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Effect of Pyrolysis Temperature and Retention Time on Mustard Straw-Derived Biochar for Soil Amendment

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ABSTRACT

Pyrolysis technology and settings play an important role for producing biochar, as an effective and sustainable mean for agriculture which is used to produce a carbon rich soil and renewable bioenergy. Large quantities of mustard straw are produced in India each year and their residues are burnt in the field thus making the environment polluted. Conversion of mustard straw to biochar for soil amendment in prior is necessary to preserve the carbon content.

For this study, mustard straws with particle size between 0.7 to 1.4 mm were pyrolysed with a heating rate of 10°C min^{-1} at different temperatures (ranged from 250°C to 500°C) and three retention times (1,2 and 3 hours) in a temperature controlled oven. The yield, pH, EC, carbon content and proximate analysis of biochar were recorded. Total elemental C, H, N, O, and S content, calorific value and ratios of O/C, H/C were measured. The surface functionality of the biochars was measured by FTIR spectroscopy.

The results showed that, as pyrolysis temperature increased, the aromaticity, carbon content, pH, EC and ash content also increased, while the oxygen and hydrogen contents decreased. This indicates an increasing degree of carbonization. In addition, as showed by FT-IR spectroscopy biochar produced from mustard stalks that, as temperature increased, functionality decreased. The study showed that pyrolysis temperature had a greater influence than the retention time on the properties of biochar made from mustard straw. The produced biochar could be a good source of carbon sink resulting into reduction in carbon intensity and potential use as soil amendment.

KEYWORDS: Biochar; pyrolysis temperature; retention time; renewable energy; soil amendment.

INTRODUCTION

Renewable energy has seen an explosion of interest due to concerns about limited fossil fuel supplies and increasing prices. In addition, CO_2 released by the burning of fossil fuels is causing global warming and climate alteration. However, fossil fuels are still the major source of electricity and energy consumption [1] According to the 2008 ranking of the countries by fossil-fuel CO_2 emission rates provided by CDIAC, India's total fossil-fuel CO_2 emissions rose 8.1% over the 2007 level to 475 million metric tons of carbon. From 1950 to 2008, India experienced dramatic growth in fossil-fuel CO_2 emissions averaging 5.7% per year and becoming the world's third largest fossil-fuel CO_2-emitting country. India's total emissions from fossil-fuel consumption and cement production have more than doubled since 1994 [2]. For sustainable development of India following issues such as developing clean, renewable energy and reducing greenhouse gas (GHG) emissions are very important.

To our knowledge, there is no such research till date on the production and characterization of biochar produced from mustard straw via pyrolysis in literature. Mustard straw is a valuable biomass, not only because it is an agricultural residue, but also it is in abundance. Therefore, in this study mustard residues were selected as biomass source for producing biochar. In India, the annual production of mustard from 2006 to 2010 was about 59.68 million tons. For every metric ton of grain harvested, about 6.82 metric tons of mustard straw remains in the field [3]. Therefore, there is about 2 million metric tons of mustard straw generated every year, so it is abundant in India. Traditionally, most of the mustard straws left on farmland are directly burned without proper disposal, causing severe air pollution, damaging scenery and wasting a source of renewable energy. Therefore, it is necessary to convert into valuable products like biochar to clear the mustard field and at the same time preserve the carbon content.

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Biochar refers to the carbon-rich product of biomass carbonization under limited oxygen supply and has attracted attention due to its ability for long term improvements of physical and chemical properties of soil. It is distinguished from charcoal by its use as a soil amendment [4]. Specifically, biochar may improve water infiltration [5], soil water retention, ion exchange capacity and nutrient retention [6], pH [7], and improve nitrogen use efficiency [8]. Biochar is used as environmental and agricultural applications [9, 10] and recognized as a high-efficient and low-cost sorbent for pollutants [11, 12, 13]. Application of biochar, as a soil amendment is an approach to sequester carbon [14] and to possibly reduce or suppress CO_2, CH_4 and N_2O emissions [15]. During pyrolysis, biochar yield [16], physical [17], and chemical properties [18] depend on the condition used, and its composition of the feedstock biomass. The effect of pyrolysis temperature and the retention time on the production of biochars have to be well understood.

The use of biochar in agriculture to identify which biochar increases yield in short term and which in long term improves soil health for a given crop and soil. Therefore, the purpose of this study was to examine the effect of pyrolysis temperature and retention time on characteristics and chemical composition of the produced biochar from mustard stalks and illustrate its application into soil.

MATERIALS AND METHODS

Material and Sample Preparation

Mustard straw was collected from the farm field. Prior to use, the mustard straw was air dried and grounded in hammer mill. The production of biochar from mustard straw was followed by sieving to uniform particle size ranging from 0.7-1.4 mm.

Pyrolysis Experiment

Pyrolysis experiments were performed with biomass samples in a temperature-controlled oven at 250, 300, 350, 400,450 and 500 °C. The heating rate was maintained at 10°C min^{-1}. The temperature of the reactor was determined by inserting a thermocouple in the temperature-controlled oven. Once the required temperature reached inside the reactor, it was maintained for at least one, two and three hours until no further release of gas was observed using a slow pyrolysis process. After each experiment the biochar yield was noted from the final weight of the char.

Characterization

The biochar produced were subjected to the following procedures. Proximate analyses were conducted according to the American Society for Testing and Materials (ASTM) D3174-3175. Fixed carbon was determined by difference of percentage composition. For total content of elements in biochar samples, total carbon, nitrogen, hydrogen and sulphur were measured by CHNS analyzer. The percentage of oxygen content was estimated by difference as follows: O (%) =100- (C + H + N + S+ ash) [19]. The atomic ratios O/C and H/C were also calculated in this study. Biochar pH and Electric Conductivity (EC) were measured with glass electrode and EC meter respectively using a biochar-to-water ratio of 1:10. The carbon content was measured by TOC analyzer. Chemical functional groups were determined by FTIR (Shimadzu). Higher Heating Value (HHV) was determined by Bomb calorimeter.

RESULTS AND DISCUSSIONS

Biochar yield

The effect of pyrolysis temperature and retention time on the biochar yield is shown in Fig.1.The yield of biochar decreased with an increase in pyrolysis temperature and retention time. The decrease in the biochar yield with increasing temperature could either be due to greater primary decomposition or through secondary decomposition of char residues. The high yield of biochar at low temperatures indicates that the material has been only partially pyrolysed.

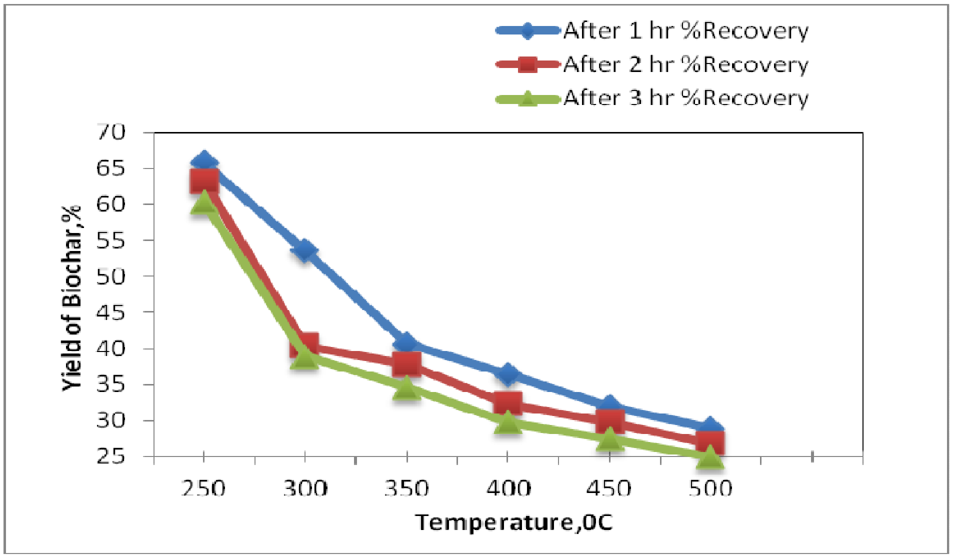

Fig.1. Effect of pyrolysis temperature and retention time on yield of biochar

At 250 °C, the yield of biochar changed from 65.8% to 60.4% (5.4% change) as the retention time increased from 1 to 3 hours. However, at 500 °C, for some increase in retention time, the biochar yield showed only 3.9% change.

Carbon content

As the pyrolysis temperature increased from 250 to 500 °C, the carbon content of the biochar increased from 72.62 to 76.56%. At 250 °C, the carbon content changed from 52.63 to 56.32% as the retention time increased from 1 to 3 hours. Whereas carbon content increased from 61.45 to 66.23% and 65.23 to 69.86% at 350 and 400 °C respectively. Carbon content of biochar produced from mustard straw at different temperature and retention time is shown in fig.2.

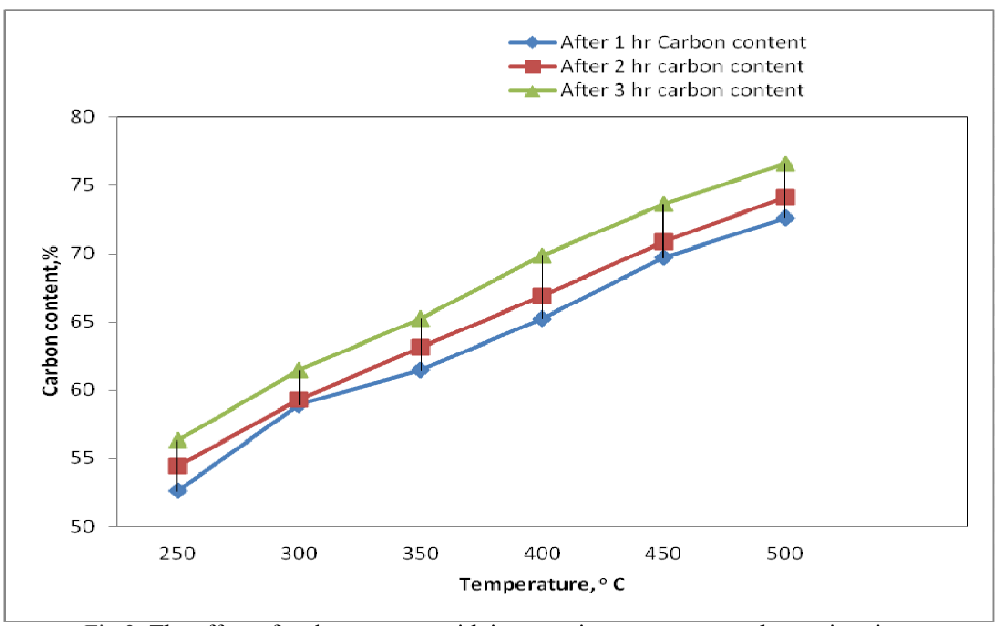

Fig.2. The effect of carbon content with increase in temperature and retention time

pH values and Electrical Conductivity

The pH and EC values of the biochar made from mustard straw were analyzed at different temperatures and retention time. With increase in pyrolytic temperature and retention time, the value of pH and EC increases. The pH of the biochar was maintained between7.4 to 10.05. Similarly, the EC of biochar was found to be increasing from 7.7 to 9.9 mS cm^{-1} with increase in temperature of biochar from 250 °C to 500 °C at retention time 1 hour. With the increase in retention time from 2 to 3 hours, EC of biochar was between 8.0 to 10.2 mS cm^{-1} and 8.3 to 10.9 mS cm^{-1} respectively at 250 and 500 ^oC. The increase in values of pH was perhaps due to the formation of oxides of metal and release of CO_2, NO_2 and SO_2 during pyrolysis.

Proximate Analysis

The results of the proximate analysis of biochar produced at different pyrolysis temperatures are given in Table 1. The volatile matter content of the biochar decreased from 64.56% to 35.26% for the retention time of 1 hr and from 60.15% to 33.24% for retention time of 2 hr. It decreased from 58.27 % to 31.65% for the retention time of 3 hr as the pyrolysis temperature was raised from 250 to 500 ^0C.The ash content is a measure of the non-volatile matter and non-combustible component of the biochar. The ash content of the biochars increased from 3.43 % to 5.71 % for 1 hr duration, it increased from 3.61 % to 5.93 % for 2 hr duration and from 3.83 % to 6.83 % for duration of 3 hrs with the increase in temperature from 250 to 500 ^0C. Thus, the ash content of the biochar was approximately similar as these of cotton stalk, orange peels and palm waste biochar [20, 21, 22].

As the pyrolysis temperature increased from 250 to 500 ^0C, the fixed carbon content of the biochar increased and fixed carbon content as high as 59.03-61.57 % was achieved for biochar pyrolysis at 500 ^0C in this study as shown in Table 1.

Table 1 Proximate analyses of Mustard biochar produced at different pyrolysis temperatures and retention time

	Pyrolysis Temperature ^0C					
Retention time-1 hr	250	300	350	400	450	500
Volatile matter (%)	64.56	57.12	45.62	41.56	37.13	35.26
Ash (%)	3.43	3.58	4.16	4.89	5.14	5.71
Fixed Carbon (%)	32.01	39.3	50.22	53.55	57.73	59.03
Retention time-2 hr						
Volatile matter (%)	60.15	54.21	43.2	39.53	35.23	33.24
Ash (%)	3.61	3.89	4.81	5.12	5.57	5.93
Fixed Carbon (%)	36.23	41.9	51.99	55.35	59.2	60.83
Retention time-3 hr						
Volatile matter (%)	58.27	47.8	40.8	36.7	33.8	31.6
Ash (%)	3.83	4.29	5.29	5.69	6.48	6.83
Fixed Carbon (%)	37.9	47.91	53.91	57.61	59.72	61.57

Calorific value

Higher calorific value indicates that good potential of biochar to be used as a fuel. The higher calorific value of the biochars increased from 4723.15 to 6138.47 cal/g for the retention time of 1 hour, it increased from 4839.03 to 6324.44 cal/g for the retention time of 2 hours, and increased from 4942.23 to 6387.42 cal/g for the retention time of 3 hours as the pyrolysis temperature was increased from 250 to 500 ^0C.From the given data it is clear that the values are nearly the same at different retention time.

Ultimate Analysis of Mustard biochars

Table 2 includes the result of elemental content of biochar. With an increase in the pyrolysis temperature from 250 to 500 ^0C, the carbon content of the biochar increased from 52.9 to 70.1 %, however, the hydrogen content decreased from 5.1 to 0.94 % and oxygen content decreased from 37.95 to 19.34 % at all retention times. Carbonization is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis. Since carbonization is a pyrolytic reaction, it is considered as a complex process in which many reactions take place concurrently, such as dehydrogenation, condensation, hydrogen transfer and isomerization. The amount of heat applied controls the degree of carbonization and the residual content of foreign elements. The increase in carbon content with temperature is due to increasing degree of carbonization.

Table 2- Elemental analyses of Mustard biochar produced at different pyrolysis temperatures and retention time

	Pyrolysis Temperature ^{0}C					
Retention time-1 hr	250	300	350	400	450	500
Carbon (%)	52.9	59.2	60.9	64.5	67.1	67.8
Nitrogen (%)	0.14	0.24	0.24	0.27	0.3	0.31
Sulphur (%)	0.48	0.76	0.82	0.83	0.84	0.91
Hydrogen (%)	5.1	4.3	4.1	3.8	3.6	3
Oxygen (%)	37.95	31.92	29.78	25.71	23.02	22.27
H/C Ratio	1.16	0.87	0.81	0.71	0.64	0.53
O/C Ratio	0.54	0.4	0.37	0.3	0.26	0.25
Retention time-2 hr						
Carbon (%)	53	59.8	61.7	65	67.4	68.5
Nitrogen (%)	0.15	0.25	0.26	0.28	0.31	0.33
Sulphur (%)	0.49	0.78	0.83	0.84	0.85	0.92
Hydrogen (%)	5.3	4.5	4.2	4	3.7	3.1
Oxygen (%)	37.45	30.78	28.2	24.76	22.17	21.22
H/C Ratio	1.2	0.9	0.82	0.74	0.66	0.54
O/C Ratio	0.53	0.39	0.34	0.29	0.25	0.23
Retention time-3 hr						
Carbon (%)	55.1	61.3	64.2	67.6	68.7	70.1
Nitrogen (%)	0.17	0.29	0.32	0.34	0.36	0.39
Sulphur (%)	0.51	0.79	0.85	0.86	0.87	0.94
Hydrogen (%)	5.7	4.9	4.2	3.8	3.1	2.4
Oxygen (%)	34.69	28.43	25.14	21.71	20.49	19.34
H/C Ratio	1.24	0.96	0.79	0.67	0.54	0.4
O/C Ratio	0.47	0.35	0.29	0.24	0.22	0.21

The data given in Table 2 clearly indicate that H/C, O/C atomic ratios gradually decreased with rise in temperature. However, this decline in oxygen and hydrogen content with temperature was as a result of carbonization due to breaking of weaker bonds in biochar structure [23, 24]. It is observed that the O/C ratios of the biochars were the lowest at 500 ^{0}C, while the O/C ratios of biochar were highest at 250 ^{0}C.[25]

FTIR Analysis

The FTIR analysis revealed that the functional groups of biochar obtained at different pyrolysis temperature and retention time were very similar and the aliphatic and aromatic groups were predominant. The highest peak at about 3375 cm^{-1} was observed in the spectra of biochar made at 250 ^{0}C for 1 hour duration (data avoided for brevity), indicating the presence of O-H stretching and intermolecular hydrogen bonded polymeric association. However, the intensity of this peak decreased with increasing pyrolysis temperatures, revealed that the loss of O-H at increased temperature [26].

CONCLUSION

Pyrolysis studies indicated that a good quality biochar could be obtained from mustard straw which is only used for the purpose of burning. Biochar produced from mustard straw at 400^{o}C to 450^{o}C considering the pH and EC of biochar can be effectively used for the preparation of activated carbon. Biochar obtained at high pyrolysis temperature (500 ^{o}C) was suitable for direct use as a fuel due to their high carbon content, higher retention time and high pH and EC values. Biochar can be evaluated as a source of electricity and energy consumption. However, biochar obtained at lower temperatures (300 & 350^{o}C) are suitable for land application. Further studies are needed to evaluate its performance on crop growth and its effect on soil health.

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