Effect of lignin on the thermal properties of nanocrystalline prepared from kenaf core

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Abstract. Lignin and cellulose work together to provide a structural function in plants. While cellulose is the primary load-bearing element, lignin acts as the matrix that provides stiffness and rigidity to the fibre. In the production of nanocellulose, the removal of lignin is essential which is done through bleaching. Nevertheless, studies have shown that lignin can impart positive effects on thermal stability besides being a natural compatibilizer due to the presence of both aliphatic and polar groups in the chain network. The objective of this study is to evaluate the effect of lignin on the thermal properties of nanocrystalline cellulose prepared from kenaf core. Nanocellulose of different lignin content was prepared by undergoing first, pulping using 20 % NaOH and 0.1 % anthraquinone (AQ) followed by a bleaching sequence. The study shows that, sample having the least amount of lignin had good thermal stability during the first and second stage of decomposition by shifting the temperature higher as compared to sample with higher lignin content. However, when the temperature reached more than 300 °C up to the end of the degradation process, the latter gave a higher amount of residue suggesting that lignin can help the NCC to withstand heat better.

1. Introduction
Cellulose is the most abundant renewable natural biopolymer. Rapid developments of nanotechnologies have led to the emergence of the next generation of cellulose based products and one of these is nanocrystalline cellulose (NCC). NCC can be produced by a sequel series of isolation processes, including complete or partial removal of matrix materials and isolation of the cellulosic fibres and followed by controlling chemical treatment to remove amorphous regions of cellulose polymer [1].

Other than cellulose and hemicellulose, lignin is one of the polymeric components in a plant which interpenetrate with each other to form complex higher order structure. Over hundred years, lignin has been considered as un-welcomed by product and it is excluded from wood in order to extract cellulose especially in the pulping process [2]. However, it is very important to keep the lignin component as it has been investigated that lignin can be a natural compatibilizer due to the presence of both aliphatic and polar groups which can provide compatibility between nonpolar polymers and lignocellulosic fibres [3-6]. In fact, cellulose and lignin is analogous to that of epoxy resin and glass fibres where the fibrous components, cellulose or glass fibres, are the primary load-bearing elements while the matrix, lignin or epoxy resin, provides stiffness and rigidity.

Recently, there has been an interesting finding about lignin on its positive effect on thermal performance other than in mechanical properties [7]. However, most of the studies had reported the
application of isolated and industrial lignins. For example, Hatakeyama and Hatakeyama [2], in their study reported the application of two types of industrial lignins to prepare a polyurethane matrix which to be applied together with various types of organic and inorganic fillers to produce densely filled sandwich composites with the objective to improve its thermal stability for practical used. These lignin PU composites can be used as panels in the field of construction including civil construction and housing materials. Another finding was done by Morandim-Gianetti et al. [6] in their studies on isolated lignin through acetosolv process from coir which incorporated in polypropylene reinforced coir fiber (PP/CF) also reported significant improvement in both initial decomposition temperature and oxidation induction times may due to role of lignin as an antioxidant and its action as a barrier against thermal degradation process.

Kenaf is another source of plant fibre that comprises two different parts, bast fibre and woody core. Kenaf bast fibres, an aggregate of long fibres, are well known for its high strength, which is widely used in natural fibre composites as reinforcement. On the contrary, kenaf core has short fibres and resembles that of low density wood, thus its application in the industries is limited. For this reason, and due to relatively high cellulose content, 31–33 %, kenaf core is a preferred source for the production of nanocellulose. Many studies have reported on the properties of NCC produced from kenaf core [8-11]. However, all these studies used NCC that has undergone the bleaching process, with almost zero lignin. Therefore, the aim of this study is to evaluate the effect of lignin content on the thermal decomposition and thermal stability of the NCC prepared from kenaf core.

2. Experimental Procedure

2.1 Materials
Raw kenaf core fibres (*Hibiscus cannibinus*) were supplied by National Kenaf and Tobacco Board (LKTN), Kota Bharu, Kelantan, Malaysia.

2.2 Methods

2.2.1 Pulping of kenaf
Kenaf core chips (200 g) of 2-3 cm long were placed in in a twin digester with 20% sodium hydroxide (NaOH) and 0.1% anthraquinone (AQ). The ratio of cooking liquid was 1:10 and was cooked at temperature of 170℃ for 90 minutes. The condition of pulping process was listed in Table 1 below.

| Condition                  | Maximum Temperature | Time          | Chemical      | Ratio        |
|----------------------------|---------------------|---------------|---------------|--------------|
|                            | 170 ℃               | 1 hour 30 minutes | 20% NaOH, 1% AQ | 1:10         |

2.2.2 Bleaching
The kenaf pulp, then was later purified through three-stage bleaching. Table 2 shows the bleaching conditions employed in the study. Three types of pulp were prepared: (1) Unbleached pulps, denoted as UB, (2) pulps that have undergone bleaching process up to stage D1, denoted as B1, and (3) pulps that were subjected to all bleaching stages (D1 followed by E then D2) and denoted as B2.
Table 2. Bleaching conditions used in the study

| Bleaching stage | Chemical charge            | Reaction time (min) | Temperature (°C) | Consistency (%) |
|-----------------|----------------------------|---------------------|------------------|-----------------|
| D₁              | 2% Sodium Chlorite + 3% Acetic Acid | 120                 | 70               | 10              |
| Eₚ              | 1.5% NaOH + 1% H₂O₂         | 90                  | 70               | 10              |
| D₂              | 1.5% Sodium Chlorite + 3% Acetic Acid | 90                  | 60               | 10              |

2.2.3 Preparation of NCC via acid hydrolysis

All unbleached and bleached samples were treated with sulfuric acid for producing the NCC. High content of lignin tends to impede the acid hydrolysis process, thus requires higher percentage of sulfuric acid and vice versa [10]. Hence the hydrolysis were conducted using the same conditions except for the concentration of the acid depend on the lignin content (Table 3).

The pulps were stirred vigorously in sulfuric acid solution for 60 minutes at 45 °C. After that, the pulps were rinsed using multiple centrifugations until the solution become a cloudy suspension. The process was continued with dialysis using cellulose membrane until the pH changed from acidic to neutral. The suspensions were then sonicated for 30 minutes before they were freeze dried. Later, the pulp was subjected to sonification followed by freeze drying to produce NCC. The kenaf core NCC powder was kept in a cool and dry place for further characterization.

Table 3. Acid Hydrolysis conditions employed for the production of NCC from kenaf core

| Sample    | Acid concentration (%) | Temperature (°C) | Time (sec) |
|-----------|------------------------|------------------|------------|
| NCC-UB¹   | 64% H₂SO₄              | 45               | 60         |
| NCC-B₁²   | 62% H₂SO₄              | 45               | 60         |
| NCC-B₂³   | 60% H₂SO₄              | 45               | 60         |

¹ NCC produced from unbleached pulp  
² NCC produced from D₁-stage bleached pulp  
³ NCC produced from D, Eₚ, D₂-stage bleached pulp

2.3 Characterization

2.3.1 Chemical analysis

The chemical compositions of kenaf core fibres (raw, bleached and unbleached) were investigated. The content of extractive was carried out according to TAPPI T204 cm-97 standards. The acid insoluble lignin in kenaf core, then were prepared according to TAPPI T222 om-02 using 72% sulfuric acid. Then the cellulose content of the kenaf pulps was carried out according to the TAPPI standard 203 using 8.3% sodium hydroxide, 17.5 % sodium hydroxide and 2N acetic acid. Next, the percentage of holocellulose is based on a study done by Wise et al., [12] using 1.5g sodium chlorite, 10% acetic acid and acetone.
2.3.2 Zeta potential and particle size distribution
The zeta potential and nano particle size distribution for kenaf core NCC suspensions were analyzed using Zetasizer Nano equipment (Malvern Instruments, UK). The NCC suspension was sonicated for 15 minutes before the process.

2.3.3 Thermal analysis
The thermal composition and thermal stability were obtained using TGA/SDTA 851 (Mettler Toledo) thermogravimetric analyzer under a linear temperature condition with temperature 50 – 700 °C with heating rate of 10 °C/min under nitrogen atmosphere. The DSC test was done using Perkin Elmer Instrument (Pyris Diamond). The temperature range is from 50-300 °C with a heating rate of 10 °C/min.

3. Results and Discussion

3.1 Chemical properties
The chemical compositions of kenaf core fibre before and after bleaching treatments are presented in Table 4.

| Sample       | Lignin (%) | α-cellulose (%) | Hemicellulose (%) | Extractive (%) |
|--------------|------------|-----------------|-------------------|---------------|
| RAW kenaf core | 33.7       | 43.7            | 17.8              | 4.3           |
| UB¹          | 11.5       | 67.2            | 15.3              | 3.4           |
| B1²          | 9.2        | 77.4            | 8.9               | 3.1           |
| B2³          | 2.2        | 89.9            | 5.8               | 2.7           |

¹ Unbleached pulp
² D1-stage bleached pulp
³ D1, E, and D2-stage bleached pulp

LITERALLY, the amount of lignin from woody materials varies from 12 % to 39 %, according to acid insoluble Klason lignin analysis [2, 13]. The lignin content of raw kenaf core is 33.7 %, which falls within this range. Alkaline treatment appears to reduce the amount of lignin content in the kenaf core; from 33.7 % to 11.5 % indicating the effectiveness of NaOH in removing the lignin content. Jonoobi et al. [14] also reported the same effect for kenaf core. The content of cellulose also was seen to correspondingly increase from 43.7 % to 67.2 % after the alkali treatment.

As the kenaf pulp was subjected to first stage bleaching (B1), the content of lignin dropped to 9.2 % (from 11.5 %) whilst the content of cellulose increased from 67.2 % to 77.4 %. At this stage, sodium chloride and acetic acid appear to partially remove the lignin, as well as some amounts of hemicellulose [14]. On further bleaching using E followed by D2 bleaching sequence (B2), almost all the lignin and hemicellulose were substantially extracted out as shown by the relatively low percentage of lignin (2.2 %) and hemicellulose (5.8 %) contents in NCC-B2 whilst the cellulose content increased up to 89.9%. This result indicates the effectiveness of bleaching process used in removing hemicellulose and lignin, producing high amounts of pure cellulose. According to Jonoobi et al. [14], hydrogen peroxide that was used at stage E helps to remove the residual chlorite in the pulp and ease the removal of lignin. The last stage of bleaching, D2, removed the remainder of hemicellulose and lignin. The significant increment in cellulose content proved that the alkaline and bleaching process are an effective sequence for kenaf core.
A similar trend was reported by Jonoobi et al., [8] and Jonoobi et al., [14] showing increment of cellulose content of kenaf bast and kenaf core after pulping and bleaching process while content of hemicellulose and lignin decrease after this chemical treatment. They agree that those effects attributed to the effect of NaOH as well other chemical employed during chemical treatment process. In other study done by Chan et al. [10], kenaf core powder was treated using NaOH and NaClO₂ for pulping and bleaching process show increase percentage of holocellulose and marked decrement of Klason lignin as the kenaf core fibre chemically treated. Also show a similar trend was study done by Shi et al., [15] on kenaf bast fibre which treated using slightly different methods of pulping and bleaching process using NaOH and H₂O₂.

3.2 Physical properties (Zeta Potential and Particle Size Analysis)

Figure 1 shows the diameter of NCCs suspension corresponding to the volume percentage. During the acid hydrolysis process, the presence of hydrogen ions (H⁺) helps to remove the amorphous materials and effect the degree of removal is depending on the availability of these hydrogen ions. The effect of acid hydrolysis occurred in the amorphous parts continued by the erosion of crystalline regions of the cellulose fibre [16, 17]. Unbleached sample (NCC-UB) was treat with 64 % of sulfuric acid show two peaks considering two highest mean of diameter size; ~13 nm (volume of 8 %) and ~37 nm (volume of 12 %) respectively. Sample NCC-B1 have a means of diameter value of ~15 nm (volume of 16 %) whilst sample NCC-B2 show broad mean peak around 15 – 30 nm (volume 8 %). The major portion of the NCC-UB have higher diameter size which may be attributed to insufficient hydrogen ions (H⁺) to remove the amorphous part of the cellulose chains thus, insufficient to penetrate to the other parts of cellulose. Apparently, the unbleached pulps still contain a lot of hemicellulose and lignin that may have prevented the hydrogen ions to reach the amorphous region in the cellulose chains resulting in a substantial amount of the cellulose chains are still intact with diameter of more than 30 nm. Chan et al. [10], Ng et al. [16] and Kumar et al. [18] associated this behaviour with the impediment by the presence of lignin and hemicellulose for the hydrolysis to occur. This result also suggests that the acid hydrolysis condition for unbleached pulp need to be intensified by increasing the acid concentration.
On the other hand, both NCC-B1 and NCC-B2 show an almost perfect nano size cellulose distribution which mainly has < 30 nm in diameter.

Figure 1 also shows the values of zeta potential for NCC-UB, NCC-B1 and NCC-B2. Zeta potential measurement has been used to investigate the colloidal stability of NCC dispersion in an aqueous media. The ideal value for zeta potential is higher than -25.0 mV \[19\]. Higher zeta-potential value show higher capacity for dispersion in water with no tendency to flocculate \[17, 20\]. As shown in Figure 1, the values of zeta potential for NCC-UB, NCC-B1 and NCC-B2 samples are respectively -64.6 mV, -52.0 mV and -57.4 mV implying a stable NCC suspension due to electrostatic repulsion between sulfate groups. According to Roman and Winter \[21\] and Brinchi et al. \[1\], during acid hydrolysis process, especially using sulfuric acid, there is a certain degree of grafting of sulfate group onto the surface of NCC. These groups impart negative surface charge to NCC and stabilize the suspension against flocculation; thus give better zeta potential values.

3.3 Thermal properties
TG and DTG graphs for unbleached NCC (NCC-UB), sample bleached at the first stage (NCC-B1) and bleached at the second stage (NCC-B2) are shown in Figures 2(a) and 2(b) respectively. The initial weight loss of NCCs at first stage occurred around 90 - 100°C were indicated the vaporization of water. Similar findings were reported by Rosa et al. \[7\] and Chan et al. \[10\].

The main decomposition happens at the second stage. Based on the value listed in Table 5, the onset temperature at the second stage shifted from lower to higher temperature from sample NCC-UB, NCC-B1 and NCC-B2 respectively may due to removal of hemicellulose and partial removal of lignin. The decomposition value for this study is lower compared to other study involving NCC may due to the presence of acid sulfate groups which leads to decrement of thermal stability \[1, 7, 10, 21\]. At this stage, NCC-UB shows the lowest onset temperature may due to the high amount of amorphous materials that still covered the whole NCC surface which weakened the thermal stability of the sample \[7\]. As bleaching step escalated for sample NCC-B1 and NCC-B2, most of the hemicellulose and lignin are gradually removed and shifted the higher onset degradation temperature.

The lignin removal is reflected in the amount of residue in the range between 300 – 500 °C \[7\]. As the sample underwent the region between 300 – 500 °C at third stage, the TG graph at Figure 2(a) shows sample NCC-B2 has a lower amount of residue as compared to sample NCC-UB and NCC-B1. The exact values are listed in Table 5. This may due to effect of remaining lignin that coats the NCC surface had protected the NCC from decomposition process thus, improves the thermal performance of the NCC \[7\]. This statement is supported by Yang et al. \[22\], claiming that the lignin decomposition can extend over the whole temperature range starting from 200 °C up to 700 °C.

| Table 5. Thermal characteristics of NCC from kenaf core |
|-------------------------------------------------------|
| NCC-UB | NCC-B1 | NCC-B2 |
| Amount of lignin, % | 11.5 | 9.2 | 2.2 |
| Onset 1st stage (°C) | 96.24 | 95.43 | 94.36 |
| Onset 2nd stage (°C) | 167.25 | 171.61 | 183.64 |
| 1st weight loss (%) | 36.16 | 35.18 | 39.03 |
| Onset 3rd stage (°C) | 288.86 | 283.34 | 298.75 |
| 2nd weight loss (%) | 33.14 | 33.57 | 33.23 |
| Residue up 700 °C (%) | 25.04 | 25.75 | 21.73 |
As observed from the DTG curves in Figure 2(b), it is clearly shown that those three sample shows two well separated peaks indicated two times of pyrolysis processes which affected by the presence of acid sulfate group in NCCs. First process occurred at a temperature of 200 – 250 °C and the second process occurred at 300 – 400 °C. The first pyrolysis process dominated higher weight loss of the NCC in the range of 35 – 39 wt% as compared to second pyrolysis indicating the overall pyrolysis. A similar observation was shown in a study done by Wang et al. [23]. Sample NCC-UB show lower rate of degradation as compared to samples NCC-B1 and NCC-B2 may indicate the effect of residual lignin that help to delay the degradation process.

4. Conclusion

In this work, the content of lignin was observed to have some influences on the thermal degradation pattern of NCC. NCC having the least amount of lignin (NCC-B2) shows slightly better thermal stability, particularly during the first and second stage of thermal decomposition. However, at the third stage of decomposition (at about 300 °C), NCC that contains higher amount of lignin (NCC-UB and NCC-B1) started to stabilize until a complete decomposition took place, whilst NCC-B2 continued to decompose. The higher amount of residue for both NCC-UB and NCC-B1 was observed, which
corresponds well with the amount of residual lignin in the NCC suggesting lignin helps to protect the surface of NCC from heat up to 700 °C. The ability of lignin to protect the surface of NCC especially at high temperature and give it better thermal stability has open the opportunity for it to be applied in the composites and other high thermal end product. The fact that the application of NCC with least lignin need less usage of chemical is believed can help to free the environment from chemical effluent disposal.

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