

Synthesis and Characterization of Reduced Graphene Oxide from Fibers of *Borassus Flabelifer* by Activation Method

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ABSTRACT–Reduced Graphene Oxide (RGO) has been successfully synthesized by calcination process at 400°C for 4 hours followed by activation with 1 M NaOH. Carbonization is the last process with variations in heating at 650 °C, 750 °C, 850 °C, and 950 °C for 1 hour (heating rate 10°C / minute). DSC-TGA data shows that there is advanced decomposition at high temperatures, this is confirmed by SEM data which shows the amount of porosity which is getting higher with a size that decreases with temperature. XRD data shows phase differences at low temperatures with a trend of higher levels of crystallinity at high temperatures. Raman spectroscopy data showed an ID / IG ratio of 2.607 and 1.007 on *Borassus Flabelifer* L with carbonization at 650 °C and 950 °C respectively. The ID / IG value which is getting closer to 1 indicates that the carbon available in *Borassus Flabelifer* L has undergone phase changes such as Graphene with a little Oxide commonly called RGO.

KEYWORDS : *Borassus Flabelifer*, *Reduced Graphene Oxide*, *Raman Spectra*

INTRODUCTION

Cellulose, hemicellulose, and lignin are carbon polymers that are commonly found in natural materials such as coconut shell (Wachid et al., 2014), rice husk (Prasetya et al., 2018) and bagasse. (Prasetya, Nasrullah, & Nugraheni, 2015) have successfully synthesized reduced graphene oxide by utilizing coconut shell through heat treatment up to 1000 °C. The process of purifying cellulose, hemicellulose, and lignin from complex compounds consisting of Carbon, Oxygen, Hydrogen, and some other impurities such as Potassium, Magnesium, and Chlorine can be carried out through several methods, such as excofiliation (Putra et al., 2018), heating at high temperatures (Pamungkas et al., 2018), and hydrothermal. Through the process of breaking non-carbon chains and impurities, several phases derived from carbon will be

obtained, including Graphite Oxide (Andrameda, Diah, & Nurdiansah, 2018), Graphene Oxide (Kurniasari et al., 2017), until Reduced Graphene Oxide (Nugraheni et al., 2015). These phases has superior electrical and thermal properties, good mechanical properties and high surface area so that it is suitable to be applied as supercapacitor electrodes (Tsaia et al., 2017) and catalysts (Upare, Yoon, & Lee, 2011). In this study, heat and chemical treatments will be carried out to the materials which contain cellulose, hemicellulose, and lignin, namely fibers of *Borassus Flabelifer* L which are easily found especially in the Indonesian coastal regions (Lu & Zhao, 2017). Research on fibers of *Borassus Flabelifer* L has only been limited to the synthesis of activated carbon phase. Several studies have identified the possibility of making advanced phases from *Borassus*

flabelifer L, but on the part of the flower not on the fibers (Sivachidambaram et al., 2017). Calcination at low temperatures, activation with alkaline NaOH and carbonization with a temperature variation of 650 °C – 950 °C are the main process that will be carried out with the aim to break the van der Waals bond so that the material is not only purer by decreasing impurity levels, but also having dipole moments due to asymmetrical bond and high surface area.

METHODS

Fibers of *Borassus Flabellifer L* is the main raw material used in this study for treatment. NaOH and distilled water used for activating agent and leaching respectively. The equipments used in this study are Oven, Muffle Furnace, and filter paper. The characterization instruments used are Differential Scanning Calorimeter-Thermal Gravimetry Analysis (DSC-TGA) Perkin Elmer Jade for thermal analysis, Scanning Electron Microscope (SEM) EDAX for morphology analysis, Raman Bruker Spectroscopy for defect identification, and X-Ray Diffraction analysis PAN Analytical. Fibers of *Borassus Flabellifer L* as main raw material was cleaned firstly by separating from visible dirt and dried by oven. DSC-TGA characterization was carried out on the fibers which had been cleaned to determine the temperature parameters to be used in this study during the chemical decomposition process by variation in heating rate: 10 °C/min and 20 °C/min with atmospheric conditions ranging from 0 °C to 1000 °C. In addition, *Borassus Flabellifer L* fibers are dehydrated by heating in an oven for 12 hours at 110 °C. Clean fibers are calcined at 400 °C for 4 hours and then the chemical activation process is carried out using 1 M NaOH activator. The carbonization process was carried out after the activation process with a muffle furnace for one hour with variations in temperature of 650 °C, 750 °C, 850 °C, and 950 °C. To find out the phase on the results of the treatment, it was tested with XRD. While the SEM test was conducted to analyze the morphology of the material and to determine the intensity of defects and graphite, Raman

Spectroscopy was tested.

RESULTS AND DISCUSSION

Thermal Analysis

In the treatment using a heating rate of 10 °C/min as in Figure 1(a), there were two main processes, namely dehydration at a temperature of 50 °C- 150 °C which evaporate H₂O around 1.1480 mg. Meanwhile decomposition at temperatures of 250 °C – 750 °C make impurities of compound in the hydrocarbon polymer bonds break and evaporate with a mass reduction 6.7309 mg. Heating at these temperatures allow to have a high percentage of carbon along with decreasing amounts of impurities. While the treatment using a heating speed of 20 °C/min as in Figure 1(b) has two decomposition processes, at 250 °C – 750 °C and 950 °C with mass loss of 7.7225 mg and 1.5819 mg respectively. There are several impurities which is broken and evaporated at high temperature with higher heating rate. This indicates that higher heating rate enable to decompose high bonding compounds and make substance is purer from impurities.

Phases Analysis by XRD

Fibers of *Borassus Flabellifer L* XRD data from activation and carbonization results are shown in Figure 2 with temperature variations. At low temperature of 650 °C, XRD data show the pattern of activated carbon in the presence of KCl impurities on 2(θ) 28°. KCl comes from the initial content of *Borassus Flabellifer* which is planted near the beach enable seawater which most of it containing potassium and chloride is absorbed. At a higher temperature of 750 °C the graphene pattern (002) is increasingly visible with the sharpening bumps on 2(θ) 24°. At higher temperatures the 850 °C and 950 °C, XRD patterns have many sharp peaks with almost the same pattern. The peak that occurred was in 2(θ) 28° showed KCl content, 2(θ) 34° and 36° were graphite (110) and graphite (006) respectively. While at 2(θ) 40° shows graphene (100). Based on XRD data at all temperatures showed that at higher temperatures make *Borassus Flabellifer L* have higher purity and lower impurity. The higher carbon purity

makes it possible to form a carbon derivative phase that is reduced graphene oxide. There are peaks of graphene (002) and graphene (100) and

several phases of graphite (110) and (006). This shows that graphene is still bound with oxide so that reduced graphene oxide is formed.

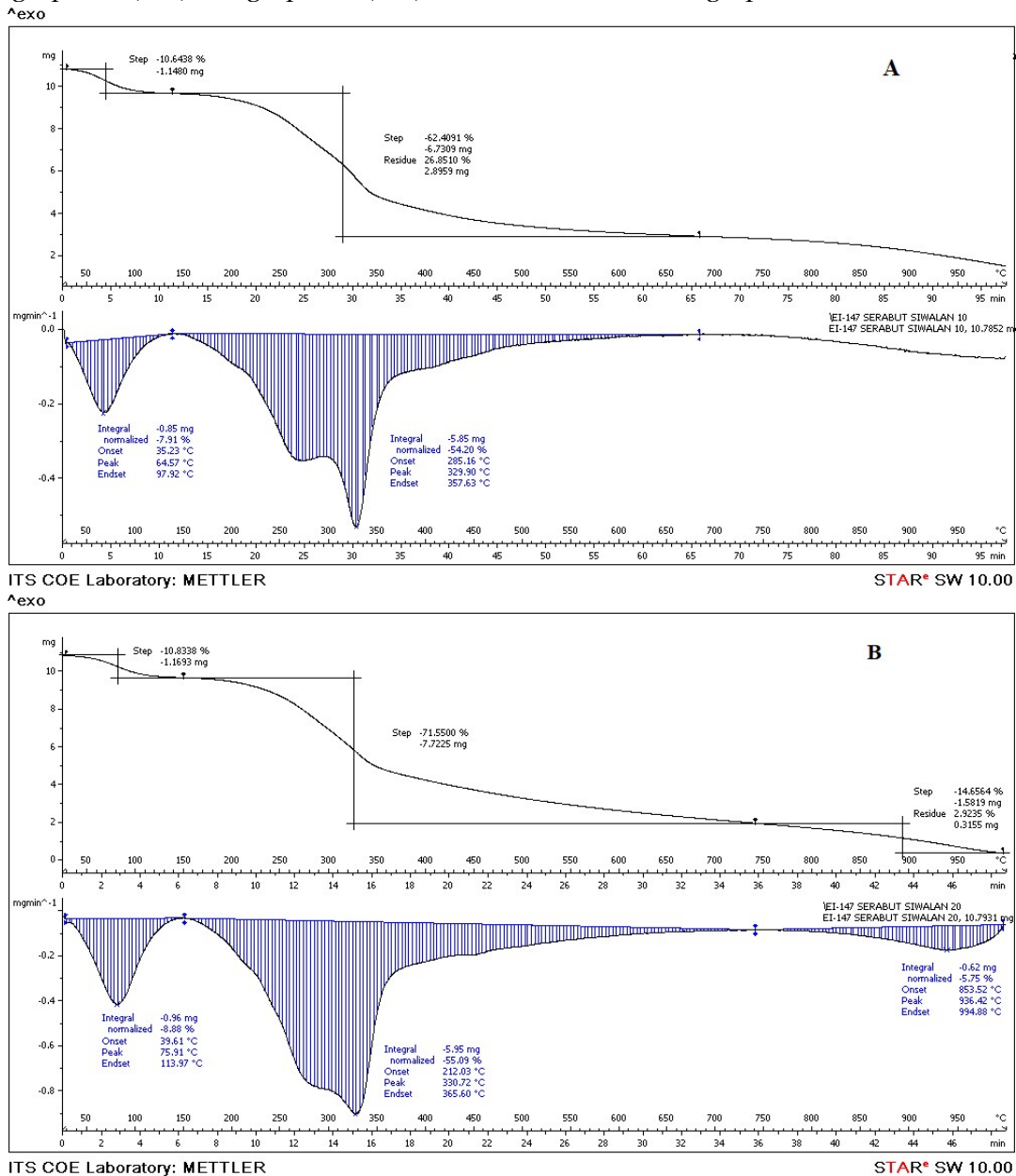


Figure 1 DSC-TGA Data of *Borassus Flabelifer L* Carbonization with (a) 10°C/min (b) 20°C/min heating Rate

Morphology Analysys

Fibers of *Borassus Flabelifer L* carbonization followed by activation results in temperature variations were characterized by SEM with 5000x magnification to analyze the surface morphology of the material. In the data presented starting from Figure 3 (a) to 3 (d) which reflects the increase in temperature ranging from 650 °C to 950 °C, there was an increase in the number of porous followed by decreasing of porous diameter in surface area

qualitatively. At a temperature of 650 °C, the carbonization process only produces lumps with a low porosity level which then shows the growth of porosity begins to appear at a temperature of 750 °C with a still high porous size. Porous order began to appear clearly on the surface of *Borassus Flabelifer L* with higher heating (850 °C), with an average diameter of 10µm pore. The highest carbonization temperature is at 950 °C, the porosity is getting more regular with its diameter decreasing with

an average of $5\mu\text{m}$. This trend illustrates that at high temperatures, the decomposition process increasingly makes *Borassus Flabelifer L* lose impurities thus making the area, especially on its surface, experience defects which results in the formation of increasingly high porosity. Activator agent (NaOH) helps to bond particular compounds which could react with NaOH after calcination process so that Fibers of *Borassus Flabelifer L* purer from any impurities. High porosity results in a greater resultant attraction between molecules towards the compound so that it is possible to be able to draw compounds around the compound surface. This indicates that the adsorption capacities is getting bigger. The greater adsorp power can be utilized to capture CO_2 gas so that it can reduce industrial gas waste that is wasted into free air. In addition, with a high adsorption capability that is offset by a small size of porosity, this compound is suitable for storing the electrical charge as a supercapacitor electrode. Compared with (Sivachidambaram et al., 2017) which used *Borassus Flabelifer L* flower with H_3PO_4 , the result of the morphology of this research is more appear strictly. Because of the difference of activator agent, where NaOH is more appropriate as activator rather than H_3PO_4 . This is caused Na^+ can bond with various ion impurities which is possible to form salt.

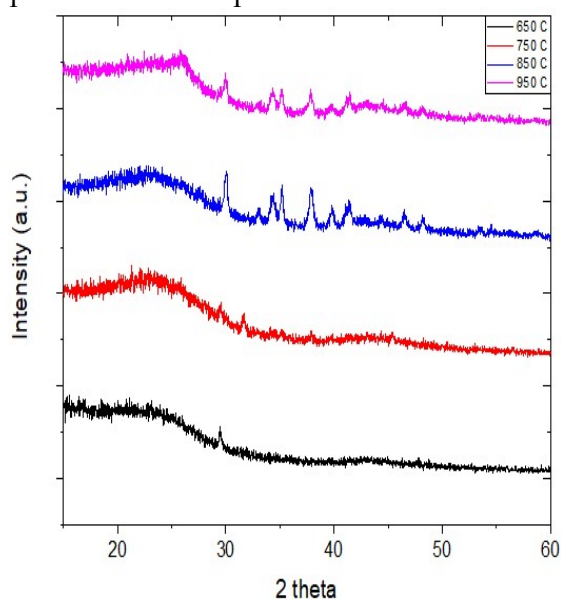


Figure 2 XRD Data of activated Fibers of *Borassus Flabelifer L* at various Temperature

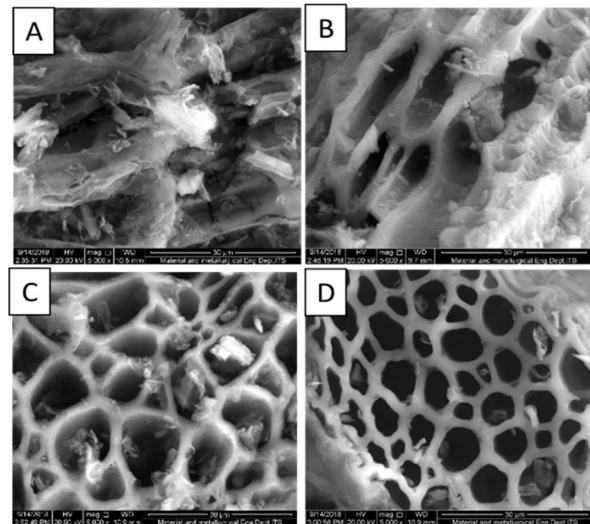


Figure 3 SEM Image of activated *Borassus Flabelifer L* at various Temperature (a) $650\text{ }^\circ\text{C}$, (b) $750\text{ }^\circ\text{C}$, (c) $850\text{ }^\circ\text{C}$, and (d) $950\text{ }^\circ\text{C}$

Defect/Graphitic Analysis

Raman Spectroscopy Test was carried out with the aim of determining the defect intensity and Graphite Intensity in *Borassus Flabelifer L* from carbonization at $650\text{ }^\circ\text{C}$ and $950\text{ }^\circ\text{C}$. The use of only these two temperature variables aims to identify the lowest and highest temperature effects in the carbonization of defects that occur. In Spectroscopic Raman Graphic on carbon-based materials, there are two main peaks which each show the presence of graphite crystalline phases and defects. Larger defects occur allowing material to change the phase from graphite crystals to derivatives. To identify this phase, the Raman Spectroscopy curve produces a process that corresponds to the Lorentz method, so that the peak area ratio of each peak appears. In Figure 4, which shows the fit curve of carbonization results at a temperature of $650\text{ }^\circ\text{C}$, it was found that the Graphitic Intensity / Intensity ratio (ID/IG) was 2.607. This shows that there are still many oxides in the material. In contrast, in *Borassus Flabelifer L* which carbonizes at $950\text{ }^\circ\text{C}$ based on a fitting curve as shown in Gamabr 6, it produces ID/IG 1.007. This shows that the oxide possessed decreases so that it approaches the Graphene phase. However, because the ID / IG value is not right at number 1, it can be concluded that *Borassus Flabelifer*

L which is carbonized at 950 °C has formed the phase of Reduced Graphene Oxide.

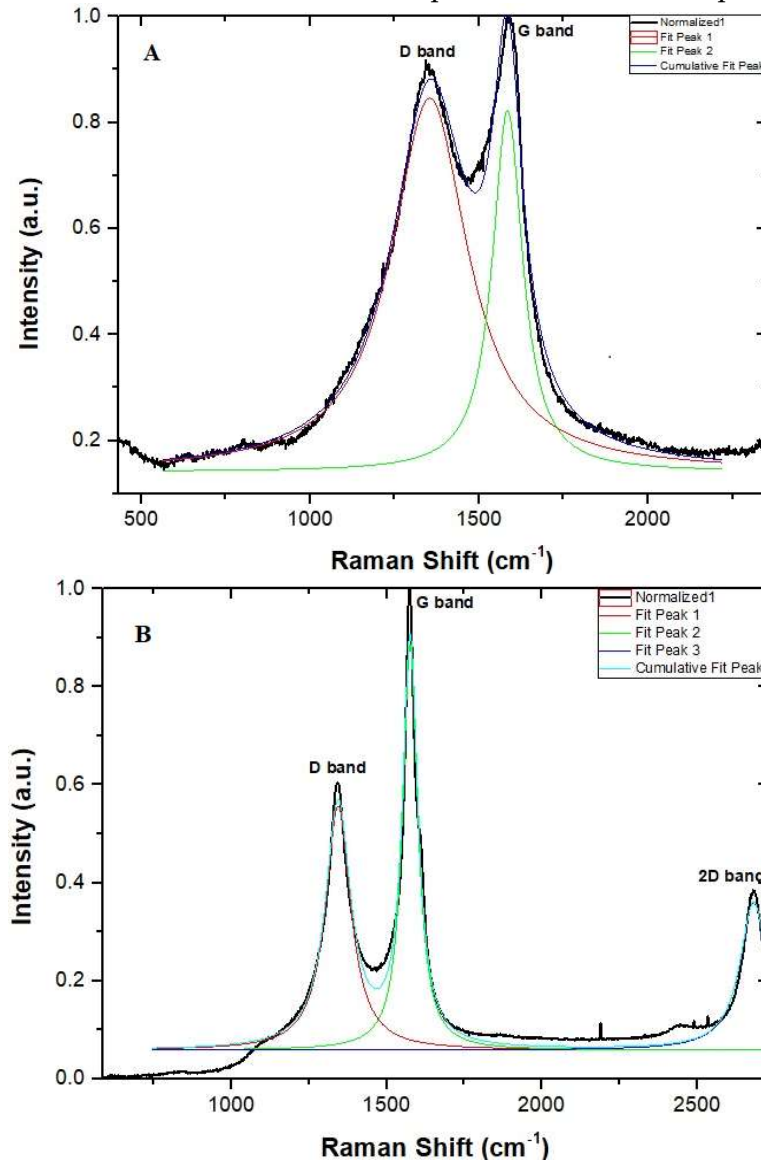


Figure 4 Raman Spectroscopy Curve Fitting of activated Borassus Flabelifer at (a) 650 °C and (b) 950 °C

CONCLUSION

Based on the research that has been done, it can be concluded that the carbonization followed by activation process has improved fibers of *Borassus Flabelifer L* which is proven by increasing of porosity with smaller size along with the increase of carbonization temperature. Furthermore, at the highest temperature; 950 °C, a Reduced Graphene Oxide phase was formed which was clarified with an ID / IG value of 1.007 by Raman Spectroscopy.

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