Application of waste sorghum stem (sorghum bicolour) as a raw material for microfibre cellulose

Sri Handayani1,a, Yuli Amalia Husnil1, Aniek Sri Handayani1, Ismojo2,b, Mochamad Chalid3,c

1 Department of Chemical Engineering, Institut Teknologi Indonesia, Jl. Raya Puspiptek Serpong, Tangerang Selatan, Banten, Indonesia
2 Department of Automotive, Institut Teknologi Indonesia, Jl. Raya Puspiptek Serpong, Tangerang Selatan, Banten, Indonesia
3 Department of Metallurgy and Material, Faculty of Engineering, Universitas Indonesia, Kampus Depok, Jawa Barat-Indonesia
E-mail: a sri.handayani@iti.ac.id, b ismojo72@gmail.com; c chalid@metal.ui.ac.id

Abstract. Microfibre cellulose (MFC) is one of trending topics in advanced material researches. This work was aimed to study the characteristics of MFC produced from waste sorghum stem. To produce MFC, the amorphous part presence in the fibre such as hemicellulose and lignin had to be removed through chemical process. This study compared two methods for preparing the waste sorghum stem i.e. 1) Alkalization 1-Hydrolysis-Alkalization 2-Acetylation and 2) Alkalization-Bleaching-Acetylation. Thermal stability, crystallinity, morphology, and functional group analysis were the parameters measured in this research. The method that produce MFC with better quality was the first method. The MFC had a significant reduction of amorphous fraction with crystallinity index of 81.07%. From STA analysis it was found that the MFC product was able to endure the thermal treatment at 315°C without any significant weight loss.

Keywords: waste sorghum stem; fibre; microfibre cellulose; alkalization; bleaching

1. Introduction
Sorghum is mainly used as raw material for producing sugar [1]. The waste sorghum stem contains cellulose, hemicellulose, and lignin with composition around 40-44% w/w, 27-35% w/w, and 18-20% w/w respectively [2]. The natural fibre that presence in the waste sorghum stem has not been optimally utilized for producing higher value product.

Cellulose fibre receives a great deal of interest considering the ability of this material on increasing the biodegradability of a polymer. Biopolymer is the current trend especially in research regarding advanced material so that the usage of petroleum based polymer can be reduced. The cellulose fibre for biopolymer application is usually in a form of micro fibre with size <100 μm [3]. This fibre, which is known as microfibre cellulose (MFC), has the ability to reinforce the biopolymer [4]. It is crucial that the fibre must be sufficiently small in size in order to improve the mechanical strength of the biopolymer [5].

In MFC production from cellulose, the impurities such as wax and oil as well as amorphous fraction such as hemicellulose and lignin have to be removed first. There are three common methods to synthesize cellulose fibre, mechanical, chemical or enzymatic. Mechanical methods involve crushing and grinding while chemical method employs alkalinization, hydrolysis, bleaching, acetylation, and another chemical treatment. Endoglucanase is commonly used in synthesizing cellulose fibre through enzymatic method [6].
Former studies synthesized cellulose from sorghum plant by combining mechanical and chemical methods [7]. This study found that alkalization with NaOH 4% will remove most of lignin thus produce ‘cleaner’ cellulose fibre. However the fibre size was larger than 200 µm. Another study used NaOH 20% [8]. The remaining lignin and hemicellulose was relatively very small. Bleaching treatment involve soaking the sorghum fibre from alkalization in NaClO solution 1.7% [7]. Three cycle of bleaching treatment produced cellulose fibre with better appearance and smaller size i.e. 2-4 µm.

This study used chemical method for synthesizing MFC from waste sorghum stem which consisted of several following treatments, alkalization (NaOH 5%), hydrolysis (H₂SO₄ 25%), bleaching (NaClO 5%) and acetylation (CH₃OOH 8%). This study compared two methods for preparing the waste sorghum stem i.e. 1) Alkalization-Hydrolysis-Alkalization 2-Acetylation and 2) Alkalization-Bleaching-Acetylation. Thermal stability, crystallinity, morphology, and functional group analysis are the parameters measured in this research. The method that produce MFC with better quality was the combination of alkalization, bleaching and acetylation.

2. Material and Methods

2.1. Preparation for raw material

The waste sorghum stem was cleaned from any dirt. Then the substrate was crushed using blender and screened using 23 mesh sieve. This preparation was aimed to produce waste shorgum stem at uniform size of 710 µm.

Alkalization 1-Hydrolysis-Alkalization 2-Acetylation (Al1-Hi-Al2-As)

1. Alkalization 1

The purpose of this treatment was to remove impurities and wax from the surface of waste sorghum stem thus creating roughness in the surface. Waste sorghum stem at uniform size was soaked in NaOH 15% solution for 1 hour at 70°C. Then the substrate was washed using distilled water until it has pH=7 and dried.

2. Hydrolysis

Substrate that was produced from Alkalization 1 was soaked in H₂SO₄ 25% solution at room temperature for 2 hours. The purpose of this treatment to produce fibre with micro/nano size.

3. Alkalization 2

Alkalization was performed one more time by soaking the substrate in NaOCl 5% solution at room temperature for 2 hours. This second alkalization was conducted to remove the remaining impurities from previous treatment.

4. Acetylation

In this treatment the fibre was soaked in acetic acid 8% at room temperature for 1 hour. The purpose of this treatment is to coat the fibre so it has hydrophobic characteristic.

Alkalization-bleaching-Acetylation (Al-B-As)

1. Alkalization

The purpose of this treatment was to remove impurities and wax from the surface of waste sorghum stem thus creating roughness in the surface. Waste sorghum stem at uniform size was soaked in NaOH 15% solution for 1 hour at 70°C. Then the substrate was washed using distilled water until it has pH=7 and dried.

2. Bleaching

This treatment had similar effect with alkalization but with stronger intensity. Substrate that was produced from previous treatment was soaked in NaOCl 5% solution at room temperature for 2 hours.

3. Acetylation

Substrate was soaked in acetic acid 8% at room temperature for 1 hour.

2.2 Fibre characterization

After all fibre modification treatment has been finalized, the resulting fibre was characterized to analyze its morphology using Scanning Electron Microscope (SEM). The alteration of functional groups in the
fibre was also analyzed using Fourier Transform Infrared (FTIR). The crystallinity index of the fibre was examined using X-Ray Diffraction (XRD) while the fibre thermal stability was evaluated using Thermogravimetric Analysis (TGA).

3. Result and Discussion

3.1 Functional group analysis

Fig. 1 presents the spectrum curve of the untreated sorghum fibre. The figure shows several peaks with wavenumber of 898 cm$^{-1}$ which indicates the chemical bond of C-O-C from β-1,4-glycosidic—the amorphous area in cellulose [9]. The peak at wavenumber of 1035 cm$^{-1}$ indicates the chemical bond of C-C and C-O from cellulose, hemicellulose and lignin in sorghum fibre. The phenolic C-O, aromatic rings, and C=C from lignin is represented by peak with wavenumber of 1244, 1514, and 1602 cm$^{-1}$ respectively. The presence of acetyl group and ester group in hemicellulose or carboxylic acid in ferulic group and p-coumeric in lignin are indicated by peak with wavenumber of 1737 cm$^{-1}$ [10]. The 2850 and 2917 cm$^{-1}$ spectrums show C-H bond while the 3338 cm$^{-1}$ is for the –OH group in cellulose, hemicellulose and lignin.

![Figure 1. FTIR analysis results for untreated sorghum fibre.](image)

The FTIR analysis results for Al1-Hi-Al2-As treatment and Al 15%-B-As are depicted in Fig. 2. It can be seen from the Fig. that the Al1-Hi-Al2-As treatment was better on removing hemicellulose and lignin as well as reducing the hydrophilic characteristic of the fibre. The percentage of light transmitted by functional groups that indicate hemicellulose and lignin were higher for fibre that received the Al1-Hi-Al2-As treatment, meaning that in this fibre the composition of hemicellulose and lignin were lower.

![Figure 2. FTIR analysis results for Al1-Hi-Al2-As treatment and Al 15%-B-As.](image)
3.2 Fibre Morphology Analysis

The morphology of untreated sorghum fibre is presented in Fig. 3. At magnification of 100x, Fig. 3(a) shows that fibre size is around 700 µm while in 550x of magnification we can see that the virgin sorghum fibre still has layers of lignin and hemicellulose. In addition, the cellulose fibres are also still attached to each other. Some parts of the fibre surface are peeled off which is probably lignin layers that was eroded when the fibre was crushed in blender. At larger magnification (Fig. 3(c)) we can see there are perforations in some part of the eroded fibre surface which probably the xylem area of the sorghum.

![Figure 3](image)

**Figure 3.** Morphology of untreated sorghum fibre with magnification of (a)100x, (b) 550x and (c) 1000x.

Fig. 4 shows the morphology of the sorghum fibre that has received Al1-Hi-Al2-As treatment. In Fig. 4(a) at 100x of magnification, it can be seen that the smallest fibre size from this treatment was 20 µm. From the Fig. 4, we can also see that most of cellulose fibre has been separated. Fig. 4(b) and (c) show that hemicellulose has been removed from the treatment. We can also observe that this treatment does not deteriorate the cellulose fibre, indicated by the absence of amorphous area on the fibre.

![Figure 4](image)

**Figure 4.** Morphology of sorghum fibre after receiving Al1-Hi-Al2-As treatment with magnification of (a) 100x, (b) 550x and (c) 1000x.

Similar results were obtained from the Al-B-As treatment. Fig. 5(a) shows that the smallest fibre size from this treatment was also 20 µm. Fig.s 5 (b) dan (c) demonstrate that most part of cellulose fibre has been detached, indicating that some of hemicellulose has been removed from the treatment.

![Figure 5](image)

**Figure 5.** Morphology of sorghum fibre after receiving Al-B-As treatment with magnification of (a) 100x, (b) 550x and (c) 1000x.
3.3 Thermal stability analysis

The thermal characteristic of cellulose fibre from waste sorghum stem was studied using Thermogravimetric Analysis (TGA) at temperature range of 50-500°C. The TGA result is shown in Fig. 6. This figure shows how fibre mass change as the function of temperature. As the temperature increases from 50-300°C, the fibre mass remain constant. However when the temperature is further increased, the fibre mass is reduced significantly. The fibre from Al1-Hi-Al2-As was starting to experience weight loss at 315°C while the fibre from the other treatment was starting to degrade at lower temperature i.e. 300°C. This result shows that the Al1-Hi-Al2-As treatment produces fibre with better thermal stability compared to Al-B-As treatment.

![TGA result for thermal characteristic of cellulose fibre from waste sorghum stem.](image)

3.4 Fibre crystallinity

The crystallinity of cellulose fibre from waste sorghum stem was measured by using XRD analysis as can be seen from Fig. 7. However XRD result only is not enough to compare the crystallinity of each sorghum fibre. Therefore the crystallinity index of each fibre should be calculated first using equation (1).

![XRD analysis of fibre from waste sorghum stem; (a) and (b) with treatment, (c) untreated.](image)

\[ \text{Crystallinity index} = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}}} \times 100\% \]  

(1)
where I is for intensity. The calculation results for crystallinity index of each fibre are listed in table 1. The chemical treatment on sorghum fibre removes most of lignin and hemicellulose. Hence, the disappearance of amorphous fraction in the fibre exposes the semicrystalline fraction of cellulose. This phenomenon, and how different treatment produce different result can be detected by XRD analysis. Fig. 7 shows that sorghum fibre that underwent the Al-B-As treatment has the highest peak compared to the other two fibre samples. But as has been explained in previous paragraph, the height of the peak is not sufficient as an evidence to find out which sample has the highest crystallinity index.

| Treatment     | Intensity | Crystallinity index (%) |
|---------------|-----------|-------------------------|
| Untreated     | 148       | 256                     | 42.18 |
| Al1-Hi-Al2-As | 106       | 560                     | 81.07 |
| Al-B-As       | 193       | 817                     | 76.37 |

The low crystallinity index of sorghum fibre indicates that it has amorphous characteristic. The Al1-Hi-Al2-As treatment produced sorghum fibre with crystallinity index 81.07%. This index is higher compared to result from [8] and [11] in which the crystallinity index was 62.5% and 77% respectively.

4. Conclusion
Two chemical methods for synthesizing MFC from waste sorghum stem was conducted. Based on analysis results it was found that the Al1-Hi-Al2-As treatment produced MFC with higher crystallinity index compared to the Al-B-As treatment. The MFC that was produced from the former method has the smallest size of 20 µm, crystallinity index 81.07%, and able to endure thermal treatment at 315°C.

Acknowledgment
This work was carried out with the financial support of Competitive Research Grant from Kemenristek-Dikti 2018 with the contract number:34/ KP/LPKT-ITI/III/2018. And thank also for a Sofiana and L. Chandra for collaboration in working on this research.

References
[1] Smith G, Bagby M, Lewellan R, Doney D, Moore P, Hills F, Campbell L, Hogaboam G, Coe G and Freeman K 1987 Evaluation of Sweet Sorghum for Fermentable Sugar Production Potential 1 Crop Sci. 27 4 788-93
[2] Pabendon M B, Aqil M and Mas’ud S 2015 Kajian sumber bahan bakar nabati berbasis sorgum manis Iptek Tanaman Pangan 7 2 123-9
[3] Brinchi L, Cotana F, Fortunati E and Kenny J 2013 Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications Carbohydr. Polym. 94 1 154-69
[4] Bhatnagar A and Sain M 2005 Processing of cellulose nanofiber-reinforced composites J. Reinf. Plast. Compos. 24 12 1259-68
[5] Postek M T, Moon R J, Rudie A W and Bilodeau M A 2013 Production and applications of cellulose: Tappi Press. Peachtree Corners)
[6] Simanulang P, Zulfia A and Chalid M 2017 Preparation of micro-fibrillated cellulose from sorghum fibre through alkalization and acetylation treatments IOP Conf. Ser. Mater. Sci. Eng. 223 012057
[7] Zainuddin S Y Z, Ahmad I, Kargarzadeh H, Abdullah I and Dufresne A 2013 Potential of using multiscale kenaf fibers as reinforcing filler in cassava starch-kenaf biocomposites Carbohydr. Polym. 92 2 2299-305
[8] Yuanita E, Pratama J N, Mustafa J H and Chalid M 2015 Multistages preparation for microfibrillated celluloses based on Arenga pinnata “ijuk” fiber Procedia Chem. 16 608-15
[9] Ramahdita G, Ilmiati S, Suryanegara L, Khalid A and Chalid M 2017 Preparation and Characterization for Sorgum-Based Micro-Fibrillated Celluloses Macromol. Symp. 371 1 69-74

[10] Alemdar A and Sain M 2008 Isolation and characterization of nanofibers from agricultural residues–Wheat straw and soy hulls Bioresour. Technol. 99 6 1664-71

[11] Ioelovich M 2012 Optimal conditions for isolation of nanocrystalline cellulose particles Nanosci. Nanotechnol. 2 2 9-13