Effect of carbonization temperatures on biochar formation of bamboo leaves

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Abstract
Bamboo is a typical plant native in Asia, been used in many sectors, which also produces a large volume of leaves which goes waste and not find its application for any useful purposes; is often considered as a bio-waste and normally incinerated or dumped; as its applications are not yet fully explored. However, some research work done on bamboo fibers for use as a reinforcement in making polymer matrix composite. In the present piece of research work, the influence of burning/carbonization of bamboo leaves (at different temperatures) have been studied and characterized. Proximate analysis gave the fixed carbon content (of nearly 21%). X-Ray diffraction results revealed the presence of various phases viz. cristobalite (Si\textsubscript{2}O\textsubscript{4}), Calcite (Ca\textsubscript{3}O\textsubscript{3}) etc. accompanied with changes in crystal structures. Fourier transform infrared spectroscopy results showed various modes of vibrations viz. O-H stretching bending of other bonds; (for aromatic benzene derivatives) etc. Scanning Electron Microscopic observation (of morphology) showed irregular stacking arrangements between the randomly spaced lamellae structure, with variation in carbonizing temperature. Results revealed the advantages of pyrolysis process in biochar production/formation. It appears that, the bamboo biochar can have suitable properties for its use as an alternative energy source and also for agricultural applications. Its high porosity and carbon content suggest its application as activated carbon also; after physical or chemical treatments. The present research focuses on extending the frontiers of use of bamboo leaves from being an unutilized biowaste to its conversion into a value added product, which can be compassed in terms of sustainable applications.

Keywords: Bamboo leaf, Biochar, Carbonization, FTIR analysis, Morphology

1. Introduction
Biochar is a stable solid containing carbon and can last in soil for thousands of years. The carbon in biochar resists degradation and can hold carbon in soils for hundreds to thousands of years. Biochar is produced through gasification or pyrolysis — processes that heat biomass in the absence of oxygen. During pyrolysis process micro pores are developed, so biochar has a large microscopic surface area and can be used as a soil amendment, nutrients retention, adsorption of pollutant and ion exchange capacity\textsuperscript{[1]}. Bamboo biomass energy can possibly be an option for non-renewable energy source. The thermal or biochemical conversion of bamboo biomass to produce energy products like syngas, charcoal and biofuels can be substitutions for existing fossil fuel products. Cellulose, hemicelluloses, lignin and extractives are the major chemical constituents of bamboo\textsuperscript{[2]}. Bamboo fibers are used to make paper, textiles and board. Bamboo has many desirable fuel characteristic such as low alkali index and ash content. The moisture content in bamboo is relatively low in comparison to other type of plant. Thus bamboo leaf pyrolysis or carbonization can produce certain genuine products like solid-biochar, hydrocarbon gases, etc. which can be potentially used for either environmental advantages or technological applications depending upon suitability.

In the present study, emphasis has been given for analysis of bamboo leaves carbonized at different temperatures (ranging from 250\degree C to 900\degree C). Carbonization or pyrolysis of bamboo leaves was done to compare the properties of biochar obtained with the raw bamboo leaves. Proximate analysis was done to know the fixed carbon content. X-Ray diffraction (XRD), Fourier Transform Infrared Spectroscopy
(FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) was performed to know the various phases, functional groups as well as morphological details of the biochar. The distribution of phases as well as resulting end-products as an outcome of carbonization was important in order to determine the potential of the biochar to be used in various suitable applications.

2. Materials and Methods

2.1. Raw materials:
Bamboo leaves biowaste was collected and washed with water. The bamboo leaves obtained was then sun-dried for a week in order to get rid of the moisture. Using planetary ball mill at an rpm of 300 for 30 minutes the leaves was ground to fine powder. After sometime the fine powder from the ball mill was taken out and was kept in air tight pouch to prevent any contaminants.

2.2. Proximate analysis of raw material:
Proximate analysis of the sample was done to know the fixed carbon content. To determine the moisture present 2(g) of sample in a crucible was placed at 110°C in hot air oven for an hour. For volatile content same amount of bamboo leaves powder was taken in a closed crucible and was kept in a muffle furnace at 900°C for 10 minutes. To calculate the ash content, an open crucible containing 2(g) of sample was placed at 775 °C for an hour in the muffle furnace. Finally the fixed carbon content percent was evaluated to know about the correctness of the sample to be carbonized.

2.3. Carbonization experiment of raw material:
Pyrolysis of bamboo leaves sample at temperatures 250°C, 350°C, 450°C, 600°C and 900°C were done in a furnace with inert atmosphere. Once the desired pyrolysis temperature was attained in a furnace, 5g of the sample was placed isothermally for 2 hours followed by furnace cooling. Next day the sample was taken out of the furnace and weight loss was measured. All the carbonized samples were kept in air tight pouch to prevent oxidation and moisture contamination. Five carbonized and a raw sample were taken for further characterization.

2.4. Characterization:
The Scanning Electron Microscope with an Energy dispersive X-ray spectroscopy analysis was done to study the microstructure and elemental composition. Wide angle X-Ray diffraction (WAXRD) was done in the range of 20 – 100° with step size of 0.02° and a scan rate of 10 °/min. Fourier transform infrared spectra (FTIR) using Perkin Elmer Spectrum Two was done to determine the chemical functional groups by subjecting the disc shaped pellets formed to IR radiations.

3. Results and discussion

3.1. Proximate analysis of bamboo biomass:
Proximate analysis is done to know the percentage of volatile matter, moisture content, ash content and fixed carbon present in a particular organic material. T. Rout et al. (2016) [3] stated that favorable conditions for bio-oil production during pyrolysis are: high volatile matter, low content of moisture and ash. In the present study, the moisture and ash content was very low (given in Table 1). All of these values are included in the range of values compiled by Scurlock et-at. (2000) [4].

| Bamboo biomass   | Wt.% |
|------------------|------|
| Moisture content | 7    |
| Volatile matter  | 57   |
| Ash content      | 15   |
| Fixed carbon     | 21   |

Table 1. Proximate analysis of the raw material

The volatile matter in bamboo biomass is more than 55% enabling a stable flame of the biomass. Biomass fuels contain more volatile components and are more reactive than coal. Due to high volatile
matter the combustion of biomass is rapid and tough to control. However the fixed carbon content was found to be 21%.

3.2. Characterization and analysis of bamboo biomass and its biochars:

3.2.1. Micro-structural analysis
Scanning Electron Microscope analysis showed the morphology of the six samples prepared. The raw bamboo leaf exhibited a cross-linked structure as marked in fig 1. The cross linking reveals the presence of a network containing lignin, cellulose and hemicellulose. In raw sample few pores were seen when compared to its biochars. From fig 4 it was observed that the biochars above 450°C had rougher surface than the raw bamboo biomass. Porous structures were formed on the surface. The biochar was observed to contain more porous structure than the original bamboo biomass samples.

![Fig. 1] Raw bamboo leaves.  
![Fig. 2] Biochar pyrolysed at 250°C.  
![Fig. 3] Biochar pyrolysed at 350°C.  

![Fig. 4] Biochar pyrolysed at 450°C.  
![Fig. 5] Biochar pyrolysed at 600°C.  
![Fig. 6] Biochar pyrolysed at 900°C.  

Carbonization at lower temperature produces large quantity of char but due to thermal breakdown of hemicellulose and cellulose at 450°C, ample pore structures are observed. Above figures when compared the bulk density of raw bamboo sample is more and particle density is less than that of its biochars. Large pores present in bamboo biochar can provide an environment for microorganisms thereby increasing the soil quality (Thies and Rilling, 2009) [5]. At 900°C the biomass burns completely as revealed by SEM image as shown in fig. 6.

3.2.2. Elemental analysis
The composition of elements present in bamboo biomass and its biochars was determined using EDS analysis. The Fig. 7 shows the variation amount of different elements with pyrolysing temperature for raw bamboo leaves and the biochar.

![Fig. 7] Variation of amount of different element with paralyzing temperature for bamboo leaves.
Sharp peaks of carbon (C), oxygen (O), silicon (Si), calcium (Ca) and potassium (K) is seen in the carbonized bamboo leaves samples. Peaks of other elements like chlorine (Cl), nitrogen (N), magnesium (Mg) and aluminium (Al) is also seen in some carbonized samples.

3.2.3. X-Ray Diffraction of Bamboo leaves and its biochars

XRD analysis can potentially determine the phases and planes of components present within a material. A comparison has been made for raw bamboo leaves and all other biochars to know the different between the original bio residue and its derivatives.

![XRD pattern for raw bamboo leaves, biochar at 350°C and biochar at 900°C.](image)

| Peak number | Peak position(°) | Mineral name       | Formula | (hkl) | Structure  |
|-------------|------------------|--------------------|---------|-------|------------|
| 1.          | 25.447           | Silicon oxide      | SiO₂    | 100   | Hexagonal  |
| 2.          | 31.040           | Silicon oxide      | SiO₂    | 101   | Hexagonal  |
| 3.          | 33.051           | Silicon            | Si      | 111   | Cubic      |
| 4.          | 42.281           | Silicon oxide      | SiO₂    | 110   | Hexagonal  |
| 5.          | 45.642           | Calcium Carbonate  | Ca₂O₃   | 113   | Rhombohedral |
| 6.          | 54.654           | Calcium Fluoride   | CaF₂    | 220   | Cubic      |
| 7.          | 67.157           | Calcium Carbonate  | Ca₂O₃   | 122   | Rhombohedral |
| 8.          | 75.957           | Iron oxide         | Fe₂O₃   | 300   | Rhombohedral |

![XRD pattern for bamboo biochars.](image)

Table 2. The peaks for biochar at 900°C are shown.
As seen from the figure 8, absence of well-defined diffraction peaks in case of raw bamboo leaves, except for a weak peak at ~31°; it is worth mentioning it to be an amorphous or non-crystalline material as stated by Macedo et al. [6]. However a single weak peak at ~31° was detected and ascribed to the (101) plane of hexagonal silicon oxide. The amorphous nature of raw bamboo leaves arises due to the presence of hemicellulose, lignin and other similar components.

As shown in fig. 9 a peak at ~ 31° show the presence of silicon oxide (SiO$_2$) ascribed to the (101) plane for all the biochars. The results revealed the presence of various phases viz. cristobalite (SiO$_2$), Calcite (Ca$_2$O$_3$) etc. accompanied with changes in crystal structures.

3.2.4. FTIR analysis

The functional groups present in bamboo biomass and its biochar was determined by FITR analysis. Fig 10 is the FTIR plot for bamboo biomass before and after treatment, thereby revealing the function groups present. Table 3 shows the characteristic bands of raw bamboo leaves and their assignment to different functional groups.

![FTIR pattern for raw bamboo leaves and biochars carbonized at 450°C and 900°C.](image)

| Stretching Frequency | Functional Group                                           |
|----------------------|-----------------------------------------------------------|
| 3650-3200            | Broad and strong, O-H stretch from hydroxyl group of alcohols |
| 1700-1500            | Broad, amine N-H / carbonyl group C=O                     |
| 1100-1000            | C-O-C stretch of the ethers present in lignin Or Si-O-Si stretch |
| 800-700              | C=O absorption/ Si-O-Si bond bending vibrations           |
| 700-600              | Out-of-plane ring deformation or weak vibration –CH$_2$ rocking |
| 500-400              | rings in benzene derivatives / Si-O-Si out-of-plane rocking motion |

Table 3. Band assignment to the peaks of raw bamboo leaves
In figure 10, a broad peak noticed between 3500 and 3300 cm\(^{-1}\) was attributed to the O-H stretch from the hydroxyl groups of the alcohols present. The extremely weak peaks between 3500 and 3800 cm\(^{-1}\) in biochar 900ºC could be assigned to OH stretching which may have occurred due to retention of some hydroxides as well as water in the sample, although mineral based Si-OH in this region could be expected as well. The decomposition of hemicellulose during carbonization was indicated by the disappearance of the carbonyl peak at 1635 cm\(^{-1}\) with increased treatment temperature. Chia et al. 2012 [7] stated that the main chemical processes which occur during the pyrolysis of lignocellulosic substances are depolymerisation and dehydration resulting in the formation of C=C bonds, carbonyl and carboxylic functional groups. In a fingerprint region a prominent peak was seen between 1100 – 1000 cm\(^{-1}\) can be attributed to C-O-C stretch of the ethers present in lignin [8] Or Si-O-Si stretch. C=O absorption or Si-O-Si bond bending vibrations around 798 cm\(^{-1}\) was observed in all biochars. The weak mode of vibration in between 700 and 600 cm\(^{-1}\) was –CH\(_2\) rocking or out-of-plane ring deformation. Also with increase in temperature the aromaticity of biochars increases.

4. Conclusions
The present study dealing with raw bamboo leaves and the biochar obtained from it at different temperatures and conditions, revealed the effects of carbonization temperature leading to a conclusion that the type of carbon found in it was isotropic which does not fuse at higher temperatures. From the proximate analysis we found the fixed carbon content in the raw bamboo leaves to be 21%. High carbon content in biochar was revealed on characterisation. The carbon content is affected with increase in pyrolysis temperature. Variation was also noticed for elements like silicon, oxygen, magnesium, nitrogen etc. with carbonization temperature. Formation of new bond and change in bond structure with increase in temperature was observed. Also formation of new phases in biochars was revealed from the XRD observation. FTIR analysis verified the presence of Si-O-Si stretch and the Si-C peaks in biochars. Also with increase in temperature the aromaticity of biochars increases. The study showed that a biowaste can be made valuable thereby decreasing environmental pollution. Thus the present work can be helpful in the determination of some high-class biochar properties for further use in the near future.

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