Characterization of Chemical Compound and Cellulose content in Kenaf core

Siti Raihan Binti Zakaria and Madam Rabiatul Adawiyah Binti Abdol Aziz

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*— In this study, the chemical composition and cellulose content of kenaf core were investigated. Kenaf core was pretreated with 4 wt% sodium hydroxide (NaOH) followed by five steps of bleaching using 1.7 wt% sodium chloride (Nacl) in acetic acid buffer solution. The effects of five steps bleaching on the cellulose content was also investigated. Raw kenaf core, alkaline-treated kenaf core, 1st bleaching kenaf core, 3rd bleached kenaf core and 5th bleached kenaf core were analyzed by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA) and X-ray diffractometer (XRD). The effectiveness of alkaline treatments in the removal of non-cellulosic materials which is lignin and hemicellulose from the kenaf core fiber was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) observation. The crystallinity of all the samples were calculated by using Segal method. X-ray diffractometer analysis showed that the 5th bleached kenaf core has the highest degree of crystallinity which is 76.4 % while raw kenaf core show the lowest which is 55.8%. The increasing of crystallinity for each subsequent sample improved that the removal lignin and hemicellulose after the treatment. Thermal analysis results show that the content of cellulose is increased after subsequent chemical treatment.**

Keywords*— *kenaf core, alkaline-treated kenaf core, bleached kenaf core, alkaline treatment, bleaching treatment, thermal stability and crystallinity

I. INTRODUCTION

Kenaf plant or its scientific name called as Hibiscuss Cannabinus L. is one of the sources of cellulose that can be implemented with economic and ecological advantage. Nowadays, kenaf core is used to make paper, textile, adsorbent and polymer composite due of its special properties which is environmental friendly and good potential reinforcement material. Kenaf plant is a dicotyledons and herbaceous annual plant of the Malvaceae family. Kenaf plant is firstly planted in Africa and todays kenaf is known as 4000 years old plant (M.Ramesh, 2016).

According to Ashori, et al., (2006), Kenaf come from Persian word which describe the plant as annual herbaceous, short day and warm season plant. Being as dicotyledon plants, therefore kenaf stalk has three main layers which are phloem (outer tissue layer), xylem (inner tissue layer) and a thin layer of pith centre. The thin pith layer consists of sponge such as tissue with non-ferrous cell. The outer cortical tissue and inner woody tissue are called as bast and core fibers respectively. These fibers are different in chemical and morphological properties (M.Ramesh, 2016). According to Chan, et al., (2013), bast and core fibers comprises 35% and 65% of the stalk dry weight respectively.

Mosello, et al., (2010) study (as cited as Abdul Khalil et.al (2010) and Mosello, et al., 2009) found that lignin content is greater in core fibers compared to bast fibers while the cellulose content is vice versa. Kenaf can grows very fast with 3.7 to 5.5 m of height (Shi, et al., 2011). While, its diameter of stem is about 25 to 51 mm. Kenaf plant grows within 4 to 5 months with several factors that need to take into account which are temperature, humidity and soil condition (Ashori, et al., 2006). Since the growing cycle of kenaf is approximalely 150 to 180 days, therefore its require less water to grow. Kenaf plant can grow in various type of climatic and require only minimum ferlilizers, water and pesticides. M.Ramesh (2016) states that kenaf plant is rich in cellulose, good in resistance and large biomass, thus it can be replaced wood pulp and use for many applications such as paper products.

Kenaf core is one of the non-wood lignocellulosic fibers comprises of three principal chemical constituents which are hemicellulose, lignin and cellulose. Cellulose fibrils are hold together by non-cellulosic components such as lignin, hemicellulose and pectin. Cellulose contain hydroxyl group (-OH) which enables it to establish strong hydrogen bonds. Generally, cellulose is hydrophilic biopolymer composed of β-1, 4-linked anhydro-D-glucose units (Kumari, et al., 2016). Cellulose is a type of biopolymer which is plentiful and inexhaustible (Sulaiman, et al.,2015). The cellulose is environmentally-friendly and biocompatible products and present as whisker-like microfibrils (Zaini, et al., 2013). Wood, cotton, hemp, flax and sisal are the type of sources of cellulose (Kumari, et al., 2016). Hemicellulose and lignin are amorphous polymers while cellulose is a semi – crystalline polymer (Kumari, et al.,2016 as cited Faruk, O. et al., 2012). Pentosan or known as hemicellulose is the third most abundant organic resource available (Cunningham, et al., 1987). Two portion of cellulose which are crystal and shapeless structure where by the shapeless structure can be removed in order to form high crystal form of cellulose (Sulaiman, et al., 2015).

Bleaching process is used to remove the amorphous region which is lignin and hemicellulose. The reinforcement effect for the lignocellulosic fibers is depend on the content of cellulose. Chemical treatment has been conducted to achieve high cellulose content in kenaf core. The chemical treatments conducted in this paper are alkali treatment and bleaching treatment. However, there is some weakness along with the techniques used to obtain high cellulose content that need to be considered. Type of chemical used and bleaching separation technique are the examples of the weakness in the techniques.

The aims of this study were to characterize the chemical compounds and cellulose content in Kenaf core as well as to investigate the effect of five bleaching process on the characteristics of kenaf core fibers.

II. METHODOLOGY

A. Materials

Kenaf core is obtained from Kenaf Solution Sdn Bhd. NaOH (0.4 wt% Sodium hydroxide), NaCl (1.7 wt% Sodium Chloride) and acetic acid are obtained from storage chemical chemistry laboratory, Faculty of Chemical Engineering. Sodium hydroxide (NaOH) used for alkali treatment, whereas sodium chloride (NaCl) and acetic acid used for bleaching process.

B. *Preparation of Cellulose*

The cellulose is prepared by using alkali treatment and bleaching treatment.

1) *Alkali treatment*

Firstly, 15 g of kenaf core were weight and transferred into round bottom flask and 4 wt% NaOH (alkali solution) are added into the flask (Zain, et al., 2014). The alkali treatment is conducted at 100°C to 120 °C for two hours. Then, the mixture is filtered and washed by using distilled water for several times to remove hemicellulose, lignin and other impurities. The alkaline-treated kenaf core is dried before used for bleaching treatment (Zain, et al., 2012). The alkaline-treated kenaf core is dried in an oven at 80°C.

2) *Bleaching treatment*

15 g of alkaline-treated fibers is bleached with 400 ml of 1.7 wt % sodium chloride (NaCl) in acetic acid buffer solution within 4 hours at 80°C (Zain, et al., 2014). The bleaching process is repeated five times. After that, the bleached fibers become neutral by filtration and washing by distilled water (Sulaiman, et al., 2015). The kenaf core powder is oven dried at 105°C for TGA, FTIR and XRD analysis.

C. *Characterization*

1) *Fourier Transform infrared (FTIR) Spectroscopy*

Fourier Transform infrared (FTIR) Spectroscopy studies was performed on a Perkin Elmer Spectrum 400 to determine the changes in functional groups caused by the chemical treatments. The samples were analyzed at wavenumber around 4000 to 650 cm^{-1}.

2) *X-ray diffraction*

X-ray diffraction was performed to investigate the structural and phase analysis of the sample. All the samples were analyzed using XRD (Rigoku) with monochromatic CuKα radiation source (λ = 0.1539 nm) from 2θ = 5° to 50° with a step size of 0.0250°. The crystallinity index, CrI was determined using Segal's equation (Hanisah et al., 2015). I_{002} is intensity for crystalline region while I_{am} is intensity for amorphous region.

$$\text{Crystallinity index, CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

3) *Thermogravimetric Analysis(TGA)*

10 mg of all samples were put into the crucible and weighted. The samples were tested by using thermogravimetric analyzer (Mettlor Toledo under linear temperature conditions. The purpose of thermogravimetric analysis is to investigate the thermal decomposition as well as thermal stability of all samples after the subsequent chemical treatments. The starting temperature is 35°C and the ending temperature is 600°C. The heating process is conducted in platinum crucibles in a nitrogen atmosphere (Zaini, et al., 2013). The onset temperature and beginning of weight loss represent the degradation temperature.

III. RESULTS AND DISCUSSION

A. *Thermogravimetric Analysis(TGA)*

Thermogravimetric analysis (TGA) is conducted to investigate the thermal stability as well as degradation temperature of all samples. Thermogravimetric analysis (TGA) measures the weight loss in relation with temperature change. Therefore, the measured weight loss curve will give information on the thermal stability, changes in sample composition as well as kinetic parameters for reaction of chemical in the sample. In this case, a thermogravimetric analysis (TGA) was carried out in order to investigate the effect of chemical treatments on thermal decomposition of the fibers. Chemical composition, structure as well degree of crystallinity are the factors of the thermal behaviour of lignocellulosic materials (Jonoobi, et al., 2010). A thermal stabilities study is important since reinforcement material need to meet minimal thermal acceptance in processing. Table 1 shows the percentage of residue before and after degradation in raw kenaf core, alkaline-treated kenaf core, 1st bleached kenaf core, 3rd bleached kenaf core and 5th bleached kenaf core. Figure 1 shows the TG graph of weight loss of all samples against temperature while figure 2 shows the DTG graph of weight loss per minute against temperature. The onset degradation temperature is shown in figure 1. Based on the figure 1, it is observed that the thermal degradation of all the samples occurred in 1 step which is around 255°C to 360°C.

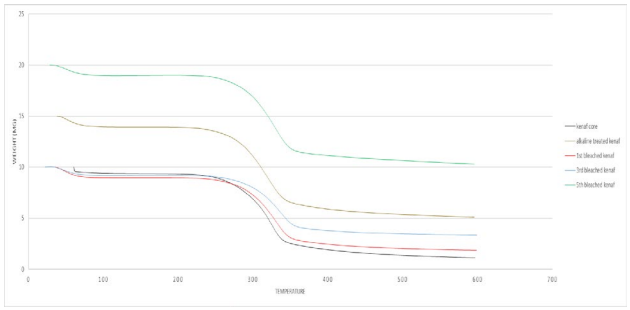

Figure 1: Graph of weight loss against temperature

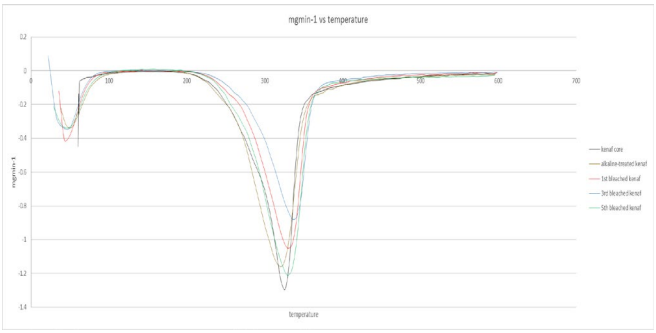

Figure 2: Graph of weight loss per minute against temperature

Table 1:
The percentage difference of residue before and after degradation in raw core kenaf, alkaline treated kenaf, 1st bleached kenaf, 3rd bleached kenaf and 5th bleached kenaf.

Sample	T onset, T_O (°C)	T endset, T_e (°C)	T degradation, T_{deg} (°C)	% Residue before degradation, R1	%Residue after degradation, R2	Difference between %residue before and after the degradation R1 – R2
Raw kenaf core	282.55	345.98	330	100	14.0293	85.9707
Alkaline-treated kenaf	255.58	352.43	325	93.1314	35.5562	57.5752
1st bleached kenaf	274.40	355.82	335	89.7083	21.9227	67.7856
3rd bleached kenaf	259.65	351.76	325	94.2210	41.5479	52.6731
5th bleached kenaf	270.02	358.47	335	95.0163	55.1114	39.9049

Based on the table 1, the thermal degradation of all the samples are occurred between 325°C to 330°C. The main degradation step (T_{deg}) was found to be 325°C for alkaline treated kenaf and 3rd bleached kenaf. While, the main degradation step (T_{deg}) is same for 1st bleached kenaf, and 5th bleached which is 335°C. The main degradation step (T_{deg}) for raw kenaf core is 330°C. Figure 1 shows that the loss of weight is started from 50°C due to the evaporation water and volatile material. The initial decomposition of cellulosic materials take place in the amorphous regions. The curve of raw kenaf core shows a weight loss starting at 190°C because the lignin was started to degrade. While, degradation of hemicellulose was started at 240°C until finally reach its peak at 330°C whereas attributed to cellulose decomposition. From the raw kenaf core, the peak of T_{deg} was attributed to hemicellulose degradation while the corresponding peak for other samples indicates the cellulose decomposition. According to Jonoobi, et al., (2010), degradation of lignin is started between 100°C to 900°C while degradation of hemicellulose is started at low temperature which is between 220°C to 315°C. In addition, the TG graph in figure 1 indicates that an increasing thermal stability for the alkaline treated kenaf, 1st bleached kenaf, 3rd bleached kenaf, as well as 5th bleached kenaf as compared to raw kenaf core. These results show that the thermal stability of lignocellulosic materials was increased after the chemical treatments. This is due to the removal of the hemicellulose and lignin during the chemical treatments. According to Jonoobi, et al., (2009) the amorphous region in the cellulose is degraded by the alkaline and bleaching treatment. The percentage of the residue before and after degradation was decreased from 85.9707% into 39.9049%. The raw kenaf core has higher amount of residue due to the presence of ash and lignin which have a very slow degradation. The lower amount of residue after the chemical treatment indicated that the highest content of cellulose in the core kenaf. Therefore, by using five steps of bleaching have increased the cellulose content in core kenaf.

The IR spectrum of raw kenaf core, alkaline-treated kenaf core, 1st bleached kenaf core, ,3rd bleached kenaf core and 5th bleached kenaf core were presented in figure 3. The IR spectrum shows the changes in chemical composition that occurred after the alkaline and bleaching treatment. All samples have medium and broad band around 3328 cm^{-1} to 3340 cm^{-1} that correspond stretching and bending of the groups on cellulose molecules and those O-H groups matches to intra and intermolecular hydrogen bonds. In addition, the sample of raw kenaf core showed the characteristics C-H stretching absorption around 2900 cm^{-1}. The peak around 2800 cm^{-1} to 2900 cm^{-1} represent the C-H stretching. The absorption peak at 1740 cm^{-1} in the spectrum of the raw kenaf core is associated with C=O stretching of the acetyl group and uranic ester groups in the hemicelluloses. The peak also corresponding to ester linkage of the carboxylic group in the ferulic as well as p-coumeric acids of lignin and/or hemicellulose (Kargarzadeh, et al., 2012). But, there is no peak of C=O stretching of acetyl group observed in alkaline treated kenaf due to the removal of hemicellulose during alkaline treatments. Besides, the absorption peak at 1233.27 cm^{-1} was observed in the raw kenaf core. This result suggested the present of that C-O stretching of the aryl group in lignin (Kim, et al., 2016). However, the peak was reduced after alkaline treatment showing that a small amount of lignin was removed during alkaline treatment. The absorption peak observed at 1590cm^{-1} to 1600 cm^{-1} indicated the present of lignin (Bodirlau & Teaca, 2007). This peak is remained in the alkaline-treated kenaf core. It proved that lignin was retained after the alkaline treatment. However, this peak was reduced after the bleaching treatment. It showed that the significant amount of lignin was removed after the bleaching treatment. Moreover, the vibration peak is observed in the region 1318 cm^{-1} to 1320 cm^{-1} in all samples. This peak is related to the bending vibration of C-H and C-O bonds in the polysaccharides aromatic rings.

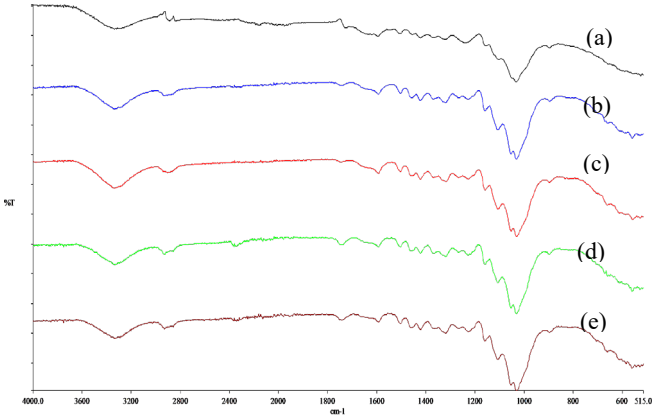

Figure 3: IR spectrum of (a) raw kenaf core (b) alkaline-treated kenaf core (c) 1st bleached kenaf (d) 3rd bleached kenaf (e) 5th bleached kenaf

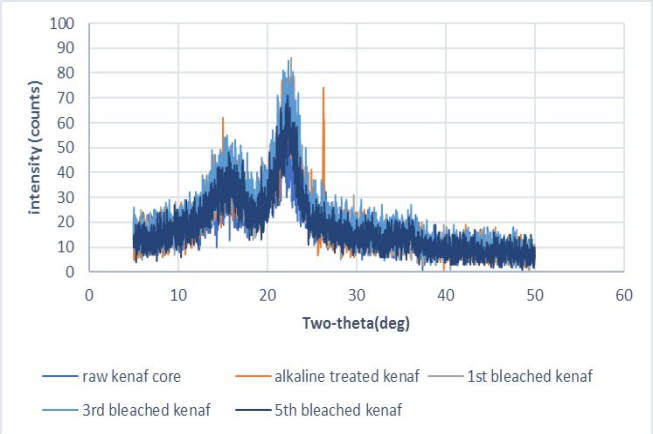

Figure 4: Graph of intensity against two-theta

C. *X-Ray diffraction*

The crystallinity index is calculated by using Segal's empirical method. The method is used to give the relative amount of crystalline material in fibers. The crystallinity index increased after each chemical treatment. For an example, crystallinity index is increased from 14.38% to 25.98% after alkali treatment. This is due to the alkaline cleavage of β- D-glucopyranosides, removing of amorphous region of hemicellulose. The crystallinity index shows a slightly increased after first step of bleaching which can be attributed to the removal of lignin. The fibers after second step of bleaching shows increased in crystallinity presumably due to the removal of remaining lignin as well as increase cleavage of cellulose molecular chain within amorphous region. The crystallinity index of cellulose was found to be highest in 5th bleached kenaf compared to raw kenaf core and alkaline treated kenaf. The increasing of crystalline index proved that the relative portion of crystalline region of cellulose increased.

Table 2:

Crystallinity index, CrI and cellulose intensity peak for all samples

Sample	I_{002}	I_{am}	Crystallinity index (%)	Cellulose intensity peak (2θ)
Raw kenaf core	43.0	19.0	55.8	43.0
Alkaline treated kenaf core	67.0	29.0	56.7	67.0
1st bleached kenaf	58.0	25.0	57.0	58.0
3rd bleached kenaf	70.0	27.0	61.4	70.0
5th bleached kenaf	55.0	13.0	76.4	55.0

IV. CONCLUSION

Kenaf core fiber contain three major components which is lignin, hemicellulose and cellulose. Lignin and hemicellulose are amorphous region in the kenaf core fiber, while cellulose is both amorphous and crystalline region in kenaf core fiber. Cellulose fibers were extracted from kenaf core by using alkaline treatment and bleaching treatment.

Alkaline treatment is conducted by using sodium hydroxide solution while bleaching treatment is conducted five times by using sodium chloride in acetic acid buffer solution. All the samples which are raw kenaf core, alkaline treated kenaf, 1st bleached kenaf, 3rd bleached kenaf and 5th bleached kenaf were analyzed by using thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD).

Based on the result, the amorphous region which is lignin and hemicellulose in kenaf core is removed after the chemical treatments. From the thermogravimetric analysis, the thermal stability of kenaf core is concluded to be higher after chemical treatment. The higher thermal stability is due to the removal of lignin and hemicellulose. TGA results revealed that the cellulose content is keep increasing when bleaching treatment is repeated five times. This was believed due to the low percentage of residue before and after the degradation.

The result proved that the present of hemicellulose in the raw kenaf core since there is absorption peak at 1740 cm^{-1}. FTIR results also confirmed the removal of hemicellulose after the alkaline treatments since there is no peak of C=O stretching of acetyl group observed in alkaline treated kenaf core. The IR spectrum of raw kenaf core proved that the present of C-O stretching of the aryl group in lignin which is at 1233.27 cm^{-1}. FTIR results also proved that the significant amount of lignin was removed after the bleaching treatment. XRD results shows that the crystallinity index is increased after conducting few times of bleaching treatment. The crystallinity index of kenaf core is 55.8%, increased to 56.7% after alkaline treatment and finally reached 76.4% after repeating the bleaching treatment by five times. These results confirm the removal of amorphous region of lignin and hemicellulose.

ACKNOWLEDGMENT

I would like to acknowledgement the support of my supervisor Madam Rabiatul Adawiyah who expertly guided my research project 1 and 2. In addition, I also would like to extend my sincere gratitude to Universiti Teknologi MARA for facilities that provided to conduct my research project.

References

[1] Ashori, A., Harun, J., D.Rawerty, W. & Mohd. Yusoff, M. N., 2006. Chemical and Morphological Characteristics of Malaysian Cultivated Kenaf (Hibiscus cannabinus) Fiber. Polymer Plastics Technology and Engineering, pp. 131-134.

[2] Bodirlau, R. & Teaca, C., 2007. Fourier Transform Infrared Spectroscopy and Thermal Analysis of Lignocellulose Fillers Treated with Organic Anhydrides. Volume 2, pp. 93-104.

[3] Cunningham, R., Carr, M. & M.O.Bagby, 1987. Hemicellulose Isolation from Annual Plants. Biotechnology and Bioengineering, Volume 17, pp. 159-168.

[4] Jonoobi, M. et al., 2010. Characteristics of Nanofibers Extracted from Kenaf core. Bioresources.com, pp. 2556-2566.

[5] Jonoobi, M. et al., 2009. Chemical Composition, Crystallinity, and Thermal Degradation of Bleached and Unbleached Kenaf Bast (Hibiscus cannabinus) Pulp and Nanofibers. Bioresources.com, pp. 626-639.

[6] Kargarzadeh, H. et al., 2012. Effects of hydrolysis conditions on the morphology,crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. Springer, Volume 19, pp. 855-866.

[7] Kumari, P. L., Sreenivasulu, N. & Reddy3, P. D. S., 2016. Synthesis of nanocellulose fibers from various natural resources and residues. International Journal of Advance Research in Science and Engineering, Volume 5, pp. 364-372.

[8] Kim, D.-Y., Lee, B.-M., Koo, D. H. & Jeun, P.-H. K. &. J.-P., 2016. Preparation of nanocellulose a kenaf core using E-beam irradiation and acid hydrolysis. *Springer Science ,* pp. 3039-3049

[9] M.Ramesh, 2016. Kenaf (Hibiscus cannabinus L.) fibre based bio-materials : A review on processing and properties. Elsevier Ltd, pp. 1-92.

[10] Mosello, A. A. et al., 2010. New approach to use of kenaf for paper and paperboard production. Bioresources.com, pp. 2112-2122.

[11] Shi, J. et al., 2011. Kenaf Bast Fibers—Part I: Hermetical Alkali Digestion. pp. 1-5.

[12] Sulaiman, H. S. et al., 2015. Isolation and Fractionation of Cellulose Nanocrystals from Kenaf Core. Sains Malaysiana, pp. 1635-1642.

[13] Zain, N. F. M., Yusop, S. M. & Ahmad, I., 2012. Preparation and Characterization of cellulose and nanocellulose from Pomelo (Citrus grandis) Albedo. Nutrition and Food, 5(1), pp. 1- 4.

.