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CHARACTERISATION OF CARBON PARTICLES (CPs) DERIVED FROM DRY MILLED KENAF BIOCHAR

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Abstract

The characteristics of carbon particles (CPs) derived from dry milled biochar originated from Kenaf was investigated. The biochar was processed in dry milling mechanical alloying equipment using two hardened steel vials set and steel balls as a milling media at room temperature. Characterisation of the CPs after 12 hours milling portrays significant changes of the materials in its size and structural transformations. The size is further reduced with a function of time due to the shear forces introduced during milling. The produced CPs is amorphous as interpreted from the Raman and X-Ray Diffraction (XRD) spectra.

Keywords: Biochar, Carbon particles, Ball milling, Kenaf.

1. Introduction

Biochar is a solid residue obtained during the thermal conversion of biomass into fuel products and has been treated as a lower-value byproduct compared to the higher valued syngas and bio-oil [1]. It is produced from biomass compound that undergo controlled pyrolysis/gasification in the absence of oxygen under temperature ranging from 300°C to 1000°C. The incomplete gasification resulted in producing charcoal (*bio-char or agri-char*) which is also a byproduct of pyrolysis-technology implemented in bio-fuel and ammonia production. These process produced massive amount of biochars thus drives the need to increase its utilisation. Despite of turning it from waste to wealth, it also viable to help agricultural activities more sustainable, reliable and tangibly promotes a better green environment.

Abbreviations

CPs	Carbon particles
ELDC	Electrical double layer capacitors
F/g	Capacitance per mass
FESEM	Field emission scanning electron microscopy
XRD	X-Ray Diffraction

Kenaf is a very versatile plant that is able to provide many valuable by product for consumers and industries. As such, Kenaf is widely used in the production of pulp, paper and cardboard as in fibre reinforced composite, natural fuels, cellulose product, absorbent agent and animal feed. Kenaf exhibits low density, high absorbent, non abrasiveness during processing, high specific mechanical properties and biodegradability [2]. One of the value added significance for char byproduct is turning it into carbon particles (CPs). CPs has the potential to be used in water and beverage purifying systems and as supercapacitor electrodes in electrode production technology. The CPs quality depends on its size distribution, surface area, pore sizes and flexibility. The mass ratio, milling hours and post treatment to the samples are noticably significant to produce high quality CPs. These can be obtained by optimizing the process parameters during its production.

The materials structural investigations was carried out by X-Ray Diffraction (XRD) and Raman scattering and reported by [3-5] that when the structural transformation is obtained, the defects are induced by ball milling process. Activated CPs is used as a carbon based materials in electrical double layer capacitors (ELDC) to increase the surface area of the electrode thus giving it more site for charge storage. The specific and area capacitance is dependant very much on the surface area, pore sizes and active area on the pores in which the double layer is formed [6].

Reports showed that graphite from natural sources subjected to high energy ball milling, gave the capacitance of only 205 F/g (capacitance per mass) [7]. Likewise [6], it produced a nanoscale activated carbon with good quality and purity, controlled pore sizes with high capacitance of 1071 F/g. Another research on CPs produced from corn-stover feedstock showed that the surface area increased by a factor of 60 to 194 m^2/g (cumulative specific surface area, meter square over mass) by optimising milling conditions such as mass ratio of milling media and samples and performing dry milling with the presence of salt [8].

The intention of this work is to produce noticably fine CPs from Kenaf biochar via simple dry ball mill process. The characterisation of the CPs will be carried out to observe its structural transformation after milling and sieving process. The CPs size transformation, defectiveness, functional groups and crystallinity phase will also be studied. The results obtained from this study will provide a new insight for the development and utilisation of Kenaf biochar.

2. Materials and Method

Crop biomass residue of Kenaf from pyrolysis process was further processed using high energy ball mill 8000D Mixer/Mill. Two hardened steel vials set were used as a milling media to mill the biochar samples of 7.5 gram each. The ball to

powder ratio was set at 10:1 at the beginning of milling which was carried out at room temperature and the clamp speed was at 875 cycles per minute. The milling times were 3 hours, 6 hours, 9 hours and 12 hours and milling was interrupted in between for material sampling.

The CPs was refined using 45µm sieve to get even and uniform distributions of particles. The material was characterised using Field Emission Scanning Electron Microscopy (FESEM), Nova NanoSEM 230 for size distribution analysis. Raman spectrum of the CPs was examined by DXR Raman Microscope (Thermo Scientific) with 25µm pinhole aperture, excitation wavelength of 532nm and 10 mV laser power. FTIR spectra was acquired to identify the presence of certain functional groups and to confirm the identity of pure carbon compound or any other impurities in the CPs using FTIR Thermo-Nicolet with a resolution of $4cm^{-1}$ in the range of $4000cm^{-1}$ to $400cm^{-1}$ using KBr pellet method. The X-ray diffraction was performed by Shimadzu 6000 using Cu Kα radiation.

3. Results and Discussion

The FESEM images of the derived CPs from biochar by dry ball milling process are presented in Fig. 1. The pre-processed biochar was observed as flaky and thin with flat surfaces. Small particles also can be seen and it may be the result of agate and mortar crushing and also scratching during handling. The particles also appeared to have sharp edges and averagely long in shape indicating its isolation state from any other particles. There were no sign of agglomeration as the flat surfaces were clean and even.

The observed carbon particles appeared to get smaller with a certain degree of agglomeration as the milling time increased. The agglomeration can be described as the large CPs appeared to be in single and big in size which was surrounded by smaller particles. Some of the CPs had facet, some were round due to the loss of edges during abrasion. The samples observed were in a mixture of flat surfaces and round edges speculated to be mixed material of crystalline and amorphous carbon. This can be confirmed from the Raman spectra in Fig. 2 that shows a combination of D band peak and a slight broad peak appeared at the lower frequency.

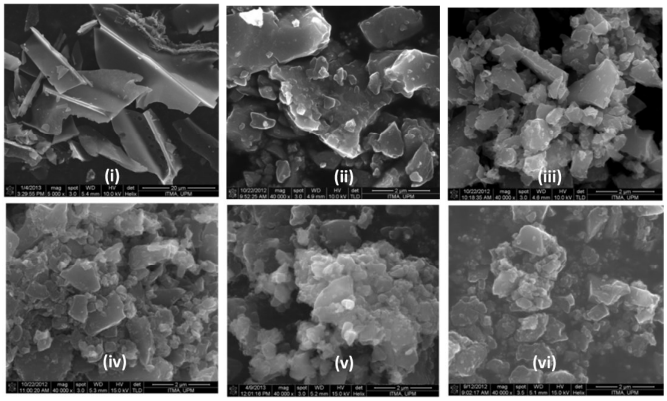

Fig. 1. SEM Images of CPs after i) Preprocessed, ii) 3 Hours, iii) 6 Hours, iv) 9 Hours, v) 12 Hours, vi) 12 Hours Sieve.

The Raman spectrum obtained in Fig. 2 shows that the intensity increased between pre-processed particles and 12 hours of milling due to the increased concentration of the material. This can be confirmed by looking closely at the FESEM micrographs in Fig. 1. The intensity ratio of the D to G band (I_D/ I_G) obtained is a measurement of the average defectiveness of the sample. If the ratio is close to 1, this indicates a high quantity of structural defects [8]. The resulted ratio (I_D / I_G) for pre-processed CPs and 12 hours of milling were 0.7 and 0.76 respectively proven the ball milling effect resulted in high structural defects particles.

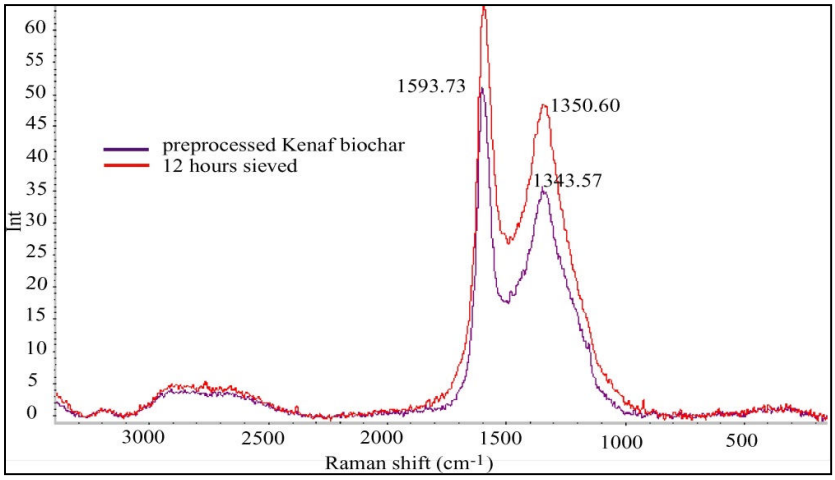

Fig. 2. Raman Spectrum of the CPs.

A typical G-band appears at 1593cm^{-1} representing the C-C stretching mode of sp^2 bonded carbon in planar sheets. The broadened G-band shift from the two observed samples showed the metallic electrical property getting better as milling time increased. A prominent D band appears at 1350cm^{-1} represents the broken basic symmetry of the planar sheets [1] caused by the high impact of ball mills, vials perimeter and the particles itself. The broad peak occurs in the range from 2500cm^{-1} to 2900cm^{-1} denotes 2D band due to the interaction of stacked graphene layers. The observed defect band also indicates the amorphous state even after 12 hours of milling.

The size distribution analysis of the milled CPs is presented in Fig. 3. The particles size was getting smaller as milling time prolonged. This shows a proportional dependency of particle size to the function of time. As the milling time increased, sizes were reduced to below 1000nm and the trend follows to 600nm and below as milling time increased from 3h to 9h. The presence of bigger particle size of 1000nm and above demonstrated the phenomenon of agglomeration which is constant with the FESEM image in Fig. 1.

After 12 hours, it can be seen that particles sizes reduced tremendously to only 600nm and below. The size distribution is seen to be more uniform and small in size after the CPs been refined through 45 µm sieve that gives the distribution in the range of 400 nm and below only.

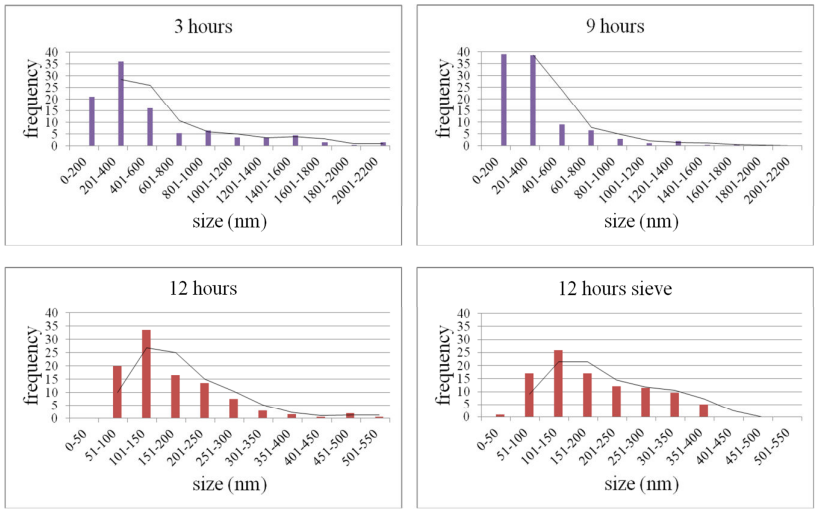

Fig. 3. Size Distribution Analysis of CPs.

The FTIR spectra for 12 hours milled and sieved Kenaf biochar is shown in Fig. 4. It can be seen from the both spectra that the peak at 1633 cm^{-1} indicates the C=O bonds and aromatic hydrocarbon. The broad and strong peak at 3443 cm^{-1} indicates the O-H bond. Meanwhile, the peak at 1384 cm^{-1} represent the C=C bond. The peak at 669 cm^{-1} represents the C-H bond out of bending mode.

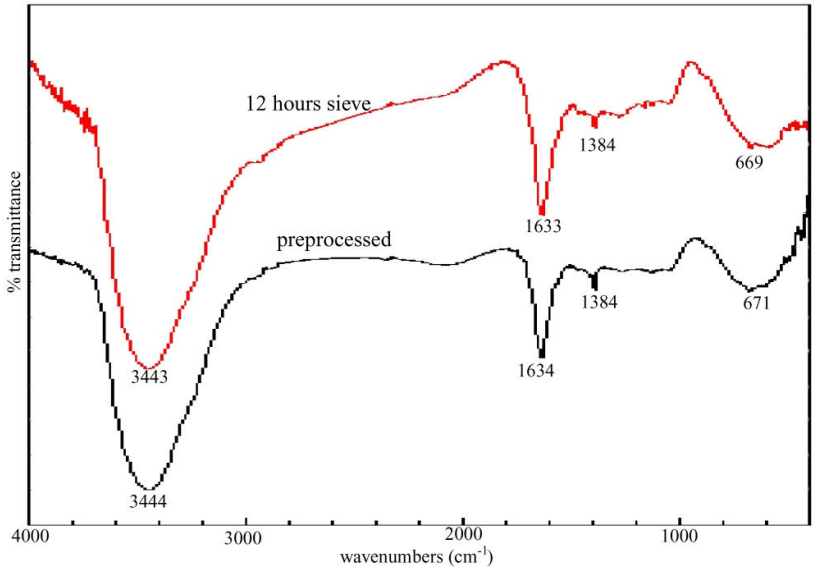

Fig. 4. FTIR Spectra of the CPs.

The XRD pattern of Kenaf biochar before and after it was processed is shown in Fig. 5. It is clearly seen that the position peaks of every sample remained with a

slight reduction of intensities after sieving. This shows that when bigger particles were sieved out, the remaining small particles are a mixture of amorphous and a small amount of graphitize carbon.

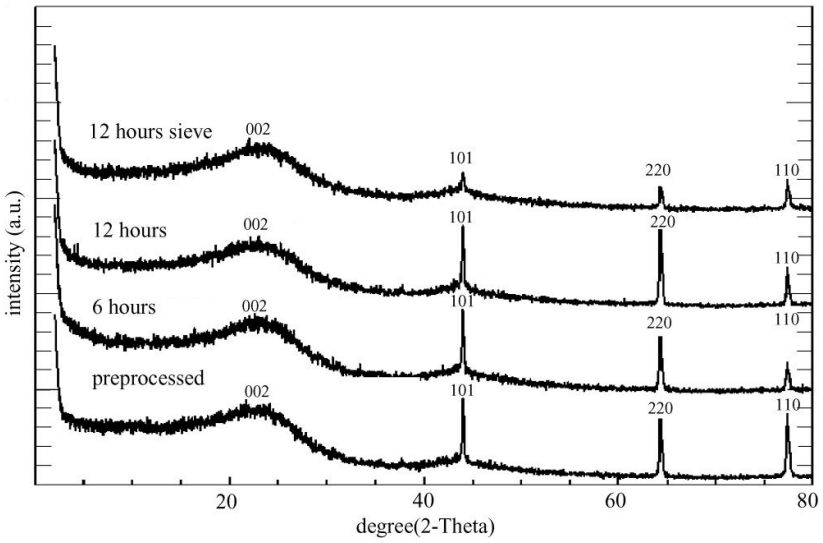

Fig. 5. XRD Pattern of the CPs.

4. Conclusion

Kenaf biochar was ball milled to produce carbon particles in the sizes of 400nm and below. The size reduction occurs during milling due to abrasion and shear forces. The structural transformation happened after 12 hours of milling, in which carbon particles tends to agglomerate easily and a reduction in materials size as milling time gets longer. The dry milling method is observed to be a suitable method to get a subtle size of CPs derived from Kenaf biochar. The sieving process played an important role as to observe the effects of ball milling to the samples. The pre-processed biochar and derived CPs were amorphous but mixed with crystalline phase after 12 hours of milling.

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