of obtained cellulose and the result of the nitration process were evaluated through lignocellulosic content determination, Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscope (SEM), X-ray diffraction (XRD) Brunauer-Ernett-Teller (BET), and elemental analyzer method.

### *2.4.1 Determination of Lignocellulosic Content*

Determination of lignocellulosic content in WCP, ATCP, and BL samples was conducted according to Chesson's method described by Datta [14]. This method utilizes four stages of processes. Initially, the dried sample was weighted to the nearest 1 gram (a) and was refluxed in 150 ml boiling water for 2 hours. The processed sample was filtered and dried to constant weight (b). The second stage involves refluxing the residue in 150 ml of 0.5M $H_2SO_4$ at 100°C for 2 hours. The result was filtered, washed to a constant pH, and dried to a constant weight (c). The final stage was conducted by immersing the sample in 10 ml of 72% sulfuric acid under stirring for 4 hours; the mixture was then diluted to 0.5M and refluxed for 2 hours at 100°C. The result was filtered and dried to constant weight (d). The lignocellulosic content percentage was calculated according to the equation in Table 1. Where (a) is the initial weight. The (b), (c), and (d) were dried weight of the sample after boiling in water, refluxed in 0.5 M $H_2SO_4$, and final stage, respectively.

**Table 1.** Lignocellulosic Content Calculation

| Content | Calculation |
|---|---|
| **Water soluble content** | $\frac{a-b}{a}x100\%$ |
| **Hemicellulose** | $\frac{b-c}{a}x100\%$ |
| **Cellulose** | $\frac{d-c}{a}x100\%$ |
| **Lignin** | $\frac{d}{a}x100\%$ |

### *2.4.2 Fourier Transform Infrared (FTIR) Spectroscopy*

FTIR characterization was conducted to evaluate the effect of the extraction and nitration processes qualitatively. The sample was prepared into pellets with KBr, and the spectra were recorded in the 4000 $cm^{-1}$ to 650 $cm^{-1}$ range using Prestidge 21 Shimadzu (Japan) in the Chemistry Study Program, Institut Teknologi Bandung, Indonesia.

### *2.4.3 Scanning Electron Microscope (SEM)*

The morphology of the samples was evaluated using Scanning Electron Microscopy (SEM). SEM characterizations of CP cellulose were conducted on a freeze-dried BL sample (BL-FD) and an air-dried BL sample (BL-AD). Characterization was conducted using JEOL JSM 6510 with an applied voltage of 10 kV (JEOL Ltd., Tokyo, Japan) in the Centre for Textile of the Ministry of Industry, Republic of Indonesia, Indonesia.

### *2.4.4 X-Ray Diffraction (XRD)*

XRD characterization was conducted using a Rigaku MiniFlex X-Ray Diffractometer in PT Inovasi Hijau Indonesia, Jakarta, Indonesia. The diffraction spectra were recorded in 2ϴ 10° - 90°. The crystallinity index was calculated using Equation 1.

$$Cr.I = \frac{I_{002} - I_{am}}{I_{002}} \tag{1}$$

Where Cr.I was crystallinity index, $I_{002}$ and Iam were intensity values of crystalline and amorphous phases, respectively [20].

### *2.4.5 Brunauer Ernett Teller (BET)*

BET characterization was conducted to evaluate the specific surface area of the resulting cellulose. BET characterizations were evaluated using Quantachrome Nova 4200e BET Surface Area and Pore Size Analyzer in Research Centre for Physics of National Research and Innovation Agency Republic of Indonesia, Center for Science and Technology Research (Puspitek) Complex, Serpong, Banten Province, Indonesia.

### *2.4.6 Elemental Analyzer*

Elemental Analyzer was used to evaluate the nitrogen content of the resulting cellulose nitrate. Characterizations were evaluated using the Thermoscientific CHONS Analyzer in the Materials Engineering Laboratory, Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung.

## 3 Result and Discussion

### 3.1 Isolation of Cellulose from Arabica Coffee Pulp

Cellulose from CP (WCP) was extracted using alkali treatment with 3% NaOH and hydrogen peroxide bleaching. Alkali treatment stages were conducted to remove non-cellulosic components such as hemicellulose and lignin from WCP. Non-cellulosic components were removed after NaOH alkali treatment because of the swelling phenomenon of the microfibril structure. This allowed disruption in inter-component bonds in the WCP and allowed non-cellulosic content to dissolve [1,21]. Due to this mechanism, individual cellulose fibrils could be released [22].

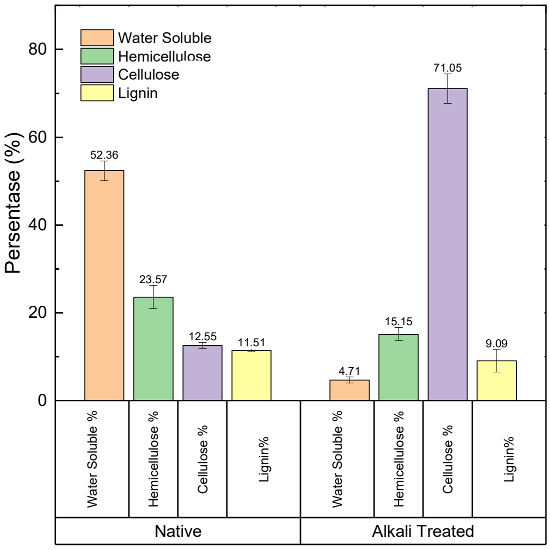

**Fig. 1.** Lignocellulosic content of native and alkali treated cellulose

Effects of the alkali treatment process were qualitatively evaluated using the Chesson-Datta method. The result showed that the fraction of cellulose was increased after the alkali treatment process, indicating the removal of non-cellulosic content after the process, as presented in Fig. 1. The increase of cellulose fraction post-alkali treatment was reached around 71.05%, from which only 12.55% in native condition.

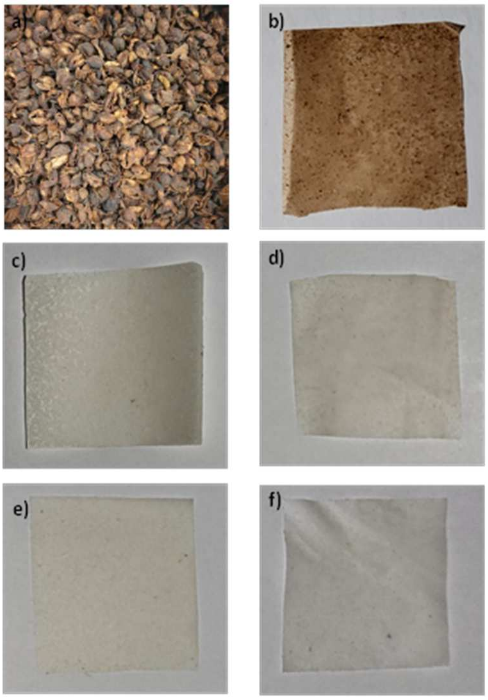

**Fig. 2.** Visual appearance a) Dried coffee pulp, b) Alkali Treated Coffee Pulp (ATCP), c) 2.5% Hydrogen peroxide bleaching (BL 2.5), d) 5% Hydrogen peroxide bleaching (BL 5), e) 7.5% Hydrogen peroxide bleaching (BL 7.5), f) 10% Hydrogen peroxide beaching (BL 10)

Hydrogen peroxide bleaching in various concentrations was conducted to remove non-cellulosic content that remains after alkali treatment, mainly to components that contribute to the brownish color of lignocellulosic substances such as lignin [17]. Hydrogen peroxide was used as a bleaching agent as it was considered more environmentally friendly than a chlorine-based bleaching agent. The visual appearance of the bleached cellulose compared to ATCP was presented in Fig. 2., which showed that the bleached product tends to have a whitish color compared to the brownish ATCP. This condition indicates the removal of lignin after the bleaching process. CP cellulose also showed that it forms a film or paper sheet-like structure after air-drying. This feature is similar to that reported by Achaby (2019), which considered exceptional as isolated cellulose commonly forms an agglomeration of fibers that readily crumble into fine powder. Another example type of

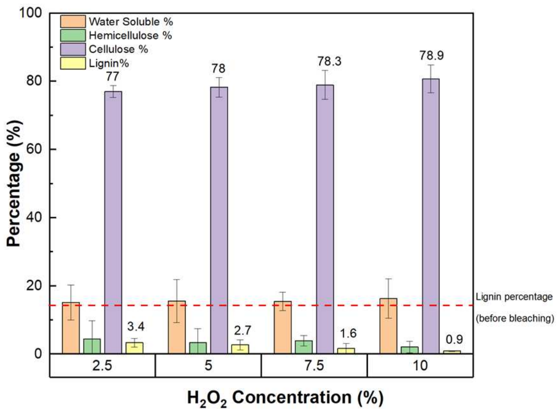

**Fig. 3.** Variation of residual lignin content after bleaching process using $H_2O_2$

cellulose with similar film-forming characteristics was bacterial or modified cellulose [8]. These capability could credited to the specific network-like morphology that allow fiber to overlap and intertwine with each other [19]. This suggests that CP cellulose has a similar quality.

Chesson-Datta method was also employed to qualitatively evaluate the effect of variation of hydrogen peroxide solution on removing lignin from ATCP. The result showed that the residual lignin fraction was fewer in higher concentrations of hydrogen peroxide, as presented in Fig. 3. This was caused as in higher concentrations, more hydroxide radicals present that were available to react with lignin, allowing removal of higher amounts of lignin after the process [23].

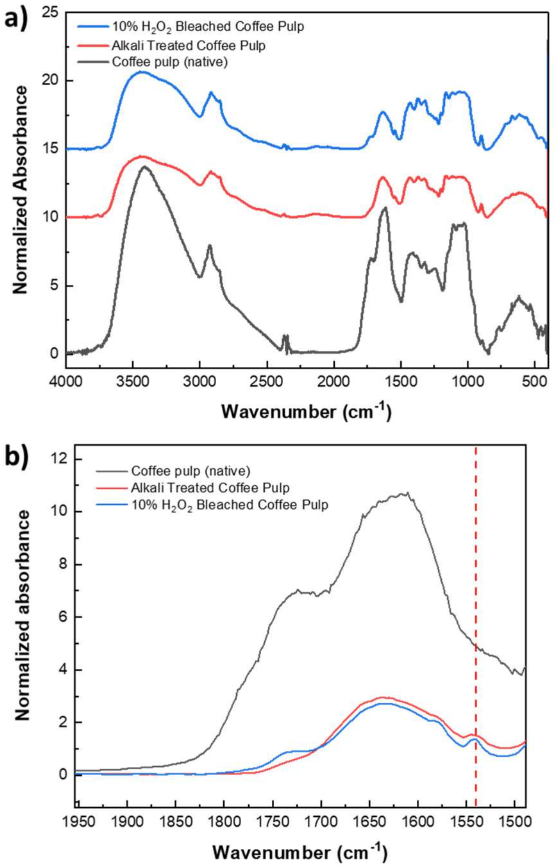

**Fig. 4.** FTIR Spectra a) Full length of FTIR spectra of respective samples (wavenumber 4000 $cm^{-1}$ – 500 $cm^{-1}$) b) Segment of spectra in wavenumber 1950 – 1500 $cm^{-1}$

FTIR characterization was conducted to evaluate the effect of the bleaching process qualitatively. The result showed that there was a reduction of absorbance peak in wavenumber 1535 – 1530 $cm^{-1,}$ which refers to the stretching movement of the aromatic ring of lignin [24,25], as shown in Fig. 4. This indicates that the lignin was removed or reduced in quantity after the process.

Based on the result, the bleaching process using hydrogen peroxide 10% (BL 10) was considered an optimal condition as it resulted in the lowest amount of residual lignin, around 0.9%. Despite the presence of residual lignin, attempts to obtain higher purity cellulose (lower amount of lignin) by increasing the hydrogen peroxide concentration were limited as it could also degrade the cellulose [26]. However, the result presented less residual lignin than reported in the previous reference (around 8.5%) [9]. Thus allowing the use of CP cellulose for applications that require high-purity cellulose, such as for modification into cellulose derivative product.

### 3.2 Properties of Cellulose from Arabica Coffee Pulp

Characterization using SEM, XRD, and BET was conducted to evaluate the morphology, crystallinity, and specific surface area of the extracted CP cellulose, respectively. The characterization applied to BL 10 CP cellulose samples was prepared through two different drying processes, freeze drying and air drying. This study was conducted on the possible occurrence of the hornification phenomenon that commonly happens during cellulose drying, which could affect the arrangement of cellulose after drying [27,28]. CP cellulose was prepared using the respective method, resulting in a different form, which is particles with freeze drying (BL-FD) and sheet form resulting from air drying (BL-AD), as presented in Fig. 5.

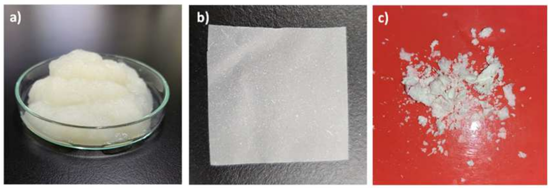

**Fig.5.** Visual appearance of 10% Hydrogen peroxide bleached CP cellulose (BL-10) a) Wet CP cellulose pulp, b) Air-Dried BL-10 cellulose (BL-AD), c) Freeze dried BL-10 cellulose (BL-FD)

The morphology of BL-FD and BL-AD, as observed using SEM, were shown in Fig. 6. The result showed that BL-FD mostly had smooth surfaces with flake-like and porous microfibrils embedded between them. BL-AD also showed a smooth surface with some helical-shaped microfibrils, which were also embedded between them. This contrasted with a cotton linter that exhibited short, thick-walled, curly, cylindrical fiber with a smooth, non-porous surface [29]. The obtained CP cellulose

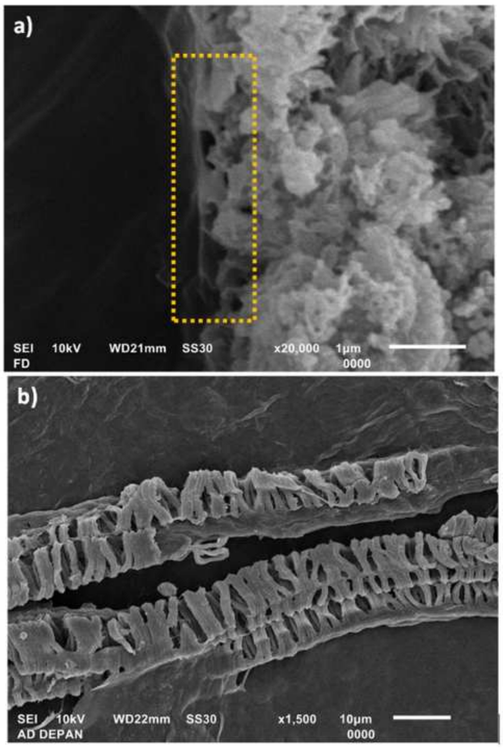

**Fig. 6.** SEM photomicrograph of 10% Hydrogen peroxide bleached CP cellulose (BL-10) a) Freeze-Dried BL-10 cellulose (BL-FD), b) Air dried BL-10 cellulose (BL-AD)

morphology was similar to the previous result by Achaby (2019), which reported a similar condition. Such cellulose morphology potentially has decent accessibility with high surface area and exposed cellulose. This was confirmed through BET characterization to BL-FD and BL-AD. The CP-based cellulose had a specific surface area of around 1.742 $m^2/g$ and 0.5962 $m^2/g$ for BL-FD and BL-AD, respectively, more significant than cotton linter with 0.4974 $m^2/g$. The lower specific surface area of BL-AD compared to BL-FD is caused by the effect of the hornification phenomenon. The larger specific surface area was advantageous to applications such as cellulose modification into derivative products, which require access to chemical reagents to hydroxyl groups cellulose molecules.

Crystallinity properties from CP cellulose were evaluated through XRD characterization. The resulting XRD diffractogram is presented in Fig. 7. The crystallinity values of the CP cellulose were 55.89% and 59.63% for BL-FD and BL-AD, respectively. The crystallinity of air-dried cellulose was higher due to better re-alignment of cellulose as an influence of hornification phenomenon during the drying than its freeze-drying counterpart [30,31]. However, the overall crystallinity of cellulose obtained from CP was lower than that of cotton linter, which reached around 75.52%. The lower crystallinity of cellulose indicates a more amorphous arrangement of CP cellulose, which could be advantageous for nitration as the readily accessible structure of cellulose allows access to foreign chemical molecules to react with cellulose [1,21].

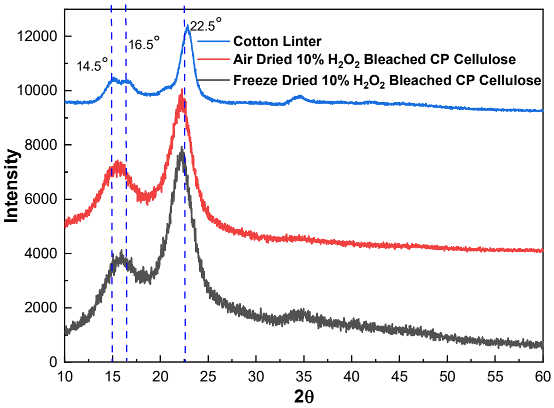

**Fig. 7.** XRD diffractogram of cotton linter and CP based cellulose

The XRD result also indicated that the obtained cellulose had a crystallinity pattern of cellulose I, shown by the diffraction peaks at 14.5°, 16.5°, and 22.5° [32]. Cellulose I structure was a crystalline pattern present in native cellulose, which indicates that the process caused no rearrangement of cellulose from its original crystalline pattern.

## 3.3 Effect of Nitric Acid-Sulfuric Acid Ratio to Nitration Effectiveness of CP Cellulose

Cellulose isolated from arabica coffee pulp (BL10) was subjected to a nitration process to evaluate its capability to be modified into CP cellulose nitrate. The cellulose was nitrated in various ratios of nitric acid: sulfuric acid while maintaining a cellulose to nitric acid ratio of 1:45 (w/v), 30 minutes of nitration duration, and conducted at 25°C (ambient temperature). The ratio of nitric acid and sulfuric acid was one of the most affecting parameters in cellulose nitration [33]. Sulfuric acid can catalyze the formation of nitronium ions ($NO_2^+$) from nitric acid [34]. Increasing sulfuric acid composition to a certain extent would allow more nitronium ions to be formed, which then react with the hydroxyl group in cellulose. More nitronium ions allow more hydroxyl groups to be substituted, resulting in cellulose nitrate with higher nitrogen content. Sulfuric acid is also needed to dehydrate the water molecules that could be formed from the substitution hydroxyl group of cellulose and maintain the concentration of nitronium ions per volume in the reagent system. Substitution reaction is unlikely to occur in lower concentrations of nitronium ions [33,35].

**Fig. 8.** Visual appearance of nitration result in various nitric acid : sulfuric acid ratio a) 1:1, b) 1:2, c) 1:3

The visual appearance of nitrated CP cellulose was presented in Fig. 8. From the figure, it could be deduced that the CP cellulose nitrated in various nitric acid: sulfuric acid ratios showed a more yellowish color than the original. This condition was caused by the reaction

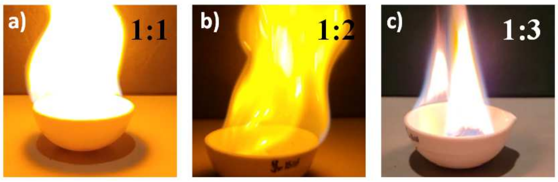

**Fig. 9.** Still of the burning test of CP cellulose nitrates in various nitric acid : sulfuric acid ratio a) 1:1, b) 1:2, c) 1:3

between the nitration reagent with residual non-cellulosic content in CP cellulose, in which the BL10 used in nitration still contained 0.9% lignin. The CPNC14 and CPNC15 were dissolved by nitration reagent and left no trace of available cellulose nitrate after the process; thus, they were not included in further discussion. This is caused by excessive sulfuric acid in the reagent, which degrade cellulose [33,34].

Burning tests were conducted as a means to assess the cellulose nitrate qualitatively. The burning test was conducted by considering the capability of cellulose nitrate with sufficient nitrogen content to be easily ignited. With higher nitrogen content contained in cellulose nitrate, the burning would be more rapid as the effect of the higher energy released by the formation of nitrogen gas following decomposition of cellulose nitrate [36]. The result showed that the post-nitrated product tends to burn rapidly after having contact with a heat source (fire from an igniter) compared to the BL10, which is relatively difficult to propagate or ignite. The rapid burning of post-nitration CP cellulose suggests the presence of nitrogen within its molecules. The still of the burning test is presented in Fig. 9.

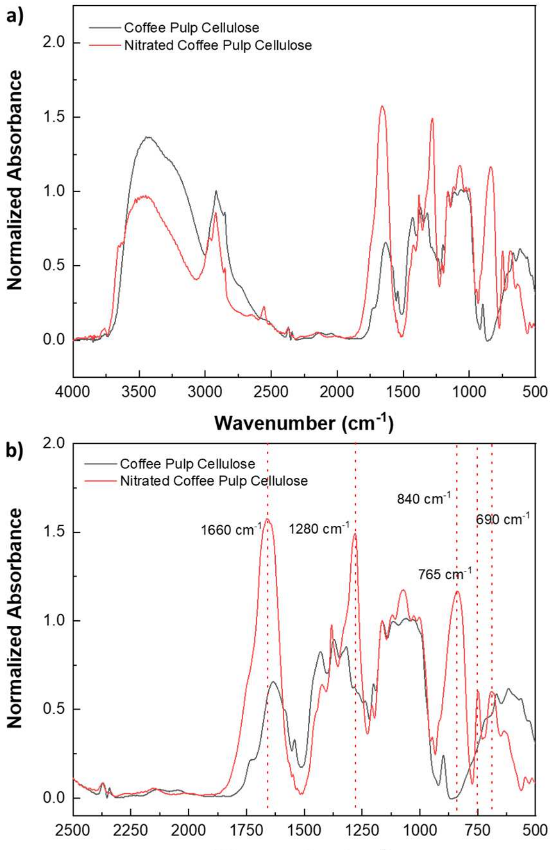

**Fig.10.** FTIR Spectrum of BL10 and post nitration BL10 a) Full length spectrum at wavenumber 4000 cm$^{-1}$ – 500 cm$^{-1}$, b) Segment of spectrum at wavenumber 2000 cm$^{-1}$ – 500 cm$^{-1}$

FTIR characterization was conducted as another qualitative assessment to verify the effect of the nitration process on CP cellulose further by confirming the presence of nitrate functional groups. The FTIR spectrum of BL10 and post-nitrated CP cellulose were presented in Fig. 10. The spectrum was normalized to wavenumber 1160 cm$^{-1,}$ indicating C-O-C stretching of cellulose glycosidic bond [37,38]. The referred wavenumber was used as a normalization point, considering the cellulose glycosidic bond should be uninvolved in the substitution reaction by nitronium ion. The result showed that the post-nitrated product showed new absorbance peak at 1660 cm$^{-1}$ (Asymmetric stretch of $NO_2$), 1280 cm$^{-1}$ (Symmetric stretch of $NO_2$), 840 cm$^{-1}$ (Stretching of O-$NO_2$), 765 cm$^{-1}$ (Asymmetric deformation of O-$NO_2$ groups), and 690 cm$^{-1}$ (Symmetric deformation of O-$NO_2$) which indicating existence of nitrate groups [2,39]. The result confirms that there are hydroxyl groups in the CP cellulose that nitrate groups substituted.

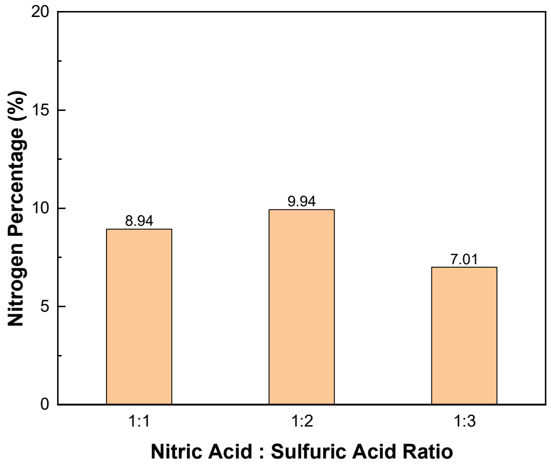

**Fig.11.** Nitrogen content of Coffee Pulp Cellulose Nitrate in various nitric acid : sulfuric acid ratio

The nitrogen content of CP cellulose NC was quantitatively evaluated using the Elemental Analyzer method to assess the effect of the acid ratio effectiveness of nitration. The result shown in Fig. 11 indicated that the increase of sulfuric acid increased the nitrogen content of the resulting cellulose nitrate to a certain extent. The highest nitrogen content was obtained in the nitric acid: sulfuric acid ratio of 1:2, with nitrogen content reaching 9.94%. This was caused by higher nitronium ion available as the effect of usage of higher sulfuric acid. However, in higher sulfuric acid concentrations (1:3), the nitrogen content sharply decreased to 7.01%. The decrease in nitrogen content of cellulose nitrate processed in higher sulfuric acid could be caused by several factors. First, possible degradation of cellulose through the hydrolysis mechanism in excessive sulfuric acid, resulting in a smaller molecular chain or even could lead to dissolution

[33,35,40]. The second possible cause was the denitration of the nitrate group that had previously formed [41].

The morphological condition of CPNC was also evaluated using SEM characterization. The SEM photomicrograph of CPNC was presented in Fig. 12. The result showed that visible fibers were slightly swollen. This condition is caused by substituting the hydroxyl group with the nitrate group, which expands the distance between the cellulose chain [2,42].

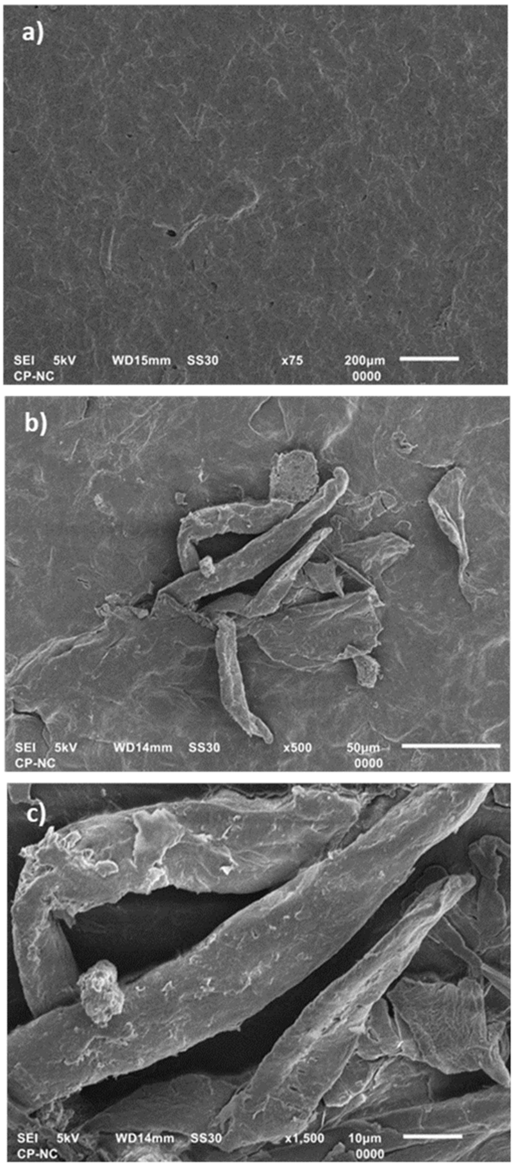

**Fig.12.** SEM micrograph of CPNC in various magnification a) 75x , b) 500x, c) 1500x

The overall result, based on the nitrogen content, is that the nitration of CP cellulose with the current method resulted in CPNC being classified into moderate-nitrogen content cellulose nitrate, as it has nitrogen content under 12% [43,44]. Usually, cellulose nitrate with moderate nitrogen content is applied in plastics, ink, lacquer, and paint. However, it is still unsuitable for propellant application as it needs higher nitrogen content for higher energy output. This limitation on the resulted nitrogen content could be affected by the surface morphology of the coffee pulp, which, despite having porous and helical-shaped fibrils that have a high surface area, most of the surface was covered in a smooth layer which formed of agglomeration of smaller fibrils [31]. This condition potentially hindered the progression of nitration reactions. However, optimizing process parameters was still possible considering limiting the amount of sulfuric acid since it could degrade the CP cellulose to the extent of complete dissolution.

## 4 Conclusion

The result of this study exhibited the effect of using alkali treatment using 3% NaOH and hydrogen peroxide in the extraction of cellulose from coffee pulp, the properties of extracted cellulose, and its cellulose nitrate product. The result showed that increased hydrogen peroxide concentration would remove the higher amount of lignin from alkali-treated CP, resulting in a lower presence of residual lignin, allowing higher purity of cellulose. The lowest residual lignin obtained was 0.9%, which resulted from the usage of 10% hydrogen peroxide concentration. The cellulose obtained is also shown to have porous and helical morphology, with crystallinity lower than cotton linter, which could be advantageous to nitration reaction. Nitration process to CP in various nitric acid: sulfuric acid ratio resulting in CP-based cellulose nitrate with moderate-ranged nitrogen content. Using a higher sulfuric acid concentration in the reagent is advantageous to obtain CP-based cellulose nitrate with higher nitrogen content. However, excessive sulfuric acid could have a detrimental effect on the result with the extent of degrading cellulose to dissolution. The optimum nitric acid: sulfuric acid ratio was achieved at 1:2, which resulted in 9.94% nitrogen content.

The authors would like to thank Mr. Ikbal from the Centre for Textile and Mrs. Maya Komalasari from Bandung Polytechnic for Textile Technology for assistance in SEM characterization, Mr. Wawan and Mr. Chandra from Research Unit for Clean Technology for assistance in freeze drying of the samples. Mr. Aries Budi Hartanto, Mr. Fauzan Aulia, Mrs. Sofa from the Research Center for Chemistry, and Dr. Latifa Hanum from the Research Center for Metallurgy of National Research and Innovation Agency Republic of Indonesia for Assistance in BET characterization. We also would like to thank the P2MI Faculty of Mechanical and Aerospace ITB for the funding provided for this research.

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