



## Mild Nitric Acid Treatments to Produce Nitrocellulose from Kapok Fiber (*Ceiba Pentandra*)

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### Abstract

Kapok (*Ceiba pentandra*) is one of the natural fibrous sources with a high content of cellulose. The natural kapok used contains 54.3% of cellulose, 11.3% of hemicellulose, and 19.11% of lignin. Kapok is a potential material to be explored by isolating the fiber, then converting into nitrocellulose. The effect of nitric acid concentration on the nitration process and characterization of material were investigated. Kapok fiber was isolated by delignification and bleaching process. Delignification was done in the presence of 5% (w/v) of NaOH and 30% (v/v) of H<sub>2</sub>O<sub>2</sub> for alkaline and acid hydrothermal treatment, respectively. Kapok was washed until neutral pH and dried in an oven at 100 °C for 4 h to get kapok fiber (CK). For the nitration process, CK 5% (w/w) was added to a solution of 15% (v/v) phosphoric acid and variation of 15%, 20%, and 25% of nitric acid. The mixture was stirred at 10 °C, 300 rpm, for 30 min. The solid CK was separated and poured into hot water for 5 min and continuously washed with demineralized (DI) water and sodium hydrogen carbonate until neutral pH. The nitrocellulose (KN) was produced after the material dried. The smooth surface of fiber and diameter around 14.5-19.1 μm was changed into a plat fiber of 13.3-21.2 μm after hydrothermal treatment. The crystallinity index (CrI) of CK was increased up to 58.17% based on X-Ray Diffraction (XRD) observation. The degree of substitution (DS) was calculated by data spectra of Fourier Transform-Infra Red (FT-IR) analysis of a specific functional group for N-O and C-O stretching vibrations. The DS optimum value was achieved at about 0.885 at concentration of 20% nitric acid (NK20). The synthesis of nitrocellulose kapok fiber-based has potential as a functional material.

### INTRODUCTION

Kapok is a part of a plant with high content of fiber, usually it is used as filler for pillow, mattresses, and other applications. Indonesia is one of largest kapok producers. Kapok has great ingredients including cellulose for development as a new biomaterial (Syed Draman et al. 2013). Treatment of optimum kapok cellulose has cellulose content about 53-55% (Mohamed et al. 2017). The utilization of kapok was observed as raw material for producing biodiesel (Yunus Khan et al. 2015), hydrogel (Sartika et al. 2021), membrane, and bioethanol (Tye et al. 2013). The exploration of

kapok is minimal and needs to develop for value-added new material, especially for cellulose.

Cellulose could be applied for textile (Costa et al. 2013), smoking filters (Fu et al. 2020), and food packing (Vanitha and Kavitha 2021), where the 50% of the cellulose is from the plant (Khan et al. 2022). Cellulose is the polymer long chain polysaccharide glucose which cannot be digested by the human. The Derivatives of cellulose products are carboxymethyl cellulose, ethyl cellulose, methyl cellulose, cellulose acetate, and nitrocellulose (Doelker 1993). The nitrocellulose/cellulose nitrate has characteristic and high commercial value. The application of nitrocellulose is used as raw material for weapon

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manufacture, propellant, paper sealant, photograph film, and explosion material (Mattar et al. 2020; Larsson 2014). Furthermore, there is no research to evaluate the synthesis of nitrocellulose based on kapok as raw material. The nitration reaction is conducted in the presence of mixed acid (phosphoric acid and nitric acid) and water. This research is focused on the effect nitric acid concentration in the mixture and the degree of substitution of the nitro group also investigated. Characterization cellulose and nitrocellulose were observed for morphology, crystal structure, and functional group.

## MATERIALS AND METHOD

### Materials

Kapok was obtained from local kapok in South Kalimantan, Indonesia. Nitric acid (HNO<sub>3</sub>, 65%), ortho-phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%), sodium hydroxide (NaOH), sodium hydrogen carbonate (NaHCO<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 %) were supplied from Merck without further purification.

### Kapok Cellulose Isolation

Kapok cellulose was isolated by two process hydrothermal treatments, including delignification and bleaching (Sartika et al. 2020). Delignification was done in alkaline condition, kapok (K) (2 g) was mixed 5% of NaOH (80 mL, w/v) and poured it into Stainless Steel Autoclave at 121 °C for 2 h. After reaction, kapok was washed until neutral pH with demineralized (DI) water and dried in the oven at 100 °C for 4 h. The delignified kapok is called KD. Bleaching process was applied to increase the color intensity, KD (2 g) was added into 30% of H<sub>2</sub>O<sub>2</sub> (108 mL, v/v) then kept in reactor hydrothermal at 121°C for 1 h. The bleached KD (CK) washed until neutral pH with DI water and dried in an oven at 100 °C for 4 h.

### Nitration Process of Cellulose Kapok

Nitration was conducted in three necks round flask in a batch process. Cellulose kapok (5 g) was mixed with variation concentration of HNO<sub>3</sub> (15%, 20%, 25%, v/v) and 15% of H<sub>3</sub>PO<sub>4</sub> (v/v) and stirred under 300 rpm at 10 °C for 30 min. After the reaction, DI water was added into the flask for washing step. Solid CK was filtered and was poured into hot water for 5 min. The residue was washed again with DI water and 10% of NaHCO<sub>3</sub> (v/v) until the pH became neutral. The CK product is

called nitrocellulose (NK) and dried at 60 °C. The same procedure was conducted for 3 types of concentration of 15%, 20% and 25% of nitric acid and identified by NK15, NK20 and NK25, respectively. The experiment's data were obtained by duplicate.

### Degree of Substitution on Nitration Process

FT-IR analysis data was used to calculate the degree of substitution (DS) of nitrogen on cellulose and nitrocellulose. The calculation based on the functional group changing the structure of cellulose from hydroxyl (-OH) becomes the nitro (-NO<sub>2</sub>) group. The identification of the -NO<sub>2</sub> group at peak wavelength ranges of 1260-1390 cm<sup>-1</sup> and 1560-1660 cm<sup>-1</sup>. The -OH group has a specific peak at wavelength range of 3200–3600 cm<sup>-1</sup>.

Determination of mole nitrogen in nitrocellulose was synthesized through comparing intensity of C-O on the primary alcohol functional group at wavenumber at 1025 cm<sup>-1</sup> and secondary alcohol at wavenumber at 1100 cm<sup>-1</sup>. Percentage mole of nitrogen in nitrocellulose synthesis result followed by Eqs (1) and (2).

$$R_{1025} = \frac{\text{Absorbance at 1025 (nitrocellulose)}}{\text{Absorbance at 1025 (pure cellulose)}} \quad (1)$$

$$R_{1100} = \frac{\text{Absorbance at 1100 (nitrocellulose)}}{\text{Absorbance at 1100 (pure cellulose)}} \quad (2)$$

Where:

Absorbance at 1025 cm<sup>-1</sup> (nitrocellulose) = - log transmittance (nitrocellulose)

Absorbance at 1025 cm<sup>-1</sup> (pure cellulose) = - log transmittance (pure cellulose)

Absorbance at 1100 cm<sup>-1</sup> (nitrocellulose) = - log transmittance (nitrocellulose)

Absorbance at 1100 cm<sup>-1</sup> (pure cellulose) = - log transmittance (pure cellulose)

The presentation mole of nitrogen in cellulose synthesis result is same concentration of O-N on nitrocellulose, which determinate by Eqs (3) and (4).

$$\% \text{ mole of N } 1025 = (1 - R_{1025}) \times 100\% \quad (3)$$

$$\% \text{ mole of N } 1100 = (1 - R_{1100}) \times 100\% \quad (4)$$

Cellulose monomer has three functional groups that can be reacted, one functional hydroxyl group is primary alcohol at C6 atomic number and

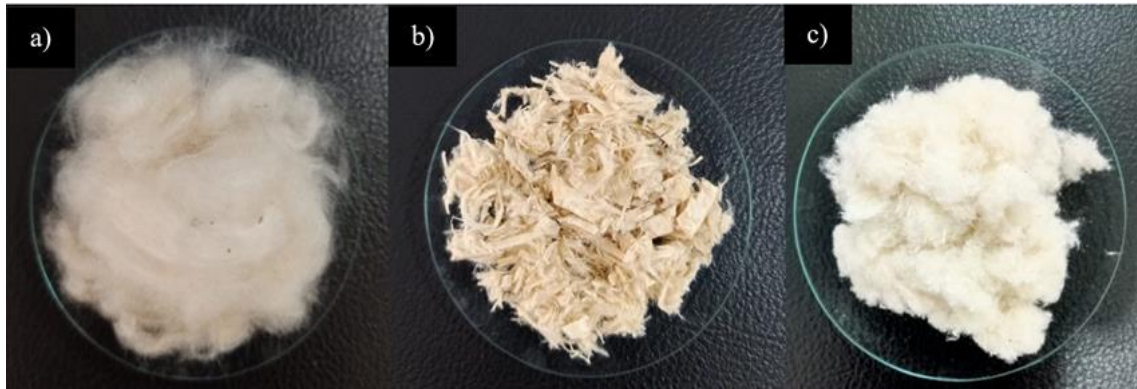


Figure 1. The photograph of (a) kapok (K); (b) kapok after delignification (KD), and (c) kapok after bleaching (CK).

two functional hydroxyl groups are alcohol scannery on atomic C number of 2 and 3, so that the percentage total nitrogen (N% total) calculate by Eq. (5).

$$N\% \text{ total} = \frac{1}{3}\% \text{ mol of N } 1025 + \frac{2}{3}\% \text{ mol of N } 1100 \quad (5)$$

Degree of substitution of nitrocellulose can be calculated from the percentage of total mole nitrogen in nitrocellulose whose availability for substitution is 3 groups. However, the substitution degree of nitro group in nitrocellulose with mole nitrogen addition can be substituted in each monomer. The degree of substitution could be calculated by using Eq. (6):

$$DS = \left( \frac{N\% \text{ total}}{100} \right) \times 3 \quad (6)$$

### Characterization

The surface morphology of cellulose and nitrocellulose were observed by Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-6500F, JEOL Ltd., Tokyo, Japan). The functional groups on the samples were retrieved by Fourier Transform Infrared Spectrometry (FT-IR, Bio-rad, Digilab FTS-3500) in a range of wavelength  $400\text{-}4,000 \text{ cm}^{-1}$ . X-Ray Diffraction (XRD, Rigaku D/MAX-B X-ray diffractor, Rigaku Co., Tokyo, Japan) equipped with Copper K-alpha ( $\text{CuK}\alpha$ ) radiation, operation voltage worked at 40 kV and machine current worked at 100 mA. Crystal index can be calculated with Eq. (7).

$$\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100\% \quad (7)$$

Where CrI = crystallity index (%);  $I_{002}$  = intensity part of cellulose crystal;  $I_{\text{am}}$  = intensity part of cellulose amorph.

## RESULTS AND DISCUSSION

### Isolation and Characterization of Cellulose from Kapok

The raw material for this study uses local kapok which contains cellulose 54.3%, hemicellulose 11.3%, and lignin 19.11%. The cellulose isolation from kapok is conducted by hydrothermal treatment by alkali solution for lignin and hemicellulose elimination on the structure. The hydrothermal process is simple, non-corrosive, safe, and efficient to get a high quality of cellulose (Sartika et al. 2020). The photograph of kapok before and after delignification and also after bleaching can be seen on Figure 1. The reaction condition of hydrothermal treatment is high temperature and pressure, so that lignin layer and hemicellulose on kapok will break and increase cellulose content. In Figure 1(a) is shown kapok looks crude fiber and hydrophobic, due to lignin content on the surface. Alkali treatment with sodium hydroxide makes kapok changes color from cream become light cream and structure turns to clumping (Figure 1 (b)). The hydroperoxide anion ( $\text{HOO}^-$ ) in alkali media was oxidized on lignin structure. This morphology observation shows the effect of delignification which destroys lignin layer on the surface of kapok. Furthermore, lignin and hemicellulose will be released into solution (Sartika et al. 2020; Chuah et al. 2017). The combination of acid hydrothermal using hydrogen peroxide also increases the purity of CK, which also can dissolve lignin and hemicellulose. The cellulose kapok

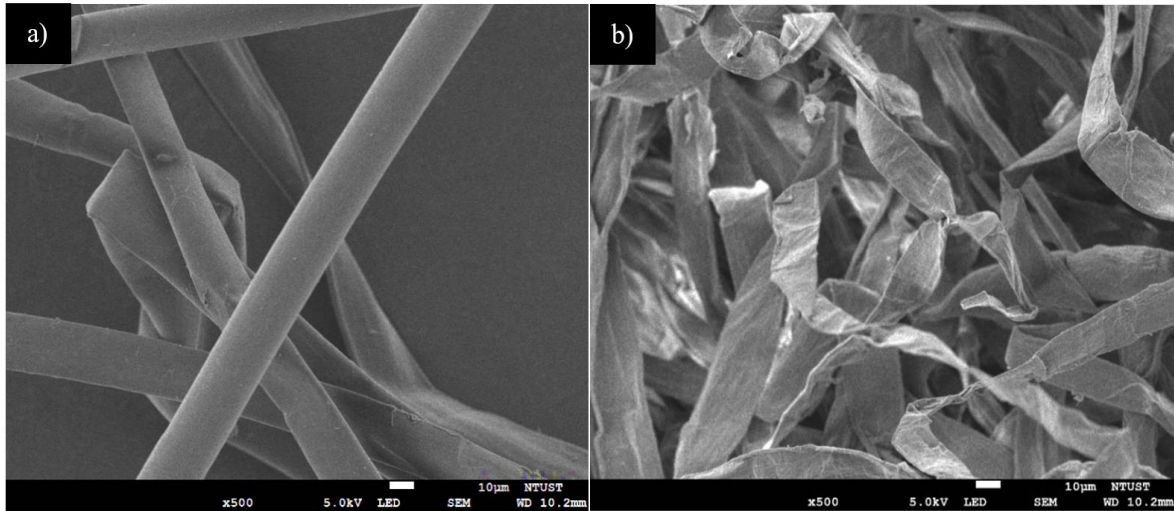


Figure 2. FE-SEM images of (a) kapok (K) and (b) kapok after bleaching (CK)

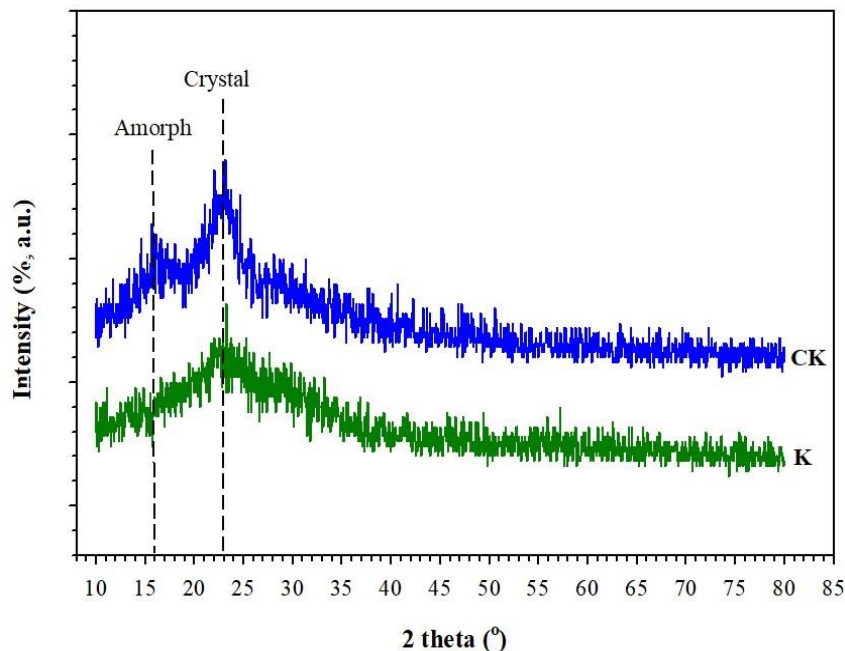


Figure 3. XRD pattern of kapok (K) a) and (b) kapok after bleaching (CK).

produces with high purity and increases the color intensity becoming white (Figure 1 (c)).

Based on FE-SEM observation, the morphology structure of kapok was changed. Figure 2 (a) shows the original kapok before treatment, its shape is rounded fiber with diameter about 14.54 and 19.09  $\mu\text{m}$ . After delignification and bleaching process, the morphology becomes slab fiber (Figure 2(b)). Again, this is because the sodium hydroxide and acid solution damages kapok structure during hydrothermal treatment. The fiber diameter is slightly larger, about 13.28-21.18  $\mu\text{m}$ , this proved that the hydrothermal treatment breaks the lignin layer and after drying it become flat

shape. This result is in accordance with previous research (Sartika et al. 2020).

In order to investigate delignification on kapok, the crystallinity Index (CrI) after treatment should be increased. Figure 3 shows the XRD pattern of kapok and kapok after bleaching. The cellulose crystal in lignocellulose structure has a specific area in two theta ( $2\theta$ ) between  $20^\circ$ – $40^\circ$  and amorph part in the range of  $2\theta$  between  $0^\circ$ – $20^\circ$ . Those peaks are identified by XRD intensity, which has highest number in the specific range of measurement. Kapok has spesifik for amorphous and crystal parts at  $2\theta = 16.66^\circ$  and  $23.15^\circ$ , respectively. CrI value of kapok is 28.57% and after

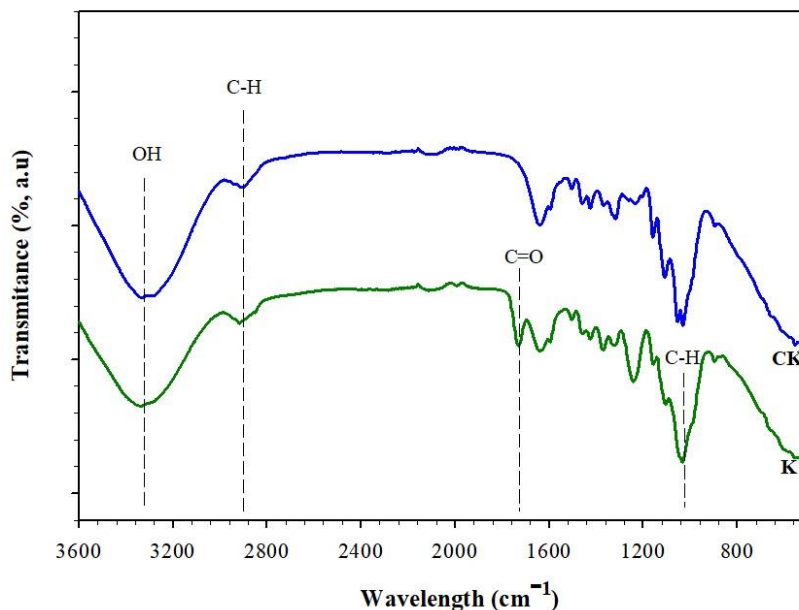


Figure 4. FT-IR Spectra of (a) kapok (K) and (b) kapok after bleaching (CK).

treatment increased up to 58.17%, the crystalline index increased about 93.10%. The increasing CrI on treatment is also found in other research which also uses kapok as raw material (Sartika et al. 2021). It is well known that cellulose is a parameter for determining strength of fiber, in this case the goal of treatment is high quality of cellulose.

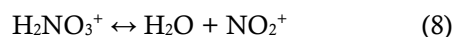
The structure change on kapok and cellulose kapok were followed by functional groups formation. The FT-IR spectra of kapok and cellulose kapok is shown in Figure 4. The peak spectra at  $3400\text{ cm}^{-1}$  is stretching vibration of -OH for cellulose, hemicellulose and lignin (Maiti et al. 2013). The peaks at wavelengths of  $2914\text{ cm}^{-1}$  and  $1756\text{ cm}^{-1}$  are stretching vibrations of C-H and C=O, respectively. Those spectra found for hemicellulose and lignin (Khenblouche et al. 2019). The functional group on CK was detected for C=O stretching, this condition showed the deformation structure in aromatic circular from lignin (Bykov 2008). This characterization shows the structure change by hydrothermal treatment which is also confirmed by FE-SEM and XRD measurement.

#### Effect of Nitric Acid Concentration Towards Nitrocellulose Product

The nitrocellulose production from cellulose is a reaction of mixed acid including nitric acid ( $\text{HNO}_3$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) at low temperature. Specificity at low temperature is to prevent decipherment reactions which lead to exothermic conditions (Cheung 2014). The

nitration reaction consists of three steps: formation of nitronium ions, releasing water ( $\text{H}_2\text{O}$ ), and formation of nitro functional groups ( $-\text{NO}_2$ ). First, H electrons from  $\text{HNO}_3$  transfer to  $\text{H}_3\text{PO}_4$  and form hydrogen hydronium ( $\text{H}_2\text{NO}_3^+$ ) because of the presence of  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$ . The transfer electron leads to release an energy which heat from the system to surroundings and eliminates energy in the system. The second step is  $\text{H}_2\text{O}$  release, the reactant and formation reaction rate are same to achieve the equilibrium. Formation of nitronium ( $\text{NO}_2^+$ ) leads to excess electrons on hydrogen nitronium ( $\text{H}_2\text{NO}_3^+$ ) compound which releases  $\text{H}_2\text{O}$  content and formation of  $\text{NO}_2^+$  (Cheung 2014).

Figure 5 shows the nitration reaction resulting in the form of degree of substitution of nitro groups on cellulose structure. The nitro source from nitric acid was varied on reaction for 15%, 20%, 25% were obtained of DS value about 0.3503, 0.8849, and 0.1016, respectively. In contrast, DS value significantly decreased at 25% of nitric acid. In the term of high concentration of nitric acid, the  $\text{H}_2\text{O}$  content also increased about 24%. The high concentration of  $\text{H}_2\text{O}$  will affect to cation nitronium take place surrounded water and will eliminate nitration effectivity though equation (Cheung 2014):



FT-IR spectra show the new functional group on cellulose. The completion substitution of

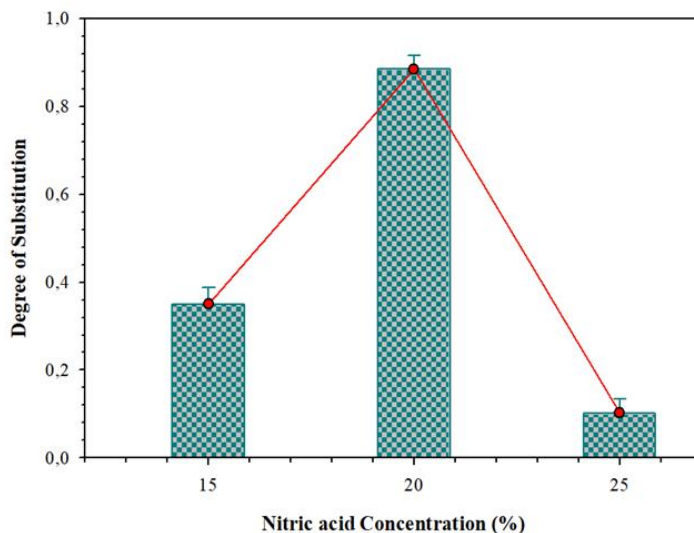


Figure 5. Degree of substitution of nitrocellulose from kapok with different concentrations of 15% of nitric acid (NK15), 20% of nitric acid (NK20), and 25% of nitric acid (NK25). Operation condition: 10 °C, 30 min.

Table 1. FT-IR spectra of nitrocellulose which prepare by difference nitric acid concentration

Sample	Wavelength (cm <sup>-1</sup> )	Functional group
NK-15	1641, 1315, 894	NO <sub>2</sub>
NK-20	1637, 1318, 897	NO <sub>2</sub>
NK-25	1634, 1315, 897	NO <sub>2</sub>

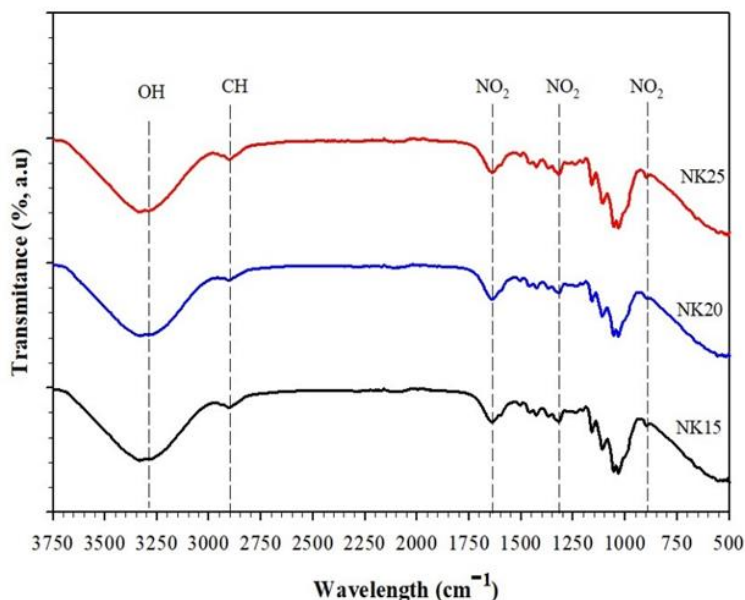


Figure 6. FT-IR spectra of nitrocellulose from kapok are prepared by different concentration of 15% of nitric acid (NK15), 20% of nitric acid (NK20), and 25% of nitric acid (NK25). Operation condition: 10 °C, 30 min.

hydroxyl group into nitro group was successfully achieved. Figure 6 shows the spectra of nitrocellulose which differ in nitric acid concentration. The FT-IR spectra for specific nitro

group on 15%, 20%, and 25% of nitric acid are shown in Table 1.

FT-IR analysis of nitrocellulose products successfully showed the nitration process which

replaced a hydroxyl group (-OH) to nitro group (NO<sub>2</sub>). It shows peak at 3200-3600 cm<sup>-1</sup> and peak at 2890-2980 cm<sup>-1</sup> for -OH and C-H, respectively. The formation of NO<sub>2</sub> was shown at peaks in the range of 1260-1390 cm<sup>-1</sup>, 1560-1660 cm<sup>-1</sup> and 800-900 cm<sup>-1</sup> (Sartika et al. 2020). It has a similar result as nitrocellulose based bacterial cellulose (Jamal et al. 2020).

## CONCLUSION

The nitrocellulose was successfully produced from nitration with mixed acid in the presence of 20% HNO<sub>3</sub> and 15% of H<sub>3</sub>PO<sub>4</sub> as optimum condition with DS value 0.885. The high cellulose content of kapok and bioconversion to nitrocellulose makes kapok become potential as a raw material to develop further.

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