

Biochar, a substitute for fossil fuels

Akankshya Supriya*¹, R Samantray¹ and S C Mishra¹

¹National Institute of Technology, Rourkela, Odisha, India.

E-mail: akankshya.igit@gmail.com

Abstract. The present piece of research is envisaged for the possibilities and usefulness of coco peat (coir dust) which is generally not considered for usefulness. Pyrolysis of coco peat was done at two different temperatures to obtain biochars and their properties were investigated. Proximate analysis gave the fixed carbon content which gave a good value for the required purpose. Characterization techniques like Scanning Electron Microscopy, X-Ray Diffraction and Fourier Transform Infra-Red Spectroscopy were employed. It was observed that depending on the pyrolysis temperature and conditions, new substances formed, the diffraction peaks changed and also there were major changes in functional groups. The cross-links were found to disintegrate with increasing temperature. The peaks unveiled the presence of silicon carbide in the biochar pyrolysed at 1000°C. The change in the functional groups with increase in temperature manifested higher aromaticity which is an important attribute of fuels viz. petroleum, etc. Thus the present investigation can open up a new era for processing biochar from unutilized biowaste for its use as an alternative to fossil fuels.

Keywords: Coco peat (coir dust), biowaste, biochar, pyrolysis

1. Introduction

Biomass, the organic subject matter which is plentifully available on earth has huge potential as feedstock for producing fuel, and generating thermal as well as electrical power. Lignocellulosic biomass is becoming the cynosure in the present era because of limited reserves of current energy resources. With the potential to append the depleting fossil fuel resources, biomass is the only renewable energy source that can be used without any energy storage systems. Although biomass primarily consists of carbohydrates comprising of carbon, hydrogen and oxygen; some biomass types may also contain a significant amount of inorganic species. The various thermal conversion or thermo-chemical processes viz. carbonization, pyrolysis, etc. may help to extenuate the growing environmental concerns, while providing greater amounts of a suitable, inexhaustible fuel and chemical resource. The thermal conversion of biomass can potentially lead to various applications leading to environmental as well as economic benefits. Pyrolysis is an example of thermo-chemical conversion which is performed in absence of air to generate solid, liquid or gaseous products. The solid black carbon or biochar obtained is usually rich in carbon and also pollution free potential solid bio-fuel. Such conversions have a shorter processing span and higher product yield. Also the pyrolysis gas can be used as a fuel in industries for combustion processes keeping in view the amount of carbon dioxide and methane it bears. The rising prices of petroleum, demand for energy, serious concerns about security of renewable sources and their supply and environmental problems are some critical reasons due to which there is much emphasis on alternative renewable energy sources [1-5].

However, biomass as a fuel has certain disadvantages viz. bulkiness, high moisture content, low energy-density and high transportation cost in many cases [6] due to which they cannot be always used in various commercial purposes. But the biodegradability, environmental friendliness and sustainability of these organic materials have made them primary candidate in production of biofuels and bioenergy generation. Biochar which has a completely different set of properties in comparison to the respective feedstock, can bring about substantial as well as sustainable changes in securing a future



supply of green energy and as well turn the bioenergy into carbon-negative industry [7]. Biofuels are referred to fuels which may be solid, liquid or gaseous in nature but are prevalently produced from biomass. These include energy security reasons, environmental concerns, etc. Biofuels are non-polluting and reliable, and also contain oxygen levels of 10-45% which make them absolutely different from petroleum feed stocks [8]. Pyrolysis produces high energy-density fuels, such as biochar. Biochars have heterogeneous char structure, contain abundant inorganic species that can be catalytically active during any thermal conversion process and also are low-rank fuels [9].

In view of using biomass precursors for production of biochar fuels, several research studies have been performed. Production of biochar from rapeseed cake [1], feasibility of using biomass residues like apricot stone, hazelnut shell, grapeseed and chestnut shell [2], synthetic fuel production from tea waste [5], and fuel properties of coffee residue biochars [10], have been already studied contributing some very positive results. Some other notable research studies regarding biochar and biofuels are: analysis of pyrolysis products of wheat straw [11], algae [12] and lignocellulosic biomass viz. pinewood, perennial grass, etc. [13]. An interesting perspective regarding biomass is its substitution for coal and coke in ironmaking process. Biomass has favourable metallurgical properties, which can be used as heating as well as reducing agent to partially replace the raw feed materials in ironmaking process which in turn would reduce the consumption of underground carbon resources and fossil fuels [14]. Thus introducing new renewable fuels would be considered as a major alternative to conventional fossil fuels.

Thus the present research study emphasizes to establish the usefulness of the biomass and highlight the effects of biochar as a sustainable replacement for fossil fuels. In this study coco peat is the primary raw material which was subjected to pyrolysis to obtain the solid residue called biochar. The biochars obtained at two different temperatures were studied to reveal several unique characteristics. Therefore the present work focuses to evaluate biochar obtained from coco peat as a substitute for fossil fuels.

2. Materials and methods

2.1 Raw materials:

In the present study, the biomass feedstock used was coco peat or coir dust. It was collected from local area in Rourkela (India) and sun-dried followed by drying in a hot air oven for 2 h at 100(±5) °C in order to remove the moisture. Then it was ground using a Fritsch planetary ball mill (Pulverisette 5) with rotating speed of 300 rpm for 30 min. After a 30 min pause in the ball mill, the finely ground powder was removed and stored in an air-tight container.

2.2 Proximate analysis of raw material:

Proximate analysis was done for raw coco peat. 10 g sample was taken in a crucible and then kept in hot air oven maintained at a temperature of 110°C for 1 h to know the moisture content. Then, 10 g sample was taken in a closed crucible and was placed in a muffle furnace maintained at a temperature of 900°C for 10 min to know the content of volatile matter. Thereafter, same amount of sample was taken in an open crucible and kept in the muffle furnace at 775°C for 1 h. The crucible was taken out and the sample was stirred and again kept back inside the hot furnace at 800°C. After 10 min when the crucible was taken out, ash content was measured. So, the fixed carbon was calculated based on proximate analysis as described.

2.3 Carbonization or pyrolysis experiment:

Carbonization/pyrolytic treatment of the coco peat were done at two different temperatures in a tubular furnace (OKAY electric furnace Model 70 T7) in inert atmosphere. The inert gas used was argon and its flow was maintained at 100 mL/min. A crucible with 15-20 g of coco peat was placed inside the tubular furnace. After starting the furnace, the temperature was raised to the desired value at a heating

rate of 5°/min. Pyrolysis was done at temperatures of 400°C and 1000°C. For each of this procedure, when the desired temperature was achieved inside the furnace, isothermal holding was done for 2 h. Also the argon gas flow was maintained at 100 mL/min. After holding for 2 h, the furnace was switched off and the sample was cooled inside the furnace followed by sample removal on the next day. Fine powdery mass of coco peat biochar was obtained and kept in a zip-lock pouch to avoid moisture contamination. Including the raw sample, a total of three samples were analyzed.

2.4 Characterization of raw material and biochars:

Particle size distribution of all the three samples was done and the value of the particle at 50% in the cumulative distribution (medium value of particle size distribution/average particle size) or the D-50 value was calculated for each sample. The microstructure and elemental composition of all samples was studied using a JEOL JSM-6480LV Scanning Electron Microscope with an INCA analyzer (Penta FET Precision- Oxford Instruments) Energy dispersive X-ray spectroscopy (EDS) system. Sample after being coated with platinum was placed in a sample holder and images were captured at different magnifications. Wide angle X-Ray diffraction (WAXRD) was done using D8 Advance Bruker equipment in the range of 30 – 80° with a scan rate of 2 °/min and step size of 0.02°. Pellets were made taking sample and KBr in the ratio of 1:9 and then were subjected to IR radiations so as to determine chemical functional groups using Fourier transform infrared spectra (FTIR) using Perkin Elmer Spectrum Two.

3. Results and discussions

3.1 Proximate analysis of raw material:

After the proximate analysis of coco peat, very low percentage of moisture could be detected i.e 3%. While the volatile matter was 31%, the ash content after proximate analysis was found to be 36%. Thus the fixed carbon was 30% which showed positive potential of the biomass to be used for the purpose of alternative bio-fuel production.

3.2 Characterization and analysis of raw material and biochars:

3.2.1. *Particle size distribution.* The particle size distribution and D-50 value of all the three samples is shown in table 1.

Table 1. Particle size distribution of raw sample and biochars.

Material sample	2.16 μm	2.16 – 9.76 μm	9.76 – 30.22 μm	> 30.22 μm	D-50 value (in μm)
	(Distribution in %)				
Raw coir dust	5.21	22.57	51.31	20.91	15.54
Biochar at 400°C	3.06	28.13	68.18	0.63	12.27
Biochar at 1000°C	4.3	28.85	52.46	14.39	14.29

The major concentration of particles was in the range of 9.76 – 30.22 μm where the percentage increased for the biochar treated at 400°C which might be due to initial lump formation of the internal constituents as soon as degradation and collapsing of the lignocellulosic network begins. However the distribution of biochar at 1000°C was almost similar to that of the raw sample in the range of 9.76-30.22 μm . The D-50 value decreased for both biochar samples in comparison to the raw sample indicating reduction in the overall particle size after carbonization.

3.2.2. *Micro-structural analysis.* SEM analysis was done for raw material and both the biochar samples, and micrographs were obtained as shown in figure 1.

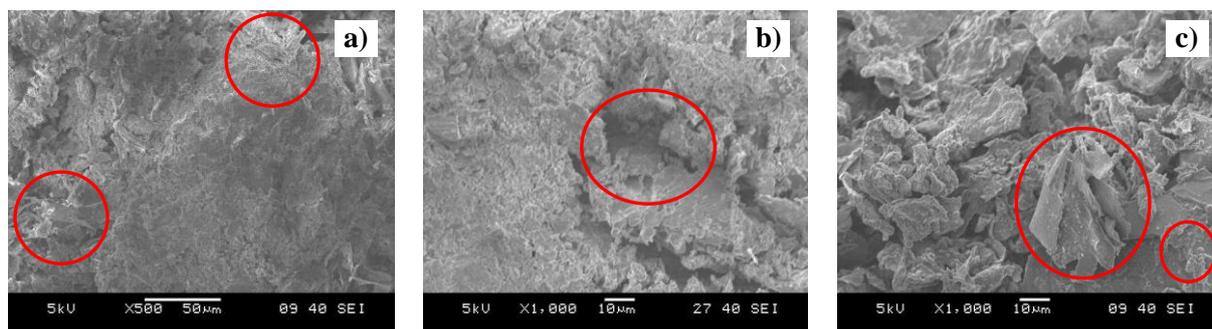


Figure 1. SEM micrograph of a) raw coco peat, b) biochar pyrolysed at 400°C and c) biochar pyrolysed at 1000°C.

Figure 1 a) revealed the compact and rigid raw material with cross-linked structure (highlighted in red) which defines the existence of cellulose, hemicellulose and lignin components. Also a very uniform surface was evident from the micrograph. Figure 1 b) showed broken cross-linked structure with large voids and terrains (highlighted in red) which confirmed the dehydration and fragmentation of the inherent biomass constituents. With increase in carbonization temperature, the particle distribution changed and disintegration could be seen in the microstructure. Figure 1 c) showed presence of elongated and flaky particles (the bigger circle highlighted in red) in the biochar. The smaller circle highlighted in red, depicted small whisker like bright deposits which may be attributed to the inorganic mineral deposits.

The weight percentage (wt %) of oxygen varied in the raw sample and the biochars as per the EDS data analysis. A decrease in oxygen wt% from 46.34 in raw coir dust to 42.93 in biochar at 1000°C was found indicating more carbonaceous percentage within the biochars. There was increase in the wt% of silicon in the biochars i.e. 0.02% in raw sample to 2.73% in biochar at 1000°C.

3.2.3. X-Ray diffraction analysis. The XRD diffractogram of all the samples is shown in figure 2. All the peaks for raw coco peat were listed and are shown in the plot. Only those peaks which shifted or were generated at higher temperatures have been indicated for the biochar samples (400 and 1000), rest of the peaks is same as that of coco peat.

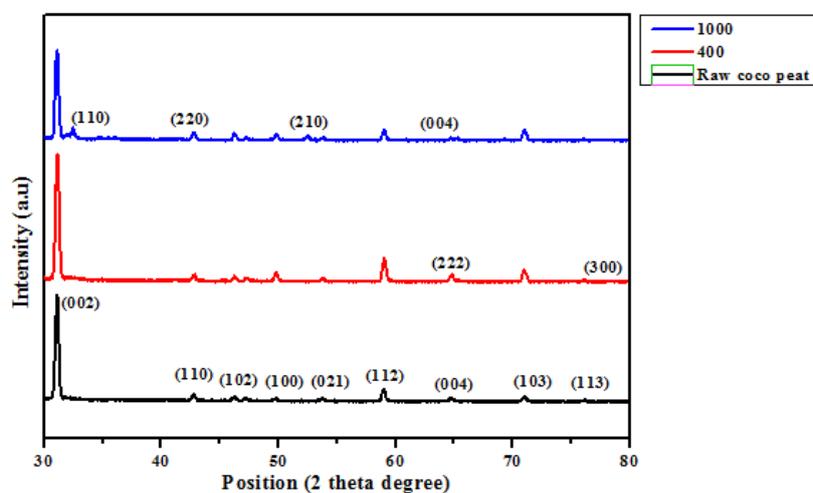


Figure 2. XRD pattern for raw coco peat and biochars pyrolysed at two different temperatures (in °C).

The intensity was highest for the peak at $2\theta = 31.088^\circ$ and was assigned as (002) reflection of graphite in case of all samples. The crystal structure of graphite indicated by (004) plane was hexagonal in raw coco peat. With increase in carbonization temperature, the crystal structure as well as hkl plane for carbon (graphite) was transformed. Rhombohedral structure was observed for the carbon present in biochar at 400°C as indicated by (222) in figure 2. The structure of carbon in biochar at 1000°C again changed back to hexagonal indicated by the plane (004). The presence of some inorganic species in the biochars viz. silica, silicon carbide and stable oxides of silicon could also be analyzed from the XRD data. The peak at $2\theta = 52.476^\circ$ in the biochar pyrolysed at 1000°C depicted the presence of silicon carbide as indicated by (210) plane.

3.2.4. FTIR analysis. FTIR pattern for raw sample and the biochars is demonstrated in figure 3. In case of the raw sample, the peak at 3416.02cm^{-1} was assigned to OH stretch from alcoholic groups. The band 2887.9cm^{-1} was attributed to the aliphatic compounds [15, 16] or may have been contributed by aromatic CH_3 [5]. Hemicellulosic signal was observed at 1618.83cm^{-1} [17] or the peak may be present due to the C=C groups [5]. The peak at 1384.39cm^{-1} was assigned to C-H in-plane bending [15]. Bands between 1000 and 1300cm^{-1} represent C-C groups. The band at 1078.83cm^{-1} could also be either C-O stretch in the C-O-H bonds of glycosidic linkages [15], or C-O-C asymmetric deformation of cellulose and hemicellulose [17] and according to a research study it may also be due the Si-O-Si stretch from the inorganic species present in the biomass feedstock [18]. The bands in fingerprint region were assigned as follows: 796.82cm^{-1} - Si-O-Si bond vibrations [18], 694.5cm^{-1} - CH_2 rocking or out-of-plane ring deformation [16] and 460.3cm^{-1} - Si-O-Si rocking motion [18]. Bands between 700 and 900cm^{-1} may also represent the aromatic CH wagging [5].

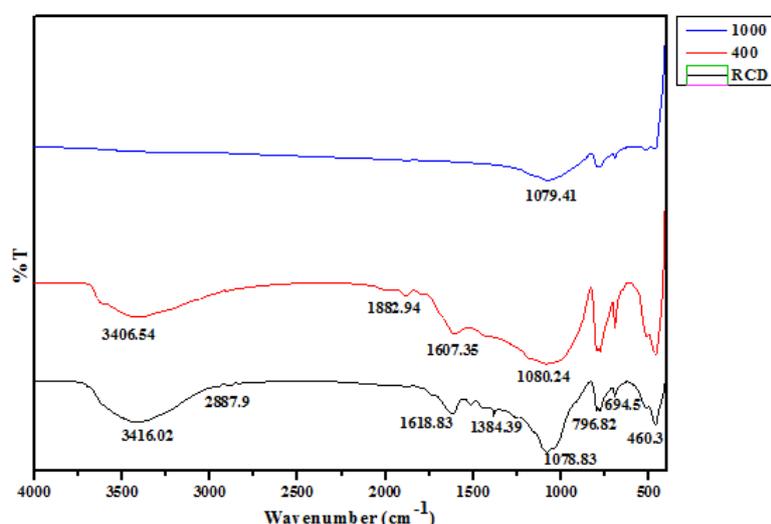


Figure 3. FTIR pattern for raw coir dust and biochar samples pyrolysed at two different temperatures (in $^\circ\text{C}$).

In case of biochars the number of peaks lessened. The broad peak of OH group faded in biochar at 400°C as shown by the band at 3406.54cm^{-1} and completely disappeared in biochar at 1000°C in comparison to raw coco peat. The ceasing of peaks at higher pyrolysis/carbonization temperature indicated loss of functionalities [5]. The peaks in between $1000 - 1100\text{cm}^{-1}$ could be constantly observed in all three samples with changed transmittance percentage which was due to the C-C groups of the ethers, esters, carboxylic acids or anhydrides. The peaks in the fingerprint region for all samples were nearly same. It is known that as the number of low energy H-C and O-C bonds palliate and high

energy C-C bonds increase, the energy density of biomass feedstock improves. With increase in the carbonization temperature, the degree of aromaticity increased. Dehydration and deoxygenation reactions led to the increase in carbon content as well as hydrophobicity. The increased hydrophobicity is an important parameter for fuel storage and handling as it has higher humidity resistance [4]. Thus the biochars experienced effective increase in the aromaticity which might be due to increased number of benzene-derivatives. Also the stability increased and carbon enrichment took place after the pyrolysis treatment of raw feedstock. The results were better for biochar treated at 1000 °C as all the OH groups were completely eliminated and stronger carbon-carbon bonds (C-C) existed in the residue indicating improved energy density.

4. Conclusions

The present study revealed various attributes of the raw biomass feedstock and biochar obtained from it. It was known from the study that the particle size of raw coco peat decreases when pyrolysed at higher temperatures. The morphology, crystal structure and phases within the raw material and biochars were evaluated along with the functional groups which varied in all the three samples. The increase in carbon content of the biomass feedstock with increased pyrolysis temperature made the biochar carbon-rich. Moreover, the biochar treated at 1000 °C showed effective results in comparison to the biochar treated at 400 °C owing to complete elimination of moisture and OH groups which can be helpful in generation of a large amount of heat. Also these biochars have a broad spectrum of concentration carrying numerous derivatives of benzene and other hydrocarbons making them rich in carbon. The increased aromaticity leads to better stability which is an important attribute in producing fuels. The analysis results obtained after characterizing the raw sample and biochars showed that biochars have the potential to replace the conventional fossil fuels owing to their high fixed carbon content and physico-chemical properties. In addition, biochars offer extremely high surface area thus providing sites where molecules of other substances can be held and thereby can be used as adsorbent materials too. Biochars may also help in mitigating some negative environmental effects by increasing the CO₂ uptake in the form of glomalins or by addressing the climate changes which in-turn may lead to economic as well as environmental benefits. Thus the unique characteristics of biochar in carbon sequestration as well as their biodegradability make them vital in this field. Thus the usage of biochars in various applications will prove absolutely beneficial in the near future.

References:

- [1] Özçimen D and Karaosmanoğlu F 2004 Production and characterization of bio-oil and biochar from rapeseed cake *Renewable Energy* **29** 779-87.
- [2] Özçimen D and Ersoy-Meriçboyu A 2010 Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials *Renewable Energy* **35** 1319-24.
- [3] Winsley P 2007 Biochar and bioenergy production for climate change mitigation *New Zealand Science Review* **64** 5-10.
- [4] Liu Z, Quek A, Hoekman SK and Balasubramanian R 2013 Production of solid biochar fuel from waste biomass by hydrothermal carbonization *Fuel* **103** 943-49.
- [5] Uzun BB, Apaydin-Varol E, Ateş F, Özbay N and Pütün AE 2010 Synthetic fuel production from tea waste: characterisation of bio-oil and bio-char *Fuel* **89** 176-84.
- [6] Abdullah H and Wu H 2009 Biochar as a fuel: 1. Properties and grindability of biochars produced from the pyrolysis of mallee wood under slow-heating conditions *Energy & Fuels* **23** 4174-81.
- [7] Kwapinski W, Byrne CM, Kryachko E, Wolfram P, Adley C, Leahy JJ, Novotny EH and Hayes MH 2010 Biochar from biomass and waste *Waste and Biomass Valorization* **1** 177-89.
- [8] Demirbas A 2008 Biofuels sources, biofuel policy, biofuel economy and global biofuel projections *Energy conversion and management* **49** 2106-16.

- [9] Yip K, Xu M, Li CZ, Jiang SP and Wu H 2010 Biochar as a fuel: 3. Mechanistic understanding on biochar thermal annealing at mild temperatures and its effect on biochar reactivity *Energy & Fuels* **25** 406-14.
- [10] Tsai WT, Liu SC and Hsieh CH 2012 Preparation and fuel properties of biochars from the pyrolysis of exhausted coffee residue *Journal of Analytical and Applied Pyrolysis* **93** 63-7.
- [11] Mahinpey N, Murugan P, Mani T and Raina R 2009 Analysis of bio-oil, biogas, and biochar from pressurized pyrolysis of wheat straw using a tubular reactor *Energy & Fuels* **23** 2736-42.
- [12] Chaiwong K, Kiatsiriroat T, Vorayos N and Thararax C 2013 Study of bio-oil and bio-char production from algae by slow pyrolysis *Biomass and bioenergy* **56** 600-6.
- [13] Nanda S, Mohanty P, Pant KK, Naik S, Kozinski JA and Dalai AK 2013 Characterization of North American lignocellulosic biomass and biochars in terms of their candidacy for alternate renewable fuels *Bioenergy Research* **6** 663-77.
- [14] Hu ZW, Zhang JL, Zuo HB, Tian M, Liu ZJ and Yang TJ 2011 Substitution of biomass for coal and coke in ironmaking process *Advanced Materials Research* **236** 77-82.
- [15] Ballesteros LF, Cerqueira MA, Teixeira JA and Mussatto SI 2015 Characterization of polysaccharides extracted from spent coffee grounds by alkali pretreatment *Carbohydrate polymers* **127** 347-54.
- [16] Namasivayam C and Kavitha D 2006 IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase *Microchemical Journal* **82** 43-8.
- [17] Mothé CG and de Miranda IC 2009 Characterization of sugarcane and coconut fibers by thermal analysis and FTIR *Journal of Thermal Analysis and Calorimetry* **97** 661-5.
- [18] Xiao X, Chen B and Zhu L 2014 Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures *Environmental science & technology* **48** 3411-9.