

## Oxidation of Cellulose and Nanocellulose Isolated from *Paraserianthes falcataria* by Potassium Permanganate

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### ABSTRACT

A high crystallinity proportion of cellulose and nanocellulose in some points contribute to the solubility in polar solvent. This paper reports oxidation reaction study by using potassium permanganate of the cellulose and nanocellulose isolated from the soft wood of *Paraserianthes falcataria*. The reaction was conducted under acidic condition at 30 and 70°C for 12 and 24 hours. The product was characterized by FTIR, XRD, SEM, DTA-TGA, and solubility test. Oxidation of cellulose resulted in the opening of hemiacetal of glucopyranose chain, as indicated by carbonyl peak recorded in FTIR spectra. The particle size was determined and amorphous product of cellulose and nanocellulose was isolated. In addition, the DTA/TGA analysis indicate the oxidized cellulose give a more stable structure than the nanocellulose.

Keywords: oxidation, cellulose, nanocellulose, characteristic, potassium-permanganate

### INTRODUCTION

Cellulose is a biopolymer and composed in plant cell wall. Its structure consists of polymer chain of D-glucose in glucopyranose form, and interlinked with glycosidic bond [1]. When its structure is oxidized both by enzymatic and/or chemical reagent form oxidized-cellulose products [2]–[5]. This product has various medical and industrial applications[6], [7], such as wound dressing, drug delivery, water and polar soluble paint and ink filler, and water purification. In the medical field, oxidized cellulose is used as a hemostatic agent to control bleeding, bioresorbable surgical mesh for wound closure. In industrial applications, oxidized cellulose is applied as a flocculant or strengthening agent in membrane or paper filter for water purification, or as a filler agents in ink or paint products [8], [9].

Even with its many uses, oxidized cellulose synthesis remains a difficult process. Oxidized cellulose is produced from many cellulose sources. This paper is reported the characteristic of oxidized cellulose and nanocellulose isolated from the softwood of Sengon (*Paraserianthes falcataria*).

The Sengon plant has cellulose composition of 40-65%. It can be isolated from the branches, leaves, bark, and wood parts. However, its structure contains high crystalline contents and difficult to be dissolved in water or polar solvent. Hydrolysis into nanocellulose still leaves the issue of solubility in aqueous solvents [1], [10]. Several references report changing the polymer structure of cellulose to a straight or branched structure and high

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crystalline become amorphous, and increase solubility in aqueous solvent [11]–[13]. Some other strategies apply oxidation reactions to produce oxidized cellulose [14]. Several reagents reported to oxidize cellulose such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [15], chlorine [4], hydrogen peroxide [5], and various metal catalysts [16].

Original form of cellulose or nanocellulose composed of hydroxyl functional group. Conversion into its oxidized form is predicted can contain the groups of carboxylic acid and carbonyl functionality. The yield of this process also depends on the nature of cellulose source, types of the oxidizing agent, concentration of oxidizing agent, pH condition, catalyst, and reaction time.

Reported by Tang, et al (2017) the use of TEMPO as a oxidating agent produce a higher levels of oxidated cellulose until 91%, and also increase its solubility in water [15]. Another reagent such as combination of hydrogen peroxide and copper sulfate ( $\text{H}_2\text{O}_2\text{-CuSO}_4$ ) as oxidating reagent, increase the carbonyl group functionality up to 37% [17]. However, consider to future large scale production, access for these two reagents facing some limitation [5]. It is necessary to apply other alternative oxidating reagent that accessible in any sides [18], [19].

Oxidating reagent mechanistically and selectively disrupt the structure of cellulose polymers, by interacting with hydroxyl groups of cellulose, and converted into carboxylic acid or carbonyl group. In other context, the reagents not only able to oxidize cellulose in one oxidation level, but also two or three oxidation level. In some cases, has to breakdown the hemiacetal bond of cellulose [3] to open the glucopyranose ring. Several oxidation reagents option was reported such as potassium permanganate ( $\text{KMnO}_4$ ) [20], [21], and ozone ( $\text{O}_3$ ) [22]. Potassium permanganate ( $\text{KMnO}_4$ ) previously been used for sigma-bond cleavage oxidation [20], [21]. The disconnected bond selectively produces carboxylic acid and ketone functionality. Similar finding is resulted by applying plasma generated ozone ( $\text{O}_3$ ) in-situ [22].

This paper reports our recent work on the oxidation cellulose and nanocellulose using potassium permanganate. The oxidation reaction time and temperature effect on the characteristics of oxidized products were investigated. The cellulose is isolated from the soft wood waste of Sengon (*Paraserianthes falcataria*). This fast-growing plant is planted by local farmer in Indonesia and processed by cutting into several type size of log. This process provide a huge source of soft wood waste [23], and generally is disposed by farmer or burnt.

## EXPERIMENT

### Chemicals and instrumentations

Chemicals used for research were sodium hydroxide (99% purity Merck, Germany), sodium hypochlorite (99% purity Merck, Germany), formic acid (99% purity Merck, Germany), potassium permanganate (99% purity Merck, Germany), hydrochloric acid (99% purity Merck, Germany). Meanwhile, several tools used for research include glassware, hot plate, magnetic stirrer, thermometer, analytical balance, suction pump, vacuum filter, oven, ultra-sonicator (DELTA D150H), FTIR spectrometer (Shimadzu FTIR-8400S), powder XRD spectrometer (PANalytical-type X'pert Pro), SEM (FEI SEM Inspect-S50), and DTA/TGA analyzer (Linseiss, STA P 1600).

### Cellulose and nanocellulose isolation

The sample cellulose for the research was prepared from the softwood waste of Sengon (*Paraserianthes falcataria*) after alkali-bleaching method. The nanocellulose was then prepared from cellulose prior to hydrolysis process using 60% formic acid. Meanwhile, characteristics of both cellulose and nanocellulose were reported previously [24].

### Procedure for oxidation reaction

The oxidation reaction of cellulose and nanocellulose begins with mixing a 1.0 gram of cellulose or nanocellulose with 5.0 grams of  $\text{KMnO}_4$  powder. Then, the mixture was added with 100 mL of distilled water. Hydrochloric acid was added subsequently to achieved solution to pH 1. Then, it was stirred (200 rpm) with magnetic stirrer for 12 and 24 hours, and the temperature was varied at 30 and 70°C. After that, the reaction was stopped, and the mixture was filtered off to obtain the product. Washing process was done several times until the pH is neutral, and the product was finally separated, dried, and weight until constant weight.

### Characterization by Fourier Transform Infra-Red (FTIR)

A 5.0 mg of sample was mixed with 95 mg of potassium bromide, and this mixture was pressed in film holder produce pellet. The FTIR spectrum was resulted by scanning the sample in the wavenumbers of 400 to 5000  $\text{cm}^{-1}$ .

### Characterization by Powder X-Ray Diffraction (XRD)

Characterization of isolated cellulose using X-ray diffraction (XRD) was done at rotation angle of 2°-Theta by 10° to 90°, and radiation rate of 0.02° per second for 46 seconds. Cu metal serves as the source of the radiation, which has a  $K_1$  wavelength of 1.540560 Å and a  $K_2$  wavelength of 1.54443 Å. The intensity and the particle response peaks after being irradiated with X-rays for measurements were obtained as diffraction pattern.

### Characterization by Scanning Electron Microscope (SEM)

The sample was attached with conductive carbon double-tape to the specimen holder for image capture by SEM analysis. The conductive double-tape uses as a grounding device for all electrons that enter the sample. Standard operating parameters for the SEM was as follows: spot size: 50, high voltage: 20 kV, and work distance: 10 mm [25].

### Characterization by DTA/TGA

Differential thermal analysis and thermal gravimetric analysis (DTA/TGA) operated using heating rate of 10 °C per minute, with ranges from 25 to 600 °C in atmospheric air. Thermogravimetry instrument was able to measure the weight loss toward the temperature. In addition, the resulted data was processed using OriginLab Pro 32-bit software to calculate the derivative weight loss to temperature (DTG).

### Solubility test

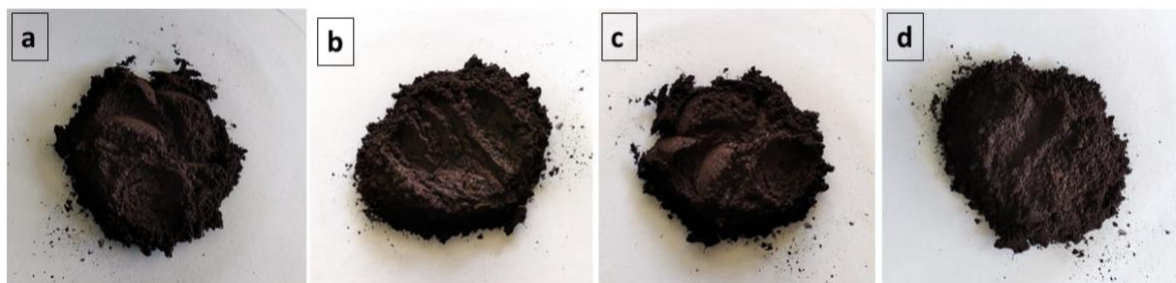
Solubility evaluation of the oxidized cellulose and nanocellulose was qualitatively tested using water, acetic acid, chloroform, and *n*-hexane as solvents. The experiment was performed in room temperature. A 10 mL of solvent and 0.05 grams of oxidized cellulose and nanocellulose was used in test tube. The observation was monitored after 1-2 minutes shaking of the mixture.

## RESULT AND DISCUSSION

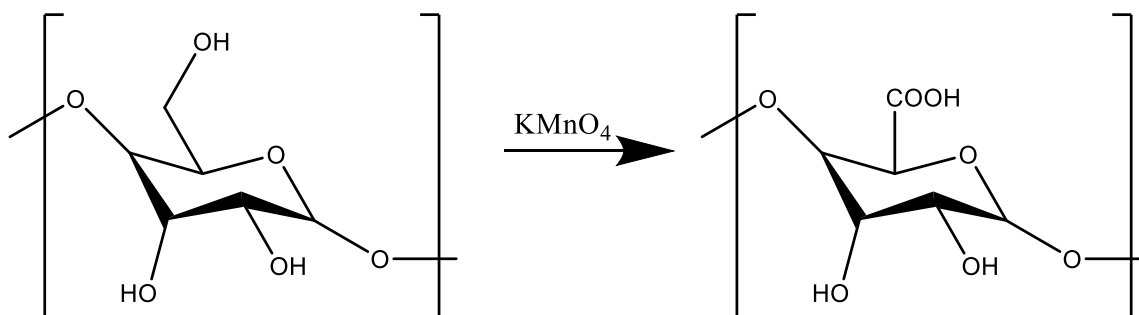
### Oxidation of cellulose and nanocellulose

Sample cellulose was isolated as a bone-white powder, and insoluble in water. While nanocellulose was yielded as a white solid powder, and easily dispersed in water. cellulose and nanocellulose have crystallinity index of 66.6% and 81.0%, respectively [24]. Oxidation using potassium permanganate ( $\text{KMnO}_4$ ) cleavage sigma-bond of cellulose to produce carbonyl groups [26]. Oxidation of the hydroxyl group attached in C6 of the glucopyranose framework

provides carboxylic acid group [3]. The schematic reaction is depicted in Figure 2. This oxidation process resulted in cellulose and nanocellulose powder as a black powder (Figure 1). It was most likely that the black color was due to the residue of manganese oxide ( $\text{MnO}$  or  $\text{MnO}_2$ ) mixed with the product. Even though, after several treatment using acidic hydrolysis, this oxidized cellulose and nanocellulose still retain a black powder. Moreover, it was found that at a longer time and higher temperature, the isolated product produced a finer powder.



**Figure 1.** Oxidized product C- $\text{KMnO}_4$ -12H-30°C (a), C- $\text{KMnO}_4$ -12H-70°C (b), C- $\text{KMnO}_4$ -24H-70°C (c), NC- $\text{KMnO}_4$ -24H-70°C (d)

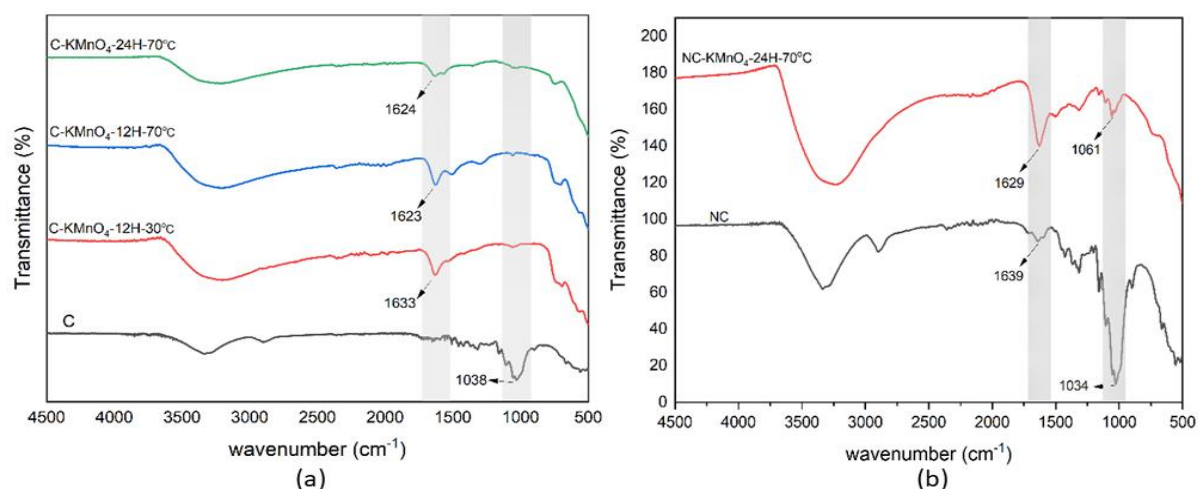


**Figure 2.** The schematic reaction of cellulose oxidation with  $\text{KMnO}_4$ . The hydroxyl-group attached in C6, was oxidized into carboxylic acid functionality.

### FTIR characterization

The FTIR spectra of oxidized product is displayed in Figure 3. It shows that both cellulose and nanocellulose has identical band peaks in  $3300$  and  $1000\text{ cm}^{-1}$  regions. Both peaks correspond to the vibration for O-H hydroxyl groups and C-O-C of pyranose rings, respectively. In addition, both oxidation product of cellulose and nanocellulose give a stronger band intensity than its original sample.

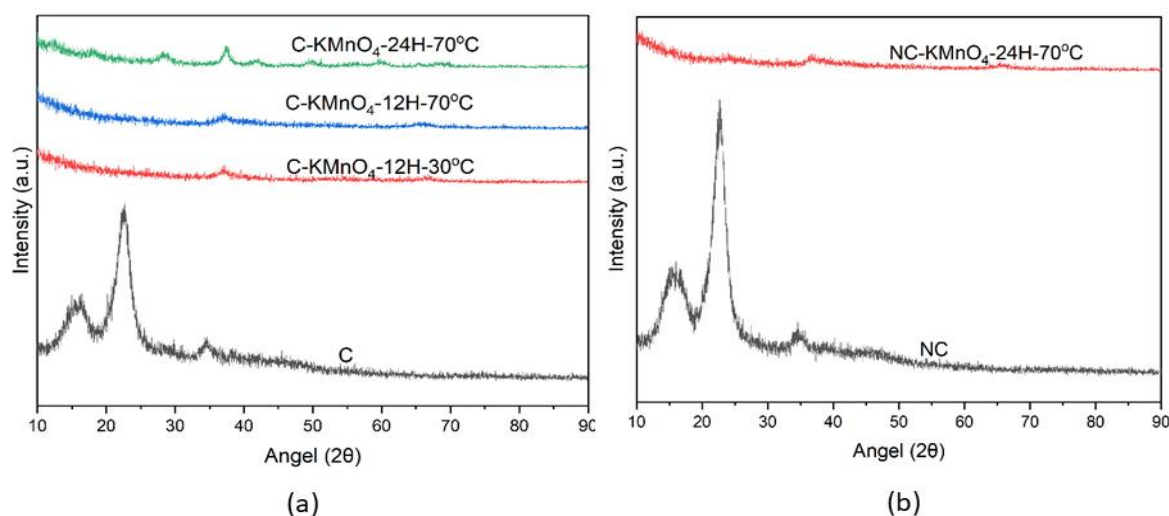
A new peak absorption was also observed for both oxidized products in  $1600\text{ cm}^{-1}$ . This absorption correlates to C=O stretching vibration for an aldehyde or carboxylic acid-resulted from oxidation process [27]. The carboxylic acid absorption is indicated by the broadband peaks for -OH stretching vibration in  $3500\text{-}3500\text{ cm}^{-1}$  [28], [29].



**Figure 3.** FTIR spectra for (a) cellulose and its oxidation product. Oxidation was undergone in 30 °C and 70 °C with 12 and 24 h reaction time. (b) Nanocellulose and its oxidation product was taken place at 70 °C for 24 h.

### XRD characterization

The X-ray powder diffraction patterns of cellulose, nanocellulose, and the oxidized products are shown in Figure 3. For cellulose and nanocellulose, they both have identical peaks at  $2\theta$  angles of 15°, 22° and 35°. These peaks are related to the characteristics of cellulose which is consist of crystalline and amorphous structures. In contrast, the oxidized products from both samples indicate amorphous properties. Several weak peaks of the oxidized products appeared at  $2\theta$  angles of 27°, 37°, 50°, 60°, and 65°. According to JCPDS 44-0141 database, this sample of oxidized product of cellulose and nanocellulose was predicted to be MnO<sub>2</sub> contaminant [30].

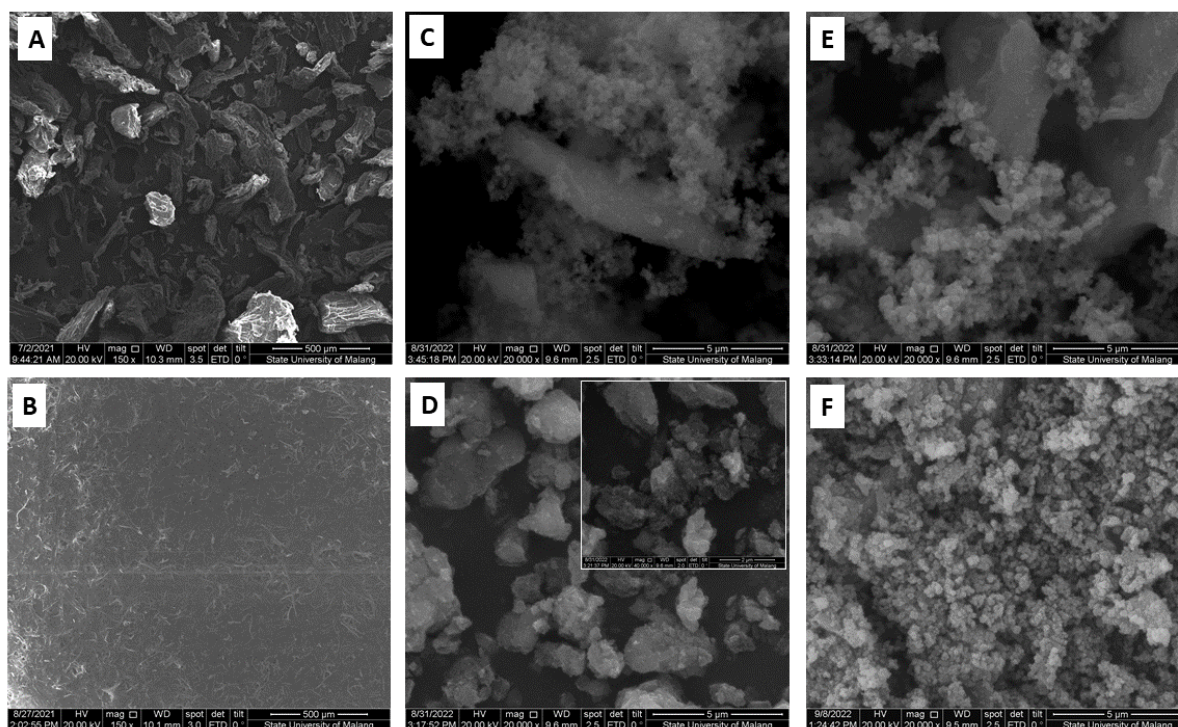


**Figure 4.** XRD diffraction pattern of (a) cellulose and its oxidation product. Oxidation was done at 30°C and 70°C in 12 and 24 h reaction times. (b) Nanocellulose and its oxidation product, which were taken place at 70°C in 24 h.

### SEM characterization

The micrograph images of the oxidized cellulose and nanocellulose is are shown in Figure 5. This image corresponds to the surface morphology of the oxidized cellulose and nanocellulose. Oxidation with potassium permanganate for both reaction time and temperature conditions directed the cellulose and nanocellulose to disintegrate its structure. Thus, amorphous powder was produced. Oxidation at a longer time and higher temperature reduced the size of the powder's appearance.

The results of the analysis showed that the size of cellulose was significantly reduced by the oxidation process [31]. This study found that the difference in temperature and reaction time affects the product particle size. The higher the reaction temperature, the finer the particles. Likewise, the longer the reaction time, the finer the particles. For C-KMnO<sub>4</sub>-24H-70, the sample undergo agglomeration, confirmed by SEM magnification up to 2um scale in figure 5C. Based on the analysis using Image J software, the average particle size of the sample C-KMnO<sub>4</sub>-12H-30 is 43.0 nm, C-KMnO<sub>4</sub>-12H-70 is 26.0 nm, C-KMnO<sub>4</sub>-24H-70 is 107.8 nm, and NC-KMnO<sub>4</sub>- 24H-70 is 1.3 nm. The C-KMnO<sub>4</sub>-24H-70 sample has a larger particle size because it is estimated that the oxidized cellulose will agglomerate due to the longer reaction time.



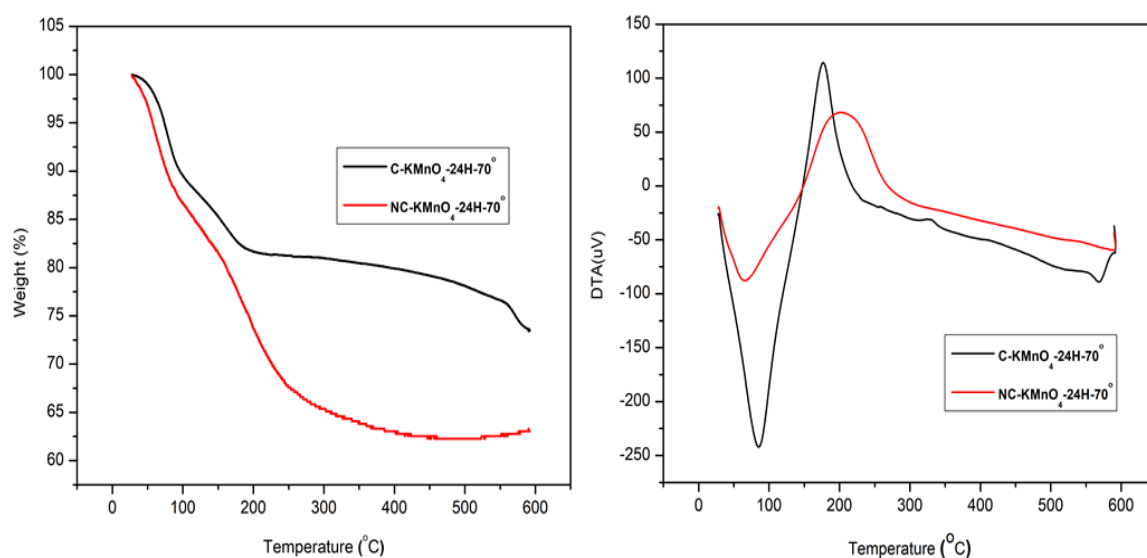
**Figure 5.** SEM images of (a) Cellulose, (b) nanocellulose (c) oxidized cellulose for 12 h at 30 °C (C-KMnO<sub>4</sub>-12-30); (d) oxidized cellulose for 24 h at 70 °C (C- KMnO<sub>4</sub>-24-70); (e) oxidized cellulose for 12 h at 70 °C (C- KMnO<sub>4</sub>-12-70); and (f) oxidized nanocellulose for 24 h at 70 °C (NC- KMnO<sub>4</sub>-24-70).

### Thermogravimetric analysis (TGA)

The thermal stability of the oxidized cellulose and nanocellulose was measured by differential thermal analysis/thermo-gravimetric analysis using a heating rate 10°C /min from 25-600°C. The graph is depicted in Figure 6. Thermal weight loss under air atmosphere. The

DTA profile of each oxidized cellulose and nanocellulose consisted of two peaks (endothermic and exothermic). The endothermic curve of oxidized cellulose and nanocellulose was observed at 85°C and 66°C, respectively. Then the endothermic peak was observed at 176°C for oxidized cellulose, and 204°C for oxidized nanocellulose samples.

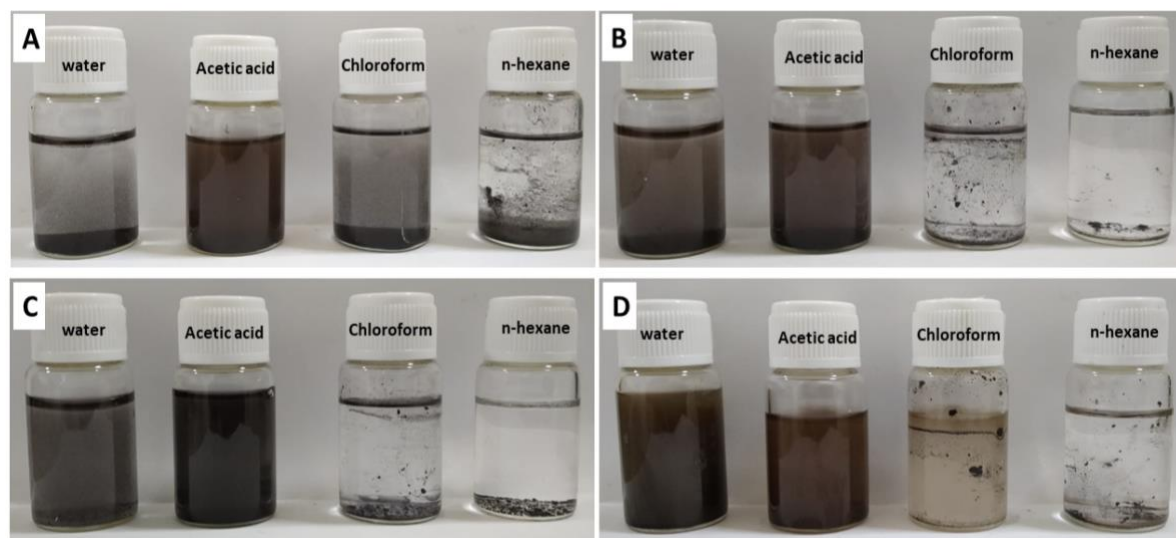
Based on the TG curve, the oxidized cellulose is thermally more stable than the oxidized nanocellulose. It can be observed that oxidized cellulose and nanocellulose have three types of lines based on mass absorption under certain temperature range conditions, namely from 30-85°C, 86-201°C, and 202-570°C for oxidized cellulose. The greatest mass loss occurred at a temperature range of 25-85°C by 8%, followed by a mass reduction of 6% at a temperature range of 86-197°C and the smallest sample mass withdrawal was 5% at 198-570°C. Oxidized nanocellulose also has the same pattern, the largest reduction in sample mass occurs in the temperature range of 97-252°C, which is 20%. At a temperature of 253-600°C, the sample mass tends to be stable.



**Figure 6.** DTA/TGA graph of oxidized cellulose and nanocellulose

### Solubility test result

The solubility test aims to qualitatively identify the solubility of the oxidation products in several types of solvents. The solvents used were water, acetic acid glacial, chloroform, and n-hexane. These solvents were chosen because they have different polarities. The results of the solubility test show that the oxidized cellulose easily dissolved in water and acetic acid, slightly soluble in chloroform, and insoluble (attached to the walls of the bottle) in n-hexane. The longer the reaction and the higher the reaction temperature, the higher the solubility of the product, which can be seen from the color of the solution that becomes increasingly darker. The smaller the particle size also affects the solubility, the smaller the particle size, the greater the solubility. Particle size can affect solubility because the smaller the particle, the ratio between surface area and volume increases.



**Figure 7.** Solubility test images of (a) C-KMnO<sub>4</sub>-12-30, (b) C- KMnO<sub>4</sub>-12-70, (c) C- KMnO<sub>4</sub>-24-70, and (d) NC- KMnO<sub>4</sub>-24-70

## CONCLUSION

This research concludes that KMnO<sub>4</sub> successfully oxidizes the cellulose isolated from sengon wood into oxidized cellulose. From FTIR spectra, oxidation products indicate a change in the hydroxyl (-OH) to a carboxylate (-COOH) functional group. The XRD diffractogram showed that the oxidation product was in amorphous phase, meanwhile the effect of oxidation also reduces the particle size (SEM images). DTA/TGA results show that oxidized cellulose is more stable than oxidized nanocellulose at temperatures above 197°C. The resulting product is oxidized cellulose (the hydroxyl group is substituted by the carboxylic group -COOH). It is necessary to purify with acid to dissolve MnO<sub>2</sub> impurities.

## ACKNOWLEDGMENT

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