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Effect Of Temperature On Biochar Properties During Paper Mill Sludge Pyrolysis

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Abstract: In the present study, sludge generated from wastewater treatment plant of pulp and paper industry was utilized as feedstock for the preparation of biochar using pyrolysis. The effect of pyrolyser temperature and sludge retention time on biochar yield was studied and the results were quantified in terms of % biochar yield. Nitrogen gas was used as sweep gas for maintaining oxygen-free atmosphere in the pyrolyser. Nitrogen sweep rate was 1 LPM at a constant pressure of 2 bar. To study the influence of temperature on biochar yield, temperature was varied from 500 ^{o}C to 700 ^{o}C at a constant heating rate of 10^{o}C/min. The solid residue (biochar) was analyzed by XRD, FTIR and SEM for correlation of operational parameters in sludge pyrolysis with biochar properties.

Keywords: Feedstock; Pyrolysis; Sludge; Biochar; Sweep gas.

1. Introduction

Production of pulp and paper generates significant amounts of sludge waste. After treated by physicochemical and biochemical methods, 90% of paper mill wastewater's solid and semisolid waste becomes sludge[1]. This kind of sludge is commonly known as paper mill sludge, which contains massive heavy metal, pathogen and parasite, so the sludge is very easy to corrupt and produce odor. For each ton of paper production, the paper industry generates close to 100 kg of waste[2]. If not to be handled properly, it will cause secondary pollution to the environment. Especially, it will be a threat to the health of human being and animals[3]. Therefore, how to properly and scientifically handle the paper mill sludge has become an urgent environmental issue. In recent years, methods formerly used for the disposal of sludge, including landfill, ocean dumping and disposal on agricultural land, have become much less acceptable[4]. So it is very important to find new methods to deal with the sludge disposal problem.

In a recent review, Monte et al.[5] suggested waste minimisation should have the highest priority for the paper manufacturing industry. Re-use of paper sludge for adsorbent preparation was investigated by Likon et al.[6] He et al.[7] investigated combustion as possible management route, which also enables energy recovery. Another potential waste management option for the paper sludge is through pyrolysis which produces bio-gas, bio-oil and charcoal products, all of which have potential viable applications.

The interest in pyrolysis of wastes and biomass materials has increased in recent years as it provides an option for thermal upgrading to higher calorific value fuels. Biochar derived from biomass was traditionally used as metallurgical fuel, which has been recognised as a CO_2-neutral iron ore reductant[8]

. Biochar is also being considered as a soil amendment, adsorbent and fertiliser replacement[9], which enhances soil quality and provides an additional option for carbon sequestration. While pyrolysis of a wide range of different biomass and waste materials has been investigated in the past, there is still limited data on pyrolysis of paper sludge waste and evaluation of its pyrolysis products. The aim of this work is to thermally characterise and investigate the properties of the biochar. Quantification of these properties is important in determining the feasibility of the paper sludge management option through thermal treatment.

2. Materials and methods

2.1 Raw material preparation

Pulp and Paper mill sludge was selected as raw material for biochar production. Sludge samples were collected from dewatering unit of effluent treatment plant (ETP) of pulp and paper mill. Prior to the pyrolysis experiments, raw waste samples was characterized for pH, conductivity moisture content, ash content and inorganic compounds (Table 1). Preparation of raw material for pyrolysis was done by drying sludge in sunlight for 3 days and then oven dried at 70 ^{o}C for 48 hrs. Dried paper sludge (DPS) samples were ground to particle size of 0.5 mm-1.25mm. Ground sludge samples were further used for pyrolysis.

2.2 Pyrolysis studies

To pyrolyze paper sludge, 100 g dried paper sludge (DPS) was inserted into a 5 cm diameter by 25-cm long tube. Glass wool was put to the two sides of the DPS to fix it at certain position. The paper sludge in the tube was then purged with nitrogen for 5 min to purge the tube of oxygen before pyrolysis. The tube was then capped and put into a furnace. The time-temperature profiles used for this study are not considered optimum synthesis conditions for paper sludge pyrolysis, since optimization would also depend upon composition and moisture content in the DPS as well as time-temperature profile. The furnace temperature is programmed to increase 10 ^{o}C / min until it reaches at 500 ^{o}C, 600 ^{o}C and 700 ^{o}C. This entire procedure took 2 hrs to complete. Then the biochar is allowed to cool at room temperature under flow of nitrogen gas. The resultant char is then washed three times with distilled water and then dried in oven at 60 ^{o}C for 24 hr. Biochars are then sieved to 0.250 - 1.0 mm and store in air tight plastic container prior to use. Biochar samples were assigned with different labels i.e. BC500, BC600 and BC700, according to pyrolysis temperature.

2.3 Characterization of biochar

Characterization of sludge samples and biochar was performed to relate initial feedstock composition with the final product composition & yield. The specific surface areas of the chars were determined by N_2 adsorption–desorption isotherms at 77 K and calculated according to the Brunauer, Emmett and Teller (BET) method. Fourier transform infrared (FTIR) spectroscopy was used to determine its surface functional groups. The scanning electron microscopy (SEM) was employed to observe the surface physical morphology of the biochar samples. The crystal structure of the biochar was analyzed by X-ray differactometer. Characterization of biochar samples helped to relate feedstock properties and process condition to product characteristics.

2.4 Analysis

Biochar yield is calculated by equation 1:

$$\text{Biochar Yield (wt \%)} = \frac{W_c\left(\frac{100 - \%\,\text{ash}}{100}\right)}{W_{rm}\left(\frac{100 - \text{moisture}\,\% - \text{ash}\%}{100}\right)} * 100 \qquad (1)$$

Where W_c is weight of char; W_{rm} is weight of raw material and ash and moisture % for sludge.

Table 1 Characterization of Sludge and biochar

Parameters	**Sludge**	**BC 500**	**BC 600**	**BC 700**
pH	7.26	7.28	7.45	7.70
Conductivity (ms/cm)	12.52	0.0973	1.118	1.169
Moisture content (%)	32.69	6.6	5.5	5.8
pHpzc	-	7.01	7.84	8.65
BET surface area (m^2/g)	4.8	47	50	67
Pore volume (ml/g)	0.024	0.063	0.074	0.083
Ca (wt %)	5.89	8.67	9.67	7.94
Si (wt %)	2.39	4.08	3.87	4.06
Mg (wt %)	1.73	3.33	3.74	4.32
Al (wt %)	0.68	0.86	0.82	0.90
Cl (wt %)	0.11	-	0.07	0.09

3. Results and discussion

3.1 Pyrolysis studies

Fig. 1, shows the effect of pyrolysis temperature on biochar, bio-oil and syngas yield. The weight of paper sludge was decreased with increase in temperature. It was observed that there was yellowing phenomenon in paper mill sludge and a kind of strong smelling concentrated yellow liquid was evolved in first 20 min. There were no smell and no liquid formation observed after 20 min. This was because paper mill sludge had relative high water content at the beginning so sludge lost more water and more weight would be lost during sludge's pyrolysis process. With the continuation of the heating time, water content of sludge was lower and lower so sludge would lost less and less water and weight if continue to heat[10] .

3.2 Characterisation

Paper sludge and biochars were characterized by studying surface area, morphology and bulk properties. XRD, FTIR, BET-surface area, SEM and EDX techniques were used for characterization of paper sludge and char adsorbents.

BET surface area and total pore volume of raw sludge and pyrolyzed biochars at BC500, BC600

and BC700 was measured for comparison .BET surface area of the paper sluge increased significantly with increase in pyrolysis temperature (Table 1).The BET surface area of the paper sluge pyrolyzed at 700 ^{o}C was greater than that of the paper sluge pyrolyzed at 600 ^{o}C and 500 ^{o}C,likely due to the release of CO_2 upon decomposition of calcium carbonate in the paper sludge.

X-ray diffractograms for both raw sludge and biochar smaples (BC500, BC600 and BC700) are shown in Fig. 2. Sharp peak was observed in all the samples which confirm the presence of crystalline materials. Peak at $2\theta = 29.4^{o}$ confirm the presence of calcium carbonate in all the samples. It is observed that the dominant crystal form is Calcite for all pyrolysis temperature samples. With increase in pyrolysis temperature from 500 ^{o}C and 700 ^{o}C intensity of Calcium carbonate peak shortened due to decomposition of Calcium carbonate into carbon oxide Silicaon dioxide is also found in biochar samples[11].

Figure 1 Effect of temperature on yield (% wt) of pyrolysis products

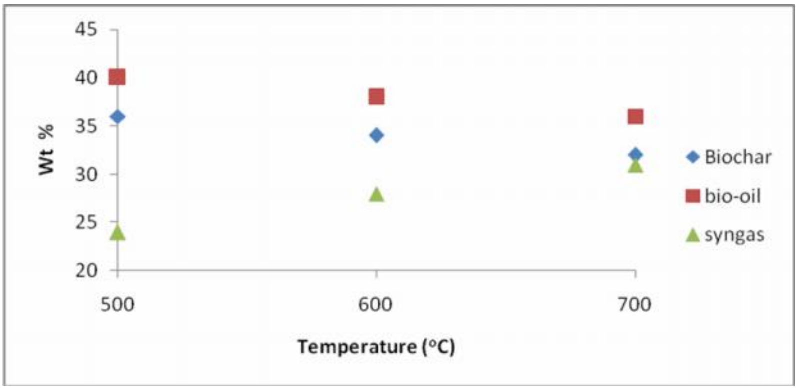


Figure 2 XRD diffract-gram of raw sludge and biochar samples

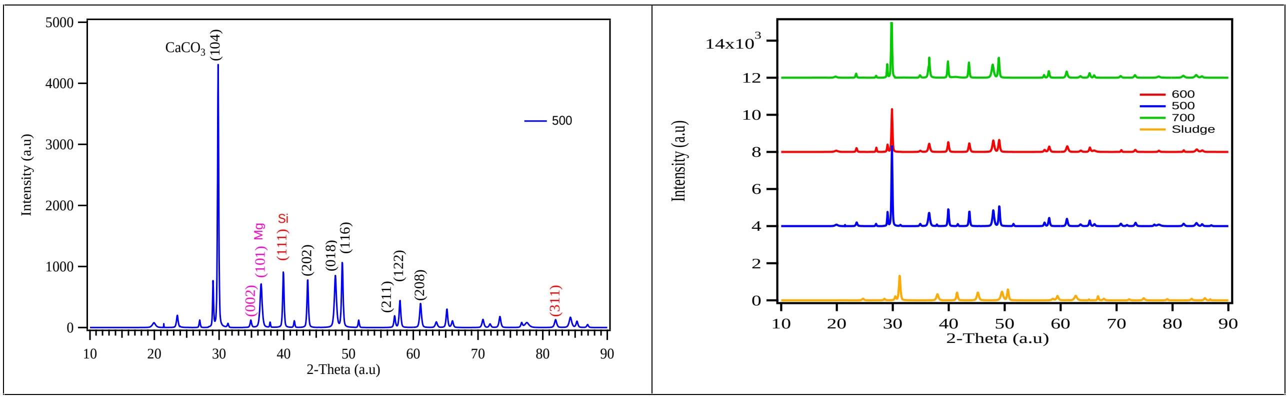
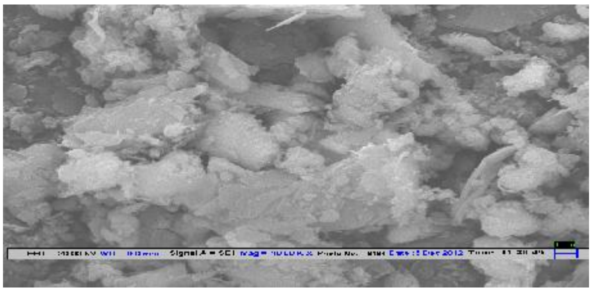
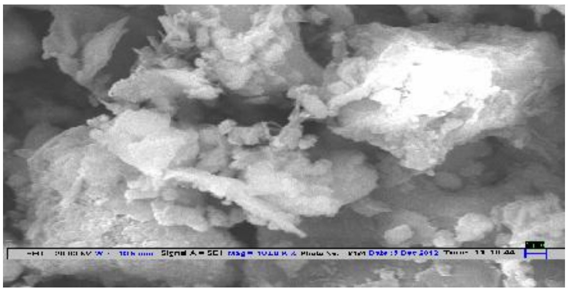


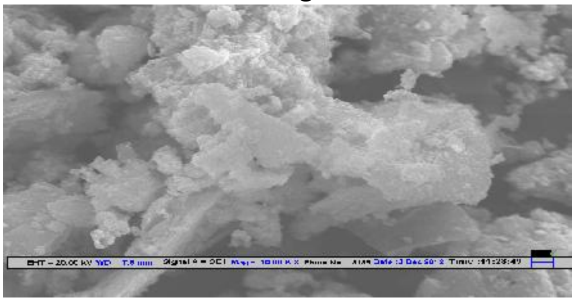
Figure 3 SEM images of paper sludge and biochar samples



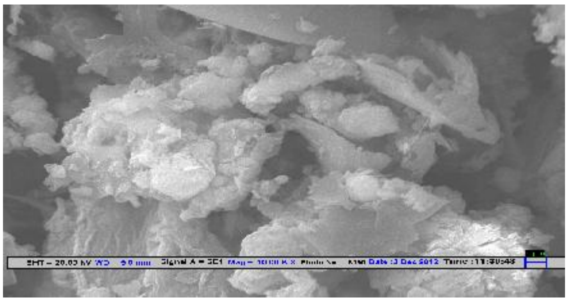
Sludge



500 BC



600 BC

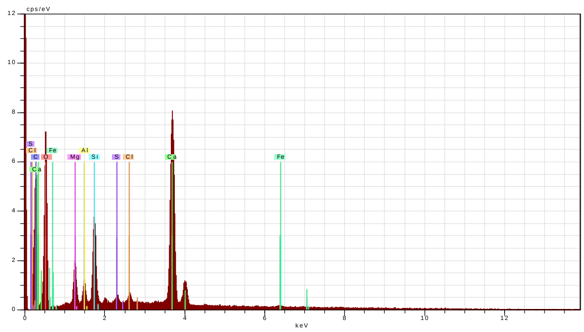


700 BC

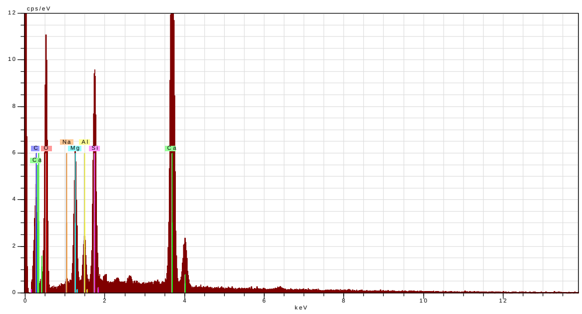
Fig.3, shows the SEM photograph of raw sludge and paper pyrolyzed at 500 ^{o}C, 600 ^{o}C and 700 ^{o}C. The SEM allows visualization of the surface morphology of the samples .Fig.3, shows the cellulose fiber remained in raw DPS. The rapid heating process remained the fiber shape through pyrolysis ,which can explain 700 ^{o}C sample kept the original fiber-shape carbon.However , in 500 ^{o}C amd 600 ^{o}C samples, fibers collapsed when heating was relatively slow.

Fig. 4, shows the elemental composition of raw sludge and biochar samples. The samples are composed primarily of the elements carbon, oxygen and calcium. Hydrogen, too, is likely present, but EDX cannot detect it.In the BC 500 ^{o}C and BC600 ^{o}C ,calcium and oxygen are mainly present as calcium carbonate, which is used as filler and in coatings in paper making processes. In the BC700, the carbon concentration decreases while the calcium concentration increases. This is likely due to the loss of carbon dioxide during the pyrolysis process as calcium carbonate decomposes to calcium oxide and carbon dioxide at temperatures between 600 ^{o}C and 700 ^{o}C .The main element in all samples is carbon .All samples have comparable sulphur concentrations of silicon and aluminium.

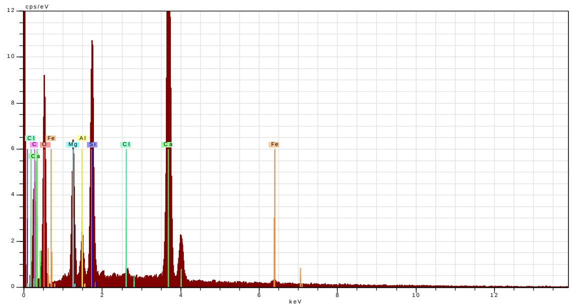
Figure 4 EDX spectra of paper sludge and biochar samples



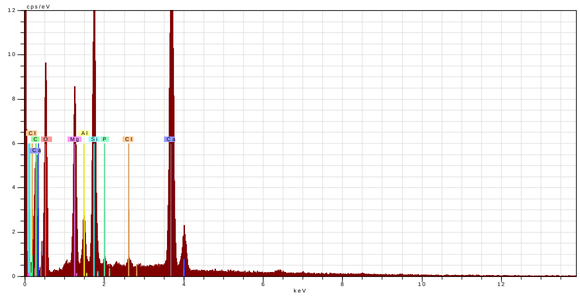
Sludge



500 BC



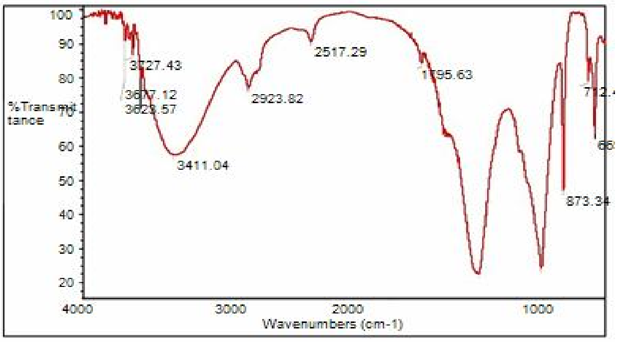
600 BC



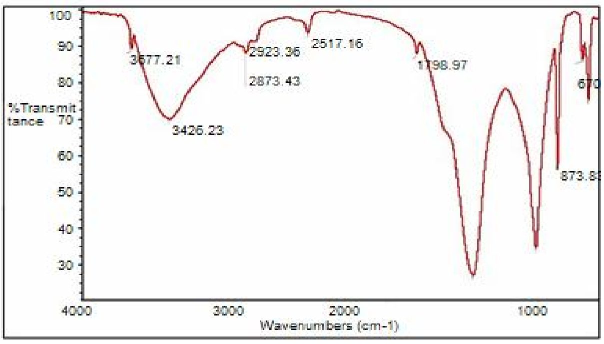
700 BC

The FT-IR spectroscopic study of the produced carbon is shown in Fig. 5. The sample showed four major absorption bands at 2900-3500 cm^{-1}, 1300-1750 cm^{-1}, 800-1150 $cm^{-1}$and 710 cm^{-1}. A wide band with maximum peaks can be noticed at 3411 cm^{-1}. The band at 3393- 3423 cm^{-1} is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water, while the band at 2923 is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm^{-1} have also been attributed to the hydrogen-bonded OH group of alcohols and phenols[12]. In the region 1300-1750 cm^{-1}, amides can be distinguished on surface which has two peaks at 1798 and 1430 cm^{-1}. These functional groups were obtained during the pyrolysis process as a result of the presence of ammonia and primary amines that usually exist in the sludge. The sharp absorption band at 1125 cm^{-1} is ascribed to either Si-O or C-O stretching in alcohol, ether or hydroxyl groups[13]. The band at 1150 cm^{-1} can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring). This band could also be attributed to the antisymmetrical Si-OSi stretching mode as a result of existing alumina and silica containing minerals within the sludge samples[14]. The region 450-750 cm^{-1} show bands at the 573 cm-1 which are associated with the in-plane and out-of-plane aromatic ring deformation vibrations. These spectra were also suggested to be due to alkaline groups of cyclic ketons and their derivatives added during pyrolysis.

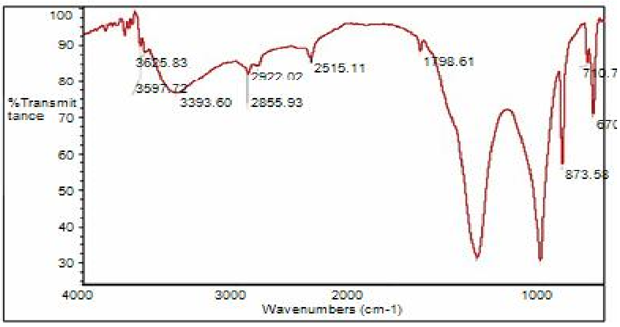
Figure 5 FTIR spectra of paper sludge and biochar samples



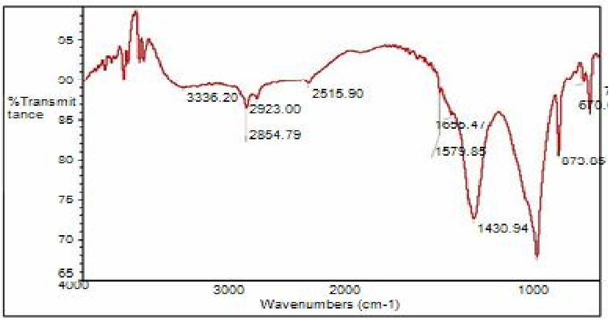
Sludge



500 BC



600 BC



700 BC

Conclusions

The effect of pyrolysis temperature on paper sludge and biochar properties was studied. Characterization of sludge samples and biochar was performed to relate initial feedstock composition with the final product composition & yield. The characteristics of the paper sludge and biochar samples were interpreted by XRD, FTIR, EDX and SEM.

1. The mass of the paper mill sludge reduced as the pyrolysis temperature increasing, at 500 ^oC more biochar yield produced as compared to 600 ^oC and 700 ^oC.
2. Sludge contains significant amount of inorganic compounds, calcium is the highest one, silicon, magnesium and aluminium also present in measurable amount.
3. XRD results confirm the presence of Calcium carbonates, which break down to calcium oxide and CO_2 at higher temperature. Evolution of CO_2 at high temperatures increase the surface area of the biochar samples
4. FTIR spectra showed the enrichment of basic functional group and disappearance of acidic functional groups with increase in pyrolysis temperature. Biochar produced at higher temperatures are relatively alkaline in nature.

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