

Modification in surface properties of sugarcane bagasse: a comparative study from the pretreatment using sodium and calcium hydroxide

Juliana Anggono,^{1,*} Hariyati Purwaningsih,² Béla Pukánszky,³ Suwandi Sugondo,¹ Steven Henrico,¹ and Sanjaya Sewucipto¹

¹ Mechanical Engineering Department – Petra Christian University, Jalan Siwalankerto 121-131 Surabaya 60236, Indonesia, email: ^{*} julianaa@petra.ac.id

² Materials and Metallurgical Engineering Department – Sepuluh November Institute of Technology, Jalan Raya ITS Keputih Sukolilo, Surabaya 60111, Indonesia, email: hariyati@mat-eng.its.ac.id

³ Physical Chemistry and Material Science Department - Budapest University of Technology and Economics, H-1521 Budapest, Hungary, email: BPukanszky@mail.bme.hu

ABSTRACT

Sugarcane is the world's largest crop grown with a total harvest of about 1.69 billion tons in 2010. Sugarcane bagasse is an agro-industrial by-product of sugar mill. About 30-32% by weight of the cane produced as by-products. Like other natural fibers, bagasse is a fibrous residue, available in abundance, and have been relatively unexplored for fibrous application. To improve interfacial adhesion between fibers and matrix in the composite, alkali pretreatment was performed on the bagasse fibers. This current research studied the effect of soaking time during alkali treatment using sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)₂) solution on the surface properties modifications on bagasse fiber. Calcium hydroxide is chosen as low cost and less aggressive alkaline solution to the environment compared to sodium hydroxide. Pretreatment with NaOH was found more effective than with Ca(OH)₂ with major removal of lignin and minor of hemicellulose as . The weight loss obtained on bagasse after pretreated with NaOH was found as 40.5-57.75%, while using Ca(OH)₂, the weight loss was measured as 25-46%. The chemical structure of the cellulose fibers after treatment was analysed using Fourier Transform Infrared (FTIR). Scanning electron microscope (SEM) was performed to study the effect of treatment on the surface morphology of the fibers. Those techniques identified that most lignin has been removed and cellulose fibers obtained from treatment using both solutions.

Keywords: sugarcane bagasse, alkali pretreatment, sodium hydroxide, calcium hydroxide

Introduction

Indonesia is a major producer of agricultural products which the sugarcane is one of the main agricultural products with a total production of 28,7 metric tons per year (rank 9th in the world).^[1] Agricultural production inevitably generates residues (by-products) that have limited use. Sugarcane stems consist of three major parts: the pith (5%), fibers (73%), and the rind (22%).^[2] Sugarcane bagasse is the remaining substance (waste) after crushing the canes for sugar. Bagasse is a fibrous residue, one among the three other main byproducts of the sugar industry, i.e. cane tops, filter muds, and molasses. Currently sugarcane bagasse is used as primary energy source as fuel for the boilers in the sugar mills and the remaining is stored. However, the important part of the bagasse as an industrial waste is still underutilized. Added-value compounds that can be produced using bagasse are bioethanol,^[3-6] protein-enriched animal feed ('single cell protein'),^[7] and enzymes. Therefore various research works have been

done to develop methods for further processing of bagasse to produce fuel and chemicals that offer economic, environmental, and strategic advantages. However, there were relatively fewer studies reporting on obtaining fibers from sugarcane bagasse compared to other agricultural by-products.

Bagasse, as well as other lignocellulosic materials consist of cellulose, hemicelluloses, lignin, and small amounts of extractives and mineral salts. Several research has studied bagasse as a potential resource as a reinforcement element in biocomposites.^[8-15] There are a wide ray of applications in building, construction, and automobiles that exist for the fabrication of bagasse based composites. The use of lignocellulosic materials require pretreatment step. One of the main problems working with natural fibers used as reinforcement components is their high moisture sorption and hydrophobicity of the fibers which thereby influences the mechanical bonding with the matrix. Therefore chemical pretreatments are considered in modifying the fiber surface properties. Chemical pretreatments using acid have been successfully applied to sugarcane bagasse fiber.^[10,13,16] Acids hydrolyze hemicellulose and produce a liquid phase rich in xylose, with minor amounts of lignin derivatives and it has been successfully applied to sugarcane bagasse.^[17,18] The principle of alkaline pretreatment method is the removal of lignin (major loss) whereas cellulose and a part of the hemicelluloses remain in the solid material (minor loss of hemicellulose). Pretreatment using alkaline solution (mercerization) has been proven to be effective for removal of lignin in the fibers therefore enhanced fiber surface adhesion which allowed an effective stress transfer from matrix to fiber. Relatively fewer studies have investigated the surface modification on lignocellulosic fibers obtained from sugarcane bagasse. This current research work focused on the study of surface and structural modification on bagasse fibers pretreated using two different alkaline solution, i.e. sodium hydroxide (NaOH) and lime or calcium hydroxide (Ca(OH)₂). Calcium hydroxide was chosen due to its less hazardous characteristics and low cost. Surface properties on morphology and structure of modified bagasse fibers after pretreatment were studied to evaluate the delignification degree for bagasse fiber performed by both solution in different time length of pretreatment ranging from 2 to 6 hours at 60-70°C. Characterization on the untreated and treated fiber was carried out using Fourier Transform Infrared (FTIR) and X-ray diffractometer (XRD) tests to determine the modified structure and chemical composition on the fiber surface. Scanning electron microscope (SEM) was used to study the effectiveness of both pretreatments through the changes of surface morphology of bagasse fibers.

Experimental

The first step in the bagasse preparation was neutralization of the bagasse by soaking in a 70% ethanol for an hour to eliminate the stench generated due to bacterial fermentation reaction.^[19] A ratio of volume of ethanol (litre) to the weight of bagasse (kg) used was 2.5:1. The neutralized fibers were drained and dried for 6 hours in air at room temperature. The fibers were then dried in the oven (Memmert type UN450) at a temperature 200°C for 30 seconds. Pretreatment was applied to the dried fibers by soaking the fibers in two different solutions of 10% vol. NaOH and 14 % vol. Ca(OH)₂ at 60-70°C for various soaking time of 2, 4, and 6 hours. At the end of pretreatment, bagasse fibers were rinsed couple of times in distilled water to ensure they were clean from the alkaline solution. Before the rinsed fibers went to the oven for drying, they were dried in air for 6 hours at room temperature. Lastly, those fibers were oven dried at 200°C for 30s. Dried fibers were then examined with XRD (X'pert PRO tipe PANalytical) and FTIR (Thermo Scientific Nicolet model) to analyse the structural changes on the fiber surface after treatment. Mass loss after neutralization and pretreatment stages was measured to check the effectiveness of lignin removal. SEM (FEI type Inspect S50) was used to evaluate the surface morphology of the fibers before and after the alkaline treatment in different soaking time. Untreated bagasse fibers were also evaluated to study the surface changes after both treatment.

Results and discussions

Modification of Sugarcane Bagasse – Weight Loss of Sugarcane Bagasse After Pretreatment

The goals of alkaline pretreatment include the removal of lignin and disruption of the crystalline structure of cellulose (Fig. 1). Chemicals used in alkaline pretreatment were sodium and calcium hydroxide.

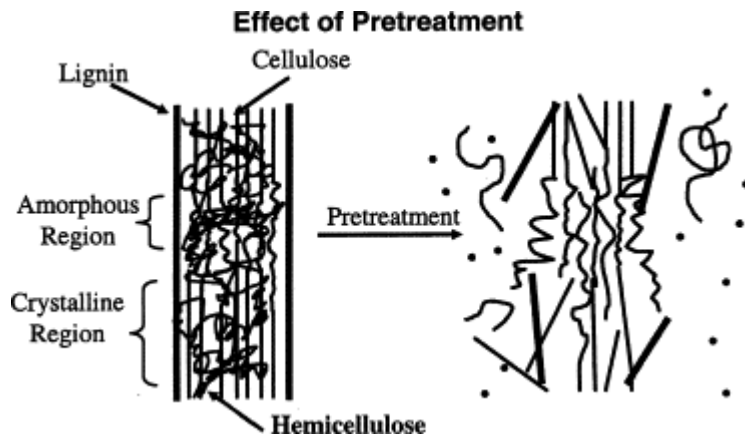


Fig. 1 Schematic structure of natural fibers before and after pretreatment.^[20]

Weight loss measurement on bagasse samples due to pretreatment was carried out aiming to determine the delignification degree of both pretreatment. The weight loss values obtained can inform the effectiveness of lignin removal both in different alkaline solution and soaking time. Bagasse samples were weighed when they were received as wet fibrous residue. Two other weight measurements were performed after oven dried bagasse samples both after neutralization and alkali treatment processes. Neutralization of bagasse using 70% ethanol aimed to prevent bacterial fermentation as that solution is an effective disinfectant or antiseptic agent. The weight loss obtained after neutralization and oven drying was 42.5%. Apart from the three basic chemical compounds (lignin, hemicellulose, and cellulose) that lignocellulose consists of, water is also present in the complex. Typically, sugarcane bagasse has a moisture content of between 45 and 55% on a wet basis.^[21] Furthermore, minor amounts of proteins, minerals and other components can be found in the lignocellulose composition as well. Therefore the weight loss of neutralized fibers was mainly due to the loss of water/moisture content after drying process. Following the neutralization step, the dried fibers were pretreatment using sodium and calcium hydroxide for 2, 4, and 6 hours. After pretreated and oven dried, the fibers were weighed to calculate a further weight loss due to this treatment. Fig. 2 shows the weight loss after both pretreatments. Significant loss was measured in NaOH pretreated fibers (40.5%-57.75%) than in the fibers pretreated using $\text{Ca}(\text{OH})_2$ (25%-46%). The weight loss due to NaOH pretreatment increased by 60% during 2 hours soaking time compared with the same soaking time during pretreatment in $\text{Ca}(\text{OH})_2$. When soaking time increased to 4 and 6 hours, the weight loss during NaOH pretreatment increased only by 30% compared with treatment using $\text{Ca}(\text{OH})_2$. However the weight loss increment with the additional two-hour soaking time was noted relatively higher in $\text{Ca}(\text{OH})_2$ solution (10%-11%) than in NaOH (4.5-12.75%). Major component removed during NaOH and $\text{Ca}(\text{OH})_2$ pretreatment was lignin. Hemicellulose removal was contributed as minor loss to the weight loss.^[22]

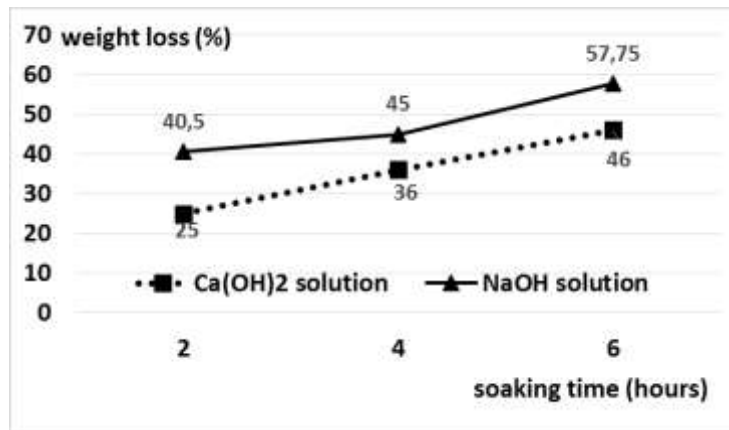


Fig. 1 Weight loss of bagasse fibers after pretreatment

Higher value of weight loss was obtained in NaOH pretreatment than the same loss experienced in Ca(OH)₂ meaning that the more efficient lignin removal experienced by bagasse in NaOH than in Ca(OH)₂. The action of Ca(OH)₂ during pretreatment is slower compared to sodium hydroxide.^[22] FTIR and SEM results support the findings on the weight loss and will be explained in the next section.

Characteristics of Modified Bagasse

Bagasse is a lignocellulosic material consisting of cellulose 43.8%, hemicellulose 28.6%, lignin 23.5%, ash 1.3%, and other components 2.8%.^[19] Studies performed with different varieties of sugarcane bagasse reported that their main chemical composition does not differ significantly.^[23] The hemicellulose fraction is a heteropolymer of pentoses (C5) and hexoses (C6), predominated by xylans, and the cellulose fraction, a major structural component of cell walls and it provides mechanical strength and chemical stability to plants, is a homopolymer of glucose. Lignin is the most complex natural polymer; polymer of aromatic compounds produced through a biosynthetic process and forms a protective layer for the plant walls. It is an amorphous three-dimensional polymer with phenylpropane units as the predominant building blocks.

The major effect of alkaline pretreatment is the removal of lignin from the bagasse. FTIR spectroscopy was used to obtain information about the chemical structure of the bagasse before and after pretreatment. The FTIR spectra for bagasse fibers after both pretreatments are shown in Figure 3a and 3c. The spectra for untreated fibers were also shown for a comparative study to identify considerable changes in the chemical composition on the surface as a consequence of modification due to alkali pretreatment. The similarity of the FTIR spectra between untreated and pretreated bagasse fibers was found in the 4000-2700 cm⁻¹ region where the OH and CH stretching vibrations existed. The strong broad band observed in the region of 3700-3000 cm⁻¹ is assigned to different OH stretching modes and another band in the region of 3000-2800 cm⁻¹ is attributed to the stretching of asymmetric and symmetric methyl and methylene cellulose groups.

Fig. 3b and 3d show a 1800-800 cm⁻¹ region in the spectra that revealed several bands. The band at 1642 cm⁻¹ is associated with adsorbed water in cellulose and probably some hemicelluloses. The C-H stretch at 2894 cm⁻¹ is present in both untreated and treated fibers. The C-OH bending peaks at 670 cm⁻¹ of cellulose are indicated in all fibers. The obvious differences between the untreated bagasse fibers and treated fibers were noted in the range from 2000-700 cm⁻¹ (Fig. 3a and b). Lignin spectrum at 1512 and 1250 cm⁻¹ was no longer found in sugar cane fibers that were given pretreatment, either in NaOH or Ca(OH)₂. The peak 1730 cm⁻¹ indicates the carbonyl peak, C=O stretching of the acetyl groups of hemicellulose^[24,25] and can be seen in untreated fibers. The disappearance of that peak indicates the removal of

hemicellulose from the fiber surfaces after treatment. Pretreatment with sodium hydroxide causes the disruption of H-bonding in cellulose and hemicellulose, breakage of ester linkages between lignin and xylan, and deprotonation of phenolic groups. As a result, swelling of cellulose and the partial solubilization of hemicellulose and lignin occurs. [26] There is an indication of carbonate peaks in the range of 1500-1400 and 872 cm^{-1} on the fiber pretreated using $\text{Ca}(\text{OH})_2$ (Fig. 3d). XRD analysis and SEM study performed on the bagasse fiber pretreated using $\text{Ca}(\text{OH})_2$ confirmed the existence of carbonate compound.

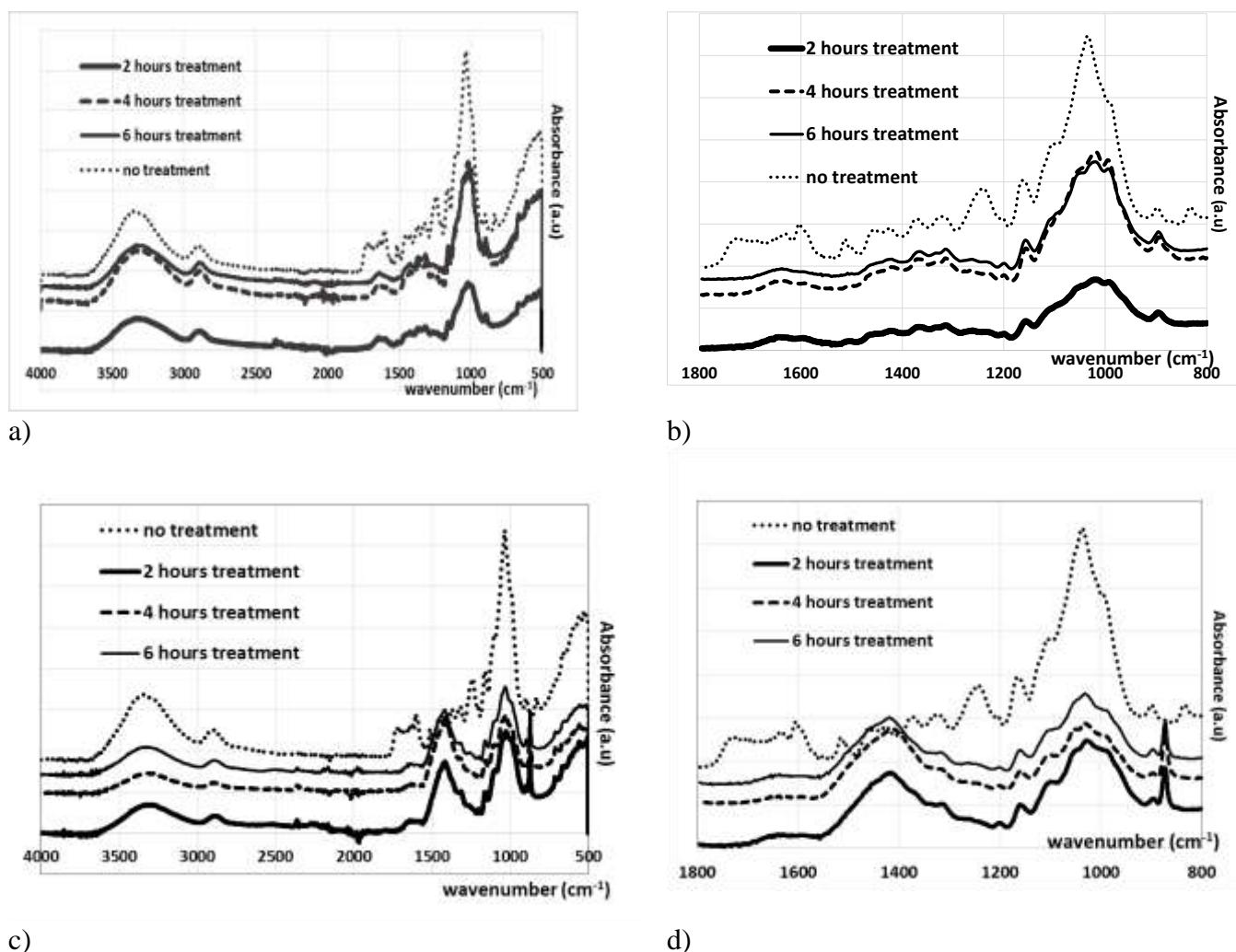


Fig.3 FTIR spectra of untreated and pretreated bagasse fibers in the region between 2800 cm^{-1} in a) NaOH and c) $\text{Ca}(\text{OH})_2$ and in the region between 1800-800 cm^{-1} in b) NaOH and d) $\text{Ca}(\text{OH})_2$.

Figure 4 shows X-ray diffractograms obtained from untreated and pretreated fibers both using NaOH and $\text{Ca}(\text{OH})_2$ at different soaking time. The diffractogram of untreated bagasse fiber shows the main diffraction peaks at 2θ angles: 15.6° and 22° which confirmed the typical cellulose-I structure. The major diffraction peak between 22° and 23° referred to cellulose (002) crystallographic planes was found in all pretreated fibers but the weak peak at 2θ angle 15.6° disappeared. (Fig. 4a and 4b).

Cellulose is a crystalline phase with four different polymorphs of cellulose are known, including cellulose I, II, III, and IV. [27] Alkaline pretreatment in natural cellulose fibers results in the structural transformation from cellulose I (native cellulose) to cellulose II. [28, 29] This structural transformation was observed in the XRD patterns for both pretreatments which the

significant change in diffraction pattern from double peaks as indication of cellulose I to a single peak indicating formation of cellulose II structure.

Another peak at 2θ angle 29.8° was noted at the bagasse sample pretreated with $\text{Ca}(\text{OH})_2$ in all soaking time. That peak was an indication of the presence of insoluble calcium carbonate that might be obtained from the mixture with the starting powder of calcium hydroxide used and from being recoverable from water by the reaction with carbon dioxide. [22]

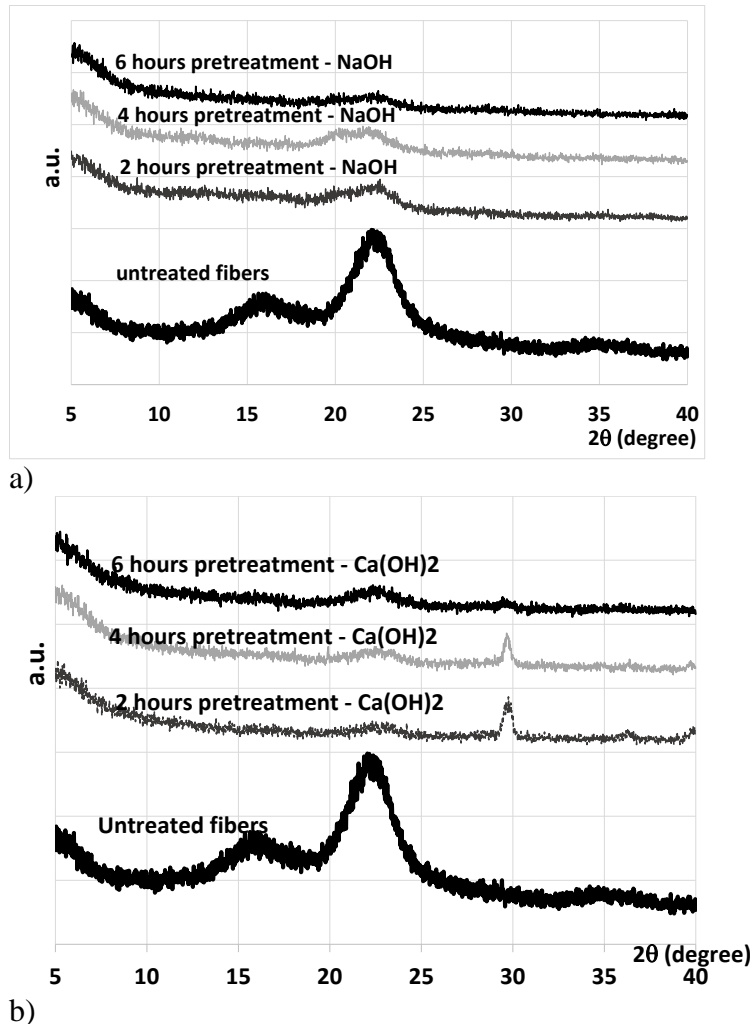


Fig.4 X-ray diffractograms of untreated and pretreated bagasse fibers in a) NaOH and b) in $\text{Ca}(\text{OH})_2$

Morphological Property of Modified Bagasse

To evaluate the effect of alkaline treatment on the morphological surface of bagasse fibers, the samples were studied using SEM. Morphological characteristics of fibres before and after pretreatment were microscopically observed. Figure 5 shows SEM micrographs of unmodified sugarcane fibers, providing the elementary fibrils and bundles are cemented by lignin and pectin intercellular substances. The fiber obtained from sugarcane bagasse was reported to have a length of 2.5 to 20 cm. [2] Schematic structure of natural fibers before treatment in Fig.1 represents the morphology of unmodified bagasse fiber shown in Fig.5. It shows that cellulose fibers are in one piece and intact due to the presence of lignin. Cellulose is a semi crystalline polysaccharide made up of D-glucopyranose units linked together by β -(1-4)-glucosidic bonds [30] and the large amount of hydroxyl group in cellulose gives natural fiber hydrophilic properties.

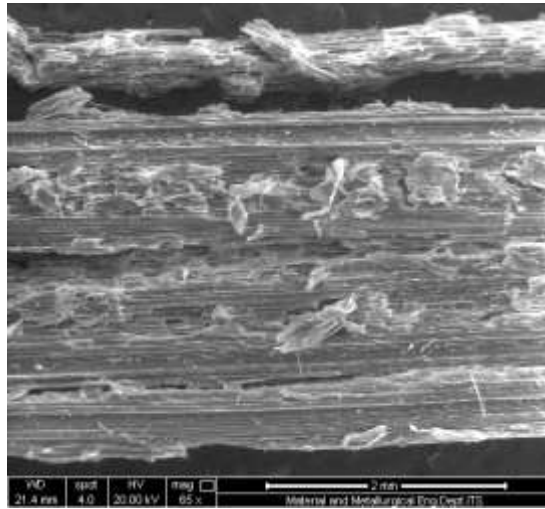
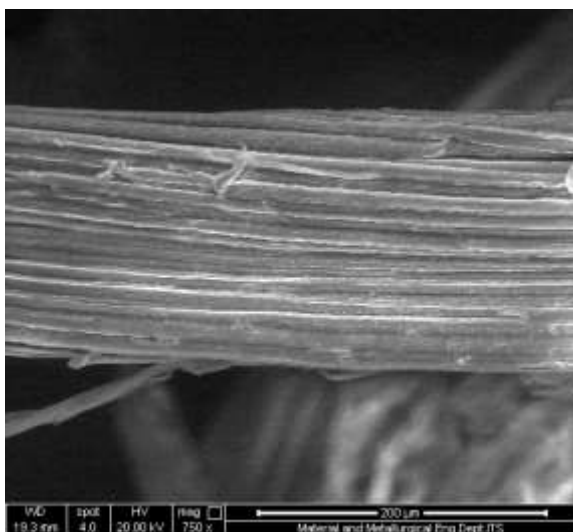


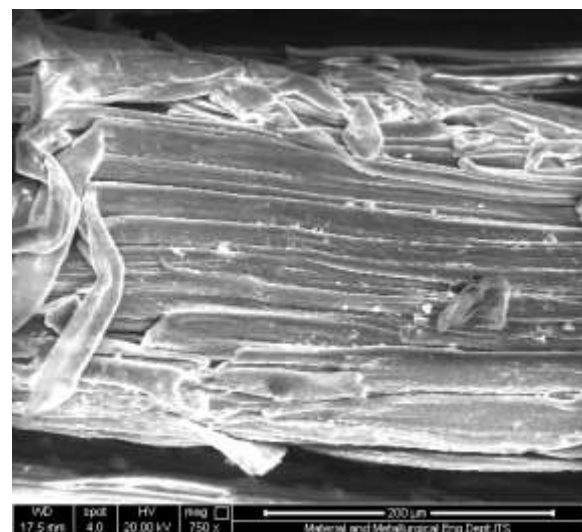
Figure 5 SEM micrographs of longitudinal view of untreated sugar cane fibers

Hemicellulose is strongly bound to cellulose fibrils presumably by hydrogen bonds. Hemicellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is partly soluble in water and hygroscopic. [31] Lignins are amorphous, highly complex, mainly aromatic, polymers of phenyl propane units form a protective layer for the plant walls [32] but have the least water sorption of the natural fiber components. [31]

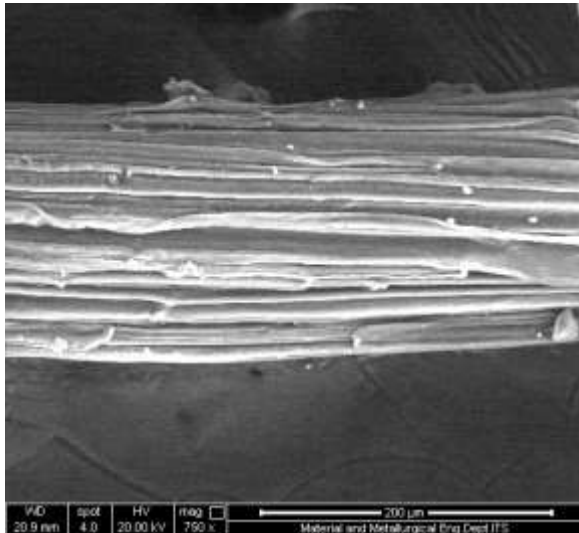
Sugarcane fiber pretreated with NaOH for 2 hours shows that the treatment has been able to eliminate most of the lignin and minor hemicellulose. FTIR spectroscopy detected the removal of lignin and hemicellulose (Fig. 3b). The surface micrograph in Fig. 6a shows a cleaner surface of the fiber compared to untreated one in Fig. 5. An increase of NaOH soaking time to 4 hours increases the weight loss of the bagasse from 40.5% to 45%. That weight loss is evidenced by a definitive change in the morphological structure occurred after 4 hours treatment which the cellulose fibers observed in the micrographs in Fig.6a are partially decomposed. Increase soaking time in NaOH treatment to 6 hours increased the weight loss to 57.75%. This loss was supported by FTIR spectra that reported the absence of lignin and hemicellulose spectra. Figure 6c shows deeper contour of cellulose fibers morphology compared to the fiber surface after soaking in NaOH for 2 hours (Fig.6a).



a)



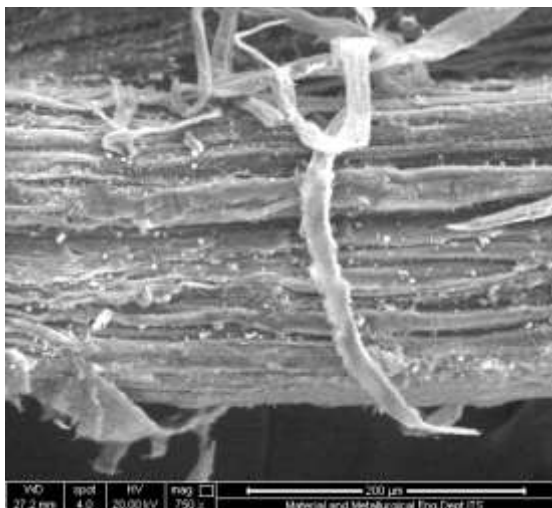
b)



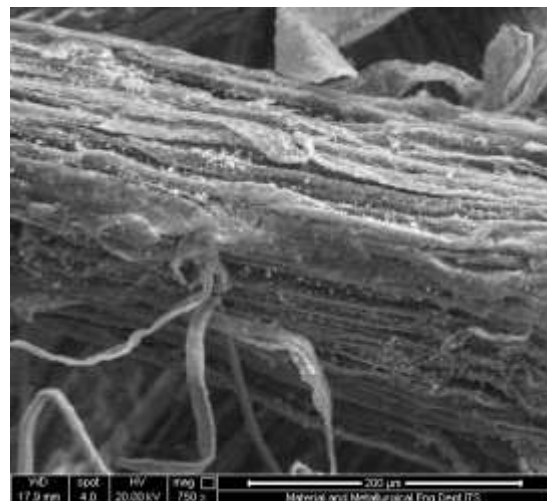
c)

Figure 6 SEM micrographs of bagasse fibers after pretreated using NaOH for a) 2 hours, b) 4 hours, and c) 6 hours

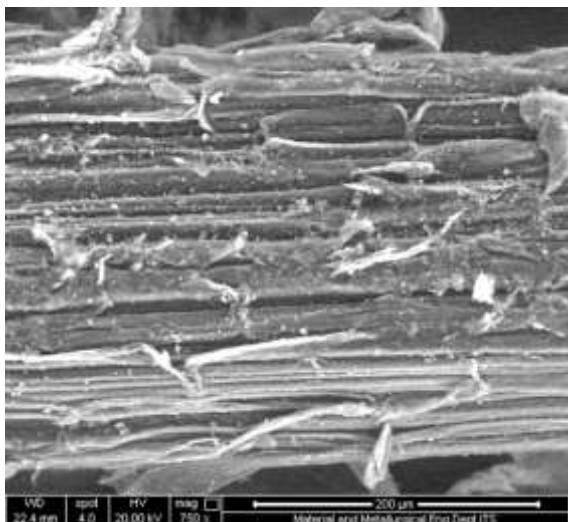
SEM observations on bagasse fibers pretreated with $\text{Ca}(\text{OH})_2$ for 2 to 6 hours show the defibrillation of cellulose fibers. The defibrillation occurred due to the removal of lignin and hemicellulose. Fig. 7a-7c show the cellulose fibrils became more exposed. The weight loss data obtained from pretreatment using $\text{Ca}(\text{OH})_2$ are about 62%-80% of the weight loss experienced by the bagasse fiber pretreated with NaOH. There was an increase in weight loss about 10%-11% with the addition of two-hour soaking time. The presence of CaCO_3 precipitate as it has been identified by FTIR and XRD results was evident in the SEM observation. Bright small particles of CaCO_3 was found on the fibers surface in all soaking time. The cleanliness of the fiber surface pretreated with $\text{Ca}(\text{OH})_2$ was not as good as the fiber surface pretreated with NaOH. The removal of hemicellulose is not as effective as done with NaOH (Fig.7c)



a)



b)



c)

Figure 7 SEM micrographs of bagasse fibers after pretreated with $\text{Ca}(\text{OH})_2$ for a) 2 hours, b) 4 hours, and c) 6 hours

Conclusions

Pretreatment bagasse fibers using 10 vol. % NaOH results in more significant removal of lignin and hemicellulose compared to pretreatment done with 14 vol.% $\text{Ca}(\text{OH})_2$ as indicated by FTIR and XRD spectra. Reaction of $\text{Ca}(\text{OH})_2$ with the bagasse is slower than with NaOH. That finding is supported by the weight loss data of bagasse after the NaOH and $\text{Ca}(\text{OH})_2$ pretreatments, i.e. 40.5-57.75% and 25-46% respectively. SEM evaluation on the morphological property on bagasse fiber surface shows significant fibrillation of cellulose bundle pretreated with $\text{Ca}(\text{OH})_2$ with bright small particles of CaCO_3 deposited on the fiber surface.

Acknowledgement

Authors thank the Directorate General of Higher Education for the grant received for the development of this work.

References

1. <http://www.mapsofworld.com/world-top-ten/sugar-cane-producing-countries.html> (retrieved 29 March 2016)
2. N. Reddy and Y. Yang, *Innovative Biofibers from Renewable Resources*, Springer, 2015.
3. I.C Roberto, L.S Lacis, M.F.S Barbosa, I.M Demancilha, Utilization of Sugarcane Bagasse Hemicellulose Hydrolysate by *Pichia Stipitis* For The Production of Ethanol, *Process Biochemistry*, 26 (1991), pp. 15–21.
4. R Katzen and D.E Fowler, Ethanol From Lignocellulosic Wastes With Utilisation of Recombinant Bacteria, *Applied Biochemistry and Biotechnology*, 45–46 (1994), pp. 697–707.
5. C.A. Cardona, J.A. Quintero, and I.C. Paz, Production of Bioethanol From Sugarcane Bagasse: Status And Perspectives, *Bioresource Technology*, 101 (13), July 2010, pp. 4754–4766
6. J. M. Paturau, *By-products of Sugarcane Industry*, 3rd ed., Elsevier, Amsterdam (1989)
7. R. Rodriguez-Vazquez, G. Villanuevaventura, and E. Riosleal, Sugarcane Bagasse Pith Dry Pre-Treatment For Single Cell Protein Production, *Bioresource Technology*, 39 (1992), pp. 17–22.
8. D. Verma *et al.*, Bagasse Fiber Composites – A Review, *J. Mater. Environ. Sci.* 3(6) (2012), pp. 1079-1092.

9. S.N. Monteiro, R.J.S. Rodriguez, M.V. De Souza, J.R.M. D'Almeida, Sugar Cane Bagasse Waste as Reinforcement in Low cost composites, *Advanced Performance Material*, 5 (3) (1998), pp. 183-191.
10. A. Vazquez, V. A. Dominguez, J.M. Kenny, Bagasse Fiber-Polypropylene Based Composites, *Journal of Thermoplastic Composite Materials*, 12 (1999), pp. 477-497.
11. M.V. de Sausa, S.N. Monteiro, J.R.M. d'Almeida, Evaluation of Pre-Treatment, Size and Molding Pressure on Flexural Mechanical Behavior of Chopped Bagasse-Polyester Composites, *Polymer Testing*, 23 (2004), pp. 253-258.
12. S. Shibata, Yong Cao, and I. Fukumoto, Effect Of Bagasse Fiber On The Flexural Properties Of Biodegradable Composites, *Journal Of Polymer Composite*, 26 (2005), pp. 689-694.
13. Yu-Tao Zheng, De-Rong Cao, Dong-Shan Wang, Jiu-Ji Chen, Study on The Interface Modification of Bagasse Fibre and The Mechanical Properties of Its Composite With PVC, *Composites: Part A*, 38 (2007), pp. 20-25.
14. C.P. da Silva, Tessie Gouvêa da Cruz, Clodoaldo Saron, Sugarcane Bagasse Cellulose/HDPE Composites Obtained By Extrusion, *Composites Science and Technology* 69 (2009), pp. 214-219.
15. Martin, Jurgen Puls, Bodo Saake, and Andreas Schreiber, Effect of Glycerol Pretreatment on Component Recovery and Enzymatic Hydrolysis Of Sugarcane Bagasse, *Cellulose Chemistry and Technology*, 45 (2011), pp. 487-494.
16. P.H.F.Pereira *et al.*, Sugarcane Bagasse Pulping and Bleaching: Thermal and Chemical Characterization, *Bioresources* 6 (3) (2011), pp. 2471-82.
17. C.C. Geddes *et al.*, Optimizing the Saccharification of Sugar Cane Bagasse Using Dilute Phosphoric Acid Followed by Fungal Cellulases. *Bioresour Technol.*, 101 (2010), pp. 1851-1857.
18. G.J.M. Rocha, *et al.* Dilute Mixed-Acid Pretreatment of Sugarcane Bagasse for Ethanol Production. *Biomass Bioenerg.*, 35 (2011), pp. 663-670.
19. S.M.Luz, A.R.Gonçalves, and A.P. Del'Arco, Jr, Mechanical Behavior and Microstructural Analysis of Sugarcane Bagasse Fibers Reinforced Polypropylene Composites. *Composites Part A: App. Sc. and Manf.*, 38 (2007), pp. 1455-1461.
20. T.A. Hsu, M.R. Ladisch, G.T. Tsao, Alcohol from Cellulose, *Chemical Technology*, 10 (5) (1980), pp. 315-319.
21. J.M. Paturao, By Products of the Cane Sugar Industry, An Introduction to Their Industrial Utilization. Amsterdam-Oxford-New York: Elsevier Scientific Publication Company (1982).
22. P.F.H. Harmsen, W.J.J. Huijgen, L.M. Bermúdez López, and R.R.C. Bakker, Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass, BioSynergy Project (2010).
23. Rocha, *et al.* (2015), Influence of Mixed Sugarcane Bagasse Samples Evaluated by Elemental and Physical- Chemical Composition, *Industrial Crops and Products* 64 (2015), pp. 52-58.
24. J. Biagiotti, *et al.*, A Systematic Investigation on the Influence Of The Chemical Treatment of Natural Fibers on The Properties of Their Polymer Matrix Composites, *Polym Composite*, 25(5) (2004), p 470. W. Liu, *et al. J. Mater. Sci.*, 39 (2004), p. 1051-4.
25. W. Liu, *et al.*, Effects of Alkali Treatment on the Structure, Morphology, and Thermal Properties of Native Grass Fibers as Reinforcements for Polymer Matrix Composites, *J. Mater. Sci.*, 39 (2004), pp. 1051-4.
26. Y. Chen, R.R. Sharma-Shivappa, *et al.*: Potential of Agricultural Residues and Hay for Bioethanol Production. *Applied Biochemistry and Biotechnology*, 142 (3) (2007), pp. 276-290.

27. O. Sauperl, K. Stana-Kleinschek, and V. Ribitsch, Cotton Cellulose 1, 2, 3, 4 Buthanetetracarboxylic Acid (BTCA) Crosslinking Monitored by Some Physical-Chemical Methods. *Text Res J.*, 79 (2009), pp. 780-791.
28. G.T. Ciacco, D.L. Morgado, E. Frollini, S. Possidonio, O.A. El Seoud, Some Aspects of Acetylation of Untreated and Mercerized Sisal Cellulose. *J Brazil Chem Soc.* 21 (2010), pp.71-77.
29. E. Dinand, M. Vignon, H. Chanzy, and L. Heux, Mercerization of Primary Wall Cellulose and Its Implication for The Conversion of Cellulose I -> Cellulose II. *Cellulose* 9 (2002), pp.7-18.
30. R.M. Rowell, R.A. Young, J.K. Rowell, 1997. Paper and Composites from Agro-Based Resources, CRC Lewis Publishers, Boca Raton FL.
31. T.W. Frederick, W. Norman, 2004. Natural Fibers Plastics and Composites, Kluwer Academic Publishers, New York.
32. C.P. da Silva, T. Gouvêa da Cruz, C. Saron, Sugarcane Bagasse Cellulose/HDPE Composites Obtained by Extrusion, *Composites Science and Technology*, 69 (2009), pp. 214-219.